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A TEXT-BOOK OF
INORGANIC CHEMISTRY.
VOLUME XI. PART IV.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
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Text-book of Inorganic Chemistry, Vol. XI., Part IV.] [*Frontispiece.*

THE PERIODIC TABLE.*

PERIODS.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period	2 He 4·002	1 H 1·0078 3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·00	7 N 14·008	8 O 16·000	9 F 19·00	
Second short period	10 Ne 20·183	11 Na 22·997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·457	
First long period: Even series	18 A 39·944	19 K 39·096	20 Ca 40·08	21 Sc 45·10	22 Ti 47·90	23 V 50·95	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
First long period: Odd series		29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·91	34 Se 78·96	35 Br 79·916	
Second long period: Even series	36 Kr 83·7	37 Rb 85·44	38 Sr 87·63	39 Y 88·92	40 Zr 91·22	41 Nb 92·91	42 Mo 96·0	43 Ma ...	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
Second long period: Odd series		47 Ag 107·880	48 Cd 112·41	49 In 114·76	50 Sn 118·70	51 Sb 121·76	52 Te 127·61	53 I 126·92	
Third long period	54 Xe 131·3	55 Cs 132·91	56 Ba 137·36	57 La 138·92	58 Ce 140·13 59 Pr 140·92	60 Nd 144·27 61 Il ...	62 Sm 150·43 63 Eu 152·0	64 Gd 157·3 65 Tb 159·2	
Fourth long period		66 Dy 162·46 67 Ho 163·5	68 Er 167·64 69 Tm 169·4	70 Yb 173·04 71 Lu 175·0	72 Hf 178·6	73 Ta 180·88	74 W 184·0	75 Re 186·31	76 Os 191·5 77 Ir 193·1 78 Pt 195·23
Fifth long period: Even series		79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·22	83 Bi 209·00	84 Po [210]	85 ...	
Fifth long period: Odd series	86 Rn 222	87 ...	88 Ra 226·05	89 Ac ...	90 Th 232·12	91 Pa 231	92 U 238·14		

* The Revised International Atomic Weights for 1936 are adopted in this Table

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME XI.

ORGANOMETALLIC COMPOUNDS.

PART IV.
DERIVATIVES OF SELENIUM, TELLURIUM, CHROMIUM AND PLATINUM.

BY

ARCHIBALD EDWIN GODDARD, M.Sc. (B'ham).

LONDON:
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GENERAL INTRODUCTION TO THE SERIES.

During the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the original scheme, in addition to a detailed account of the elements of Group O, the general principles of Inorganic and Physical Chemistry were discussed in Volume I. It was later felt, however, that this arrangement was hardly satisfactory, and an Introduction to these principles is now afforded by my Text-book of Physical Chemistry, Volumes I. and II. (1932–35), whilst in future editions the first volume of this Series will deal with the Inert Gases alone.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX.

under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:—

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.
Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and, moreover, it renders the data for the different elements strictly comparable throughout the whole series.

Since the original scheme was drawn up in 1912, enormous progress has been made in all branches of chemistry, and the original intention of devoting one book only to each Vertical Group in the Periodic Table has had to be abandoned. In several cases it has been necessary to devote a whole book to a single element, as, for example, in the cases of oxygen, nitrogen, phosphorus and arsenic. Further, a separate volume has been devoted to the Metal-Ammines and a comprehensive account of the Organometallic Derivatives is given in Volume XI., which is being issued in four parts.

The Editor would draw attention to the unsatisfactory state of the nomenclature of organometallic compounds in general. The designations of compounds in Volume XI. are those used in the original memoirs, since any attempt to alter these in a work of that description would only complicate matters.

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii–xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi–xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the Authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

December 1936.

PREFACE.

THIS work concludes a series of four volumes dealing with Organometallic Compounds, and in all some 11,500 derivatives have been mentioned.

The present volume describes 1166 selenium, 489 tellurium, 90 chromium, and 8 platinum compounds. It is the first time that the organo-derivatives of these four elements have been collectively reviewed in detail.

In all cases the nomenclature adhered to is that used in the original memoirs, any alteration of which must be undertaken by an International Committee. For an author to make such alterations would merely mean that another set of names had been added to those already in existence, and would tend to add to the present confusion. The author, as in Volume II., again appeals to Chemical Societies to secure some definite standard nomenclature for organometallic compounds in general.

It is hoped that the collection of material in these four volumes will be of increasing assistance to investigators in this field of Chemistry, and particularly those who have not access to a University Library. It is for these latter that details of preparations have in so many cases been given in full, thereby obviating the necessity of looking up original papers. It has been gratifying to receive appreciations already from workers as far apart as Moscow and Tokio, which points to the wide appeal of the field under review.

In conclusion the author desires to thank Sir Gilbert T. Morgan, O.B.E., D.Sc., LL.D., F.R.S., for reprints of his work on Selenium and Tellurium; the late Professor T. M. Lowry, C.B.E., D.Sc., F.R.S., and the Chemical Society, for permission to reproduce the diagrams on pp. 184, 185; Professor F. Challenger for reprints; Dr. Van Dam (Groningen) for a copy of his thesis entitled, "*Eenvoudige seleninezuren en seleninecarbonzuren*"; Dr. H. D. K. Drew for reprints and advice on the nomenclature of Selenium and Tellurium compounds; and Dorothy Goddard, M.Sc., for encouragement during the whole of the work.

A. E. GODDARD.

"THALLIA,"
GLENFIELD FRITH DRIVE,
GROBY ROAD,
LEICESTER.
December 1936.

CONTENTS.

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914+).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900+).
Ann. Physik, Beibl.	Annalen der Physik, Beiblattes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin.*
Ber. deut. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft.
Ber. deut. physikal. Ges.	Berichte der deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bul. Soc. Stünte Cluj.	Buletinul Societâtei de Stünte din Cluj.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.

ABBREVIATED TITLE.	JOURNAL.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's allg. J. Chem.	Allgemeines Journal der Chemie.
Geol. Mag.	Geological Magazine.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Helv. Chim. Acta	Helvetica Chim. Acta.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch für Mineralogie.
Jahresber.	Jahresbericht uber die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift für Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbucher.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Mon. scient.	Moniteur scientifique.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Öfvers. K. Vet.-Akad. Förh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Post	Pharmazeutische Post.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824-1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.

Abbreviated Title.	Journal.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Koniglich-Preussischen Akademie de Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien.	Sitzungsberichte der Koniglich-Bayerischen Akademie der Wissenschaften zu Wien.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte.	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift fur Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift fur Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift fur Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J Sci.	Ann Chim. Phys.	Ann Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32–35	...	...	...	4–6	...	5–8	90	...
1	...	36–39	...		...	7–9	...	8–11	91	...
2	...	40–43	...	...	...	10–12	...	11–14	92	
3	...	44–47		...	...	13–15	...	14–17	93	...
4	...	48–51		...		16–18	...	17–20	94	...
1805	...	52–55	...	...	...	19–21	...	20–23	95	...
6	...	56–60	...	...	...	22–24	...	23–26	96	...
7	...	61–64	...		...	25–27	...	26–29	97	...
8	...	65–68	...	...	...	28–30	...	29–32	98	...
9	...	69–72	...	...	...	31–33	(1) 1*	33, 34	99	...
1810	...	73–76	...	...	...	34–36	2	35, 36	100	...
11	...	77–80	...	...	...	37–39	3	37, 38	101	...
12	...	81–84	...	...	...	40–42	4	39, 40	102	...
13	...	85–88	...	...	...	43–45	5	41, 42	103	...
14	...	89–92	...	...	...	46–48	6	43, 44	104	...
1815	...	93–96	...	...	...	49–51	(2) 1	45, 46	105	...
16	...	(2) 1–3	...	...	...	52–54	2	47, 48	106	...
17	...	4–6	1, 2	...	...	55–57	3	49, 50	107	...
18	...	7–9	3	...	...	58–60	4	51, 52	108	...
19	(1) 1	10–12	4	...	...	61–63	5	53, 54	109	...
1820	2	13–15	5	...	1–3	64–66	6	55, 56	110	...
21	3	16–18	6	...	4–6	67–69	7	57, 58	111	...
22	4, 5	19–21	7	1, 2	7–9	70–72	8	59, 60	112	...
23	6	22–24	8	3–6	10–12	73–75	9	61, 62	113	...
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1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	...
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1835	28, 29	13–16	58–60	7, 8	(2) 1–4	...	1	55–58	21	4–6	...	6, 7	125	34–36	..	...	...
36	30, 31	17–20	61–63	9, 10	5–8	...	2, 3	59–62	22	7–9	...	8, 9	126	37–39	...	...	...
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42	42, 43	41–44	4–6	(4) 1, 2	29–32	...	14, 15	83–86	(3) 1, 2	25–27	...	20, 21	132	55–57	...	...	...
43	44, 45	45–48	7–9	3, 4	33–36	...	16, 17	87–90	3, 4	28–30	...	22, 23	133	58–60	4	...	...
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49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
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1860	...	29, 30	...	113–116	...	58–60	17, 18	101–104	...	2	1, 2	...	..
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66	...	41, 42	...	137–140	4	7–9	9, 10	125–128	..	5, 6	13, 14	...	...
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1875	...	9, 10	...	175–179	...	4–6	7, 8	206, 207	8	23, 24	31, 32	..	.
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1885	6, 7	29, 30	10	227–231	...	4–6	7, 8	223	18	43, 44	51, 52	...	9
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1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
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78	86, 87	227–230	8	...	33, 34	27, 28	17, 18	10	...	...	20	17, 18, 19	5, 6
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1885	100, 101	255–258	15	7	47, 48	11, 12	31, 32	17	4	6	27	31, 32, 33	19, 20
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1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
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63	153	118–120	...	12, 13		...	47, 48	...	...	2	...	...	...
64	154	121–123	...	13		...	49, 50	...	...	3	...	...	...
1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127–129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130–132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133–135	...	16, 17	...	...	57, 58	...	...	7	...	...	...
69	159	136–138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139–141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
71	161	142–144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145–147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
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74	164	151–153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154–156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
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81	172	...	...	31, 32, 33	...	...	83, 84	1	12–14	20	...	5, 6	...
82	173	...	...	33, 34	...	1	85, 86	2	15–17	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	3	18–20	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	4	21–23	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	5	24–26	24	...	10, 11	...
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1890	12	39, 40	15	256–260	19–21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
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1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(6) 1, 2	. .	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
1	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
2	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
3	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
4	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
6	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
7	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
8	323	38	30	93, 94	..	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
9	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	..	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

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* See footnote, p. xxii.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	.	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	..	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
1	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
2	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
3	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
4	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
6	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
7	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
8	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
9	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
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1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	...	36		55	29	94–98	22	..	91, 92
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* Remainder of vol. 55 appeared in 1920.

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VOLUME XI. PART IV.

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INORGANIC CHEMISTRY.

VOL. XI. PART IV.
ORGANOMETALLIC COMPOUNDS.

CHAPTER I.

ALIPHATIC DERIVATIVES OF SELENIUM.

COMPOUNDS OF THE TYPES RSeH, R_2Se, RSeR′ AND R_2Se_2.

THREE types of compounds may be considered to be derived from hydrogen selenide, H_2Se, namely RSeH, R_2Se and RSeR′, where R and R′ are aliphatic radicals.

The first class, RSeH, may be prepared as follows :

(1) By the interaction of sodium or magnesium hydroselenide with alkyl halides in an atmosphere of hydrogen :

$$NaHSe + RI = RSeH + NaI$$

(2) By heating aluminium selenide with alcohols at 250° to 300° C. :

$$Al_2Se_3 + 3ROH = 3RSeH + Al_2O_3$$

These products are heavy oils, possessing vile and persistent odours. They do not dissolve in water, and with salts of the heavy metals yield coloured precipitates. As might be expected they readily undergo oxidation, forming diselenides, RSe.SeR, and the grouping —SeH reacts with methyl magnesium iodide, giving a quantitative yield of methane.

Compounds of the type R_2Se were first mentioned as early as 1853, and are obtained in the following ways :

(1) Phosphorus pentaselenide is heated with a mixture of concentrated potassium or sodium hydroxide and potassium alkyl sulphate, the resulting product being fractionated :

$$P_2Se_5 + 10KRSO_4 + 16KOH = 5R_2Se + 2K_3PO_4 + 10K_2SO_4 + 8H_2O$$

(2) Aluminium selenide and ethers are heated at 300° to 350° C. :

$$Al_2Se_3 + 3R_2O = 3R_2Se + Al_2O_3$$

The dialkyl selenides are colourless strongly refractive oils of obnoxious odour and low boiling-point. In the presence of moisture they tend to pass into diselenides, but with alcohol or ether they are miscible in all proportions. Diethyl selenide slowly combines with ethyl iodide to form triethyl selenium iodide.

The mixed selenides, RSeR′, are formed by treating the mono-alkyl selenides with alkyl halides containing a different alkyl radical :

$$RSeH + R'X = RSeR' + HX$$

They have similar properties to the type R_2Se.

The diselenides, RSe.SeR, are prepared by the interaction of potassium diselenide and dialkyl sulphates or alkyl halides :

$$K_2Se_2 + R_2SO_4 = RSe.SeR + K_2SO_4$$
$$K_2Se_2 + 2RX = RSe.SeR + 2KX$$

These compounds are heavy liquids having higher boiling-points than the types RSeH or R_2Se.

Ethyl, propyl and butyl selenides, RSeH, sometimes called selenomercaptans, may be obtained by heating on the water-bath a solution of sodium hydroselenide, obtained by saturating a 10 per cent. solution of sodium ethoxide with hydrogen selenide, with about 5 per cent. less than the calculated quantity of alkyl iodide or bromide in an atmosphere of hydrogen.[1] The ethyl compound has more recently been obtained by the interaction of ethyl iodide and magnesium hydroselenide.[2] The products are heavy liquids possessing foul, persistent odours, insoluble in water and yielding coloured precipitates with salts of the heavy metals. They are extremely autoxidisable in air, giving diselenides, RSe.SeR, and the hydrogen of the —SeH group reacts with methyl magnesium iodide, methane being quantitatively evolved. The following constants have been determined: *Ethyl selenide,* C_2H_5SeH, B.pt. 53·5° C., density 1·3954 at 24° C., n_D 1·47715 at 24° C. ; *n-propyl selenide,* C_3H_7SeH, B.pt. 84° C., density 1·3020 at 20° C., n_D 1·47560 at 20° C. ; *n-butyl selenide,* C_4H_9SeH, B.pt. 114° C., density 1·2352 at 24·5° C., n_D 1·47446 at 24·5° C.

The earliest preparation of ethyl selenide was carried out according to the equation [3]

$$C_2H_5NaSO_4 + NaSeH = C_2H_5SeH + Na_2SO_4$$

An elaborately-designed apparatus for carrying out an adaptation of this preparation has been devised by Shaw and Reid.[4]

Condensation of ethyl selenide with ketones takes place according to the equation

$$R_2CO + 2HSeC_2H_5 = R_2C(SeC_2H_5)_2 + H_2O$$

The reaction requires the presence of hydrogen chloride, and the following derivatives are known: *ββ-Diethylselenolpropane,* $(CH_3)_2C(SeC_2H_5)_2$, B.pt. 81° C. at 4 mm., density 1·4577 at 0° C., 1·4329 at 25° C. ; *ββ-diethylselenolbutane,* $CH_3(C_2H_5)C(SeC_2H_5)_2$, B.pt. 91·5° C. at 3·5 mm., density 1·4294 at 0° C., 1·4064 at 25° C. ; *γγ-diethylselenolpentane,* $(C_2H_5)_2C(SeC_2H_5)_2$, B.pt. 104·5° C. at 3·5 mm.,

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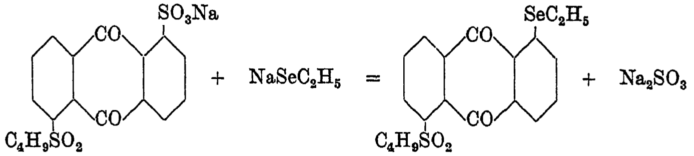
[1] Tschugaeff, *Ber.*, 1909, 42, 49.
[2] Mingoia, *Gazzetta*, 1928, 58, 667.
[3] Siemens, *Annalen*, 1847, 61, 360.
[4] Shaw and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 522.

density 1·3825 at 0° C., 1·3608 at 25° C. Oxidation of these substances by dilute nitric acid or hydrogen peroxide affords ethyl seleninic acid, whilst free halogens decompose them with formation of selenium halides.

Sodium ethyl selenide condenses with $\beta\beta'$-dichlorodiethyl sulphide in alcohol solution to give *di-β-ethylselenolethyl sulphide*:

$$S(CH_2.CH_2.Cl)_2 + 2NaSeC_2H_5 = S(CH_2.CH_2.SeC_2H_5)_2 + 2NaCl$$

This product melts at 15° C., boils at 171° C. at 4 mm. and has a density of 1·4724 at 25° C. Replacement of the sulphide by $\beta\beta'$-dichlorodiethyl sulphone or sulphoxide yields respectively *di-β-ethylselenolethyl sulphone*, $SO_2(CH_2.CH_2.SeC_2H_5)_2$, M.pt. 72·5° C., and the corresponding *sulphoxide*, $SO(CH_2.CH_2.SeC_2H_5)_2$, an oil, decomposing on distillation at 4 mm. Condensation of sodium ethyl selenide with sodium anthraquinone-1-*n*-butylsulphone-5-sulphonate similarly yields *5-ethylselenol-1-n-butylsulphone anthraquinone*, which does not melt below 300° C.:



Dimethyl selenide, $(CH_3)_2Se$.—An intimate mixture of selenium and amorphous phosphorus (5 : 2) is heated, and the black mass powdered and heated in a retort with concentrated sodium hydroxide and potassium methyl sulphate. The mixture foams and a yellow liquid distils over. This is separated from the water and fractionated to remove dimethyl diselenide, which is present in small quantity.

Dimethyl selenide is a colourless, strongly refractive liquid, having an unpleasant smell. It boils at 58·2° C. and burns with the blue flame characteristic of selenium. It is heavier than and immiscible with water, and tends to form dimethyl diselenide in the presence of moisture. When boiled with water selenium separates. The selenide is, however, miscible with alcohol or ether, and soluble in concentrated nitric acid.[1] Treatment with aqueous platinic chloride yields a *platinichloride*, $[(CH_3)_2Se]_2PtCl_4$, consisting of citron-yellow needles, slightly soluble in water, more soluble in hot alcohol, insoluble in ether and blackening on heating, giving dimethyl selenide. The *picrate* crystallises from alcohol in small needles, M.pt. 118° C.[2]

Diethyl selenide, $(C_2H_5)_2Se$, may be obtained by digesting phosphorus pentaselenide with potassium ethyl sulphate, potassium hydroxide and water at 50° C., and submitting the product to fractional distillation.[3] The distillate is contaminated with diethyl diselenide, which is removed by digesting with potassium ethyl sulphate, potassium hydroxide, water and a little amorphous phosphorus and distilling afresh. Pure diethyl selenide is a colourless mobile liquid, boiling at 108° C., miscible with alcohol or ether in all proportions. It gradually combines with ethyl iodide to form triethylselenium iodide. It is

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[1] Jackson, *Ber.*, 1875, 8, 109; *Annalen*, 1875, 179, 1; compare Wohler and Dean, *Annalen*, 1856, 97, 5; Rathke, *Annalen*, 1869, 152, 181.

[2] Baker and Moffitt, *J. Chem. Soc.*, 1930, p. 1728.

[3] Pieverling, *Ber.*, 1876, 9, 1469; *Annalen*, 1877, 185, 331; Joy, *ibid.*, 1853, 86, 35; Rathke, *ibid.*, 1869, 152, 181.

capable of dissolving both the red and black modifications of selenium.

Di-n-propyl selenide, $(C_3H_7)_2Se$.[1]—Equimolecular quantities of *n*-propyl selenide, C_3H_7SeH, and *n*-propyl bromide or iodide are allowed to react in alcohol solution in the presence of sodium ethoxide and in the absence of air. The yield is nearly quantitative. The compound boils at 159° C., has a density of 1·1427 at 24·3° C., n_D 1·47494 at 24·3° C.

Methyl ethyl selenide, $CH_3.Se.C_2H_5$, is prepared in a similar manner to the foregoing compound using methyl selenide and ethyl bromide or iodide. It boils at 86° C., has a density of 1·3134 at 23° C., n_D 1·4820 at 23° C.

Methyl n-propyl selenide, $CH_3.Se.C_3H_7$, boils at 114° C., density 1·2445 at 20·4° C., n_D 1·48121 at 20·4° C.

Methyl n-butyl selenide, $CH_3.Se.C_4H_9$, obtained in the usual manner, boils at 141° C., density 1·1875 at 24·5° C., n_D 1·47710 at 24·5° C.

The following derivatives are obtained by the interaction of aluminium selenide with the corresponding alcohols at 250° to 300° C. or with the ethers at 300° to 350° C.:[2] *Diethyl selenide,* B.pt. about 110° C., *diethyl diselenide,* orange-yellow, B.pt. 137° C., M.pt. $-90°$ to $-98°$ C., and *ethyl selenide*; *di-isopropyl selenide, isopropyl selenide,* B.pt. 70° to 75° C., and *di-isopropyl diselenide.* The presence of water in the alcohols or ethers does not seem to affect appreciably the purity of the final products.

Dimethyl diselenide, $CH_3Se.SeCH_3$,[3] is obtained by the interaction of potassium diselenide and dimethyl sulphate. It is an oil, B.pt. 155° to 157° C. or 57° C. at 21 mm.

Diethyl diselenide, $C_2H_5Se.SeC_2H_5$, obtained by a similar method to the foregoing compound, boils at 192° to 193° C. or at 77° to 78° C. at 16 mm.[4]

Di-n-propyl diselenide, $C_3H_7Se.SeC_3H_7$, is prepared from potassium diselenide and *n*-propyl bromide. It boils at 103° to 104° C. at 15 mm. or at 99° C. at 13 mm.,[5] density 1·4991 at 22·2° C., n_D 1·55535 at 22·2° C.

Di-n-butyl diselenide, $C_4H_9Se.SeC_4H_9$, boils at 129° to 130° C. at 13 mm.

Complex Compounds of Platinum and Palladium Halides with Dialkyl Selenides.[6]

The following complexes have been noted: *Ethyl platinous chloride compound* $PtCl_2.4(C_2H_5)_2Se$; *methyl palladious chloride compound* $PdCl_2.2(CH_3)_2Se$, orange-red crystals, M.pt. 127° to 128° C.; *ethyl palladious chloride compound* $PdCl_2.2(C_2H_5)_2Se$, orange-red crystals, M.pt. 45° C.; *n-propyl palladious chloride compound,* $PdCl_2.2(C_3H_7)_2Se$, M.pt. 62° to 62·5° C.; *isobutyl palladious chloride compound,* $PdCl_2.2(C_4H_9)_2Se$,

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[1] Tschugaeff, *Ber.*, 1909, 42, 49.

[2] Natta, *Atti II Cong. Naz. Chim. Pura Appl.*, 1926, p. 1326; *Chem. Zentr.*, 1928, i, 2245.

[3] van Dam, *Inaug. Dissert. Groningen*, 1930.

[4] Compare Rathke, *Annalen*, 1869, 152, 216.

[5] Compare Tschugaeff, *Ber.*, 1909, 42, 49.

[6] Fritzmann, *Zeitsch. anorg. Chem.*, 1924, 133, 119, 133.

orange-red crystals, M.pt. 79° C.; *isoamyl palladious chloride compound*, $PdCl_2.(C_5H_{11})_2Se$, M.pt. 76° C. *Diethyltrimethylene diselenide* yields the *palladious chloride compound*, $PdCl_2.(C_2H_5)Se[CH_2]_3Se(C_2H_5)$, softening and decomposing at 181° C. The corresponding *palladious bromide derivatives* are as follows: $PdBr_2.2(CH_3)_2Se$, M.pt. 129° C.; $PdBr_2.2(C_2H_5)_2Se$, M.pt. 167° C.; $PdBr_2.2(C_3H_7)_2Se$, M.pt. 165° C.; $PdBr_2.2(C_4H_9)_2Se$, M.pt. 17° C.; $PdBr_2.2(C_5H_{11})_2Se$, M.pt. 4° C.(?); $PdBr_2.(C_2H_5)Se[CH_2]_3Se(C_2H_5)$, M.pt. 162° C. The bromine compounds are slightly darker in colour than the chlorine compounds. The following *palladious iodide compounds* are nearly black: $PdI_2.2(CH_3)_2Se$, M.pt. 123·5° C.; $PdI_2.2(C_2H_5)_2Se$, M.pt. 60° C.; $PdI_2.2(C_3H_7)_2Se$, M.pt. 74° C.; $PdI_2.2(C_4H_9)_2Se$, M.pt. 147° C.; $PdI_2.2(C_5H_{11})_2Se$, M.pt. 121° C.

COMPOUNDS OF THE TYPES R_2SeX_2 AND R_3SeX.

When dialkyl selenides are treated with nitric acid they are converted into dialkyl selenium dinitrates, $R_2Se(NO_3)_2$, and these with hydrochloric and hydrobromic acids give dichlorides and dibromides, respectively, potassium iodide forming the di-iodide. The dimethyl compounds crystallise well, but the diethyl derivatives are all described as liquids. When selenium and methyl iodide are heated together at 180° C., the di-iodide of trimethyl selenium iodide results. Combination takes place directly between diethyl selenide and ethyl iodide, giving triethyl selenium iodide, which is stable in air, and converted by moist silver oxide into the hydroxide, which is a powerful base, giving salts on treatment with acids.

Dimethyl selenium dichloride, $(CH_3)_2SeCl_2$.—A concentrated aqueous solution of the corresponding dinitrate, when treated with hydrochloric acid, gives a precipitate of the dichloride, which is soluble in excess of the precipitant. Crystallisation from alcohol yields white, pearly plates, M.pt. 59·5° C., decomposing at about 70° C. The product has an unpleasant smell, is readily soluble in alcohol, sparingly soluble in water or ether.[1]

Dimethyl selenium dibromide, $(CH_3)_2SeBr_2$, obtained in a similar manner to the dichloride, crystallises from alcohol in short, sulphur-yellow, thin, pearly plates, having a repulsive odour and melting at 82° C. with decomposition. It is less soluble in water than the dichloride, sparingly soluble in cold alcohol, but on heating with alcohol part dissolves and the rest melts to a dark brown oil. On cooling, this oil suddenly crystallises and an odour of dimethyl selenide is apparent; this appears to be due to splitting off of the halogen, followed by recombination.

Dimethyl selenium di-iodide, $(CH_3)_2SeI_2$, occurs when an aqueous solution of the dinitrate is treated with potassium iodide. It is a brick-red powder, not very stable, somewhat soluble in alcohol or ether, insoluble in water. The solutions decompose on heating in a similar way to those of the dibromide. A *dimethyl selenium sulphate* and a *dicyanide* are also mentioned in the literature.

Dimethyl selenium dinitrate, $(CH_3)_2Se(NO_3)_2$.—Dimethyl selenide in small quantities is dissolved in concentrated nitric acid. Long, prismatic crystals separate, which correspond to the *hydroxynitrate*,

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[1] Jackson, *loc. cit.*

$(CH_3)_2Se(NO_3)OH$. Concentration of the mother-liquor from these gives colourless prisms having a faint, unpleasant smell, and melting at 90·5° C. The composition of the product appears to be represented by a combination of nitrate and oxide, $(CH_3)_2Se(NO_3)_2.(CH_3)_2SeO$. The compound is volatile above 100° C. and burns with the blue characteristic selenium flame. In water it is readily soluble, it is sparingly soluble in alcohol, and insoluble in ether.

Diethyl selenium dichloride, $(C_2H_5)_2SeCl_2$, is obtained by a similar method to that used for the corresponding dimethyl compound.[1] It is a transparent, pale yellow liquid, heavier than water, somewhat soluble in water and hydrochloric acid, the aqueous solution having an acid reaction. When dissolved in ammonium hydroxide an *oxychloride*, $(C_2H_5)_2SeCl_2.(C_2H_5)_2SeO$, is formed, which consists of colourless, glistening cubes. From an aqueous solution of the oxychloride hydrochloric acid precipitates the dichloride as an oil, and sulphur dioxide gives diethyl selenide and diethyl selenium dichloride. Zinc diethyl is said to react with the dichloride, forming a *double salt* of *triethyl selenium chloride* and *zinc chloride*, $(C_2H_5)_3SeCl.ZnCl_2$.

Diethyl selenium dibromide, $(C_2H_5)_2SeBr_2$, is a heavy, citron-yellow oil.

Diethyl selenium di-iodide, $(C_2H_5)_2SeI_2$, is a black liquid, heavier than water, readily dissolving in ammonium hydroxide with formation of an oxyiodide.

Diethyl selenium dinitrate, $(C_2H_5)_2Se(NO_3)_2$, occurs when diethyl selenide is dissolved in nitric acid.

Trimethyl selenium iodide, $(CH_3)_3SeI$, is obtained in the form of its di-iodide, $(CH_3)_3SeI.I_2$, when selenium and methyl iodide (1 : 3) are heated together in a sealed tube at 180° C.[2] The reaction which occurs is similar to that occurring with sulphur, the di-iodide of trimethylsulphine iodide being isolated. The di-iodide may be reduced by treating its aqueous solution with hydrogen sulphide until colourless. Platinic chloride in hydrochloric acid gives a *platinichloride*, $[(CH_3)_3SeCl]_2.PtCl_4$, isolated as red octahedra.[3]

Triethyl selenium iodide, $(C_2H_5)_3SeI$.—When diethyl selenide and ethyl iodide are mixed together in molecular proportions, combination slowly takes place at room temperatures. White crystals of the iodide separate out. These sublime completely between 80° and 126° C. without melting, undergoing dissociation into diethyl selenide and ethyl iodide, which, if collected in a receiver, recombine in twelve hours to re-form the iodide. The iodide is stable in air, non-hygroscopic, but readily soluble in water or alcohol, sparingly soluble in ether.[4]

Triethyl selenium hydroxide, $(C_2H_5)_3SeOH$, is a powerful base, obtained by the action of moist silver oxide on the preceding iodide. It readily absorbs carbon dioxide. All its salts are crystalline, have a bitter taste, and all are deliquescent except the *tartrate*, $(C_2H_5)_3SeC_4H_5O_6.2H_2O$, which forms delicate, pale rose-red needles.

Triethyl selenium chloride, $(C_2H_5)_3SeCl$, is obtained by adding hydrochloric acid to the hydroxide; with platinic chloride it gives a

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[1] Joy, *loc. cit.*; Rathke, *loc. cit.*

[2] Scott, *Proc. Chem. Soc.*, 1904, 20, 156.

[3] Joy, *Annalen*, 1875, 175, 19. See preparation of benzyldimethyl selenium tri-iodide, p. 37.

[4] Pieverling, *Ber.*, 1876, 9, 1469; *Annalen*, 1877, 185, 331.

platinichloride, $[(C_2H_5)_3SeCl]_2PtCl_4$, crystallising from hot water in brilliant red rhombohedra.

COMPOUNDS DERIVED FROM ALDEHYDES AND KETONES.

Only three compounds are known in which the oxygen of an aldehyde is replaced by selenium, R.CHSe. They are prepared by treating the aldehydes in suitable solvents with hydrogen selenide, and they are crystalline. If the aldehyde be replaced by a ketone a similar result is obtained, *e.g.* acetone yields diselenoacetone, $(CH_3.CSe.CH_3)_2$. These ketone products are red, viscous oils. Their alcohol solutions deposit red selenium on standing, and the members of lower molecular weight are volatile in steam. If the hydrogen selenide be replaced by selenium tetrachloride, the oxygen is not replaced by selenium, but compounds of the type $(CH_3.CO.CH_2)_2SeCl_2$ are isolated as crystalline solids. When chloroacetone and potassium selenocyanate react, they form selenocyanoacetone, $CH_3.CO.CH_2.SeCN$. Similar results are obtained with acetophenone and its derivatives.

Selenoformaldehyde, H.CHSe.—Hydrogen selenide is passed for 2·5 to 3 hours into a 36 per cent. aqueous solution of formaldehyde mixed with three times its volume of concentrated hydrochloric acid.[1] The resulting product separates from alcohol in columnar crystals, M.pt. 215° C. (approx.). It is sparingly soluble in most organic solvents, and becomes green on exposure to sunlight. The yield is about 50 per cent.

Selenoacetaldehyde, $CH_3.CHSe$.—Hydrogen selenide is passed into a solution of acetaldehyde in three volumes of alcohol saturated with hydrogen chloride, and the resulting semi-solid mass recrystallised from alcohol, the selenoaldehyde separating as slender, transparent needles, M.pt. 139° C. The use of acetone as a solvent gives crystals of melting-point 123° to 124° C.; those from chloroform melt at 117° C. The selenoaldehyde may also be prepared from acetaldehyde and magnesium bromohydroselenide, the melting-point in this case being given as 136° C.[2] It would thus appear that selenoacetaldehyde resembles thioacetaldehyde in existing in several modifications.

Selenovaleraldehyde, $C_4H_9.CHSe$, occurs when an aqueous solution of valeric aldehyde is treated with hydrogen selenide.[3] It is a crystalline solid, which cannot be recrystallised, as its solution in ether, ethyl alcohol or methyl alcohol soon decomposes, selenium separating in mirror form, but as it volatilises with aqueous vapour in a current of gas at room temperature it may be purified in this way. It forms white crystalline crusts, M.pt. 56·5° C., and its odour is particularly offensive, causing difficulty in breathing and palpitation of the heart. In contact with mercury, selenovaleraldehyde decomposes at 30° C., and with dry ammonia *selenovaleraldine* is formed, which resembles thiovaleraldine.

Diselenoacetone,[4] $(CH_3.CSe.CH_3)_2$, is prepared by passing hydrogen selenide into a well-cooled mixture of equal volumes of acetone and concentrated hydrochloric acid. A heavy red oil separates, the yield being 50 per cent. by volume. The product is washed with water and

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[1] Vanino and Schinner, *J. prakt. Chem.*, 1915, [ii], 91, 116.
[2] Mingoia, *Gazzetta*, 1928, 58, 667.
[3] Schroeder, *Ber.*, 1871, 4, 400.
[4] Lyons and Bradt, *Ber.*, 1927, 60, [B], 824.

distilled under reduced pressure at 45° to 60° C. The distillate boiling at about 60° C. at 6 to 10 mm. pressure is dried and analysed. Diselenoacetone is a red oil, having a garlic-like odour. It is not miscible with water, is only slightly soluble in acetic acid, but more soluble in benzene or chloroform. Its alcohol solution precipitates red selenium on standing. The compound is volatile in steam with slight decomposition. When treated in chloroform or benzene solution with chlorine, it is decomposed with separation of selenium tetrachloride.

Di(methyl ethyl selenoketone), $(CH_3.CSe.CH_2.CH_3)_2$, is a red oil, obtained from methyl ethyl ketone as described for the foregoing compound, which it resembles in properties.

Diselenoacetophenone, $(CH_3.CSe.C_6H_5)_2$, is a reddish, viscous oil, not volatile in steam.

Dichloroselenoacetone, $(CH_3.CO.CH_2)_2SeCl_2$.[1]—Two molecular proportions of pure acetone in a large volume of absolute ether are treated with selenium tetrachloride (1 mol.) in small quantities. The resulting product crystallises in white needles, M.pt. 82° C., which emit a vapour tending to attack the mucous membrane. The compound decomposes on keeping and also on boiling with water, selenium separating.

Selenocyanoacetone, $CH_3.CO.CH_2.SeCN$,[2] occurs when potassium selenocyanate reacts with chloroacetone in alcohol solution, the solution being evaporated, the residue taken up in water and the aqueous solution extracted with ether. Evaporation away of the solvent gives an oil, which yields an oily *hydrazone* with phenylhydrazine.

Dichloroselenoacetophenone, $(C_6H_5.CO.CH_2)_2SeCl_2$,[3] occurs when acetophenone (2 mols.) in dry ether reacts with selenium tetrachloride (1 mol.). The product crystallises in white needles, M.pt. 122° C., and is much more stable than the corresponding compound derived from acetone. It can be preserved without undergoing decomposition, but with dilute sodium hydroxide it yields acetophenone and selenious acid, more concentrated alkali causing the separation of selenium. With phenylhydrazine it gives a resinous mass.

Selenocyanoacetophenone, $C_6H_5.CO.CH_2.SeCN$,[4] is obtained by treating bromoacetophenone with potassium selenocyanate in alcohol solution. It melts at 85° C.

ALIPHATIC ACIDS CONTAINING SELENIUM.

The first type of acid to be dealt with contains the selenocyano-grouping —SeCN. This is introduced into aliphatic acids by treating their halogen-substituted derivatives with potassium selenocyanate in the presence of potassium hydroxide, *e.g.* :

$$CH_2Cl.COOH + KSeCN = CH_2SeCN.COOH + KCl$$

The acids thus produced are crystalline products, which are not very stable and show a tendency to pass into diseleno-acids. Some are fairly stable in neutral solution, but yield diseleno-acids in the presence of alkalis, whereas others yield the latter class of acids on prolonged treatment with dilute mineral acids.

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[1] Michaelis and Kunckell, *Ber.*, 1897, 30, 2823.
[2] Hofmann, *Annalen*, 1889, 250, 294.
[3] Michaelis and Kunckell, *Ber.*, 1897, 30, 2823; compare Michaelis, *ibid.*, p. 2821.
[4] Hofmann, *loc. cit.*

Hydrogen selenide converts α-bromopropionic acid in the presence of alkali into selenodilactylic acid, $(C_2H_4.COOH)_2Se$.

Diselenodiacetic acid is obtained as already mentioned or by treating potassium chloroacetate with potassium diselenide,

$$2CH_2Cl.CO_2K + K_2Se_2 = CO_2K.CH_2.Se.Se.CH_2.CO_2K + 2KCl$$

and this method appears to be of general application. All these acids are crystalline solids, capable of forming crystalline salts.

The diselenodicarboxylic acids are oxidised by nitric acid (density 1·4) at 40° to 45° C. to selenino-fatty acids :

$$[CO_2H.CHR.Se.]_2 + 3O + H_2O = 2CO_2H.CHR.SeO_2H$$

Nitric acid oxidises dialkyl diselenides to alkylseleninic acids :

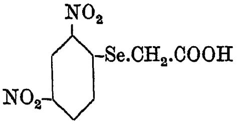
$$RSe.SeR + 2HNO_3 = 2RSeO_2H + 2NO$$

These form well-defined crystalline salts.

When magnesium bromohydroselenide reacts with ethyl chloroformate or acetyl chloride it gives, respectively, ethoxyseleno-formic acid, $C_2H_5O.COSeH$, and selenoacetic acid, $CH_3.COSeH$, products in which one atom of oxygen in the carboxyl group is replaced by selenium.

Selenocyanoacetic acid, $CH_2SeCN.COOH$.[1]—One molecular proportion of monochloracetic acid in the minimum quantity of water is neutralised with solid potassium hydroxide and one molecular proportion of potassium selenocyanate added. The solid which slowly separates is extracted with boiling alcohol, the solution on evaporation yielding plates, readily soluble in water but sparingly soluble in cold alcohol. This product is the *potassium salt*, and the free acid is isolated by treating the salt with sulphuric acid and extracting the solution with ether. The solid obtained by removal of the solvent is recrystallised from ether-chloroform, needles being deposited, M.pt. 84° to 85° C., readily soluble in water, alcohol or ether, sparingly soluble in benzene, insoluble in chloroform or ligroin. The acid is not very stable, and yields a brown resin on keeping. It liberates carbon dioxide from carbonates, and its alkaline earth salts are readily soluble. The *barium salt*, $(CH_2SeCN.COO)_2Ba$, is a gummy substance.

2 : 4-Dinitrophenylselenoacetic acid,[2]



is the condensation product from 2 : 4-dinitrochlorobenzene and selenocyanoacetic acid or its potassium salt. The reaction is carried out in sodium hydroxide solution in the presence of sodium acetate. The resulting product crystallises from water in long yellow needles, or from alcohol in plates, M.pt. 168° C. In this preparation 2 : 4 : 2′ : 4′-tetranitrodiphenyl selenide, p. 23, separates as a by-product.

α-Selenocyanopropionic acid, $CH_3.CH(SeCN)COOH$,[3] is isolated in 50 to 60 per cent. yield in the form of its *potassium salt*, when

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[1] Hofmann, *loc. cit.*

[2] Behaghel and Rollmann, *Ber.*, 1929, *62*, [B], 2696.

[3] Simon, *Monatsh.*, 1905, *26*, 959; Fredga, *J. prakt. Chem.*, 1929, [ii], *121*, 56, 129.

potassium α-bromopropionate reacts with potassium selenocyanate in the presence of a little water. The acid is liberated from its salt by dilute sulphuric acid and melts at 69° to 70° C.[1] The acid decomposes in air after several weeks, giving diselenodilactylic acid. The *strychnine salt* yields a free acid having the value +19° for $[\alpha]_D$ in *N*/10 aqueous solution. The *quinine salt* is known and crystallises with three molecules of water, but yields an inactive free acid. Active α-selenocyanopropionic acid, obtained from the potassium salt of the active bromo-acid, has the value 54·8° for $[\alpha]_D$, the value increasing to 65° after five crystallisations. In contact with a small amount of water α-selenocyanopropionic acid slowly evolves hydrogen cyanide, and it gives a red selenium stain on a filter paper after standing. In neutral solution the acid yields a white precipitate with silver nitrate, which becomes yellow and probably consists of a mixture of silver selenocyanate and silver lactate. Potassium α-selenocyanopropionate forms deliquescent, thin needles, which are readily soluble in water or alcohol, almost insoluble in benzene or chloroform. The *sodium salt* yields pale yellow crystals, readily soluble in water, less soluble in alcohol, and only slightly hygroscopic. *Ethyl α-selenocyanopropionate*,[2] obtained by boiling together ethyl α-chloropropionate and potassium selenocyanate in alcoholic solution, is a reddish-brown oil of unpleasant odour and burning taste. It is heavier than water, soluble in ether and hydrolysed by boiling alcoholic sodium hydroxide, sodium lactate, sodium selenocyanate and alcohol resulting. The *methyl ester* has similar properties to the ethyl ester.

β-Selenocyanopropionic acid, $CH_2(SeCN)CH_2.COOH$, melts at 58° C., and conductivity measurements indicate that this acid is about sixteen times weaker than the α-acid.

α-Selenocyanobutyric acid, $C_3H_6(SeCN)COOH$, M.pt. 50° to 51° C., dissociation constant, κ, $=2{\cdot}7\times10^{-3}$ (potassium salt), and *α-selenocyanoisobutyric acid*, M.pt. 79° to 80° C., $\kappa=6{\cdot}1\times10^{-3}$ (potassium salt), are prepared by the general method.

α-Selenocyanoisovaleric acid, $C_4H_8(SeCN)COOH$,[3] from α-bromo*iso*valeric acid, melts at 109° to 110° C., $\kappa=2{\cdot}59\times10^{-3}$ at 25° C. Prolonged treatment with dilute mineral acid yields diselenodi-α-*iso*valeric acid, M.pt. 122° to 123° C. Oxidation with hydrogen peroxide in the presence of barium carbonate gives *α-seleninoisovaleric acid*, M.pt. 111° C. (decomp.).

α-Selenocyanoacrylic acid, $C_2H_2(SeCN)COOH$.[4]—Condensation of potassium αβ-dibromopropionate (1 mol.) and potassium selenocyanate (1 mol.) yields *potassium α-selenocyanoacrylate*, containing a molecule of water of crystallisation. This salt is decomposed by sulphuric acid in ether into α-selenocyanoacrylic acid, M.pt. 105° C. (decomp.). The dissociation constant, κ, is $1{\cdot}27\times10^{-2}$, $\mu_\infty=369$ being assumed, and slight decomposition is observed in contact with the platinum electrodes. Potassium α-bromoacrylate does not react with potassium selenocyanate at the ordinary temperature.

Selenodilactylic acid, $(C_2H_4.COOH)_2Se$.—A solution of 18 grams of potassium hydroxide in water is saturated with hydrogen selenide, an

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[1] Simon stated that the acid did not solidify at −15° C.

[2] Simon, *loc. cit.*

[3] Fredga, *Svensk. Kem. Tidskr.*, 1930, 42, 66.

[4] *Ibid.*, p. 153.

equal volume of potassium hydroxide solution added, followed by 160 grams of α-bromopropionic acid. The *potassium salt* so obtained is decomposed by shaking with dilute sulphuric acid and the free acid extracted by ether, from which solvent it is obtained on evaporation.[1] The acid crystallises from water in monoclinic prisms, the parameters of which are $a : b : c = 1{\cdot}0089 : 1 : 1{\cdot}3345$; $\beta = 114°\ 32'$. It melts at 145° C., μ_∞ has the value 356 and κ is 0·0416. From the mother-liquors of this acid a rhombic form is obtained, $a : b : c = 0{\cdot}9210 : 1 : 1{\cdot}2360$, M.pt. 106° to 107° C., $\kappa = 0{\cdot}0380$. The *sodium salt* and potassium salt are very soluble; the *barium salt* exists in two forms, as in the case of the analogous thio-acid, one being amorphous and readily soluble, the other crystalline and sparingly soluble. The *amide* of the monoclinic acid crystallises in long needles, that of the rhombic acid in plates.

Diselenodiacetic acid, $CO_2H.CH_2.Se.Se.CH_2.CO_2H$.[2]—Selenocyanoacetic acid or its potassium salt in dilute acetic or hydrochloric acid solution is boiled for some time and after cooling extracted with ether. The solvent is removed, the residue dissolved in ethyl acetate, the solution boiled with charcoal, filtered, and treated with six volumes of benzene. After long standing pale yellow spear-shaped crystals are deposited, M.pt. 101° C. The following are also formed during the reaction: ammonia, carbon dioxide, hydrocyanic acid, and small amounts of oxalic acid. A second method of preparation[3] consists of treating potassium chloroacetate with potassium diselenide:

$$2CH_2Cl.CO_2K + K_2Se_2 = CO_2K.CH_2.Se.Se.CH_2.CO_2K + 2KCl$$

The melting-point in this case is given as 97° to 98° C. The tetrahydrated *diquinine salt* melts with decomposition at 147° C.

α-Diselenodipropionic acid, $CO_2H.CH(CH_3).Se.Se.CH(CH_3).CO_2H$,[4] is prepared from potassium diselenide solution and α-bromopropionic acid, or by heating inactive α-selenocyanopropionic acid at 80° to 90° C. with concentrated hydrochloric acid.[5] By the latter method the acid is obtained in two inter-convertible forms, M.pt. 70·5° to 72·5° C. (*meso* form ?), and M.pt. 107° to 108° C. (*racemic* form ?). Prolonged treatment of α-selenocyanopropionic acid with 4*N* hydrochloric acid gives α-diselenodipropionic acid, M.pt. 43° to 45° C., $[\alpha]_D^{25°} = +251{\cdot}2°$ in water. The *diquinine salt* of α-diselenodipropionic acid melts with decomposition at 164° C., and the acid gives the value +922° for the molecular rotation $[M]_D$.

β-Diselenodipropionic acid, $CO_2H.CH_2.CH_2.Se.Se.CH_2.CH_2.CO_2H$, is prepared from β-chloropropionic acid and potassium diselenide, or by treating β-selenocyanopropionic acid with hot hydrochloric acid. It melts at 137° C.

α-Diselenodibutyric acid, $CO_2H.CH(C_2H_5).Se.Se.CH(C_2H_5).CO_2H$, melts at 72° C.,[6] and forms a *diquinine salt,* M.pt. 128° C. (decomp.). The molecular rotation, $[M]_D$, of the acid is $= +790°$, and for the *dipotassium salt* $[M]_D = +155°$. *α-Diselenodi-isobutyric acid* melts with decomposition at about 185° C.

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[1] Nils Coos, *Ber.*, 1902, 35, 4109.

[2] Behaghel and Rollmann, *Ber.*, 1929, 62, [B], 2696.

[3] van Dam, *loc. cit.*

[4] van Dam, Backer and Dam, *Rec. Trav. chim.*, 1929, 48, 1287; van Dam, *loc. cit.*

[5] Fredga, *J. prakt. Chem.*, 1929, [ii], 121, 56.

[6] Fredga (*loc. cit.*) gives M.pt. 80° to 81° C.

α-Diselenodivaleric acid, $CO_2H.CH(C_3H_7).Se.Se.CH(C_3H_7).CO_2H$, melts at 74° C., and the monohydrated *diquinine salt* melts with decomposition at 171° C. *a-Diselenodi-isovaleric acid* melts at 122° to 123° C.

Aliphatic Seleninocarboxylic Acids.

Oxidation of diselenodicarboxylic acids by nitric acid (density 1·4) at 40° to 45° C. yields selenino-fatty acids :

$$[CO_2H.CHR.Se.]_2 + 3O + H_2O = 2CO_2H.CHR.SeO_2H$$

Iodine in the presence of sodium hydrogen carbonate converts diselenides quantitatively into seleninic acids :

$$(RSe)_2 + 3I_2 + 4H_2O = 2RSeO_2H + 6HI$$

The oxidation may also be effected by hydrogen peroxide in aqueous solution.

Seleninoacetic acid, $SeO_2H.CH_2.CO_2H$,[1] is obtained as indicated above and isolated in the form of its *barium salt*, which contains two molecules of water, the parameters of the crystals being $a:b:c = 1{\cdot}276:1:1{\cdot}555$. The values of κ_1 and κ_2 for the acid by electrometric titration are $2{\cdot}50 \times 10^{-3}$ and $3{\cdot}74 \times 10^{-6}$ respectively. The free acid melts with decomposition at 99° C. The *diquinine salt* contains seven molecules of water and melts at 122° C. (decomp.), six molecules of water being lost on heating *in vacuo*.

α-Seleninopropionic acid, $SeO_2H.CH(CH_3).CO_2H$.[2]—This acid may be prepared by the general method. It melts at 83° C. The *barium salt* is isolated as the dihydrate, M.pt. 150° to 160° C. with decomposition. The *calcium salt* also contains two molecules of water. *Lead* and *silver salts* are also known. The dissociation constants of the acid by electrometric titration are $\kappa_1 = 3{\cdot}36 \times 10^{-3}$, $\kappa_2 = 3{\cdot}36 \times 10^{-6}$. The tetrahydrated *quinine salt* of the *l*-acid sinters at 115° C. and melts at about 128° C. with decomposition, whence the *l*-acid, $[M]_D - 110°$, for the undissociated compound in water. Treatment of the acid in solution with hydrochloric or hydriodic acid causes development of *dextro*-rotation, owing to the formation of *d*-diselenodipropionic acid, $[M]_D = +922°$, the *quinine salt* of which melts at 164° C.

β-Seleninopropionic acid, $SeO_2H.CH_2.CH_2.CO_2H$, may be prepared by the general method or by oxidising β-dipropyl diselenide with iodine in sodium hydrogen carbonate solution or hydrogen peroxide in aqueous or acetone solution.[3] The melting-points of the acid prepared by the foregoing methods are given as 109° to 110° C. and 108° C., respectively. The *silver salt* has been isolated. The dissociation constants for the acid by electrometric titration are $\kappa_1 = 0{\cdot}336 \times 10^{-3}$, $\kappa_2 = 1{\cdot}02 \times 10^{-6}$.

α-Seleninobutyric acid, $SeO_2H.CH(C_2H_5).CO_2H$.[4]—When obtained from α-diselenodibutyric acid it is isolated in the form of its *lead salt*. The *barium salt* occurs also as the dihydrate. Prepared from the diselenide[5] the acid melts with decomposition at 122° C.

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[1] van Dam, *Inaug. Dissert. Groningen*, 1930; Backer and van Dam, *Rec. Trav. chim.*, 1930, 49, 482.

[2] van Dam, *loc. cit.*; Backer and van Dam, *Rec. Trav. chim.*, 1929, 48, 1287.

[3] See Fredga, *Svensk. Kem. Tidskr.*, 1930, 42, 66.

[4] van Dam, *loc. cit.*; Backer and van Dam, *loc. cit.*

[5] Fredga, *loc. cit.*

The values for the dissociation constants are $\kappa_1 = 2{\cdot}95 \times 10^{-3}$, $\kappa_2 = 3{\cdot}28 \times 10^{-6}$. The *diquinine salt* contains five molecules of water and melts with decomposition at 112° C. By fractional crystallisation of the appropriate quinine salt, *l-a-seleninobutyric acid*, $[n]_D = 25°$, $[M]_D = 82°$, is isolated; its *barium salt* is also known.

a-Seleninovaleric acid, $SeO_2H.CH(C_3H_7).CO_2H$, melts with decomposition at 111° C., and yields a *barium salt* in the form of a dihydrate, also a tetrahydrated *diquinine salt* melting with decomposition at 120° C. The dissociation constant values are $\kappa_1 = 2{\cdot}75 \times 10^{-3}$, $\kappa_2 = 3{\cdot}30 \times 10^{-6}$, and *l-a-seleninovaleric acid* has the values $[M]_D = -11{\cdot}5°$ (barium salt), $[M]_D = -12{\cdot}5°$.

Alkylseleninic Acids.[1]

These compounds are obtained by oxidising dialkyl diselenides by nitric acid (density 1·4), the general equation for the reaction being as follows:

$$RSe.SeR + 2HNO_3 = 2RSeO_2H + 2NO$$

They are solids and form molecular compounds with strong acids, the following table showing the melting-points of the free acids and their derivatives.

MELTING-POINTS OF ALKYLSELENINIC ACIDS AND THEIR DERIVATIVES.

	$CH_3.SeO_2H$	$C_2H_5.SeO_2H$	$C_3H_7.SeO_2H$	$C_4H_9.SeO_2H$
Free Acid	134° C.	47° C.	75° C.	68° C.
Nitrate	103 „	73 „	101 „	96 „
Sulphate	130 „	98 „	119 „	117 „
Hydrochloride	100 „	106 „	101–102° C.	99 „
Methanesulphonate	142 „	115 „	122° C.	99 „
Ethanesulphonate	105 „	86 „	103 „	98 „
Methionate	128 „	113 „	115 „	111 „
Benzenesulphonate	150 „	130 „	136 „	121 „

Methaneseleninic acid, $CH_3.SeO_2H$, is prepared by the oxidation of dimethyl diselenide by nitric acid (density 1·4) at 50° C. It melts at 134° C. with blackening and gas evolution, gives the value $6{\cdot}44 \times 10^{-6}$ for the dissociation constant (κ_{25}), is hygroscopic, and yields a crystalline *lead salt* and a *barium salt* separating in rosettes. The *hydrochloride* melts at 100° C., the *nitrate* at 103° C., the *sulphate*, $(CH_3SeO_2H)_2.H_2SO_4$, at 130° C., the *methanesulphonate*, $CH_3SeO_2H.CH_3SO_3H$, at 142° C., the *ethanesulphonate* at 105° C., the *benzenesulphonate*, $CH_3SeO_2H.C_6H_5SO_3H$, at 150° C., and the *methionate*, $(CH_3SeO_2H)_2.CH_2(SO_3H)_2$, at 128° C.

Ethaneseleninic acid,[2] $C_2H_5.SeO_2H$, is the oxidation product of diethyl diselenide using nitric acid (density 1·4) at 100° C. It melts

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[1] van Dam, *Inaug. Dissert. Groningen*, 1930.

[2] van Dam, *ibid.*; Backer and Dam, *Rec. Trav. chim.*, 1930, 49, 479; compare Rathke, *Annalen*, 1869, 152, 181.

at 47° C., $\kappa_{25} = 5{\cdot}29 \times 10^{-6}$, and gives a *lead* and a *barium salt*; the *hydrochloride* melts at 106° C., the *nitrate* at 73° C., the *sulphate* at 98° C., the *methanesulphonate* at 115° C., the *ethanesulphonate* at 86° C., the *benzenesulphonate* at 130° C., and the *methionate* at 113° C. Oxidation of selenomercaptoles,[1] *e.g.* $\beta\beta$-diethylselenolpropane, with dilute nitric acid yields *ethaneseleninic acid nitrate*, consisting of white plates, M.pt. 80° C., decomposing at 100° C. Hydrochloric acid converts this to the *hydrochloride*, melting with decomposition at 100° to 107° C., but hydrobromic acid gives *ethyl selenium tribromide*, $C_2H_5.SeBr_3$, decomposing at 73° C.

n-Propaneseleninic acid,[2] $C_3H_7.SeO_2H$, from dipropyl diselenide, melts at 75° C. and the dissociation constant is $\kappa_{25} = 5{\cdot}59 \times 10^{-6}$. It yields anhydrous *lead* and *barium salts*, also the following molecular compounds: *hydrochloride*, M.pt. 101° to 102° C., *nitrate*, M.pt. 101° C., *sulphate*, M.pt. 119° C., *methanesulphonate*, M.pt. 122° C., *ethanesulphonate*, M.pt. 103° C., *benzenesulphonate*, M.pt. 136° C., and *methionate*, M.pt. 115° C.

n-Butaneseleninic acid, $C_4H_9.SeO_2H$, is formed when *n*-dibutyl diselenide is oxidised at 50° C. by nitric acid (density 1·4), the yield being about 70 grams of acid from 54 grams of diselenide. The acid melts at 68° C., $\kappa_{25} = 5{\cdot}13 \times 10^{-6}$, and yields a *lead salt*. Its molecular derivatives are as follows: *hydrochloride*, M.pt. 99° C., *nitrate*, M.pt. 96° C., *sulphate*, M.pt. 117° C., *methanesulphonate*, M.pt. 99° C., *ethanesulphonate*, M.pt. 98° C., *benzenesulphonate*, M.pt. 121° C., and *methionate*, M.pt. 111° C.

Seleno-fatty Acids.

Ethoxyselenoformic acid, $C_2H_5O.COSeH$,[3] is prepared by the interaction of magnesium bromohydroselenide and ethyl chloroformate. It soon decomposes, yielding its *anhydride*, B.pt. 125° to 127° C., a liquid of nauseating odour, carbon monoxide, selenium and alcohol.

Selenoacetic acid, CH_3COSeH, from magnesium bromohydroselenide and acetyl chloride, has a penetrating, irritating odour. The *ammonium salt* is unstable and decomposes into selenium and ammonium acetate. With salts of the heavy metals the ammonium salt gives coloured precipitates, which decompose, forming the corresponding black selenides.

SELENIUM DERIVATIVES OF ETHYL-, PROPYL- AND ALLYL-AMINES.

β-Selenocarbimidoethylphthalimide,[4] $C_8H_4O_2 : N.CH_2.CH_2.SeCN$, occurs when 8 grams of potassium selenocyanate, 10 grams of bromoethylphthalimide and 40 c.c. of alcohol are heated together at 100° C. The product separates from alcohol in colourless crystals, M.pt. 124° to 125° C., and when boiled with 10 per cent. potassium hydroxide is converted into *ethyl-β-diselenidodiphthalamic acid*, $Se_2(CH_2.CH_2.NH.CO.C_6H_4.COOH)_2$, a yellowish crystalline compound, M.pt. 118° to 119° C.

γ-Selenocarbimidopropylphthalimide, $C_{12}H_{10}N_2SeO_2$, from bromopropylphthalimide and potassium selenocyanate, melts at 102° C., and is converted into *propyl-γ-diselenidodiphthalamic acid*,

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[1] Shaw and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 520.

[2] van Dam, *loc. cit.*

[3] Mingoia, *Gazzetta*, 1928, 58, 667.

[4] Coblentz, *Ber.*, 1891, 24, 2131.

$C_{22}H_{24}N_2O_6Se_2$, by hot potassium hydroxide. The latter acid separates from alcohol in crystals, M.pt. 84° C.

Diselenoethylamine hydrochloride, $Se_2(CH_2.CH_2.NH_2)_2.2HCl$, is obtained when ethyl-β-diselenidodiphthalamic acid is heated at 180° C. with concentrated hydrochloric acid. It forms white crystals, M.pt. 188° C. The corresponding *picrate*, $C_4H_{12}N_2Se_2.2C_6H_3N_3O_7$, crystallises from alcohol in orange needles, M.pt. 178° C.

Diselenopropylamine hydrochloride, $Se_2(CH_2.CH_2.CH_2.NH_2)_2.2HCl$, obtained from propyl-γ-diselenidodiphthalamic acid in a similar manner to the foregoing ethyl compound, separates from alcohol in crystals of melting-point 170° C. The *picrate*, $C_6H_{16}N_2Se_2.2C_6H_3N_3O_7$, forms orange crystals, M.pt. 165° C.

Ethylselenocarbamide,[1] $C_2H_5.NH.CSe.NH_2$.—When 22·5 grams of ethylamine in 400 c.c. of ether are treated with 250 c.c. of a normal cyanogen bromide solution, the following reaction occurs :

$$2C_2H_5NH_2 + CNBr = C_2H_5.NH.CN + C_2H_5NH_2.HBr$$

The solution should be cooled and moisture excluded during the operation, and in the next stage a nitrogen atmosphere is employed, also subdued light. The filtrate from the foregoing reaction is treated with the hydrogen selenide derived from 70 grams of ferrous selenide by slowly adding 150 c.c. of hydrochloric acid (density 1·123), the gas being washed with water and dried with calcium chloride. An oil separates, which crystallises in needles after standing for several hours. The product is stirred with cold water, filtered off, dried, dissolved in a little warm alcohol, the solution filtered and the carbamide precipitated with petroleum ether. Recrystallisation from warm water gives colourless needles, M.pt. 125° C. The substance rapidly becomes red when exposed to light owing to the separation of selenium, but it can be preserved indefinitely in sealed vessels in the dark. The selenium atom is far more labile than the sulphur atom in the corresponding thio-compound. The substance unites with *allyl bromide* in alcoholic solution at 60° to 70° C. forming an *additive product*, $C_2H_5.NH.C(NH_2) : SeBrC_3H_5$ or $C_2H_5.NH.C(:NH)SeC_3H_5.HBr$, M.pt. 115° C., readily soluble in water, silver nitrate precipitating silver bromide.

Allylselenocarbamide, $C_3H_5.NH.CSe.NH_2$, is prepared in a similar manner to the foregoing compound and crystallises from alcohol-petroleum ether in colourless crystals, M.pt. about 93° C., easily soluble in warm water or alcohol, moderately soluble in ether, insoluble in petroleum ether. It has an intensely irritant action on the skin. With *ethyl iodide* it forms a colourless *additive compound*, $C_6H_{13}N_2ISe$, M.pt. 100° C., which is moderately soluble in water. This product is more stable towards air and light than the free allylselenocarbamide. When warmed with alkali a penetrating odour develops.

SELENIUM DERIVATIVES OF ETHYLENE, PROPYLENE, BUTYLENE AND AMYLENE.

These compounds are produced by the interaction of selenium monochloride, Se_2Cl_2, and the unsaturated hydrocarbon.[2] The complete

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[1] H. Schmidt, *Ber.*, 1921, 54, [B], 2067; German Patents, 305262, 305263.

[2] Boord and Cope, *J. Amer. Chem. Soc.*, 1922, 44, 395; compare Heath and Simon, *J. Ind. Eng. Chem.*, 1920, 12, 1101; Bauser, Gibson and Pope, *Trans. Chem. Soc.*, 1920, 117, 1453.

reaction is represented by the equation :

$$2C_2H_4 + 2Se_2Cl_2 = (ClC_2H_4)_2SeCl_2 + 3Se$$

It has been shown that this reaction is the summation of two definite consecutive reactions :

$$2C_2H_4 + Se_2Cl_2 = (ClC_2H_4)_2Se + Se$$
$$(ClC_2H_4)_2Se + Se_2Cl_2 = (ClC_2H_4)_2SeCl_2 + 2Se$$

The process may be stopped at the end of the first stage by reversing the order of bringing the reagents together. To bring about the complete reaction the selenium monochloride is brought into reaction with the olefine in such a manner that the latter is always in excess, a condition obtained by spraying it into an atmosphere of the olefine.

The production of these compounds is considered to be evidence of the unsymmetrical structure, Se : $SeCl_2$, for selenium monochloride.

ββ'-Dichlorodiethyl selenide dichloride, $(CH_2Cl.CH_2)_2SeCl_2$,[1] crystallises in long colourless prisms, M.pt. 122·5° C., which are slightly hygroscopic. The parameters of the crystals are as follows : $a : b : c = 0{\cdot}6345 : 1 : 0{\cdot}8389$; $\beta = 75° \ 50'$. The compound is about ten times as soluble in boiling benzene as in the cold solvent. In cold water it gives an acid liquid from which silver nitrate precipitates silver chloride, a viscous liquid then remaining on evaporating the aqueous solution. One half of the chlorine present is hydrolysed by water to hydrogen chloride. Sulphur dioxide converts the dichloride into a heavy oil which yields colourless prismatic crystals on cooling, M.pt. 23° to 25° C. This is probably *ββ'-dichlorodiethyl selenide,* $(CH_2Cl.CH_2)_2Se$.

ββ'-Dichlorodipropyl selenide, $(C_3H_6Cl)_2Se$,[2] boils at 134° C. at 10 mm., and is a lemon-yellow oil. The *dichloride* forms white crystals, M.pt. 81° C.

ββ'-Dichlorodibutyl selenide, $(C_4H_8Cl)_2Se$, B.pt. 138° C. at 8 mm., and **ββ'-dichlorodiamyl selenide,** $(C_5H_{10}Cl)_2Se$, B.pt. 158° C. at 10 mm., are also known, together with their dichlorides.

[1] Bauser, Gibson and Pope, *loc. cit.*

[2] Boord and Cope, *loc. cit.*

For the estimation of selenium in organic compounds, see Wrede, *Zeit. physiol. Chem.*, 1920, 109, 272; Spica, *Gazzetta*, 1877, vii, 90; Lyons and Shinn, *J. Amer. Chem. Soc.*, 1902, 24, 1089; Frerichs, *Arch. Pharm.*, 1902, 240, 656; Konek and Schleifer, *Ber.*, 1918, 51, 842; Bradt and Lyons, *J. Amer. Chem. Soc.*, 1926, 48, 2642; Bogert and Stull, *J. Amer. Chem. Soc.*, 1927, 49, 2015; Challenger and Peters, *J. Chem. Soc.*, 1928, p. 1375.

CHAPTER II.

AROMATIC DERIVATIVES OF SELENIUM.

ARYL SELENIDES OF THE TYPES RSeH, R_2Se, R′SeR AND RSe.SeR.

THE aryl selenides, RSeH, may be prepared by the following methods:

(1) By the interaction of selenium tetrachloride and benzene in the presence of aluminium chloride. Diaryl selenides and diaryl diselenides are formed as by-products.

(2) By treating aryl magnesium bromides in ether solution with selenium, followed by decomposition of the resulting complex with hydrochloric acid.

(3) By the reduction of diaryl diselenides.

The aryl selenides are crystalline solids or liquids heavier than water. Oxidation by atmospheric oxygen or dilute alkali yields diaryl diselenides.

For the diaryl selenides, R_2Se, a variety of methods of preparation is available:

(1) Diarylsulphones are heated with precipitated selenium:

$$R.SO_2.R + Se = R.Se.R + SO_2$$

If the two radicals in the sulphone be different, mixed selenides, R.Se.R′, are produced.

(2) The Grignard reagent may be used as in method (2) for aryl selenides, and the selenium may be replaced by selenium bromide.

(3) By the interaction of mercury diaryls and powdered selenium at 220° to 230° C.:

$$R_2Hg + 2Se = R_2Se + HgSe$$

(4) By treating aryl diazonium chlorides with potassium selenide:

$$2RN_2Cl + K_2Se = R_2Se + 2N_2 + 2KCl$$

(5) In the case of the benzyl compound, sodium selenide is treated with benzyl chloride:

$$2RCH_2Cl + Na_2Se = (RCH_2)_2Se + 2NaCl$$

(6) Chloronitro-hydrocarbons are treated with hydrogen selenide:

$$2(NO_2)_2C_6H_3Cl + H_2Se = [(NO_2)_2.C_6H_3]_2Se + 2HCl$$

In addition to method (1), mixed diaryl selenides may also be obtained:

(1) By the interaction of sodium aryl selenides and alkyl halides:

$$NaRSe + R'X = R.Se.R' + NaX$$

(2) By treating arylseleninic acids with arylamines.

Most of the simple diaryl selenides are liquids, combining with bromine to yield dibromides. The ditolyl-, benzyl- and dinaphthyl-compounds are solids.

The diaryl diselenides are solids of well-defined crystalline form, the benzyl compounds being slowly decomposed by light. The following methods have been used for their preparation, but some are only applicable to special cases :

(1) Aryl diazonium chlorides are treated with potassium selenocyanate, the resulting product boiled with 2*N* sodium hydroxide, and the solution cooled, filtered and acidified.

(2) The diselenides occur as by-products when aryl magnesium bromides react with selenium bromide in ether.

(3) In very poor yield when benzene reacts with selenium bromide in carbon disulphide solution in the presence of aluminium chloride.

(4) Sodium ethoxide is treated with selenium and *o*-nitrochlorobenzene stirred into the mixture.

(5) By reduction of seleninic acids.

(6) By atmospheric oxidation of aryl selenides or treatment with dilute alkali.

(7) By treating sodium selenide with benzyl chloride.

(8) Potassium nitrobenzyl selenosulphates are treated with iodine in alcohol.

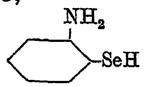
(9) By the electrolytic reduction of selenosulphates.

(10) By treating di-β-naphthyl selenide with red selenium.

(11) By allowing potassium diselenide to react with diazotised β-naphthylamine.

Phenyl selenide, $C_6H_5.SeH$.[1]—This selenide may be obtained as follows : (1) Selenium tetrachloride is allowed to react with benzene in the presence of aluminium chloride. (2) Magnesium phenyl bromide in ether solution is treated with finely divided selenium and the addition product treated with cold hydrochloric acid. The ether layer is then removed, the extracted solution treated with more ether and the extracts combined, then shaken with one equivalent of sodium hydroxide, calculated on the basis of the total amount of selenium used, and dissolved in water to make a 25 per cent. solution. The ether solution is then dried with calcium chloride, the ether removed and the residue distilled, diphenyl diselenide and diphenyl selenide, B.pt. 303° C., being obtained. The sodium hydroxide solution on acidification with a slight excess of concentrated hydrochloric acid, followed by three more extractions with ether, gives on removal of the solvent almost pure phenyl selenide, B.pt. 182° C. The product melts at 60° C., and is insoluble in water, but dissolves in alcohol; mercuric chloride gives a white precipitate.[2]

o-Aminophenyl selenide,[3]



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[1] Taboury, *Bull. Soc. chim.*, 1903, iii, 29, 761; *Ann. Chim. Phys.*, 1908, 15, 5; *Bull. Soc. chim.*, 1906, iii, 35, 668; Foster and Brown, *J. Amer. Chem. Soc.*, 1928, 50, 1182; Chabrié, *Bull. Soc. chim.*, 1894, iii, 11, 1080; *Compt. rend.*, 1889, 109, 182.

[2] Compare Krafft and Lyons, *Ber.*, 1894, 27, 1768; Stoecker and Krafft, *Ber.*, 1906, 39, 2197.

[3] Bogert and Stull, *J. Amer. Chem. Soc.*, 1927, 49, 2011; compare Bauer, *Ber.*, 1913, 46, 92.

is isolated as the *zinc salt* by reducing di-*o*-aminophenyl diselenide, the yield being 81 per cent. The pure salt is practically colourless, but it rapidly turns yellow and then brown in the light.

p-Chlorophenyl selenide,[1]

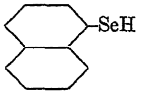
is isolated as described in the foregoing by the aid of the Grignard reagent. It crystallises in small, colourless laminæ, M.pt. 55° C. *p-Bromophenyl selenide* melts at 75° to 77° C. Both compounds readily oxidise in air to the corresponding diselenides.

p-Methylphenyl selenide,

separates from ether in colourless plates, M.pt. 46° to 47° C., rapidly oxidising to the diselenide.

p-Ethoxyphenyl selenide, $C_2H_5O.C_6H_4.SeH$, is a colourless liquid, heavier than water, B.pt. 156° to 158° C. at 24 mm., oxidation of its dilute potassium hydroxide solution yielding the diselenide.

α-Naphthyl selenide,



occurs when magnesium α-naphthyl bromide in ether solution is treated with metallic selenium in the usual way. It is a pale yellow liquid, B.pt. 165° to 167° C. at 20 mm., and evolves hydrogen selenide when heated at atmospheric pressure.

Diphenyl selenide, $(C_6H_5)_2Se$, may be prepared in several ways:

(1) Diphenylsulphone (1 mol.), when heated with one atomic proportion of precipitated selenium (red), evolves sulphur dioxide. After several hours' heating the mixture is distilled and the yellowish-red oily distillate collected.[2]

$$C_6H_5.SO_2.C_6H_5 + Se = C_6H_5.Se.C_6H_5 + SO_2$$

(2) Benzene (3 parts) and one part of selenium tetrachloride are heated together under reflux in the presence of anhydrous aluminium chloride until no further evolution of hydrogen chloride occurs.[3] Benzene, aluminium bromide and selenium bromide interact to give bromobenzene and a 22 to 27 per cent. yield of diphenyl selenide.[4]

(3) Phenyl magnesium bromide and selenium bromide react to form diphenyl selenide as one product.[5]

(4) Mercury diphenyl and powdered selenium react at 220° to 230° C. to form the diphenyl selenide.[6]

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[1] Taboury, *loc. cit.*

[2] Krafft and Vorster, *Ber.*, 1893, 26, 2813; compare Chabrié, *Bull. Soc. chim.*, 1894, [iii], 11, 1080.

[3] Chabrié, *Bull. Soc. chim.*, 1889, [iii], 2, 788. Selenium oxychloride in the presence of aluminium chloride and selenious anhydride also reacts with benzene.

[4] Loevenich and Sipmann, *J. prakt. Chem.*, 1930, [ii], 124, 127.

[5] Pieroni and Balduzzi, *Gazzetta*, 1915, 45, [ii], 106.

[6] Krafft and Lyons, *Ber.*, 1894, 27, 1768; compare Lesser and Weiss, *Ber.*, 1914, 47, 2510.

(5) The best method, however, appears to be as follows:[1] Powdered potassium hydroxide (360 grams) and 240 grams of black powdered selenium are thoroughly mixed and heated in an oil-bath at 140° C., at which temperature they fuse together. The mass is then dissolved in 400 c.c. of ice water and treated slowly with the diazotised product from 138 grams of aniline. To complete the reaction the solution is separated from the viscous selenium-containing black mass in the bottom of the reaction vessel and heated to boiling. Whilst still hot the liquid is poured upon the black viscous mass, which is then stirred up with it. The precipitate of selenium is filtered off and the lower layer of the filtrate, consisting of diphenyl selenide, separated. The selenium is washed with ether or chloroform and the washings combined with the selenide. The combined liquids are distilled, the fraction boiling at 300° to 315° C. being the pure diphenyl selenide. The yield is 125 grams, or 72 per cent. based on the aniline used.

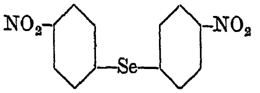
$$2C_6H_5N_2Cl + K_2Se = (C_6H_5)_2Se + 2N_2 + 2KCl$$

Diphenyl selenide is a colourless, strongly refractive oil, B.pt. 167° C. at 16·5 mm.; insoluble in water but miscible with alcohol or ether in all proportions. It has a faint odour, and a density of 1·3712 at 0° C., 1·3561 at 15·2° C., and 1·350 at 20° C. With cold bromine in ether solution it yields the *dibromide*. Diphenyl selenide, unlike dimethyl selenide, does not combine with alkyl iodides, and in this respect it resembles diphenyl sulphide.[2] When heated nearly to its boiling-point with sulphur it gives diphenyl sulphide, the reaction being practically quantitative at 300° C.[3] With *palladium chloride* it forms the *complex* $PdCl_2.2(C_6H_5)_2Se$, orange-red needles, M.pt. 181° to 182° C.[4]

Dibromophenyl selenide, $(C_6H_4Br)_2Se$, occurs when bromine reacts with diphenyl selenide. It crystallises from alcohol in brilliant white, hexagonal prisms, M.pt. 112° C.

Di-m-aminophenyl selenide, $(C_6H_4NH_2)_2Se$,[5] obtained from magnesium *m*-aminophenyl bromide and selenium bromide, is a yellowish-brown, heavy, viscous oil, B.pt. 130° to 150° C. *in vacuo*. When treated with an ether solution of *bromine* it yields the *compound* $(Br.C_6H_3.NH_2.HBr)_2Se$, which crystallises in tufts of needles, M.pt. 115° to 116° C.

pp′-Dinitrodiphenyl selenide,[6]



Phosphorus pentaselenide, 24 grams, is boiled with 23 grams of powdered selenium in an aqueous alcohol solution of sodium hydroxide for two to three hours. To the resulting solution 39 grams of *p*-chloronitrobenzene in hot alcohol are added and boiling continued for a further two hours. The precipitate which forms is washed with water and extracted with boiling ethyl acetate. The selenide melts at 170° to 171° C.[7]

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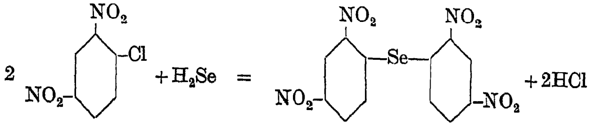
[1] Leicester and Bergstrom, *J. Amer. Chem. Soc.*, 1929, 51, 3587.
[2] Chabrié, *Compt. rend.*, 1889, 109, 182.
[3] Krafft and Steiner, *Ber.*, 1901, 34, 560.
[4] Fritzmann, *Zeitsch. anorg. Chem.*, 1914, 133, 119.
[5] Pieroni and Balduzzi, *loc. cit.*
[6] Baker and Moffitt, *J. Chem. Soc.*, 1930, p. 1722.
[7] Compare Bogert and Anderson, *J. Amer. Chem. Soc.*, 1927, 49, 2011.

2 : 4 : 2′ : 4′-Tetranitrodiphenyl selenide, $[C_6H_3(NO_2)_2]_2Se$.[1]—This occurs as a by-product in the preparation of 2 : 4-dinitrophenylselenoacetic acid, p. 11, and is probably formed as shown below.



It separates from 90 per cent. acetic acid as brownish-yellow needles, M.pt. 195° to 196° C.

Phenyl methyl selenide, $C_6H_5.Se.CH_3$,[2] is a pale yellow oil, B.pt. 200° to 201° C., obtained by the action of methyl iodide on sodium phenyl selenide.

Phenyl ethyl selenide, $C_6H_5.Se.C_2H_5$.[3]—Phenyl selenide (10 grams) is dissolved in one equivalent of sodium hydroxide in the minimum of water, 50 c.c. of absolute alcohol then added, followed by 20 grams of ethyl bromide. The mixture is heated under reflux for fifteen minutes, then diluted with four times its volume of cold water, extracted three times with ether, the extract washed with water, dried over calcium chloride and distilled. Rectification of the oil obtained gives a 72 per cent. yield of the required selenide, boiling at 214° to 216° C. Treatment with bromacetic acid converts the selenide into phenylselenoglycollic acid.[4]

Phenyl isoamyl selenide, $C_6H_5.Se.C_5H_{11}$,[5] is obtained by a similar operation to that used for phenyl ethyl selenide. The yield is about 86 per cent., and the product boils at 105° C. at 3 mm.

Di-o-tolyl selenide, $Se(CH_3.C_6H_4)_2$.[6]—This is prepared by the action of selenium on magnesium *o*-tolyl bromide, and is isolated during the preparation of *o*-tolylselenoglycollic acid after extraction of the ether solution of selenomagnesium bromide with aqueous potassium hydroxide. Repeated crystallisation from absolute alcohol gives flat, colourless, shining plates, M.pt. 64° C. This selenide also occurs when mercury di-*o*-tolyl is heated with metallic selenium : [7]

$$(C_7H_7)_2Hg + 2Se = (C_7H_7)_2Se + HgSe$$

Five per cent. of selenium in excess of that required by the foregoing equation is used. The mixture is heated for twelve hours at 220° C., then for a short time at 235° to 240° C. By this method the selenide is obtained in rectangular plates, M.pt. 61° to 62° C., B.pt. 186° C. at 16 mm. When aluminium and selenium bromides react with toluene, the chief product is *o*-bromotoluene, but a small amount of di-*o*-tolyl selenide also results, B.pt. 174° to 180° C. at 13 mm.[8] It yields a dibromide on treatment with bromine and a nitrate with nitric acid.

Di-p-tolyl selenide, $Se(C_6H_4.CH_3)_2$, may be isolated by heating together 10 parts of mercury di-*p*-tolyl, 4·2 parts of selenium and 2 parts

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[1] Behaghel and Rollmann, *Ber.*, 1929, 62, [B], 2696.

[2] Krafft and Lyons, *Ber.*, 1894, 27, 1768; Pope and Neville, *Proc. Chem. Soc.*, 1902, p. 198.

[3] Foster and Brown, *J. Amer. Chem. Soc.*, 1928, 50, 1182.

[4] Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2293.

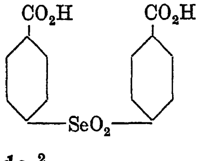
[5] Foster and Brown, *loc. cit.*

[6] Porritt, *J. Chem. Soc.*, 1927, p. 27.

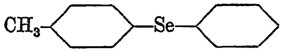
[7] Zeiser, *Ber.*, 1895, 28, 1670.

[8] Loevenich and Sipmann, *J. prakt. Chem.*, 1930, [ii], 124, 127.

of benzene for twelve hours at 225° C., and finally for a short time at 230° C. The mixture is fractionated under reduced pressure, the selenide boiling at 196° to 196·5° C. at 16 mm. It forms colourless crystals, M.pt. 69° to 69·5° C., which soon become yellow. It also occurs as a by-product during the interaction of selenic acid and toluene.[1] It combines with bromine to form a *dibromide,* and oxidation with hot permanganate solution converts it into *diphenylselenone-4 : 4′-dicarboxylic acid,*

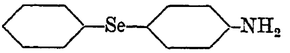


Phenyl p-tolyl selenide,[2]



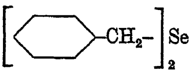
116 grams of phenyl *p*-tolyl sulphone (M.pt. 127° to 128° C.) and 40 grams of powdered selenium are heated together on a metal-bath until sulphur dioxide is freely evolved. After two to three hours the temperature is raised, and phenyl *p*-tolyl selenide distils at 305° to 312° C. Redistillation gives a pale yellow mobile liquid, B.pt. 175° to 178° C. at 20 mm., the yield being about 35 grams. When treated with bromine in carbon disulphide solution the selenide is converted into the *dibromide,* $(CH_3.C_6H_4)(C_6H_5)SeBr_2$, which separates from carbon disulphide as long, orange-red, glistening needles, M.pt. 149° to 150° C.

4-Aminodiphenyl selenide,



A mixture of 20 grams of benzeneseleninic acid and 80 c.c. of aniline is heated at 110° to 115° C. for six hours. Excess aniline is then removed by steam distillation and the dark-coloured residue extracted with hot dilute hydrochloric acid. The addition of sodium carbonate to the extract precipitates the selenide as a pink microcrystalline powder (yield, 12 to 15 grams). It dissolves in hot dilute hydrochloric acid, and on cooling the *hydrochloride* separates as small, feathery needles, M.pt. 159° C. The free base forms almost colourless prismatic needles, M.pt. 93° to 94° C.

Dibenzyl selenide,



This selenide may be obtained as follows : (1) Phosphorus pentaselenide (P_2Se_5) is treated with alcoholic sodium hydroxide until sodium selenide is produced, air being excluded during the operation. Benzyl chloride is then added and the mixture heated under reflux. Evaporation away of the solvent yields white needles of the selenide, together with yellow scales of the diselenide.[3] (2) Potassium selenosulphate is

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[1] Doughty and Elder, *Eighth Inter. Congress Applied Chemistry,* 1912, 6, 93.
[2] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.,* 1928, p. 2280.
[3] Jackson, *Ber.,* 1875, 8, 109; *Annalen,* 1875, 179, 1.

slowly added dropwise to a boiling alcoholic solution of benzyl chloride.[1] (3) Two molecular equivalents of sodium ethoxide are boiled with one equivalent of dibenzyl diselenide in alcohol until a deep brown colour develops. Benzyl chloride is then added dropwise, the solution decolorising and sodium chloride separating. The reaction is completed by boiling, and after steam distillation the selenide is left as a residue. It crystallises in white needles or colourless prisms, M.pt. 45·5° C., insoluble in water, readily soluble in alcohol or ether. It forms a *platinochloride*, $[(C_7H_7)_2Se]_2.PtCl_4$, a yellow powder, insoluble in water, sparingly soluble in alcohol, not isolated in a crystalline form.

Benzyl α-naphthyl selenide, $(C_6H_5.CH_2)Se(C_{10}H_7)$.[2]—This selenide is produced when the complex obtained from magnesium α-naphthyl bromide and metallic selenium is treated with benzyl chloride. It forms small colourless prisms from alcohol, M.pt. 68° to 69° C. It yields a *picrate*, which separates from ether in orange-red needles, M.pt. 118° C.

Benzyl p-tolyl selenide, $(C_6H_5.CH_2)Se(C_6H_4.CH_3)$, crystallises in small colourless laminæ, M.pt. 32° to 33° C.

Benzyl methyl selenide,[3] $(C_6H_5.CH_2)Se(CH_3)$, is prepared from dibenzyl selenide and methyl iodide. Ethyl iodide gives *benzyl ethyl selenide*, and ethylene dibromide forms *dibenzyl ethylene selenide*, $C_2H_4(Se.C_7H_7)_2$, M.pt. 68° to 69° C., crystallising in pale yellow needles.

Di-α-naphthyl selenide, $(C_{10}H_7)_2Se$.[4]—The preparation of this compound depends upon the following reaction :

$$(C_{10}H_7)_2Hg + 2Se = (C_{10}H_7)_2Se + HgSe$$

Mercury di-α-naphthyl, 4·5 grams, and 1·58 grams of selenium are heated together in a Wood's metal-bath at 190° C. under a pressure of 16 mm. for about 12 hours. Above 200° C. the reaction takes another course, giving mercury and naphthalene. The melt, after cooling, is steam distilled and the residue extracted with ether. The extracts give a 54 per cent. yield of selenide on removal of the solvent. Crystallisation from absolute alcohol gives pale yellow glistening leaflets, M.pt. 114° C., which rapidly decompose on exposure to air and light.

Diphenyl diselenide, $(C_6H_5)_2Se_2$, is formed as a by-product in the preparation of phenyl selenide when magnesium phenyl bromide in ether solution reacts with selenium.[5] A 2 per cent. yield is obtained when benzene, aluminium and selenium bromides react in dilute carbon disulphide solution. The product melts at 62° C.[6] The corresponding *oxide* is an oil, B.pt. 230° C. at 65 mm.,[7] and the *sulphide*, $(C_6H_5)_2Se_2S$, M.pt. 55° C., is obtained from sulphur chloride and phenyl selenide in carbon disulphide solution.[8]

Di-o-nitrophenyl diselenide, $(NO_2.C_6H_4)_2Se_2$.[9]—A mixture of 25 grams of sodium in 250 to 300 c.c. of 95 per cent. alcohol is refluxed

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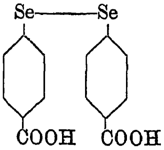
[1] Fromm and Martin, *Annalen*, 1913, 401, 177.
[2] Taboury, *Bull. Soc. chim.*, 1906, [iii], 35, 668.
[3] Fromm and Martin, *loc. cit.*
[4] Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831.
[5] Foster and Brown, *J. Amer. Chem. Soc.*, 1928, 50, 1182; compare Baroni, *Atti R. Accad. Lincei*, 1930, [vi], 11, 579.
[6] Loevenich and Sipmann, *J. prakt. Chem.*, 1930, [ii], 124, 127.
[7] Chabrié, *Bull. Soc. chim.*, 1894, [iii], 11, 1080.
[8] Baroni, *loc. cit.*
[9] Bogert and Stull, *J. Amer. Chem. Soc.*, 1927, 49, 2011.

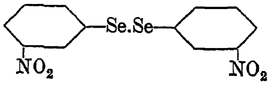
until the solution is clear, when 16 grams of finely-divided selenium are added and the refluxing continued for half an hour longer. The solution is then stirred into 50 grams of *o*-nitrochlorobenzene in 100 c.c. of alcohol and the mixture refluxed for two or three hours. The diselenide separates as the solution cools and is filtered off, washed with water and alcohol, then recrystallised from glacial acetic acid. The yield is 37 grams, or 57 per cent. The product is a pale brownish microcrystalline solid, M.pt. 209° C. (corr.), readily soluble in benzene. The melting-point has also been reported as 206·2° to 206·5° C. (corr.),[1] and 209° C. when the selenide is obtained by a different method.[2]

4 : 4′-Dicarboxydiphenyl diselenide,[3]



46 grams of *p*-aminobenzoic acid in 750 c.c. of water and 83 c.c. of concentrated hydrochloric acid are vigorously stirred and cooled whilst 230 c.c. of 10 per cent. sodium nitrite are added. After thirty minutes the solution is made alkaline to Congo red by the addition of potassium acetate, and a solution of potassium selenocyanate (96 c.c. of 50 per cent. solution) gradually added. After three hours' stirring the light brown insoluble material is filtered off; it consists mainly of an inseparable mixture of *p-carboxyphenyl selenocyanate* and 4 : 4′-dicarboxydiphenyl diselenide. To convert the selenocyanate to diselenide, the mixture is dissolved in 2*N* sodium hydroxide solution, the solution boiled for an hour, cooled, filtered and acidified. The precipitated 4 : 4′-dicarboxydiphenyl diselenide (32 grams) separates from methyl alcohol as a pale yellow microcrystalline powder, M.pt. 297° C.

Di-m-nitrophenyl diselenide,[4]



24 grams of *m*-nitrophenylseleninic acid in 250 c.c. of boiling water are treated with a saturated solution of sodium hydrogen sulphite so long as a turbidity is produced. Cooling and stirring gives an oil, which soon crystallises. The yield is about 21 grams. Recrystallisation from ether gives yellow spears, M.pt. 83° C. (corr.), insoluble in water, moderately soluble in cold alcohol or ether, more soluble on warming.

Di-m-aminophenyl diselenide, $(NH_2.C_6H_4)_2Se_2$, may be obtained in three ways: (1) The foregoing compound is reduced by an alkaline solution of sodium sulphide. (2) *m*-Nitrophenyl selenocyanate is reduced by tin and hydrochloric acid. (3) Diazotised *m*-nitroaniline is treated with potassium selenocyanate.[5] The *dihydrochloride* crystallises from dilute hydrochloric acid in yellow grains formed of small needles melting with decomposition at 291° to 292° C. (corr.).[6] It readily

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[1] Bogert and Anderson, *Proc. Nat. Acad. Sci.*, 1925, 11, 217.

[2] Bauer, *Ber.*, 1913, 46, 92.

[3] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2280.

[4] Pyman, *Trans. Chem. Soc.*, 1919, 115, 166.

[5] Challenger and Peters, *J. Chem. Soc.*, 1928, p. 1364.

[6] Pyman, *loc. cit.*

dissolves in hot hydrochloric acid, but is sparingly soluble in the cold dilute acid. The dihydrochloride reacts with acetic anhydride yielding *di-m-acetamidophenyl diselenide*, $(CH_3.CO.NH.C_6H_4)_2Se_2$, which crystallises from hot glacial acetic acid in rosettes of short yellow needles, M.pt. 185° to 186° C. (corr.). The acetamido-compound is anhydrous, insoluble in water or ether, readily soluble in hot alcohol. The diselenide obtained by method (3) crystallises from light petroleum or acetone-light petroleum in almost colourless plates, M.pt. 65° C.

Di-p-chlorophenyl diselenide, $(C_6H_4Cl)_2Se_2$, occurs when *p*-chloroselenophenol oxidises in the air.[1] It forms yellow needles, M.pt. 85° to 86° C. *Di-p-bromophenyl diselenide* separates from alcohol in yellow needles, M.pt. 107° to 108° C.

Di-p-ethoxyphenyl diselenide, $(C_6H_4.OC_2H_5)_2Se_2$, is obtained by oxidising *p*-ethoxyselenophenol with dilute potassium hydroxide solution. It forms brilliant yellow laminæ, M.pt. 65° C.

Di-p-tolyl diselenide, $(C_6H_4.CH_3)_2Se_2$, from *p*-selenocresol, separates from alcohol as orange needles, M.pt. 47° C.

Dibenzyl diselenide, $(C_6H_5.CH_2)_2Se_2$.—This compound may be obtained in a variety of ways : (1) Sodium selenide is heated for several hours under reflux with benzyl chloride in alcoholic solution.[2] (2) A good yield of the diselenide results when a solution of selenium in sodium sulphide or sodium hydroxide is shaken on a machine with benzyl chloride.[3] (3) Potassium selenosulphate is shaken with the calculated quantity of benzyl chloride in the cold. (4) An alcohol solution of potassium benzyl selenosulphate is treated with an excess of iodine, and the diselenide remaining in solution is precipitated by the addition of water. The precipitate is collected immediately and recrystallised from alcohol, since the presence of iodine appears to aid decomposition, with deposition of selenium, and it is also necessary to wash the crystals with water to remove any traces of hydriodic acid before drying the product.[4] (4) An aqueous solution of potassium benzyl selenosulphate is subjected to electrolysis, using a current of 0·25 to 0·5 ampère, the method of operation being similar to that used for di-*p*-nitrobenzyl diselenide.

Dibenzyl diselenide crystallises from alcohol in yellow needles, which are slightly deeper in colour than those of the *p*-nitrobenzyl compound, and melt at 92° to 93° C. Exposure to light for an hour or so causes the crystals to turn red. The selenide readily dissolves in hot alcohol, but is only sparingly soluble in ether, insoluble in water. Oxidation with fuming nitric acid converts it into benzyl seleninic acid, and boiling with copper or mercury in suspension precipitates selenium. Boiling with iodine in chloroform solution gives the *tetra-iodide*, M.pt. 98° C. ; the *tetrabromide* melts at 137° C.[5]

Di-p-nitrobenzyl diselenide,[6] $(NO_2.C_6H_4.CH_2)_2Se_2$.—An alcoholic solution of iodine is added to a solution of potassium *p*-nitrobenzyl selenosulphate in alcohol until the colour of the iodine persists ; water is then added to precipitate the last traces of diselenide. The latter is then recrystallised from alcohol containing a drop of sulphurous acid,

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[1] Taboury, *loc. cit.*

[2] Jackson, *Ber.*, 1874, 7, 1277; *Annalen*, 1875, 179, 1.

[3] Fromm and Martin, *Annalen*, 1913, 401, 177.

[4] Price and Jones, *Trans. Chem. Soc.*, 1909, 95, 1729.

[5] Fromm and Martin, *loc. cit.*

[6] Price and Jones, *loc. cit.*

a felted mass of canary-yellow crystals, M.pt. 107·5° C., being isolated. On exposure to light these gradually become red, owing to the liberation of selenium. Alcoholic sodium hydroxide gives no immediate precipitate with the diselenide in the cold, but a deep red colour on warming.

Di-m-nitrobenzyl diselenide, $(NO_2.C_6H_4.CH_2)_2Se_2$, may be isolated in a similar way to the foregoing compound or by electrolytic reduction of the selenosulphate. It crystallises from alcohol in flat needles, having a faint yellow tinge and melting at 106° C. It is much more stable towards diffused daylight than the *p*-diselenide, but prolonged exposure gradually causes the product to acquire a red tinge. With alcoholic sodium hydroxide a red colour is produced on warming.

Di-o-nitrobenzyl diselenide, $(NO_2.C_6H_4.CH_2)_2Se_2$, may be prepared by the usual methods, but not by electrolytic reduction of the corresponding selenosulphate. It crystallises from alcohol in yellow plates, M.pt. 103·5° C., which have similar properties to the *meta-* and *para-*compounds.

The following details are available in connection with the electrolytic reduction of selenosulphates to diselenides: the filtrate obtained in the preparation of, *e.g.*, potassium *p*-nitrobenzyl selenosulphate is electrolysed at the cathode in a divided cell after the addition of 6 grams of potassium hydrogen carbonate. A rotating cathode (area = 0·5 sq. dcm.) is used, and 0·25 ampère of current passed for one hour, and 0·5 ampère for another hour. A copious precipitate of the diselenide is formed. The filtrate from this precipitate on standing in the dark overnight gave a deposit of selenium. This was filtered off and the filtrate again electrolysed, but no more diselenide was produced, the only result being a further deposit of selenium.

Di-α-naphthyl diselenide, $(C_{10}H_7)_2Se_2$, crystallises from alcohol as orange-yellow prisms, M.pt. 87° to 88° C.[1]

Di-β-naphthyl diselenide, $(C_{10}H_7)_2Se_2$,[2] may be obtained as follows: (1) By dissolving β-naphthyl selenide, $C_{10}H_7.SeH$, in ether and allowing it to oxidise by exposure to the air. The yellow crystalline product melts at 126° to 127° C. and has the composition $C_{10}H_7Se.SeC_{10}H_7$. (2) Red selenium is allowed to react with di-β-naphthyl selenide. The resulting yellow powder melts at 112° to 114° C., and appears to be the isomeric *di-β-naphthyl selenoselenide,* $(C_{10}H_7)_2Se : Se$. (3) The latter product may also be obtained from diazotised β-naphthylamine and potassium diselenide. The selenoselenide loses selenium on prolonged treatment with boiling alcohol, whereas the diselenide is completely stable under similar conditions. The latter is not affected by oxidising agents, which convert the selenoselenide into a selenoxide and finally a selenone.

COMPOUNDS OF THE TYPES R_2SeX_2 AND R_2SeO.

When diaryl selenides in carbon disulphide, carbon tetrachloride or chloroform solution are treated with bromine, direct addition occurs, yielding dibromides, R_2SeBr_2. In some cases the dichlorides have been obtained by direct chlorination, but they are usually isolated by the action of hydrochloric acid on the selenoxides or dinitrates.

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[1] Taboury, *loc. cit.*

[2] Loevenich, Fremdling and Föhr, *Ber.*, 1929, 62, [B], 2856.

Dibenzyl selenide gives an iodide when allowed to react with iodine in chloroform solution. Dinitrates are formed when nitric acid (density 1·4) acts upon diaryl selenides or upon their dibromides. The dihalides have their halogen removed by moist silver oxide, the hydroxides resulting. When sodium hydroxide is used they are transformed to the oxides, R_2SeO, which also result when diaryl selenides are oxidised by " perhydrol."

Diphenyl selenium dibromide, $(C_6H_5)_2SeBr_2$,[1] occurs in 95 per cent. yield when 7 grams of diphenyl selenide in 15 c.c. of carbon disulphide are mixed with 4·9 grams of bromine in 15 c.c. of the same solvent. It crystallises in prisms,[2] M.pt. 154° C., which give the following measurements : $a : b : c = 0{\cdot}90231 : 1 : 0{\cdot}37583$.[3] It is decomposed by water or alcohols, and the addition of sodium hydroxide yields the oxide. The dibromide, when heated at its melting-point, suffers decomposition according to the equation

$$(C_6H_5)_2SeBr_2 = C_6H_5.Se.C_6H_4Br + HBr$$

and a secondary reaction takes the following course :

$$2(C_6H_5)_2SeBr_2 = (C_6H_5)_2Se + (C_6H_4Br)_2Se + 2HBr$$

Diphenyl selenium dichloride, $(C_6H_5)_2SeCl_2$, is formed when diphenyl selenoxide is treated with hydrochloric acid. It crystallises in glistening prisms, M.pt. 179° to 180° C.[4] A similar product is obtained when diphenyl selenide is dissolved in an excess of concentrated nitric acid and concentrated hydrochloric acid added.[5]

Diphenyl selenoxide, $(C_6H_5)_2SeO$.—This oxide may be prepared in several ways : (1) Diphenyl selenium dichloride is treated with sodium hydroxide.[6] (2) Diphenyl selenium dibromide is allowed to react with sodium hydroxide.[7] (3) 7 grams of diphenyl selenide are slowly treated with 10 c.c. of " perhydrol." [8] (4) Diphenyl selenoxide hydronitrate, $(C_6H_5)_2SeO.HNO_3$, is treated with sodium carbonate.[9] The melting-point of the oxide obtained by methods (1) and (4) is 106° to 108° C. ; by methods (2) and (3) it is 113° to 114° C. In each case the crude product is recrystallised from benzene. The substance absorbs one molecule of water if allowed to stand in the air.

Diphenyl selenium disulphide,[10] $(C_6H_5)_2SeS_2$, results from the action of selenium chloride on a solution of thiophenol in carbon disulphide. It melts at 50° to 51° C.

Chlorodiphenyl selenoxide, $(ClC_6H_4)(C_6H_5)SeO$,[11] is isolated as a by-product when phenyl selenide is prepared by the Friedel-Craft reaction. It melts at 94° C. If dibromophenyl selenide is mixed with hydrogen peroxide and hydrochloric acid and the whole treated with a current of air, white crystals are formed which have the composition

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[1] Krafft and Lyons, *Ber.*, 1894, 27, 1761; Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2293.

[2] Krafft and Vorster, *Ber.*, 1893, 26, 2813.

[3] Billows, *Chem. Zentr.*, 1905, I, 930.

[4] Krafft and Vorster, *loc. cit.*

[5] Leicester and Bergstrom, *loc. cit.*

[6] Krafft and Vorster, *loc. cit.*

[7] Krafft and Lyons, *loc. cit.*

[8] Edwards, Gaythwaite, Kenyon and Phillips, *loc. cit.*

[9] Foster and Brown, *J. Amer. Chem. Soc.*, 1928, 50, 1182.

[10] Baroni, *Atti R. Accad. Lincei*, 1930, [vi], 11, 579.

[11] Chabrié, *Bull. Soc. chim.*, 1894, iii, 11, 1080.

$ClC_6H_4.Se.C_6H_4OH$. These melt at 145° C., dissolve in potassium hydroxide, and when treated with nitric acid yield long needles, M.pt. 188° C.[1]

Di-o-tolyl selenium dichloride, $(C_7H_7)_2SeCl_2$,[2] is a white product, M.pt. 152° to 153° C. with decomposition, formed from the corresponding oxide by the action of concentrated hydrochloric acid.

Di-o-tolyl selenium dibromide, $(C_7H_7)_2SeBr_2$.—Di-*o*-tolyl selenide unites with bromine to give the dibromide, but the product is not very stable and an odour of bromine is soon apparent. The compound forms glistening needles, decomposing at 84° C.

Di-o-tolyl selenoxide, $(C_7H_7)_2SeO$.—This is best obtained by treating the dichloride with dilute sodium hydroxide and warming for a short time. The dibromide is less suitable for the preparation owing to its instability. Recrystallisation of the oxide from benzene yields glistening plates, M.pt. 116° C., soluble in water, probably forming a *hydrate*.

Di-o-tolyl selenium dinitrate, $(C_7H_7)_2Se(NO_3)_2$.—The dibromide, when allowed to react with nitric acid (density 1·4), yields the dinitrate.

Di-p-tolyl selenium dichloride, $(C_7H_7)_2SeCl_2$, forms white needles, M.pt. 177° to 178° C. with decomposition.

Di-p-tolyl selenium dibromide, $(C_7H_7)_2SeBr_2$, crystallises in yellowish-red prisms, melting at 162° C. with decomposition.

Di-p-tolyl selenoxide, $(C_7H_7)_2SeO$, occurs when the dichloride is treated with dilute sodium hydroxide solution. It separates from benzene in small, glistening, white needles, melting at about 96° C., and soluble in water.

Dihydroxydiphenyl selenide, $(C_6H_4.OH)_2Se$,[3] occurs when phenol reacts with selenious acid. Phenoxyacetic acid gives **dianisylselenoxide-$\omega\omega'$-dicarboxylic acid,** $(C_6H_4.OCH_2.CO_2H)_2SeO$, decomposing at 210° C.

Dibenzyl selenium dichloride,[4] $(C_6H_5.CH_2)_2SeCl_2$, occurs when an alcoholic solution of the dinitrate is treated with hydrogen chloride, or when benzylseleninic acid is treated with phosphorus pentachloride. It crystallises in colourless needles, M.pt. 134° to 135° C.[5]

Dibenzyl selenium dibromide, $(C_6H_5.CH_2)_2SeBr_2$.[6]—The existence of this compound seems doubtful, but it is said to result when the hydrogen chloride in the foregoing preparation is replaced by hydrogen bromide. Dibenzyl selenide and bromine in chloroform yield a red powder of melting-point 84° C.[7]

Dibenzyl selenium di-iodide, $(C_6H_5.CH_2)_2SeI_2$.—When dibenzyl selenide is heated with iodine in chloroform solution, dark violet crystals of the di-iodide separate, M.pt. 97° C. The halogen in this and the foregoing compound is removed by alkali, silver oxide or silver acetate.

Dibenzyl selenium dinitrate, $(C_6H_5.CH_2)_2Se(NO_3)_2$.—The interaction of dibenzyl selenide and nitric acid gives rise to a dinitrate, according to Jackson.[8] This crystallises from alcohol in shining rhombic crystals, M.pt. 88° C. Fromm and Martin,[9] however, state

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[1] Chabrié, *Compt. rend.*, 1889, 109, 182.

[2] Zeiser, *Ber.*, 1895, 28, 1670.

[3] Takamatsu, *J. Pharm. Soc. Japan*, 1928, No. 555, 450.

[4] Jackson, *Ber.*, 1875, 8, 109; *Annalen*, 1875, 179, 1.

[5] Lesser and Weiss, *Ber.*, 1924, 57, [B], 1077; compare Strecker and Willings, *Annalen*, 1875, 179, 13.

[6] Jackson, *loc. cit.*

[7] Compare Fromm and Martin, *Annalen*, 1913, 401, 177.

[8] Jackson, *loc. cit.*

[9] Fromm and Martin, *loc. cit.*

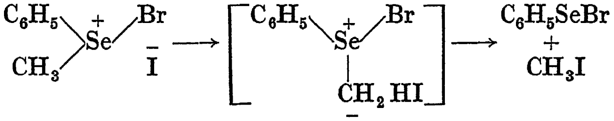
that the product of the reaction is tribenzylselenium nitrate, $(C_7H_7)_3SeNO_3$, crystallising in needles, M.pt. 102° to 103° C.

Phenyl methyl selenium dibromide, $(C_6H_5)(CH_3)SeBr_2$.[1]—Bromine, 33 grams in 30 c.c. of carbon disulphide, is added to 35 grams of phenyl methyl selenide in 120 c.c. of the same solvent. The additive product separates immediately as long, yellow, glistening needles, in 95 per cent. yield, turning brown at about 100° C. and melting with decomposition at 115° to 116° C. It is soluble in water to the extent of about 6 per cent., the colourless solution being acid to Congo red. When heated at 120° to 130° C. for about ten minutes, it decomposes quantitatively into methyl bromide and bromoselenobenzene.

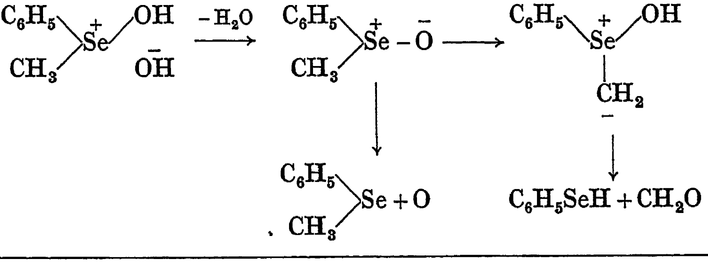
Phenyl ethyl selenium dibromide, $(C_6H_5)(C_2H_5)SeBr_2$, is isolated in a similar manner to the methyl compound. It crystallises from ether in light red, transparent, stout, prismatic rods, M.pt. 84° C. When heated at 130° C. it decomposes quantitatively into ethyl bromide and bromoselenobenzene.

Phenyl methyl selenium di-iodide, $(C_6H_5)(CH_3)SeI_2$, occurs when the corresponding dibromide is triturated at 40° C. with a concentrated solution of potassium iodide. It crystallises from alcohol in glistening, purple, short prisms, M.pt. 69° to 71° C.

Phenyl methyl selenium bromo-iodide, $(C_6H_5)(CH_3)SeIBr$, is obtained when the dibromide is triturated with a cold solution of potassium iodide of the same concentration. The yield is quantitative, and the product separates from alcohol as red, ill-defined, compact crystals, M.pt. 85° C. with decomposition. Heating at 100° C. causes quantitative decomposition to methyl iodide and bromoselenobenzene, the reaction being represented as follows :



Phenyl methyl selenium dihydroxide, $(C_6H_5)(CH_3)Se(OH)_2$.—The dibromide (10 grams) is triturated with a suspension of 12 grams of silver oxide in 100 c.c. of water until the yellow colour disappears. Filtration, evaporation and desiccation yield about 8 c.c. of the hydroxide as a viscous oil. When heated at 100° C. at 15 mm., or at 170° C. at 760 mm., it decomposes, yielding phenyl methyl selenide, diphenyl diselenide and formaldehyde. The formation of formaldehyde is in agreement with the view that phenyl methyl selenoxide may exist in two isomeric forms, which, being unstable, decompose thus :



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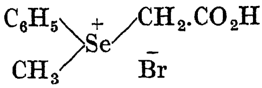
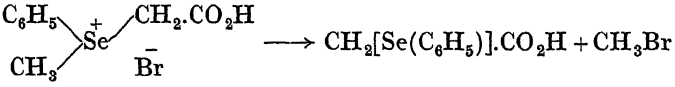
[1] Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2293.

Phenylmethylselenetine bromide,[1]



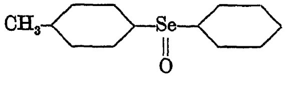
$$\left.\begin{array}{r}C_6H_5\\CH_3\end{array}\right>\overset{+}{Se}\left<\begin{array}{l}CH_2.CO_2H\\\overset{-}{Br}\end{array}\right.$$

Equimolecular quantities of phenyl methyl selenide (8·6 grams) and bromacetic acid (7 grams) are gently warmed together until molten and allowed to stand overnight; dry ether is then added, 7·6 grams of crystals being removed by filtration. Recrystallisation from a mixture of alcohol and ether gives the pure bromide, M.pt. 111° C. Treatment of the product with silver *d*-bromocamphorsulphonate gives a mixture of the two following salts, which are separated by crystallisation from alcohol: *d-Phenylmethylselenetine d-bromocamphorsulphonate* (*d*-B, *d*-A), $Se(C_6H_5)(CH_3)(CH_2.CO_2H)C_{10}H_{14}BrOSO_3$, which is the less soluble compound, forming needles, M.pt. 168° C., and giving the rotations $[\alpha]_D$ +61·26° and $[M]_D$ +330·8° in aqueous solution; *l-phenylmethylselenetine d-bromocamphorsulphonate* (*l*-B, *d*-A), the more soluble salt, forming minute white scales, M.pt. 151° C., and giving the rotations $[\alpha]_D$ +38·81° and $[M]_D$ +209·6° in aqueous solution. Since the *d*-bromocamphorsulphonic ion has the molecular rotation $[M_D]$ +270°, the corresponding value for the optically active selenetine ion is $[M]_D$ ±60·6°. The *d- and l-phenylmethylselenetine platinichlorides*, $[Se(C_6H_5)(CH_3)(CH_2.CO_2H)Cl]_2.PtCl_4$, form yellow prisms, M.pt. 171° C. They have the molecular rotations $[M]_D$ +55·0° and −54·3° respectively in acetone solution. *Phenylmethylselenetine mercuriodide*, $Se(C_6H_5)(CH_3)(CH_2.CO_2H)I.HgI_2$, may be prepared by precipitating either of the salts (*d*-B, *d*-A), (*l*-B, *d*-A), or phenylmethylselenetine bromide with a solution of potassium mercuric iodide. It forms white scales, M.pt. 141° to 142° C., and is optically inactive whichever method of preparation be used. This result is assumed to be due to the presence of sexavalent selenium. Phenylmethylselenetine bromide decomposes smoothly and quantitatively at its melting-point into methyl bromide and phenylselenoglycollic acid :



$$\left.\begin{array}{r}C_6H_5\\CH_3\end{array}\right>\overset{+}{Se}\left<\begin{array}{l}CH_2.CO_2H\\\overset{-}{Br}\end{array}\right. \longrightarrow CH_2[Se(C_6H_5)].CO_2H + CH_3Br$$

Phenyl p-tolyl selenoxide,[2]



is readily produced by triturating the corresponding dibromide with 15 per cent. sodium hydroxide solution until a white granular powder is formed. This is filtered off, washed, dried, and crystallised from benzene, from which it separates in clusters of feathery needles, M.pt. 131° to 133° C. A 25 per cent. yield of the selenoxide also results when the theoretical amount of potassium permanganate in boiling solution reacts with the selenide. Attempts to resolve the selenoxide

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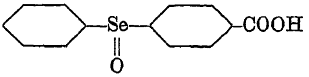
[1] Pope and Neville, *Proc. Chem. Soc.*, 1902, p. 198; *Trans. Chem. Soc.*, 1902, 81, 1552; Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2293.

[2] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2280.

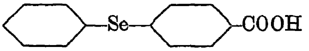
into optically active forms by means of *d*-camphorsulphonic acid have not been successful.

4-Carboxydiphenyl selenoxide,



Phenyl *p*-tolyl selenide in aqueous suspension is boiled with potassium permanganate for several hours. The manganese mud is dissolved and the 4-carboxydiphenyl selenoxide precipitated by passing in sulphur dioxide. After filtration the precipitate is macerated with dilute sodium carbonate solution, the products of oxidation being separated in this manner into phenyl *p*-tolyl selenoxide and 4-carboxydiphenyl selenoxide. Addition of dilute sulphuric acid to the sodium carbonate extract causes the separation of 4-carboxydiphenyl selenoxide, which is crystallised from alcohol. The product is a microcrystalline powder, melting with decomposition at 253° to 255° C. Attempts to resolve it into optically active forms have failed; the *l-menthylamine salt* melts at 220° to 222° C. with decomposition, and the *d-α-phenylethylamine salt* forms feathery needles, M.pt. 194° to 195° C. with decomposition.

4-Carboxydiphenyl selenide,

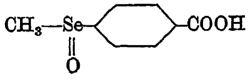


The foregoing selenoxide, 0·5 gram, and 0·3 gram of zinc dust in 15 c.c. of acetic acid, are warmed together on a steam-bath for three hours. The solution is filtered hot and diluted with water, 0·25 gram of the selenide separating as pale yellow glistening leaflets melting at 182° to 184° C. without decomposition. Treatment with bromine in carbon tetrachloride solution yields the *dibromide*, forming yellow, microcrystalline needles, becoming red and sintering at 180° to 190° C., and melting at 208° to 210° C. The latter compound also occurs when the selenoxide in acetic acid is treated with aqueous hydrobromic acid.

p-Carboxyphenyl methyl selenide,

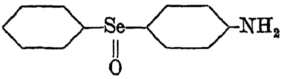
To a gently boiling solution containing 40 grams of 4 : 4′-dicarboxydiphenyl diselenide (p. 26) in 240 c.c. of 10 per cent. sodium hydroxide solution, 80 grams of sodium hydrosulphite or 12 grams of zinc dust are gradually added. After filtering and cooling the solution, 13 c.c. of methyl sulphate are added in small portions with stirring, and after an hour the crude selenide is precipitated by the addition of acid. When dry, the selenide is extracted with benzene to remove any diselenide, which is insoluble. The hot extract yields 20 grams of *p*-carboxyphenyl methyl selenide as a pale yellow microcrystalline powder, M.pt. 174° C. The selenide forms a *dibromide*, consisting of small orange-red needles, becoming deep red above 170° C. and melting at 198° to 199° C.

p-Carboxyphenyl methyl selenoxide,



may be prepared from the dibromide in the usual way, or by treating a methyl alcohol solution of the selenide with 30 per cent. hydrogen peroxide. It crystallises from alcohol in small, hard, irregular prisms, M.pt. 183° to 184° C. with decomposition, the molten product rapidly setting to a yellow solid which melts at about 250° C. The *brucine salt* melts at 105° to 110° C.

4-Aminodiphenyl selenoxide,[1]

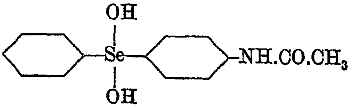


occurs when a solution containing 1·7 grams of 4-acetamidodiphenyl selenide dihydroxide in 15 c.c. of alcohol is heated with 10 c.c. of 3*N* sodium hydroxide for six hours. On cooling, 1·3 grams of the selenoxide separate as glistening needles, melting with decomposition at 188° to 189° C. The selenoxide may also be isolated by treating 7·5 grams of 4-aminodiphenyl selenide in 30 c.c. of acetone with 4·5 c.c. of "perhydrol," 5·2 grams of crude product separating out. Zinc dust and sodium hydroxide reduce the oxide to the corresponding selenide, and a similar result is obtained when the oxide is triturated with dilute hydrochloric acid, the reaction mixture filtered and sodium bicarbonate added to the filtrate.

4-Acetamidodiphenyl selenide,

4-Aminodiphenyl selenide, 3·8 grams, and 4 c.c. of acetic anhydride are heated together, when 4·2 grams of the acetyl derivative separate. Recrystallisation from aqueous alcohol yields glistening leaflets, M.pt. 169° to 170° C. 4-Acetamidodiphenyl selenide decomposes when heated with mineral acids, but hydrolysis goes smoothly under the following conditions : A solution of 2 grams of the selenide in 10 c.c. of alcohol is heated under reflux with 10 c.c. of 3*N* sodium hydroxide solution for six hours; on cooling, 1·65 grams of the base crystallise from the reaction mixture.

4-Acetamidodiphenyl selenide dihydroxide,



To a cooled mixture of 5·8 grams of 4-acetamidodiphenyl selenide and 10 c.c. of glacial acetic acid, 4 c.c. of "perhydrol" are gradually added. About 5·7 grams of the dihydroxide separate on standing, crystallisation from 700 c.c. of boiling water giving a product melting with decomposition at 147° to 148° C. Reduction by zinc dust and glacial acetic acid, or heating at 100° C. with *N*/2 hydrochloric acid, gives 4-acetamidodiphenyl selenide. Heating alone under specific conditions can transform the dihydroxide to the selenide.

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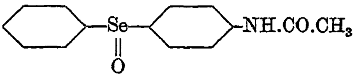
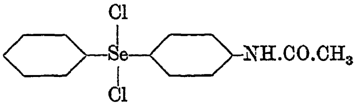
[1] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2287.

4-Acetamidodiphenyl selenoxide,



The foregoing dihydroxide, when heated under a pressure of 20 mm., effervesces vigorously at 120° to 130° C. and becomes fluid. After twenty minutes the effervescence ceases and the liquid crystallises although the temperature is 130° C. The solid formed is the selenoxide, and recrystallisation from dry chloroform yields small, ill-defined crystals, M.pt. 144° to 146° C. Unlike the dihydroxy-compound the selenoxide does not decompose on melting; the melting-point of the dihydroxy-compound given is really the temperature at which the body loses water at the ordinary pressure. When a hot aqueous alcohol solution of 4-acetamidodiphenyl selenoxide is cooled, crystals of the corresponding dihydroxide separate out. Treatment of the selenoxide with halogen acids yields the dihalides.

4-Acetamidodiphenyl selenide dichloride,



A warm solution of 1·53 grams of the dihydroxide in 4 c.c. of glacial acetic acid is treated with a mixture of 2 c.c. of concentrated hydrochloric acid and 3 c.c. of acetic acid. The dichloride separates and is recrystallised from 30 c.c. of acetic acid, 1·6 grams of almost colourless, bulky, feathery needles being obtained. The product turns yellow at about 125° C. and melts at 131° to 132° C. A large bulk of water or dilute sodium hydroxide converts the dichloride to the dihydroxide, and aqueous potassium bromide (2 mols.) converts it to the dibromide. Attempts to form the dichloride by the action of chlorine on the selenide give a white crystalline compound of melting-point 186° to 187° C., which contains chlorine not replaceable by the action of aqueous sodium hydroxide.

4-Acetamidodiphenyl selenide dibromide, $(CH_3.CO.NH.C_6H_4)(C_6H_5)SeBr_2$, is prepared as described in the foregoing, or better by mixing 1·8 grams of bromine and 3·5 grams of 4-acetamidodiphenyl selenide in 95 c.c. of acetic acid. Small red needles separate (5·05 grams). Recrystallisation from warm glacial acetic acid gives a product which turns bright red at 100° C. and melts to a deep red liquid at 135° to 136° C. Water or sodium hydroxide converts it into the dihydroxide. When the dibromide is heated for 30 minutes at its melting-point, hydrogen bromide is evolved, and the residue, an insoluble grey powder, when recrystallised from alcohol forms colourless glistening needles, M.pt. 167° C. This product gives no precipitate with alcoholic silver nitrate on warming and is probably *3 : 5-dibromo-4-acetamidodiphenyl selenide*, the bromine having migrated from the selenium atom to the benzene nucleus.

4-Acetamidodiphenyl selenide di-iodide, $(CH_3.CO.NH.C_6H_4)(C_6H_5)SeI_2$.—The di-iodide may be obtained in three ways: (1) An acetic acid solution of iodine is added to 4-acetamidodiphenyl selenide in the same solvent. (2) Concentrated aqueous hydriodic acid is added to a warm solution of 4-acetamidodiphenyl selenide dihydroxide or selenoxide in acetic acid. (3) The dibromide is triturated with potassium iodide in the presence of water. The resulting di-iodide melts with decomposition at 144° to 145° C. and crystallises in bulky rosettes of fine needles. When heated at its melting-point for an hour a sublimate of iodine is obtained and the residue is 4-acetamidodiphenyl selenide. This change proceeds slowly at ordinary temperatures and in the air goes to completion in about ten days.

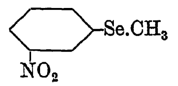
Di-α-naphthyl selenium dichloride,[1] $(C_{10}H_7)_2SeCl_2$.—The corresponding selenide is dissolved in ether and dry chlorine passed in, when an amorphous white precipitate separates. Recrystallisation from xylene yields colourless prisms, M.pt. 130° C., insoluble in alcohols, ether, chloroform, benzene, ligroin and carbon disulphide.

Di-α-naphthyl selenium dibromide, $(C_{10}H_7)_2SeBr_2$, is prepared in the usual manner. It forms white needles, melting at 183° C. with decomposition, soluble in amyl alcohol but best recrystallised from carbon disulphide. The halogen may be removed by alkali, but only di-α-naphthyl selenide results, no selenoxide being isolated as in the preceding cases.

Di-β-naphthyl selenium dichloride, $(C_{10}H_7)_2SeCl_2$, separates from carbon disulphide in colourless leaflets, M.pt. 146° C.

Phenyldimethyl selenium picrate, $(C_6H_5)(CH_3)_2Se.O.C_6H_2(NO_2)_3$,[2] occurs when phenyl methyl selenide is treated with methyl sulphate for four hours at 100° C. and the resulting product converted to the picrate by interaction with a saturated aqueous solution of sodium picrate. After crystallisation from ethyl acetate it melts at 87° to 89° C. Use of a large excess of sodium picrate gives a *double picrate,* $2[C_6H_5(CH_3)_2Se.O.C_6H_2(NO_2)_3].C_6H_2(NO_2)_3ONa$.

m-Nitrophenyl methyl selenide,



m-Nitrophenyl selenocyanate, 8 grams, is heated with an aqueous alcohol solution of 4 grams of sodium hydroxide at 80° to 90° C. for thirty minutes, 4·5 grams of methyl sulphate are added and the mixture boiled for three hours. The product is extracted with ether and the residue, after removal of the solvent, is distilled under reduced pressure. The pure selenide melts at 30° to 31° C. and boils at 165° C. at 13 mm.

m-Nitrophenyldimethyl selenium picrate, $(NO_2.C_6H_4)(CH_3)_2Se.O.C_6H_2(NO_2)_3$, obtained from the foregoing selenide and methyl sulphate, followed by treatment with aqueous sodium picrate, melts at 156° C. It also occurs when phenyldimethyl selenium picrate is nitrated.

p-Nitrophenyl methyl selenide,

is obtained from *p*-nitrophenyl selenocyanate in a similar manner to the corresponding *m*-derivative, or by reducing *pp′*-dinitrodiphenyl selenide

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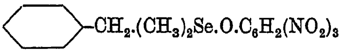
[1] Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831.
[2] Baker and Moffitt, *J. Chem. Soc.*, 1930, p. 1722.

with sodium sulphide in alkaline solution and methylation with methyl sulphate in the usual way. After crystallisation from methyl alcohol the product melts at 54° to 56° C.

p-Nitrophenyldimethyl selenium picrate, $(NO_2.C_6H_4)(CH_3)_2Se.O.C_6H_2(NO_2)_3$, may be crystallised from 90 per cent. alcohol, and melts at 122° to 123° C.

Benzyldimethyl selenium picrate,



$$C_6H_5-CH_2.(CH_3)_2Se.O.C_6H_2(NO_2)_3$$

Dimethyl selenide, 28 grams, is added to 43 grams of benzyl bromide, the resulting brown mass dissolved in water, and the picrate precipitated by the aid of sodium picrate. The yield is about 38 grams, the product separating from alcohol in small needles, M.pt. 118° C.

Benzyldimethyl selenium tri-iodide, $(C_6H_5.CH_2)(CH_3)_2SeI_3$.[1]—Dibenzyl diselenide is digested on the steam-bath with four to five times the theoretical quantity of methyl iodide for three days :

$$(C_6H_5.CH_2)_2Se_2 + 5CH_3I = (C_6H_5.CH_2)(CH_3)_2SeI_3 + (CH_3)_3SeI + C_6H_5.CH_2I$$

The tri-iodide forms black, very hard, metallic, glistening needles, M.pt. 65° C., possessing a vile smell and somewhat volatile above 100° C. It is insoluble in water, somewhat soluble in hot alcohol or ether. The *platinichloride* forms yellow, microscopic, quadratic plates, blackening at 100° C., insoluble in water or alcohol.

o-Nitrobenzyldimethyl selenium picrate,[2] $(NO_2.C_7H_6)(CH_3)_2Se.O.C_6H_2(NO_2)_3$, is prepared by allowing equivalent quantities of *o*-nitrobenzyl iodide and dimethyl selenide to react for fifteen minutes, washing the crude iodide with ether, and treating with a saturated solution of sodium picrate. After several crystallisations from methyl alcohol the product melts at 145° to 148° C.

m-Nitrobenzyldimethyl selenium picrate, $(NO_2.C_7H_6)(CH_3)_2Se.O.C_6H_2(NO_2)_3$, is isolated similarly to the foregoing compound, the first reaction taking two to three days in the cold before the addition of the sodium picrate. The compound melts at 132° to 134° C.

p-Nitrobenzyldimethyl selenium picrate, $(NO_2.C_7H_6)(CH_3)_2Se.O.C_6H_2(NO_2)_3$, may be prepared in the usual manner or by nitrating benzyldimethyl selenium picrate. It melts at 152° C.

COMPOUNDS OF THE TYPE R_3SeX.

These derivatives fall into two classes, the first containing an unsubstituted nucleus, and the second having alkoxy-groups in the nucleus. The former may be represented by triphenyl selenium chloride, prepared by adding diphenyl selenium dichloride to a suspension of aluminium chloride in dry benzene. This chloride is crystalline, absorbs atmospheric moisture to yield a dihydrate, and decomposes at its melting-point, forming diphenyl selenide and chlorobenzene. Boiling with ethylene dibromide converts it into triphenyl selenium bromide. The hydroxide has not been isolated in the solid state, but salts have been prepared. The alkoxy-derivatives are represented by

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[1] Joy, *Annalen*, 1875, 179, 19; Baker and Moffitt, *J. Chem. Soc.*, 1930, p. 1728.

[2] Baker and Moffitt, *loc. cit.*

trianisyl and triphenetyl selenium chlorides. These occur when selenium dioxide reacts with anisole or phenetole in the presence of anhydrous aluminium chloride. The halogen is removed by moist silver oxide, giving the hydroxide, from which salts may be prepared by the action of acids.

Triphenyl selenium chloride, $(C_6H_5)_3SeCl$.[1]—80 grams of anhydrous aluminium chloride are suspended in 100 c.c. of dry benzene. The reaction flask is cooled with ice and 40 grams of diphenyl selenium dichloride are added in portions over a period of twenty minutes, the cooling being maintained and the flask shaken throughout the addition. When all the dichloride has been added, the mixture is allowed to stand at room temperature for three hours, then cautiously treated with 200 c.c. of water. The benzene layer is removed and discarded, and the aqueous solution extracted with chloroform. The extract is evaporated to small bulk and treated with three volumes of ether, a yellow oil separating, which soon solidifies to a yellow powder. This is removed and crystallised from methyl ethyl ketone. The yield is 30 grams or 66 per cent. The product is very soluble in water, alcohol or chloroform, sparingly soluble in acetone and insoluble in ether. If the compound be allowed to stand in moist air, or if it is recrystallised from wet solvents, it takes up water to form a *dihydrate*, which loses its water completely in half an hour at 100° C., the loss commencing at 82° C. When heated at its melting-point the chloride yields diphenyl selenide and chlorobenzene.

Triphenyl selenium bromide, $(C_6H_5)_3SeBr$, is formed when the foregoing chloride is dissolved in boiling ethylene dibromide. It is crystallised from methyl ethyl ketone and melts with decomposition at 236° C., heating at this temperature causing decomposition with formation of diphenyl selenide and bromobenzene.

Triphenyl selenium iodide, $(C_6H_5)_3SeI$, decomposes at 237·5° C., yielding diphenyl selenide and iodobenzene. On exposure to light the white iodide slowly turns yellow; it may be crystallised from water.

The following triphenyl selenium salts are also known: *dichromate*, decomposing at 238° C., crystallisable from dilute acetic acid; *picrate*, crystallising from alcohol, M.pt. 141° to 142° C.; and the *nitrate*, M.pt. 107° to 108° C., separating from a concentrated aqueous solution on addition of concentrated nitric acid.

Triphenetyl selenium chloride, $(C_6H_4.OC_2H_5)_3SeCl$.[2]—Powdered anhydrous aluminium chloride, 8 grams, is dissolved in 10 grams of phenetole, 3 grams of powdered selenium dioxide added and the whole heated for an hour on the water-bath. The mixture, which evolves hydrogen chloride and becomes almost solid, is then decomposed by ice and any excess of phenetole distilled off in steam. The residue is extracted with chloroform, the extract dried and evaporated, the solid dissolved in alcohol and boiled with charcoal, subsequent filtering and evaporation in a vacuum yielding the chloride in fairly good yield as an almost colourless semi-solid mass. Boiling for a few minutes with an alcoholic suspension of silver oxide gives a solution of *triphenetyl selenium hydroxide*. This solution is strongly alkaline to litmus and is not precipitated by water, thus resembling the corresponding sulphur

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[1] Leicester and Bergstrom, *J. Amer. Chem. Soc.*, 1929, 51, 3587.

[2] Hilditch and Smiles, *Trans. Chem. Soc.*, 1908, 93, 1384.

compound. Exact neutralisation of the base with hydriodic acid and evaporation *in vacuo* gives the *iodide* as a pale yellow oil which cannot be crystallised. The chloride in alcohol yields a *platinichloride* when a slight excess of platinic chloride is added and the mixture treated with water. This has the composition $(C_{24}H_{27}O_3Se)_2PtCl_6$, and is exceedingly soluble in acetone or alcohol.

Trianisyl selenium chloride, $(C_6H_4.OCH_3)_3SeCl$, is obtained in a similar manner to the phenetyl compound, and yields a *hydroxide, iodide* and *platinichloride.* The platinichloride decomposes below 90° C. and is not very stable at the ordinary temperature. A *dichromate* is also known, an orange-brown powder decomposing at 68° to 70° C.

Tribenzyl selenium nitrate, $(C_6H_5.CH_2)_3SeNO_3$, decomposes at 102° to 103° C.; the corresponding *chloride* melts at 92° C.[1]

ARYL SELENOCYANATES AND THEIR DERIVATIVES.

The selenocyano-group may be introduced conveniently into the benzene nucleus by the aid of the diazo-reaction, *e.g.* diazotised aniline reacts with potassium selenocyanate to yield phenyl selenocyanate:

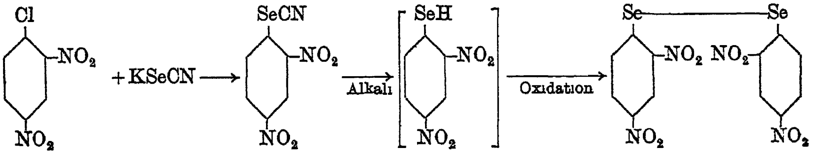
$$C_6H_5.N_2Cl + KSeCN = C_6H_5.SeCN + N_2 + KCl$$

When chlorine or a cyano-group is in the *ortho*-position to a nitro-group in benzyl compounds, it reacts with potassium selenocyanate:

$$NO_2.C_6H_4.CH_2Cl(\text{or } CN) + KSeCN = NO_2.C_6H_4.CH_2SeCN + KCl(\text{or } CN)$$

Benzyl chloride and potassium selenocyanate give benzyl selenocyanate, which yields a *para*-compound on nitration, the latter also being obtained by the condensation of *p*-nitrobenzyl chloride with potassium selenocyanate. The strength of the nitric acid and the conditions of the nitration determine the resulting products in the case of chlorophenyl and tolyl compounds. Nitric acid (density 1·4) at 3° C. converts *p*-tolyl selenocyanate into di-2-nitro-*p*-tolyl diselenide and 2-nitro-*p*-tolylseleninic acid, whereas acid of density 1·5 at −10° C. yields 2-nitro-*p*-tolyl selenocyanate and a small amount of 3-nitro-*p*-tolyl selenocyanate.

Selenocyanates are transformed by alkali to selenides (selenomercaptans), the oxidation of these products yielding diselenides, an example being as follows:



The conversion of *oo'*-diaminodiphenyl diselenide into phenylbenzselenazole is of interest and the complete synthesis is shown in the following scheme:

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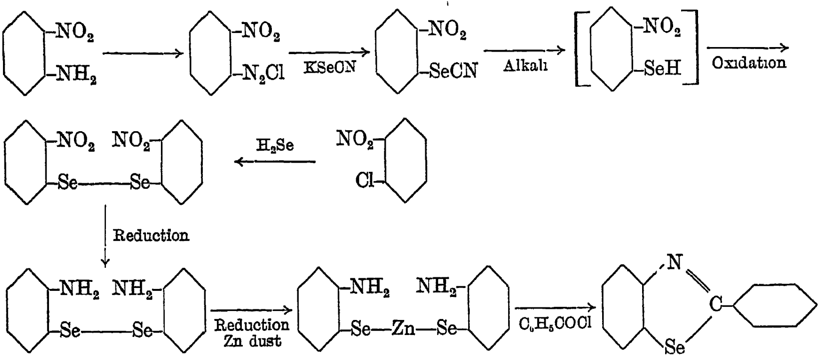
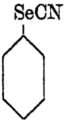
[1] Fromm and Martin, *Annalen*, 1913, 401, 177.



Phenyl selenocyanate,[1]



occurs when triphenylbismuthine and cyanogen triselenide react in ether solution :

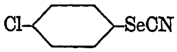
$$(C_6H_5)_3Bi + Se(SeCN)_2 = (C_6H_5)_2Bi.SeCN + C_6H_5.SeCN + Se$$

It also occurs when triphenylbismuthine dichloride and potassium selenocyanate are shaken together for fifteen hours in light petroleum :

$$(C_6H_5)_3BiCl_2 + 2KSeCN = (C_6H_5)_2Bi.SeCN + C_6H_5.SeCN + 2KCl$$

The best method of preparation, however, is as follows :[2] 9·1 grams of aniline in dilute sulphuric acid (1 : 4) are diazotised at 3° C. with 9·5 grams of sodium nitrite and the solution, made neutral to Congo paper with sodium acetate, is added to a cold aqueous solution of 22 grams of potassium selenocyanate. After fifteen hours steam distillation gives a pale yellow oil, which, when dried over calcium chloride, boils at 134° C. at 10 mm. and at about 250° C. with decomposition at ordinary pressures. The yield is about 50 per cent. When nitrated at $-5°$ C. with nitric acid (density 1·5), *p*-nitrophenyl selenocyanate and a very small amount of *o*-nitrophenyl selenocyanate are obtained.

p-Chlorophenyl selenocyanate,



is prepared by treating diazotised *p*-chloroaniline with potassium selenocyanate and subjecting the resulting mixture to steam distillation. It crystallises from light petroleum in colourless needles, M.pt. 53·5° to 54·5° C.[3] Boiling with alcoholic potassium hydroxide gives di-*p*-chlorophenyl diselenide. Nitric acid of density 1·41 and sulphuric acid below 3° C. give a mixture of di-*p*-chlorophenyl diselenide and *p*-chlorobenzeneseleninic acid, but with nitric acid of density 1·5 and at $-25°$ C. to $-10°$ C. a mixture of 4-chloro-2-nitrophenyl selenocyanate and the

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[1] Challenger, Peters and Halévy, *J. Chem. Soc.*, 1926, p. 1648.

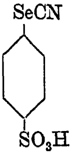
[2] Challenger and Peters, *J. Chem. Soc.*, 1928, p. 1364.

[3] Morgan and Elliot (*Proc. Chem. Soc.*, 1914, 30, 248) gave M.pt. 50° to 51° C.

corresponding seleninic acid results, the latter predominating. The nitro-selenocyanate forms pale yellow crystals, M.pt. 127° C.

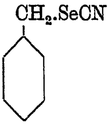
p-Bromophenyl selenocyanate, $BrC_6H_4.SeCN$, separates from light petroleum as white needles, M.pt. 70·5° to 71·5° C. Di-*p*-bromophenyl diselenide occurs as a by-product during the preparation. Attempts to nitrate the selenocyanate yield only *p*-bromobenzeneseleninic acid.[1]

Benzenesulphonic acid p-selenocyanate,[2] is obtained from diazotised sulphanilic acid and potassium selenocyanate. It crystallises as pale yellow needles.



p-Tolyl selenocyanate,[3] This is obtained in the usual manner from diazotised *p*-toluidine and potassium selenocyanate; it yields large transparent crystals of characteristic odour, M.pt. 55° to 56° C., readily soluble in most organic solvents and easily volatile in steam. Di-*p*-tolyl diselenide occurs with it as a by-product. When *p*-tolyl selenocyanate is boiled with alcoholic sodium hydroxide, di-*p*-tolyl diselenide results. Nitration[4] at −10° C. with nitric acid of density 1·5 yields principally 2-nitro-*p*-tolyl selenocyanate, yellow needles, M.pt. 69° to 70° C., and in much smaller amount 3-nitro-*p*-tolyl selenocyanate, yellow needles, M.pt. 150° C. If nitric acid of density 1·41 be used at 3° C., a mixture of di-2-nitro-*p*-tolyl diselenide and 2-nitro-*p*-tolueneseleninic acid results.

Benzyl selenocyanate,[5] is isolated by the interaction of potassium selenocyanate and benzyl chloride. It forms white prisms or needles, M.pt. 71·5° C., soluble in alcohol or ether, insoluble in water.



p-Nitrobenzyl selenocyanate, $C_7H_6NO_2.SeCN$, may be prepared (1) by the action of fuming nitric acid at −4° C. on the preceding selenocyanate; (2) by boiling *p*-nitrobenzyl chloride with potassium selenocyanate. It crystallises in stellate groups of colourless needles, M.pt. 122·5° C., insoluble in cold water, alcohol or ether, soluble in ammonium hydroxide, but reprecipitated by hydrochloric acid.

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[1] See Porritt, *J. Chem. Soc.*, 1927, p. 27.

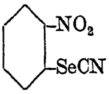
[2] German Patent, 255982.

[3] Challenger, Peters and Halévy, *loc. cit.*

[4] Challenger and Peters, *loc. cit.*

[5] Jackson, *Annalen*, 1875, 179, 1.

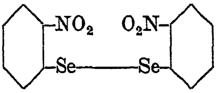
o-Nitrophenyl selenocyanate,[1]



o-Nitroaniline, 13·8 grams, is diazotised and the free mineral acid neutralised by sodium acetate. 14·4 grams of potassium selenocyanate in water are then added in small portions ; nitrogen is evolved and a yellow product separates. After a short time the latter is collected, washed, and recrystallised from alcohol containing charcoal. The selenocyanate separates as yellow needles, M.pt. 142° C., the yield being quantitative. It is readily soluble in ether, benzene or chloroform, insoluble in ligroin. With alkali in alcohol it gives the *sodium salt* of *o-nitroselenophenol* (*o-nitrophenyl selenide*) and a violet colour develops, which after a short time disappears and a yellow precipitate of *oo*′-dinitrodiphenyl diselenide separates. The *lead salt* of *o*-nitroselenophenol forms orange needles, soluble in sodium hydroxide giving a violet solution.[2]

p-Nitrophenyl selenocyanate, prepared from *p*-nitroaniline, crystallises from alcohol in faint yellow plates, M.pt. 135° C., having a similar solubility to the *ortho*-compound. With sodium hydroxide a brownish-red solution of the *sodium salt* of *p-nitroselenophenol* (*p-nitrophenyl selenide*) is obtained ; the *lead salt* of this selenophenol is orange-yellow.

oo′-Dinitrodiphenyl diselenide,



One method of preparation of this compound is indicated above ; a second is as follows : A solution of 4·6 grams of sodium in 100 c.c. of alcohol is saturated with the hydrogen selenide from 40 grams of aluminium selenide. The reddish solution is diluted with 400 c.c. more of alcohol and added with ice-cooling to a solution of 30 grams of *o*-chloronitrobenzene in 500 c.c. of alcohol, the operation being conducted in an atmosphere of hydrogen. The reaction mixture is violet, and after twenty-four hours a black precipitate separates. On the addition of hydrogen peroxide to the solution the nitroselenophenol which has been formed is oxidised to the insoluble diselenide. The precipitate is collected and boiled with acetic acid, the solution on cooling giving 5 grams of the diselenide as yellow crystals. *oo*′-Dinitrodiphenyl diselenide forms golden-yellow needles from benzene, M.pt. 209° C., readily soluble in hot acetic acid, sparingly soluble in alcohol or ligroin, insoluble in ether. Boiling with potassium hydroxide converts it to *o*-nitroselenophenol.

oo′-Diaminodiphenyl diselenide is obtained by reducing *o*-nitrophenyl selenocyanate in alcohol solution with alkaline sodium hydrosulphite. Orange-yellow needles result, which melt at 81° C. after crystallisation from alcohol. The product is readily soluble in ether, benzene or chloroform, sparingly soluble in ligroin and practically

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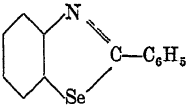
[1] Bauer, *Ber.*, 1913, 46, 92; see German Patent, 255982.

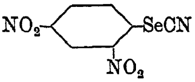
[2] For *m*-nitrophenyl selenocyanate, see Pyman, *Trans. Chem. Soc.*, 1919, 115, 172.

insoluble in water. Hydrogen chloride converts the diamine in alcohol solution to the *dihydrochloride*. The latter on reduction with zinc dust gives the *zinc salt* of *o-aminoselenophenol* (*o-aminophenyl selenide*), $C_6H_4(NH_2)Se.Zn.Se(NH_2)C_6H_4$, which is stable in air, insoluble in the usual organic solvents, but dissolves easily in mineral acids or caustic alkalis, the alkaline solution when oxidised by air or hydrogen peroxide giving the diselenide. When the foregoing zinc salt in ethyl acetate is treated with benzoyl chloride and gently warmed, it is transformed into phenylbenzselenazole,

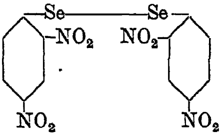


which separates on cooling and crystallises from alcohol in colourless needles, M.pt. 116° to 117° C., subliming without decomposition (see p. 121).

2 : 4-Dinitrophenyl selenocyanate,[1]

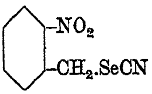


is the condensation product formed when potassium selenocyanate and chloro-2 : 4-dinitrobenzene are boiled together in alcohol solution. It separates from alcohol or acetic acid in pale yellow crystals, stable towards strong acids and recrystallisable from concentrated nitric acid, but decomposed by concentrated sulphuric acid with separation of selenium. Boiling with sodium carbonate or sodium hydroxide gives a brownish-red solution containing 2 : 4-dinitroselenomercaptide. This solution is oxidised by atmospheric oxygen, forming *2 : 4 : 2′ : 4′-tetranitrodiphenyl diselenide*,



which crystallises from nitrobenzene as yellow, glistening spangles, M.pt. 264° to 265° C., insoluble in most solvents. When the foregoing alkaline mercaptide solution is treated with hydrosulphite until colourless and then shaken with benzoyl chloride to isolate the diamine, a sparingly soluble compound separates. It crystallises from nitrobenzene in needles, and is *benzamidophenylbenzoxazole.*

o-Nitrobenzyl selenocyanate,



is the condensation product of potassium selenocyanate and *o*-nitrobenzyl chloride in boiling alcohol. It forms large pale crystals from alcohol or acetic acid, M.pt. 77° C., exploding at 215° C., soluble in alkali, giving a red solution and an odour of cyanogen. The alkali

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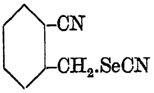
[1] Fromm and Martin, *Annalen*, 1913, 401, 177.

solution contains *o*-nitrobenzylselenomercaptan, atmospheric oxygen yielding *o-nitrobenzyl diselenide*, M.pt. 103° C.

o-Cyanobenzyl selenocyanate,[1]



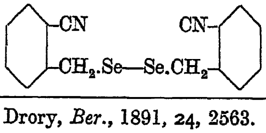
occurs when alcohol solutions of *o*-cyanobenzyl chloride and potassium selenocyanate are mixed and heated under reflux for fifteen to thirty minutes. It crystallises from benzene as compact colourless rhombohedra or prisms, M.pt. 121° C., completely decomposing at 200° C. It dissolves in methyl or ethyl alcohol, ether, petroleum, carbon disulphide, acetone or benzene.

o-Cyanobenzylselenomercaptan (*o-cyanobenzyl selenide*), $CN.C_6H_4.CH_2.SeH$, is obtained by adding gradually 10 grams of *o*-cyanobenzyl selenocyanate to 75 c.c. of concentrated sulphuric acid. Carbon dioxide is evolved. The clear solution is poured into ice water, an excess of sodium carbonate added and the resulting emulsion extracted with ether. Removal of solvent yields a yellow oil, possessing a nauseous odour, partly solidifying on being kept in a closed vessel and melting again at 30° C. It dissolves in chloroform, petroleum, benzene, alcohol or ether. It cannot be distilled without decomposition, and in air changes to *o*-cyanobenzyl diselenide. It is completely soluble in acids and may be reprecipitated by alkali, avoiding excess or it redissolves.

The salts of this mercaptan crystallise well from alcohol, but they are decomposed on evaporation of the solution on the water-bath. The *hydrochloride* dissolves sparingly in water or alcohol, evaporation of the aqueous solution in a vacuum over sulphuric acid yielding long flat prismatic needles ; the *platinichloride* is an orange-yellow, insoluble, infusible powder ; the *picrate* is an intensely yellow crystalline precipitate, sparingly soluble in alcohol and decomposing at 170° C. without melting ; the *hydrobromide* forms colourless prismatic needles, M.pt. 264° C. ; the *sulphate* separates from water in slender silky needles, M.pt. 145° to 150° C. with frothing, and on boiling in aqueous solution decomposes, yielding selenophthalide (see below). When *o*-cyanobenzyl selenocyanate, 5 grams, is heated with 20 c.c. of hydriodic acid (density 1·70) for five hours at 100° C., it forms the *periodide* of the mercaptan, $C_8H_7NSeI_2$. This crystallises from alcohol as slender dark-violet needles, M.pt. 223° C. with decomposition, is sparingly soluble in boiling alcohol, but almost insoluble in all other solvents.

o-Cyanobenzylmethyl selenide, $CN.C_6H_4.CH_2.Se.CH_3$, occurs when the foregoing mercaptan in the form of its hydrochloride is treated with methyl iodide in alcoholic potassium hydroxide solution. The product is distilled in steam and extracted with ether. It forms a yellowish-brown oil, having an unpleasant odour, and distilling without decomposition at 180° to 200° C.

o-Cyanobenzyl diselenide,



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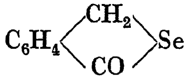
[1] Drory, *Ber.*, 1891, 24, 2563.

is obtained when a solution of a salt of *o*-cyanobenzylselenomercaptan is treated with sodium hydroxide and the mixture extracted with ether. It crystallises in needles, melting with decomposition at 108° to 110° C., soluble in methyl or ethyl alcohol, benzene, chloroform or carbon disulphide.

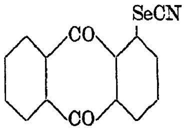
Selenophthalide,



$$C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle Se$$

is formed when *o*-cyanobenzylselenomercaptan in alcohol solution is mixed with an excess of potassium hydroxide and the whole kept in a warm place. Ammonia is slowly evolved, and on distillation of the mixture in a current of steam an emulsion is obtained, which deposits short nacreous needles of selenophthalide. It crystallises from alcohol in short colourless leaflets, M.pt. 58° C., soluble in alcohol, ether or benzene.

Anthraquinone 1-selenocyanate,[1]



is obtained from diazotised 1-aminoanthraquinone in aqueous solution on the addition of potassium selenocyanate. It forms yellowish-red needles, M.pt. 249° C. In a similar manner *potassium 1-selenocyano-anthraquinone-5-sulphonate* is prepared. The reaction for the former compound may be represented by the equation :

$$C_{14}H_7O_2.N_2.SeCN = C_{14}H_7O_2SeCN + N_2$$

o-Selenocyanobenzoic Acid and its Derivatives.[2]

o-Selenocyanobenzoyl chloride, $CNSe.C_6H_4.COCl$, occurs when an equimolecular mixture of *o*-chloroselenolbenzoyl chloride and silver cyanide is heated in an oil-bath at about 70° C., the yield of selenocyanate being about 70 per cent. The powdered melt is extracted with petroleum ether, which removes the selenocyanate and unchanged chloro-compound. The residue, on boiling with much benzene, gives a compound, M.pt. 235° C., the nature of which has not been determined. The selenocyanate crystallises from the petroleum ether as pale yellow, glistening plates, M.pt. 122° to 123° C., subliming above 100° C. into broad, colourless needles, which have a characteristic and not unpleasant smell. The compound is readily soluble in the usual organic solvents, somewhat sparingly soluble in petroleum ether. In contact with air, or on boiling with solvents not perfectly anhydrous, *o*-selenocyanobenzoic acid results, the change being more rapid on shaking with sodium carbonate solution.

Methyl o-selenocyanobenzoate, $CNSe.C_6H_4.COOCH_3$, is obtained by boiling the preceding compound with methyl alcohol, or by treating diazotised methyl anthranilate with potassium selenocyanate. It

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[1] German Patent, 256667.

[2] Lesser and Schoeller, *Ber.*, 1914, 47, 2505.

crystallises from methyl alcohol in long, colourless, glistening needles, M.pt. 114° to 115° C., readily soluble in benzene or acetic acid. The corresponding *ethyl ester* crystallises from ethyl alcohol in small, glistening prisms, M.pt. 125° to 126° C.

o-Selenocyanobenzoic acid, $CNSe.C_6H_4.COOH$, as already indicated, is best obtained by shaking the chloride with dilute sodium carbonate solution, and is also formed when *o*-aminobenzoic acid is diazotised and treated with potassium selenocyanate.[1] It crystallises in colourless plates, melting with decomposition at 185° C., readily soluble in alcohol or ether, sparingly soluble in benzene, insoluble in petroleum ether. The *barium salt,* which shows a variable water content, is readily soluble in hot water, sparingly soluble in cold water, and crystallises in needles; the *ferric salt* is brownish and the *silver salt* colourless; the *copper salt* is a bluish, sparingly soluble powder. When hydrogen chloride is passed into a methyl alcohol solution of the acid the expected ester is not obtained, but only *methyl diphenyl diselenide-di-o-carboxylate,* $CH_3OOC.C_6H_4.Se.Se.C_6H_4.COOCH_3$, M.pt. 143° to 144° C. The corresponding chloride, $ClCO.C_6H_4.Se.Se.C_6H_4.COCl$, reacts with silver cyanide to give a product of melting-point 235° C., as already mentioned in connection with *o*-selenocyanobenzoyl chloride.

α-Selenobenzoic acid, C_6H_5COSeH.[2]—The passage of hydrogen selenide through ethereal magnesium ethyl bromide yields a mixture of ethane and magnesium bromohydroselenide. The latter is decomposed by moisture, giving hydrogen selenide and magnesium hydroxybromide, but may be isolated as an additive product with pyridine, $MgBr.SeH.2C_5H_5N$. Benzoyl chloride reacts with magnesium bromohydroselenide to give α-selenobenzoic acid, which separates as red crystals, M.pt. 133° C., from methyl alcohol, in which solvent it is moderately soluble. When the acid is heated in the presence of aqueous ammonia decomposition into selenium, ammonium benzoate and ammonium hydroselenide occurs. *p-Tolyl selenobenzoate,* $C_6H_5COSeC_6H_4.CH_3$, forms colourless prisms, M.pt. 71° to 72° C., becoming red on exposure to light owing to the separation of selenium;[3] *p-methoxyphenyl selenobenzoate,* $C_6H_5COSeC_6H_4.OCH_3$, melts at 97° C., and the corresponding *p-ethoxy-compound* crystallises in needles, M.pt. 94° to 95° C.

ARYLSELENINIC AND ARYLSELENONIC ACIDS AND THEIR DERIVATIVES.

When diselenides are treated with nitric acid (density 1·4) they are converted into seleninic acids, $RSeO_2H$. The latter are also produced by the oxidation of arylselenoglycollic acids with hydrogen peroxide. The arylseleninic acids are well-defined crystalline products, converted by alkaline permanganate solution into arylselenonic acids, $RSeO_3H$. Nitration of phenylseleninic acid gives a *meta*-nitro-acid. The selenonic acids have also been prepared by the oxidation of diaryl diselenides by moist chlorine, and by the action of selenic acid on aromatic hydrocarbons. Benzyl chloride and its *o*-, *m*- and *p*-nitro-derivatives in alcohol form potassium benzyl or nitrobenzyl selenosulphate when

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[1] German Patent, 255982.,

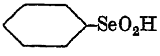
[2] Mingoia, *Gazzetta,* 1926, 56, 835.

[3] Taboury, *Bull. Soc. chim.,* 1906, [iii], 35, 668.

boiled with selenium in potassium sulphite solution. The selenosulphates are affected by light, decomposition occurring with liberation of selenium. Aqueous solutions yield diselenides when treated with iodine in potassium iodide :

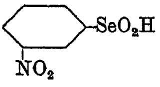
$$2KO.SO_2.SeRNO_2 + 2H_2O + I_2 = (RNO_2)_2Se_2 + 2KHSO_4 + 2HI$$

Phenylseleninic acid,[1]



To a solution of phenyl magnesium bromide in dry ether, prepared from 24 grams of magnesium and 157 grams of bromobenzene, 79 grams of selenium are slowly added and the mixture boiled for half an hour. The product is decomposed with ice and dilute hydrochloric acid, well shaken and the ether layer removed, the aqueous layer being extracted with ether twice again. The ether extracts are combined, dried with calcium chloride and the solvent removed on the water-bath. The resulting oil, about 130 grams, is then allowed to flow dropwise into concentrated nitric acid (density 1·4), of which 4 c.c. are employed for each gram of oil. The nitric acid solution is digested for an hour on the water-bath and then stood for a time, crude *phenylseleninic acid nitrate* separating as hard crystals. These are collected on asbestos, dissolved in water, and the solution filtered from insoluble matter. The solution is then extracted with ether and the extract evaporated to a syrup. On cooling almost pure nitrate results, which, after thoroughly drying in the air, amounts to about 110 grams, the yield thus being 44 per cent. The free acid is obtained by dissolving 10 grams of the nitrate in 20 c.c. of water and adding 6 c.c. of 10 per cent. aqueous ammonium hydroxide. On stirring, phenylseleninic acid separates as sandy, yellow grains ; it is purified by crystallisation from water. The yield is about 6·5 grams of pure acid. The acid has also been prepared by dissolving one part by weight of diphenyl diselenide in 40 parts by weight of nitric acid and heating the mixture. On cooling, phenylseleninic acid nitrate separates ; it is dissolved in ammonium hydroxide and mixed with silver nitrate, silver phenylseleninate being precipitated. Addition of the requisite quantity of hydrochloric acid then yields phenylseleninic acid.[2] A third method of preparation consists of treating phenylselenic acid with hydrochloric acid.[3] Prepared by the first method the acid melts at 124° to 125° C. (corr.) after drying at 100° C., the air-dried acid practically being anhydrous. *Sodium phenylseleninate* crystallises from water in colourless plates containing two molecules of water and readily soluble in water ; the *barium salt* forms plates, and the *copper salt* crystallises in bright blue leaflets.[4]

m-Nitrophenylseleninic acid,[5]



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[1] Pyman, *Trans. Chem. Soc.*, 1919, 115, 166.

[2] Stoecker and Krafft, *Ber.*, 1906, 39, 2197.

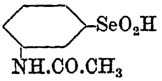
[3] Doughty, *Amer. Chem. J.*, 1909, 41, 326.

[4] Stoecker and Krafft, *loc. cit.*

[5] Pyman, *loc. cit.*

When phenylseleninic acid is heated with a large excess of fuming nitric acid at 150° C. for one hour it gives only a 20 per cent. yield of the nitro-acid. A better method of preparation is as follows : 30 grams of *phenylseleninic acid nitrate* are dissolved in 30 c.c. of sulphuric acid and the solution cooled by running water. 12 grams of finely powdered potassium nitrate are then stirred into the solution, the cooling being continued. The mixture is then heated for two hours on the steam-bath and afterwards poured into 600 c.c. of water. After several hours the crystals which form are collected, 17 to 19 grams being obtained. The acid crystallises from water in yellow prismatic needles, M.pt. 156° to 157° C. (corr.) after drying at 100° C., being moderately soluble in boiling water, sparingly soluble in cold water.

m-Acetamidophenylseleninic acid,



10 grams of di-*m*-acetamidophenyl diselenide are added in quantities of about one gram with stirring to 40 c.c. of nitric acid (density 1·4) maintained at −6° to −3° C. Crystals soon separate and are collected on asbestos, washed with concentrated nitric acid and drained. The product melts at 146° C., and is the *nitrate* of *m-acetamidophenylseleninic acid.* It is dissolved in an excess of hot dilute ammonium hydroxide (200 c.c.), the solution treated with animal charcoal, filtered, and acidified with acetic acid. The seleninic acid separates as fine, colourless needles, which are removed, washed well with water and dried in air. The yield is 8·5 grams. The acid crystallises from boiling water in short, slender, colourless needles, which turn brown at about 200° C. and melt with decomposition at 209° C. (corr.). The *sodium salt* separates from water in microscopic needles, which contain seven molecules of water of crystallisation after drying in air, but lose four of these at 100° C. and the remainder at 120° C.

o-Tolylseleninic acid, $CH_3.C_6H_4.SeO_2H$.[1]—When an excess of 20 per cent. hydrogen peroxide is added to a suspension of *o*-tolylselenoglycollic acid in ice-cold water, the acid gradually dissolves and after several hours the seleninic acid separates. Recrystallisation from hot water yields clusters of colourless needles, M.pt. 126° to 127° C., sparingly soluble in ether, more readily soluble in alcohol or chloroform.

m-Tolylseleninic acid, $CH_3.C_6H_4.SeO_2H$, separates from hot water in colourless needles, M.pt. 119° to 120° C., which develop a deep blue coloration with warm sulphuric acid.

p-Tolylseleninic acid, $CH_3.C_6H_4.SeO_2H$.—When prepared similarly to the *ortho*-compound it forms colourless, flattened needles, M.pt. 171° C. It develops a violet coloration with warm concentrated sulphuric acid, and liberates iodine from acidified solutions of potassium iodide.

In connection with the foregoing *ortho*- and *para*-acids, the following preparation is of interest.[2] Toluene and concentrated selenic acid

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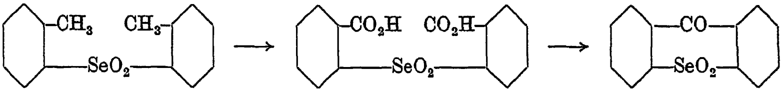
[1] Porritt, *J. Chem. Soc.*, 1927, p. 27.

[2] Doughty and Elder, *Report Eighth Inter. Congress Applied Chemistry*, 1912, 6, 93.

react slowly on standing for some months, carbon dioxide being evolved. The lower dark red viscous layer is poured into water, giving an acid solution and a small amount of a red oil with a solid admixture. The acid solution is neutralised by barium hydroxide, the barium selenate removed and the filtrate evaporated to dryness. Extraction of the residue for several days with chloroform removes any traces of the red oil and leaves an inseparable mixture of *o*- and *p*-tolueneselenonic acids. Reduction of the mixture with concentrated hydrochloric acid gives *p*-tolueneseleninic acid, M.pt. 160° C., the mother-liquor from this yielding the *o*-acid containing $\frac{1}{2}H_2O$, M.pt. 99° to 101° C. The red oil mentioned is washed with ether, in which the solid matter is insoluble, and then distilled. A yellow mass of melting-point 69·5° to 70·5° C. results, which is di-*p*-tolyl selenide. The substance insoluble in ether, when recrystallised from alcohol, melts at 183° C., and is *benzophenone-selenone.* Its formation may be explained on the assumption that di-*o*-tolyl selenone may occur as an intermediate product, then being oxidised to *diphenylselenone-2 : 2′-dicarboxylic acid,* which condenses with loss of water and carbon dioxide according to the scheme :

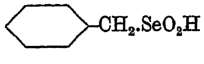


o-Xylylseleninic acid, $(CH_3)_2C_6H_3.SeO_2H$,[1] obtained from the corresponding selenoglycollic acid, crystallises from water in colourless needles, decomposing at 125° C.

m-Xylylseleninic acid, $(CH_3)_2C_6H_3.SeO_2H$, separates from hot water in colourless needles, decomposing at 146° to 147° C. The xyleneseleninic acids develop blue colorations with warm concentrated sulphuric acid.

Bromophenyl-p-seleninic acid, $C_6H_4Br.SeO_2H$, is obtained by oxidising *p*-bromophenylselenoglycollic acid in acetic acid solution with hydrogen peroxide. It crystallises from hot water in colourless needles, decomposing at 187° C., and giving a reddish-purple coloration with concentrated sulphuric acid.

Benzylseleninic acid,[2]



is produced by gently warming the corresponding diselenide with concentrated nitric acid. It forms stellate groups of white needles, M.pt. 85° C., having a strong odour and dissolving in hot water or alcohol, insoluble in ether. It is a " strong " acid, liberating carbon dioxide from carbonates, and the following salts being known : *ammonium salt,* white crystals ; *silver salt,* hair-like crystals ; *sodium* and *barium salts,* white crystalline masses ; *lead salt,* a white crystalline powder. Later investigation[3] gives the melting-point of the acid as 122° to 123° C., and finds that the barium and calcium salts are isolated as dihydrate and hexahydrate respectively.

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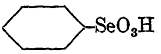
[1] Porritt, *loc. cit.*

[2] Jackson, *Annalen,* 1875, 179, 13; *Ber.,* 1874, 7, 1277.

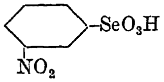
[3] Lesser and Weiss, *Ber.,* 1924, 57, [B], 1077.

Phenylselenonic acid,



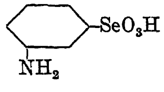
is obtained when diphenyl diselenide is oxidised by moist chlorine [1] or by the action of selenic acid on benzene.[2] It is a hygroscopic syrup, which may be dried *in vacuo* at 105° C., but explodes at 180° to 190° C. and cannot be distilled. It absorbs moisture from the air, forming a *hydrate*, which separates in prisms. The *potassium salt* [3] forms colourless prismatic needles, sintering at about 50° C. and melting at 65° to 90° C. in their water of crystallisation ($2H_2O$). The *sodium salt* occurs as the *tetrahydrate* in long, clear, oblong plates, readily soluble in water. The *barium salt* forms white plates.[4] *Silver*, *copper* and *cadmium salts* are also known.

m-Nitrophenylselenonic acid,[5]



35 grams of the corresponding seleninic acid in 600 c.c. of boiling water containing 20 c.c. of 10 per cent. potassium hydroxide are mixed with a solution of 16 grams of potassium permanganate in 200 c.c. of hot water. Further small quantities of permanganate are subsequently added until the red colour no longer quickly vanishes. After removing the manganese dioxide the solution is evaporated to small bulk and cooled, when the *potassium salt* of the selenonic acid separates, about 34 grams being obtained. It forms hard yellow rosettes of flat needles, readily soluble in hot water, but sparingly soluble in cold water. It explodes violently at about 330° C. (corr.). By double decomposition the *barium salt* can be prepared from the potassium salt, giving colourless leaflets containing two molecules of water, which are lost at 120° C. but not at 110° C. Treatment of this salt with the calculated quantity of sulphuric acid, removal of the barium sulphate and evaporation to a syrup gives the free acid in the form of colourless plates, containing two molecules of water, which are lost at 100° C., and melting at 146° C.

m-Aminophenylselenonic acid,



When *m*-acetamidophenylseleninic acid is oxidised by alkaline permanganate it yields *m-acetamidophenylselenonic acid*, isolated in the form of the *tetrahydrated barium salt*, which crystallises in colourless needles, double decomposition giving the sodium salt. The latter separates from water in colourless needles and from alcohol in prismatic needles. Treatment of the barium salt with sulphuric acid releases the free acid as a *dihydrate*, which melts and decomposes at 229° C. (corr.). The *sodium salt* separates from water in plates.

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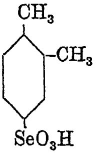
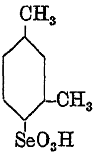
[1] Stoecker and Krafft, *Ber.*, 1906, 39, 2197.
[2] Doughty, *Amer. Chem. J.*, 1909, 41, 326.
[3] Pyman, *Trans. Chem. Soc.*, 1919, 115, 166.
[4] Stoecker and Krafft, *loc. cit.*
[5] Pyman, *loc. cit.*

o-Xylylselenonic acid,[1]



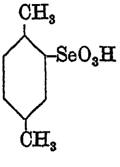
The preparation of this acid is similar to that described for the corresponding *para*-acid. The yield is about 80 per cent. The *ortho*-acid forms fine white needles, M.pt. 108° to 110° C., very hygroscopic and readily soluble in acetic acid, acetic anhydride, benzene or chloroform. The following salts have been described : *ammonium salt, potassium salt, sodium salt* (+ $4H_2O$), *barium salt* (+ $3H_2O$), *magnesium salt, zinc salt* (+ $6H_2O$), *silver salt, copper salt* (+ $6H_2O$), *nickel salt* (+ $5H_2O$), *cobalt salt* (+ $5H_2O$). The free acid forms a *dihydrate*, crystallisable from water.[2]

m-Xylylselenonic acid,



Two parts of *m*-xylene in 1·6 parts of acetic anhydride are cooled in ice and treated dropwise with one part of 96 per cent. selenic acid, the mixture being shaken until uniform. After forty-eight hours in an ice-chest the product is filtered off, washed with a little acetic anhydride and dried in a vacuum desiccator over lime and phosphorus pentoxide. The yield is 75 per cent. and cannot be increased by concentration of the mother-liquor in a vacuum, since this leads to explosion. The acid crystallises from hot concentrated acetic anhydride solution as fine needles, M.pt. 130° to 130·5° C., soluble in benzene or chloroform. It is hygroscopic, stable towards boiling sodium hydroxide, not attacked by hydrogen peroxide, and forms a *dihydrate*, $(CH_3)_2C_6H_3.SeO_3H.2H_2O$. The acid evinces analogy with *m*-xylene-4-sulphonic acid, and forms the following salts : *ammonium salt, potassium salt* (+ $2H_2O$), *sodium salt* (+ $5H_2O$), *barium salt* (+ $10H_2O$), *magnesium salt* (+ $8H_2O$), *zinc salt* (+ $6H_2O$), *silver salt, copper salt* (+ $6H_2O$), *nickel salt* (+ $5H_2O$), *cobalt salt* (+ $6H_2O$).

p-Xylylselenonic acid,[3]



Two parts of *p*-xylene in acetic anhydride cooled to 0° C. are treated dropwise with one part of selenic acid, the mixture being stirred during

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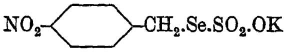
[1] Anschütz, Kallew and Riepenkröger, *Ber.*, 1919, 52, [B], 1860. The position of the selenium in these xyleneselenonic acids is not definitely known.

[2] Anschutz and Teutenberg, *Ber.*, 1924, 57, [B], 1018.

[3] Anschütz, Kallew and Riepenkröger, *loc. cit.*

the operation. After twenty-four hours in ice the product is quickly filtered off, washed with cold acetic anhydride and dried *in vacuo* over lime and phosphorus pentoxide. Recrystallisation from warm acetic anhydride yields fine, white hygroscopic needles, M.pt. 95° to 96° C., readily soluble in benzene or chloroform, sparingly soluble in ether. From 20 grams of selenic acid about 25 grams of the *p*-xylylselenonic acid are obtained, *i.e.* about an 80 per cent. yield. The following salts are known: *ammonium salt, potassium salt, sodium salt* ($+4H_2O$), *barium salt* ($+3H_2O$), *magnesium salt* ($+8H_2O$), *zinc salt* ($+10H_2O$), *silver salt* ($+H_2O$), *copper salt* ($+10H_2O$), *nickel salt* ($+7H_2O$), *cobalt salt* ($+9H_2O$). The acid also forms a *dihydrate*.[1]

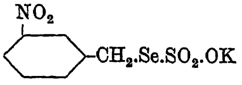
Potassium p-nitrobenzyl selenosulphate,[2]



2·3 grams of finely powdered selenium are boiled with a solution of 6 grams of potassium sulphite in 50 c.c. of water for forty-five minutes and the hot solution filtered to remove any undissolved selenium. 5 grams of *p*-nitrobenzyl chloride in 50 c.c. of 95 per cent. alcohol are then added and the resulting turbid solution heated over a free flame under reflux. Heating is maintained for ten minutes and the flask then rapidly cooled, a copious precipitate separating. The product is purified by several crystallisations from 95 per cent. alcohol, followed by shaking with ether to remove traces of diselenide. The selenosulphate crystallises in plates, moderately soluble in water, possessing in bulk a creamy tinge, exposure to light for several days causing the liberation of selenium. Its aqueous solution gives no precipitate with barium chloride, but sodium carbonate or sodium hydroxide gives a yellow precipitate of the diselenide. Hydrochloric acid gives a yellow precipitate which consists of a mixture of seleno-mercaptan and the diselenide. An alcoholic solution of iodine or a solution of iodine in potassium iodide causes immediate precipitation of the diselenide :

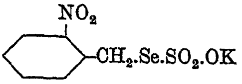
$$2KO.SO_2.Se.C_7H_6.NO_2 + 2H_2O + I_2 = (C_7H_6.NO_2)_2Se_2 + 2KHSO_4 + 2HI$$

Potassium m-nitrobenzyl selenosulphate,



is obtained in a similar manner to the preceding compound. It crystallises in plates, which are moderately soluble in water and more readily obtained pure than the *para*-compound. Selenium is liberated on exposure to light. Oxidation or treatment with iodine converts the selenosulphate to the diselenide.

Potassium o-nitrobenzyl selenosulphate,



possesses similar properties to the *meta*- and *para*-compounds. It crystallises from alcohol in colourless plates, and yields the diselenide by the usual treatment.

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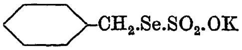
[1] Anschütz and Teutenberg, *loc. cit.*

[2] Price and Jones, *Trans. Chem. Soc.*, 1909, 95, 1729.

Potassium benzyl selenosulphate,



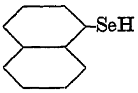
This compound is obtained using 3 grams of selenium, 8 grams of potassium sulphite, 40 c.c. of water and 40 c.c. of alcohol, the operation being carried out in a similar manner to that used for the nitrobenzyl compounds. The salt is, however, much more soluble in water than in the case of the nitrobenzyl derivatives, and is also much less stable. Hence a larger proportion of diselenide is produced, and to remove it, the solution and precipitate are extracted with ether. The aqueous layer is evaporated to dryness over sulphuric acid in a vacuum, and the selenosulphate extracted from the residue by boiling with 95 per cent. alcohol. Repeated crystallisation from alcohol gives colourless plates, which are very soluble in water. Decomposition readily takes place on exposure to light, with liberation of selenium. The aqueous solution gives no precipitate with barium chloride, and oxidation with iodine gives the diselenide.

CHAPTER III.

MISCELLANEOUS ORGANIC DERIVATIVES OF SELENIUM.

Selenium Derivatives of Naphthalene.[1]

α-Naphthyl selenide,



This compound [2] has already been described on p. 21. It is characterised by its *silver salt*, a bright red powder, its *lead salt*, an orange-coloured powder, its *copper salt*, a pale brown powder, and its *mercury salt*, a citron-yellow powder.

Methyl-α-naphthyl selenide, $C_{10}H_7.Se.CH_3$, occurs when 10 grams of the foregoing compound in alkaline solution are treated with 12·16 grams of dimethyl sulphate. After heating for thirty minutes on the water-bath the oil which separates is extracted with ether and vacuum-distilled. The resulting product (5 grams) is a pale yellow strongly refractive oil, B.pt. 173° C. at 16 mm. Oxidation by potassium permanganate solution yields *methyl-α-naphthylselenone*, $C_{10}H_7.SeO_2.CH_3$, B.pt. 290° C.

Ethyl-α-naphthyl selenide, $C_{10}H_7.Se.C_2H_5$.—10 grams of α-naphthyl selenide in the sodium alcoholate solution from 2·3 grams of sodium and 30 c.c. of alcohol are boiled on a water-bath for thirty minutes with 7·5 grams of ethyl iodide in alcohol. The solvent is distilled off, the residue treated with water, and the precipitated oil extracted with ether. Removal of the latter yields 5 grams of the ethyl selenide, B.pt. 167° to 168° C. at 13 mm.

In a similar manner *isopropyl-α-naphthyl selenide*, $C_{10}H_7.Se.CH(CH_3)_2$, is obtained in 55 per cent. yield, B.pt. 165° to 167° C. at 14 mm., and *n-butyl-α-naphthyl selenide*, $C_{10}H_7.Se.C_4H_9$, in 41 per cent. yield, B.pt. 180° C. at 13 mm.

α-Naphthylacetyl selenide, $C_{10}H_7.Se.CO.CH_3$, is the product of reaction between acetyl chloride and α-naphthyl selenide. It is a golden-yellow oil, B.pt. 167° C. at 18 mm. The corresponding *benzoate*, $C_{10}H_7.Se.CO.C_6H_5$, separates from alcohol in golden-yellow needles, M.pt. 133° C.

αα-Di-1-naphthylselenolethane, $(C_{10}H_7.Se)_2CH.CH_3$.—A gently warmed mixture of 1 gram of paraldehyde with 3 grams of α-naphthyl

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[1] Loevenich, Fremdling and Föhr, *Ber.*, 1929, 62, [B], 2856.

[2] Taboury, *Bull. Soc. chim.*, 1903, iii, 29, 761; 1906, iii, 35, 668; 1909, iv, 6, 762; *Ann. Chim. Phys.*, 1908, 15, 5.

selenide containing a few drops of sulphuric acid is treated with hydrogen chloride. After standing for several hours the mixture is treated with sodium hydroxide and extracted with ether. The residue obtained after removing the solvent is recrystallised from alcohol, yellow crystals resulting, M.pt. 89° C. The same product results when the aldehyde is replaced by pyruvic acid, but if acetone is used *ββ-di-1-naphthylselenolpropane*, M.pt. 130° C., is obtained as yellow crystals.

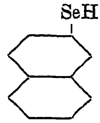
αα′-Dinaphthylselenoxide, $C_{10}H_7.SeO.C_{10}H_7$, is produced by oxidising αα′-dinaphthyl selenide in acetic acid with potassium dichromate solution. The product separates from alcohol as colourless glistening needles, M.pt. 105° C. Oxidation of this oxide by an excess of potassium permanganate yields *αα′-dinaphthylselenone*, $C_{10}H_7.SeO_2.C_{10}H_7$, which is deposited from alcohol as colourless glistening plates, M.pt. 106° C.

β-Naphthyl selenocyanate, $C_{10}H_7.SeCN$.—To obtain this a diazotised solution of β-naphthylamine containing sodium acetate is added to aqueous potassium selenocyanate. It separates from alcohol as small yellow crystals, M.pt. 68° C. Boiling with 20 per cent. nitric acid for eight hours gives *naphthalene-β-seleninic acid*, $C_{10}H_7.SeO_2H$, consisting of white plates, M.pt. 156° C. The *silver* and *lead salts* of this acid are white powders, the *methyl ester* is deposited as dark yellow crystals, M.pt. 106° C., and the *ethyl ester* is a yellow oil, B.pt. 65° to 68° C. at 12 mm.

Methyl-β-naphthylselenone, $C_{10}H_7.SeO_2.CH_3$, occurs when the sodium salt of naphthalene-β-seleninic acid in methyl alcohol is boiled with methyl iodide for a long period. After treatment with water and extraction with ether, removal of the latter and crystallisation from alcohol gives a 48 per cent. yield as golden-yellow crystals, M.pt. 136° C. The selenone may also be obtained by the oxidation of methyl-β-naphthyl selenide with permanganate.

In a similar manner *ethyl-β-naphthylselenone* is produced, and from alcohol it yields yellow crystals, M.pt. 40° to 41° C.

β-Naphthyl selenide,



may be prepared in two ways: (1) By the hydrolysis of β-naphthylselenocyanate by aqueous alcoholic sodium hydroxide in the presence of dextrose, a 92 per cent. yield resulting. (2) By the reduction of naphthalene-β-seleninic acid by dextrose in sodium hydroxide solution, the yield in this case being 80 per cent. The selenide separates from alcohol in yellow crystals, M.pt. 72° to 74° C. The *lead salt* is an orange powder, which, in ether suspension, yields the *acetyl compound*, $C_{10}H_7.Se.CO.CH_3$, when boiled with acetyl chloride. The acetyl compound separates from alcohol in golden-yellow plates, M.pt. 172° to 173° C. The corresponding *benzoyl derivative* forms yellow crystals, M.pt. 118° C.

Methyl-β-naphthyl selenide, $C_{10}H_7.Se.CH_3$, occurs when a quantity of the foregoing lead salt is suspended in methyl alcohol and boiled with methyl iodide. It deposits as yellow crystals, M.pt. 54° C., which yield, when oxidised by potassium permanganate, *methyl-β-naphthylselenone*, $C_{10}H_7.SeO_2.CH_3$, M.pt. 136° C.

In a similar manner *n-butyl-β-naphthyl selenide*, $C_{10}H_7.Se.C_4H_9$, is prepared, using *n*-butyl iodide in place of methyl iodide, the product forming golden crystals, M.pt. 137° C.

αα-Di-2-naphthylselenolethane, $(C_{10}H_7.Se)_2CH.CH_3$, is prepared by a similar process to that described for the α-naphthyl-derivative. From alcohol it separates as yellow crystals, M.pt. 134° C. *ββ-Di-2-naphthylselenolpropane* melts at 96° C.

ββ′-Dinaphthylselenoxide, $C_{10}H_7.SeO.C_{10}H_7$, occurs when ββ′-dinaphthyl diselenide, in acetic acid, is oxidised by potassium dichromate. From alcohol it is deposited as colourless needles, M.pt. 134° C.

ββ′-Dinaphthylselenone, $C_{10}H_7.SeO_2.C_{10}H_7$, is produced when the foregoing compound is oxidised by aqueous permanganate solution. It yields colourless crystals from alcohol, M.pt. 160° to 161° C.

HYDRONITRATES OF SELENOXIDES.[1]

When mixed selenides of the type Alk.Se.Ar and diphenyl selenide are treated in the cold with fuming nitric acid, a violent reaction occurs. The mixtures are then heated on the steam-bath until evolution of nitrogen peroxide ceases. In the case of phenyl methyl selenide a crystalline solid separates, which has the composition $C_6H_5(CH_3)SeO.HNO_3$. Phenyl ethyl selenide and phenyl *iso*amyl selenide, however, yield water-soluble oils, insoluble in organic solvents, and decomposing too easily to be purified by distillation (phenyl ethyl selenoxide hydronitrate decomposes at 110° C. at 3 mm. pressure). Consequently their constitution has only been assumed by analogy with the methyl and phenyl derivatives. When heated above 100° C., the methyl, ethyl, and *iso*amyl compounds decompose with evolution of nitrogen peroxide and leave a residue of diphenyl diselenide, M.pt. 63° C. The following derivatives have been isolated: *Phenylmethylselenoxide hydronitrate*, $C_6H_5(CH_3)SeO.HNO_3$, white needles or plates, M.pt. 97° C., yield 64 per cent.; *phenylethylselenoxide hydronitrate*, $C_6H_5(C_2H_5)SeO.HNO_3$, a colourless oil; *phenylisoamylselenoxide hydronitrate*, $C_6H_5(C_5H_{11})SeO.HNO_3$, a colourless oil; *diphenylselenoxide hydronitrate*, $(C_6H_5)_2SeO.HNO_3$, white needles, M.pt. 97° C., yield 77 per cent.

Treatment of the hydronitrates in aqueous solution with sodium carbonate causes evolution of carbon dioxide. Evaporation to dryness, followed by extraction with alcohol or benzene, then yields oils which are probably the selenoxides. These oils with concentrated hydrochloric acid are converted into white solids, crystallisable from benzene, xylene, alcohol or dry ether. These solids are the dichlorides of the original selenides, and when prepared by this method their melting-points are as follows: *Phenyl methyl selenium dichloride*, M.pt. 122° C.; *phenyl ethyl selenium dichloride*, M.pt. 64° to 65° C.; *diphenyl selenium dichloride*, M.pt. 142° C.

The foregoing bodies are supposed to be produced by the following reactions:

$$C_6H_5.SeR + 3HNO_3 = C_6H_5.SeOR.HNO_3 + 2NO_2 + H_2O$$
$$2C_6H_5.SeOR.HNO_3 + Na_2CO_3 = 2C_6H_5.SeOR + 2NaNO_3 + CO_2 + H_2O$$
$$C_6H_5.SeOR + 2HCl = C_6H_5.SeCl_2R + H_2O$$

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[1] Foster and Brown, *J. Amer. Chem. Soc.*, 1928, 50, 1182.

COMPOUNDS DERIVED BY THE INTERACTION OF SELENIUM OXYCHLORIDE AND KETONES.[1]

The interaction of selenium oxychloride and ketones may be represented generally by the following equation:

$$2C_6H_5.CO.CH_3 + SeOCl_2 = (C_6H_5.CO.CH_2)_2SeCl_2 + H_2O$$

The reactions are carried out at room temperature, except in the case of 2-methyl-5-*iso*propyl-acetophenone, which requires heat. The products are nearly insoluble in ether, benzene, petroleum ether and carbon tetrachloride, but dissolve in water or alcohol with decomposition. They cannot be recrystallised and hence impurities are removed by washing first with benzene and then with ether. The compounds are more or less unstable, some commencing to decompose at once and others not showing marked decomposition for a period of two weeks. Decomposition gives a reddish sticky mass with a strong lachrymatory action and an odour like that of chloro-ketones. The following table shows the substances which have been obtained.

SELENO-KETONES.

Ketone	Seleno-ketone	Formula	M.pt., ° C.	Yield, per cent.	Decomposition Time
Acetone	Dichloroselenoacetone	$(CH_3.CO.CH_2)_2SeCl_2$	81	77	3–4 weeks.
Acetophenone	Dichloroselenoacetophenone	$(C_6H_5.CO.CH_2)_2SeCl_2$	121·5	77	1–2 days.
p-Chloroacetophenone	Dichloroseleno-*p*-chloroacetophenone	$(ClC_6H_4.CO.CH_2)_2SeCl_2$	126	50	1–2 weeks.
Propiophenone	Dichloroselenopropiophenone	$(C_6H_5.CO.C_2H_4)_2SeCl_2$	118	60	2 weeks.
Methyl-*p*-tolyl ketone	Dichloroselenomethyl-*p*-tolyl ketone	$(CH_3.C_6H_4.CO.CH_2)_2SeCl_2$	129	60	,,
2-Methyl-5-*iso*-propylacetophenone	Dichloroseleno-2-methyl-5-*iso*-propylacetophenone	$[CH_3(C_3H_7)C_6H_3.CO.CH_2]_2SeCl_2$	133	50	,,

COMPOUNDS DERIVED BY THE INTERACTION OF SELENIUM OXYCHLORIDE AND PHENOLS.[2]

Phenol Derivatives.

Condensation between phenol and selenium oxychloride in ether or chloroform solution produces two isomeric selenonium chlorides, $[(HO.C_6H_4)_3Se]Cl$, each containing chlorine precipitable as silver chloride and replaceable by other acid radicals. The three phenolic hydroxyl groups of the complex cation impart acidic properties to the chlorides, causing them to be soluble in aqueous caustic alkali. From such solutions carbonic or acetic acid precipitates the amphoteric oxide $[(HO.C_6H_4)_3Se]_2O$, which redissolves in alkalis and reacts with acids to give a bromide, nitrate, sulphate and chloroplatinate. The following scheme shows the compounds obtained:

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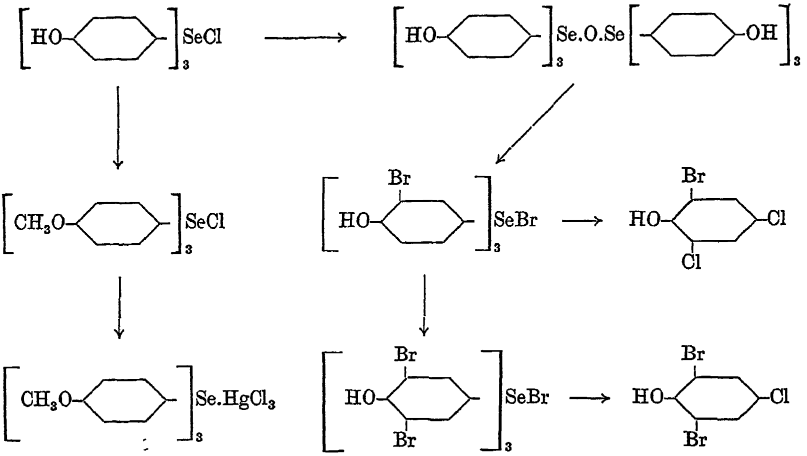
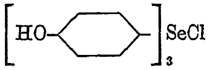
[1] Nelson and Jones, *J. Amer. Chem. Soc.*, 1930, **52**, 1588.

[2] Morgan and Burstall, *J. Chem. Soc.*, 1928, p. 3260.



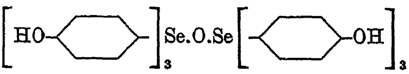
Tri-4-hydroxytriphenylselenonium chloride,



Selenium oxychloride, 33·2 grams (*i.e.* 1 mol.) in 50 c.c. of chloroform, is added to a well-stirred solution of phenol (56·4 grams, *i.e.* 3 mols.) in 500 c.c. of the same solvent. Heat is liberated and hydrogen chloride evolved, the mixture darkening and becoming opaque. After an hour the yellow solution containing a red oil in suspension is refluxed until the insoluble product adheres to the sides of the vessel as a gum. The chloroform is then decanted off and the residue triturated with acetone, from which the selenonium chloride separates as a white powder, crystallising from alcohol-ether in small white prisms, M.pt. 232° C. with decomposition. The product is stable and yields an almost neutral solution when dissolved in hot water, separating on cooling as a microcrystalline powder. In organic solvents, except those already mentioned, it is insoluble. Cold concentrated sulphuric acid dissolves the compound, hydrogen chloride being evolved and a colourless solution obtained, which, on warming, develops yellow to green tints ; aqueous ferric chloride gives a reddish-purple coloration.

The acetone filtrates in the foregoing preparation yield the *isomer*, $(HO.C_6H_4)_3SeCl.2H_2O$, on evaporation. This decomposes at 125° C., and dissolves in hot water, evaporation of the solution giving a colourless, viscous gum, setting to a glass over sulphuric acid. It possesses the chemical properties of the preceding compound, and from its solution in aqueous sodium hydroxide, carbon dioxide or acetic acid precipitates the amorphous oxide (decomposing at 180° C.) ; methylation yields a viscous *trimethoxytriphenylselenonium chloride* which may be converted into a *mercurichloride*, M.pt. 54° to 55° C.[1]

Tri-4-hydroxytriphenylselenonium oxide,



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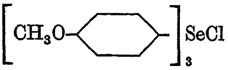
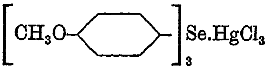
[1] Compare Michaelis and Kunckell, *Ber.*, 1897 30, 2823.

occurs when tri-4-hydroxytriphenylselenonium chloride in aqueous sodium hydroxide solution is treated with carbon dioxide or the calculated amount of dilute acetic acid. It separates as a white amorphous precipitate, decomposing at 240° C., insoluble in neutral organic solvents, but dissolving in acids to form salts. The oxide is amphoteric. The corresponding *sulphate*, decomposing at 269° to 270° C., and the *bromide*, decomposing at 237° C., are prepared by solution of the oxide in the appropriate acid. Silver nitrate quantitatively removes the chlorine from the selenonium chloride, forming a white, crystalline, water-soluble *nitrate*, M.pt. 138° to 139° C. with decomposition. The *chloroplatinate* is orange in colour and separates from hot water as lustrous needles, decomposing at 244° C.

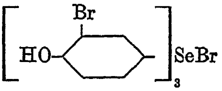
Tri-4-methoxytriphenylselenonium chloride,



5 grams of methyl iodide are added to a solution of 3·9 grams of tri-4-hydroxytriphenylselenonium chloride and sodium methoxide (1 gram of sodium in 200 c.c. of methyl alcohol), the mixture being refluxed until acid to litmus. The mixture is then strongly acidified with hydrochloric acid, distilled in steam, the residue dissolved in chloroform, the solution dried and evaporated to a yellow, uncrystallisable gum, which yields a *mercurichloride*, M.pt. 68° to 70° C. :

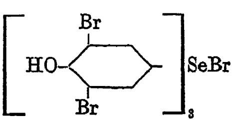


Tri-3-bromotri-4-hydroxytriphenylselenonium bromide,



This is formed when tri-4-hydroxytriphenylselenonium oxide is gradually stirred into excess of bromine. When the vigorous reaction is complete, the mixture is evaporated to dryness and the dry residue triturated with ether. The resulting product is dissolved in hot alcohol, from which a crop of the impure tri-3 : 5-dibromo-derivative separates, the mother-liquors on evaporation and treatment with ether giving the tri-3-bromo-compound as a white microcrystalline powder. Repeated crystallisation yields a product of melting-point 251° C., insoluble in water or organic solvents with the exception of alcohol, but soluble in aqueous sodium hydroxide, dilute acetic acid precipitating the corresponding oxide, M.pt. 198° C., which is decomposed by chlorine water, yielding 2 : 4-dichloro-6-bromophenol.

Tri-3 : 5-dibromotri-4-hydroxytriphenylselenonium bromide,

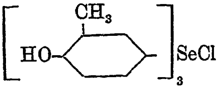


As already mentioned, this compound occurs in the preceding preparation. The material obtained is repeatedly evaporated with bromine, and then crystallised from alcohol. The hexabrominated bromide separates as lustrous, white prisms, decomposing at 261° C. Chlorine water converts it into 4-chloro-2 : 6-dibromophenol, the selenium being eliminated.

o-Cresol Derivatives.

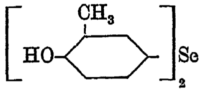
The main product of the interaction of *o*-cresol with selenium oxychloride is tri-4-hydroxytri-3-methyltriphenylselenonium chloride, and di-4-hydroxydi-3-methyldiphenyl selenide is formed as a by-product.

Tri-4-hydroxytri-3-methyltriphenylselenonium chloride,



A solution of 33·6 grams of *o*-cresol (3 mols.) in 400 c.c. of chloroform is treated with 16·6 grams of selenium oxychloride (1 mol.) in 50 c.c. of the same solvent, the whole being well stirred during the addition of the oxychloride. After an hour the mixture is refluxed until the heavy red oil which first separates is converted into solid selenonium salt. The chloroform solution is then decanted, the residue washed with acetone and crystallised from alcohol-ether, a white powder separating (10 grams). It decomposes at 231° C., is insoluble in water and most organic solvents, but dissolves in alcohol. No coloration is developed with alcoholic ferric chloride, but warm concentrated sulphuric acid produces a green tint. From its solution in alkali, carbon dioxide or dilute acetic acid precipitates the corresponding oxide.

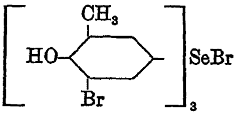
Di-4-hydroxydi-3-methyldiphenyl selenide,



The decanted chloroform solution from the preceding preparation is evaporated and the residual oil distilled in steam. The residue is repeatedly extracted with petroleum (B.pt. 80° to 100° C.) and from the extracts small, pale yellow needles, M.pt. 98° to 99° C., are finally isolated. The product is insoluble in water, but dissolves in aqueous sodium hydroxide or the usual organic solvents ; with concentrated sulphuric acid it gives a green coloration. Boiling with concentrated hydriodic acid eliminates the selenium with the production of 5-iodo-*o*-cresol.

Tri-4-hydroxytri-3-methyltriphenylselenonium oxide occurs when the corresponding chloride in alkaline solution is treated with carbon dioxide or dilute acetic acid. It is an amorphous powder, decomposing at 236° C. Its solution in alkali gives the *nitrate* when treated with nitric acid. This decomposes at 224° C.

Tri-5-bromotri-4-hydroxytri-3-methyltriphenylselenonium bromide,

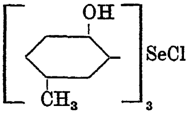


This is prepared by the interaction of the foregoing oxide and an excess of bromine. It separates from alcohol as silvery prisms darkening and decomposing at 253° C. From its alkaline solution dilute acetic acid precipitates the amorphous oxide, which yields 5-chloro-3-bromo-*o*-cresol on treatment with chlorine water.

p-Cresol Derivatives.

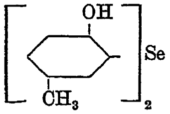
p-Cresol with selenium oxychloride yields tri-2-hydroxytri-5-methyltriphenylselenonium chloride, together with a considerable proportion of di-2-hydroxydi-5-methyldiphenyl selenide, the latter with hydriodic acid forming 3-iodo-*p*-cresol.

Tri-2-hydroxytri-5-methyltriphenylselenonium chloride,



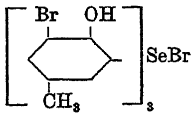
The condensation is carried out in the usual manner in chloroform solution. The product separates from alcohol with 1·5 molecules of solvent of crystallisation, which can be removed at 110° C. It gives the iodoform test with iodine in aqueous sodium hydroxide. At 260° to 265° C. it decomposes. It is insoluble in water, but dissolves in hot alcohol or aqueous sodium hydroxide. Alcoholic ferric chloride gives a faint olive-green tint; concentrated sulphuric acid gives no coloration in the cold, but on warming an olive-green tint appears, changing to deep red. The chloride may be converted to the *oxide* in the usual manner.

Di-2-hydroxydi-5-methyldiphenyl selenide,



The chloroform filtrate from the preceding preparation is evaporated nearly to dryness and the residue distilled in steam, the distillate containing 3-chloro-*p*-cresol. The dry residue is extracted repeatedly with petroleum (B.pt. 40° to 60° C.), the white selenide being obtained, M.pt. 111° C. It dissolves in the usual organic solvents, but is insoluble in water. Cold concentrated sulphuric acid gives a green tint, becoming red on warming; alcoholic ferric chloride gives a green coloration. Concentrated hydriodic acid causes decomposition with elimination of selenium and formation of 3-iodo-*p*-cresol. The last fractions of the foregoing petroleum extracts contain 5-chloro-4 : 4′-dihydroxy-3 : 3′-ditolyl.

Tri-3-bromotri-2-hydroxytri-5-methyltriphenylselenonium bromide,

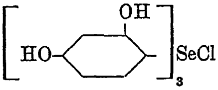


prepared in the usual manner, separates from hot alcohol as pinkish-white prisms, decomposing at 195° C.

Resorcinol Derivative.

Resorcinol reacts with selenium oxychloride in a similar manner to phenol.

Tri-2 : 4-dihydroxytriphenylselenonium chloride,



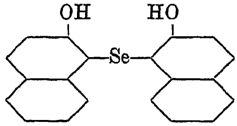
The condensation is conducted in the usual way in chloroform. The chloride crystallises from acetone with 1 molecule of solvent of crystallisation, and melts at 206° C. It dissolves in boiling water, the pale red solution setting to a jelly on cooling. In aqueous sodium hydroxide or alcohol it readily dissolves, but it is only sparingly soluble in acetone or glacial acetic acid, and insoluble in benzene or chloroform. Aqueous ferric chloride gives a reddish-purple coloration, warm concentrated sulphuric acid gives a green tint, and bromine water causes decomposition.[1]

β-Naphthol Derivative.

The condensation proceeds quantitatively according to the equation

$$3C_{10}H_7.OH + SeOCl_2 = Se(C_{10}H_6.OH)_2 + C_{10}H_6Cl(OH) + HCl + H_2O$$

Di-2-hydroxydi-1-naphthyl selenide,

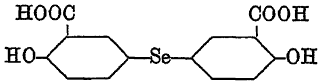


crystallises from acetone as lustrous, colourless prisms, M.pt. 186° C. to a red liquid. It dissolves readily in acetone, is sparingly soluble in hot alcohol or glacial acetic acid, but is insoluble in chloroform, benzene, ether or water. Cold concentrated sulphuric acid gives a green tint, but alcoholic ferric chloride gives no colour effect. From its solutions in alkali the selenide is precipitated unchanged by acids.

Salicylic Acid Derivative.

In this case the condensation is best effected in the absence of solvents, a compound of the type $Se(R.OH)_2$ resulting.

Di-4-hydroxydiphenyl selenide di-3-carboxylic acid,



0·3 gram-molecule of salicylic acid (41·4 grams) and 0·1 gram-molecule of selenium oxychloride (16·6 grams) are heated together in an open basin until evolution of hydrogen chloride ceases and the melt becomes brown. After cooling, the melt is powdered, extracted with hot benzene, and the pale yellow residue (20 grams) repeatedly crystallised from aqueous alcohol, small, yellowish-white, micaceous plates, sinter-

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[1] Compare Michaelis and Kunckell, *Ber.*, 1897, 30, 2823.

ing at 250° C. and decomposing at 272° C., being obtained. The compound is readily soluble in alcohol, ether, acetone, glacial acetic acid, aqueous sodium hydroxide or alkali carbonates, insoluble in water, chloroform or benzene. The addition of ether to an alcoholic solution of the very soluble sodium salt of the selenide yields a hygroscopic precipitate of the *sodium salt,* which becomes green on exposure. The selenide in alcohol gives an intense bluish-violet coloration with ferric chloride, and cold concentrated sulphuric acid gives a green coloration which deepens on warming.

Anisole Derivatives.[1]

Condensation between anisole and selenium oxychloride leads to the formation of compounds of the types $(R.OMe)_2SeCl_2$ and $(R.OMe)_2Se$.

Di-4-methoxydiphenyl dichloroselenide, $(C_6H_4.OCH_3)_2SeCl_2$.—Selenium oxychloride (16·5 grams, *i.e.* 1 mol.) is slowly added to anisole (21·6 grams, *i.e.* 2 mols.) in three volumes of ether. Hydrogen chloride is evolved and the solution becomes brownish-red. After completion of the reaction, evaporation yields a thick residue which crystallises. The residue left after extraction with benzene and water is recrystallised from chloroform-alcohol. The product, consisting of yellow needles, M.pt. 159° C., is readily soluble in chloroform, but sparingly soluble in ether or water. Its solution in the latter solvent has an acid reaction.

Selenoanisole, $(C_6H_4.OCH_3)_2Se$, occurs when the mother-liquors from the preceding preparation are evaporated. It may be prepared in larger quantity by taking one molecular equivalent of selenium oxychloride to one mol. equiv. of anisole and carrying out the operation in ether solution. It forms white, nacreous plates, M.pt. 48° C., readily soluble in chloroform, alcohol, acetic acid or ether. In chloroform solution it unites with chlorine to yield the *dichloro-compound*; with bromine it gives *di-4-methoxydiphenyl dibromoselenide,* brick-red needles, M.pt. 124° C.; with iodine a red syrup is formed. These halogen compounds react with moist silver oxide yielding *di-4-methoxydiphenyl dihydroxyselenide,* white needles, M.pt. 137° C., readily soluble in alcohol and converted by concentrated hydrochloric acid into the dichloride.

Phenetole Derivatives.

This substituted phenol gives compounds of a similar type to those derived from anisole.

Di-4-ethoxydiphenyl dichloroselenide forms yellow needles, M.pt. 140° C., readily soluble in chloroform, sparingly soluble in alcohol or ether, practically insoluble in water. *Selenophenetole* yields white needles, M.pt. 56° C., readily soluble in chloroform, alcohol, acetic acid or ether, and easily combining with halogens to give dihalides. *Di-4-ethoxydiphenyl dibromoselenide* separates as red needles, M.pt. 123° C., and the *di-iodo-compound* in thin coffee-coloured needles, M.pt. 96° C. The halogen derivatives are readily converted to the *dihydroxide,* which forms white needles, M.pt. 145° C.

Naphthyl Alkyl Ether Derivatives.[2]

These ethers only give products of the type $(C_{10}H_6.OAlk.)_2Se$.

Seleno-α-naphthyl methyl ether, $(C_{10}H_6.OCH_3)_2Se$, occurs when

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[1] Kunckell, *Ber.,* 1895, 28, 609.

[2] Michaelis and Kunckell, *loc. cit.*

one molecular equivalent of selenium oxychloride reacts with two mol. equivs. of α-naphthyl methyl ether in ether solution. It is a crystalline mass, M.pt. 138° C., readily soluble in chloroform, sparingly soluble in alcohol. *Seleno-α-naphthyl ethyl ether* crystallises as small, lemon-yellow needles, M.pt. 149° C.

Seleno-β-naphthyl methyl ether forms needles, M.pt. 162° C., easily soluble in chloroform, less soluble in alcohol. The corresponding *ethyl ether* separates as pure white needles, M.pt. 176° C.

ARYLSELENOGLYCOLLIC ACIDS.

These compounds are obtained by treating Grignard's reagents with finely powdered selenium, when an addition compound results, which is decomposed by ice and hydrochloric acid and the arylselenomercaptan formed extracted as alkali salt from its ether solution, this salt then being condensed with sodium chloracetate in aqueous alcohol solution, the process being summarised as follows :

$$\mathrm{ArMgBr} \longrightarrow \mathrm{ArSeMgBr} \longrightarrow \mathrm{ArSeH}$$
$$\mathrm{ArSeNa} + \mathrm{CH_2Cl.CO_2Na} = \mathrm{ArSe.CH_2.CO_2Na} + \mathrm{NaCl}$$

Phenylselenoglycollic acid, $C_6H_5Se.CH_2.CO_2H$.[1]—20 grams of finely powdered selenium are slowly added to the magnesium phenyl bromide derived from 39 grams of bromobenzene and 6 grams of magnesium in dry ether. A brisk reaction ensues and the mixture is cooled in ice, the reaction afterwards being completed by warming on the water-bath. The cooled mixture is poured upon ice and hydrochloric acid, a small quantity of hydrogen selenide and red selenium separating. The ether layer is extracted rapidly with a solution of 7 grams of potassium hydroxide in 60 c.c. of water, and to the aqueous solution are added 100 c.c. of alcohol and a solution of sodium chloracetate (from 6·7 grams of sodium carbonate and 11·8 grams of monochloracetic acid). Heat is evolved and the sodium salt of the selenoglycollic acid separates as a white powder, the reaction being completed by heating on the water-bath and concentration of the solution to half its bulk. The *sodium salt* crystallises in pinkish-white plates. The acid separates as a pale yellow oil when hydrochloric acid is added to an aqueous solution of the sodium salt. It dissolves in a large quantity of boiling water, from which it separates as a colourless oil, B.pt. 160° C. at 750 mm., which crystallises after standing for several days and melts at 40° C. The *potassium salt* forms colourless plates having a silvery lustre. The acid is soluble in most organic solvents, but only sparingly soluble in water, the solution being acid to litmus. With concentrated sulphuric acid a deep purple coloration develops. The *copper salt* is bright green and insoluble in water.

p-Bromophenylselenoglycollic acid, $C_6H_4Br.Se.CH_2.CO_2H$, is prepared by a similar method to the foregoing acid. It crystallises from hot water in colourless, lustrous needles, M.pt. 127° C., and has a solubility like that of the unbrominated acid. The *sodium salt* is slightly pink, the *silver salt* is only slowly decomposed by light, and the *copper salt* is green and insoluble in water. The acid develops a deep brown colour in concentrated sulphuric acid.

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[1] Morgan and Porritt, *Trans. Chem. Soc.*, 1925, 127, 1755.

o-Tolylselenoglycollic acid, $CH_3.C_6H_4.Se.CH_2.CO_2H$,[1] crystallises in lustrous plates, M.pt. 70° to 71° C. The *sodium salt* is known. The acid develops a reddish-brown colour in concentrated sulphuric acid.

p-Tolylselenoglycollic acid[2] separates from hot water in lustrous, acicular prisms, M.pt. 98° C., giving a carmine-red coloration with concentrated sulphuric acid. The *alkali* and *ammonium salts* are colourless, crystalline substances, soluble in water; the green *copper salt* is insoluble.

o-Xylyl-4-selenoglycollic acid, $(CH_3)_2C_6H_3.Se.CH_2.CO_2H$,[3] prepared from 4-iodo-*o*-xylene, crystallises from hot water in colourless plates, M.pt. 88° C., which develop a violet coloration in sulphuric acid.

m-Xylyl-4-selenoglycollic acid forms colourless lustrous plates, M.pt. 90·5° C., the colour in sulphuric acid being greenish-yellow.

***a*-Naphthylselenoglycollic acid,** $C_{10}H_7Se.CH_2.CO_2H$,[4] is obtained as an oil which takes three weeks to crystallise in a vacuum desiccator. The solid melts at 54° C. and gives a green coloration in concentrated sulphuric acid.

Halogenides of Arylselenoglycollic Acids.

Phenylselenoglycollic acid dibromide, $C_6H_5SeBr_2.CH_2.CO_2H$.[5] —A solution of 8 grams of bromine in 50 c.c. of warm carbon tetrachloride is added to a hot solution of 10·75 grams of phenylselenoglycollic acid in 500 c.c. of carbon tetrachloride. The additive compound (18·3 grams, 97 per cent. yield) separates as very small, ill-defined needles, M.pt. 126° C. to a deep red liquid. It is almost insoluble in carbon tetrachloride, chloroform, benzene or carbon disulphide; it dissolves in about ten times its weight of hot glacial acetic acid, but on cooling red crystals of bromoselenobenzene separate, M.pt. 61° C. When the dibromide is heated alone it yields mainly bromoselenobenzene and bromacetic acid:

$$CH_2[SeBr_2.C_6H_5]CO_2H = C_6H_5SeBr + CH_2Br.CO_2H$$

p-Tolylselenoglycollic acid dibromide, $CH_3.C_6H_4.SeBr_2.CH_2.CO_2H$.[6]—A solution of 2·29 grams of *p*-tolylselenoglycollic acid in 25 c.c. of dry chloroform is treated with 1·6 grams (1 mol.) of bromine and left in a vacuum desiccator. The dibromide separates in clusters of golden-yellow needles, which decompose between 90° and 100° C. with evolution of bromine.[7] A second method of preparation consists of adding a solution of 0·4 gram of bromine in 25 c.c. of carbon tetrachloride to a cold solution of 0·65 gram of *p*-tolylmethylselenetine bromide in 300 c.c. of carbon tetrachloride. The yield is 0·8 gram of yellow needles, M.pt. 100° to 101° C. The dibromide is not stable in moist air, and is easily hydrolysed, giving complex brownish-red oils. It decomposes when heated or brominated, according to the following scheme:

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[1] Porritt, *J. Chem. Soc.*, 1927, p. 27.

[2] Morgan and Porritt, *loc. cit.*

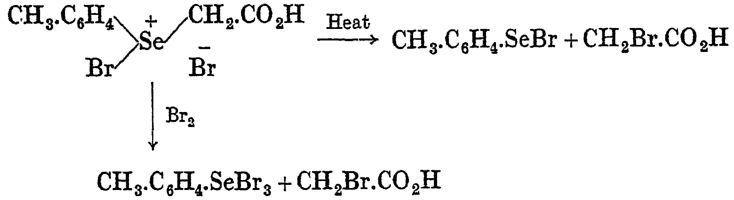
[3] Porritt, *loc. cit.*

[4] Morgan and Porritt, *loc. cit.*

[5] Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 1928, p. 2293.

[6] Morgan and Porritt, *loc. cit.*; Edwards, Gaythwaite, Kenyon and Phillips, *loc. cit.*

[7] The melting-point of the dibromide as prepared by this method is given by Edwards, etc. as 103° to 104° C., a deep red liquid being formed.

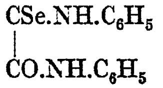


p-Bromophenylselenoglycollic acid dibromide, $C_6H_4Br.SeBr_2.CH_2.CO_2H$, prepared from *p*-bromophenylselenoglycollic acid, forms golden-yellow crystals decomposing at 120° to 130° C. with evolution of bromine. Excess of bromine in this preparation is said to give a tetrabromide, which separates as scarlet needles.

SELENIUM DERIVATIVES OF SUBSTITUTED ANILIDES.

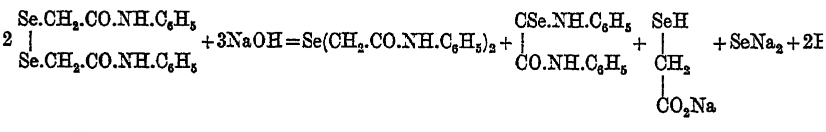
Selenodiglycollic anilide, $Se(CH_2.CO.NH.C_6H_5)_2$,[1] may be obtained by the interaction of potassium selenide and chloracetanilide in alcoholic solution, or as follows: 5 grams of diselenoglycollic anilide and 30 c.c. of 25 per cent. sodium hydroxide solution are heated to boiling for a short time and the mixture filtered. A white solid is obtained and a red filtrate. The solid crystallises from alcohol as white needles, M.pt. 198° C., and gives an analysis corresponding to selenodiglycollic anilide.

Selenoxanilide,



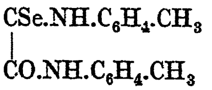
$$\begin{array}{l} CSe.NH.C_6H_5 \\ | \\ CO.NH.C_6H_5 \end{array}$$

The red filtrate in the preceding preparation is treated with hydrochloric acid, the red precipitate dissolved in a little alcohol, some selenium being deposited, and the solution rendered turbid by the addition of water. Shining red needles separate, which after crystallisation melt at 139·5° to 140·5° C. The yield is small. The product is readily soluble in hot alcohol, acetic acid, chloroform or benzene, but insoluble in water. The preparation may be represented as follows:



$$2\begin{array}{l} Se.CH_2.CO.NH.C_6H_5 \\ | \\ Se.CH_2.CO.NH.C_6H_5 \end{array} + 3NaOH = Se(CH_2.CO.NH.C_6H_5)_2 + \begin{array}{l} CSe.NH.C_6H_5 \\ | \\ CO.NH.C_6H_5 \end{array} + \begin{array}{l} SeH \\ | \\ CH_2 \\ | \\ CO_2Na \end{array} + SeNa_2 + 2$$

Selenodiglycollic o-toluidide, $Se(CH_2.CO.NH.C_6H_4.CH_3)_2$, prepared in a similar manner to the anilide, has not been obtained in a pure state, but *selenoxal-o-toluidide,*



$$\begin{array}{l} CSe.NH.C_6H_4.CH_3 \\ | \\ CO.NH.C_6H_4.CH_3 \end{array}$$

separates from alcohol in red needles and plates, M.pt. 131·5° to 132·5° C., soluble in alcohol, acetic acid, chloroform and benzene, insoluble in water.

Selenodiglycollic m-toluidide separates from alcohol in white

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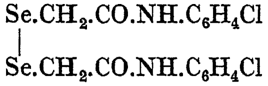
[1] Frerichs and Wildt, *Annalen*, 1908, 360, 118.

needles, M.pt. 170° to 171° C., insoluble in water, soluble in alcohol or acetic acid.

Selenodiglycollic p-toluidide may be prepared from diselenodiglycollic *p*-toluidide, or by treating chloraceto-*p*-toluidide with potassium selenide. The product melts at 217° to 218° C., is soluble in alcohol or hot acetic acid, sparingly soluble in chloroform or benzene, insoluble in water. *Selenoxal-p-toluidide* separates from dilute alcohol in long, red needles, M.pt. 165° to 166° C., soluble in alcohol, acetic acid, chloroform or benzene, insoluble in water.

Diselenodiglycollic p-chloranilide,

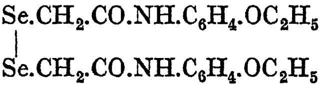


$$\begin{array}{l}\text{Se.CH}_2\text{.CO.NH.C}_6\text{H}_4\text{Cl}\\ |\\ \text{Se.CH}_2\text{.CO.NH.C}_6\text{H}_4\text{Cl}\end{array}$$

occurs when the compound $NH_2.CO.Se.CH_2.CO.NH.C_6H_4Cl$ is boiled in alcohol in the presence of air. It gives yellowish needles, M.pt. 172° to 173° C., soluble in alcohol or acetic acid, insoluble in water.

Selenodiglycollic p-chloranilide, $Se(CH_2.CO.NH.C_6H_4Cl)_2$, obtained from the preceding compound in the usual way, melts at 190° to 191° C. *Selenoxal-p-chloranilide,* $ClC_6H_4.NH.CO.CSe.NH.C_6H_4Cl$, separates as long, silky, yellowish-red needles, M.pt. 166° C. The yield of the latter compound is very small, and the product dissolves in alcohol or acetic acid, but is insoluble in water.

Diselenodiglycollic p-phenetide,



$$\begin{array}{l}\text{Se.CH}_2\text{.CO.NH.C}_6\text{H}_4\text{.OC}_2\text{H}_5\\ |\\ \text{Se.CH}_2\text{.CO.NH.C}_6\text{H}_4\text{.OC}_2\text{H}_5\end{array}$$

This compound is obtained from *selenocyanaceto-p-phenetide,* $CNSe.CH_2.CO.NH.C_6H_4.OC_2H_5$, which is prepared as follows: 7 grams of potassium selenocyanate in 7 per cent. alcoholic solution are heated to boiling. Two or three drops of dilute hydrochloric acid are added, which causes the separation of some selenium, and after the addition of 10 grams of chloraceto-*p*-phenetide, the boiling is continued for two minutes. On filtering, long yellowish needles melting with decomposition at 162° to 163° C. are obtained. The cyano-compound is soluble in hot alcohol or acetic acid, insoluble in water. When dissolved in the smallest possible amount of acetic acid, followed by the addition of two volumes of fuming hydrochloric acid, addition of water causes the separation of crystals after a short time. This is a diseleno-compound, and recrystallisation from aqueous alcohol gives small yellow needles, M.pt. 161° to 162° C., soluble in alcohol or acetic acid, insoluble in water.

Selenodiglycollic p-phenetide, $Se(CH_2.CO.NH.C_6H_4.OC_2H_5)_2$, prepared in the usual manner, melts at 199° to 200° C., and is soluble in alcohol or acetic acid, but insoluble in water. *Selenoxal-p-phenetide,* $C_2H_5O.C_6H_4.NH.CO.CSe.NH.C_6H_4.OC_2H_5$, crystallises from alcohol in large red needles, M.pt. 160° to 161° C., soluble in alcohol or acetic acid, moderately soluble in chloroform or benzene, insoluble in water.

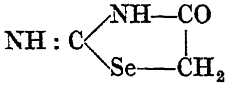
SELENIUM DERIVATIVES OF SUBSTITUTED AMIDES.

When a 10 per cent. alcoholic solution of potassium selenocyanate containing a few drops of hydrochloric acid is heated with derivatives of the type $RCO.NH.CO.CH_2Cl$, with chloracetamide, $NH_2.CO.CH_2Cl$, or with α-bromopropionylcarbamide, $NH_2.CO.NH.CO.CH(CH_3)Br$, a product occurs which may have a constitution $RCO.NH.CO.CH_2.SeCN$ or $RCO.NH.CO.CH_2.NCSe$, etc.[1] To decide between these constitutions is difficult, since aqueous sodium hydroxide causes the formation of sodium cyanide whilst, on the other hand, heating alone or with water, aniline or toluidine gives rise as a rule to a diselenoglycolyl compound of the type $Se_2(CH_2.CO.NH.COR)_2$.

Selenocyanoacetocarbamide, $NH_2.CO.NH.CO.CH_2.SeCN$, obtained as noted above using chloracetylcarbamide, melts at 178° to 179° C., and yields *diselenoglycolylcarbamide*, $Se_2(CH_2.CO.NH.CO.NH_2)_2$, M.pt. 221° C., when boiled with water. Boiling with 10 per cent. ammonium hydroxide solution converts selenocyanoacetocarbamide into hydantoin, ammonium selenocyanate and a little diseleno-derivative. The seleno-compound will also exchange its —SeCN grouping for $—SO_2C_6H_5$ or —NCS when heated in alcoholic solution with sodium benzene sulphinate or potassium thiocyanate respectively, in the latter case an immediate transformation of the product into thiohydantoin occurring.

Selenocyanoacetomethylcarbamide, $CH_3.NH.CO.NH.CO.CH_2.SeCN$, melts at 148° to 149° C., and heating it with water or aniline gives *diselenoglycolylmethylcarbamide*, $Se_2(CH_2.CO.NH.CO.NH.CH_3)_2$, M.pt. 183° to 184° C.

Selenocyanoacetophenylcarbamide, $C_6H_5.NH.CO.NH.CO.CH_2.SeCN$, M.pt. 147° to 148° C., yields diphenyl carbamide and *selenohydantoin*,

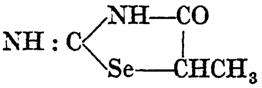


$$NH:C\begin{cases}NH—CO\\ \quad\ |\\ Se—CH_2\end{cases}$$

M.pt. 190° C., when boiled with water.

Selenocyanoacetamide, $NH_2.CO.CH_2.SeCN$, melts at 123° to 124° C., but does not form a diseleno-derivative.

α-Selenocyanopropionylcarbamide, $NH_2.CO.NH.CO.CH(CH_3)SeCN$, M.pt. 136° C., yields an *α-methylselenohydantoin*,



$$NH:C\begin{cases}NH—CO\\ \quad\ |\\ Se—CHCH_3\end{cases}$$

M.pt. 179° C., when boiled with ammonium hydroxide.

Potassium selenocyanate reacts with substances of the type $NHR.CO.CH_2Cl$ to give products $NHR.CO.CH_2.SeCN$, which, on heating with concentrated hydrochloric acid and sometimes glacial acetic acid, yield a diselenoglycollo-derivative, $Se_2(CH_2.CO.NHR)_2$. At the same time some carbamidoselenoglycollo-derivative, $NHR.CO.CH_2.Se.CO.NH_2$, is probably formed, but is seldom isolated. Acidification with hydrochloric acid causes evolution of hydrogen cyanide, and on adding ammoniacal copper sulphate a precipitate separates having the composition $(NHR.CO.CH_2.Se)_2Cu_2$.

The following derivatives of the foregoing types are known : *Selenocyanoacetanilide*, $C_6H_5.NH.CO.CH_2.SeCN$, M.pt. 129° C.; *diselenoglycolloanilide*, $Se_2(CH_2.CO.NH.C_6H_5)_2$, M.pt. 158° C.; *carbamido-*

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[1] Frerichs, *Arch. Pharm.*, 1903, 241, 177.

selenoglycolloanilide, $C_6H_5.NH.CO.CH_2.Se.CO.NH_2$, M.pt. 118° to 119° C.; *cuproselenoglycolloanilide*, $(C_6H_5.NH.CO.CH_2.Se)_2Cu_2$; *selenocyanoacetotoluidides*, $CH_3.C_6H_4.NH.CO.CH_2.SeCN$, *ortho-*, M.pt. 126° C., *meta-*, M.pt., 136° C., *para-*, M.pt. 160° C.; *diselenoglycollotoluidides*, $Se_2(CH_2.CO.NH.C_6H_4.CH_3)_2$, *ortho-*, M.pt. 174·5° C., *meta-*, M.pt. 158° C., *para-*, M.pt. 174° C.; *selenocyanoacetoxylidides*, $(CH_3)_2C_6H_3.NH.CO.CH_2.SeCN$, *meta-* (asym.), M.pt. 148° C., *para-*, M.pt. 144° to 146° C.; *diselenoglycolloxylidides*, $Se_2[CH_2.CO.NH.C_6H_3(CH_3)_2]_2$, *meta-* (asym.), M.pt. 184° C., *para-*, M.pt. 180° to 181° C.; *selenocyanoacetochloranilides*, $Cl.C_6H_4.NH.CO.CH_2.SeCN$, *meta-*, M.pt. 117° to 118° C., *para-*, M.pt. 178° C.; *diselenoglycollo-m-chloranilide*, $Se_2(CH_2.CO.NH.C_6H_4.Cl)_2$, M.pt. 183° C.; *selenocyanoacetobromanilides*, $BrC_6H_4.NH.CO.CH_2.SeCN$, *meta-*, M.pt. 105° C., *para-*, M.pt. 188° C.; *diselenoglycollo-m-bromanilide*, $Se_2(CH_2.CO.NH.C_6H_4Br)_2$, M.pt. 198° C.; *selenocyanoacetoanisidides*, $CH_3O.C_6H_4.NH.CO.CH_2.SeCN$, *ortho-*, M.pt. 110° C., *para-*, M.pt. 131° C.; *diselenoglycolloanisidide*, $Se_2(CH_2.CO.NH.C_6H_4.OCH_3)_2$, *ortho-*, M.pt. 124° C., *para-*, M.pt. 172° C.

In the following compounds the grouping $—NHR$ in the foregoing types is replaced by $—NRC_6H_5$: *Selenocyanoacetomethylanilide*, $(CH_3)C_6H_5.N.CO.CH_2.SeCN$, M.pt. 78° C.; *diselenoglycollomethylanilide*, $Se_2[CH_2.CO.NC_6H_5(CH_3)]_2$, M.pt. 94° to 95° C.; *carbamidoselenoglycollomethylanilide*, $(CH_3)C_6H_5N.CO.CH_2.Se.CO.NH_2$, M.pt. 123° C.; *cuproselenoglycollomethylanilide*, $[(CH_3)C_6H_5N.CO.CH_2.Se]_2Cu_2$; *selenocyanoacetobenzylanilide*, $(C_6H_5.CH_2)C_6H_5N.CO.CH_2.SeCN$, M.pt. 70° C.; *diselenoglycollobenzylanilide*, $Se_2[CH_2.CO.NC_6H_5(CH_2.C_6H_5)]_2$, M.pt. 81° C.; *carbamidoselenoglycollobenzylanilide*, $(C_6H_5.CH_2)C_6H_5N.CO.CH_2.Se.CO.NH_2$, M.pt. 140° to 141° C.; *cuproselenoglycollobenzylanilide*, $[(C_6H_5.CH_2)C_6H_5N.CO.CH_2.Se]_2Cu_2$; *selenocyanoacetodiphenylamide*, $(C_6H_5)_2N.CO.CH_2.SeCN$, M.pt. 103° C.; *diselenoglycollodiphenylamide*, $Se_2[CH_2.CO.N(C_6H_5)_2]_2$, M.pt. 123° to 124° C.

Phenylselenoacetamide, $C_6H_5.CH_2.CSe.NH_2$,[1] occurs in almost quantitative yield when phenylacetonitrile reacts at 80° C. with alcoholic hydrogen selenide, saturated at $-10°$ C., containing sodium hydrogen selenide. The compound separates as glistening white crystals, M.pt. 92° to 92·5° C.

Selenoacetamide, $CH_3.CSe.NH_2$, prepared in a similar manner to the foregoing compound, is isolated in 17 per cent. yield from acetonitrile. It melts at 126° to 126·5° C.

AROMATIC SELENO-ALDEHYDES.

Three selenobenzaldehydes have been described,[2] the particular compound obtained depending on the conditions obtaining.

α-Selenobenzaldehyde, $C_6H_5.CHSe$, occurs when hydrogen selenide is passed for three to four hours into a solution of 21 grams of benzaldehyde in 140 c.c. of alcohol. Clusters of yellow transparent columns separate, M.pt. 83° to 84° C., soluble in alcohol, ether, acetone, chloroform or benzene, insoluble in water. The yield is small and the compound is decomposed by light. If the alcohol used has been previously saturated with hydrogen chloride, a mixture of *β-* and *γ-selenobenzaldehydes* results, and these may be separated by taking advantage of their

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[1] Kindler, *Annalen*, 1923, 431, 187.

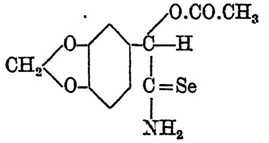
[2] Vanino and Schinner, *J. prakt. Chem.*, 1915, [ii], 91, 116.

differing solubilities in benzene. The *β-variety* is the most sparingly soluble form and crystallises from benzene as lustrous, golden-yellow needles, M.pt. about 205° C., having the constitution $3C_6H_5.CHSe.C_6H_6$. This variety is also said to occur when magnesium bromohydroselenide reacts with benzaldehyde, the melting-point of the product being 203° to 205° C.[1] It is insoluble in water, sparingly soluble in alcohol or ether, but readily soluble in chloroform or nitrobenzene. Distillation with copper powder yields stilbene. *γ-Selenobenzaldehyde* separates when the benzene mother-liquors from the β-variety are evaporated. Slender pale yellow needles, M.pt. 166° C., are obtained, readily soluble in benzene, sparingly soluble in alcohol or ether.

A selenobenzaldehyde is also formed when phosphorus pentaselenide heated with alcoholic potassium hydroxide is treated with benzal chloride.[2] The product forms yellow needles, M.pt. 70° C., and would appear to correspond with the foregoing α-variety except that it is soluble in hot water. It may be an impure form of the α-variety.

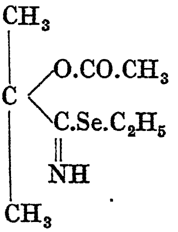
SELENIUM DERIVATIVES OF CYANHYDRINS FROM ALDEHYDES AND KETONES.

Compound [3]



Three parts of methylenedioxyacetylmandelonitrile in 10 parts of benzene are treated with two volumes of alcohol saturated with ammonia at 0° C., and the whole cooled in ice and saturated with hydrogen selenide. After several hours the product is collected, dissolved in acetone and reprecipitated by ligroin. This operation is repeated several times, snow-white bushy needles resulting, these corresponding to the above formula. The selenamide decomposes at about 125° C. When *o-nitrobenzoylmandelonitrile* is used in the reaction the resulting *product* forms needles decomposing towards 140° C.

Compound [4]



5 grams of acetylacetone cyanhydrin are dissolved in 50 c.c. of absolute alcohol, 20 c.c. of alcohol saturated with ammonia at 0° C. added, and hydrogen selenide passed in whilst the mixture is cooled. After long standing at a low temperature a stream of air is passed through the solution and the filtrate concentrated in a vacuum. The residue

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[1] Mingoia, *Gazzetta*, 1928, 58, 667.

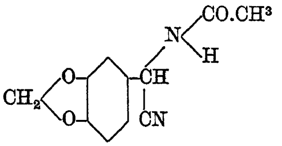
[2] Cole, *Ber.*, 1875, 8, 1165.

[3] German Patent, 273073.

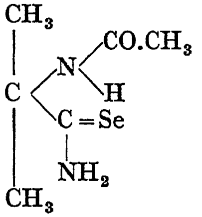
[4] German Patents, 273073, 275442.

crystallises from ligroin in snow-white needles, becoming violet at 99° to 100° C.

A *compound*[1] of unknown formula is prepared from α-acetamidohomopiperonylic nitrile



in a similar manner to that described for the preceding compounds. It forms needles, which become reddish-brown at 119° C. *α-Acetylaminoisobutyronitrile* gives a *compound* of the formula



melting at 143° to 146° C. to a brown liquid.

SUGARS CONTAINING SELENIUM.[2]

Dicellosyl selenide tetradeca-acetate, $C_{52}H_{70}O_{34}Se$, is prepared by dissolving metallic potassium in alcohol, half saturating the solution with dry hydrogen selenide in the absence of oxygen, and adding acetobromocellose to the boiling solution. On cooling, slender and almost colourless needles are deposited, M.pt. 252° C., $[\alpha]_D$ −47·08° at 18° C. in chloroform solution.

Dicellosyl selenide, $C_{24}H_{42}O_{20}Se$, occurs when the acetyl derivative in methyl alcohol solution is saponified by ammonia and extracted with ether. It is a yellow powder, decomposing at about 215° C., $[\alpha]_D$ −85·93° to −86·35° at 20° C. in aqueous solution.

Cellosyl-glucosyl selenide hendeca-acetate, $C_{40}H_{54}O_{26}Se$.—A mixture of acetobromocellose and acetobromoglucose is suspended in 96 per cent. alcohol and treated with potassium selenide. The product crystallises in rhombic platelets combined in rosettes, M.pt. 141° C., $[\alpha]_D$ −39·76° and −40·36° in ethyl acetate. Hydrolysis with ammonia gives *cellosyl-glucosyl selenide,* $C_{18}H_{32}O_{15}Se$, a yellow powder decomposing at about 160° C.

Galactosyl-glucosyl selenide octa-acetate, $C_{28}H_{38}O_{18}Se$.—This is prepared from acetobromoglucose and acetobromogalactose, using potassium selenide in alcoholic solution. It forms dense needles, M.pt. 161° C., $[\alpha]_D$ −30·92° to −30·72° in ethyl acetate. Hydrolysis with ammonia yields *galactosyl-glucosyl selenide,* which gives the value $[\alpha]_D$ −48·35° at 16° C. in water.

Potassium selenide also reacts with alcohol solutions of β-acetobromodextrose, the octa-acetate of a disaccharide in which one of the oxygen atoms is replaced by selenium being obtained.[3] The compound

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[1] German Patent, 275847.

[2] Wrede, *Zeitsch. physiol. Chem.*, 1920, 112, 1.

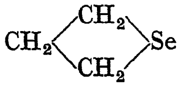
[3] Wrede, *Biochem. Zeitsch.*, 1917, 83, 96.

is a well-crystallised substance, yielding on hydrolysis by acids hydrogen selenide and a reducing sugar. The acetate, $C_{28}H_{38}O_{18}Se$, gives the rotation $[\alpha]_D$ − 51·24° at 25° C. in tetrachloroethane solution. Hydrolysis with alcoholic ammonia causes scission of the acetyl groups, the *disaccharide*, $C_{12}H_{22}O_{10}Se$, M.pt. 193° C., $[\alpha]_D$ −83·58° resulting. Crystalline *metallic salts* have been isolated, such as $C_{12}H_{21}O_{10}SeK.2H_2O$ and $C_{12}H_{20}O_{10}SeK_2.4H_2O$. The disaccharide has been designated *selenoisotrehalose.*

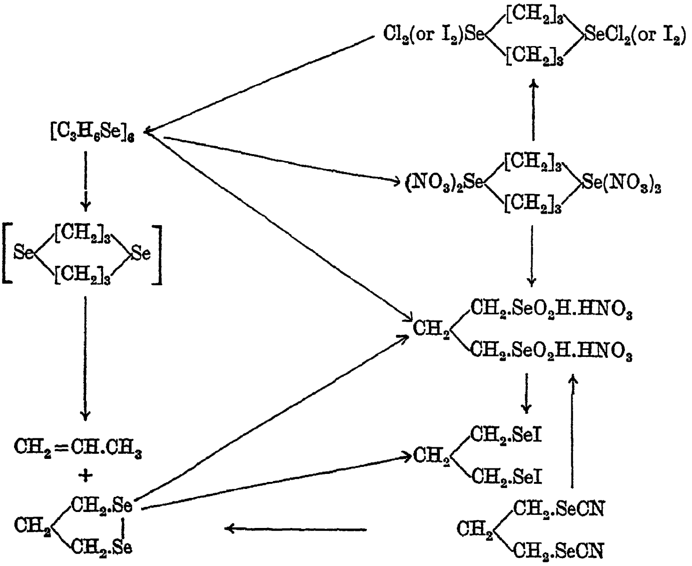
POLYMETHYLENE SELENIUM COMPOUNDS.

*cyclo*Selenopropane and its Derivatives.[1]

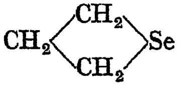
Although the cyclic selenohydrocarbons having five- or six-membered rings are isolated in good yield by the interaction of alkylene dibromides and sodium selenide, trimethylene dibromide and sodium selenide furnish only a small yield of *cyclo*selenopropane,



the main product being a polymeride, $[C_3H_6Se]_6$. The following scheme shows the products which have been obtained :



cycloSelenopropane,



40 grams of freshly distilled trimethylene dibromide are added to an alcoholic suspension (350 c.c.) of sodium selenide obtained from 24 grams of aluminium selenide, 11 grams of sodium and 9 c.c. of water in the presence of hydrogen. After standing for some hours in an

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[1] Morgan and Burstall, *J. Chem. Soc.*, 1930, p. 1497.

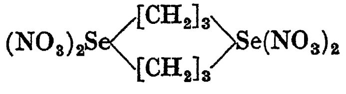
inert atmosphere the mixture is filtered and the filtrate distilled under reduced pressure, the distillate being rectified until a colourless alcoholic solution results. The latter is poured into a large excess of water and the aqueous alcoholic solution repeatedly extracted with petroleum, the extracts being dried over calcium chloride and the solvent removed. The residue is distilled under diminished pressure and finally rectified in a stream of carbon dioxide at the ordinary pressure. A considerable quantity of the oil polymerises to a yellow gum during these distillations.

*cyclo*Selenopropane is a colourless liquid having a powerful and penetrating odour, the vapour exerting an irritant effect on the mucous membrane of the nose. It boils at 118° to 119° C. at 779 mm.; n_D 1·5612 at 15° C.; density 1·525 at 20° C., 1·510 at 29° C., 1·498 at 37·5° C., 1·484 at 47° C., whence density $= 1{\cdot}554 - 0{\cdot}001493t$ at $t°$ C. With organic solvents the compound is miscible in all proportions, but it is insoluble in water. In volatile solvents the vapours show varying degrees of volatility. Mineral acids cause rapid polymerisation of the substance.

cycloSelenipropane 1 : 1-di-iodide, $C_3H_6SeI_2$.—Alcoholic iodine solution interacts with the foregoing product yielding a *polymerised* form of the *di-iodide* as an amorphous purple deposit, insoluble in all organic solvents and softening at 87° C., then remaining liquid. Although this polymer is the main product of the reaction, a more soluble *monomeric di-iodide* remains in solution, from which it separates as deep purple hair-like needles, M.pt. 98° C., soluble in acetone, benzene or chloroform, sparingly soluble in alcohol and insoluble in cold water. Exposure to light causes slow decomposition of the di-iodide. Grinding with water and silver oxide yields a colourless neutral solution of the *dihydroxide*, which soon decomposes with formation of a yellow solid, M.pt. 73° to 74° C. Aqueous sodium metabisulphite reduces the di-iodide with difficulty to *cyclo*selenopropane.

cycloSelenopropane mercurichloride, $C_3H_6Se.HgCl_2$, separates when alcohol solutions of the components are mixed. It is a white crystalline precipitate, decomposing at 105° C., insoluble in organic solvents or water, but decomposed by aqueous caustic alkalis with liberation of *cyclo*selenopropane. Heating gives mercuric selenide and trimethylene dichloride.

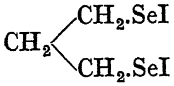
Polymeride of cycloselenopropane, $(C_3H_6Se)_6$.—The yellow gum obtained during the preparation of *cyclo*selenopropane is washed with water and dissolved in chloroform. The solvent is removed and the residue extracted with boiling acetone until the extracts are colourless, the residual product solidifying to a pale yellow soap-like substance, M.pt. 38° to 40° C. This is insoluble in water or alcohol, sparingly soluble in acetone, but dissolves readily in warm chloroform or benzene. When gently heated selenium is not eliminated, but frothing takes place and the evolved gas when passed through bromine water furnishes, propylene dibromide, the residue consisting of *cyclo*trimethylenediselenide. The polymeride is soluble in warm $2N$ nitric acid, a white microcrystalline *nitrate* separating on cooling,



$$(NO_3)_2Se\begin{matrix}\diagup [CH_2]_3 \diagdown \\ \diagdown [CH_2]_3 \diagup\end{matrix}Se(NO_3)_2$$

This decomposes rapidly at 87° C., is readily soluble in water giving a strongly acid solution and decomposing slowly with evolution of nitrous fumes. Treatment with concentrated hydrochloric acid converts the nitrate into the *chloride*, a white microcrystalline substance, moderately soluble in water, insoluble in alcohol or acetone. Potassium iodide solution transforms the nitrate into a gummy *iodide*, decomposing indefinitely above 100° C. Hot concentrated nitric acid reacts violently with the polymeride, the resulting clear solution after evaporation depositing oxalic acid.

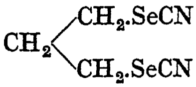
Trimethylenediselenodi-iodide,



$$CH_2\Big\langle\begin{array}{l}CH_2.SeI\\CH_2.SeI\end{array}$$

The foregoing nitric acid solution of polymerised *cyclo*selenopropane after removal of the oxalic acid gives a viscous residue. After treatment with sodium acetate, addition of potassium iodide precipitates the brick-red diselenodi-iodide. The di-iodide occurs when hydriodic acid acts on trimethylenediselenious acid or when a chloroform solution of *cyclo*trimethylene diselenide is treated with iodine. It dissolves in warm chloroform or benzene, but is very sparingly soluble in acetone or alcohol; it melts to a red liquid at 124° C.

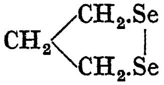
Trimethylenediselenocyanate,



$$CH_2\Big\langle\begin{array}{l}CH_2.SeCN\\CH_2.SeCN\end{array}$$

occurs when one gram-molecule of trimethylene dibromide and two gram-molecules of potassium selenocyanate react in acetone. It forms colourless prisms, M.pt. 53° C.,[1] remains undecomposed on keeping, and possesses a faint characteristic odour.

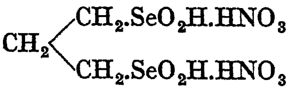
cycloTrimethylene diselenide,



$$CH_2\Big\langle\begin{array}{l}CH_2.Se\\ \quad\;\;|\\CH_2.Se\end{array}$$

obtained as a yellow amorphous precipitate when air is aspirated through an alcoholic soda solution of the foregoing diselenocyanate, melts at 59° C.,[2] distils undecomposed when heated under diminished pressure, and in chloroform solution gives trimethylenediselenodi-iodide on treatment with iodine.

Trimethylenediselenious acid dinitrate,



$$CH_2\Big\langle\begin{array}{l}CH_2.SeO_2H.HNO_3\\CH_2.SeO_2H.HNO_3\end{array}$$

The foregoing diselenocyanate and diselenide both dissolve readily in nitric acid and the solution on concentration yields white needles of the dinitrate. This decomposes at 112° C., dissolves readily in water, and the solution, when treated successively with sodium acetate and potassium iodide, yields brick-red trimethylenediselenodi-iodide.

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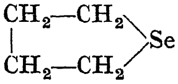
[1] Hagelberg (*Ber.*, 1890, 23, 1090) gave M.pt. 51° C.

[2] Hagelberg (*loc. cit.*) gave 54·5° C.

cycloSelenobutane and its Derivatives.

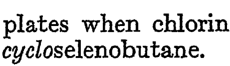
cycloSelenobutane or *Tetrahydroselenophen,*[1]



A mixture of hydrogen and hydrogen selenide (prepared from 14·5 grams of aluminium selenide and water) is passed into a solution containing 6·9 grams of sodium, 250 c.c. of alcohol and 6 c.c. of water. Colourless sodium selenide separates, and after distilling off the alcohol, cold water is added together with 25 grams of αδ-tetramethylene dibromide. The mixture is heated for four hours at 80° C. in a current of hydrogen, oxidation thus being prevented and the liquid kept agitated. The *cyclo*selenobutane which is formed is then dissolved in carbon tetrachloride, the extract dried over calcium chloride, and sufficient bromine added to convert the selenohydrocarbon into dibromide, a 75 per cent. yield of the latter resulting. To regenerate the selenobutane, the dibromide is stirred for a long time with water and four times its weight of sodium metabisulphite, and the product then dried over calcium chloride and distilled under reduced pressure. The final distillation is carried out under ordinary pressure in a stream of carbon dioxide. *cyclo*Selenobutane also occurs when *cyclo*tetramethylene diselenide is decomposed by heat.

The compound obtained as above is a colourless or faintly yellow liquid, B.pt. 90° to 91° C. at 172 mm. and 135° to 136° C. at 770 mm.; density 1·484 at 15° C., its densities at other temperatures being given by the expression $D_{4^\circ}^{t^\circ} = 1{\cdot}5060 - 0{\cdot}001354t$. The liquid possesses a very pungent and rather unpleasant odour, is insoluble in water, but volatile in steam or in the vapour of alcohol or ether. It is miscible in all proportions with organic solvents. Cold concentrated sulphuric acid gives no coloration, but yellow to red tints develop on warming. Oxidation takes place slowly in air, and rapidly in the presence of hydrogen peroxide; aqueous permanganate ruptures the ring and fuming nitric acid also causes decomposition, but moderately concentrated nitric acid yields *cycloselenobutane 1 : 1-dinitrate.* Mercuric chloride in alcoholic solution combines to form a *mercurichloride,* $C_4H_8Se.HgCl_2$, consisting of colourless needles, M.pt. 146° C.

cycloSelenibutane 1 : 1-dichloride,



crystallises in colourless plates when chlorine is passed into a carbon tetrachloride solution of *cyclo*selenobutane. It melts at 88° to 89° C., is soluble in chloroform, benzene or acetone, sparingly soluble in alcohol or hot water, giving a strongly acid solution in the latter which deposits the compound unchanged on cooling.

cycloSelenibutane 1 : 1-dibromide, $C_4H_8SeBr_2$, crystallises from benzene, carbon tetrachloride or hot water in lustrous yellow needles, M.pt. 92° C. When its concentrated chloroform solution is treated

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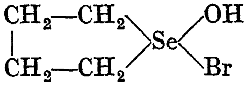
[1] Hagelberg, *Ber.*, 1929, 62, 1096.

with bromine in the same solvent, crimson prismatic crystals of *perbromide*, $C_4H_8SeBr_2Br_5$, separate. Air causes slow decomposition of this perbromide and heating a more rapid change, a residue of dibromide remaining; acetone also removes five atomic proportions of bromine from the perbromide.

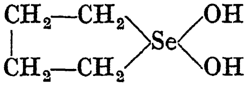
cycloSelenibutane 1 : 1-di-iodide, $C_4H_8SeI_2$, forms lustrous purplish-black crystals, M.pt. 99° to 100° C., only sparingly soluble in organic solvents and practically insoluble in hot water.

cycloSelenibutane 1-hydroxy-1-bromide,



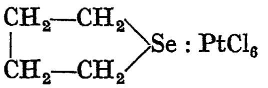
is obtained by treating the dibromide with sufficient silver oxide to remove only half its bromine or by mixing equimolecular proportions of the 1 : 1-dihydroxide and 1 : 1-dibromide in aqueous solution, the liquid on concentration yielding the colourless crystalline hydroxybromide, which is washed with benzene to remove unchanged dibromide. The hydroxybromide decomposes slowly on keeping, and on heating decomposition sets in at 99° to 100° C.; it is almost insoluble in non-hydrolytic solvents; its aqueous solution is strongly acidic. By a similar process *cycloselenibutane 1-hydroxy-1-chloride* may be isolated as a stable crystalline compound decomposing at 116° C. and readily soluble in water giving a strongly acid solution.

cycloSelenibutane 1 : 1-dihydroxide,



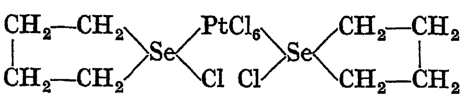
occurs when the corresponding dibromide in aqueous solution is treated with excess of freshly prepared silver oxide. Evaporation of the filtered solution on the water-bath and finally in a vacuum desiccator gives colourless highly hygroscopic crystals. The aqueous solution is neutral to litmus ($p_H = 6{\cdot}0 - 6{\cdot}2$). Addition of aqueous hydrogen halide regenerates the corresponding 1 : 1-dihalide.

cycloSelenibutane 1-chloroplatinate,



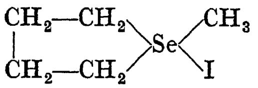
separates in yellow needles from a mixture of cold dilute aqueous solutions of *cyclo*selenibutane 1 : 1-dichloride and chloroplatinic acid, the product decomposing at 230° C.

Bis-1-chlorocycloselenibutane 1-chloroplatinate,



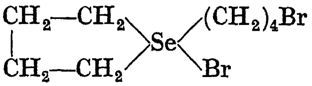
Platinic chloride is added to a warm concentrated solution containing an excess of *cyclo*selenibutane 1 : 1-dichloride, orange crystals of the complex salt separating after evaporation and cooling. These, after drying and washing with warm acetone to remove unchanged dichloride, melt with decomposition at 179° C.

cycloSelenibutane 1-methiodide,



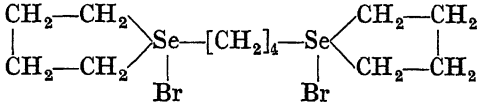
is produced by mixing 27 parts of *cyclo*selenobutane with 27 parts of methyl iodide. It crystallises from hot water in colourless needles, which in an open tube sublime slowly at about 150° C., but in a closed tube melt at 174° C.

1-δ-Bromobutylcycloselenibutane 1-bromide,



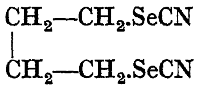
*cyclo*Selenobutane reacts with an excess of αδ-tetramethylene dibromide in the course of a few days to give a colourless glassy compound. Excess of the dibromide is removed by washing with light petroleum, the residue dissolved in water and the solution evaporated over sulphuric acid, the gum slowly crystallising. The compound melts at 65° to 66° C.

Tetramethylene-αδ-biscycloselenibutane 1 : 1′-dibromide,



A mixture of *cyclo*selenobutane, αδ-tetramethylene dibromide and water is heated at 90° C. in a sealed tube with occasional shaking until no more material dissolves in the aqueous layer. The solution is then evaporated over sulphuric acid until the complex dibromide separates as colourless prisms. These prisms after drying *in vacuo* melt at 95° to 96° C.

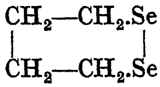
Tetramethylene αδ-diselenocyanate,



$$\begin{array}{l} CH_2\text{—}CH_2.SeCN \\ | \\ CH_2\text{—}CH_2.SeCN \end{array}$$

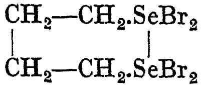
Potassium selenocyanate (14·4 grams) and 10·8 grams of αδ-tetramethylene dibromide are heated together in acetone solution under reflux for several hours. After filtration and addition of water, the diselenocyanate separates as a heavy pale yellow oil, which slowly solidifies. Recrystallisation from aqueous acetone yields white flakes, M.pt. 40° C., possessing a penetrating and nauseous odour, and decomposing slowly on keeping. The compound is readily soluble in organic solvents, but insoluble in water.

cycloTetramethylene diselenide or *cycloDiselenobutane,*



An alcoholic solution of 5 grams of the preceding compound is added to alcoholic sodium hydroxide made by dissolving 1·5 grams of sodium in 100 c.c. of alcohol. The yellow liquid is decanted from any precipitate formed, diluted with 400 c.c. of water and air passed through for several hours. The diselenide separates as a yellow powder, sparingly soluble in alcohol or acetone, and is washed successively with water and acetone. It dissolves readily in benzene or chloroform, separating from the latter as a yellow gum which subsequently solidifies. It is quite stable on keeping. It melts to a yellow liquid at 41° to 42° C.; strong heating causes decomposition with formation of *cyclo*selenobutane.

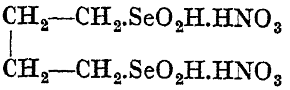
cycloTetramethylene diselenide tetrabromide,



$$\begin{array}{l} CH_2—CH_2.SeBr_2 \\ \;|\qquad\quad | \\ CH_2—CH_2.SeBr_2 \end{array}$$

This formula is given to a product obtained by treating *cyclo*tetramethylene diselenide (1 mol.) with bromine (4 mols.) in chloroform solution. The compound decomposes so rapidly that it cannot be analysed. Evaporation of the chloroform solution at ordinary temperature yields *cyclo*selenibutane 1 : 1-dibromide.

αδ-Tetramethylene diselenious acid dinitrate,

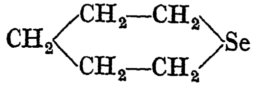


$$\begin{array}{l} CH_2—CH_2.SeO_2H.HNO_3 \\ \;| \\ CH_2—CH_2.SeO_2H.HNO_3 \end{array}$$

separates as colourless crystals when αδ-tetramethylene diselenocyanate or *cyclo*tetramethylene diselenide is dissolved in warm nitric acid (1 : 1). The product decomposes with explosive violence and liberation of selenium at 136° C.

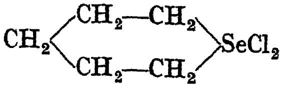
cycloSelenopentane and its Derivatives.[1]

cycloSelenopentane,



The preparation and purification of this compound is identical with that of *cyclo*selenobutane, the αδ-tetramethylene dibromide in the latter case now being replaced by 27 grams of αε-pentamethylene dibromide. The product need only be distilled under ordinary pressure in a stream of carbon dioxide to effect purification. It is a colourless or very faintly yellow liquid, B.pt. 158° C. at 759 mm., n_D 1·5475 at 18° C., density 1·409 at 12·5° C., 1·399 at 20° C., 1·392 at 26° C., and 1·384 at 32·2° C., whence $d^{t°}_{4°} = 1{\cdot}424 - 0{\cdot}001236t$. The compound has similar properties to those described for *cyclo*selenobutane. The *mercurichloride*, $C_5H_{10}Se.HgCl_2$, forms white, feathery needles, M.pt. 175° to 176° C.

cycloSelenipentane 1 : 1-dichloride,



is obtained as white needles, M.pt. 103° C., when chlorine is passed into a carbon tetrachloride solution of *cyclo*selenopentane. It is readily

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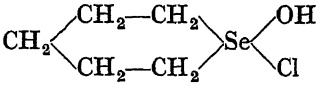
[1] Hagelberg, *Ber.*, 1929, 62, 2197.

soluble in benzene, chloroform or acetone, sparingly soluble in alcohol or petroleum.

cycloSelenipentane 1 : 1 dibromide crystallises in small bright yellow needles, which melt to a deep red liquid at 117° to 118° C.; the corresponding *perbromide* yields small, crimson, prismatic crystals, whilst the *di-iodide* separates in large, almost black, prismatic crystals, M.pt. 114° C.

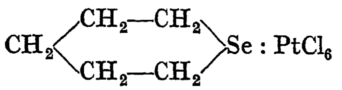
cycloSelenipentane 1-hydroxy-1-chloride,



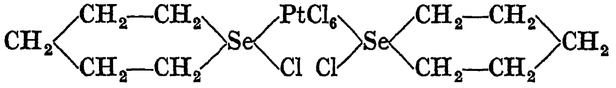
is prepared in a similar manner to the corresponding *cyclo*selenibutane compound, and is a colourless crystalline body decomposing at 110° to 111° C.

cycloSelenipentane 1 : 1-dihydroxide forms highly hygroscopic crystals, which give a practically neutral aqueous solution ($p_H = 6{\cdot}0 - 6{\cdot}2$).

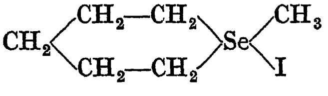
cycloSelenipentane 1-chloroplatinate,



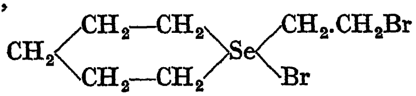
When a very dilute cold aqueous solution of the 1 : 1-dichloride is treated with chloroplatinic acid, the chloroplatinate separates as a pale yellow microcrystalline powder, sintering at 190° C. and decomposing at 216° C. It is almost insoluble in water, but dissolves in chloroform or benzene. If the chloroplatinic acid be added to a hot, moderately concentrated solution of the 1 : 1-dichloride, sparingly soluble orange *bis-1-chlorocycloselenipentane 1-chloroplatinate* is precipitated. This decomposes at 160° C., is insoluble in organic solvents with the exception of alcohol, and has the constitution



cycloSelenipentane 1-methiodide,

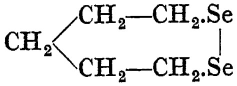


is produced from its components with generation of heat. It crystallises as white needles from water. In an open tube it slowly sublimes at 160° C. without melting, but in a closed tube it melts to a colourless liquid at 165° to 166° C. Replacement of the methyl iodide in the preparation by ethylene dibromide yields *1-β-bromoethylcycloselenipentane 1-bromide,*

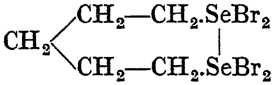


To complete the reaction the mixture is heated with water for a week in a sealed tube at 100° C. The aqueous layer is then evaporated over sulphuric acid and the residue recrystallised from alcohol-acetone, small, white, very hygroscopic needles, M.pt. 88° C., being obtained. These decompose slowly on keeping.

cycloPentamethylene diselenide or *cycloDiselenopentane*,

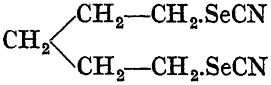


7 grams of *αε*-pentamethylene diselenocyanate are slowly added to 50 c.c. of alcohol containing 3·0 grams of potassium hydroxide. A brown oil separates, from which a yellow uncrystallisable gum is produced on evaporation. Strong heating causes decomposition with formation of *cyclo*selenopentane. The diselenide (1 mol.), when treated with bromine (2 mols.) and the mixture allowed to evaporate spontaneously, gives *cyclo*selenipentane 1 : 1-dibromide, elemental selenium and tarry matter, but with 4 molecular equivalents of bromine a substance, probably *cyclopentamethylene diselenide tetrabromide*,



is obtained, but this compound is unstable, decomposing to form the 1 : 1-dibromide.

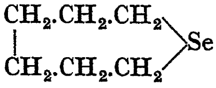
The *αε-pentamethylene diselenocyanate*,



required for the foregoing preparation is obtained by heating 14·4 grams of potassium selenocyanate with 11·5 grams of pentamethylene dibromide in acetone solution for several hours. Filtration and addition of water to the filtrate gives the diselenocyanate in almost quantitative yield as a dark oil. This decomposes on distillation. It is purified by precipitating its benzene solution with petroleum. The viscous compound possesses the intense nauseating odour characteristic of this group of substances.

cycloSelenohexane and its Derivatives.[1]

When sodium selenide reacts with *αζ*-hexamethylene dibromide in alcohol only a small proportion of monomeric *cyclo*selenohexane,



results, the main product being a mixture of two or more polymeric forms. This reaction is therefore comparable with that which takes place between trimethylene dibromide and sodium selenide, p. 72. The compounds of this series which have been isolated are shown in the following scheme :

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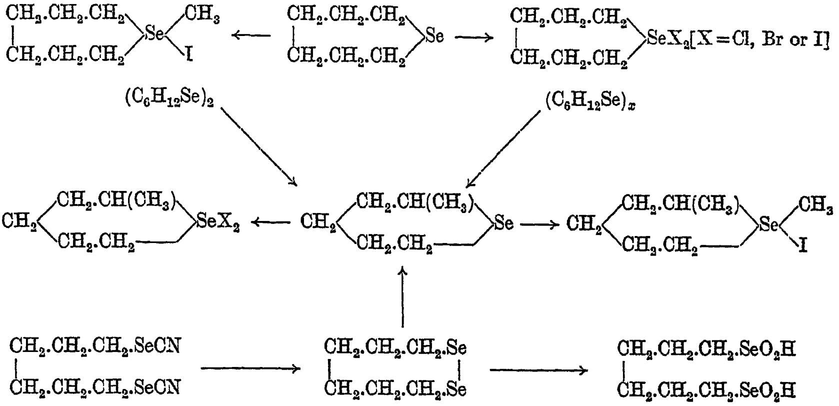
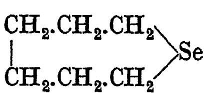
[1] Morgan and Burstall, *J. Chem. Soc.*, 1931, p. 173.



cycloSelenohexane,



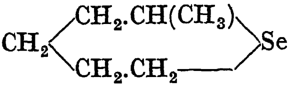
The hydrogen selenide generated from 18 grams of aluminium selenide is passed into a solution of 6·9 grams of sodium in 250 c.c. of alcohol and 9 c.c. of water, the operation being conducted in an atmosphere of hydrogen. A suspension of sodium selenide in alcohol is thus produced, and 32 grams of hexamethylene dibromide are added and the whole refluxed for two hours. The product is filtered from sodium bromide and yellow polymerides, and then distilled under reduced pressure and the distillate rectified until colourless. The product is purified through the di-iodide, the latter being reduced by treatment with an excess of aqueous sodium metabisulphite. Rectification yields a liquid, B.pt. 105° to 106° C. at 68 mm., 188° to 190° C. at 756 mm., n_D 1·5470 at 18° C., density 1·353 at 24·5° C., 1·341 at 37° C., 1·334 at 44° C., and 1·323 at 54° C., whence $d_{4^\circ}^{t^\circ} = 1{\cdot}378 - 0{\cdot}00101t$.

*cyclo*Selenohexane is miscible with organic solvents and volatile in the vapours of alcohol and ether, but insoluble in water. It dissolves in cold concentrated sulphuric acid, yellow to red tints developing when the solution is warmed. It may be kept in a cool, dark place, and is not oxidised in air. It yields the following derivatives: *Mercurichloride*, white flaky crystals, M.pt. 193° to 194° C. with decomposition; *dichloride*, small white crystals, M.pt. 78° C.; *dibromide*, yellow prismatic crystals, M.pt. 118° to 119° C.; *di-iodide*, small reddish-purple needles, M.pt. 82° C.; *methiodide*, white prisms, decomposing at 149° to 150° C.

Dimeride of cycloselenohexane, $(C_6H_{12}Se)_2$.—The mixture of sodium bromide and yellow polymerides mentioned in the foregoing preparation is extracted with chloroform and the extract evaporated to dryness. The residue is extracted with petroleum (B.pt. 60° to 80° C.), when two fractions of differing solubility result. The more soluble fraction when recrystallised from acetone gives the dimeride as white acicular prisms, M.pt. 92° C., and only depolymerised at about 220° C. Soluble in most organic solvents, the product does not dissolve in water. Addition of bromine to its carbon tetrachloride solution yields a pale yellow microcrystalline *dibromide*, melting with decomposition at 145° C., sparingly soluble in most solvents, decomposing slowly, and reduced to the original dimeride by aqueous sodium metabisulphite.

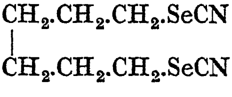
Polymeride of cycloselenohexane, $(C_6H_{12}Se)_x$.—The less soluble fraction mentioned in the foregoing preparation, when recrystallised from acetone yields the polymeride as a white, waxy, microcrystalline powder, M.pt. 36° to 37° C. Molecular weight determinations by the ebullioscopic method indicate an aggregation of approximately twelve molecules of $C_6H_{12}Se$. The product yields a *dibromide* decomposing at 94° to 95° C.

2-Methylcycloselenopentane,



may be prepared in two ways: (1) The polymeride $(C_6H_{12}Se)_x$ commences to depolymerise at about 220° C., and when the pyrolysis is carried out under 30 mm. pressure with the purified polymeride practically no residue remains. Fractionation of the distillate yields 2-methyl*cyclo*selenopentane. (2) *cyclo*Hexamethylene 1 : 8-diselenide loses selenium at about 250° C. and is converted into the selenopentane. Although insoluble in water, 2-methyl*cyclo*selenopentane is miscible in all proportions with organic solvents and is volatile in the vapours of steam, alcohol and ether. Its solution in sulphuric acid gives yellow to red tints on warming; nitric acid furnishes a crystalline *nitrate*. Acid or alkaline permanganate ruptures the ring, whereas $2N$ caustic alkalis are without action. The corresponding *dichloride* is a colourless liquid, the *dibromide* is a reddish-yellow gum, and the *di-iodide* a deep red gum; the *mercurichloride* forms small white needles, M.pt. 112° C., and the *methiodide* is a microcrystalline powder melting with decomposition at 164° C.

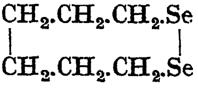
Hexamethylene $\alpha\xi$**-diselenocyanate,**



$$\begin{array}{l} CH_2.CH_2.CH_2.SeCN \\ | \\ CH_2.CH_2.CH_2.SeCN \end{array}$$

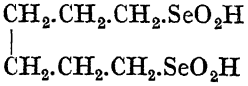
is formed when potassium selenocyanate and $\alpha\xi$-hexamethylene dibromide are heated together under reflux in acetone solution for several hours. The residue obtained by evaporation of the filtrate is treated with water and the oil layer dissolved in benzene. After drying the solution with calcium chloride it is filtered and poured into a large excess of light petroleum, when the diselenocyanate separates as a thick yellow oil. The product dissolves in most organic solvents, but is insoluble in water. It possesses a penetrating and nauseous odour.

cycloHexamethylene 1 : 8-diselenide (cycloDiselenohexane),



$$\begin{array}{l} CH_2.CH_2.CH_2.Se \\ |\qquad\qquad\quad | \\ CH_2.CH_2.CH_2.Se \end{array}$$

The foregoing diselenocyanate in alcohol is added to sodium ethylate and the mixture poured into a large excess of water through which air is aspirated. The precipitated oil is extracted with chloroform and the solution dried, the product solidifying at 0° C. after removing the solvent. It melts rather indefinitely at 40° C., and yields 2-methyl*cyclo*selenopentane at about 253° C. When dissolved in warm nitric acid it gives *hexamethylenediseleninic acid,*



$$\begin{array}{l} CH_2.CH_2.CH_2.SeO_2H \\ | \\ CH_2.CH_2.CH_2.SeO_2H \end{array}$$

M.pt. 147° C., the same product being obtained if the diselenide be replaced by the diselenocyanate.

SELENIUM COMPOUNDS DERIVED FROM β-DIKETONES.

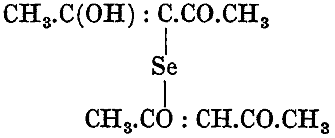
The Reaction between Selenium Tetrachloride and Copper Acetylacetone.

The reaction between the above compounds may be summarised by the following equation:[1]

$$2SeCl_4 + 2Cu(C_5H_7O_2)_2 = Se_2(C_5H_6O_2)_2 + 2C_5H_7O_2Cl + 2CuCl_2 + 2HCl$$

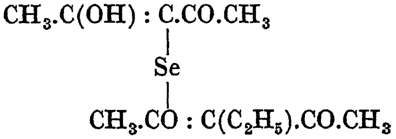
The hydrogen chloride formed reacts with the selenium derivative giving a further amount of 3-chloroacetylacetone, and the principal reaction becomes modified with the production of a small amount of diselenium *bis*acetylacetone.

Chemical Constitution of Selenium Acetylacetone.—This compound is dimeric and devoid of enolic properties. It combines with acetylacetone to form selenium OC-*bis*acetylacetone,



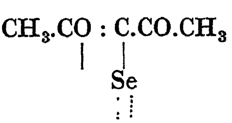
$$\begin{array}{l} CH_3.C(OH):C.CO.CH_3 \\ \qquad\qquad\qquad | \\ \qquad\qquad\quad Se \\ \qquad\qquad\qquad | \\ \qquad\quad CH_3.CO:CH.CO.CH_3 \end{array}$$

a monoenolic derivative which forms a copper salt. This additive reaction may be reversed on heating or by the use of hydrolytic solvents. C-Ethylacetylacetone under similar conditions gives selenium C-ethyl-OC-*bis*acetylacetone,



$$\begin{array}{l} CH_3.C(OH):C.CO.CH_3 \\ \qquad\qquad\qquad | \\ \qquad\qquad\quad Se \\ \qquad\qquad\qquad | \\ \qquad\quad CH_3.CO:C(C_2H_5).CO.CH_3 \end{array}$$

which is monoenolic and resolved by heat or hydrolytic solvents into its generators. The reversal of the additive change, leading to the removal of acetylacetone or C-ethylacetylacetone respectively, would leave the residue



$$\begin{array}{l} CH_3.CO:C.CO.CH_3 \\ \qquad\quad |\quad\; | \\ \qquad\qquad\; Se \\ \qquad\quad \vdots\;\; \vdots \end{array}$$

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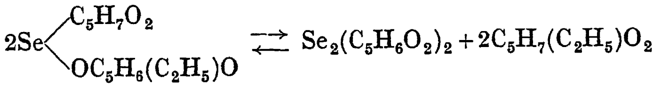
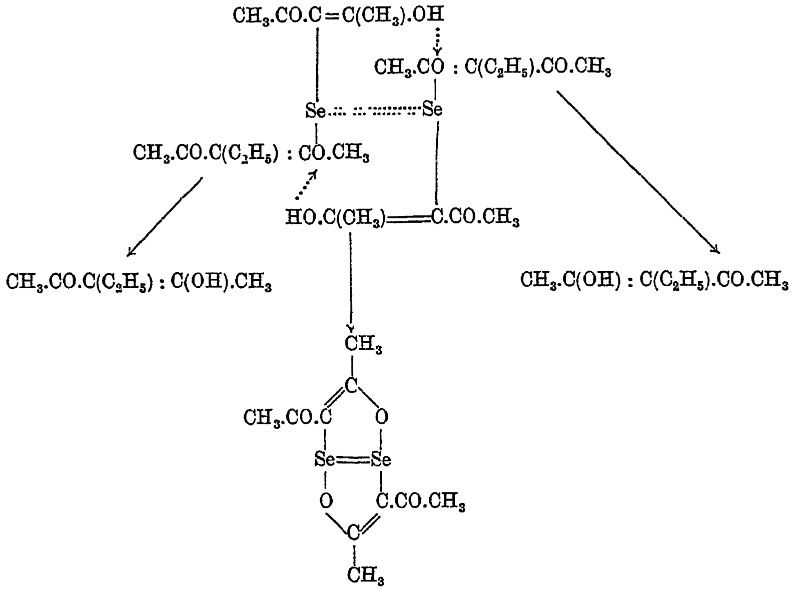
[1] Morgan, Drew and Barker, *Trans. Chem. Soc.*, 1922, 121, 2432.

and it would appear from the dimeric condition of selenium acetylacetone that it is formed by the fusion of two of these unsaturated residues. The reversal of the additive change which takes place when two molecules of selenium C-ethyl-OC-*bis*acetylacetone interact is expressed by the equation



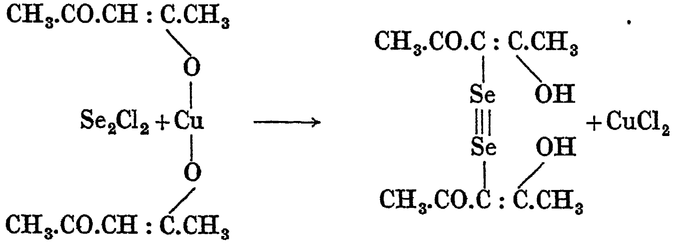
$$2\mathrm{Se}\left\langle\begin{matrix}C_5H_7O_2\\ OC_5H_6(C_2H_5)O\end{matrix}\right. \rightleftarrows Se_2(C_5H_6O_2)_2 + 2C_5H_7(C_2H_5)O_2$$

or may be more fully represented by the following scheme :

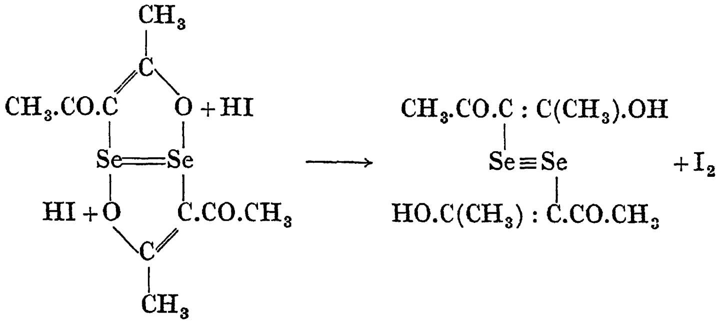


Here the residual affinity of the two selenium atoms serves to hold the two molecules together in an additive complex from which two molecules of C-ethylacetylacetone are eliminated, leaving a molecule of the dimeric selenium acetylacetone.

The formation of diselenium *bis*acetylacetone from selenium monochloride and copper acetylacetone in molecular proportions may be expressed as follows :

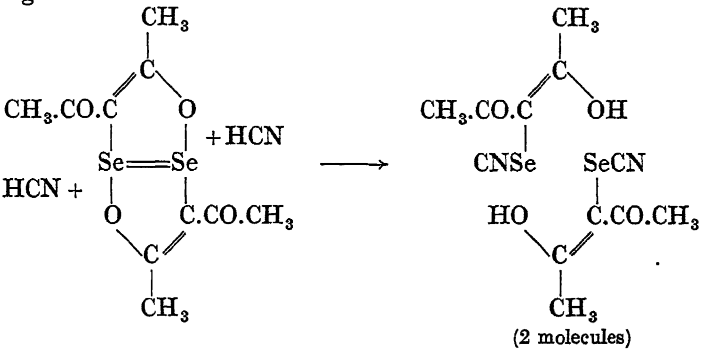


This scheme furnishes confirmatory evidence of the structure assigned to selenium acetylacetone, insomuch as the latter substance yields diselenium *bis*acetylacetone when treated with hydriodic acid :



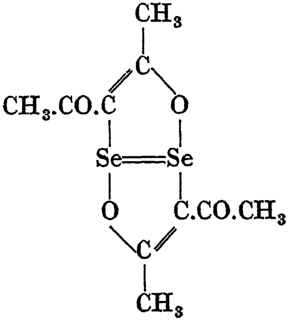
The *bis*-compound also arises to a small extent in the condensation of copper acetylacetone with selenium tetrachloride.

The interaction of selenium acetylacetone and hydrogen cyanide is one of addition and depolymerisation, cyano-3-selenium acetylacetone resulting :

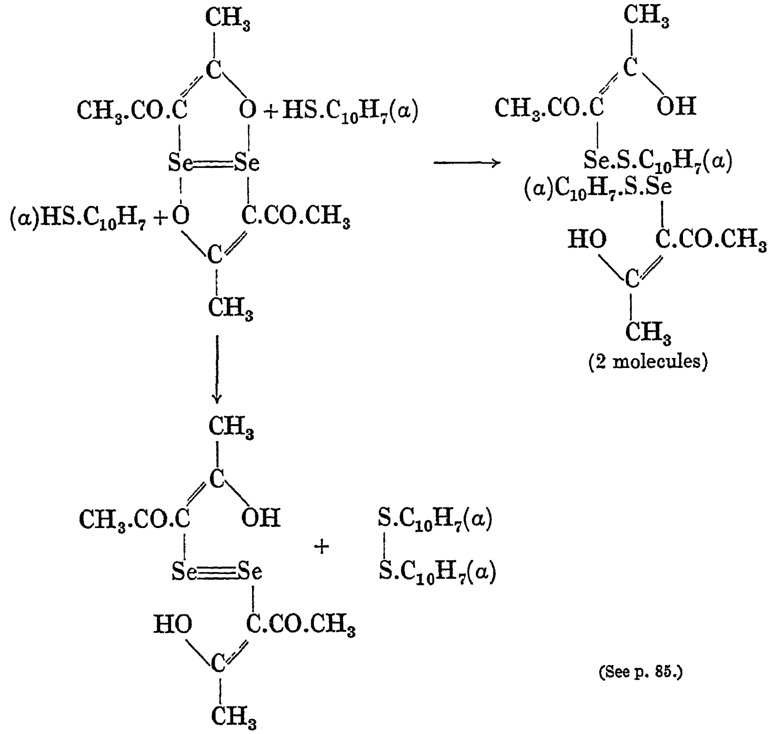


The reaction between selenium acetylacetone and thio-α-naphthol occupies an intermediate position between the reactions with hydriodic and hydrocyanic acids, the change being partly simple addition accompanied by depolymerisation, forming α-naphthylthioselenium acetylacetone, and partly in the direction of forming diselenium *bis*acetylacetone and αα-dinaphthyl disulphide, as shown in the scheme on page 86.

Selenium acetylacetone,



Dry copper acetylacetone, 25·1 grams, is added during 15 minutes to 21·2 grams of selenium tetrachloride suspended in 100 c.c. of chloroform



(See p. 85.)

(B.P.), the mixture being cooled in ice and salt. After 30 minutes the copper chloride is filtered off and the chloroform removed from the filtrate by a current of air, 17 grams (78 per cent. yield) of pure selenium acetylacetone remaining.[1]

Selenium acetylacetone is unaffected by methyl or ethyl iodide, acetone or acetonitrile. It readily crystallises unchanged from the last-named of these reagents. Hydrogen chloride in dry ether dissolves the compound without change, but *hydrochloric acid* yields an unstable *additive compound,* soluble in ether, with decomposition into selenium and chloroacetylacetone, a change occurring more rapidly in alcoholic hydrochloric acid. Anhydrous ammonia, when sealed up with selenium acetylacetone, causes complete decomposition, selenium, acetamide and hydrocyanic acid being found amongst the products.

Selenium acetylacetone has a faintly acid, sweetish taste, and dissolves sparingly in hot water, the solution being distinctly acid ; it is somewhat sparingly soluble in boiling ether, ethyl alcohol, acetone or chloroform, but dissolves more freely in hot glacial acetic acid. In cold aqueous alkali hydroxides or ammonium hydroxide it gives yellow solutions, acidification causing reprecipitation unchanged. The alkaline solutions soon decompose, red selenium separating ; aqueous sodium carbonate although not dissolving the body causes similar decomposition. Dilute mineral acids do not affect selenium acetyl-

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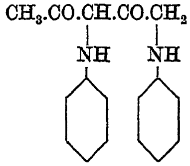
[1] Morgan, Drew and Barker, *loc. cit.*; compare Morgan and Drew, *Trans. Chem. Soc.*, 1920, 117, 1456; Morgan and Smith, *ibid.*, 1921, 119, 1067.

acetone, concentrated nitric and sulphuric acids have a destructive action, and cold concentrated hydrochloric acid causes decomposition into red selenium and chloroacetylacetone. Ferric chloride in aqueous or alcoholic solution gives an orange coloration on boiling the solution, and selenium separates.

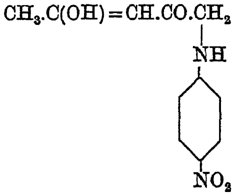
Reduction by zinc dust yields an oil; iodine in chloroform has no action, but chlorine in the same solvent gives selenium tetrachloride and chloroacetylacetone, and bromine yields lachrymatory products and a colourless crystalline substance of melting-point 180° C. Aqueous hydrogen sulphide causes slow decomposition, with liberation of sulphur and selenium. Potassium metabisulphite and sodium hydrogen sulphite transform selenium acetylacetone quantitatively into alkali selenodithionates, a reaction which affords the best known means of preparing these salts.

Selenium acetylacetone may be converted into selenium benzoylacetone by dissolving it in a warm solution of benzoylacetone in chloroform in the presence of a trace of sodium hydroxide, the resulting selenium *bis*benzoylacetone being converted into selenium benzoylacetone by boiling with alcohol.

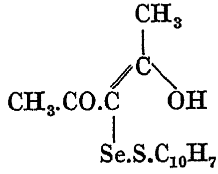
Selenium acetylacetone also undergoes the following reactions:[1] One molecule of the compound reacts with two molecules of *p*-nitrophenylhydrazine to give *p*-nitrobenzeneazoacetylacetone, 1-*p*-nitrophenyl-3 : 5-dimethylpyrazole and di-*p*-nitrophenylhydrazinoacetylacetone. With one or two molecular proportions of aniline, selenium and 1 : 3-dianilinoacetylacetone are obtained,



With two equivalents of *p*-nitroaniline, selenium is set free, and 1-*p*-nitroanilinoacetylacetone,



and *p*-nitroanilinoethoxyacetylacetone produced. With methyl mercaptan in dry ether an oil is obtained, probably having the composition $CH_3.C(OH):C(CO.CH_3).Se.S.CH_3$. With thio-$\alpha$-naphthol, *$\alpha$-naphthylthioselenium acetylacetone,*



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ & C & \\ \diagup\!\!\diagup & & \diagdown \\ CH_3.CO.C & & OH \\ | & & \\ Se.S.C_{10}H_7 & & \end{array}$$

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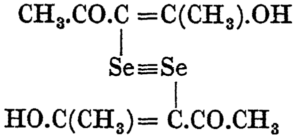
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1921, 119, 610.

is formed, together with some *aa*-dinaphthyl sulphide and diselenium *bis*acetylacetone. The *a*-naphthylthioselenium acetylacetone melts at 81° to 83° C., and separates from ether or light petroleum as bright cowslip-yellow crystals, readily soluble in organic solvents. It is enolic, giving a greenish-yellow copper salt and a red ferric chloride coloration. Selenium acetylacetone in alcoholic solution serves to distinguish primary and secondary amines from the tertiary bases; in the former cases selenium is eliminated on gentle heating, whereas the element is not set free by tertiary bases.

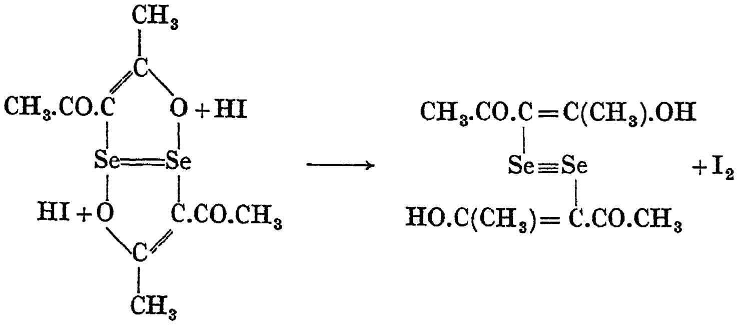
Selenium acetylacetone crystallises in two distinct modifications, both being somewhat elongated six-sided plates, which are not suitable for measurement on the goniometer. Under the microscope the first form is seen to have a symmetrical dome termination of 88°. Optically, the extinction is straight, and a negative acute bisectrix is normal to the plate. The axial angle is wide. The system is therefore almost certainly orthorhombic. The second form, on the other hand, is probably monoclinic, for the termination is unsymmetrical, with angles of 56°, 51° and 73°; the extinction is oblique, and a positive acute bisectrix is normal to the plate—which must therefore be the face *b*(010). On crystallising from benzene at suitable concentration, the second form undergoes a transformation into the first form.

Diselenium bisacetylacetone,[1]



$$\begin{array}{l} CH_3.CO.C=C(CH_3).OH \\ \qquad\quad | \\ \qquad\quad Se\equiv Se \\ \qquad\qquad\quad | \\ HO.C(CH_3)=C.CO.CH_3 \end{array}$$

may be prepared in several ways: (1) Powdered selenium acetylacetone, 5·5 grams, is added during 2 minutes to a cooled and shaken mixture of 150 c.c. of ether, 5 c.c. of decolorised 60 per cent. hydriodic acid and 100 c.c. of water. The ether layer is washed with water and the iodine removed by 340 c.c. of 0·1*N* sodium thiosulphate solution (calculated amount 311 c.c.). The ether solution is then separated, filtered and evaporated, 3·9 grams of orange crystals of diselenium *bis*acetylacetone being obtained. This method gives the best yield, and the reaction is represented as follows:



(2) Selenium monochloride is required for this method, and is prepared by dissolving the requisite amount of selenium in selenium

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[1] Morgan, Drew and Barker, *loc. cit.*

tetrachloride. A solution of 9·3 grams of the monochloride in 40 c.c. of chloroform is added with shaking to 10·7 grams of copper acetylacetone in 150 c.c. of the same solvent, the mixture being cooled to 0° C. The colour of the copper acetylacetone disappears before all the selenium chloride has been added, and 9·5 grams of a red precipitate result, which is filtered off, the filtrate giving 9·8 grams of a dark yellow lachrymatory oil on removal of the solvent. The red precipitate consists of red selenium, cupric chloride and a complex double salt of copper chloride and the organo-selenium compound. The latter on treatment with water-chloroform mixture forms cupric chloride and a copper compound of diselenium *bis*acetylacetone, the latter dissolving in chloroform. From the green solution 2 grams of product result, from which the free compound is obtained by shaking with dilute sulphuric acid. The chloroform layer then gives a yellow oil, which solidifies partly to orange crystals identical with those obtained in method (1). Some diselenium *bis*acetylacetone may also be isolated from the lachrymatory oil mentioned. If the method of preparation be modified by adding 21·7 grams of copper acetylacetone in 240 c.c. of chloroform to 16·5 grams of selenium monochloride in 100 c.c. of chloroform, about half the selenium is set free, the remaining products being diselenium *bis*acetylacetone, a complex organic copper salt, selenium acetylacetone, anhydrous cupric chloride, red selenium, and traces of chloroacetylacetone.

(3) Dry copper acetylacetone, 11·8 grams (2 mols.), is added in one lot to a suspension of 5 grams of selenium tetrachloride (1 mol.) suspended in 50 c.c. of anhydrous chloroform cooled to 0° C. After two hours the greenish-black precipitate which has formed is collected and decomposed by water, 3·1 grams of a greenish-yellow powder being obtained. A cold chloroform solution of this product is shaken with dilute sulphuric acid, the chloroform layer on removal and evaporation giving a yellow oil. This oil yields diselenium *bis*acetylacetone when extracted with light petroleum. The main reaction taking place in this preparation results in selenium acetylacetone and may be represented as follows :

$$2SeCl_4 + 2Cu(C_5H_7O_2)_2 = Se_2(C_5H_6O_2)_2 + 2C_5H_7O_2Cl + 2CuCl_2 + 2HCl$$

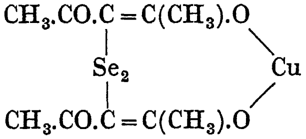
Diselenium *bis*acetylacetone crystallises from light petroleum in hexagonal plates or prisms having a bright orange colour and a farinaceous and burnt rubber odour which is nearly lost on drying. It usually sinters at 78° C. and melts at 92° to 93° C., but occasionally purified specimens sinter at 58° C. and melt at 78° to 80° C. These variations in melting-point may indicate modifications having mono- and di-enolic structures, and such compounds would yield different copper salts. Diselenium *bis*acetylacetone is readily soluble in organic solvents, insoluble in water, and decomposed in warm alcoholic solution, giving red selenium, acetylacetone and a yellow oil, the change occurring more slowly in the cold. Dry ammonia in ether solution gives a yellow precipitate ; hydrazine hydrochloride and phenylhydrazine cause the elimination of selenium in acetic acid and alcoholic solutions respectively ; aqueous potassium bisulphite only reacts slowly ; ferric chloride instantly gives an intense red coloration.

The crystals of diselenium *bis*acetylacetone are isomorphous with those of the corresponding dithio-compound. The system is orthorhombic and the parameters $a : b : c = 0{\cdot}954 : 1 : 1{\cdot}727$, the forms developed being *c*(001), *q*(011), *b*(010) and *r*(101), with occasional traces of *s*(012). The following are the mean values obtained in the measurement of two crystals :

	c(001)	*q*(011)	*b*(010)	*r*(101)	*s*(012)
ϕ . .	Polar	0° 0′	0° 0′	89° 58′	0° 0′
ρ . .	Face	59° 56′	90° 0′	61° 7′	*ca.* 40

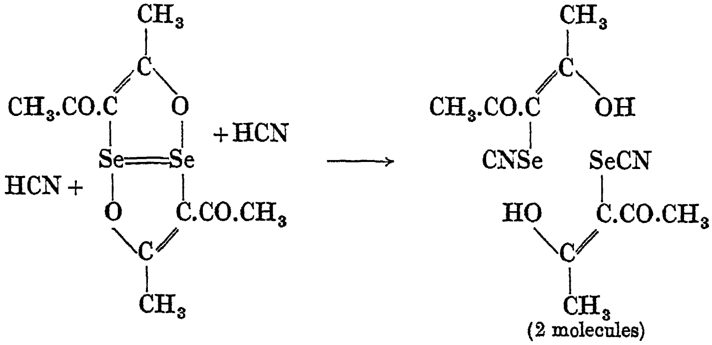
Fedorov complex symbol = (4*d*)59($-\frac{1}{2}$) ; trans. 110/$\bar{1}$10/001. Cleavage : *c* perf. and showing pearly lustre. Acute positive bisectrix (with medium angle) perpendicular to *b* ; axial plane *c*(001).

Copper diselenium bisacetylacetone,



occurs when a benzene solution of the free diselenium compound is shaken with an excess of aqueous cupric acetate with or without addition of the calculated amount of ammonium hydroxide. The yellow product is quantitatively precipitated, and washed with water and benzene. The product is insoluble in water, petroleum or acetone, and sparingly soluble in benzene or chloroform, thereby differing from the copper derivative formed in the preparation of diselenium *bis*acetylacetone, the latter being readily soluble in chloroform. The compound reddens at 130° to 135° C. and decomposes and blackens between 150° and 170° C. In cold 5*N* sodium hydroxide it forms a yellow solution, which changes successively to red and black.

Cyano-3-selenium acetylacetone is formed by the addition of hydrogen cyanide to selenium acetylacetone, followed by depolymerisation :



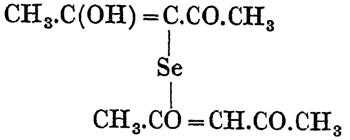
3 grams of powdered selenium acetylacetone are added to 10 c.c. of freshly distilled hydrogen cyanide diluted with an equal volume of dry ether at 0° C., the mixture being shaken at intervals for 14 hours. Removal of the hydrogen cyanide and ether under reduced pressure gives a quantitative yield of the selenocyanate provided that the hydrogen cyanide was free from polymerides and phosphoric acid. The compound crystallises from light petroleum as brittle, colourless needles, sintering at 75° C. and melting at 78° to 80° C. to a colourless liquid. It has an odour resembling that of burnt indiarubber, and on long exposure to

light and air it becomes brownish-pink and emits a faint odour of hydrogen cyanide, finally being converted to a brittle red mass. It is readily soluble in alcohol, benzene or chloroform, less soluble in ether, almost insoluble in cold water and decomposed by boiling water. Decomposition on treatment with two or more molecules of aqueous potassium bisulphite takes place as follows :

$$C_5H_7O_2SeCN + 2KHSO_3 = C_5H_8O_2 + HCN + Se(SO_3K)_2$$

The *copper derivative*, $[CH_3.CO.C(SeCN) : C(CH_3)O -] < Cu$, occurs when an excess of aqueous 5 per cent. copper acetate is mixed with the selenocyanate dissolved in 25 parts of chloroform or benzene. The product is pale blue, insoluble in water, benzene, acetone or alcohol, and decomposed by acetic acid or aqueous sodium hydroxide.

Selenium OC-bisacetylacetone,



$$\begin{array}{c} CH_3.C(OH) = C.CO.CH_3 \\ | \\ Se \\ | \\ CH_3.CO = CH.CO.CH_3 \end{array}$$

This may be prepared in three ways : (1) One part of selenium acetylacetone and three parts of acetylacetone, together with six parts of ethyl alcohol, are heated under reflux and the resulting solution allowed to evaporate to dryness spontaneously *in vacuo* over quicklime. (2) A quantitative yield is obtained when selenium acetylacetone, three parts of acetylacetone and eleven parts of chloroform are refluxed together. (3) A solution containing 1·1 grams of selenium tetrachloride (1 mol.) and 5·3 grams of dry copper acetylacetone (4 mols.) in 45 c.c. of cold dehydrated chloroform is allowed to stand for two hours. The dark green precipitate which has formed is decomposed by water, the solution filtered, and the chloroform filtrate after shaking with dilute sulphuric acid is evaporated. A yellow oil remains, which deposits colourless crystals of the desired compound, whilst the mother-liquor, on addition of alcohol, yields selenium acetylacetone.

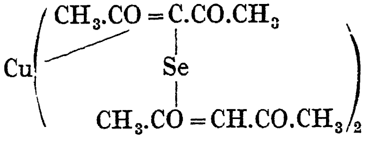
Selenium OC-*bis*acetylacetone yields a yellow solution in sodium hydroxide, which becomes red, developing a nauseating odour and liberating selenium. A similar series of changes occurs with sodium hydrogen carbonate, but the reaction is not so rapid. The compound is acid to moist litmus paper, reacts slowly with metallic sodium in dry ether, and dry ammonia added to the ether solution gives a yellow precipitate of an unstable ammonium salt. Ferric chloride gives an intense red coloration. Warm alcoholic solutions of pyridine, aniline and *p*-nitrophenylhydrazine cause decomposition. Selenium OC-*bis*acetylacetone reacts in two stages with aqueous potassium hydrogen sulphite (2 mols.), half only of the calculated amount of acetylacetone being eliminated initially. After removing the product with chloroform, the colourless solution on warming with alcohol yields potassium selenodithionate and the remainder of the acetylacetone. The *bis*acetylacetone when rapidly heated melts at 50° to 54° C. to a colourless liquid; it dissolves readily in cold ether, ethyl iodide, chloroform, benzene or toluene.

Selenium OC-*bis*acetylacetone crystallises in enantiomorphous forms of the monoclinic system, with $a : b : c = 0{\cdot}8872 : 1 : 1{\cdot}107$; $\beta = 110° 55'$. The list of forms observed on a right-handed crystal is $a(100)$, $c(001)$, $R(\bar{1}01)$, $m(110)$, $m'(1\bar{1}0)$ and $q(011)$. The habit is extremely variable.

The following are the combined results of the measurement of four crystals, three of right-handed types and one left-handed variety :

	$a(100)$	$c(001)$	$R(\bar{1}01)$	$m(110)$	$q(011)$
ϕ . .	0° 0′	69° 5′	133° 39′	0° 0′	69° 3′
ρ . .	90° 0′	90° 0′	90° 0′	50° 21′	44° 2′

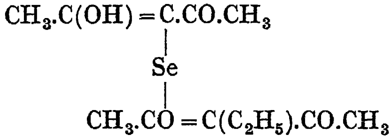
The compound dissociates in concentrated hot ethyl or methyl alcohol solution, also on warming with water, and on addition of a few drops of benzoyl chloride to its ether solution. It only partly dissociates in warm acetonitrile, and not at all in chloroform, benzene or light petroleum. The *copper derivative,*



$$\mathrm{Cu}\left(\begin{array}{l} \mathrm{CH_3.CO=C.CO.CH_3} \\ \qquad\qquad | \\ \qquad\quad\; \mathrm{Se} \\ \qquad\qquad | \\ \mathrm{CH_3.CO=CH.CO.CH_3} \end{array}\right)_2$$

occurs when a chloroform solution is shaken with ammoniacal cupric acetate, the product being isolated by evaporation or precipitation with light petroleum.

Selenium C-ethyl-OC-bisacetylacetone,



$$\begin{array}{l} \mathrm{CH_3.C(OH)=C.CO.CH_3} \\ \qquad\qquad\qquad | \\ \qquad\qquad\quad\; \mathrm{Se} \\ \qquad\qquad\qquad | \\ \qquad\quad \mathrm{CH_3.CO=C(C_2H_5).CO.CH_3} \end{array}$$

C-Ethylacetylacetone, 3·5 grams in 10 c.c. of alcohol, is treated with 1 gram of powdered selenium acetylacetone, the mixture heated under reflux for 10 minutes, and the resulting solution evaporated to dryness *in vacuo* over sodium hydroxide. The substance crystallises from light petroleum as short, rod-like needles, or compact prisms, sintering at 65° to 67° C. and melting at 77° to 82° C., soluble in the usual organic solvents, insoluble in water. It gives an intense red coloration with ferric chloride, and a pale blue copper salt. It undergoes dissociation in a similar manner to the preceding *bis*acetylacetone.

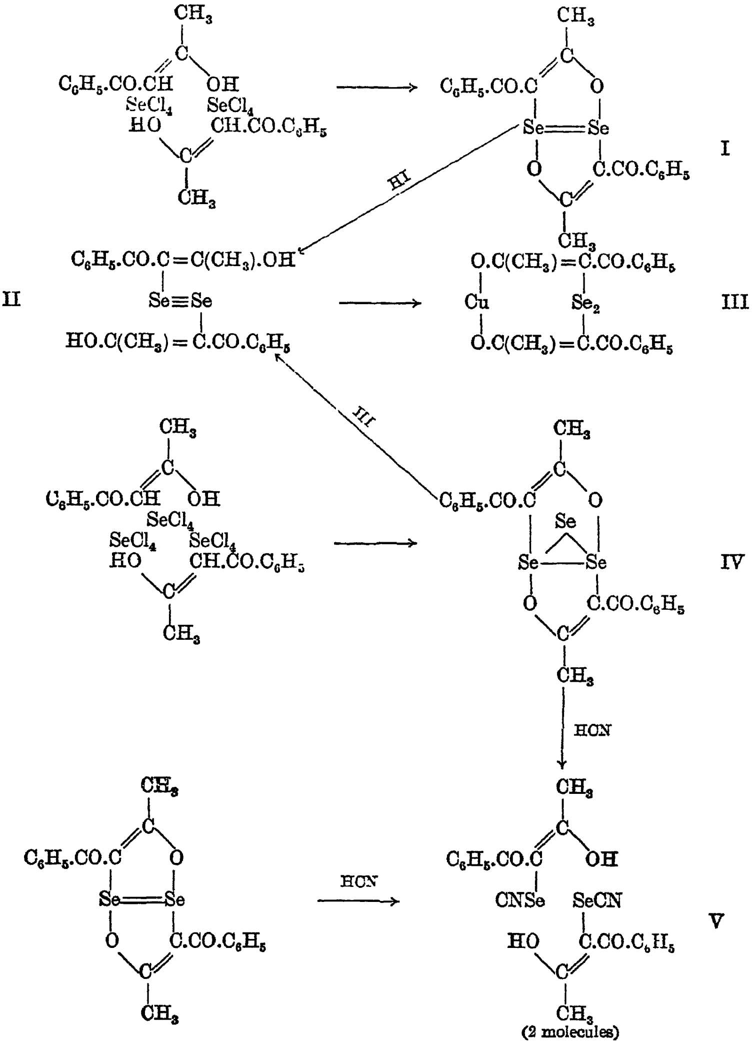
Reaction between Selenium Tetrachloride and Copper Benzoylacetone.

The reaction between selenium tetrachloride and copper benzoylacetone in equimolecular proportions takes place in two ways :

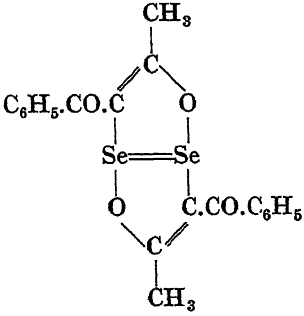
$$(1)\ 2\mathrm{SeCl_4}+2\mathrm{Cu(C_{10}H_9O_2)_2}=\mathrm{Se_2(C_{10}H_8O_2)_2}+2\mathrm{C_{10}H_9O_2Cl}+2\mathrm{CuCl_2}+2\mathrm{HCl}$$

$$(2)\ 3\mathrm{SeCl_4}+3\mathrm{Cu(C_{10}H_9O_2)_2}=\mathrm{Se_3(C_{10}H_8O_2)_2}+4\mathrm{C_{10}H_9O_2Cl}+3\mathrm{CuCl_2}+2\mathrm{HCl}$$

The dimeric form of selenium benzoylacetone (I) is the product of the simpler condensation (1). The change (2) leads to *cyclo*triselenium *bis*benzoylacetone (IV). Hydriodic acid transforms these substances quantitatively into diselenium *bis*benzoylacetone (II), the enolic nature of the product being proved by the formation of the copper salt (III). The relationships of these selenium derivatives of benzoylacetone are shown in the following scheme, which also illustrates the formation of the compounds and their quantitative conversion into diselenium *bis*benzoylacetone (II) and cyano-3-selenium benzoylacetone (V).



Selenium benzoylacetone,

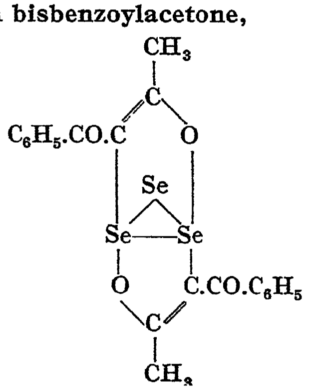


may be obtained in two ways: (1) Selenium tetrachloride, 4·6 grams suspended in 50 c.c. of dry ether, is added to 6·8 grams of benzoylacetone in 60 c.c. of the same solvent. After three hours the pale red solution obtained is evaporated in a current of air, hydrogen chloride being evolved, and the greenish-yellow residual oil triturated with successive small portions of alcohol. An almost white powder results (0·7 gram), and the filtrate yields a further 1·4 grams. This crystallises from benzene as small, pale yellow needles, decomposing at 200° C. The benzene mother-liquors contain *cyclo*triselenium *bis*benzoylacetone. (2) To 20·5 grams of selenium tetrachloride (1 mol.) suspended in 160 c.c. of anhydrous chloroform are added with shaking during 15 minutes at the ordinary temperature 41 grams of dry copper benzoylacetone (1½ mols.). After one hour the mixture is filtered, the filtrate evaporated in a current of air at the ordinary temperature, and the oily residue separated by alcohol into a less soluble product (*a*) and the more soluble chlorobenzoylacetone (*b*) contaminated with ill-defined seleniferous products. Repeated extraction of (*a*) with chloroform removes triselenium *bis*benzoylacetone (3·1 grams), leaving selenium benzoylacetone. The triselenium compound remains when the chloroform is evaporated off.

Selenium benzoylacetone crystallises from toluene as small, pale primrose-yellow, hexagonal plates, moderately soluble in toluene or glacial acetic acid, sparingly soluble in boiling chloroform, benzene or ethyl acetate, insoluble in water, ether and alcohol. It exists in two closely related varieties, one becoming discoloured at 175° C. and decomposing to a reddish-brown tar at 200° C., the other not changing in colour below 207° C. but melting rather sharply at 210° to 212° C. When silver benzoylacetone and selenium tetrachloride react in chloroform solution, selenium benzoylacetone is formed, but no *cyclo*triselenium *bis*benzoylacetone. Selenium benzoylacetone has no enolic properties, is insoluble in caustic alkalis, and inactive towards ferric and cupric compounds. In contact with 5*N* sodium hydroxide it decomposes with formation of acetophenone and red selenium; aniline and phenylhydrazine also cause the elimination of selenium. The benzoylacetone is converted into selenium acetylacetone by refluxing with acetylacetone in pure ethyl alcohol in the presence of a trace of solid sodium hydroxide.

From the crystallographic point of view selenium benzoylacetone crystallises in elongated, six-sided plates, with a dome termination of 64°. The extinction is straight and a positive bisectrix emerges normal to the plate; whether acute or obtuse has not been determined with certainty. In any case, the optic axial plane contains the morphological direction of elongation.

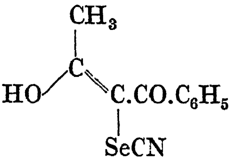
cycloTriselenium bisbenzoylacetone,



prepared as already described, crystallises in small, prismatic, bright yellow crystals, sintering at 190° to 195° C., liberating selenium and changing to a dark tar at 196° to 200° C. It is insoluble in alcohol, ether or water, but dissolves in cold benzene or chloroform. It readily decomposes when treated with hot concentrated hydrochloric acid, and less rapidly under the influence of cold 5*N* sodium hydroxide. It possesses no enolic properties, giving neither a ferric coloration nor a copper salt. Hydriodic acid decomposes it into diselenium *bis*-benzoylacetone, iodine and red selenium :

$$Se_3(C_{10}H_8O_2)_2 + 2HI = Se_2(C_{10}H_9O_2)_2 + Se + I_2$$

Cyano-3-selenium benzoylacetone,

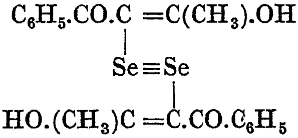


occurs in quantitative yield when selenium benzoylacetone or the triselenium compound is acted upon by anhydrous hydrogen cyanide in the presence of dry ether. The reaction in the latter case takes place according to the equation

$$Se_3(C_{10}H_8O_2)_2 + 2HCN = 2CNSe.C_{10}H_9O_2 + Se$$

The compound crystallises from light petroleum as transparent needles, softening at 68° C. and melting at 70° C. to a colourless liquid which reddens at 110° C. It readily dissolves in benzene or chloroform, is less soluble in carbon tetrachloride, and dissolves in alcohol only with slow decomposition. With cupric acetate it gives a greenish-blue *copper salt*, M.pt. 131° C., and with ferric chloride in aqueous alcohol solution enolisation sets in after a few seconds, the liquid assuming an intense red shade. The cyano-compound is very sensitive to sunlight, selenium being eliminated.

Diselenium bisbenzoylacetone,



$$\begin{array}{l} C_6H_5.CO.C = C(CH_3).OH \\ \quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\; Se \equiv Se \\ \quad\quad\quad\quad\quad\quad\;\; | \\ HO.(CH_3)C = C.CO.C_6H_5 \end{array}$$

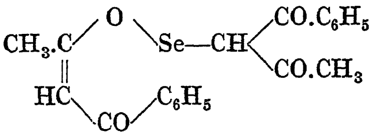
may be obtained (1) from selenium benzoylacetone and hydriodic acid by a similar method to that adopted for diselenium bisacetylacetone ; (2) by shaking 0·5 gram of the triselenium compound at 0° C. with 0·5 c.c. of 50 per cent. decolorised hydriodic acid, 50 c.c. of ether and 10 grams of ice. Liberated iodine is removed by 0·1*N* sodium thiosulphate solution, the mixture filtered, and the ether layer evaporated, when 0·2 gram of the required compound results. It crystallises in bright orange hexagonal prisms, sintering at 65° C. and melting at 80° to 90° C., insoluble in water, very sparingly soluble in alcohol, but readily dissolving in ether, chloroform or cold benzene. It decomposes when treated with 5*N* sodium hydroxide, giving selenium and acetophenone. Ferric chloride in a mixture of ether and alcohol causes a violet-red coloration, aqueous cupric acetate gives a brownish-yellow *copper derivative*, and alcoholic phenylhydrazine gives an unstable salmon-pink compound.

The orange crystals of diselenium *bis*benzoylacetone are isomorphous with those of the corresponding dithio-compound. The system is orthorhombic, with $a : b : c = 0{\cdot}7341 : 1 : 0{\cdot}4110$, the forms developed being $b(010)$, $a(100)$, $o(111)$ and $r(101)$. The following results were obtained from the measurement of two crystals :

	$b(010)$	$a(100)$	$o(111)$	$r(101)$
ϕ .	0° 0′	89° 58′	53° 43′	90° 32′
ρ . .	90° 0′	90° 0′	34° 47′	29° 14′

Optically, the crystals exhibit a strong dichroism when resting on $b(010)$, but not on $a(100)$, the transmitted colours being deep orange for a-axis vibrations and lemon-yellow for the b- and c-axes. The optic axial plane is $c(001)$, but it has not been possible to determine the several orientations of the two bisectrices.

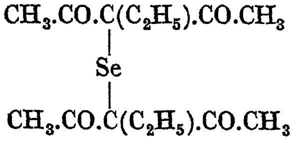
Selenium OC-bisbenzoylacetone,



This is prepared by treating selenium benzoylacetone with an excess of benzoylacetone in anhydrous chloroform in the presence of a trace of sodium hydroxide. The product crystallises from benzene and light petroleum in minute, white, odourless prisms, sintering at 100° C., melting at 134° to 136° C., and decomposing at higher temperatures. It is moderately soluble in hot benzene or chloroform, sparingly soluble in ether, alcohol or cold benzene, insoluble in water or light petroleum. It has no acidic properties, is insoluble in but decomposed by cold 5*N* sodium hydroxide, does not yield a copper derivative, and with alcoholic ferric chloride only slowly develops a red coloration. Boiling with alcohol or any moist solvent gives selenium benzoylacetone and benzoylacetone, but the compound crystallises unchanged from its solution in boiling benzene.

Reaction between Selenium Tetrachloride and Copper C-Ethylacetylacetone.[1]

Selenium bis-C-ethylacetylacetone,



$$\begin{array}{c} \mathrm{CH_3.CO.C(C_2H_5).CO.CH_3} \\ | \\ \mathrm{Se} \\ | \\ \mathrm{CH_3.CO.C(C_2H_5).CO.CH_3} \end{array}$$

Dry copper C-ethylacetylacetone, 2·2 grams, is added to 0·77 gram of selenium tetrachloride in 20 c.c. of dry chloroform, the pale green precipitate which forms is shaken with ether and dilute sulphuric acid, and the ether extract evaporated until 0·6 gram of the required compound is obtained (yield, 50 per cent.). The compound crystallises from alcohol as colourless, transparent, six-sided prisms or needles,

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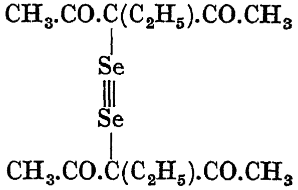
[1] Morgan, Drew and Barker, *loc. cit.*

melting at 81° to 82° C. to a transparent colourless liquid which does not liberate selenium until about 200° C. In boiling water or light petroleum it is sparingly soluble, but it dissolves more readily in ether, benzene or chloroform. The derivative is non-enolic, giving no coloration with dilute alcoholic ferric chloride even on boiling; it is slowly decomposed by cold 5*N* sodium hydroxide, in which it is insoluble. Warm concentrated hydrochloric acid causes decomposition with liberation of selenium, and bromine in chloroform solution also decomposes the compound. Selenium C-ethylacetylacetone is quantitatively decomposed by 50 per cent. hydriodic acid in the presence of ether into C-ethylacetylacetone and selenium:

$$(C_7H_{11}O_2)_2Se + 2HI = 2C_7H_{12}O_2 + Se + I_2$$

Diselenium bis-C-ethylacetylacetone,

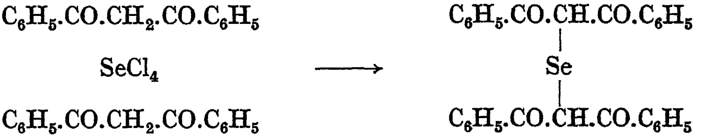


$$\begin{array}{c} CH_3.CO.C(C_2H_5).CO.CH_3 \\ | \\ Se \\ ||| \\ Se \\ | \\ CH_3.CO.C(C_2H_5).CO.CH_3 \end{array}$$

Copper C-ethylacetylacetone, 7·8 grams, is added in one lot to 4·3 grams of selenium tetrachloride in 40 c.c. of anhydrous chloroform at 0° C. After one hour the filtrate is concentrated and mixed with alcohol, further evaporation giving 1·2 grams of pure substance. The compound crystallises from alcohol in lemon-yellow, six-sided needles or prisms, melting at 117° to 118° C. to a transparent, yellow liquid which reddens and decomposes at 210° C. It is sparingly soluble in light petroleum, more soluble in ether, benzene or chloroform. It is non-enolic, and behaves towards ferric chloride, 5*N* sodium hydroxide and bromine in a similar manner to the preceding compound. With two to four molecular equivalents of potassium bisulphite it yields C-ethylacetylacetone, selenium and probably potassium selenodithionate. A large excess of sulphite gives no precipitate of selenium, the element dissolving probably to form potassium selenosulphate. Hydriodic acid quantitatively decomposes the compound in the presence of ether into C-ethylacetylacetone and red selenium.

Reaction between Selenium Tetrachloride and Copper Dibenzoylmethane.[1]

Condensation between selenium tetrachloride and copper dibenzoylmethane like the preceding condensations gives rise to two products. In the simpler case one molecule of tetrachloride reacts:



$$\begin{array}{lcc} C_6H_5.CO.CH_2.CO.C_6H_5 & & C_6H_5.CO.CH.CO.C_6H_5 \\ & & | \\ \qquad SeCl_4 & \longrightarrow & Se \\ & & | \\ C_6H_5.CO.CH_2.CO.C_6H_5 & & C_6H_5.CO.CH.CO.C_6H_5 \end{array}$$

I

whilst in the more complex reaction two molecules of tetrachloride take part:

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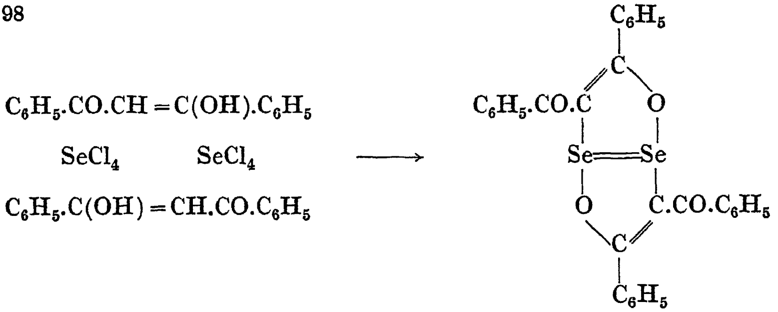
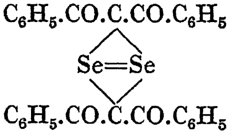
[1] Morgan, Drew and Barker, *loc. cit.*

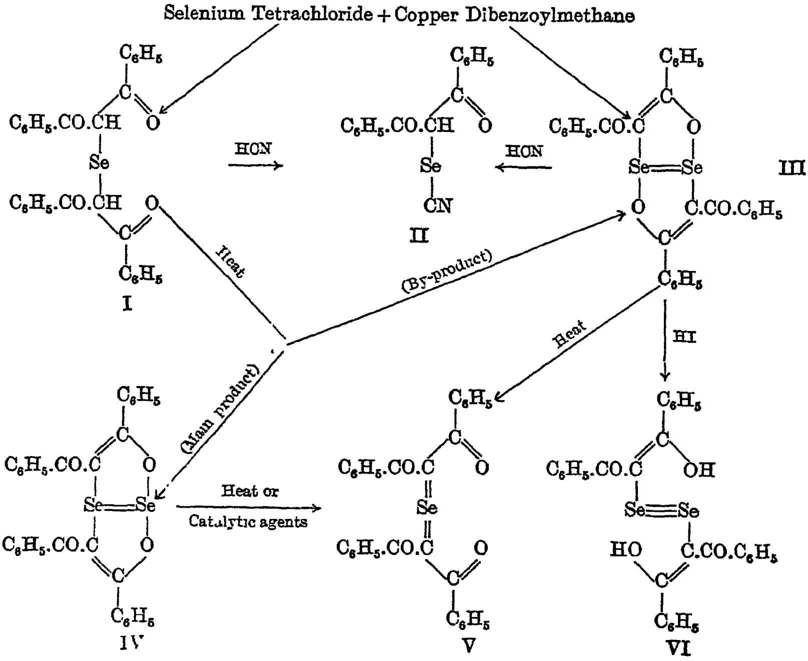


II

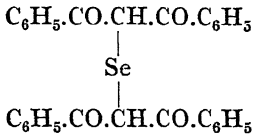
An isomeride of selenium dibenzoylmethane is produced, together with a small proportion of selenium dibenzoylmethane, by the regulated heating of Compound I, two molecules condensing with the elimination of two molecules of dibenzoylmethane. This isomeric substance, *iso*-selenium dibenzoylmethane, is assigned the formula (IV), since, on further heating, or under the catalytic influence of hydrogen cyanide or of hydriodic acid, it readily loses an atom of selenium and passes into an orange compound, selenium dehydro*bis*dibenzoylmethane (V). The following formula is not entirely excluded as a representation of the *iso*-compound, the relation between the two formulæ being somewhat in the nature of keto- and enol-forms of the same substance:



The close genetic relationship between the selenium compounds of dibenzoylmethane is shown in the following scheme:



Selenium bisdibenzoylmethane,



$$\begin{array}{c} C_6H_5.CO.CH.CO.C_6H_5 \\ | \\ Se \\ | \\ C_6H_5.CO.CH.CO.C_6H_5 \end{array}$$

may be obtained as follows: (1) 2 grams of selenium tetrachloride (3 mols.) suspended in 20 c.c. of anhydrous chloroform at 0° C. are treated with 6·2 grams of dry copper dibenzoylmethane (4 mols.) in 10 c.c. of chloroform. After 1½ hours the mixture is filtered, the filtrate evaporated and the resulting paste extracted with warm alcohol. The residue separates from ethyl acetate in pale yellowish-white prisms, and constitutes the *bis*-compound. (2) If 4 equivalents of tetrachloride be used with 5 equivalents of the copper salt, the following products are isolated: selenium *bis*dibenzoylmethane, selenium dibenzoylmethane, and chlorodibenzoylmethane mixed with dibenzoylmethane.

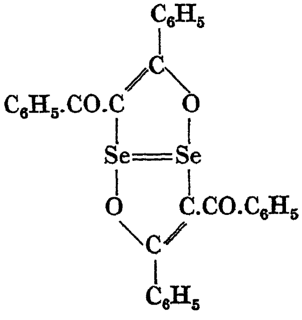
Selenium *bis*dibenzoylmethane crystallises from dry ethyl acetate as large yellowish-white, six-sided prisms, sintering at 143° C. and melting at 150° to 152° C. to a transparent yellow liquid. From dry benzene it separates in aggregates of minute white needles containing one molecular proportion of the solvent, which may be removed at 100° C. The compound is sparingly soluble in alcohol, but more soluble in benzene or chloroform; it is insoluble in and decomposed by cold $5N$ sodium hydroxide. It is comparatively inert and stable; it is not affected by cold potassium hydrogen sulphite solution and only slowly on warming; it gives no copper salt, and its chloroform solution at first gives no coloration with aqueous alcoholic ferric chloride, but after a few seconds the colour develops, the liquid becoming cloudy owing to the formation of a dark precipitate. Selenium *bis*dibenzoylmethane is decomposed by warm concentrated hydrochloric acid and quantitatively by dilute hydriodic acid giving red selenium, dibenzoylmethane and free iodine.

The elements, as obtained by a mutual adjustment of the poles of a gnomonic projection, are $a:b:c=1{\cdot}07:1:0{\cdot}75$; $\beta=91\frac{1}{2}°$. The list of forms is $a(100)$, $m(110)$, $c(001)$, $r(101)$ and $R(\bar{1}01)$. The following are the approximate angular values obtained from two crystals:

	$m(110)$	$a(100)$	$c(001)$	$r(101)$	$R(\bar{1}01)$
ϕ . .	43°	90°	*ca.* 90°	90°	90°
ρ . .	90°	90°	1°	37°	35°

There is an imperfect cleavage parallel to $a(100)$, through which an optic axis emerges very obliquely. Another optic axis is visible through $c(001)$, so that the axial plane is b. A 35° extinction on m (with the vertical edge) is proof that the system is not orthorhombic.

Selenium dibenzoylmethane,

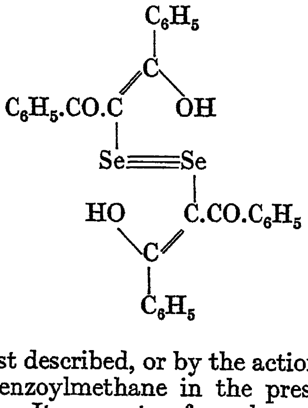


The optimum yield of this derivative is obtained under the following conditions: Copper dibenzoylmethane, 28·5 grams, is quickly added to 9·9 grams of selenium tetrachloride in 150 c.c. of anhydrous chloroform, and the mixture shaken at intervals for 2·5 hours at room temperature. The filtrate from this mixture is evaporated until free from chloroform, and the syrup extracted after 12 hours with cold alcohol. After repeated extractions the residue is treated with cold ethyl acetate. A primrose-yellow powder remains, which by treatment with boiling ethyl acetate gives 5 grams of selenium *bis*dibenzoylmethane (soluble in boiling ethyl acetate) and 1·4 grams, or a 10 per cent. yield, of selenium dibenzoylmethane, which is comparatively insoluble in the boiling solvent.

Selenium dibenzoylmethane crystallises from benzene as lustrous, pale golden-yellow plates containing 2 molecules of benzene of crystallisation; when freed from the latter a pale primrose-yellow powder results, M.pt. 211° C. to a deep yellow liquid. The compound is very sparingly soluble in boiling ethyl acetate, moderately soluble in benzene, but dissolves readily in chloroform. It is not enolic. It is insoluble in 5*N* sodium hydroxide, but decomposed on warming. It is stable towards 15 per cent. hydrochloric acid; it yields an intensely scarlet solution in concentrated sulphuric acid, the colour disappearing on dilution.

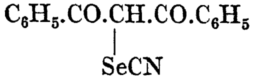
From the ethyl acetate extract mentioned above, *cyclotriselenium bisdibenzoylmethane* may be isolated by evaporation and extraction of the residue with cold alcohol and ethyl acetate. The product has the formula $Se_3(C_{15}H_{10}O_2)_2$, reddens at 205° C., and melts at 220° C. with liberation of selenium. It separates from benzene as minute, bright yellow prisms, is almost insoluble in chloroform, and is non-enolic towards ferric chloride. It is decomposed by hydriodic acid in the presence of ether, yielding red selenium and orange diselenium *bis*dibenzoylmethane.

Diselenium bisdibenzoylmethane,



may be obtained as just described, or by the action of aqueous hydriodic acid on selenium dibenzoylmethane in the presence of a mixture of chloroform and ether. It separates from benzene-light petroleum in felted masses of slender orange-yellow prismatic needles, softening above 104° C. and melting at 116° to 118° C. In chloroform or benzene it dissolves readily, but is sparingly soluble in ether or petroleum. It possesses enolic properties, yielding an olive-green *copper derivative*, which develops a red coloration with ferric chloride.

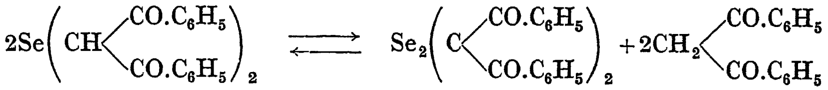
Cyanoselenium dibenzoylmethane,



$$\underset{\displaystyle \text{SeCN}}{C_6H_5.CO.\underset{|}{C}H.CO.C_6H_5}$$

occurs when selenium dibenzoylmethane or selenium *bis*dibenzoylmethane is treated with anhydrous hydrogen cyanide. The compound sinters at 97° C., melts at 100° to 101° C., is readily soluble in benzene or chloroform, moderately soluble in ether, and very sparingly soluble in light petroleum. It closely resembles the corresponding derivatives of acetylacetone and benzoylacetone in appearance and odour, but differs from them in yielding no copper derivative, although developing a coloration with ferric chloride.

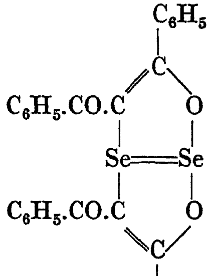
Action of Heat on Selenium bisDibenzoylmethane.—When selenium *bis*dibenzoylmethane is melted and maintained at 140° to 145° C. for 30 minutes, dibenzoylmethane is eliminated and an equilibrium represented by the following equation occurs :



$$2Se\left(CH\begin{matrix}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{matrix}\right)_2 \rightleftharpoons Se_2\left(C\begin{matrix}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{matrix}\right)_2 + 2CH_2\begin{matrix}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{matrix}$$

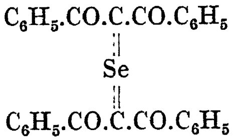
Cooling and examination of the mixture shows that about 50 per cent. of the original quantity of selenium *bis*dibenzoylmethane has undergone transformation, and that the dimeric selenium product represented on the right of the equation consists of *iso*selenium dibenzoylmethane together with a small proportion of selenium dibenzoylmethane.

isoSelenium dibenzoylmethane,



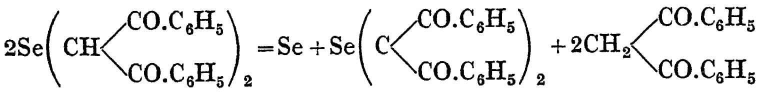
crystallises from ethyl acetate in rosettes of pale golden-yellow needles or flakes, melting at 175° to 176° C. with elimination of red selenium. It readily dissolves in benzene or chloroform, but is sparingly soluble in ethyl acetate or ether. It possesses no acid or enolic properties and yields no coloration with ferric chloride. Treatment with hydrogen cyanide, or a mixture of aqueous hydriodic acid and ether, or heating to the melting-point, transforms the compound into selenium dehydro*bis*dibenzoylmethane, one atom of selenium being set free.

Selenium dehydrobisdibenzoylmethane.—If instead of maintaining a temperature of 140° to 145° C. as before, the molten mass be raised above 150° C., a further change sets in, the velocity of the reaction increasing with rise of temperature and becoming rapid at 180° C. In the course of this change half the total amount of selenium present is set free, with the formation of selenium dehydro*bis*dibenzoylmethane,



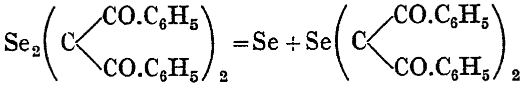
$$\begin{array}{c} C_6H_5.CO.C.CO.C_6H_5 \\ \| \\ Se \\ \| \\ C_6H_5.CO.C.CO.C_6H_5 \end{array}$$

Since the reaction is not reversible, all the selenium *bis*dibenzoylmethane is transformed according to the equation



$$2Se\left(CH\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array}\right)_2 = Se + Se\left(C\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array}\right)_2 + 2CH_2\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array}$$

The intermediate compounds, *iso*selenium dibenzoylmethane and selenium dibenzoylmethane, when isolated and heated separately above their melting-points yield, as would be expected, identical products, selenium dehydro*bis*dibenzoylmethane and selenium:



$$Se_2\left(C\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array}\right)_2 = Se + Se\left(C\begin{array}{l}\diagup CO.C_6H_5\\ \diagdown CO.C_6H_5\end{array}\right)_2$$

Selenium dehydrobisdibenzoylmethane separates from ethyl acetate in small, refractive, bright orange crystals, M.pt. 190° to 191° C., soluble in ether, benzene or chloroform, moderately soluble in ethyl acetate, insoluble in water. In organic solvents the solutions are intensely yellow. The compound possesses no acidic or enolic properties, does not react with 5*N* sodium hydroxide, ferric chloride or cupric acetate, is unaffected by boiling concentrated hydrochloric acid, alkali bisulphites, ethereal aqueous hydriodic acid or ethereal hydrocyanic acid. With 50 per cent. potassium hydroxide it yields selenium and acetophenone. It dissolves in cold concentrated sulphuric acid giving a scarlet solution, being reprecipitated by the addition of water. Heating at 220° C. with calcium hydroxide does not affect the compound. Reduction by sodium amalgam in moist ethyl alcohol suspension gives red selenium, the odour of acetophenone, dibenzoylmethane (separated as copper derivative) and benzoic acid.

The crystals of the dehydro-compound belong to the monoclinic system, the parameters being $a : b : c = 2{\cdot}10 : 1 : 1{\cdot}49$; $\beta = 99°$. The forms developed are $c(001)$, $a(100)$, $x(310)$, $o(111)$ and $p(\bar{1}11)$. The following mean results have been obtained from a crystal 0·3 mm. in diameter:

	$x(310)$	$a(100)$	$c(001)$	$o(111)$	$p(\bar{1}11)$
ϕ . .	55½°	90°	*ca.* 90°	31°	339°
ρ . .	90°	90°	10°	60°	59°

The optic axial plane is $b(010)$ and the negative acute bisectrix is inclined at about 10° to the vertical in the acute angle β. An optic axis is visible through $c(001)$. The dispersion is abnormally strong, $\rho > v$.

Reaction between Selenium Tetrachloride and Copper Propionylacetone.[1]

This condensation closely resembles that with acetylacetone, one seleniferous product being obtained. This is selenium acetylpropionyl-

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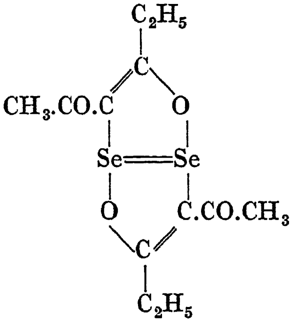
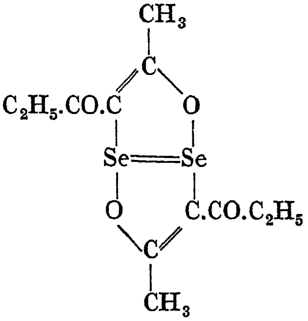
[1] Morgan and Reeves, *Trans. Chem. Soc.*, 1923, 123, 444.

methane, and it is accompanied by acetylpropionylchloromethane, $C_2H_5.CO.CHCl.CO.CH_3$. As an analogue of selenium acetylacetone it undergoes similar reactions with hydriodic and hydrocyanic acids and with excess of propionylacetone. The products on the whole are less stable than those from selenium acetylacetone.

Selenium acetylpropionylmethane (*Selenium propionylacetone*),



or

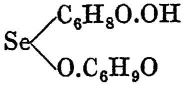


Copper acetylpropionylmethane (10·2 grams, *i.e.* 1 mol.) is slowly added with shaking to 7·8 grams of selenium tetrachloride suspended in 56 c.c. of anhydrous chloroform. After 30 minutes the mixture is filtered, the solvent removed from the filtrate by a current of air, and the residue triturated with absolute alcohol. A 24·5 per cent. yield of selenium acetylpropionylmethane is isolated as a yellow crystalline powder. It separates from absolute alcohol as pale yellow, glistening plates, M.pt. 137° C., is only faintly acid to litmus, and dissolves to a yellow solution in aqueous sodium hydroxide, decomposition gradually setting in with precipitation of selenium. The compound is practically insoluble in water or ether. It yields selenium when warmed with alcoholic aniline, and becomes superficially coated with red selenium on exposure to light.

Diselenium bisacetylpropionylmethane, $Se_2(C_6H_8O.OH)_2$.—To 0·9 gram of selenium acetylpropionylmethane (1 mol.) suspended in 150 c.c. of ether and cooled by adding 1 gram of crushed ice, 0·63 gram of 60 per cent. hydriodic acid (2 mols.) diluted with 40 c.c. of water is added with vigorous shaking. The brown colour in the ether layer due to iodine is removed by adding 0·1*N* sodium thiosulphate solution, the decolorised solution dried over sodium sulphate, and the ether removed in a vacuum. The residual yellow oil (0·4 gram, *i.e.* 42 per cent. yield) does not solidify. It has the characteristic offensive odour of the diselenium *bis*-β-diketones. It yields a mustard yellow *copper salt*, $Se_2(C_6H_8O.O)_2Cu$.

Cyano-3-selenium acetylpropionylmethane, $CNSe.C_6H_8O.OH$, results from the interaction of selenium acetylpropionylmethane and redistilled hydrogen cyanide in dry ether solution. It crystallises in a mass of flat six-sided needles, M.pt. 27·5° C., which liquefy on keeping but do not solidify again on cooling. Both the oil and the crystals give a red ferric chloride coloration. The compound yields a pale blue, crystalline *copper salt*, $(CNSe.C_6H_8O.O)_2Cu$, readily soluble in chloroform and gradually decomposing on keeping.

Selenium OC-bisacetylpropionylmethane,

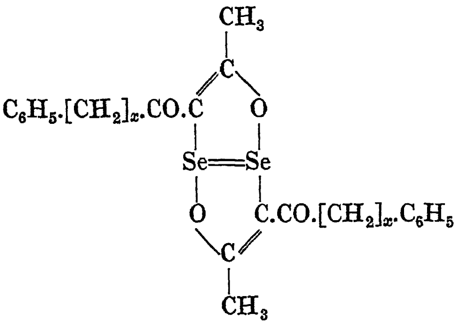


$$Se\begin{cases}C_6H_8O.OH\\O.C_6H_9O\end{cases}$$

This is the condensation product of selenium acetylpropionylmethane and acetylpropionylmethane in chloroform solution, using a trace of solid sodium hydroxide as catalyst. It is an oil, having an odour of burnt rubber. It dissolves readily in chloroform, but is only sparingly soluble in petroleum. A *copper salt* is known, which approximates to the formula $(C_{12}H_{17}O_4Se)_2Cu$.

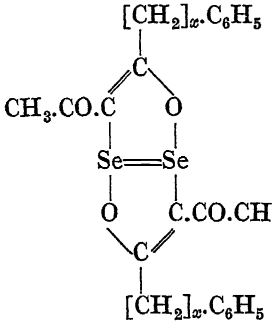
Selenium Tetrachloride and Di- and Tri-ketones.

Selenium ω-phenylacetylacetone,[1]



I

or



IA

This compound is represented by formula I or IA, where $x=1$. The reaction between selenium tetrachloride and copper ω-phenylacetylacetone takes place smoothly in accordance with the equation

$$2(C_{11}H_{11}O_2)_2Cu + 2SeCl_4 = (C_{11}H_{10}O_2)_2Se_2 + 2C_{11}H_{11}O_2Cl + 2CuCl_2 + 2HCl$$

the other organic product being 3-chloro-ω-phenylacetylacetone. One gram-molecule of copper ω-phenylacetylacetone (27·2 grams) is gradually added to 14·3 grams of selenium tetrachloride (1 mol.) in 70 c.c. of chloroform at 0° C. After 30 minutes the liquid is filtered and the red filtrate evaporated to dryness in a current of air. After washing with alcohol and ether, 12 grams of a light yellow residue remain. This represents a 74 per cent. yield of selenium ω-phenylacetylacetone. The alcoholic and ethereal extracts are evaporated and the residue extracted with light petroleum, this removing the 3-chloro-ω-phenylacetylacetone. The selenium compound, after repeated crystallisation from chloroform and benzene, sinters at 161° C. and melts at 164° to 165° C. It separates from chloroform, benzene or glacial acetic acid as pale yellow plates which soon become pink on exposure to light; in alcohol or ether it is only sparingly soluble and in water insoluble. It develops no coloration with ferric chloride, but red selenium separates on warming with 3*N* sodium hydroxide or with mineral acid.

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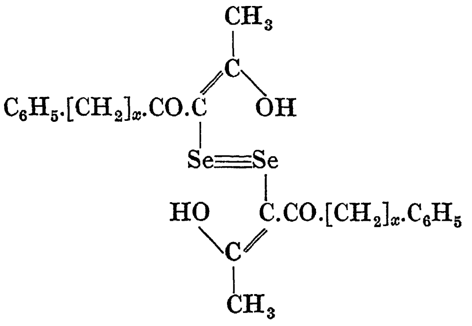
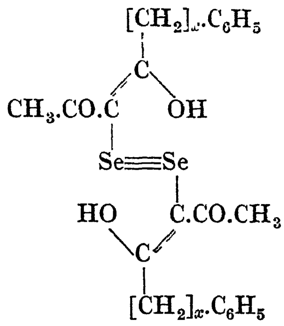
[1] Morgan and Porter, *Trans. Chem. Soc.*, 1924, 125, 1269.

Diselenium bis-ω-phenylacetylacetone,



II

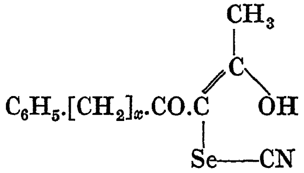
or



IIA

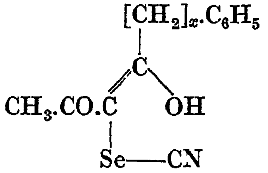
For this compound $x = 1$. A suspension of powdered selenium ω-phenylacetylacetone in water and ether is reduced by 2·5 equivalents of 30 per cent. hydriodic acid. The liberated iodine is removed by thiosulphate solution, and the ether solution concentrated in a vacuum. Rapid evaporation then causes partial crystallisation of orange diselenium bis-ω-phenylacetylacetone, which, however, becomes oily again at the ordinary temperature. Yield, 90 per cent. The orange-yellow oil gives an intense red coloration with ferric chloride, and forms a brown *copper derivative* decomposing at 150° to 152° C.

Cyanoselenium ω-phenylacetylacetone,



III

or



IIIA

This compound is represented by formula III or IIIA, where $x = 1$. 3 grams of powdered selenium ω-phenylacetylacetone in a mixture of 4 c.c. of hydrogen cyanide and 11 c.c. of anhydrous ether are allowed to stand for two hours, and the liquid then evaporated in a vacuum. The residue is dried and rapidly crystallised from petroleum (B.pt. 40° to 60° C.), the cyano-derivative separating as colourless needles, M.pt. 63° to 64° C., very soluble in organic solvents, insoluble in water. The product slowly decomposes, forming a red tar, impurities hastening the decomposition. With ferric chloride a dull red coloration develops, and a light green *copper derivative* is formed with cupric acetate.

Selenium β-phenylpropionylacetone, (Formula I or IA, $x = 2$).—This is prepared in a similar manner to selenium ω-phenylacetylacetone, using copper β-phenylpropionylacetone. It crystallises from benzene as pale, yellowish-white leaflets, sintering at 128° C. and melting at 141° to 142° C.; it is more soluble in organic solvents than selenium ω-phenylacetylacetone, with benzene at comparable temperatures the solubility being five times as great. The compound is non-enolic and gives no coloration with ferric chloride.

Diselenium bis-β-phenylpropionylacetone, (Formula II or IIA, $x=2$), is the reduction product of the preceding compound when hydriodic acid is employed in the usual way. It is an orange oil, yielding a buff-coloured *copper derivative,* M.pt. 147° to 149° C.

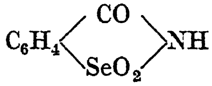
Cyanoselenium β-phenylpropionylacetone, (Formula III or IIIA, $x=2$), occurs in quantitative yield when selenium β-phenylpropionylacetone reacts with anhydrous hydrocyanic acid. It is very soluble in organic solvents and crystallises from petroleum as colourless needles, M.pt. 59° to 61° C. It is much more stable on keeping than cyanoselenium ω-phenylacetylacetone. It develops a red ferric chloride coloration, and gives a greenish-yellow *copper derivative* having no definite melting-point.

The interaction of selenium tetrachloride and barium diacetylacetone does not give organo-selenium derivatives.

SELENOSACCHARIN.[1]

Diphenyl diselenide di-o-carboxylamide, $Se_2(C_6H_4.CO.NH_2)_2$.—10 grams of diphenyl diselenide di-*o*-carboxylic acid are intimately mixed with 11 grams of phosphorus pentabromide and the mixture heated to melting in an oil-bath, the heating being continued until the evolution of hydrogen bromide ceases. The melt is then extracted with benzene and the solution saturated with ammonia to precipitate the amide. The yield is about 7 grams, and when crystallised from acetic acid the compound is deposited in yellow needles, M.pt. 265° to 266° C.

1 : 2-Benzoic seleno-imide (*Selenosaccharin*),

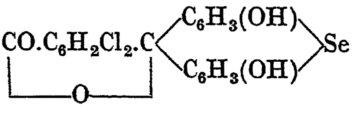


$$C_6H_4\begin{cases}CO\\SeO_2\end{cases}NH$$

The foregoing amide, 2·4 grams, when boiled with an aqueous solution of potassium permanganate, is oxidised to selenosaccharin, a yield of 2·6 grams being obtained. This body forms colourless needles, M.pt. 227° to 228° C. (decomp.), sparingly soluble in water. The sweet taste of the sulphur analogue is entirely lacking in this compound. The imino hydrogen may be replaced by metals, the alkali metal salts being very soluble. *o*-Selenobenzoic acid, which is the parent substance of this compound, is very readily soluble in water, and is formed by the oxidation of diphenyl diselenide di-*o*-carboxylic acid.

SELENOFLUORESCEÏNS.[2]

Dichloroselenofluoresceïn,



$$CO.C_6H_2Cl_2.C\begin{cases}C_6H_3(OH)\\C_6H_3(OH)\end{cases}Se$$

20 kilograms of dichlorofluoresceïn are heated with 150 litres of 30 per cent. sodium hydroxide for six hours at 120° C., during which period 20 kilograms of finely divided selenium are introduced. The reaction

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[1] Lesser and Weiss, *Ber.*, 1912, 45, 1835.

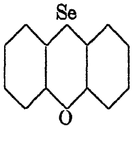
[2] German Patent, 279549.

mixture is poured into water, acidified and filtered; the residue is dissolved in dilute sodium hydroxide solution and the solution filtered, the filtrate then being acidified with dilute hydrochloric acid. A reddish-brown powder separates, which is difficult to crystallise, being purified by means of its iron salt and finally by boiling its alcohol solution several times with charcoal. Fine reddish-brown crystals are thus obtained, which melt with decomposition on heating and are insoluble in water and all the usual organic solvents with the exception of alcohol, in which the body is sparingly soluble. This method is said to be applicable both to fluoresceïn and its halogen derivatives.

Another method of preparation is as follows: [1] 33 parts of fluoresceïn are dissolved in 5 parts of ether and treated with 25 parts of selenium chloride in the same solvent. A yellowish-red precipitate separates, and after long stirring at the ordinary temperature the ether is distilled off. The residue is stirred with water, the mixture filtered and the residue now dissolved in sodium hydroxide. After further filtration the filtrate is treated with hydrochloric acid, which precipitates selenofluoresceïn. Further purification is effected by solution in alkali and reprecipitation. A reddish-brown powder is obtained, soluble with fluorescence in alcohol, but insoluble in water. In concentrated sulphuric acid it dissolves to give an orange solution. Its alkali salts are very soluble in water, giving red solutions. This process may also be applied to phthalins, which are obtained by the reduction of phthaleïns and their halogen derivatives. If the selenium chloride is replaced by the oxychloride similar products are obtained.[2] In place of the phthalins specified in the patents quoted, their O-acetyl compounds or O-acetyl compounds of the phthaleïns may be used in indifferent solvents. The products are different from those obtained by the action of selenium on fluoresceïns in aqueous alkali solutions.[3]

PHENOXSELENINE AND ITS DERIVATIVES.[4]

Phenoxselenine,



3 grams of phenoxtellurine (p. 225) and powdered black selenium (0·9 to 1·3 grams) are mixed and heated so that the phenoxtellurine boils gently during thirty to sixty minutes. About 2·6 grams of organic selenium product result, and this may be distilled or extracted with ether or chloroform. It crystallises from acetic acid as long sulphur-yellow needles, M.pt. 82° to 84° C., which consist of a mixture or compound containing about 2 molecules of phenoxselenine to 1 molecule of phenoxtellurine. Resolution into the components is effected by dissolving the body in cold chloroform, adding a slight excess of bromine, collecting the mixed dibromides and boiling them for a few minutes with acetone; the acetone and bromoacetone formed are now

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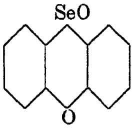
[1] German Patent, 290540.
[2] German Patent, 291883.
[3] For the compound from eosin, see German Patents, 261556, 286950, 287020.
[4] Drew, *J. Chem. Soc.*, 1928, p. 511.

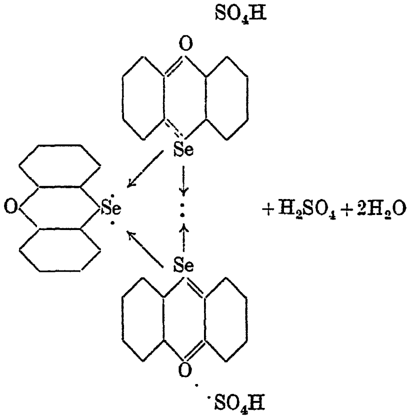
allowed to evaporate off, the residue extracted with ether and the solution filtered from the insoluble phenoxtellurine dibromide. The ether solution affords almost pure phenoxselenine. The compound separates from alcohol or acetic acid as long, colourless, refractive, rectangular prisms, M.pt. 87° to 88° C., which have a faint odour of rose leaves. It forms halides when treated with chloroform solutions of the halogens. The *dichloride* crystallises from acetic acid as pale yellow glistening plates, melting with decomposition at 127° C.; the *dibromide* forms orange-red spangles, melting with decomposition at 147° to 148° C.

Phenoxselenine oxide,



occurs when a solution of phenoxselenine in warm glacial acetic acid is treated with a slight excess of hydrogen peroxide. A solution of the unstable *diacetate* results, and the solid isolated by spontaneous evaporation is dissolved in a little hot water, the solution allowed to cool and extracted with its own volume of ether. The aqueous layer yields the *dihydroxide* in inch-long, slender, colourless needles, very soluble in water. Drying at 100° C. *in vacuo* over phosphorus pentoxide eliminates a molecule of water, giving the oxide, which is a colourless, crystalline powder, M.pt. 171° to 172° C. Water converts the oxide into the dihydroxide, the solution having a neutral reaction. Above its melting-point the oxide is quantitatively transformed to phenoxselenine. Both the oxide and the dihydroxide are violently decomposed by hydrogen peroxide in glacial acetic acid solution.

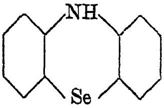
Triphenoxselenylium dibisulphate sulphuric acid dihydrate,



The greenish-black solution of 1 gram of phenoxselenine in 6 c.c. of concentrated sulphuric acid is warmed for five minutes, sulphur dioxide escaping. After cooling, 4 c.c. of water are gradually added with stirring, and after thirty-six hours the copper-red crystals which have formed are filtered off on sintered glass and dried on a porous plate. The product may also be isolated by leaving 0·8 gram of phenoxselenine in 7 c.c. of concentrated sulphuric acid for three hours, then adding 7 c.c. of water, the liquor on standing depositing the copper-red crystals. The compound forms large, deep copper-red, rectangular tablets from acetic acid, the crystals yielding a purplish-black powder. In a sealed tube the powder changes near 155° C. and then melts at 168° C. to a deep greenish-black liquid. The solution in sulphuric acid is olive-green, becoming violet on dilution or warming (reversible change). The product is stable in moist air for only a few hours, then being gradually hydroxylated with loss of colour. Treatment with cold water decomposes the substance quantitatively into sulphuric acid, phenoxselenine and phenoxselenine oxide.

DERIVATIVES OF DIPHENYLAMINE.[1]

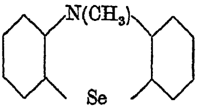
Selenodiphenylamine,



Equivalent quantities of diphenylamine and selenium chloride ($SeCl_2$) are dissolved in cold benzene. A violent evolution of hydrogen chloride occurs, and a brown mass separates. The benzene is distilled off, and unchanged diphenylamine removed by steam distillation. The residue may be recrystallised from benzene containing charcoal, or better distilled under reduced pressure. An oil is isolated in the latter case in 40 per cent. yield, producing yellow plates on solidification. Recrystallisation from benzene gives small pale yellow plates, or prisms from alcohol, M.pt. 195° C. These become green in air, owing to oxidation. The compound is moderately soluble in acetic acid or boiling alcohol, sparingly soluble in cold alcohol or ether. The following equation represents the reaction :

$$SeCl_2 + (C_6H_5)_2NH = NH(C_6H_4)_2Se + 2HCl$$

Methylselenodiphenylamine,



5 grams of selenodiphenylamine, 2·5 c.c. of methyl iodide and 10 c.c. of methyl alcohol are heated together in a sealed tube for seven hours at 120° C. The melt is recrystallised from alcohol containing charcoal, intense sea-green needles separating. Repeated crystallisation yields pure white needles, M.pt. 138° to 139° C., very soluble in hot alcohol, hot acetic acid or benzene, sparingly soluble in cold alcohol. Solutions in cold concentrated sulphuric acid are reddish, becoming brownish-red on warming. Alcoholic solutions with ferric chloride give a sea-green coloration if dilute, grass-green if concentrated. Bromine vapour gives a blue-green coloration.

Acetylselenodiphenylamine, $CH_3.CO.N(C_6H_4)_2Se$, occurs when selenodiphenylamine is refluxed with acetic anhydride. It forms

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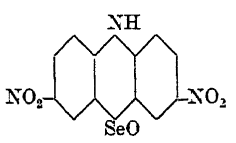
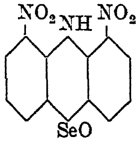
[1] Cornelius, *J. prakt. Chem.*, 1913, [ii], 88, 395.

shining prismatic crystals, M.pt. 176° C., soluble in hot alcohol, boiling acetic acid or benzene.

The Nitration of Selenodiphenylamine.—Selenodiphenylamine is slowly added to 15–20 times its weight of nitric acid (density 1·49), the mixture being maintained below 0° C. Yellowish-brown crystals separate, which consist principally of *a-compound*, a second *β-isomeride* remaining in the mother-liquor. The former isomer is insoluble in alcohol and the latter soluble, this fact being made use of in the separation of the bodies. The *a*-compound is obtained as small yellowish-brown needles, sparingly soluble in the usual solvents, soluble in boiling aniline. In cold concentrated sulphuric acid it yields a moss-green solution, which becomes brown on warming, blue on boiling, violet on dilution with water, and carmine-red on dilution with alkali. From aqueous solution *silver* and *mercury salts* are obtained as white precipitates, the silver salt giving a rose-red solution in pyridine. The β-isomer is a reddish-brown crystalline mass, soluble in concentrated sulphuric acid. The following formulæ are suggested for these compounds :

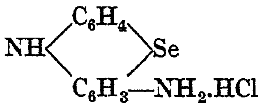


a



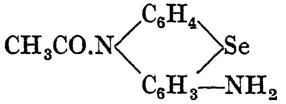
β

Aminoselenodiphenylamine and **Imidoselenodiphenylamine** (Formulæ below).—30 grams of finely powdered selenodiphenylamine are added to a well-cooled mixture of 75 c.c. of nitric acid (density 1·4) and 75 c.c. of water, and when the action is complete water is added to precipitate the nitro-compound. The latter is boiled with tin and hydrochloric acid for one to two hours, and from the yellowish-brown solution white glistening needles separate. These consist of a double salt of the monoamino-compound, the filtrate containing the readily soluble diamino-compound. The double salt is dissolved in dilute hydrochloric acid and reprecipitated by the addition of zinc, the white needles which separate soon becoming grey-brown. The product is soluble in water and the solution becomes bright violet with ferric chloride. The free amine is isolated by decomposing the salt with excess of sodium hydroxide and extracting with benzene, a rose solution resulting. Treatment of this with hydrogen chloride yields white needles of the *hydrochloride*,



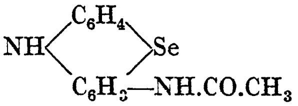
$$\mathrm{NH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_3{-}NH_2.HCl}\end{matrix}{>}\mathrm{Se}$$

these soon becoming a dirty blue and dissolving in water to give a reddish-blue solution. The hydrochloride in aqueous solution gives the base on addition of ammonium hydroxide, recrystallisation from alcoholic ammonium sulphide yielding small, pearly plates, which soon become greyish-blue. If the base or hydrochloride be refluxed with acetic anhydride and sodium acetate, addition of water causes the separation of an acetyl compound. This crystallises from alcohol as small white crystals, decomposing with frothing at 330° C., and dissolving in cold sulphuric acid to give a rose-coloured solution which becomes green on boiling. This *acetyl compound* may be represented as



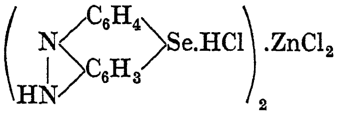
$$CH_3CO.N{<}\begin{array}{c}C_6H_4\\ C_6H_3{-}NH_2\end{array}{>}Se$$

or



$$NH{<}\begin{array}{c}C_6H_4\\ C_6H_3{-}NH.CO.CH_3\end{array}{>}Se$$

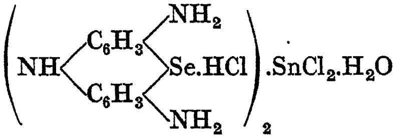
To obtain the dye, the hydrochloride or double salt is dissolved in dilute hydrochloric acid, ferric chloride added and the dyestuff precipitated by common salt and zinc chloride. The bluish-bronze, glistening precipitate so obtained after washing with saturated sodium chloride solution is dissolved in hot water and concentrated zinc chloride solution added. The *zinc chloride double salt* separates as hair-fine bronze needles, readily soluble in water or alcohol, the solutions being blue when very dilute. In concentrated sulphuric acid the solution is green, becoming blue on dilution with water or red on dilution with alkali; in concentrated hydrochloric acid the solution is sea-green. The following formula is assigned to the *double salt*:



$$\left(\begin{array}{l}N\\ |\\ HN\end{array}{<}\begin{array}{c}C_6H_4\\ C_6H_3\end{array}{>}Se.HCl\right)_2.ZnCl_2$$

The *free base* is isolated by dissolving the double salt in alcohol, adding alkali and precipitating by water. A reddish-bronze powder is obtained, dissolving in alcohol to give a ruby-red solution, but sparingly soluble in ether. The *hydrochloride* is precipitated as Bordeaux-red flocks when hydrogen chloride is passed into an ether solution of the base.

α-Diaminoselenodiphenylamine.—5 grams of α-dinitroselenodiphenylamine are warmed with a mixture of 25 grams of stannous chloride in 35 grams of hydrochloric acid (30 per cent.), 15 grams of tin and 100 c.c. of water. The colour changes from red to brownish-yellow as the reaction proceeds. After filtering and cooling, fine, glistening, yellowish-brown needles of the *tin chloride double salt* separate, containing 1 molecule of water:

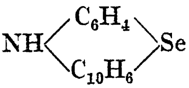


$$\left(NH{<}\begin{array}{c}C_6H_3{<}NH_2\\ C_6H_3{<}NH_2\end{array}{>}Se.HCl\right)_2.SnCl_2.H_2O$$

This double salt is oxidised by ferric chloride solution to Selenonine, this dyestuff being the analogue of Lauth's Violet. The dyestuff forms deep blue solutions, which become turquoise blue on boiling. The *zinc double salt* is prepared by adding zinc to an aqueous solution of the stannous salt. In alcohol or water it gives blue solutions, and in concentrated hydrochloric acid greenish-blue. Aqueous solutions of the salts yield the *free base* on treatment with sodium hydroxide, this separating from its ruby-red solution in alcohol as small needles. The *hydrochloride* consists of fine, long, greenish-bronze needles, occurring when the base is dissolved in hot hydrochloric acid.

The analogue of Methylene Blue is prepared by the action of hydrogen selenide on nitrosodimethylaniline and subsequent oxidation by ferric chloride in very dilute hydrochloric acid solution.

Selenophenyl-β-naphthylamine,



This occurs when equimolecular quantities of selenium chloride ($SeCl_2$) and phenyl-β-naphthylamine are condensed in benzene solution. It crystallises as small, yellow, bushy needles, M.pt. 176° C., readily soluble in boiling benzene or boiling alcohol, sparingly soluble in cold acetic acid.

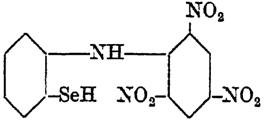
Selenodi-α-naphthylamine, $NH(C_{10}H_6)_2Se$, forms small, yellowish needles, M.pt. 176° to 177° C., readily soluble in benzene or alcohol, less soluble in aniline or nitrobenzene. Its solution in concentrated sulphuric acid is greenish-blue, and ferric chloride in alcoholic solution gives an emerald-green coloration.

Selenodi-β-naphthylamine separates from benzene as yellowish-green, matted needles, M.pt. 245° C., from nitrobenzene as greenish prisms, and from alcohol in tablets. Its concentrated sulphuric acid solution is blue-green. Addition of ferric chloride to its alcoholic solution gives a moss-green coloration. Nitric acid yields a yellow nitro-compound.

Selenodi-p-tolylamine, $NH(C_6H_3.CH_3)_2Se$, crystallises from benzene in glistening scales, melting at 240° C. to a green oil. It dissolves in concentrated sulphuric acid, forming carmine-red to reddish-violet solutions.

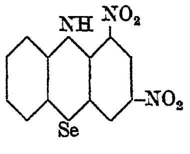
SELENAZINE DYESTUFFS.[1]

o-Picrylaminophenylselenol,



25 grams of picryl chloride in 500 c.c. of hot alcohol are treated with 21 grams of the zinc salt of *o*-aminoselenophenol (*o*-aminophenyl selenide) and 100 c.c. of 50 per cent. alcohol. The mixture becomes orange; it is heated for about 1·5 hours, then filtered and the residue washed with alcohol. Yield, 33 grams. The product is a reddish-brown powder, sparingly soluble in the usual organic solvents, insoluble in water, but giving a brown solution in alkalis.

3 : 5-Dinitrophenselenazine,



The foregoing compound (19·2 grams) in 450 c.c. of alcohol is treated with 10 c.c. of 10*N* sodium hydroxide and the mixture warmed on the

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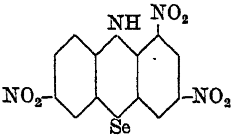
[1] Bauer, *Ber.*, 1914, 47, 1873; compare German Patent, 261969.

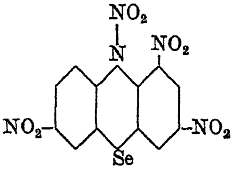
water-bath for two to three hours, when the solution becomes violet and dark crystals separate out. When the reaction is complete the product is filtered off, washed with alcohol, then with water. Yield, 6 to 8 grams. It forms microscopic red-brown prisms, M.pt. 195° to 196° C., sparingly soluble in alcohol, benzene or acetic acid, giving dark red solutions. When suspended in alcohol and treated with sodium hydroxide, the *sodium salt* is formed, which is intense violet in colour.

3 : 5 : 9-Trinitrophenselenazine,



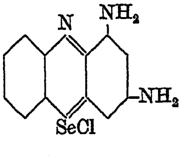
The foregoing dinitro-compound is nitrated in acetic acid solution with nitric acid of density 1·4 at the ordinary temperature. It forms opaque prisms, melting indefinitely at 220° to 223° C., sparingly soluble in alcohol, easily soluble in benzene or acetic acid. With sodium hydroxide its suspension in alcohol gives the pure blue colour of the *sodium salt*. The same result is obtained by treating a nitric-acetic acid solution of the dinitro-compound with sodium nitrite.

3 : 5 : 9-Trinitrophenselenazine nitroamine,



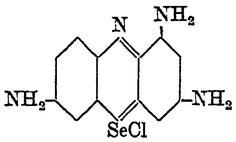
is produced instead of the foregoing body when an excess of nitric acid is used. It is a red amorphous powder, M.pt. 182° C. after previously sintering, readily soluble in benzene or acetic acid, less soluble in alcohol.

3 : 5-Diaminophenazselenium chloride,



The foregoing dinitro-compound, 3·4 grams, is moistened with alcohol, treated with 15 c.c. of hydrochloric acid (dens. 1·19) and 15 grams of stannous chloride stirred in, the temperature being kept below 30° C. or hydrogen selenide is evolved. The nitro-compound dissolves and the *stannous chloride double salt* of the diamine separates out. This is allowed to stand overnight, washed with hydrochloric acid (dens. 1·19), dissolved in water and the tin precipitated by hydrogen sulphide. The latter is removed from the filtrate by blowing air through, this being maintained until a test portion gives no further deepening of the brown-green colour when treated with ferric chloride. The dye crystallises out in needles and is purified by solution in water and precipitation by dilute hydrochloric acid. It forms long, dark green needles, which give a green-brown solution in water. The air-dried product contains three molecules of water of crystallisation, which may be removed *in vacuo* over sulphuric acid, the anhydrous dyestuff taking up water from the air. From its aqueous solution the dye may be precipitated by sodium chloride or hydrochloric acid. Sodium hydroxide precipitates the base as red flocks, which dissolve in ether giving an orange solution, but sodium carbonate only partially precipitates the dyestuff. In concentrated sulphuric acid the dyestuff is brown, traces of water changing this to pure green, and the further addition of water turning the solution brown again. This dyestuff dyes cotton mordanted with tannic acid brown-olive. The *nitrate, dichromate* and *chloroplatinate* are only sparingly soluble.

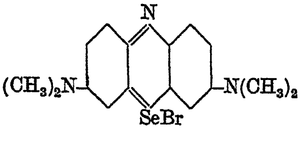
3 : 5 : 9-Triaminophenazselenium chloride,



This is formed by reduction of the trinitroselenazine by a similar process to that used for the foregoing dinitro-compound. The air-dried substance contains 1·5 molecules of water, which can be removed *in vacuo*. It crystallises from hot water as green, metallic, glistening needles. The dry dyestuff is very hygroscopic and quickly absorbs a molecule of water. It is sparingly soluble in cold water, but readily soluble in hot water, giving a violet solution. Sodium hydroxide precipitates the base as red-brown flocks, sparingly soluble in ether. In concentrated sulphuric acid the base is dark blue, a little water changing the colour to brownish-green, further water giving a violet colour and finally precipitating the dye. In its other reactions this compound resembles the diamino-derivative. It dyes cotton mordanted with tannic acid a bright violet.

SELENOMETHYLENE BLUE.[1]

The *bromide* of this derivative has the constitution



and may be isolated in the following manner: 2 grams of selenodiphenylamine are dissolved in 100 c.c. of warm acetic acid and after rapidly cooling to the ordinary temperature, 5 per cent. bromine in acetic acid is added until phenazselenium perbromide is completely precipitated as shimmering brown flakes. This is filtered off and washed with dry ether The product is then treated with 50 c.c. of 96 per cent. alcohol and triturated with a 5 per cent. alcoholic dimethylamine solution until a pure blue colour persists. After ten minutes the solution is filtered and ether added to the filtrate; this causes the separation of the bromide of selenomethylene blue (*3 : 9-tetramethyldiaminophenazselenium bromide*).

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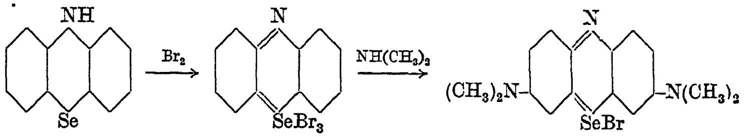
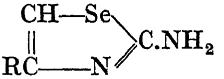
[1] Karrer, *Ber.*, 1918, 51, 190.

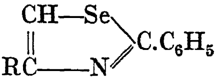
The product is removed, washed with ether and recrystallised from a little boiling water, shimmering needles with a metallic green reflex being obtained. The compound possesses the same stability and tinctorial properties as Methylene Blue.[1] The course of the reaction may be represented thus :



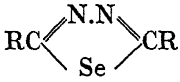
SELENAZOLES.

These compounds were first prepared by Hofmann[2] by the interaction of halogenated ketones and selenourea or selenobenzamide, the resulting products having the constitutions

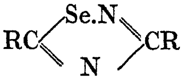




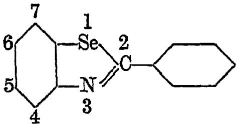
Selenodiazoles are prepared by the interaction of *sym.*-diacetyl- or dibenzoyl-hydrazines and phosphorus pentaselenide, or by treating arylselenamides with iodine in alcohol solution. The formulæ proposed for these compounds are



or



The analogy between sulphur and selenium derivatives would make it reasonable to suppose that the method of preparing phenylbenzthiazole, namely by heating benzanilide with sulphur, would be applicable to the formation of phenylbenzoselenazole. The yield, however, by this method is not good, a better result being obtained by heating together benzalaniline and finely powdered selenium. The 2-phenylbenzoselenazole,



which is obtained, may be nitrated, the nitro-group usually entering at position 6. From the nitro-compound the amino-, cyano- and carboxy-derivatives may be isolated. Nitration at a higher temperature gives a dinitro-compound, but the position of the second nitro-group does not appear to be known. When condensed with benzaldehyde, the amino-derivative gives 6-benzalamino-2-phenylbenzoselenazole. This product forms the starting point for obtaining the benzo-*bis*-selenazoles, which occur when the 6-benzalamino-compound is heated

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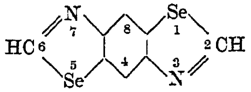
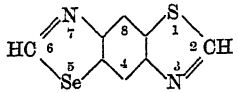
[1] Compare German Patents, 261793, 280713; Cornelius, *J. prakt. Chem.*, 1913, [2], 88, 395.

[2] Hofmann, *Annalen*, 1889, 250, 294.

with selenium. Their structure is embodied in the following ring system :



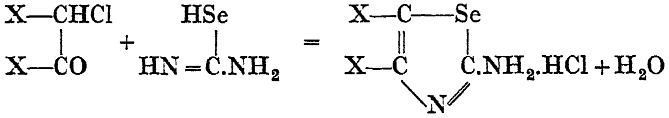
If the selenium in the foregoing reaction is replaced by sulphur, selenazolobenzothiazoles result,



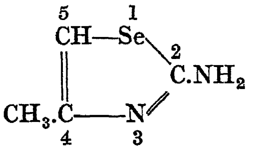
If it is desired to obtain nitro-derivatives of 2-phenylbenzoselenazole in which the phenyl group in position 2 is nitrated, it is necessary that this nitro-group be present before condensation; *e.g.* the zinc salt of *o*-aminophenyl selenide and *p*-nitrobenzoyl chloride when fused at 100° C. for an hour yield 2-(*p*-nitrophenyl)-benzoselenazole.

Condensation Products from Selenourea.[1]

Selenourea condenses with halogenated ketones to yield selenazoles according to the equation



2-Amino-4-methylselenazole,



The *hydrochloride* of this selenazole is readily obtained by gently warming together molecular quantities of selenourea and chloroacetone. The mass is dissolved in hot water and the solution filtered and concentrated, shining centimetre-long prisms of the hydrochloride separating. To a concentrated solution of this salt, concentrated potassium hydroxide solution is added until the mixture is strongly alkaline, oily drops separating, which are extracted with ether. Evaporation of the solvent leaves a yellow mass, soluble in alcohol, ether and benzene. A solution in the last-named solvent yields shining needles of the selenazole on the addition of ligroin. The product melts at 79° to 80° C., and is a strong base, forming good crystalline salts with mineral acids. The *platinichloride*, $(C_4H_7N_2SeCl)_2.PtCl_4$, is orange-red and shows decomposition on recrystallisation. The *acetyl compound* of the selenazole forms shining needles, M.pt. 122° C.

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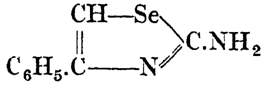
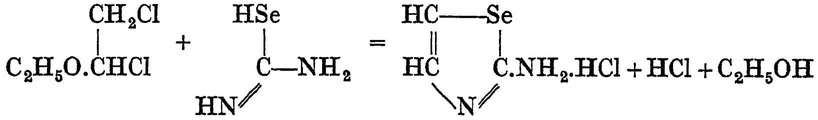
[1] Hofmann, *loc. cit.*

2-Amino-4-phenylselenazole,



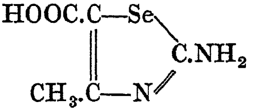
is the condensation product of selenourea and bromoacetophenone. This gives the *hydrobromide*, consisting of glistening yellow plates sparingly soluble in cold water, readily soluble in hot water. The *free base* is liberated by means of potassium hydroxide and crystallises in fine needles, M.pt. 132° C., insoluble in water but dissolving in acids to form sparingly soluble salts, *e.g.* the *platinichloride*, an insoluble red precipitate. This selenazole shows practically a neutral reaction in solution.

The condensation between selenourea and dichloroether occurs as follows :



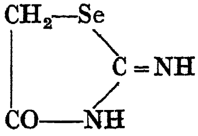
2-Aminoselenazole is prepared according to the above equation, the reaction mixture being treated directly with potassium hydroxide and extracted with ether. Removal of the solvent and recrystallisation of the residue from benzene gives shining white needles, M.pt. 191° C., readily soluble in ether or alcohol, moderately soluble in benzene or water, solutions in water having a strongly alkaline reaction. When boiled with water the selenazole is completely decomposed. The *platinichloride* is an orange-red precipitate, somewhat soluble in water but decomposing on attempted recrystallisation. The *acetyl derivative* crystallises from much hot water or alcohol as needles, melting with decomposition towards 210° C.

2-Amino-4-methyl-5-carboxyselenazole,



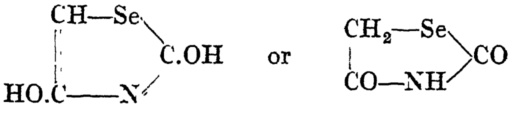
is prepared from selenourea and chloracetoacetic ester. The *hydrochloride* forms spear-like plates, readily soluble in water, the solution having an acid reaction. The base crystallises in fine needles, M.pt. 195° C. with decomposition. Air-dried specimens of the base contain two molecules of water, which are removed at 110° to 120° C. The selenazole readily dissolves in alcohol or ether, but is sparingly soluble in water. It has a feebly acid reaction, but does not decompose carbonates. The *acetyl derivative* forms small needles, melting with decomposition at 220° C., soluble in hot water, sparingly soluble in alcohol.

Selenohydantöin,

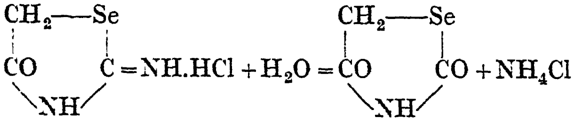


occurs when selenourea is condensed with chloracetic acid in boiling alcohol solution. The *hydrochloride* separates from the solution on cooling as shining needles. These are decomposed in the usual way, and the base melts at 190° C. with decomposition. It is somewhat soluble in hot water, sparingly soluble in cold water or alcohol, insoluble in ether. With acids it yields crystalline salts, and platinic chloride gives an orange-yellow precipitate. It turns red litmus blue.

If the selenohydantöin be heated with water, or the alcohol be omitted from the above condensation, *2 : 4-dihydroxyselenazole* is produced,



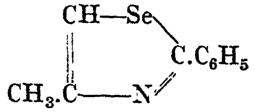
The preparation of this body from selenohydantöin may be represented as follows :



2 : 4-Dihydroxyselenazole crystallises in centimetre-long prisms, M.pt. 147° C., readily soluble in alcohol, moderately soluble in water forming supersaturated solutions. It sublimes at 100° C., and is feebly acid towards litmus, showing some phenolic properties. It does not form salts with acids.

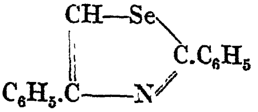
Condensation Products from Selenobenzamide.[1]

2-Phenyl-4-methylselenazole,



is produced by the condensation of selenobenzamide and chloroacetone in the presence of alcohol. It is a thin oil, distilling without decomposition at 282° to 283° C. and 737 mm. In water it dissolves sparingly, and the solution shows no alkaline reaction. With concentrated acids it forms easily soluble crystalline salts. The *platinichloride* separates as pale yellow needles, somewhat soluble in water.

2 : 4-Diphenylselenazole,



occurs as *hydrobromide* when selenobenzamide reacts with bromoacetophenone in alcohol. Addition of water precipitates the *base*, which crystallises from alcohol in plates, M.pt. 99° C., readily soluble

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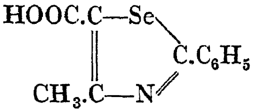
[1] Hofmann, *loc. cit.*

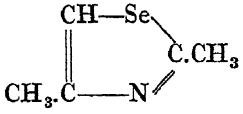
in ether or benzene. It is such a feeble base that it may be recovered unchanged from its solution in acids by evaporation.

2-Phenyl-4-methyl-5-carboxyselenazole,



is obtained as ethyl ester from selenobenzamide and chloracetoacetic ester. The crude product is dissolved in alcohol and warmed with sodium hydroxide. After removal of the alcohol the solution is faintly acidified with hydrochloric acid, when the acid separates as an amorphous powder. Recrystallisation from benzene yields small needles, M.pt. 206° to 207° C., commencing to sublime towards 130° C. The compound is somewhat soluble in alcohol, sparingly soluble in ether or water. Its alcohol solutions have an acid reaction; the selenazole is soluble in acids and in carbonates, forming crystalline salts with both. With salts of mercury, silver and lead it gives white precipitates, with copper salts a blue-green precipitate, with cobalt salts a rose-red precipitate, and with ferric salts a buff precipitate. The *ethyl ester* is precipitated by ligroin from its benzene solution as microscopic plates, M.pt. 123° to 124° C.

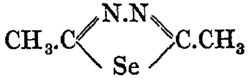
2 : 4-Dimethylselenazole,



is said to be formed when hydrogen selenide is passed into a mixture of chloroacetone and acetonitrile, but no analysis is given in the literature.

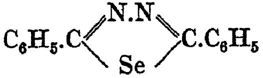
Selenodiazoles.

Dimethylselenodiazole,[1]



This product is obtained when 10 grams of *sym.*-diacetylhydrazine are heated with 30 grams of phosphorus pentaselenide, the yield being about 11 per cent. It melts at 77° C., boils at 121° C. at 23 mm., and is a crystalline mass, readily soluble in alcohol, ether or water. The solution in concentrated sulphuric acid is green. *Silver nitrate* in alcohol solution gives an additive compound, $C_4H_6N_2Se.AgNO_3$. In the foregoing preparation a 45 per cent. yield of dimethylfurodiazole occurs as by-product.

Diphenylselenodiazole,



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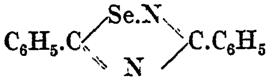
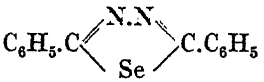
[1] Stollé and Gutmann, *J. prakt. Chem.*, 1904, [ii], 69, 509.

is prepared from *sym.*-dibenzoylhydrazine and phosphorus pentaselenide, the mixture being heated *in vacuo* at 250° C. The reaction product is digested with dilute sodium hydroxide solution to remove phosphoric acid and excess phosphorus pentaselenide, the residue consisting of diphenylselenodiazole and diphenylfurodiazole. The latter is removed by alcoholic silver nitrate, with which it forms an additive compound. Filtration and treatment with water precipitates the seleno-compound. It crystallises in glistening scales from alcohol, M.pt. 156° C., readily soluble in ether, does not react with dilute acids, alkalis or ammoniacal silver nitrate, and is insoluble in water.

3 : 5-Diphenyl-1 : 2 : 4-selenodiazole, or *Dibenzenylazoselenime*,[1]

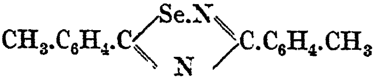


When benzonitrile in the presence of a small quantity of alcoholic ammonia is treated with hydrogen selenide it is converted into benzoselenamide, $C_6H_5.CSe.NH_2$.[2] This is transformed to the diazole by iodine in alcohol solution. White, silky needles are obtained, M.pt. 85° C., which yield a *platinichloride*, $(C_{14}H_{10}N_2Se)_2.H_2PtCl_6$, golden-yellow crystals. Reduction of the base with alcoholic sodium amalgam gives benzylamine, but with zinc and hydrochloric acid only ill-defined products result. On this account the compound appears to be similar to the dibenzenylazoximes and dibenzenylazosulphimes, and therefore the alternative formula



seems less probable than the formula given above.

3 : 5-Di-p-tolyl-1 : 2 : 4-selenodiazole or *Di-p-methyldibenzenylazoselenime*,



p-Toluic selenamide, $C_6H_4(CH_3).CSe.NH_2$, M.pt. 161° C., obtained from toluonitrile and hydrogen selenide in concentrated ammoniacal alcoholic solution, is converted by iodine into this diazole. The diazole crystallises from alcohol as white needles, M.pt. 116° C., and forms a *platinichloride*, $(C_{16}H_{14}N_2Se)_2.H_2PtCl_6$. Reduction of the base by alcoholic sodium amalgam yields *p*-tolylmethylamine, whilst zinc and hydrochloric acid give a substance which is probably *tolenylamidine*, $CH_3.C_6H_4.C(NH_2){=}N.CH_2.C_6H_4.CH_3$.

Hydrogen selenide does not combine with aliphatic nitriles, thioacetamide, thiobenzamide or benzyl cyanide.

o-Aminobenzoselenamide,[3] $NH_2.C_6H_4.CSe.NH_2$.—A solution of anthranilonitrile in absolute alcohol is saturated at 0° C. with hydrogen selenide and dry ammonia and heated in a sealed tube for ten hours at 105° to 110° C. The mixture is then concentrated and the crystals

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[1] Becker and Meyer, *Ber.*, 1904, 37, 2550.

[2] Dechend, *Ber.*, 1875, 8, 270.

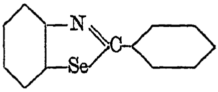
[3] Bogert and Chen, *J. Amer. Chem. Soc.*, 1922, 44, 2352.

obtained recrystallised from water. The yield is poor, the product melts at 116° C. (corr.), and is rather unstable.

2-Methyl-4-selenoquinazolone, $\overline{NH.CSe.C_6H_4.N = C}.CH_3$.—20 grams of acetyl anthranilonitrile dissolved in absolute alcohol are treated with dry hydrogen selenide, the mixture raised to 60° C., and dry ammonia passed in for three hours. The product obtained on cooling is recrystallised from dilute alcohol, a yield of about 10 per cent. being obtained. Several other processes have been developed using anthranilonitrile as the starting material, but the yield has never exceeded 25 per cent. The quinazolone separates from dilute alcohol as brownish needles or prisms, M.pt. 213·5° C. (corr.), sparingly soluble in benzene or chloroform, insoluble in water. From its solution in aqueous alkalis it is reprecipitated by carbon dioxide. Air and light cause it to decompose slowly, finely divided selenium separating and 2-methyl-4-quinazoline being formed.

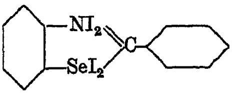
Benzoselenazoles.

2-Phenylbenzoselenazole,



This may be obtained as follows: (1) By the interaction of *o*-aminoselenophenylmercaptan (*o*-aminophenyl selenide) and benzoyl chloride.[1] (2) Selenium and benzanilide are boiled together briskly for several hours, aniline and benzoic acid removed in steam, the residue boiled with concentrated hydrochloric acid and the solution treated with sodium hydroxide. The precipitate is recrystallised from alcohol or acetic acid, a 15 to 20 per cent. yield of colourless needles, M.pt. 117° C., being isolated.[2] (3) Benzaldehyde, 106 grams, and 93 grams of aniline, both freshly distilled, are heated together at 120° C. for about two hours, until all the water has been driven off and a clear melt of benzalaniline obtained (yield, theoretical). This melt is poured upon 160 grams of selenium dust in a flask connected with an air condenser and the mixture gently boiled for three days on a sand-bath, some hydrogen selenide being evolved during the reaction. After cooling, the melt is extracted with hot concentrated hydrochloric acid, the acid solution filtered through glass wool and poured into a large volume of cold water. The precipitated product is recrystallised from alcohol, long, colourless needles being obtained, M.pt. 117·5° C. (corr.), yield 60 per cent.[3]

The body is insoluble in water, sparingly soluble in cold methyl alcohol, ether, acetone, chloroform, acetic acid, acetic anhydride or carbon tetrachloride, but more soluble on heating; it readily sublimes, and has a faint agreeable odour. When boiled with iodine in chloroform solution it forms a *tetra-iodide*,



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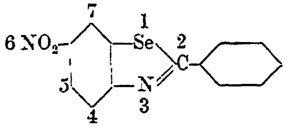
[1] Bauer, *Ber.*, 1913, 46, 92.
[2] Fromm and Martin, *Annalen*, 1913, 401, 177.
[3] Bogert and Chen, *J. Amer. Chem. Soc.*, 1922, 44, 2352.

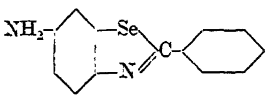
consisting of greenish-black crystals, M.pt. 84° C. The halogen may be removed by caustic alkali or alkali carbonate solution. The corresponding *tetrabromide* is a brick-red powder, M.pt. 134° C., from which the bromine may be quantitatively removed by sodium carbonate.

6-Nitro-2-phenylbenzoselenazole,[1]



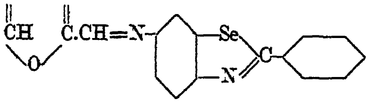
occurs when the preceding selenazole is nitrated below 0° C. using "mixed acid." After standing for four hours at 0° C. the mixture is poured into two litres of ice-water. The precipitate is removed, recrystallised from acetic acid and then from *n*-butyl alcohol containing charcoal, a 95 per cent. yield being obtained. It separates as pale yellow needles, M.pt. 202·4° C., insoluble in water, sparingly soluble in cold organic solvents, more soluble on heating.

6-Amino-2-phenylbenzoselenazole,



is obtained in 75 per cent. yield when the nitro-compound is reduced by tin and hydrochloric acid. It crystallises from alcohol as fine, glistening needles, M.pt. 201·2° to 202·3° C., having a similar solubility to the nitro-derivative. When fused with potassium hydroxide, benzoic acid is obtained, which indicates that the amino-group is not present in the 2-phenyl nucleus. The amino-compound forms an *acetyl derivative*, consisting of colourless crystals, M.pt. 188·1° to 188·7° C. Condensation with benzaldehyde gives the *6-benzalamino-compound*, yellow plates, M.pt. 157° C. (corr.). When the amine is diazotised and coupled with β-naphthol in alkaline solution it yields *2-phenylbenzoselenazole-azo-β-naphthol*, a deep red powder having a metallic lustre, melting at 284·2° C., and dyeing silk a fine pink.

6-Furfurylideneamino-2-phenylbenzoselenazole,



This is the condensation product of furfuraldehyde (excess) and 6-amino-2-phenylbenzoselenazole. The yield is 57 per cent., and the compound forms glistening yellow needles, M.pt. 147·5° C. (corr.), soluble in alcohol, carbon tetrachloride, acetone, ethyl acetate or benzene.

Dinitro-2-phenylbenzoselenazole, $C_{13}H_7(NO_2)_2NSe$.—A solution of 2-phenylbenzoselenazole (25 grams) in 150 c.c. of concentrated sulphuric acid prepared at 5° to 10° C. is cooled below 0° C. and a well-cooled mixture of 9·5 grams of concentrated nitric acid and 15 grams of concentrated sulphuric acid added very slowly with mechanical stirring. After stirring for two hours below 0° C., a similar quantity of " mixed

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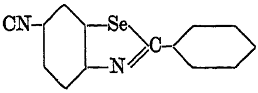
[1] Bogert and Chen, *loc. cit.*

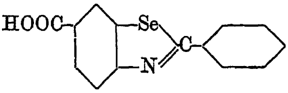
acid" is again added gradually, and the mixture then heated for two hours at 100° C. The cooled solution is poured into two litres of ice-water, filtered and the solid recrystallised from acetic acid. An 80 per cent. yield of fine, pale yellow needles, M.pt. 246·8° C., is obtained. The nitro-groups are probably in the 4 and 6 positions. The solubility is similar to that of the mononitro-compound. Reduction by tin and hydrochloric acid gives the *diamino-compound*. The product is crystallised from alcohol and then from pyridine, when colourless needles result, M.pt. 269° to 270·5° C. The diamine yields a *diacetyl derivative*, consisting of cubes from dilute alcohol, M.pt. 239·5° to 240·5° C., a *dibenzal compound*, lustrous yellow plates from carbon disulphide, M.pt. 186° to 187° C., and when diazotised and coupled, dyes are obtained.

2-Phenyl-6-cyanobenzoselenazole,[1]



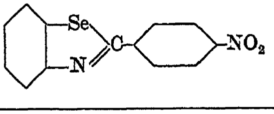
This has been obtained from the corresponding 6-amino-derivative by the Sandmeyer reaction. 10 grams of amine yielded about 12 grams of crude nitrile as a brownish powder, which decomposed at 145° to 150° C. with previous sintering, and could not be crystallised. Repeated solution in alcohol and reprecipitation with water changed it to a pale yellowish coarse powder, soluble in hot ethyl or *n*-butyl alcohol, acetone, carbon tetrachloride or benzene.

2-Phenyl-6-carboxybenzoselenazole,



occurs when 12 grams of the foregoing nitrile are boiled for twenty-two hours under reflux with a mixture of 50 c.c. of concentrated sulphuric acid and 25 c.c. of water. The solution is cooled, 100 c.c. of water added, the precipitate collected, washed with water, suspended in warm normal potassium hydroxide solution and the liquid again filtered. The clear filtrate is acidified with hydrochloric acid, which precipitates the selenazole acid. This is removed, washed and dried; yield, 4·9 grams or 36 per cent. It is a pale brownish-yellow powder, purified by solution in alkali and reprecipitation by acid. It decomposes at 170° to 180° C., is sparingly soluble in water, more soluble in hot alcohol, ethyl acetate, acetone or benzene. The *methyl ester* is obtainable as glistening, pale yellowish flakes, M.pt. 164·5° to 165·5° C. (corr.), the yield being about 10 per cent. The *potassium salt* of the acid is a fine, granular precipitate, soluble in alcohol or water (approximately 1 per cent.).

2-(p-Nitrophenyl)-benzoselenazole,[2]



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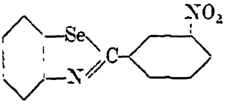
[1] Bogert and Hopkins, *J. Amer. Chem. Soc.*, 1924, 46, 1700.
[2] Bogert and Stull, *J. Amer. Chem. Soc.*, 1927, 49, 2011.

An intimate mixture consisting of 1 molecular equivalent of the zinc salt of *o*-aminophenyl selenide and 2 equivalents of *p*-nitrobenzoyl chloride is fused for an hour at 100° C. The cooled melt is then pulverised and washed successively with water and sodium carbonate solution. Repeated crystallisation from glacial acetic acid gives pale yellow lustrous needles, M.pt. 211° C. (corr.).

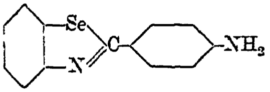
2-(m-Nitrophenyl)-benzoselenazole,



obtained in the same way as the *p*-isomer, separates from 95 per cent. alcohol as short needles, paler than the foregoing compound, and melting at 148° C. (corr.).

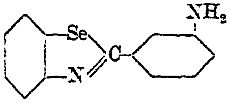
2-(o-Nitrophenyl)-benzoselenazole has not been isolated in a pure state.

2-(p-Aminophenyl)-benzoselenazole,



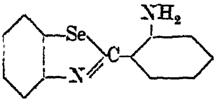
A mixture of 2 grams of the corresponding nitro-derivative, 10 c.c. of concentrated hydrochloric acid, 90 c.c. of water and 10 grams of granulated tin is boiled for three hours. The hot filtrate from the excess of tin is stirred gradually into an excess of 4N sodium hydroxide solution, which precipitates the amine. The mixture is cooled and filtered after being kept warm for a few hours. The crude amine is decolorised and crystallised from 50 per cent. alcohol, pale yellow glassy needles separating out, M.pt. 156° C. (corr.). These dissolve in alcohol, exhibiting a light violet fluorescence.

2-(m-Aminophenyl)-benzoselenazole,



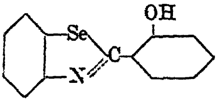
is prepared in a similar manner to the foregoing compound. The crystals, M.pt. 159·5° C. (corr.), are deeper in colour than those of the *p*-isomer, and dissolve in alcohol without fluorescence.

2-(o-Aminophenyl)-benzoselenazole,



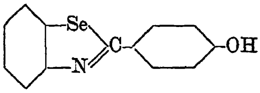
The crude *o*-nitro-compound is reduced in the usual manner and the product recrystallised from 75 per cent. alcohol. The amine melts at 142·5° C. (corr.), and forms minute pale greenish-yellow lustrous scales, which do not exhibit fluorescence in alcohol solution.

2-(o-Hydroxyphenyl)-benzoselenazole,



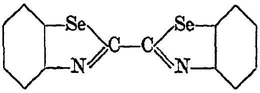
A mixture containing 1 gram of the zinc salt of *o*-aminophenyl selenide and 1 gram of salicyl aldehyde in 125 c.c. of glacial acetic acid is boiled for one hour, when a clear, dark brown solution results. After standing overnight at room temperature, the solution deposits a small amount of zinc acetate and some metallic selenium. The filtrate from this deposit is diluted with three volumes of water and the ensuing precipitate rapidly recrystallised from 50 per cent. alcohol (yield, 23 per cent.). The product forms fine, transparent needles, of a pale yellowish tinge, soluble in sodium hydroxide solution but not in sodium carbonate, and giving no colour reaction with ferric chloride either in aqueous or in alcoholic solution.

2-(p-Hydroxyphenyl)-benzoselenazole,



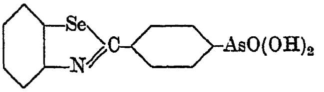
is obtained in a similar manner to the foregoing compound; yield, 46 per cent. It forms colourless, glassy needles.

2 : 2′-Bisbenzoselenazolyl,



occurs when equimolecular proportions of the zinc salt of *o*-aminophenyl selenide and oxalyl chloride are heated together under reflux for thirty minutes at 70° to 80° C. The cooled and pulverised product is warmed with an excess of normal sodium hydroxide solution and the insoluble material heated in a porcelain dish. A sublimate is formed which crystallises from toluene as colourless, glistening scales, M.pt. 314° C. (corr.), which gradually turn brown on standing in the light and air.

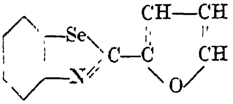
2-Phenylbenzoselenazole-4′-arsinic acid,



1 gram of 2-(*p*-aminophenyl)-benzoselenazole is diazotised and the solution added to an ice-cold solution prepared from 5 grams of potassium arsenite, 50 c.c. of water, 12 c.c. of normal sodium carbonate solution and 1 to 2 grams of copper-bronze powder. The mixture is shaken from time to time and tested periodically with litmus to make sure of its alkalinity. After standing for one hour at room temperature it is heated at 100° C. until frothing ceases. The alkaline solution is then filtered warm and the insoluble material washed with a little warm sodium carbonate solution. The combined greenish filtrate and washings are acidified with concentrated hydrochloric acid, the pale yellow flocculent precipitate removed, washed with water and dried at 100° C. Recrystallisation from 50 per cent. alcohol gives microscopic pale yellow scales, which melt with decomposition above 360° C. The yield is about 27 per cent. The arsinic acid dissolves readily in alcohol, sparingly in water, chloroform or acetone, and is insoluble in ethyl acetate and carbon disulphide. In alkali hydroxide or carbonate solution the acid is readily soluble, being precipitated unchanged on acidification. The

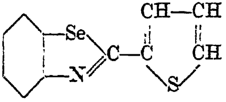
monosodium salt is a fine, white solid, and is stated to be the first water-soluble organic selenium-arsenic compound ever prepared.

2-(α-Furyl)-benzoselenazole,



A mixture of 1 molecular equivalent of zinc *o*-aminophenyl selenide and 2 equivalents of pyromucyl chloride is heated at 100° C. for thirty minutes, then cooled and the pulverised melt extracted with normal sodium hydroxide solution. The residue is decolorised and crystallised from 50 per cent. alcohol until a constant melting-point of 133° C. (corr.) is attained. The compound forms glistening plates, with an agreeable odour characteristic of 2-phenylbenzothiazole.

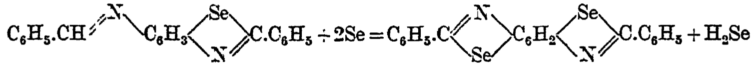
2-(α-Thienyl)-benzoselenazole,



occurs when the pyromucyl chloride in the foregoing preparation is replaced by α-thienyl chloride; yield, 60 per cent. It forms glassy, lustrous prisms, of a pale greenish-yellow colour, M.pt. 114·5° C. It is believed to be the only organic compound known which contains both unoxidised sulphur and unoxidised selenium in the molecule and yet has an agreeable odour.

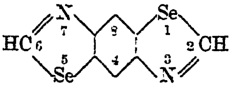
Benzobis-selenazoles.

The synthesis of these derivatives is accomplished by the fusion of 6-benzalamino-2-phenylbenzoselenazole with selenium :[1]



$$C_6H_5.CH{=}N{-}C_6H_3\left\langle\genfrac{}{}{0pt}{}{Se}{N}\right\rangle C.C_6H_5 + 2Se = C_6H_5.C\left\langle\genfrac{}{}{0pt}{}{N}{Se}\right\rangle C_6H_2\left\langle\genfrac{}{}{0pt}{}{Se}{N}\right\rangle C.C_6H_5 + H_2Se$$

The numbering of the heterocyclic ring is as follows :



2 : 6-Diphenyl-p-β-benzobis-selenazole, the structure of which is shown above, is formed when 25 grams of 6-benzalamino-2-phenylbenzoselenazole and 15 grams of selenium are gently boiled together for 23 hours on a sand-bath. The cold melt is extracted with concentrated hydrochloric acid and the filtered solution diluted to precipitate the selenazole. The latter is collected, washed and dried, about 13 grams of yellow powder being isolated. Repeated crystallisation from glacial acetic acid and from *n*-butyl alcohol gives fine, lemon-yellow crystals, M.pt. 217° C. (corr.); yield, 17 per cent. The compound is practically insoluble in ether, ethyl acetate or carbon tetrachloride, and sparingly soluble in alcohol or benzene. The fusion of 30 grams of dibenzal-*p*-diphenylamine with an equal weight of selenium for 24 hours gives only a 3 per cent. yield of the selenazole. The selenazole forms an *addition product* with *acetyl chloride* in toluene solution, $C_{20}H_{12}N_2Se_2.CH_3COCl$,

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[1] Bogert and Hopkins, *J. Amer. Chem. Soc.*, 1924, 46, 1912.

consisting of minute golden-yellow needles, which readily lose acetyl chloride on standing.

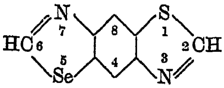
Mononitro - 2 : 6 - diphenyl - p - β - benzobis - selenazole, $C_{20}H_{11}O_2N_3Se_2$.—To a solution of 5 grams of the foregoing *bis*-selenazole in 17 c.c. of concentrated sulphuric acid at 0° C., a mixture of 0·8 c.c. of concentrated nitric acid and 7 c.c. of concentrated sulphuric acid is slowly added. After stirring for three hours the whole is poured into a large volume of ice-cold water, the precipitate collected, washed with hot acetic acid and dried. About 4·5 grams of crude nitro-compound result, and repeated crystallisation from nitrobenzene-glacial acetic acid yields orange-yellow needles, M.pt. 296·1° to 297·1° C. (corr.), slightly soluble in glacial acetic acid and practically insoluble in ethyl or *n*-butyl alcohol, ether, acetone or benzene. The product is not quite free from dinitro-compound.

Dinitro-2 : 6-diphenyl-p-β-benzobis-selenazole, $C_{20}H_{10}O_4N_4Se_2$.—A solution of 1·5 grams of the *bis*-selenazole in 7 c.c. of concentrated sulphuric acid is nitrated at 0° C. by means of a mixture of 0·8 c.c. of concentrated nitric acid and 3 c.c. of concentrated sulphuric acid. After stirring for three hours the mixture is heated for thirty minutes at 80° C., then poured into ice-water. The precipitate is collected, dried, and washed with boiling glacial acetic acid, the yield being 1·3 grams or 72 per cent. Repeated crystallisation from nitrobenzene gives minute greenish-yellow needles, darkening at about 320° C. and melting at 332·4° to 333·4° C. (corr.).

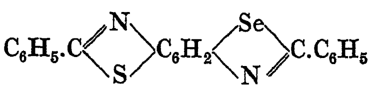
Monoamino-2 : 6-diphenyl-p-β-benzobis-selenazole, $C_{20}H_{13}N_3Se_2$, occurs in 30 per cent. yield when the corresponding nitro-compound is reduced by tin and hydrochloric acid. It crystallises from aniline as orange needles, sintering at about 260° C. and melting at 279·4° to 281° C. (corr.), practically insoluble in ethyl or *n*-butyl alcohol, ether or carbon tetrachloride. The *benzal derivative*, prepared by condensing the amine with benzaldehyde in *n*-butyl alcohol, forms glistening golden-yellow scales, M.pt. 233·5° to 235·5° C. (corr.); yield, 85 per cent.

Selenazolobenzothiazoles.[1]

These derivatives occur when 6-benzalamino-2-phenylbenzoselenazole is fused with sulphur, and contain both the thiazole and selenazole groupings, the structure being numbered as follows :



2 : 6-Diphenyl-p-β-selenazolobenzothiazole,



A mixture of 12·5 grams of 6-benzalamino-2-phenylbenzoselenazole and 5·2 grams of sulphur is heated for 8 hours at 250° to 260° C. The cold melt is powdered, extracted with hot concentrated hydrochloric acid and the filtered extracts precipitated by dilution. The yellow precipitate is collected, washed, dried, and repeatedly recrystallised from

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[1] Bogert and Hopkins, *loc. cit.*

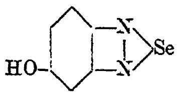
n-butyl alcohol. Lustrous straw-coloured needles separate, M.pt. 220·4° to 221·5° C. (corr.), B.pt. 345° to 350° C. at 11 mm. The yield is 6 grams, or 47 per cent. The body dissolves in hot glacial acetic acid, toluene or aniline, but is sparingly soluble in ethyl alcohol, carbon tetrachloride and acetone. Bromine in warm chloroform solution gives a *tetrabromide*, consisting of minute light brown needles, decomposing at 238° to 243° C. (corr.) with gas evolution, and slowly losing bromine on standing. The selenazolothiazole also forms an *addition compound* with *acetyl chloride* in the presence of glacial acetic acid. This crystallises from toluene in fine needles, M.pt. 224° to 225° C. (corr.) with evolution of acetyl chloride.

Dinitro-2:6-diphenyl-p-β-selenazolobenzothiazole, $C_{20}H_{10}O_4N_4SSe$.—A solution of 1 gram of the foregoing compound in concentrated sulphuric acid is nitrated at 0° C. by the slow addition of a mixture of 5 c.c. of concentrated sulphuric acid and 0·5 c.c. of concentrated nitric acid. After two hours the mixture is poured into 50 c.c. of ice-water, the yellow precipitate collected, washed with water, dried, washed with hot glacial acetic acid and crystallised from nitrobenzene. Microscopic greenish-yellow needles are obtained, M.pt. 295° to 297° C. (corr.). The yield is 0·6 gram, or 50 per cent. This product is probably contaminated with some mononitro-derivative, as the analytical figures for both carbon and hydrogen are high.

PIASELENOLS.[1]

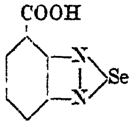
These compounds are formed by the interaction of *o*-diamines and sodium hydroselenite or selenious acid.

4-Hydroxypiaselenol,



The dihydrochloride of 1:2-diamino-4-hydroxybenzene in aqueous solution is treated with the equivalent quantity of sodium hydroselenite in the same solvent. After a short time the product is filtered off and recrystallised from a large volume of water containing animal charcoal. It forms yellowish-brown needles, becoming red and sintering at 200° C., and melting with decomposition at 209° C. Its alkali solutions are red or yellow, according to the concentration. The compound is also obtained when 1:2-diamino-4-hydroxybenzene is treated with selenious acid.

2:3-Piaselenol-1-carboxylic acid,



occurs when the dihydrochloride of 2:3-diaminobenzoic acid in aqueous solution is treated with the calculated quantity of aqueous selenious acid. The precipitate is removed after a short time and recrystallised from a large bulk of hot water. The acid forms rose-coloured crystals, M.pt.

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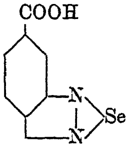
[1] German Patent, 261412; compare American Patent, 1074425; English Patent, 3042 (1913); French Patent, 455148.

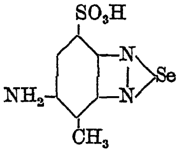
222° to 223° C. after previous sintering. It is sparingly soluble in water or alcohol, but its *alkali salts* are readily soluble.

3 : 4-Piaselenol-1-carboxylic acid,



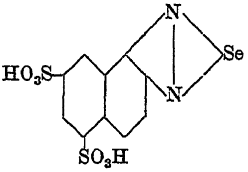
is isolated when the dihydrochloride of 3 : 4-diaminobenzoic acid replaces the 2 : 3-diamino-acid in the foregoing preparation. It melts at 290° C. after sintering at 260° C., and its *alkali salts* are readily soluble in water.

2 : 3-Piaselenol-4-methyl-5-amino-1-sulphonic acid,



2 : 3 : 5-Triamino-4-methylphenyl-1-sulphonic acid or its hydrochloride is dissolved in the calculated quantity (1 or 2 mols. respectively) of very dilute sodium hydroxide, then one molecular proportion of acid sodium selenite added, followed by the slow addition of 0·1*N* hydrochloric acid until a precipitate is obtained. After a time this precipitate is collected and dissolved in hot sodium hydroxide, the *sodium salt* separating on cooling as fine reddish-yellow needles.

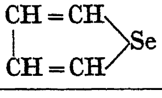
1 : 2-Naphthopiaselenol-5 : 7-disulphonic acid,



Three parts of the dihydrochloride of 1 : 2-diaminonaphthalene-5 : 7-disulphonic acid in 50 parts of water are treated with a concentrated aqueous solution of two parts of acid sodium selenite. After a short time barium chloride is added, when the *barium salt* of the disulphonic acid separates. This crystallises from boiling water as long pale yellow needles or spears. The *sodium salt* is very soluble in water.

Selenophene and its Derivatives.

Selenophene,[1]



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[1] Briscoe and Peel, *J. Chem. Soc.*, 1928, p. 1741; Briscoe, Peel and Robinson, *ibid.*, p. 2628; compare Bogert and Andersen, *J. Amer. Chem. Soc.*, 1926, 48, 223; Foa, *Gazzetta*, 1909, 39, [ii], 527; Mazza and Solazzo (*Rend. Accad. Sci. fis. nat. Napoli*, 1927, [iii], 33, 236) prepare the compound at 250° to 300° C. and give the B.pt. as 113° to 114° C.; they also describe *selenonaphthene*, C_8H_6Se, M.pt. 53° to 54° C., B.pt. 207° to 209° C., giving a sparingly soluble *picrate*.

This body is obtained by the interaction of acetylene and selenium in an electric furnace at a temperature of about 400° C. In addition to selenophene, benzene, naphthalene, anthracene, phenanthrene and probably stilbene or distyrene occur as by-products.

The following values have been found for the vapour pressure of the compound between the temperatures 25° and 85° C.:

Temp., °C.	25	30	35	38	40	43	45	48	50	55	58	60	65	68	70	73	75	77	80	83	85
Vap. Press.	46·5	55	66	74	78·5	87	94	104	112	131	146	156·5	185·5	206	221	243	259	277	305·5	335·5	356

The vapour pressures are measured in millimetres of mercury at 0° C. From the vapour pressure curve derived from these data, and also from the relationship $\log P - T^{-1}$, which is substantially linear, extrapolation to 760 mm. pressure gives a value of 108° C. for the boiling-point of selenophene.

The refractive index n_D has a value of 1·568 at 15° C., and the densities of selenophene are as follows:

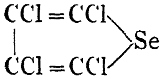
Temp., °C.	15·00	20·00	25·00	30·00	40·00	50·00
Density (grms./c.c.)	1·5307	1·5232	1·5156	1·5078	1·4943	1·4763

The values for the surface tension and the observed parachor of selenophene are as below:

Temp., °C.	15	20	25
Surface Tension (dynes/cm.)	36·49	35·83	35·14
Parachor ($\sigma^{\frac{1}{4}}M/D$)	210·6	210·8	210·5

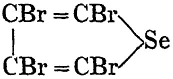
Selenophene is insoluble in water, but miscible in all proportions with a number of non-aqueous liquids, including acetone, benzene and carbon disulphide. At its boiling-point it readily dissolves sulphur, and it closely resembles thiophene in its remarkable stability and chemical inactivity. It is unaffected by boiling water, sodium hydroxide solution or concentrated hydrochloric acid. It does not form a picrate and yields no methiodide even when treated with methyl iodide in a sealed tube at 160° C. for 24 hours. On potassium permanganate in acetone solution it has only a slight reducing action and may be recovered as a colourless liquid, the permanganate apparently oxidising the small trace of impurity which causes selenophene to have a slightly yellow colour. Ordinary reducing agents, such as zinc and hydrochloric acid, do not reduce selenophene, and the body is recovered practically unchanged after being passed thrice together with hydrogen at 250° C. over nickel deposited on pumice. Selenophene reacts with concentrated sulphuric acid, giving a greenish-black mass; when warmed with concentrated sulphuric acid and isatin, it gives an indophenin reaction characterised by a greenish-blue colour, which becomes purple when the product is poured into water. Selenophene is vigorously oxidised by concentrated nitric acid, but when mixed in acetic anhydride and in the cold with a solution of nitric acid in the same solvent, and the mixture poured into water at 0° C., a dark brown oil separates, which slowly sets to a brown tar. This product appears to be a nitro-compound.

Tetrachloroselenophene,



A slight excess of a saturated solution of chlorine in carbon disulphide is added to 10 grams of selenophene in the same solvent. A reaction sets in and hydrogen chloride is evolved. After two days the solution deposits a pale yellow crystalline solid, which is insoluble in most solvents and steadily evolves hydrogen chloride on keeping. A similar product occurs when chlorine is bubbled through a carbon disulphide solution of selenophene. Unlike tetrabromoselenophene, the chloro-compound readily decomposes with deposition of selenium on warming with water or acids, and slowly decomposes at the ordinary temperature in air in a closed tube or in a vacuum, evolving acid fumes and turning brown.

Tetrabromoselenophene,

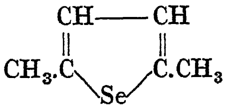


When the chlorine in the first-mentioned preparation of tetrachloroselenophene is replaced by bromine, a vigorous reaction occurs and hydrogen bromide is liberated. After twenty-four hours the solution is washed with dilute sodium hydroxide solution and with water, then evaporated on the water-bath. The brown residue, after crystallisation from alcohol, gives the tetrabromo-compound as a white, finely crystalline substance, M.pt. 102° C., which does not reduce permanganate in acetone solution, but slowly deposits selenium on boiling with water.

Diacetoxymercuriselenophene, $C_4H_2Se(Hg.O.CO.CH_3)_2$,[1] is a cream-coloured, insoluble powder, obtained by shaking selenophene with mercuric acetate solution. Long standing with bromine water gives tetrabromoselenophene, and iodine in potassium iodide yields a small amount of *di-iodoselenophene,* a pale yellow solid of characteristic pleasant smell, M.pt. 45° C. after crystallisation from benzene. Concentrated sodium chloride solution converts the diacetoxy-compound into *dichloromercuriselenophene,* $C_4H_2Se(HgCl)_2$, isolated as a white powder, and boiling potassium hydroxide gives *dihydroxymercuriselenophene,* $C_4H_2Se(HgOH)_2$, a dark grey insoluble powder.

Dihydroxymercuriselenophene mercurisulphate, $C_4H_2Se(HgOH)_2.HgSO_4$, results when selenophene is shaken with concentrated mercuric sulphate solution. It is a white or cream-coloured powder having similar reactions to the foregoing diacetoxy-compound.

2 : 5-Dimethylselenophene (*2 : 5-Selenoxene*),



is prepared by heating acetonyl acetone with phosphorus pentaselenide at 180° C.[2] Fractionation of the product gives a liquid of boiling-point

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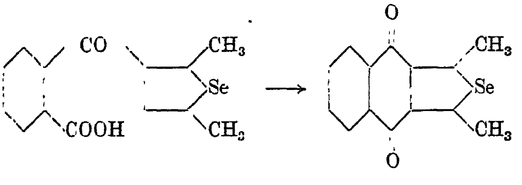
[1] Briscoe, Peel and Young, *J. Chem. Soc.*, 1929, p. 2589.

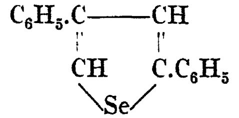
[2] Bogert and Andersen, *loc. cit.*; see Paal, *Ber.*, 1885, 18, 2255, Zoppellari, *Gazzetta*, 1894, 24, [ii], 399.

155° to 157° C. (corr.). When treated with a suspension of phthalic anhydride in carbon disulphide in the presence of aluminium chloride the liquid gives a yellow crystalline solid. This is *phthaloylselenoxene*, and from toluene it separates as pale yellow crystals, M.pt. 155·5° C. (corr.), the yield being about 7 per cent. Concentrated sulphuric acid causes this phthaloylselenophene to develop an intense red coloration, the change being regarded as taking place as follows :



The following compounds[1] are prepared in a similar manner to the corresponding thiophenes, fusion of sulphur or selenium with acetophenone anil giving rise respectively to *2 : 4-diphenylthiophene* and *2 : 4-diphenylselenophene*. The melting-points of these compounds and their derivatives are as follows : *2 : 4-diphenylthiophene*, M.pt. 122·5° C., *2 : 4-diphenylselenophene*, M.pt. 112·3° C. ; *5-chloromercuri-2 : 4-diphenylthiophene*, M.pt. 223° C., *5-chloromercuri-2 : 4-diphenylselenophene*, M.pt. 224° C.

2 : 4-Diphenylselenophene,



An equimolecular mixture of acetophenone anil (60 grams) and elemental selenium (48·6 grams) is placed in a distilling flask connected with an air condenser and heated for sixteen hours at 280° to 295° C. The melt is then distilled at 31 mm. pressure, the main fraction distilling at 270° to 280° C. A reddish oil results, which solidifies ; recrystallisation from absolute alcohol gives lustrous scales, M.pt. 112·3° C. (corr.). The yield is 13 grams, or 30 per cent. If the foregoing melt be heated for twenty hours at 235° to 240° C., the yield is 90 per cent.[2] The compound is insoluble in water, aqueous sodium hydroxide or hydrochloric acid, soluble in hot alcohol or glacial acetic acid, and easily soluble in chloroform, ether, acetone or benzene. In concentrated sulphuric acid the solution is orange, but nitric acid appears to cause some oxidation. With isatin and sulphuric acid the selenophene gives a brown colour, and on dilution a brown solid is precipitated. In the Laubenheimer reaction a green colour is obtained, the addition of water causing the separation of a green flocculent solid. The Liebermann test gives first a green and then a brownish-black colour. 2 : 4-Diphenylselenophene also occurs when acetophenone *o*- or *p*-tolil is substituted for the anil ; with the *o*-tolil the yield is 23 per cent. and with the *p*-tolil 29·3 per cent.

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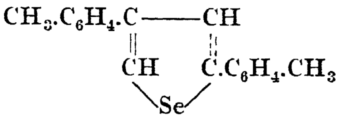
[1] Bogert and Herrera, *J. Amer. Chem. Soc.*, 1923, 45, 238.

[2] Bogert and Andersen, *loc. cit.*

2 : 4-Di-p-tolylselenophene,



is prepared from *p*-methylacetophenone anil and selenium in similar manner to that described above. It forms colourless, lustrou leaflets, M.pt. 136·3° C. (corr.), the yield being 20·5 per cent. It solubility and reactions are similar to those of the diphenyl homologue

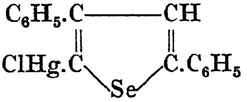
Dibromo-2 : 4-diphenylselenophene, $C_{16}H_{10}Br_2Se$.—A solutio of 5 grams of 2 : 4-diphenylselenophene in 50 c.c. of glacial acetic aci is treated with 10 grams of bromine in 10 c.c. of the same solvent. A crystalline solid separates after several days. This is collected, dried and twice crystallised from alcohol, colourless, glassy needles, M.pt 86·7° C. (corr.) separating. The product is sparingly soluble in water ether or glacial acetic acid, and the yield is 5 grams or 80 per cent.

Tribromo-2 : 4-diphenylselenophene, $C_{16}H_9Br_3Se$, may b obtained by direct bromination of 2 : 4-diphenylselenophene, usin 1·5 grams of the latter to 10 grams of bromine in glacial acetic aci solution, or by the action of bromine in the presence of water upo 5-chloromercuri-2 : 4-diphenylselenophene. It separates from glacia acetic acid as transparent, pale straw-coloured needles, M.pt. 126·7° C (corr.), the yield by the first process being about 36 per cent. It dis solves in ethyl and *n*-butyl alcohols, acetone or ether, but is practicall insoluble in water.

Tetrabromo-2 : 4-diphenylselenophene, $C_{16}H_8Br_4Se$.—4 gram of bromine are added dropwise to 1 gram of 2 : 4-diphenylselenophen in 20 c.c. of boiling alcohol in direct sunlight and the solution subse quently concentrated. A colourless crystalline mass separates as th solution cools. Recrystallisation from *n*-butyl alcohol gives colourless minute felted hairs, M.pt. 176·5° C. (corr.), soluble in alcohol, ether o carbon tetrachloride, but practically insoluble in water.

2 : 4-Diphenylselenophene tetrasulphonic acid, $C_{16}H_{12}O_{12}S_4Se$ occurs when the selenophene is suspended in petroleum ether an sulphonated at 0° C. by the addition of chlorosulphuric acid. It i isolated as the *barium salt*, and the free acid liberated by the aid o sulphuric acid. The acid crystallises from alcohol as colourless, long glassy prisms, freely soluble in water and melting above 300° C. Th yield is very poor.

5-Chloromercuri-2 : 4-diphenylselenophene,[2]



is prepared by treating 2 : 4-diphenylselenophene in alcohol solutio with a 33 per cent. sodium acetate solution followed by a cold saturate aqueous solution of mercuric chloride. The product separates out afte standing for several days. Crystallisation from 95 per cent. alcoh

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[1] Bogert and Andersen, *J. Amer. Chem. Soc.*, 1926, 48, 223.

[2] Bogert and Herrera, *loc. cit.*; Bogert and Andersen, *loc. cit.*

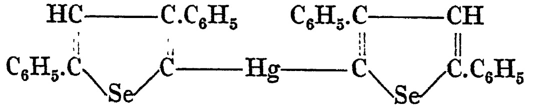
yields fine, colourless needles, M.pt. 224° C.; yield 89 per cent. The body is insoluble in water, sparingly soluble in alcohol or ether, easily soluble in hot chloroform, glacial acetic acid or benzene. If in the foregoing preparation the mixture be mechanically stirred for the first twelve hours, then allowed to stand at the ordinary temperature for twelve hours, the yield is 90 per cent.[1] Potassium bromide in acetone solution converts the selenophene into the 5-bromomercuri derivative and mercuri-*bis*(2 : 4-diphenylselenophene-5).

5-Bromomercuri-2 : 4-diphenylselenophene occurs when the mercuric chloride in the preceding preparation is replaced by mercuric bromide. It is also obtained when the mercuri-*bis* derivative is treated with mercuric bromide in acetone. It crystallises from alcohol as microscopic, colourless, felted hairs, M.pt. 215° C. (corr.), soluble in benzene, toluene or glacial acetic acid. The yield is about 50 per cent. Two molecules of sodium bromide in acetone convert it into the mercuri-*bis* compound, the yield being 65 per cent. A toluene solution of the 5-bromomercuri compound decomposes into mercurous bromide and 2 : 4-diphenylselenophene on boiling.

5-Iodomercuri-2 : 4-diphenylselenophene cannot be obtained by replacing the mercuric chloride in the preparation of the 5-chloromercuri compound by mercuric iodide or by treating the chloromercuri derivative with sodium iodide in acetone solution. It is formed when 0·6 gram of mercuri-*bis*(2 : 4-diphenylselenophene-5) and 0·4 gram of mercuric iodide are heated together in acetone solution for ten minutes, the solution filtered and the filtrate diluted with water. The yield is about 30 per cent., and the preparation should be conducted in the dark, as the compound reddens in the light. It separates from alcohol in colourless crystals, M.pt. 176° C. (corr.).

5-Cyanomercuri-2 : 4-diphenylselenophene is obtained by the method outlined on p. 132. The yield is 50 per cent., and the product when crystallised from alcohol is a colourless powder, M.pt. 256·4° C. (corr.). When boiled in toluene solution it decomposes in the same way as the bromide.

Mercuri-bis(2 : 4-diphenylselenophene-5),



may be isolated by the methods already mentioned, or by the interaction of 1·5 grams of the 5-chloromercuri derivative and 1 gram of sodium iodide in acetone solution. The mixture is stirred for six hours, the precipitate removed, washed with water, dried and crystallised from benzene. Pale grey, minute felted hairs separate, M.pt. 236·7° C. (corr.).

Selenoxanthone and Selenoxanthonecarboxylic Acid.[2]

When diphenyl selenide di-*o*-carboxylic acid (II) interacts with concentrated sulphuric acid two products are obtained, selenoxanthonecarboxylic acid (I) and a dilactone (III). The latter may be considered

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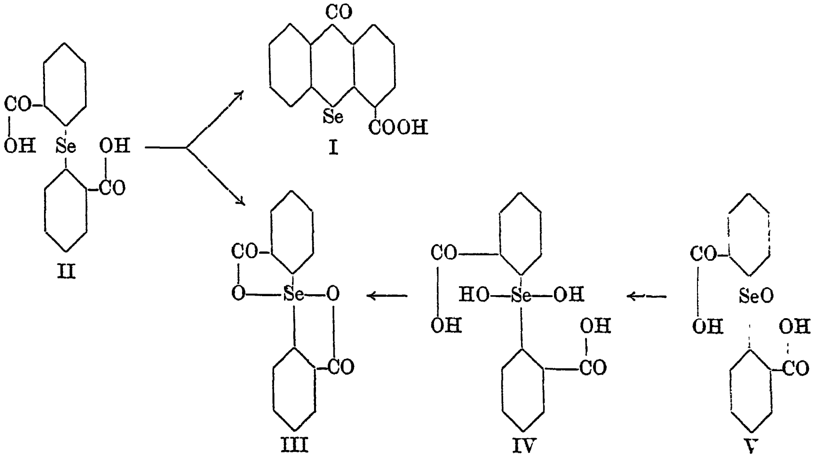
[1] Bogert and Andersen, *J. Amer. Chem. Soc.*, 1926, 48, 223.

[2] Lesser and Weiss, *Ber.*, 1914, 47, 2510.

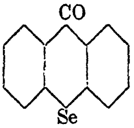
to be derived from the hypothetical diphenylselenoxide di-*o*-carboxylic acid (V) or its corresponding dihydroxy-compound (IV).



Selenoxanthone-o-carboxylic acid (Formula I).—The diphenyl selenide di-*o*-carboxylic acid required for the preparation of this compound may be obtained as follows: Diselenosalicylic acid, $Se_2(C_6H_4.CO_2H)_2$ (16 grams), is dissolved in 150 to 200 c.c. of water containing 12 grams of sodium hydroxide, the solution gently boiled and 16 grams of zinc dust introduced during the course of several hours. The mixture is filtered directly into 20 grams of *o*-iodobenzoic acid dissolved in the calculated quantity of alkali and the whole heated in an autoclave for five to six hours at 180° to 190° C. in the presence of a little copper powder. The melt is filtered, heated to boiling with charcoal, again filtered and acidified with hydrochloric acid, which precipitates the diphenyl selenide di-*o*-carboxylic acid as a crystalline precipitate. The yield of crude product is 22 to 23 grams, or about 85 per cent. Purification is effected by crystallisation from glacial acetic acid containing charcoal. 10 grams of the powdered acid are then heated with 100 grams of concentrated sulphuric acid for four to five hours on a water-bath maintained at 45° to 50° C. with frequent shaking. From the reaction mixture 6 to 7 grams of the required acid and 1 to 2 grams of the dilactone result, the relative proportion of the latter increasing with the temperature of reaction, *e.g.* if the reaction be conducted at 90° to 95° C., 1 to 1·5 grams of acid and 6 to 7 grams of dilactone are obtained. The *dilactone* forms colourless needles, melting with decomposition at 323° to 325° C., soluble in ammonium hydroxide or aqueous sodium carbonate, but not affected by methyl sulphate in alkaline solution. Reduction by zinc dust in concentrated sodium hydroxide or acetic acid solution reconverts the dilactone into diphenyl selenide di-*o*-carboxylic acid.

Selenoxanthonecarboxylic acid gives the following derivatives: *potassium salt*, yellow; *barium salt*, yellow needles; *chloride*, yellow needles, M.pt. 220° to 221° C. When the chloride is allowed to react with the respective normal paraffin alcohols, it yields the following esters, all of which are pale yellow products: *methyl ester*, needles, M.pt. 180° to 181° C.; *ethyl ester*, needles, M.pt. 162° to 163° C.; *propyl ester*, fine microscopic needles, M.pt. 126° to 127° C.; *butyl ester*, cubic crystals, M.pt. 116° to 117° C.; *amyl ester*, needles or rods, M.pt. 73° to 74° C.; *hexyl ester*, needles or microscopic rods, M.pt. 82° to 83° C.; *heptyl ester*, pyramidal crystals, M.pt. 70° to 71° C.; *octyl ester*, needles and rods, M.pt. 74° to 75° C.; *nonyl ester*, prisms, M.pt. 74·5° to 75·5° C.; *decyl ester*, needles, M.pt. 68° to 69° C.; *undecyl ester*, microscopic tablets, M.pt. 75·5° to 76·5° C.; *dodecyl ester*, glistening crystals, M.pt. 66° to 67° C.; *tetradecyl ester*, needles, 72·5° to 73·5° C.; *hexadecyl* (*cetyl*) *ester*, microscopic needles, M.pt. 63° to 64° C.; *octadecyl ester*, needles, M.pt. 83·5° to 84·5° C. The *amide* of selenoxanthonecarboxylic acid forms yellow needles, M.pt. 263° to 264° C., and the *anilide* pale yellow needles, M.pt. 270° to 271° C.

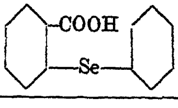
Selenoxanthone,



This compound may be obtained by three methods: (1) 10 grams of selenoxanthonecarboxylic acid when heated with eight to ten times its weight of quicklime added in 0·5-gram portions yields 3·6 to 3·9 grams of the xanthone (45 per cent. yield). (2) 5 grams of diphenyl selenide *o*-carboxylic acid (see below) and 60 grams of concentrated sulphuric acid are heated together for about three hours on the water-bath and the whole poured upon ice. The yellow precipitate is filtered off and digested whilst still moist with dilute ammonium hydroxide, the insoluble portion being removed and dried. About 3 grams of crude product result, this being purified by crystallisation from alcohol. (3) By the interaction of aluminium chloride and *o*-chloroselenobenzoyl chloride, $ClSe.C_6H_4.COCl$, in benzene solution.[1] It separates as pale yellow, glistening needles, M.pt. 191° to 192° C., which sublime without decomposition, and are moderately soluble in acetone, acetic acid or chloroform, somewhat sparingly soluble in carbon tetrachloride or alcohol. In alkali it is insoluble, but dissolves in concentrated sulphuric acid to give a red solution. When warmed with nitric acid (density 1·4) it also gives a red solution, from which it is precipitated unchanged on dilution with water. Refluxing its acetone solution with potassium permanganate does not affect the xanthone.

Selenoxanthone shows a marked resemblance to thioxanthone, but differs from it in its behaviour on oxidation. The latter substance readily yields benzophenonesulphone, whilst selenoxanthone with *chromic acid* in acetic acid solution gives an *additive compound*, $C_{13}H_8O_2Se.CrO_3$,[2] orange-yellow prisms, partially decomposed by water. Boiling this compound with dilute alkalis gives a *chromate* together with a colourless substance consisting of leaflets or needles, M.pt. 230° to 231° C., at which temperature reconversion into selenoxanthone occurs with loss of the elements of water.

Diphenyl selenide o-carboxylic acid,



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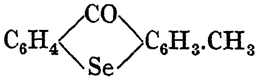
[1] Lesser and Weiss, *Ber.*, 1924, 57, [B], 1077.

[2] This is a compound of the oxide.

required in the preceding preparation (method 2) is obtained by the interaction of selenophenol (phenyl selenide) and diazotised anthranilic acid. It forms colourless crystals, M.pt. 189° to 190° C., readily soluble in alcohol or acetic acid. The *potassium* and *sodium salts* form colourless needles, moderately soluble in water; the *barium salt* is a colourless, amorphous precipitate. Thionyl chloride converts the acid to the *acid chloride*, consisting of glistening yellow crystals, M.pt. 72° to 73° C., and the chloride with methyl alcohol yields the *methyl ester*, colourless glistening rods, M.pt. 71° to 72° C. The *amide* forms colourless needles, M.pt. 201° to 202° C., and the *anilide* glistening needles, M.pt. 145·5° to 146·5° C.

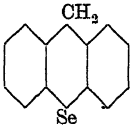
Methylselenoxanthone,[1]



$$C_6H_4\left\langle\begin{matrix}CO\\Se\end{matrix}\right\rangle C_6H_3.CH_3$$

is the condensation product of *o*-chloroselenobenzoyl chloride and toluene in the presence of aluminium chloride. It crystallises in fine needles, M.pt. 112° to 113° C.

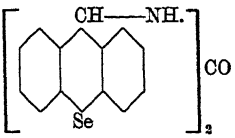
Selenoxanthhydrol,[2]



occurs when selenoxanthone is reduced by sodium amalgam and alcohol. It melts at 115° to 116° C., and reacts with magnesium phenyl bromide to give *phenylselenoxanthhydrol*, M.pt. 105° C. Both products dissolve in mineral acids, forming more deeply coloured solutions than in the case of the corresponding oxygen and sulphur compounds. A solution of selenoxanthhydrol in acetic and hydrochloric acids gives with *mercuric* and *ferric chlorides* vermilion crystalline *double salts*:

$$\left[Se\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH\right]Cl.FeCl_3 \text{ or } HgCl_2$$

Di(selenoxanthyl)carbamide,[3]



is the condensation product of selenoxanthhydrol and carbamide, the reaction being carried out in alcohol-acetic acid. The yield is quantitative, and the product melts with decomposition at about 300° C. Replacement of carbamide by thiocarbamide yields *di(selenoxanthyl) thiocarbamide*, melting with decomposition at 190° to 230° C., the actual melting-point depending upon the conditions of heating.

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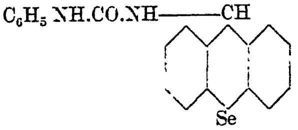
[1] Lesser and Weiss, *loc. cit.*

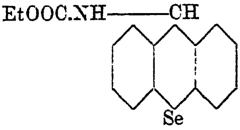
[2] François, *Compt. rend.*, 1930, 190, 191.

[3] François, *ibid.*, p. 800.

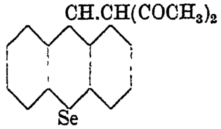
Selenoxanthylphenylcarbamide,



occurs when phenylcarbamide is used in the preceding condensation. The substance melts with decomposition at 234° C., and the corresponding *thiocarbamide* at 145° C. If the phenylcarbamide be replaced by urethane, *selenoxanthylurethane*, M.pt. 179·5° to 181° C., is obtained :



Selenoxanthylacetylacetone,[1]



is obtained when selenoxanthhydrol reacts with acetylacetone in acetic acid solution. The product melts at 145° to 146° C. *Selenoxanthylbenzoylacetone*, prepared in a similar manner, melts at 136·5° C. When ethyl acetoacetate replaces the acetylacetone and the products are heated at 130° to 135° C., *ethyl selenoxanthylacetoacetate*, M.pt. 108° to 110° C., is obtained.

Selenium Indigoid Compounds.[2]

The object of Lesser and Weiss in carrying out work on these compounds was to obtain a selenium compound analogous to thioindigo, and the following deals with the intermediates used in the preparation of this body and condensation products of oxyselenonaphthene. The complete synthesis of selenindigo is shown by the scheme on opposite page.

Diselenodisalicylic acid (*Diphenyl diselenide di-o-carboxylic acid*), $Se_2(C_6H_4.CO_2H)_2$.—Anthranilic acid is diazotised, the solution added to a solution of potassium hydroselenide, and the resulting product decomposed by heating. Whilst still hot the solution is acidified, when diselenodisalicylic acid separates out and is removed, the mother-liquor containing diphenyl selenide di-*o*-carboxylic acid, $Se(C_6H_4.CO_2H)_2$. The diselenide acid is a pale yellow crystalline substance, M.pt. 296° to 297° C. (decomp.), insoluble in the usual organic solvents, soluble with difficulty in acetic acid, and when warmed with concentrated sulphuric acid becoming dark green, the colour changing to blue-violet on strong heating.

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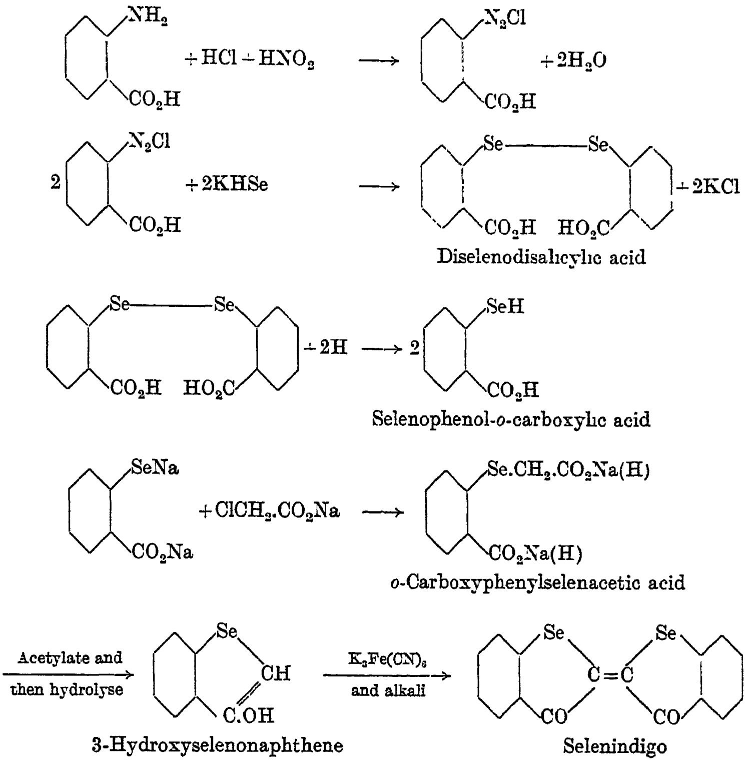
[1] François, *Compt. rend.*, 1930, 190, 1306.
[2] Lesser and Weiss, *Ber.*, 1912, 45. 1835; 1913, 46, 2640.



Derivatives of Diselenodisalicylic Acid.

o-Methylselenolbenzoic acid (*Methylselenophenol-o-carboxylic acid*), $C_6H_4(CO_2H).SeMe$.—Diselenodisalicylic acid is treated with zinc dust and sodium hydroxide, the solution cooled, the requisite amount of dimethyl sulphate added and the whole shaken for about an hour. The acid is precipitated from this solution by the addition of mineral acid. It is an odourless crystalline compound, M.pt. 180° to 181° C., soluble in concentrated sulphuric acid, the solution becoming yellow on warming.

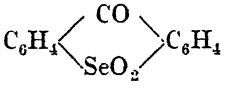
Benzoylselenophenol-o-carboxylic acid, $C_6H_4(CO_2H).Se.COC_6H_5$, is formed by the reduction of the diselenide acid by means of benzoyl chloride. It crystallises in colourless needles, M.pt. 163° to 164° C., soluble in alcohol or acetic acid, less soluble in benzene. Its solutions in concentrated or fuming sulphuric acid are nearly colourless.

o-Selenonbenzoic acid, $C_6H_4(CO_2H).SeO_3H$, is obtained by the oxidation of the diselenide acid or its alkali salts using the calculated quantity of potassium permanganate. It is a very strong acid and its salts are not decomposed by dilute nitric acid. Owing to its extreme solubility in water it cannot be obtained in a crystalline form; its *barium salt* is used for its analysis. This salt is sparingly soluble in water, from which it crystallises in colourless needles.

o-Seleninbenzoic acid, $C_6H_4(CO_2H).SeO_2H$, may be prepared similarly to the foregoing acid, using potassium permanganate and manganese dioxide for the oxidation, or by the action of hydrochloric acid on *o*-selenonbenzoic acid. It crystallises from water in needles, M.pt. 228° to 229° C., which, if heated for some time at 130° to 140° C., are converted to the *anhydride*, $[C_6H_4(CO_2H)SeO]_2O$, which is stable in dry air.

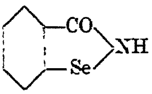
If the diselenide acid is treated with phosphorus pentachloride the free acid chloride is not isolated, but the compound $(HCl.Se.C_6H_4.COCl)_2$. The *normal acid chloride*, however, is formed by using thionyl chloride; it crystallises from benzene or toluene in needles, M.pt. 173° to 174° C. If the *hydrochloride*, M.pt. 65° to 66° C., be boiled with methyl alcohol, a compound is obtained, M.pt. 74° to 75° C., which is the *hydrochloride* of the *methyl ester* of the diselenide acid, $(Se.C_6H_4.COMe)_2$, which may be liberated by dilute sodium hydroxide. The *free ester* melts at 143° to 144° C. The corresponding *ethyl ester* melts at 129° to 130° C. and its *hydrochloride* at 91° to 92° C. Both esters may be formed also from the silver salt of the acid by heating with the alkyl iodide for two to three hours at 110° to 120° C.

Diphenyl selenide di-o-carboxylic acid, $Se(C_6H_4.CO_2H)_2$, occurs as a by-product in the preparation of diselenodisalicylic acid. It crystallises as pale yellow microscopic needles, M.pt. 234° to 235° C., very soluble in alcohol or acetic acid, sparingly soluble in water. When treated with thionyl chloride it yields *o-chloroselenobenzoyl chloride*, $SeCl.C_6H_4.COCl$, M.pt. 65° to 66° C. By means of the respective alcohols *methyl o-chloroselenobenzoate*, M.pt. 74° to 75° C., and the corresponding *ethyl ester*, M.pt. 91° to 92° C., may be isolated.[1] When diphenyl selenide di-*o*-carboxylic acid is warmed with concentrated sulphuric acid, selenoxanthone-*o*-carboxylic acid is obtained (p. 135), together with *benzophenoneselenone*,



This latter product melts at 317° to 318° C. and sublimes at about 260° C. It is sparingly soluble in most organic solvents, but dissolves in hot acetic acid or nitrobenzene. It is insoluble in sodium hydroxide and indifferent to sulphuric acid.

Benzoyleneselenimide,[2]



When *o*-chloroselenobenzoyl chloride (from diphenyl selenide di-*o*-carboxylic acid and thionyl chloride) reacts with dry ammonia in well-cooled benzene solution this imide is produced. It crystallises in plates or needles, M.pt. 234° to 235° C., soluble in water, and with excess of alkali yielding sparingly soluble *alkali salts* which crystallise in needles. *Chromic acid* in acetic acid gives the *addition compound* $C_7H_5ONSe.CrO_3$, and an excess of acetic anhydride yields *benzoyleneselenacetylimide*, consisting of glistening plates, M.pt. 172° to 174° C.

By choosing suitable amines in place of the ammonia in the foregoing preparation, the following derivatives are obtained: the *methyl-*

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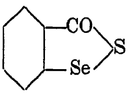
[1] Lesser and Schoeller, *Ber.*, 1914, 47, 2505.
[2] Lesser and Schoeller, *Ber.*, 1924, 57, [B], 1077.

imide, diamond-shaped glistening prisms, M.pt. 159° to 160° C.; the *ethylimide*, needles, M.pt. 102° to 103° C.; the *phenylimide*, colourless needles, M.pt. 182° to 183° C.; and the *o-tolylimide*, plates, M.pt. 187° to 188° C.

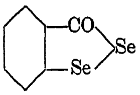
Methylenedibenzoyleneselenimide, $CH_2(C_7H_4ONSe)_2$, is obtained by boiling potassium benzoyleneselenimide with methylene iodide in amyl alcohol. It crystallises from alcohol in colourless needles, M.pt. 331° to 332° C.

Benzoylene selenosulphide,



o-Chloroselenobenzoyl chloride in acetone is converted by sodium sulphide into this sulphide. The selenosulphide crystallises in orange prisms, M.pt. 83° to 84° C.

Benzoylene diselenide,



is formed when hydrogen selenide reacts with *o*-chloroselenobenzoyl chloride in acetone solution. It forms red crystals, M.pt. 91° to 92° C.

Diphenyl selenide di-m-carboxylic acid,[1] $Se(C_6H_4.CO_2H)_2$, is obtained by the interaction of diazotised *m*-aminobenzoic acid and potassium hydroselenide in an atmosphere of carbon dioxide or hydrogen. It crystallises in needles, M.pt. 296° to 297° C., subliming at 260° C., and readily soluble in alcohol, less soluble in acetic acid. It is incompletely soluble in concentrated sulphuric acid, forming yellow solutions; in the fuming acid it is intense blue-green. By oxidation of the acid in the form of its salts with the calculated amount of potassium permanganate, *diphenylselenone-di-m-carboxylic acid*, $O_2Se(C_6H_4.CO_2H)_2$, is obtained. This becomes yellow at 255° C. and melts at 262° to 263° C. (decomp.). It should be noted that in the above reaction no diselenide acid is formed.

Diphenyl diselenide di-p-carboxylic acid, $Se_2(C_6H_4.CO_2H)_2$, is formed in the usual way from *p*-aminobenzoic acid. It melts at 314° to 315° C., is only sparingly soluble in acetic acid, but may be crystallised from methyl alcohol. The yield is poor.

Diphenyl selenide di-p-carboxylic acid, $Se(C_6H_4.CO_2H)_2$, is the principal constituent of the mother-liquors from the preceding compound; its melting-point varies from 312°–313° C. to 315°–316° C.

o-Selenolbenzoic acid (*Selenosalicylic acid*), $SeH.C_6H_4.CO_2H$, is obtained by the reduction of diselenodisalicylic acid by zinc dust in sodium hydroxide. It is stable only in the form of its salts, acidification reproducing the diseleno-acid.

o-Carboxyphenylselenoacetic acid, $CO_2H.C_6H_4.Se.CH_2.CO_2H$.—The foregoing reduced alkaline solution is added to the requisite amount of sodium monochloracetate, the mixture warmed and the acid precipitated by the addition of mineral acid. The yield is quantitative and the product isolated as microscopic needles, M.pt. 233° to 234° C. (decomp.). Chlorosulphonic acid dissolves this acid giving a red

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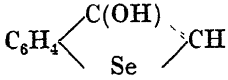
[1] Lesser and Weiss, *loc. cit.*

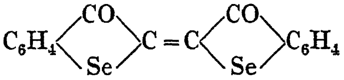
solution, which yields a red precipitate on the addition of water, this precipitate dissolving in alkali to a violet-blue solution. The seleno-acetic acid is sparingly soluble in water, easily soluble in alcohol, gives a yellow solution in concentrated sulphuric acid and a red solution in sulphuric acid monohydrate, the latter solution on warming evolving carbon dioxide and becoming green.

3-Hydroxyselenonaphthene,



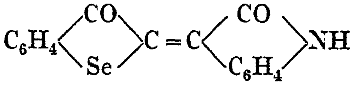
The preceding acid when boiled with an excess of acetic anhydride containing some anhydrous potassium acetate and the excess of acetic anhydride removed, yields an *acetyl compound*, sparingly soluble in organic solvents. Hydrolysis with sodium hydroxide yields 3-hydroxy-selenonaphthene, consisting of colourless silky needles, M.pt. 76° to 77° C. This resembles hydroxythionaphthene in its properties.

Selenindigo (*2 : 2-Bis-selenonaphthenindigo, 2 : 2′-Bis-oxyseleno-naphthene*),



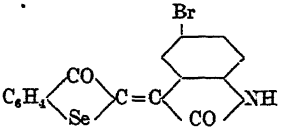
3-Hydroxyselenonaphthene is dissolved in sodium hydroxide solution and oxidised by potassium ferricyanide. Selenindigo is sparingly soluble in the usual solvents, but crystallises from xylene in reddish-brown needles which sublime without decomposition, giving a violet vapour at about 270° C. and melting at 330° to 335° C. In concentrated sulphuric acid it forms a deep green solution, in fuming sulphuric acid a deep blue solution, this latter solution yielding a water-soluble red-violet sulphonic acid. Selenindigo is reduced by alkali and hydro-sulphite to a yellow vat, which dyes cotton and wool violet-red.

2 - Selenonaphthene - 3 - indole - indigo (*3′ - Indoxyl - 2 - seleno-naphthene-3-one*),



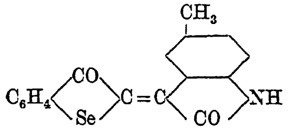
This product separates immediately when 3-hydroxyselenonaphthene and isatin in alcohol solution are warmed together in the presence of a little piperidine. It forms red silky needles, which sublime undecomposed at about 250° C. and melt at about 350° C. In nitrobenzene it is readily soluble, but sparingly soluble in xylene; the concentrated sulphuric acid solution is olive green. With alkali and hydrosulphite it gives a yellow vat, which dyes a bluer shade than Thioindigo Scarlet.

2-Selenonaphthene-5-bromo-3-indole-indigo,



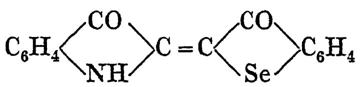
In this case 5-bromoisatin is used. The compound sublimes at 260° C. and melts at 355° C. It dissolves unchanged in concentrated sulphuric acid to give a blue-green solution, and in the fuming acid to give an intense violet solution which yields a water-soluble red sulphonic acid.

2-Selenonaphthene-5-methyl-3-indole-indigo,



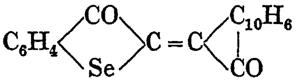
obtained from 5-methyl isatin and 3-hydroxyselenonaphthene, sublimes at 250° C. and melts at 325° to 330° C.; it is sparingly soluble in the usual solvents, gives a green solution in concentrated sulphuric acid and a violet solution in the fuming acid.

2-Selenonaphthene-2-indole-indigo,



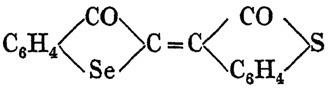
Isatin chloride and 3-hydroxyselenonaphthene are mixed in benzene and the solution boiled, when the required compound separates as a violet precipitate. It dissolves sparingly in xylene with a red-violet fluorescence and deposition of violet-black needles, M.pt. 335° C. In concentrated or fuming sulphuric acid and chlorosulphonic acid it gives intense blue solutions, forming a water-soluble red-violet fluorescent *sulphonic acid*, which yields pale yellow alkali salts.

Acenaphtheneselenonaphthenindigo *(8 - Oxy - 7 - oxyselenonaphthenylacenaphthene)*,



obtained from 3-hydroxyselenonaphthene and acenaphthene quinone, forms yellowish-red needles which sublime at about 220° C. and melt at 272° C.; its solution in concentrated sulphuric acid is blue-green.

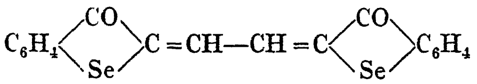
2-Selenonaphthene-3-thionaphthene-indigo,



is formed when thionaphthene quinone is used and the condensation carried out in the presence of a little acetic acid containing a drop of concentrated hydrochloric or sulphuric acid, boiling for one hour under reflux. The product is soluble in acetic acid, xylene or toluene, and crystallises from the last-named as violet-brown needles, M.pt. 203° to 204° C. With concentrated or fuming sulphuric acid it gives an intense green solution from which a violet water-soluble sulphonic acid may be obtained.

The following condensation products of 3-hydroxyselenonaphthene with aldehydes or fluorenone are obtained by boiling alcoholic or acetic acid solutions of equimolecular quantities of the components, with the addition of a drop of concentrated hydrochloric acid. They are unchanged by concentrated sulphuric acid, but in fuming acid give water-soluble sulphonic acids.

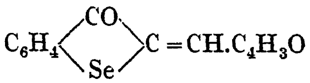
With glyoxal:



This forms violet-red needles, M.pt. 299° to 300° C., readily soluble in nitrobenzene, sparingly soluble in toluene or xylene. Its solutions in concentrated sulphuric acid, chlorosulphonic acid and fuming sulphuric acid are yellow-green, yellow-brown and intense green respectively.

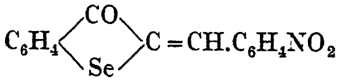
With œnanthol and *citral* only oily condensation products are obtained.

With furfurol:



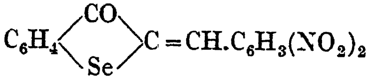
This product melts at 145° to 147° C., and is easily soluble in organic solvents. In concentrated sulphuric acid it gives a dark red solution with green fluorescence; in the fuming acid the colour is deep green.

With p-nitrobenzaldehyde:



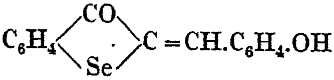
This melts at 243° to 244° C., and gives an intense blue-green solution in concentrated sulphuric acid.

With 2 : 4-dinitrobenzaldehyde:



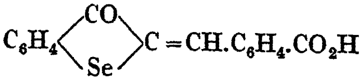
This compound exists in two modifications, the one red and the other orange, M.pt. 226° to 227° C. Both are deep blue in concentrated sulphuric acid.

With salicylaldehyde:



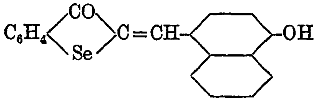
This is brown-yellow, melts at 206° to 207° C., gives a blue-green solution in fuming sulphuric acid and forms an orange-coloured sulphonic acid. It is soluble also in solutions of alkaline earths, in sodium hydroxide and in ammonium hydroxide, imparting a purple-red colour to these solvents.

With phthalic aldehyde:



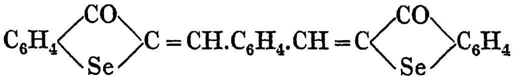
The compound melts at 226° to 227° C.

With a-naphthol 4-aldehyde:



This substance melts at 244° to 245° C. The corresponding products with *β-naphthol aldehyde* and its *methyl ether* melt at 210° to 211° C. and 127° to 128° C. respectively.

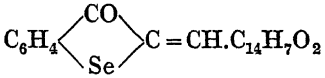
With terephthalic aldehyde:



$$C_6H_4{<}\begin{matrix}CO\\Se\end{matrix}{>}C=CH.C_6H_4.CH=C{<}\begin{matrix}CO\\Se\end{matrix}{>}C_6H_4$$

This sublimes at about 260° C. and melts at about 330° C. It is orange-red, sparingly soluble in ordinary solvents, but gives a deep green solution in concentrated sulphuric acid.

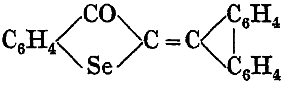
With β-anthraquinone aldehyde:



$$C_6H_4{<}\begin{matrix}CO\\Se\end{matrix}{>}C=CH.C_{14}H_7O_2$$

This derivative is orange-red, sublimes at about 270° C., melts at 348° to 349° C., is easily soluble in nitrobenzene, sparingly soluble in other organic solvents, and intense green in concentrated sulphuric acid.

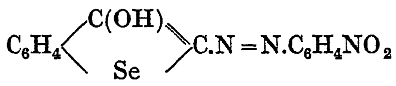
With fluorenone:



$$C_6H_4{<}\begin{matrix}CO\\Se\end{matrix}{>}C=C{<}\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$$

This melts at 169° to 171° C., and is brown-yellow in sulphuric acid.

p-Nitrobenzeneazo-3-hydroxyselenonaphthene,



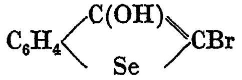
$$C_6H_4{<}\begin{matrix}C(OH)\\Se\end{matrix}{>}C.N=N.C_6H_4NO_2$$

is obtained from *p*-nitrobenzene diazochloride and the sodium salt of the selenium compound. It is sparingly soluble in xylene, from which it separates as red-brown crystals, M.pt. 239° to 240° C., giving a dark red solution in concentrated sulphuric acid and violet-red in alkalis, the latter solutions having an intense red-violet fluorescence.

Selenonaphthene-quinone and its Derivatives.[1]

The starting-point for these derivatives is the diphenyl diselenide-di-*o*-carboxylic acid already described (p. 138).

2-Bromo-3-hydroxyselenonaphthene,



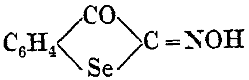
$$C_6H_4{<}\begin{matrix}C(OH)\\Se\end{matrix}{>}CBr$$

---

[1] Lesser and Schoeller, *Ber.*, 1914, 47, 2292.

is obtained when the diselenide acid is treated with bromine in acetic acid solution at the ordinary temperature. If higher temperatures are used oxidation to selenindigo takes place. The bromo-derivative crystallises in yellow needles, M.pt. 103° C., insoluble in water but soluble in the ordinary organic solvents. It reacts with aniline giving a resin, but not if alcohol is used as solvent. With chlorine at the ordinary temperature its acetic acid solution is oxidised to the indigo, but a crystalline product is not obtained.

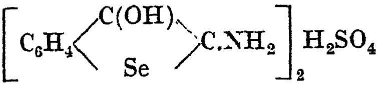
2-Nitroso-3-oxyselenonaphthene,



$$C_6H_4\left\langle\begin{matrix}CO\\Se\end{matrix}\right\rangle C=NOH$$

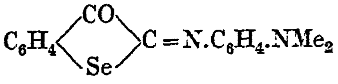
is prepared from the naphthene in the usual manner. It forms yellow needles, M.pt. 154° to 155° C. (decomp.), very soluble in ether, alcohol, acetic acid, benzene or boiling water, insoluble in ligroin. It is stable towards concentrated mineral acid even on heating, but prolonged boiling with 30 per cent. sodium hydroxide gives diselenosalicylic acid. From its solutions in sodium hydroxide or carbonate, the nitroso-compound is precipitated unchanged by mineral acids. It undergoes the following reactions: (1) *With dimethyl sulphate:* forms *methyl compound*, yellow-bronze glistening plates, M.pt. 146° to 147° C. (2) *With acetic anhydride* or *benzoyl chloride:* forms *acetyl* or *benzoyl derivative*, the former consisting of yellow needles, M.pt. 177° to 178° C., the latter yellow plates, M.pt. 184° to 185° C. (3) *With hydroxylamine:* gives *dinitroso-compound*, yellow needles, M.pt. 168° C.

The reduction product of this nitroso-compound with iron powder and dilute acid gives, when treated with dilute sulphuric acid, a compound having the constitution



$$\left[C_6H_4\left\langle\begin{matrix}C(OH)\\Se\end{matrix}\right\rangle C.NH_2\right]_2 H_2SO_4$$

Condensation of 3-oxyselenonaphthene with *p*-nitrosodimethylaniline in alcohol-sodium hydroxide solution gives a 70 per cent. yield of *selenonaphthene-quinone-2-p-dimethylaminoanil*,

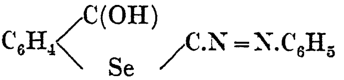


$$C_6H_4\left\langle\begin{matrix}CO\\Se\end{matrix}\right\rangle C=N.C_6H_4.NMe_2$$

This product crystallises in bright green prisms, M.pt. 166° to 167° C., having a metallic lustre, but in powder form or in solution it is intense red. It is readily soluble in acetone, chloroform, acetic acid, warm benzene, alcohol or carbon tetrachloride. By adding an absolute ether hydrogen chloride solution to a chloroform solution of the anil, a brown crystalline salt is obtained which soon deliquesces in the air. The anil is soluble in concentrated sulphuric acid with decomposition, giving a dark red solution.

In a similar manner *selenonaphthene-quinone-2-anil* is obtained from the selenonaphthene and nitrosobenzene. It forms orange needles or dark plates, both melting at 145° to 146° C.

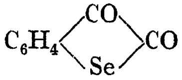
2-Benzeneazo-3-hydroxyselenonaphthene, from hydroxyselenonaphthene and diazobenzene chloride,



$$C_6H_4\begin{matrix}\diagup C(OH) \\ \diagdown\ Se\ \diagup\end{matrix}C.N=N.C_6H_5$$

forms orange-red needles, M.pt. 207° to 208° C. It is soluble without decomposition but with a red coloration in sodium hydroxide. Concentrated sulphuric acid or acetic acid saturated with hydrogen chloride colours its yellow acetic acid solution intense red, and on pouring the mixture into water the unchanged compound is precipitated. In fuming sulphuric acid it gives a red solution, then forming a yellow water-soluble sulphonic acid, which yields red salts. When an acetic acid solution of this body or the preceding anil is boiled with hydroxylamine hydrochloride and excess of fused sodium acetate, *2-nitroso-3-oxyselenonaphthene* is obtained, and the *acetyl* and *benzoyl derivatives* of both compounds give the same reaction.

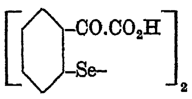
Selenonaphthene-quinone,



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown Se \diagup\end{matrix}CO$$

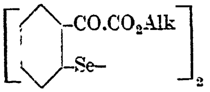
To 200 c.c. of hydrochloric acid (sp. gr. 1·12), 200 grams of ice and 400 c.c. of ether, 2·5 grams of finely powdered selenonaphthene-*p*-dimethylaminoanil are added in small portions, with shaking. The anil dissolves, and the water and ether layers are separated, more ether and anil being added to the former layer, and the operation repeated several times. The combined ether extracts are dried over calcium chloride, boiled with charcoal, and after removing the ether, the quinone is obtained in red needles, together with a small quantity of yellow substance, *diseleno-di-o-benzoylformic acid,* formed by decomposition of the quinone. These two bodies are separated by fractional crystallisation from benzene, the yield of quinone being 70 per cent. It forms red needles, subliming unchanged at about 100° C., M.pt. 102° to 103° C., stable in air, and soluble in anhydrous organic solvents without decomposition. In contrast to the intense red crystals, the colour of the solutions is reddish-yellow. With thiophene containing benzene and concentrated sulphuric acid the quinone gives the indophenin reaction, with a somewhat more violet shade than isatin. It dissolves in concentrated sulphuric acid giving a red solution, which gradually decomposes, becoming green.

Diseleno-di-o-benzoylformic acid (*Diphenyl diselenide-di-o-glyoxylic acid, Selenonaphthenquinonic acid*),



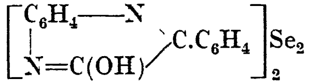
This product is the result of the action of water or dilute acetic acid on selenonaphthene-quinone. Even dilute alkali rapidly decomposes the quinone. The reaction may be slowed down by carrying out the operation in ether, when the required acid is obtained as orange, glistening prisms, the melting-point depending on the rate of heating. The acid is soluble in ether, acetone, alcohol or acetic acid, insoluble in benzene, xylene or carbon tetrachloride, and best recrystallised from chloroform.

The Action of Aliphatic Alcohols on Selenonaphthene-quinone.—When the quinone is boiled with the alcohol the corresponding *formic ester* is formed, which has the general formula



The *methyl ester* forms yellow plates, M.pt. 157° to 158° C., the *ethyl ester* yellow needles, M.pt. 125° to 126° C., and the *propyl ester* melts at 111° to 112° C.

Di-2-hydroxy-3-o-quinoxalyldiphenyl diselenide,



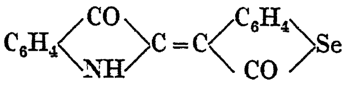
In contrast to thionaphthene-quinone, the seleno-compound reacts with *o*-diamines readily in the cold. With *o*-phenylenediamine it gives the above compound, consisting of orange-yellow microscopic needles, M.pt. 320° to 325° C., giving a red solution in concentrated sulphuric acid, and a potassium salt with concentrated potassium hydroxide solution.

Di-2-hydroxy-3-o-naphthoquinoxalyldiphenyl diselenide is formed when the *o*-phenylenediamine is replaced by 1 : 2-naphthalenediamine. It is an orange crystalline powder, M.pt. 352° to 355° C.

The methyl ester of the quinone acid gives a yellow crystalline powder, M.pt. 355° to 360° C., with *o*-phenylenediamine. The quinone with aniline and with *p*-aminodimethylaniline gives prisms, M.pt. 218° to 219° C. and M.pt. 226° C., respectively.

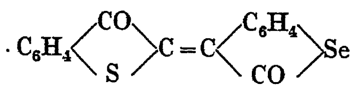
The following condensations of *selenonaphthene-quinones* are carried out by boiling the components in acetic acid solution with the addition of a drop of concentrated hydrochloric acid, when the dyestuffs crystallise out in needles.

With indoxyl:—2-Indole-3-selenonaphthene-indigo (2′-Indoxyl-3-selenonaphthene-2-one),



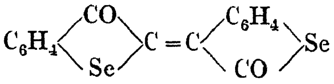
This body forms blue-black prisms, M.pt. 241° to 242° C., giving a violet-red solution in chloroform, a green solution in concentrated sulphuric acid, and a violet-red solution in the fuming acid.

With 3-hydroxythionaphthene:—2-Thionaphthene-3-selenonaphthene-indigo (3-Oxy-Δ^2-thionaphthenyl-3-selenonaphthene-2-one),



This product crystallises from benzene as reddish-brown needles, M.pt. 196° to 197° C., gives red-violet solutions in chloroform, yellowish-green in fuming sulphuric acid and yellowish-brown in chlorosulphonic acid.

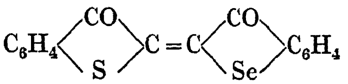
With 3-hydroxyselenonaphthene:—2 : 3′-Bis-oxyselenonaphthene (*2 : 3-Bis-selenonaphthene-indigo*),



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{Se}{>}C=C{<}\genfrac{}{}{0pt}{}{C_6H_4}{CO}{>}Se$$

This derivative forms reddish-brown needles, M.pt. 186° to 187° C., which may be sublimed without decomposition.

With 2-bromo-3-ketodihydrothionaphthene-quinone:—2-Selenonaphthene-2-thionaphthene-indigo (*3-Oxy-Δ^2-thionaphthenyl-2-selenonaphthene-3-one*),



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C=C{<}\genfrac{}{}{0pt}{}{CO}{Se}{>}C_6H_4$$

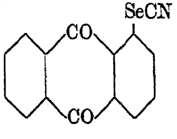
This crystallises as dark red needles, M.pt. 350° C. (about), is violet-red in chloroform, blue in fuming sulphuric acid.

All the foregoing dyestuffs are easily reduced by hydrosulphite in alkaline solution, the dye being restored on exposure to air.

The scheme on page 150 compares selenonaphthene-quinone with compounds of similar structure.

SELENIUM COMPOUNDS OF THE ANTHRAQUINONE SERIES.[1]

1-Selenocyanoanthraquinone,



1-Aminoanthraquinone, 2·2 kilograms, in concentrated sulphuric acid, is diazotised with nitrosylsulphuric acid. The addition of ice precipitates the diazosulphate, which is removed, dissolved in water and treated with 1·5 kilograms of potassium selenocyanate. The red diazoselenocyanate separates out and some nitrogen is evolved. The reaction is completed by warming, whereby an orange precipitate of selenocyanoanthraquinone is obtained. This crystallises from nitrobenzene as yellowish-red needles, M.pt. 249° C.

Alcoholic potassium hydroxide when warmed with the selenocyanate in the absence of air converts it into the *selenophenol* (*selenide*):

$$C_{14}H_7O_2.SeCN + H_2O = C_{14}H_7O_2.SeH + CN.OH$$

This product crystallises from acetic acid as orange-red plates, M.pt. 212° C., which give a green solution in alcoholic potassium hydroxide. This solution on standing in air deposits the yellowish-red *diselenide*. The selenophenol dyes wool orange-red.

The selenocyanate when heated with concentrated ammonium hydroxide in an autoclave for four to five hours at 120° to 160° C. is converted into an *isoselenazole*:

$$C_{14}H_7O_2.SeCN + NH_3 = C_{14}H_7ONSe + HCN + H_2O$$

This crystallises from pyridine as needles, M.pt. 203° C.

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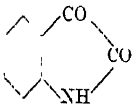
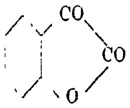
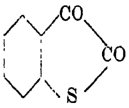
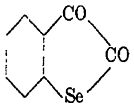
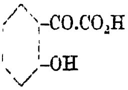
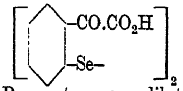
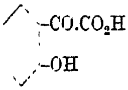
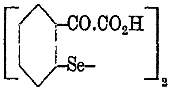
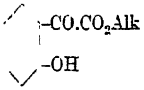
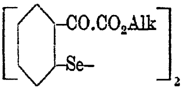
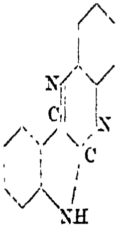
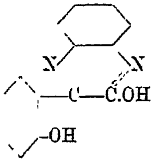
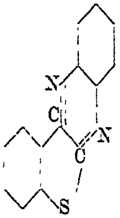
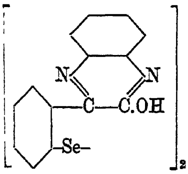
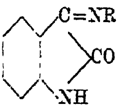
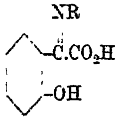
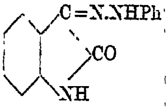
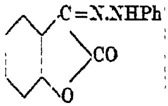
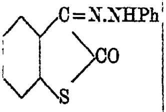
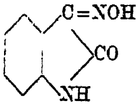
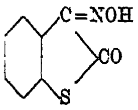
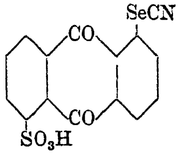
[1] German Patents, 256667, 264139, 264940.

COMPARISON OF SELENONAPHTHENE-QUINONE AND SIMILAR COMPOUNDS.

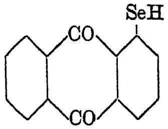
Reagent.	Isatin.	Cumarandione.	Thionaphthene-quinone.	Selenonaphthene-quinone.
	 Reddish-brown, M.pt. 200°–201° C.	 Yellow, M.pt. 134° C.	 Orange-yellow, M.pt. 121° C.	 Red, M.pt. 102°–103° C.
Moisture	No action.	 Soon formed.	No action.	 By water or dilute acetic acid.
Alkalis	Soluble, precipitated unchanged by acids.		Soluble, precipitated unchanged by acids.	
Alcohols	No action.		No action.	
o-Diamines	 Yellow.	 Yellow.		 Orange-yellow.
Primary aromatic amines			Compounds of unknown constitution.	
Phenyl-hydrazine				Mixtures of various compounds.
Hydroxyl-amine		?		Mixtures of various compounds.

1-Selenocyanoanthraquinone-5-sulphonic acid,



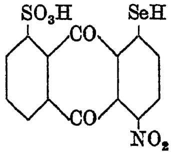
is prepared in a similar manner to the foregoing selenocyanate using 1-aminoanthraquinone-5-sulphonic acid as the starting material. The *potassium salt* crystallises in yellow needles. The acid is converted by alcoholic potassium hydroxide to the *selenophenol sulphonic acid,* the *sodium salt* of which is red, and the free acid red needles. The selenophenol dyes wool from a faintly acid bath a yellowish-red colour. When its blue alkaline solution is heated, oxidation takes place, yielding the *diselenide disulphonic acid.* The selenocyanate is converted by ammonia under pressure into the *isoselenazole sulphonic acid,* crystallising in fine, greenish needles.

1-Anthraquinone selenophenol (*selenide*),[1]



It has already been pointed out that this compound may be prepared by hydrolysis of the selenocyanate; it may also be obtained by the interaction of sodium selenide and 1-chloroanthraquinone. By the latter process orange-red plates, M.pt. 212° C., result. If 2-chloroanthraquinone be used in the reaction, *2-anthraquinone selenophenol* is obtained as an orange-yellow product, which gives a violet-red solution in sulphuric acid. Concentrated nitric acid causes oxidation to the *seleninic acid.*

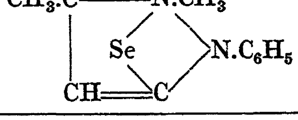
4-Nitroanthraquinone-1-selenophenol-8-sulphonic acid,



is obtained from 1-chloro-4-nitroanthraquinone-8-sulphonic acid and sodium selenide. It crystallises in violet needles which dye wool from an acid bath a violet-red colour.

SELENIUM COMPOUNDS FROM PYRAZOLONES.

Selenoantipyrine, *1-Phenyl-2 : 3-dimethyl-2 : 5-selenopyrazole,*[2]



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[1] German Patent, 264941.

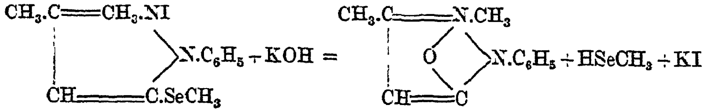
[2] Michaelis and Stein, *Annalen,* 1902, 320, 32.

This compound is obtained by the action of potassium selenide or hydroselenide on antipyrine chloride in aqueous solution, according to the equation:

$$C_{11}H_{12}N_2Cl_2 + 2KSeH = C_{11}H_{12}N_2Se + 2KCl + SeH_2$$

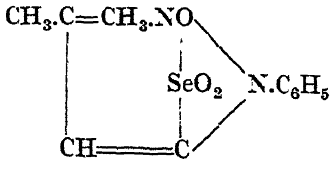
It forms hard, glistening, pale yellow crystals, M.pt. 168° C., isomorphous with thioantipyrine. It is moderately soluble in water, alcohol or chloroform, sparingly soluble in benzene or toluene, and practically insoluble in ether. With ferric chloride it gives no red coloration as does antipyrine. The addition of *platinic chloride* to a hydrochloric acid solution of the seleno-compound gives a brownish-yellow precipitate having the composition $(C_{11}H_{12}N_2Se.HCl)_2.PtCl_4$; *mercuric chloride* yields $C_{11}H_{12}N_2Se.HgCl_2$, a white powder, commencing to sinter at 240° C. and soluble only in concentrated acids; *potassium ferrocyanide* gives $(C_{11}H_{12}N_2Se)_2.H_4Fe(CN)_6$.

Methyl iodide combines at ordinary temperatures to form a *methiodide*, having the constitution shown below. This crystallises from alcohol as leaflets and from water as needles, M.pt. 197° C. When warmed with caustic alkalis it is decomposed in a similar manner to thioantipyrine:

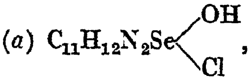


The *ethiodide* crystallises in needles, M.pt. 152° C.

Selenoantipyrine trioxide, *2-Methylammonium-1-phenyl-3-methyl-2:5-pyrazoleselenonate,*

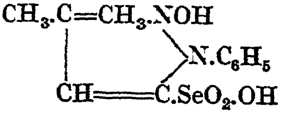


When chlorine gas is passed into an aqueous solution of selenoantipyrine and the solution evaporated on the water-bath, two substances are obtained,



$$(a)\ C_{11}H_{12}N_2Se\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}, \qquad (b)\ C_{11}H_{12}N_2SeO_3.H_2O$$

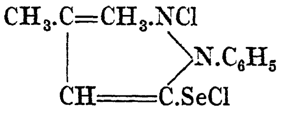
These may be separated by fractional crystallisation from alcohol. The trioxide crystallises from alcohol as slender white needles, M.pt. 170° C. with gas evolution and separation of red selenium, containing 1 molecule of water of crystallisation and having the constitution



This molecule of water may be removed by twelve hours' heating at 110° C., when the compound has the structure previously given. The trioxide is moderately soluble in water, readily soluble in hot alcohol, and has a neutral reaction. When treated with concentrated hydrochloric acid it yields selenoantipyrine dichloride :

$$C_{11}H_{12}N_2SeO_3 + 6HCl = C_{11}H_{12}N_2SeCl_2 + 3H_2O + 2Cl_2$$

Selenoantipyrine dichloride,



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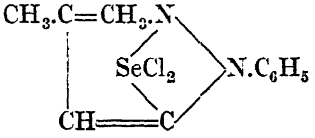
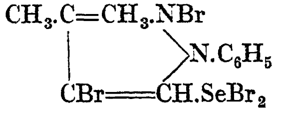
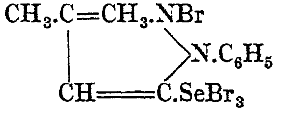


is prepared as stated above, or by passing chlorine into selenoantipyrine in dry alcohol free from chloroform. A pale yellow crystalline precipitate is formed, which crystallises from alcohol in thin yellow needles, moderately soluble in water, readily soluble in hot alcohol, sparingly soluble in concentrated hydrochloric acid. Its *platinichloride*, $(C_{11}H_{12}N_2SeCl_2)_2.PtCl_4.2H_2O$, is formed as a yellow flocculent precipitate.

Selenoantipyrine tetrabromide,



or



is obtained by the action of bromine on a chloroform solution of selenoantipyrine. It crystallises as slender, yellow, glistening needles, M.pt. 139° C., soluble in water, boiling alcohol or chloroform. When boiled with water it yields the dibromide.

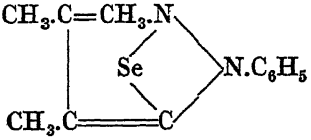
Selenoantipyrine dibromide is obtained as above or by the addition of hydrobromic acid to an aqueous solution of selenoantipyrine trioxide, when free bromine is evolved :

$$C_{11}H_{12}N_2SeO_3 + 6HBr = C_{11}H_{12}N_2SeBr_2 + 3H_2O + 2Br_2$$

It forms orange-red needles, M.pt. 236° C., soluble in water, sparingly soluble in alcohol, insoluble in ether or chloroform.

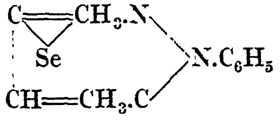
Selenoantipyrine di-iodide, $C_{11}H_{12}N_2SeI_2$, is formed when a solution of iodine in potassium iodide reacts with selenopyrine. It crystallises from acetic acid as brown crystals, M.pt. 144° C., insoluble in water, alcohol or ether.

4-Methylselenoantipyrine, *1-Phenyl-2 : 3 : 4-trimethyl-2 : 5-selenopyrazole,*



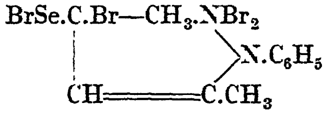
Potassium hydroselenide is allowed to act upon the methiodide of 1-phenyl-3 : 4-dimethyl-5-chloropyrazole, when long, thin, yellow needles, M.pt. 172° C., are formed, soluble in alcohol or chloroform, sparingly soluble in water. If chlorine be passed into an aqueous solution of the product and the solution evaporated, a substance corresponding in properties to selenoantipyrine trioxide is obtained, but chlorine and a dry chloroform solution of the product yield the normal *dichloride*, which melts at 207° to 208° C., and is readily soluble in water, sparingly soluble in alcohol.

3-Selenopyrine, *2 : 3-Seleno-1-phenyl-2 : 5-dimethylpyrazole,*[1]

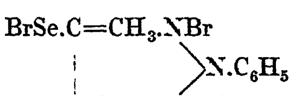


may be isolated (1) from 3-antipyrine chloride and potassium hydroselenide, (2) from the methiodide of 1-phenyl-5-methyl-3-pyrazolone and potassium hydroselenide. The reaction is much slower in the second case and the mixture is heated on the water-bath in a stream of hydrogen. On cooling the compound separates, and is recrystallised from hot water. 3-Selenopyrine has the same melting-point as selenoantipyrine, namely 168° C., but whereas the latter forms thick crystals, the former crystallises in glistening white plates. It is sparingly soluble in cold water, yielding pale yellow solutions, moderately soluble in alcohol, chloroform or benzene. With salts of the metals it gives coloured precipitates. The *platinichloride* is a reddish-brown powder, decomposing at high temperatures; the *mercurichloride* is a white crystalline precipitate, M.pt. 198° C.; the *hydriodide* forms yellow needles, M.pt. 183° C., easily decomposed; the *methiodide* consists of prisms, M.pt. 180° C.; and the *ethiodide* colourless needles, M.pt. 132° C.

3-Selenopyrine tetrabromide,



occurs when a chloroform solution of 3-selenopyrine and a similar solution containing an excess of bromine are mixed. Fine red needles separate, M.pt. 69° C., easily soluble in alcohol or chloroform, insoluble in ether. Treatment with water, or the action of heat, causes loss of bromine, giving the *dibromide*, which has the constitution



The dibromide crystallises from hot absolute alcohol as glistening golden-yellow needles, M.pt. 174° C., soluble in hot water or hot alcohol, insoluble in ether. Sodium carbonate solution eliminates selenium and the bromomethylate of 1-phenyl-5-methylpyrazole is formed in accordance with the following equation :

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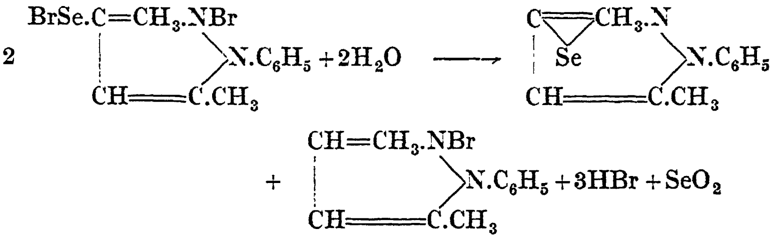
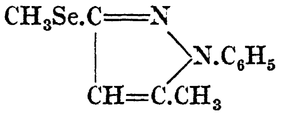
[1] Michaelis, *Annalen*, 1905, 338, 301.

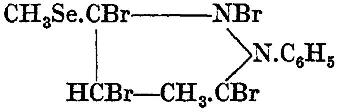


3-ψ-Selenopyrine, *3-Selenomethyl-1-phenyl-5-methylpyrazole,*

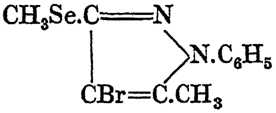


This compound is obtained by the distillation in air of the methiodide of 3-selenopyrine, the 3-selenopyrine itself giving only a dark impure product. It is a colourless mobile liquid of unpleasant smell, B.pt. 195° C. at 13 mm., readily soluble in alcohol, ether or strong acids, insoluble in water. When distilled under atmospheric pressure it evinces considerable decomposition. It yields the following salts: *hydrochloride*, a white crystalline mass, M.pt. 135° C., readily soluble in alcohol, but decomposing into its components in water; *platinichloride*, crystallises with 2 molecules of water, and is a microscopic yellow powder which decomposes on heating; *methiodide*, identical with the methiodide of 3-selenopyrine; *ethiodide*, forms white needles, M.pt. 110° C.

3-ψ-Selenopyrine tetrabromide,

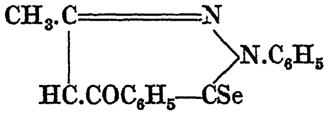


is a yellow-brown powder, M.pt. 191° C., very easily soluble in alcohol or chloroform, insoluble in water or ether. When heated, it is converted into *3-ψ-selenopyrine monobromide,*



which crystallises from alcohol in white needles, M.pt. 178° C., and decomposes at 181° C. It is soluble in benzene, sparingly soluble in alcohol, insoluble in water.

4-Benzoyl-1-phenyl-3-methyl-5-selenopyrazolone,[1]



is produced by the action of potassium hydroselenide in alcoholic

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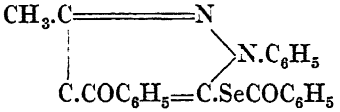
[1] Michaelis and Langenkamp, *Annalen*, 1914, 404, 21.

solution on 1-phenyl-3-methyl-5-chloro-4-benzoylpyrazole, the operation being conducted in an atmosphere of hydrogen. It occurs in two modifications: (1) red needles, M.pt. 96° C., (2) yellow needles, M.pt. 116° C. A solution of the latter form in sodium hydroxide yields the red form when treated with hydrochloric acid. The compound is insoluble in water or dilute acid, but readily soluble in sodium hydroxide, sodium carbonate, chloroform, benzene, ligroin or acetic acid. The red solution in alcohol or ether gradually changes to yellow and the *bis*-compound separates. When the selenopyrazolone in toluene is boiled for a short time with yellow mercuric oxide, and the filtrate evaporated, white crystals are obtained, M.pt. 195° C., sparingly soluble in the usual solvents. This product is the *mercuric salt*, $Hg(C_{17}H_{13}N_2OSe)_2$. If the mercuric oxide be replaced by *mercurous chloride*, a *salt* is formed which gives white crystals from chloroform and melts at 220° C. This salt is more soluble in alcohol than the preceding one.

4-Benzoyl-1-phenyl-3-methyl-5-selenobenzoylpyrazolone,

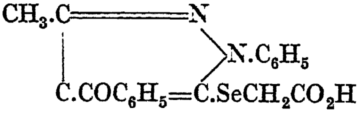


When an alkaline solution of the selenopyrazolone is treated with benzoyl chloride, this compound is obtained as white, slender needles, M.pt. 111° C. It is readily soluble in hot alcohol, benzene or chloroform, sparingly soluble in ether, insoluble in water, aqueous alcohol or dilute acid.

The **methyl ether,**

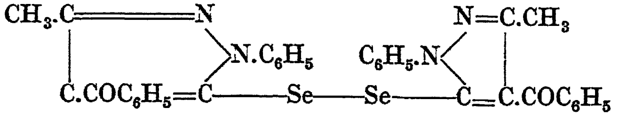
occurs as hard, white crystals, M.pt. 70° C., when methyl iodide reacts with a warm aqueous alkali solution of the pyrazolone. It is readily soluble in alcohol or ether, sparingly soluble in ligroin or petroleum ether. The *ethyl* and *benzyl ethers* are similar compounds, melting at 84° C. and 146° C. respectively.

4-Benzoyl-1-phenyl-3-methylpyrazole-5-selenoacetic acid,



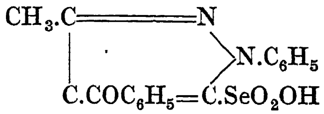
This compound is formed by the action of monochloracetic acid on a faintly alkaline solution of the 5-selenopyrazolone. It forms white needles, M.pt. 157° C., easily soluble in alcohol, hot benzene or aquoeus alkali, sparingly soluble in ligroin, insoluble in water.

Bis-4-benzoyl-1-phenyl-3-methyl-5-selenopyrazole,



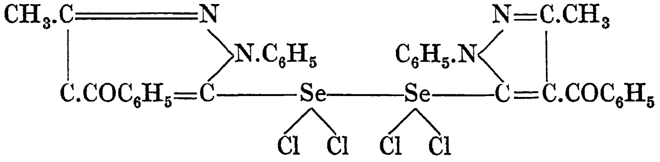
When the 5-selenopyrazolone is dissolved in alcohol and the solution evaporated down, this *bis*-compound crystallises out. The oxidation also takes place when an alkali carbonate solution of the 5-selenopyrazolone is treated with a solution of iodine in chloroform. The compound forms golden-yellow needles, M.pt. 141° C., readily soluble in acetic acid, benzene or chloroform, sparingly soluble in cold alcohol or ether, insoluble in aqueous alkalis or mineral acids. When reduced it is not reconverted into the 5-selenopyrazolone.

4-Benzoyl-1-phenyl-3-methylpyrazole-5-selenonic acid,



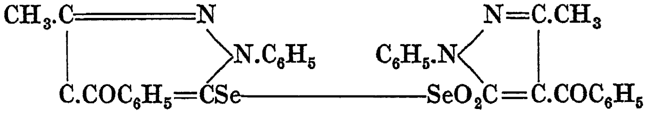
arises from the action of 30 per cent. hydrogen peroxide on a concentrated solution of the preceding compound in acetic acid. It crystallises in colourless needles, M.pt. 152° C., readily soluble in aqueous alkalis or ammonium hydroxide. When heated with concentrated hydrochloric acid the smell of free chlorine may be detected, and sulphur dioxide reduces the body to the oxide, described below.

Bis-4-benzoyl-1-phenyl-3-methyl-5-tetrachlorodiselenopyrazolone,

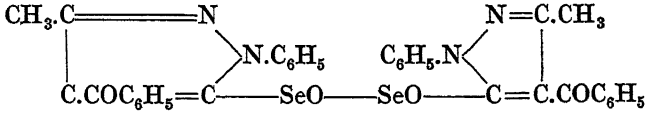


When the corresponding 5-selenopyrazole in chloroform solution is cooled in ice and treated with chlorine, an oil is obtained which may be solidified if triturated with petroleum ether. Recrystallisation gives colourless needles of the tetrachloride, M.pt. 125° C. The *tetrabromide* is prepared in a similar manner and forms yellow-red needles, M.pt. 201° C. It dissolves with decomposition in aqueous alcohol, yielding yellow needles, M.pt. 141° C., of the 5-*bis*-selenopyrazolone. If the tetrabromide is warmed with very dilute sodium hydroxide solution, a yellow *halogen-free product* is isolated, which melts at 126° C. when recrystallised from alcohol, and corresponds to the oxide of the 5-*bis*-selenopyrazolone.

Bis-4-benzoyl-1-phenyl-3-methyl-5-dioxydiselenopyrazolone,

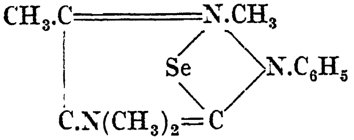


or

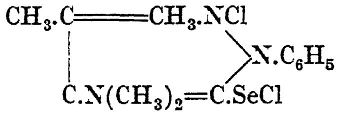


The foregoing selenonic acid is dissolved in alcohol and treated with an aqueous solution of sulphurous acid or gaseous sulphur dioxide, when golden-yellow crystals of the *bis*-compound, M.pt. 126° C., are deposited. The compound is readily soluble in hot alcohol, chloroform or acetic acid, insoluble in water, aqueous alkalis or dilute mineral acids.

4-Dimethylamino-1-phenyl-2 : 3-dimethyl-2 : 5-seleno-pyrazolone or *Selenopyramidone,*

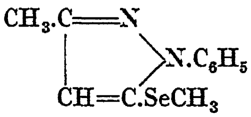


This compound is readily obtained by the action of potassium hydroselenide on an aqueous solution of pyramidone chloride. It forms pale yellow, hard needles, melting at 196° C., sparingly soluble in cold water, readily soluble in alcohol, chloroform, benzene or dilute acids. The aqueous solution gives a faint yellowish-red turbidity with ferric chloride, and a yellow colour with sulphur dioxide. The *hydrochloride* is a crystalline product, melting at 177° C., and deliquescent in air. The *mercurichloride* and *platinichloride* are white and yellowish-red precipitates respectively. When a chloroform solution of selenopyramidone is treated with chlorine, the *dichloride* is formed, which has the constitution :



It occurs as yellow crystals, M.pt. 197° C., soluble in water or alcohol, sparingly soluble in chloroform, ether or benzene. The corresponding *dibromide* is a reddish-yellow powder, M.pt. 203° C., sparingly soluble in water or alcohol, insoluble in ether, benzene or chloroform; the *di-iodide* is a reddish-brown powder. A *mono-iodo-derivative* has also been described, which crystallises in yellow-red needles, M.pt. 190° C., soluble in water or alcohol, insoluble in ether. The *methiodide* of selenopyramidone occurs as pale yellow crystals, M.pt. 208° C., and the *ethiodide* as pale yellow needles, M.pt. 170° C., both compounds being soluble in water or alcohol.

ψ-Selenopyrine, *5-Selenomethyl-1-phenyl-3-methyl-pyrazole,*[1]



Finely powdered selenopyrine is treated with a little ether and the calculated quantity of methyl iodide to form the methiodide. When the action is complete the ether is evaporated off and the residue heated at 11 mm. pressure. At 180° to 200° C., *pseudo*selenopyrine distils as a dark yellow liquid, from which the pure compound, B.pt. 181° C. at 11 mm., may be isolated by fractionation. It has a garlic-like odour,

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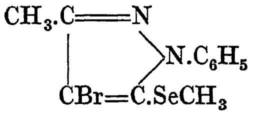
[1] Michaelis and Duntze, *Annalen*, 1914, 404, 36.

is miscible with organic solvents and concentrated acids, but insoluble in water. When heated with concentrated hydrochloric acid in a sealed tube at 200° C., methyl chloride and 1-phenyl-3-methylpyrazole are produced, whilst the selenium is eliminated as the element.

The following *salts* of ψ-selenopyrine have been described: *hydrochloride*, occurring as a crystalline compound, M.pt. 81° C., decomposed by water into its components ; *platinichloride*, a brownish-yellow precipitate, sintering at 147° C. ; *mercurichloride*, crystallising as fine white needles, M.pt. 125° C. ; *nitrate*, forming large white crystals, decomposed by water ; with *silver nitrate* a *double salt* is formed as fine, white needles, M.pt. 175° to 176° C. The methiodide is prepared by heating the components together in a sealed tube at 110° C., and melts at 197° C., ; the *ethiodide* crystallises as white plates, M.pt. 185° C., and when subjected to dry distillation yields 5-*selenoethyl-1-phenyl-3-methylpyrazole* or *ethyl-ψ-selenopyrine*, which has similar properties to the methyl compound, and boils at 182° C. at 15 mm.

ψ-Selenopyrine dibromide is formed when an excess of bromine is added to a chloroform solution of the selenopyrine. It crystallises as shining red needles, M.pt. 110° C., soluble in alcohol or chloroform, insoluble in water. The corresponding *dichloride* is obtained only in poor yield as pale yellow crystals, M.pt. 128° C., whilst the *iodide* is unknown.

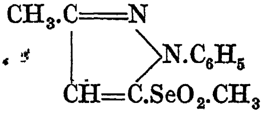
4-Bromo-ψ-selenopyrine,



The preceding dibromide is treated with an aqueous solution of sodium carbonate, when the monobromide crystallises as shining golden-yellow plates, M.pt. 147° C., easily soluble in alcohol, insoluble in water.

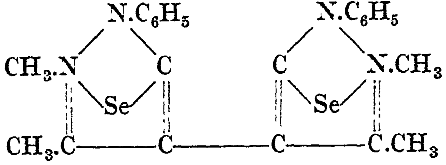
4-Nitroso-ψ-selenopyrine is obtained when nitrous gases are passed into an ice-cold hydrochloric acid solution of the selenopyrine. It forms dark green crystals, melting without decomposition at 117·5° C., readily soluble in ether, chloroform, alcohol or ethyl acetate, insoluble in water or dilute acids. It responds to Liebermann's nitroso test.

1 - Phenyl - 3 - methyl - 5 - methyldioxyselenopyrazole or the *Selenone of ψ-selenopyrine,*

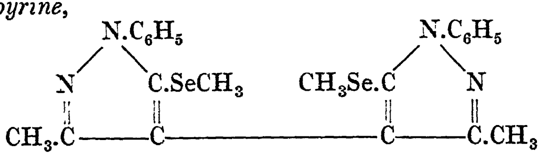


An acetic acid solution of ψ-selenopyrine is treated with an excess of 30 per cent. hydrogen peroxide and the mixture diluted with water after standing for a short time. The solution is well cooled and made alkaline with sodium hydroxide solution, then extracted with ether, from which solution the selenone separates on evaporation. It is obtained as large, colourless needles, M.pt. 126° C., readily soluble in alcohol, ether, benzene or acetic acid, insoluble in water, aqueous alkalis or dilute mineral acids.

Bis-selenopyrine,

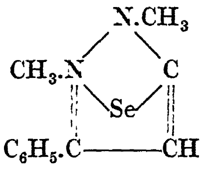


occurs when potassium hydroselenide reacts with *bis*-1-phenyl-3-methyl-5-chloropyrazole. It forms fine, pale yellow needles, M.pt. 270° to 271° C., readily soluble in acetic acid or chloroform, sparingly soluble in alcohol. It combines with methyl iodide at 100° C. in a sealed tube, forming a *methiodide*, which crystallises from alcohol as yellow needles, M.pt. 249° C. The methiodide when heated loses methyl iodide, forming *bis-ψ-selenopyrine*,



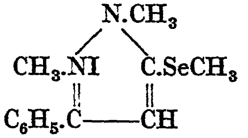
which separates from alcohol as white needles, M.pt. 115° C., and forms salts with concentrated acids.

Isoselenopyrine,[1]



is obtained from 5-chloro-3-phenyl-1-methylpyrazole and potassium hydroselenide in aqueous solution. It forms fine white needles, M.pt. 198° C., soluble in hot water, alcohol, acetic acid or hot dilute hydrochloric acid, insoluble in ether. Its aqueous solution develops no colour with ferric chloride. With *mercuric chloride* it forms a *double salt*, $C_{11}H_{12}N_2Se.HgCl_2$, a white, amorphous powder, melting with decomposition at 202° C., somewhat soluble in water, very sparingly soluble in alcohol. With platinic chloride it gives the *platinichloride* $(C_{11}H_{12}N_2Se.HCl)_2.PtCl_4$, a brown, amorphous powder, insoluble in the usual solvents, commencing to decompose at 150° C. but unmelted at 300° C.

*iso*Selenopyrine in alcohol solution combines with methyl iodide to form the *methiodide*,



This crystallises with 8 molecules of water, melts at 152° C., and is very soluble in water or alcohol. The corresponding *ethiodide* melts at 118° C., and may be crystallised from benzene.

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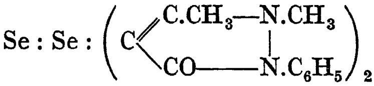
[1] Michaelis and Hagen, *Annalen*, 1907, 352, 193.

Chlorine converts *iso*selenopyrine into *dichloroisoselenopyrine*, $C_{11}H_{12}N_2SeCl_2$, a pale yellow product, decomposing and melting at 163° C. The *dibromide* forms golden-yellow needles, melting with decomposition at 215° C., and yielding *iso*selenopyrine when heated with sodium carbonate solution. The *tetrabromide*, $C_{11}H_{12}N_2SeBr_4$, separates as golden-yellow needles, M.pt. 108° C.

Selenium monochloride reacts with antipyrine[1] as though it were "selenoselenyl dichloride," $Se : SeCl_2$. When a concentrated solution of the chloride in carbon tetrachloride is added to a concentrated solution of antipyrine in chloroform at 0° C., *diantipyryl diselenide* (or selenoselenide) is deposited,



$$Se : Se : \left(C \begin{array}{l} \diagup C.CH_3 - N.CH_3 \\ \qquad\qquad\quad | \\ \diagdown CO \text{———} N.C_6H_5 \end{array} \right)_2$$

This forms yellow needles, M.pt. 215° to 216° C., and deposits selenium on boiling with hydrochloric acid, the solution containing the salt of *diantipyryl selenide*. The latter is precipitated from the salt by sodium carbonate solution, and crystallises from benzene in flakes, M.pt. 240° C., which yield a dihydrochloride and a mercurichloride.

Selenium tetrachloride and antipyrine give *diantipyrylselenium dichloride*, $(C_{11}H_{11}ON_2)_2SeCl_2$, crystallising from benzene as pearly plates, M.pt. 225° C., which change to the foregoing selenide on treatment with alkalis.

Organic selenium compounds can be prepared[2] by treating such substances as aniline, acetanilide, phenol, salicylic acid and nitrophenol with a solution of selenium or selenium dioxide in sulphuric acid at a low temperature. The *product* from *acetanilide* forms colourless crystals, melting at about 260° C. Colourless crystals result from *phenol, salicylic acid* and *resorcinol arsinic acid. Aniline sulphate* yields an almost black powder, and *o-* and *p-nitrophenols* yellow products. *p-Acetamidophenetole* forms a *derivative* $(C_2H_5O.C_6H_3.NHAc)_3Se.SO_4H.H_2O$, crystallising in needles, M.pt. 260° C. with decomposition, whilst diantipyryl selenide, $(C_{11}H_{11}ON_2)_2Se$, yields colourless needles decomposing at 240° C.

The foregoing process has been modified[3] by using selenic acid in place of selenium or selenium dioxide and substituting other solvents for sulphuric acid or using no solvent at all. Thus *o-nitrophenol* and selenic acid in the presence of sulphuric acid give a *yellow powder* containing 16 per cent. of selenium and exploding on heating. *Antipyrine* gives a *compound* (17 per cent. selenium) in the form of small crystals melting at about 238° C. with discoloration.

Selenious oxide and *p-nitroantipyrine* in formic acid solution yield *di-p-nitroantipyryl selenide*, consisting of yellow crystals decomposing at about 260° C. *Di-p-tolylantipyryl selenide*, $(C_{12}H_{13}ON_2)_2Se$, from *p*-tolylantipyrine and selenious acid in alcohol solution, forms colourless crystals melting with decomposition at about 255° C. The *compound* obtained from selenious acid and *resorcinol* in aqueous solution is a brown powder.

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[1] Konek and Schleifer, *Ber.*, 1918, 51, 842.

[2] German Patent, 299510.

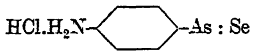
[3] German Patents, 348906, 350376.

HYDROGENATED CINCHONA ALKALOIDS CONTAINING SELENIUM.[1]

To obtain these products selenium dioxide is allowed to react with the hydrogenated cinchona alkaloids or their derivatives in the presence of concentrated sulphuric acid and the products obtained are diluted with water and boiled. *Selenohydroquinine* is prepared from hydroquinine sulphate or hydroquinine sulphuric ester, and forms yellow needles which remain unchanged below 235° C.; *selenoethylhydrocupreine* forms yellow needles, M.pt. 233° to 234° C., and *selenohydrocupreine* separates as small, orange-coloured needles, which are unmelted below 235° C. The products are of use therapeutically.

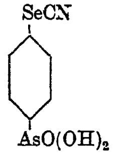
ARSENIC-SELENIUM COMPOUNDS.

4-Aminophenylarsenoselenide hydrochloride,[2]



5 grams of 4-aminophenyldichloroarsine hydrochloride in 20 c.c. of alcohol are treated with a rapid stream of hydrogen selenide. The required compound separates out as an orange powder, sparingly soluble in dilute hydrochloric acid.[3]

Phenylarsinic acid-4-selenocyanate,[4]



occurs when *p*-aminophenylarsinic acid is diazotised and treated with potassium selenocyanate. The *sodium salt* is a yellow powder, easily soluble in water or methyl alcohol, sparingly soluble in ethyl alcohol.

SELENOPYRONINES.[5]

3 : 6 - Tetramethyldiaminoselenopyronine, $C_{17}H_{18}N_2Se$. — A mixture of sodium selenite and sulphuric acid is added gradually to sulphuric acid containing 25 per cent. of sulphur trioxide and at the same time tetramethyldiaminodiphenylmethane is added in small portions, so that it is always in slight excess, the temperature being maintained below 35° C. After an hour and a half the whole is poured upon ice, filtered, and a solution of zinc chloride added to the filtrate. The *zinc chloride double salt* is precipitated in crystalline form. In sulphuric acid this salt gives a red solution which turns blue on dilution with water. The addition of sodium hydroxide to such a solution precipitates a reddish-blue base, which dissolves in ether. The colouring matter gives slightly soluble iodides and nitrates, but insoluble dichromates.

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[1] German Patent, 331145; *Chem. Zentr.*, 1921, ii, 449.

[2] German Patent, 269699.

[3] Sodium 2-mercuriseleno-4-aminophenyl-1-sulphonate is obtained by the action of mercuric chloride (1 mol.) on sodium 2-seleno-4-aminophenyl-1-sulphonate (1 mol.), German Patent, 488931.

[4] German Patent, 255982.

[5] Battegay and Hugel, *Bull. Soc. chim.*, 1920, [iv], 27, 557.

Two rules are said to govern the formation of selenopyronines.[1] Firstly, the diphenylmethane used as the parent substance must give a colour reaction with lead peroxide in acetic acid solution. Secondly, the substituents in the benzene nuclei must be such as will exert in fuming sulphuric acid a directing influence sufficient to cause the new substituent to enter in the *ortho*-position to the methane bridge. Nitro- or amino-groups are not conducive to successful condensation, although alkylation of the amino-group is distinctly advantageous, as it removes the tendency of that group to form ammonium salts.

MISCELLANEOUS SELENIUM COMPOUNDS.

Benzylselenurea, $NH_2.CSe.NH(C_6H_5.CH_2)$,[2] may be obtained by mixing aqueous solutions of benzylamine hydrochloride and potassium selenocyanate, but better results are obtained with dry alcohol solutions containing equimolecular proportions of the two compounds. After removing the potassium chloride the solution is gently evaporated, the final stages being conducted *in vacuo*. Colourless crystals result, M.pt. 70° C. with partial decomposition, the product dissolving readily in alcohol, ether or water. In the solid state or in solution the urea soon decomposes, and the addition of mineral acid or acetic acid to its solutions causes separation of selenium.

Dibenzylselenurea, $NH_2.CSe.N(C_6H_5.CH_2)_2$, is formed when dibenzylamine hydrochloride is used in the foregoing preparation. It forms long, slender, colourless prisms, darkening at 150° C. and decomposing at 216° C. It dissolves in alcohol, ether or hot water, but is sparingly soluble in cold water. With hydrochloric acid it decomposes as follows:

$$NH_2.CSe.N(C_6H_5.CH_2)_2 + HCl = NH(C_6H_5.CH_2)_2.HCl + HCN + Se$$

Selenodimethylaniline, $Se[C_6H_4.N(CH_3)_2]_2$,[3] is obtained by adding 50 grams of selenium chloride in 30 c.c. of ether gradually to a cooled solution of 10 grams of dimethylaniline in 100 c.c. of ether.[4] A dark brown mass separates, which, after decanting off the ether, is dissolved in dilute hydrochloric acid and the solution filtered. An excess of sodium hydroxide solution is then added to the filtrate and dimethylaniline removed in a current of steam, the remaining oil being washed with water, alcohol and ether. The oil soon solidifies, and crystallisation from alcohol yields yellowish needles, M.pt. 124° C., sparingly soluble in cold alcohol or ether. The *sulphate* forms long, colourless needles, M.pt. 55° C., readily soluble in water, and the *picrate* gives small yellow plates, M.pt. 135° C.[5]

Selenodiethylaniline, $Se(C_6H_4.N(C_2H_5)_2)_2$, is prepared in a similar manner to the preceding compound. It forms colourless, asbestos-like needles, M.pt. 83° C., and is moderately soluble in cold

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[1] Battegay and Hugel, *Bull. Soc. chim.*, 1923, [iv], 33, 1103.

[2] Spica, *Gazzetta*, 1877, 7, 90.

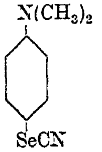
[3] Godchaux, *Ber.*, 1891, 24, 765.

[4] A selenium compound from *benzonitrile* has been obtained by Dechend (*Ber.*, 1874, 7, 1273), but its composition is uncertain.

[5] When a solution of *p-nitrosodimethylaniline* in concentrated hydrochloric acid is treated with hydrogen selenide a bluish-red scum is formed (German Patent, 261793), and when this *leuco derivative* (which is not isolated) is oxidised and subsequently treated with an aqueous solution of zinc chloride, a *double compound* with *zinc chloride* is formed. This *Selenazine Blue* is an analogue of Methylene Blue, and can be used as a dye and for the introduction of selenium into animal tissues. It forms a glistening dark green-bronze powder, readily soluble in water, sparingly soluble in alcohol.

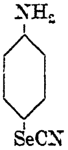
alcohol or ether, readily soluble in hot solvents. The *hydrochloride* melts at 73° C.; the *picrate* forms small plates or needles, melts at 135° C., and is easily soluble in hot alcohol.

p-Selenocyanodimethylaniline (*p-Dimethylaminophenyl selenocyanate*),[1]

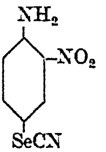


occurs when cyanogen triselenide, $Se_3(CN)_2$, and dimethylaniline react in dry ether. The product separates from alcohol as pale straw-coloured crystals, M.pt. 105° C. The yield is about 90 per cent., and the product is very soluble in most organic solvents.

p-Selenocyanoaniline (*p-Aminophenyl selenocyanate*),

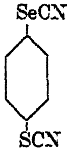


is prepared in a similar manner to the foregoing product. Repeated crystallisation from benzene-light petroleum gives a product of melting-point 93·5° C. When boiled for a long period with hydrochloric acid, red selenium separates. Diazotisation and treatment with cuprous chloride yields *p-chlorophenyl selenocyanate*. *p*-Selenocyanoaniline when dissolved in warm acetic anhydride yields an *acetyl derivative* as white crystals,[2] M.pt. 206° C. This derivative may also be obtained from diazotised *p*-aminoacetanilide and potassium selenocyanate. Nitration of the anilide with nitric acid (density 1·5) at −20° C. gives *2-nitro-4-selenocyanoacetanilide*, yellow needles, M.pt. 215° C., and hydrolysis by hydrochloric acid affords *2-nitro-4-selenocyanoaniline*,



orange needles from alcohol, M.pt. 118° C.

p-Thiocyanoselenocyanobenzene,[3]



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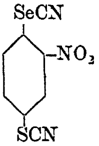
[1] Challenger, Peters and Halévy, *J. Chem. Soc.*, 1926, p. 1648.

[2] Challenger and Peters, *J. Chem. Soc.*, 1928, p. 1364.

[3] Challenger and Peters, *loc. cit.*

is obtained by treating diazotised *p*-aminophenyl thiocyanate with potassium selenocyanate. It separates from chloroform-light petroleum or from alcohol in white needles, M.pt. 109° to 110° C., somewhat volatile in steam and very soluble in acetone or chloroform. Treatment with a mixture of nitric acid (density 1·41) and sulphuric acid at 3° C. gives white crystals of *p-thiocyanobenzene seleninic acid,* M.pt. 154° C.

When diazotised 1-amino-2-nitrophenyl thiocyanate is treated with potassium selenocyanate, *2-nitro-4-thiocyanophenyl selenocyanate* is produced,



This separates from alcohol in yellow needles, M.pt. 147° C., giving a purple colour with alcoholic alkali. In this preparation the nitrothiocyanoaniline is not isolated, a solution of its acetyl derivative in warm hydrochloric acid being diazotised.

The Selenide $[(NHC_6H_5.CO)_2CSe]_2$.[1]—This occurs when malonanilide (5 mols.) and selenium tetrachloride (4 mols.) react in absolute ether at 27° to 30° C. The product darkens at 217° C. and melts at 222° to 223° C. Malon-*m*-chloroanilide also occurs during the preparation. Reduction of the selenide by alkali hydrosulphite affords the original anilide and hydrogen selenide, whilst treatment with bromine gives dibromomalonanilide and selenium bromide.

Corresponding *selenides,* M.pts. 218° to 219° C. and 210° to 211° C., after darkening at 205° C. and 200° C., respectively, are prepared similarly from malon-*p*- and -*m*-toluidides respectively and from malon-β-naphthylamide. Methylmalonanilide furnishes the *selenide* $[(NHC_6H_5.CO)_2C(CH_3)]_2Se$, M.pt. 222° to 224° C.; the corresponding *selenides* from methylmalon-*p*-toluidide, -*m*-toluidide and -β-naphthylamide have M.pts. 224° to 225° C., 221° C. and 229° to 230° C., respectively.

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[1] Naik and Trivedi, *J. Indian Chem. Soc.*, 1930, 7, 239.

CHAPTER IV.

ORGANIC COMPOUNDS OF TELLURIUM.

ALIPHATIC COMPOUNDS OF THE TYPE R_2Te.

CONSIDERABLY less work has been done on the aliphatic derivatives of tellurium than on those of selenium, and whereas the latter element yields the types RSeH, R_2Se and RSeR′, only the type R_2Te is at present known with certainty in the case of tellurium. The methods of preparation used for the dialkyl tellurides are as follows :

(1) An alloy of potassium and tellurium is treated with a concentrated aqueous solution of the barium alkyl sulphate :

$$K_2Te + Ba(RSO_4)_2 = R_2Te + BaSO_4 + K_2SO_4$$

(2) Dialkyl tellurium di-iodides are heated with aqueous sodium sulphite, the hydrogen iodide being removed by the presence of sodium carbonate :

$$R_2TeI_2 + H_2O + Na_2SO_3 = R_2Te + Na_2SO_4 + 2HI$$

(3) Aluminium telluride is heated with alcohols at 250° to 300° C., or with the ether at 300° to 350° C. :

$$\begin{aligned} Al_2Te_3 + 6ROH &= 3R_2Te + 2Al(OH)_3 \\ Al_2Te_3 + 3R_2O &= 3R_2Te + Al_2O_3 \end{aligned}$$

The dialkyl tellurides are heavy oils, which tend to decompose on keeping. Combination takes place slowly with water, probably forming the hydroxides, $R_2Te(OH)_2$. Oxidation by hydrogen peroxide gives the oxides R_2TeO and finally tellurones, R_2TeO_2.

Dimethyl telluride, $(CH_3)_2Te$.—The method first used for isolating this substance consisted in treating a potassium-tellurium alloy with a concentrated aqueous solution of barium methyl sulphate.[1] It appears doubtful whether the method can actually be used for obtaining dimethyl telluride itself, although it might be used for derivatives of this body. An excellent yield of dimethyl telluride is obtained according to the equation[2]

$$\begin{gathered} (CH_3)_2TeI_2 + H_2O + Na_2SO_3 = Na_2SO_4 + 2HI + (CH_3)_2Te \\ 2HI + Na_2CO_3 = 2NaI + CO_2 + H_2O \end{gathered}$$

To a solution of 13 grams of hydrated sodium sulphite and 6 grams of sodium carbonate in 200 c.c. of water contained in a distilling flask connected with a long water-cooled condenser, 20 grams of dimethyl tellurium di-iodide are added. The temperature is slowly raised, the

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[1] Wöhler and Dean, *Annalen*, 1855, 93, 233.

[2] Vernon, *Trans. Chem. Soc.*, 1920, 117, 889.

telluride passing over rapidly at about 75° C., a few minutes' boiling sufficing to distil the product over completely. The resultant oil is separated from water, dried over anhydrous sodium sulphate and fractionated. A recent method of preparation consists of heating aluminium telluride with methyl alcohol at 250° to 300° C., or with dimethyl ether at 300° to 350° C.[1]

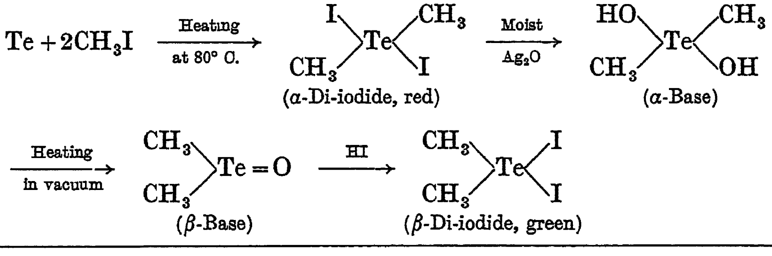
Dimethyl telluride is a very pale yellow oil, B.pt. 94° C. at 770 mm., soon solidifying in liquid air but not in carbon dioxide and ether. It is somewhat heavier than water, and possesses the most abominable and persistent odour of all tellurium compounds. The boiling-points of the dimethyl derivatives of the sixth group of the Periodic System are as follows: Dimethyl oxide, $(CH_3)_2O$, B.pt. $-23°$ C.; dimethyl sulphide, $(CH_3)_2S$, B.pt. 37° C.; dimethyl selenide, $(CH_3)_2Se$, B.pt. 58° C.; and dimethyl telluride, $(CH_3)_2Te$, B.pt. 94° C. The tellurium compound dissolves slowly in water, giving an alkaline solution which may contain the dihydroxide, $(CH_3)_2Te(OH)_2$. If the telluride be boiled for a short time with an excess of hydrogen peroxide the oxide results, $(CH_3)_2TeO$, but prolonged boiling gives the tellurone, $(CH_3)_2TeO_2$. Dimethyl telluride deposits colourless crystals of unknown composition on keeping.[2]

Diethyl telluride, $(C_2H_5)_2Te$,[3] results when a sodium or potassium alloy of tellurium is distilled with an aqueous solution of barium ethyl sulphate. It is a yellowish-red heavy liquid, B.pt. 100° C. It also occurs when triethyl tellurium chloride reacts with zinc diethyl at 100° to 110° C., butane being obtained as a by-product;[4] prepared by this method the boiling-point is given as 140° C. It readily inflames, burning with a bright blue flame, and oxidises in direct sunlight.

Ethyl telluride, C_2H_5TeH, has been described, but no physical constants are reported.[5]

ALIPHATIC COMPOUNDS OF THE TYPES R_2TeX_2, R_3TeX AND $RTeX_3$.

The dialkyl tellurium dihalides have given rise to considerable discussion in recent years. Vernon[6] stated that he isolated two distinct forms of dimethyl tellurium di-iodide, from which two bases were prepared. He formulated these substances as follows,



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[1] Natta, *Atti II Cong. Naz. Chim. Pura Appl.*, 1926, p. 1326.

[2] Drew (*J. Chem. Soc.*, 1929, p. 568) considers that the β-dihalides do not give dimethyl telluride on reduction, but an orange oil of carbylamine odour, probably dimethyl ditelluride.

[3] Wöhler, *Annalen*, 1840, 35, 111; Mallet, *ibid.*, 1851, 79, 223.

[4] Marquardt and Michaelis, *Ber.*, 1888, 21, 2042; compare Heeren, *Jahresber.*, 1861, p. 565.

[5] Natta, *loc. cit.*

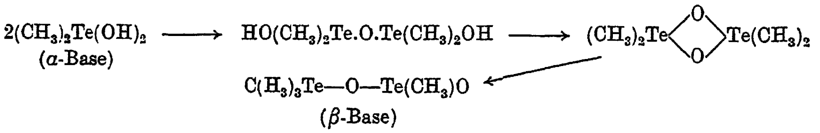
[6] Vernon, *Trans. Chem. Soc.*, 1920, 117, 86, 897; 1921, 119, 105, 687.

and postulated planar distribution of the valencies of the tellurium atom. This work was followed by the production of two dichlorides and two dibromides, the conclusion being that two distinct series (the α- and the β-series) of isomeric compounds were being investigated.[1] Drew [2] has shown that the so-called α-series consists of compounds of the normal type in which the tellurium probably has a tetrahedral valency distribution. The compounds broadly are non-polar in character. The members of the β-series do not appear to be isomeric with the corresponding members of the α-series, but are complex substances, of salt-like character, having the same empirical formulæ.[2] The β-base is a mixed anhydride, of the formula $(CH_3)_3Te.O.Te(CH_3)O$, reacting with hydriodic acid to give colourless trimethyl tellurium iodide and colourless methyl hydroxytellurium oxide (telluracetic acid) or one of its anhydro-derivatives. These two substances are readily separated, the oxide when treated with an excess of hydriodic acid forming methyl tellurium tri-iodide. The two iodides readily unite to give Vernon's β-iodide when mixed in molecular proportions in acetone solution. The changes described above are as follows :

$$\underset{(\alpha\text{-Base})}{2(CH_3)_2Te(OH)_2} \xrightarrow[\text{at 95° C.}]{\text{In vacuum}} \underset{(\beta\text{-Base})}{(CH_3)_3Te.O.Te(CH_3)O} \xrightarrow{\text{HI}} (CH_3)_3TeI + CH_3.TeO.OH$$

$$\xrightarrow{\text{Further HI}} (CH_3)_3TeI + CH_3TeI_3 \longrightarrow \underset{(\beta\text{-Di-iodide})}{(CH_3)_3TeI.CH_3TeI_3}$$

It is suggested that the change of the α- to the β-base takes place probably through an anhydride of the α-base by a molecular rearrangement almost identical with that of the pinacol-pinacolin type:



Similarly trimethyl tellurium bromide and methyl tellurium tribromide combine together in molecular proportions to give Vernon's β-dibromide. To counter the objection that "β-dihalides" might be formed by a rearrangement according to the equation

$$(CH_3)_3TeX + CH_3TeX_3 = 2(CH_3)_2TeX_2$$

compounds containing mixed halogens have been isolated. Drew showed that such products belong to the same family as Vernon's β-dihalides.

The series of compounds isolated by Drew is as follows : $(CH_3)_3TeI.CH_3TeI_3$, purple-black, with a green lustre ; $(CH_3)_3TeBr.CH_3TeI_3$, purple-red, with a golden lustre ; $(CH_3)_3TeI.CH_3TeBr_3$, orange-brown ;

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[1] Lowry and his collaborators have determined a number of the physical constants of these supposed isomeric compounds (*J. Chem. Soc.*, 1928, pp. 307, 1997, 3179; *J. Soc. Chem. Ind.*, 1928, 47, 1246), but in face of Drew's work, which appears to disprove the isomerism, only the references are given here to Lowry's work. Lowry attributes the somerism to the non-equivalence, from the point of view of electron structure, of the halogen-tellurium linkings.

[2] Drew, *J. Chem. Soc.*, 1929, p. 560.

$(CH_3)_3TeBr.CH_3TeBr_3$, yellow. The halogens of both components contribute to the colour of each salt, but the colour is mainly governed by the halogens of the component CH_3TeX_3, which are in excess. This observation, coupled with the fact that the components react to form salts when ground together in the absence of solvents, shows that the $(CH_3)_3TeX$ components possess a mobile halogen atom, probably functioning as a mobile anion, and it becomes highly probable that the salts are correctly represented by the general formula

$$(CH_3)_3\overset{+}{T}e \;.\;.\;.\; \overset{-}{T}e(CH_3)X_4$$

equivalent to the co-ordination formula $[(CH_3)_3Te]Te(CH_3)X_4$, in which all the halogens and alkyl groups are covalently linked to tellurium. The negatively charged tellurium atom is thus associated with 58 electrons, if singlet linkings are assumed to be absent. This view is supported by the fact that a mixture of acetone solutions containing equimolecular proportions of the "β-di-iodide" and potassium iodide, respectively, gives a precipitate of pure trimethyl tellurium iodide. The red filtrate, diluted with chloroform, gives a black substance, probably the salt $\overset{-}{[Te(CH_3)I_4]}\overset{+}{K}$, since it dissociates under the action of moisture into potassium iodide and methyl tellurium tri-iodide.

Dimethyl tellurium di-iodide (Vernon's α-iodide), $(CH_3)_2TeI_2$.[1]—50 grams of amorphous tellurium and 112 grams of methyl iodide are heated together in a water-bath at 80° C. for thirty-six to forty-eight hours in a sealed tube. The product is extracted with chloroform to remove the di-iodide, the yield being about 50 per cent. When recrystallised from chloroform the di-iodide melts at 130° C., and dissolves in most organic solvents. The crystals are monoclinic, the axial ratios being $a : b : c = 0{\cdot}5578 : 1 : 0{\cdot}4310$; $\beta = 72° \; 21'$. The specific gravity is 3·338 at 14° C.[2]

The reaction between tellurium and methyl iodide is reversible, the temperature controlling the resulting products :

$$Te + 2CH_3I \underset{100°\text{ C.}}{\overset{80°\text{ C.}}{\rightleftarrows}} (CH_3)_2TeI_2$$

The di-iodide is not soluble in cold water, but prolonged boiling gives an orange-red solution which, on cooling, redeposits the di-iodide, leaving a colourless solution. The salt becomes partly hydrolysed and the reaction is reversible :

$$(CH_3)_2TeI_2 + 2H_2O \rightleftarrows (CH_3)_2Te(OH)_2 + 2HI$$

Fuming or concentrated nitric acid eliminates the iodine from the di-iodide, white crystals of the *dinitrate*, $(CH_3)_2Te(NO_3)_2$, being deposited.[3] These melt sharply without decomposition at 142° C. The di-iodide gives a green *platinum salt* with chloroplatinic acid. With silver benzoate it forms a *benzoate*, white needles, M.pt. 154° C., and the yellow *picrate*, obtained in a similar manner, crystallises

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[1] Demarçay, *Bull. Soc. chim.*, 1883, [ii], 40, 99; Scott, *Proc. Chem. Soc.*, 1904, 20, 157; Vernon, *Trans. Chem. Soc.*, 1920, 117, 86; 1921, 119, 694; Drew, *J. Chem. Soc.*, 1929, p. 564.

[2] Knaggs and Vernon, *Trans. Chem. Soc.*, 1921, 119, 105.

[3] Compare Wöhler and Dean, *Annalen*, 1855, 93, 236.

in plates. The di-iodide adds on iodine, forming a tetra-iodide, $[(CH_3)_2TeI_2]I_2$.[1]

Dimethyl tellurium dihydroxide,[2] $(CH_3)_2Te(OH)_2$, is prepared by the action of silver hydroxide on the foregoing iodide, either by boiling the components in water or grinding them together with a little water in a mortar. The base forms a strongly alkaline solution which yields salts on treatment with halogen acids.

Dimethyl tellurium dibromide, $(CH_3)_2TeBr_2$, is formed when the preceding di-iodide is treated with hydrobromic acid. Another method consists in dissolving the di-iodide in ammonium hydroxide, precipitating the iodine with ammoniacal silver nitrate, and treating the dimethyl tellurium dinitrate with hydrobromic acid. The reaction is very complicated, but may be summarised as follows:

$$(CH_3)_2TeI_2 + 2AgNO_3 = (CH_3)_2Te(NO_3)_2 + 2AgI$$
$$(CH_3)_2Te(NO_3)_2 + 2HBr = (CH_3)_2TeBr_2 + 2HNO_3$$

The dibromide forms leaf-like crystals, M.pt. 92° C.

Dimethyl tellurium dichloride, $(CH_3)_2TeCl_2$, is prepared by similar methods to those used for the dibromide. It is the most stable of the dimethyl tellurium dihalides, and crystallises from water or alcohol in leaf-like crystals, M.pt. 92° C.[3]

Compound $(CH_3)_3Te.O.Te(CH_3)O$[4] (Vernon's β-base),[5] occurs when dimethyl tellurium di-iodide is dissolved in water and the solution, after filtration, evaporated to dryness at a temperature not exceeding 70° C. at 10 to 20 mm. pressure. The change also takes place in a vacuum at 95° C., the crystals appearing to be stable for at least an hour at this temperature. Evaporation of a solution of dimethyl tellurium dihydroxide yields this mixed anhydride, the change beginning to take place when colourless deliquescent crystals make their first appearance in the solution.

Compound $(CH_3)_3TeI.CH_3TeI_3$[6] (Vernon's β-iodide).[7]—A filtered solution of the foregoing mixed anhydride is treated with hydriodic acid, the precipitate dissolved in acetone and reprecipitated by the addition of chloroform. Glistening crystals result, which are either deep purplish-red or bronzed greenish-black. Each crystal gives a reddish-purple streak, and the purple powder decomposes between 80° and 85° C. It is almost insoluble in chloroform and most non-hydroxylic solvents. The crystals are monoclinic, the parameters being $a:b:c = 0{\cdot}5465:1:0{\cdot}4222$; $\beta = 76°\ 52'$. The density is 3·305 at 14° C.[8]

When the β-di-iodide (1 part) is warmed with aqueous sodium carbonate (0·78 part), a chocolate-coloured precipitate (A) is produced,[9] which, when dissolved in boiling water and precipitated by hydriodic acid, gives a black substance. The latter, extracted with warm chloroform, yields a small amount of dimethyl tellurium di-iodide. The filtrate from (A) on addition of hydriodic acid gives a black

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[1] For the electrometric titration of Vernon's α- and β-dimethyl tellurium bases, see Gilbert and Lowry, *J. Chem. Soc.*, 1928, p. 1997.

[2] Vernon, *Trans. Chem. Soc.*, 1920, 117, 86.

[3] For extinction coefficients and molecular conductivities of Vernon's isomeric α- and β-dimethyl tellurium salts, see Lowry, Goldstein and Gilbert, *J. Chem. Soc.*, 1928, p. 307.

[4] Drew, *loc. cit.*

[5] Vernon, *Trans. Chem. Soc.*, 1920, 117, 889.

[6] Drew, *loc. cit.*

[7] Vernon, *loc. cit.*, p. 86.

[8] Knaggs and Vernon, *loc. cit.*

[9] Drew, *loc. cit.*

precipitate (B). This is removed, and the filtrate slowly deposits crystals resembling potassium permanganate in colour and possessing the constitution $(CH_3)_3TeI.2(CH_3)_2TeI_2$. This product is partly soluble in hot chloroform. The black substance (B) possesses the formula $(CH_3)_3Te.O.TeI_3$ and cannot be crystallised. When this mixed anhydride is treated with boiling water alone, or with aqueous potassium metabisulphite and then with hydriodic acid, small quantities of dimethyl tellurium di-iodide are produced, the action of hot water also yielding a little tellurium tetra-iodide.

A further proof of the constitution of the β-di-iodide is afforded by synthesising it as follows: Trimethyl tellurium iodide and methyl tellurium tri-iodide are intimately mixed in exactly molecular proportions. Both dissolve on being warmed with a little acetone, although the former alone is insoluble in this solvent. The red solution, on dilution with chloroform, gives at once pure β-di-iodide as lustrous greenish-black scales or thin hexagonal plates, further quantities being obtainable from the mother-liquors. The total yield is almost quantitative, the product decomposing at about 83° C.

Compound $(CH_3)_3TeBr.CH_3TeBr_3$ (Vernon's β-dibromide).—Trimethyl tellurium bromide and methyl tellurium tribromide when dissolved in equimolecular proportions in a little acetone combine to yield this molecular compound. The yellow solution on dilution with chloroform deposits lustrous yellow spangles, decomposing at 142° C.

The following *compounds* are prepared from their constituents, precisely as described already for the β-di-iodide and β-dibromide: $(CH_3)_3TeI.CH_3TeBr_3$, forming lustrous orange-brown flat needles in felted masses decomposing at 120° C.; $(CH_3)_3TeBr.CH_3TeI_3$, crystallising as dark purple-red spangles having a golden lustre, becoming black at 90° C. When kept for a few weeks, the latter compound changes to a purple form, but recrystallisation from ethyl alcohol restores the original form.

Dimethyl tellurium di-iodide and trimethyl tellurium iodide combine in the presence of hydriodic acid containing iodine to form a *complex*, probably $(CH_3)_3TeI.(CH_3)_2TeI_2.(CH_3)_2TeI_4$. This forms thin steel-blue needles which melt to a purple liquid near 80° C. and evolve iodine when warmed with water.

The Action of Ammonia and Alkalis upon Dimethyl Tellurium Di-iodide.[1]

When dry ammonia is passed over the di-iodide, saturation takes place in about two and a half hours, the white semi-fluid *substance* formed having the composition $(CH_3)_2TeI_2.6NH_3$. When dry air is led over this substance for forty-eight hours a relatively stable *substance* remains, $(CH_3)_2TeI_2.2NH_3$. The remaining molecules of ammonia disappear if the treatment is prolonged for several days. The system is reversible and may be expressed by the equation

$$(CH_3)_2TeI_2.nNH_3 \rightleftarrows (CH_3)_2TeI_2 + nNH_3$$

Di-iodohexamethyltritellurium dioxide, $(CH_3)_2Te[O.Te(CH_3)_2I]_2$.—A solution of the base prepared from 24 grams of dimethyl

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[1] Vernon, *Trans. Chem. Soc.*, 1921, 119, 687.

tellurium di-iodide is diluted to 150 c.c. and boiled with 6 grams of the powdered di-iodide. The latter rapidly disappears and the solution becomes colourless, then being evaporated to about one-third of its bulk and suddenly cooled ; the glistening scales which separate are collected, washed with absolute alcohol and dried over calcium chloride. The yield is 4 to 6 grams. The product crystallises as minute, colourless, anhydrous scales, melting with decomposition at 152° C., and insoluble in all solvents except water, by which it is extensively hydrolysed. In contact with acids or acid vapour the substance becomes bright red. It quantitatively yields its iodine to silver nitrate, and is converted to the base by silver oxide. A *hydrated form* is also known which contains half a molecule of water, crystallising in large, transparent, highly refrangent, hexagonal plates with bevelled edges.

Di-iodotetramethylditellurium oxide, $O[Te(CH_3)_2I]_2$, occurs when the preceding compound is hydrolysed by boiling with water, or when dimethyl tellurium di-iodide is treated with concentrated ammonium hydroxide. Purification is effected by crystallisation from water, anhydrous greenish-yellow scales resulting, which melt and decompose at 115° C. The body is quite stable at the ordinary temperature, and is insoluble in all solvents with the exception of water and chloroform, being extensively hydrolysed by the former. It has also been isolated in association with half a molecule of chloroform of crystallisation ; this product melts and decomposes at about 116° C., and is insoluble in all solvents, including chloroform, except on prolonged boiling ; the crystals are not stable, and after about twenty-four hours they become opaque and disintegrate into a yellow powder.

The following work on diethyl tellurium dihalides [1] was carried out before Drew's discovery that the corresponding dimethyl compounds do not exist in isomeric form. It is therefore possible that the β-compounds to be described should be represented by formulæ of the type $(C_2H_5)_3TeI.C_2H_5TeI_3$ and not by $(C_2H_5)_2TeI_2$ as shown.

α-Diethyl tellurium di-iodide, $(C_2H_5)_2TeI_2$.—Precipitated tellurium is heated in a Carius tube for ten days at 100° C. with ethyl iodide (2 mols.), the tube being shaken every twelve hours. Little pressure is developed even at 100° C. The di-iodide is extracted with hot chloroform, filtered through a hot funnel and separated by rapid evaporation. It separates from alcohol as large brownish-red crystals, M.pt. 57° C., the yield being about 20 per cent. It adds on iodine in chloroform solution, giving an *α-tetra-iodide*, the same product also resulting when hydriodic acid is added to a solution of the α-base which has been partly oxidised by boiling for a few minutes with hydrogen peroxide and then filtered from resulting diethyltellurone. The tetra-iodide melts at 98° C., and loses iodine in air, regenerating the α-di-iodide. The latter combines with mercury diphenyl yielding $[(C_2H_5)_2TeI_2].(C_6H_5)_2Hg$, a crystalline mass, M.pt. 94° C.

α-Diethyl tellurium dibromide, $(C_2H_5)_2TeBr_2$,[2] occurs as a pale yellow oil of high boiling-point which solidifies when cooled in a freezing mixture of ice and salt. After freeing from the mother-liquor and drying in a vacuum desiccator the solid does not melt until +24° C., but it does not then resolidify on cooling.

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[1] Gilbert and Lowry, *J. Chem. Soc.*, 1928, p. 3179.

[2] Compare Wohler, *Annalen*, 1840, 35, 111; 1852, 84, 73; 1855, 93, 233.

α-Diethyl tellurium dichloride, $(C_2H_5)_2TeCl_2$,[1] is a colourless oil which freezes to a glass in a freezing mixture at −12° C. and melts again at −5° C.

Di-iodotetraethylditellurium oxide, $I[Te(C_2H_5)_2.O.Te(C_2H_5)_2]I$, occurs when the α-di-iodide is ground up with a little concentrated ammonium hydroxide, the product dissolved in the minimum quantity of water, and left to crystallise in a vacuum desiccator. Colourless crystals separate, which melt at 107° C., and turn red on exposure to the air.

α-Diethyl tellurium dihydroxide, $(C_2H_5)_2Te(OH)_2$.[2]—The α-di-iodide when ground with moist silver oxide yields the dihydroxide. With hydriodic acid the α-di-iodide is regenerated, whilst silver nitrate gives a white precipitate, which turns brown and then black. On evaporation to dryness at 100° C. under 15 mm. pressure, a colourless oily residue remains, which changes to a white non-crystalline solid when allowed to cool and come into contact with cold water. This product is sparingly soluble in water, insoluble in organic solvents, decolorises permanganate solution and liberates violet fumes of iodine when warmed with concentrated hydriodic acid. It is apparently *diethyl tellurone*, $(C_2H_5)_2TeO_2$.

β-Diethyl tellurium di-iodide, $(C_2H_5)_2TeI_2$, occurs when hydriodic acid reacts with the β-base or diethyl tellurone. It separates from methyl alcohol as dark purple crystals, M.pt. 42° C., readily soluble in acetone.

The *β-dibromide* is a deep yellow oil, which solidifies to a glass at −12° C. The *β-dichloride* is a colourless oil, solidifying in a freezing mixture and melting again at −10° C.

β-Diethyl tellurium dihydroxide, $(C_2H_5)_2Te(OH)_2$, is prepared by evaporating a solution of the α-base to dryness at 100° C. under 15 mm. pressure in a stream of nitrogen. It is dissolved by breaking a sealed tube of air-free water inside the flask, which is then filled with nitrogen under atmospheric pressure. Hydriodic acid is added and the mixed iodides washed with a few drops of chloroform, in which the α-di-iodide is freely soluble. The pure β-di-iodide is then reconverted into the β-base by the action of silver oxide. The base gives a faint white precipitate with silver nitrate which turns black on boiling, but not in the cold. Hydriodic acid converts the base into the β-di-iodide, the presence of any α-base being detected by the presence of a fine yellow precipitate which remains at the top of the liquid.

The following physical constants have been determined[3] for the preceding diethyl compounds: Extinction coefficients of diethyl tellurium dihalides; molecular conductivities of diethyl tellurium compounds at 25° C., and potentiometric titrations carried out on the two bases.

Trimethyl tellurium iodide, $(CH_3)_3TeI$,[4] may be prepared by treating the dimethyl di-iodide with sodium sulphite and methyl iodide, or by reducing the di-iodide to dimethyl telluride and treating the latter with methyl iodide. The most recent method of preparation

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[1] Compare Mallet, *Annalen*, 1851, 79, 223.

[2] Compare Wöhler, *loc. cit.*; Mallet, *loc. cit.*

[3] Gilbert and Lowry, *loc. cit.*

[4] Cahours, *Compt. rend.*, 1865, 60, 624; Scott, *Proc. Chem. Soc.*, 1904, 20, 157; Vernon, *Trans. Chem. Soc.*, 1920, 117, 894.

is, however, as follows:[1] The β-base from 5 grams of dimethyl tellurium di-iodide is dissolved in about 30 c.c. of water and the vigorously stirred solution is treated with freshly distilled, diluted, colourless hydriodic acid (4·6 c.c. of 11·4 per cent. acid), added drop by drop until the liquid appears nearly neutral to litmus. The solution, after standing in a vacuum over sulphuric acid for one to two hours, gives glistening crystals (0·69 gram) of almost pure trimethyl tellurium iodide. Recrystallisation from hot water yields long needles or large flat prisms, slowly decomposing above 240° C. and disappearing rapidly at 248° C., forming probably dimethyl telluride and methyl iodide. The aqueous solution of the iodide is neutral to litmus and gives no coloration or precipitate with hydrochloric acid or with colourless hydriodic acid.

The filtrate from the iodide on evaporation in a desiccator yields a colourless crystalline solid (1·3 grams). Extraction with small quantities of hot water gradually removes any remaining iodide, a white powder remaining as residue. This is an *anhydride* of *methyl hydroxytellurium oxide* (telluracetic acid), $CH_3.TeO.OH$, which cannot be obtained pure. In aqueous solution it is neutral to litmus, gives no precipitate with silver nitrate, and is reduced by potassium bisulphite to dimethyl ditelluride. It has a persistent odour, and gradually blackens above 230° C.

When potassium iodide is added in molecular proportion to the β-di-iodide, both components being dissolved in acetone, colourless crystals of trimethyl tellurium iodide are immediately deposited in 80 per cent. yield. The deep red filtrate on evaporation to dryness in a desiccator, followed by solution of the residue in acetone and fractional precipitation with chloroform, gives at first a black precipitate of the salt $\overset{+}{K}\overset{-}{[}Te(CH_3)I_4]$ contaminated with free potassium iodide. Some methyl tellurium tri-iodide is found in the mother-liquors.

Trimethyl tellurium bromide, $(CH_3)_3TeBr$, is obtained from the β-base and hydrobromic acid. It forms large, transparent, colourless tablets, slowly decomposing between 250° and 280° C., readily soluble in cold water but almost insoluble in organic solvents. The neutral solution in water contains bromine ions, and gives no precipitate or coloration with colourless hydriodic acid. It unites with *ferric chloride*, giving a *complex* which crystallises as salmon-coloured needles and forms a *complex salt* with *stannic bromide.*

Triethyl tellurium chloride,[2] $(C_2H_5)_3TeCl$, is isolated when an ether solution of tellurium tetrachloride is added dropwise to a similar solution of zinc diethyl. It crystallises from alcohol as colourless plates, M.pt. 174° C., readily soluble in alcohol, sparingly soluble in ether. It is deliquescent in air, and with moist silver oxide gives a *hydroxide.*

Triethyl tellurium bromide, $(C_2H_5)_3TeBr$, is a white deliquescent substance, M.pt. 162° C., dissolving readily in water or alcohol, but insoluble in ether.

Triethyl tellurium iodide, $(C_2H_5)_3TeI$,[3] occurs when the β-diethyl di-iodide is boiled with half an equivalent of sodium carbonate in concentrated solution. It is a white precipitate, blackening without

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[1] Drew, *J. Chem. Soc.*, 1929, p. 565.

[2] Marquardt and Michaelis, *Ber.*, 1888, 21, 2042.

[3] Gilbert and Lowry, *loc. cit.*; compare Marquardt and Michaelis, *loc. cit.*; Becker and Cahours, *Ann. Chim. Phys.*, 1877, [5], 10, 50.

melting at 180° C., appreciably soluble in water, but insoluble in organic solvents.

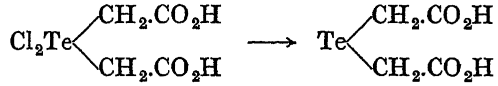
Methyl tellurium tri-iodide, CH_3TeI_3.[1]—The anhydride of methyl hydroxytellurium oxide (telluracetic acid) is dissolved in boiling water, and into the clear cooled solution is stirred colourless hydriodic acid drop by drop, until the liquid is faintly yellow. A bright scarlet precipitate of the tri-iodide is continuously produced, changing in a few seconds to a stable purplish-chocolate form. It slowly decomposes above 100° C., evolves gas near 130° C. and again at 180° C., at which point it melts leaving a black residue. Much of its iodine is liberated in the free state when it is heated in oxygen. It dissolves in acetone or ether, giving bright red solutions, and from the former it is slowly precipitated by chloroform as purple-black needles. It is only sparingly soluble in chloroform or glacial acetic acid, and is hydrolysed by boiling water or dilute hydriodic acid, being reprecipitated on cooling.

Methyl tellurium tribromide, CH_3TeBr_3, forms yellow needles, becoming discoloured above about 140° C., rapidly near 150° C., the dark mass melting to a black effervescing tar at 156° C. The yellow solution in acetone is not precipitated by chloroform.

Dimethyltellurone, $(CH_3)_2TeO_2$,[2] is the oxidation product of dimethyl telluride, or it may be isolated when dimethyl tellurium dihydroxide is oxidised by hydrogen peroxide. It is a white amorphous powder, possessing all the characteristics of the peroxides; thus, it oxidises the halogen acids to the corresponding halogens, decolorises potassium permanganate, and has explosive properties. *Diethyltellurone* has already been dealt with on p. 173. The formation of dimethyltellurone has been questioned by Drew.[3]

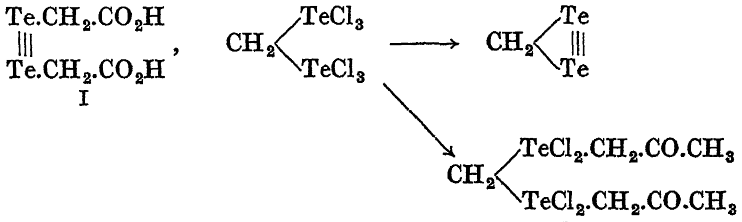
CONDENSATION PRODUCTS OF TELLURIUM TETRACHLORIDE AND ACID ANHYDRIDES.[4]

Tellurium tetrachloride reacts with a large excess of acetic anhydride (6 mols.) in chloroform yielding mainly dichlorotelluridiacetic acid, which may be reduced by alkali metabisulphite to tellurodiacetic acid :



$$Cl_2Te{<}\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix} \longrightarrow Te{<}\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}$$

If only $1\frac{3}{4}$ to 2 molecular proportions of acetic anhydride be used the condensation takes a different course, reduction of the resulting product affording ditellurodiacetic acid (I), and the mother-liquors from the condensation give methylene *bis*-telluritrichloride, which is reducible to ditelluromethane :



$$\begin{matrix}Te.CH_2.CO_2H\\ \vert\vert\vert\\ Te.CH_2.CO_2H\\ \text{I}\end{matrix}, \quad CH_2{<}\begin{matrix}TeCl_3\\TeCl_3\end{matrix} \longrightarrow CH_2{<}\begin{matrix}Te\\ \vert\vert\vert\\ Te\end{matrix}$$

$$\searrow \quad CH_2{<}\begin{matrix}TeCl_2.CH_2.CO.CH_3\\TeCl_2.CH_2.CO.CH_3\end{matrix}$$

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[1] Drew, *loc. cit.*

[2] Vernon, *Trans. Chem. Soc.*, 1920, 117, 894.

[3] Drew, *loc. cit.*

[4] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 531.

The methylene *bis*-telluritrichloride condenses with acetone as shown to form methylene *bis*-telluriacetone dichloride. The formation of the trichloride may take place in one of the three following ways :

(1) Scission of carbon dioxide and hydrogen chloride from a mixture of trichlorotelluriacetic acid and tellurium tetrachloride :

$$Cl_3Te.CH_2.CO_2H + TeCl_4 = CH_2(TeCl_3)_2 + CO_2 + HCl$$

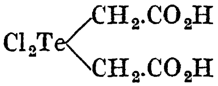
(2) Elimination of water and carbon suboxide from acetanhydro-*bis*-telluritrichloride :

$$(Cl_3Te.CH_2.CO)_2O \longrightarrow (Cl_3Te)_2CH_2 + H_2O + C_3O_2$$

(3) Intermediate formation of keten :

$$CH_2 : CO + 2TeCl_4 \longrightarrow CH_2(TeCl_3)_2 + COCl_2$$

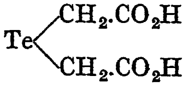
Dichlorotelluridiacetic acid,



$$Cl_2Te\begin{cases}CH_2.CO_2H\\CH_2.CO_2H\end{cases}$$

A mixture consisting of 20 grams of tellurium tetrachloride, 48 grams of acetic anhydride and 150 c.c. of dry chloroform is heated for four hours, decanted from elemental tellurium, diluted with chloroform and concentrated until a flocculent precipitate of grey crystals separates. The total yield is about 13 grams. The product is deliquescent, but when kept in a vacuum desiccator, which is occasionally opened, it becomes stable towards moist air and the melting-point rises to about 159° C. The product is obtained in crystalline form by dissolving it in cold acetone and fractionally precipitating it with petroleum (B.pt. 40° to 60° C.). Final purification is effected by adding petroleum to its solution in ethyl acetate and chloroform, when it separates as transparent, colourless, compact prisms, melting with intumescence at 160° to 161° C. The dichloride separates from ethyl acetate–chloroform–petroleum either with or without ethyl acetate of crystallisation, depending on the proportion of this solvent in the medium. The crystals containing solvent separate as spear-shaped needles, or as vitreous acicular prisms. These forms, when powdered, commence to melt below 100° C., and gradually lose solvent in the desiccator. The dichloride is readily soluble in ether, acetone, alcohol or acetic anhydride, sparingly soluble in chloroform, and insoluble in petroleum or benzene. The mother-liquor from the foregoing preparation yields methylene *bis*-telluritrichloride and an unidentified product intumescing at 152° to 153° C.

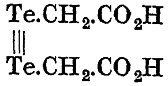
Tellurodiacetic acid,



$$Te\begin{cases}CH_2.CO_2H\\CH_2.CO_2H\end{cases}$$

Dichlorotelluridiacetic acid, 2 grams, is reduced by a solution of 2·8 grams of potassium metabisulphite in 25 c.c. of water, sulphur dioxide being evolved and a pale yellow solution containing grey needles resulting. This latter product is extracted repeatedly with small quantities of ether, tellurodiacetic acid being isolated in quantitative yield on removal of the solvent. Recrystallisation from acetone-benzene gives compact yellow prisms or long yellow needles; these specimens, when left in a desiccator, change to a colourless modification dissolving in acetone to give a yellow solution from which the yellow form may be recovered. Both varieties melt at 140° to 141° C. with blackening. The acid dissolves readily in water, alcohol or ether, is moderately soluble in ethyl acetate or acetone, but almost insoluble in benzene, chloroform or light petroleum. From water or ethyl acetate it separates with solvent of crystallisation, such crystals being yellower and having a lower melting-point. Solutions in the two latter solvents slowly oxidise to give a colourless, amorphous, insoluble oxide, this change being promoted by hydrogen peroxide but inhibited by a trace of sulphur dioxide. Tellurodiacetic acid blackens in the presence of hydrochloric acid, but is stable towards warm aqueous alkalis, and decomposes carbonates. The following salts of the acid are known: *diammonium salt*, sulphur-yellow powder, decomposing at 135° C., soluble in water; *disodium salt*, yellow, soluble in water; *disilver salt*, a white, amorphous, insoluble substance, stable towards light; *copper salt*, a light green precipitate. When suspended in chloroform and treated with chlorine, the acid is converted into *dichloroditelluroacetic acid.*

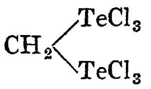
Ditellurodiacetic acid,



$$\begin{array}{l}\mathrm{Te.CH_2.CO_2H}\\ \ \equiv\!\!\!\!\!\!\quad\\ \mathrm{Te.CH_2.CO_2H}\end{array}$$

A mixture of 10·4 grams of tellurium tetrachloride, 6·6 grams of acetic anhydride and 70 c.c. of dry chloroform, after heating under reflux for four hours, is decanted from tellurium and evaporated at the ordinary temperature in a vacuum desiccator to a viscous yellow oil. This oil yields a grey flocculent material when stirred with chloroform, which melts indefinitely at 100° C., and is permanently deliquescent. This product is mainly *acetanhydro-bis-telluritrichloride*, $TeCl_3.CH_2.CO.O.CO.CH_2.TeCl_3$, which, on exposure to moisture, is transformed first to *trichlorotelluriacetic acid*, $TeCl_3.CH_2.CO_2H$, and finally to hydroxylation products of this acid. Reduction of the anhydro-compound with potassium metabisulphite (6 mols. to 1 mol. of anhydro-*bis*-trichloride) gives ditellurodiacetic acid, with evolution of sulphur dioxide. The yield is quantitative. The product is partly precipitated and partly extracted by ether from the deep yellow solution. Recrystallisation from acetone or acetone-benzene containing a little sulphur dioxide gives lustrous orange-red to ruby-red prisms, which become discoloured at 140° C. and blacken at 144° C. Ditellurodiacetic acid dissolves in acetone or alcohol, but is insoluble in chloroform, benzene or light petroleum. In water it is more sparingly soluble than tellurodiacetic acid, but dissolves more readily in ethyl acetate. Ditellurodiacetic acid yields orange or orange-red solutions, in which it becomes oxidised, on exposure, to an insoluble amorphous oxide. It gives soluble yellow *alkali salts*, a light green *copper salt* and an orange *silver salt*, the last two being insoluble, and the silver salt blackening on exposure to light. When suspended in chloroform, the acid combines additively with chlorine or bromine, the *bromide* being a yellow solid. The oily mother-liquor from the preparation of the acid yields one gram of methylene *bis*-telluritrichloride.

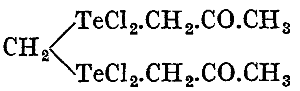
Methylene bis-telluritrichloride,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{TeCl_3}\\ \mathrm{TeCl_3}\end{matrix}$$

The chloroform filtrate from the grey flocculent material mentioned in the preceding preparation, when concentrated and left in a vacuum, slowly deposits large, brittle, prismatic crystals of almost pure methylene *bis*-telluritrichloride (2·3 grams). Recrystallisation from dry chloroform, excluding moist air, gives colourless. transparent prisms, often of acicular habit, melting at 173° C. with effervescence and formation of a red liquid. The last-mentioned property distinguishes this substance from the other tellurium compounds derived from acetic anhydride. Methylene *bis*-telluritrichloride slowly evolves hydrogen chloride in contact with moist air and is immediately hydrolysed by cold water to white amorphous oxide or oxychloride. Successive treatment with aqueous potassium hydroxide and nitric acid produces an aldehydic odour. The trichloride readily condenses with methyl ketones.

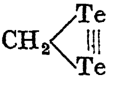
Methylene bis-telluriacetone dichloride,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{TeCl_2.CH_2.CO.CH_3}\\ \mathrm{TeCl_2.CH_2.CO.CH_3}\end{matrix}$$

The foregoing trichloride is boiled under reflux with chloroform containing a small proportion of acetone. Hydrogen chloride is evolved, and on cooling the dichloride separates in quantitative yield. It crystallises from chloroform containing acetone as lustrous, transparent, colourless, prismatic needles, M.pt. 181° C., stable in moist air.

Ditelluromethane,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{Te}\\ |||\\ \mathrm{Te}\end{matrix}$$

Methylene *bis*-telluritrichloride (0·33 gram) is mixed with 0·92 gram of potassium metabisulphite in 10 c.c. of cold water. Sulphur dioxide is evolved and ditelluromethane separates as a dark red amorphous powder. This is washed with cold water and dried in a vacuum, the yield being quantitative. It slowly changes at the ordinary temperature, and rapidly at or above 30° C., to a black modification melting gradually over 50° to 90° C. without decomposition. When heated to a high temperature in air, ditelluromethane explodes with a brilliant bluish-green flash. It is insoluble in water or organic solvents, and when suspended in chloroform it combines with bromine forming a yellow *bromide*, intumescing violently at 214° C.

Trichlorotelluripropionic acid,[1] $\mathrm{Cl_3Te.CH(CH_3).CO_2H}$.—This product results from the interaction of tellurium tetrachloride and propionic anhydride. It melts at 145° to 150° C., and the crystals become liquid on exposure to air.

Ditellurodipropionic acid, $\mathrm{[Te.CH(CH_3).CO_2H]_2}$, is formed by reducing the foregoing compound with aqueous potassium metabisulphite. It is a brick-red solid, M.pt. 75° C., yielding a photosensitive

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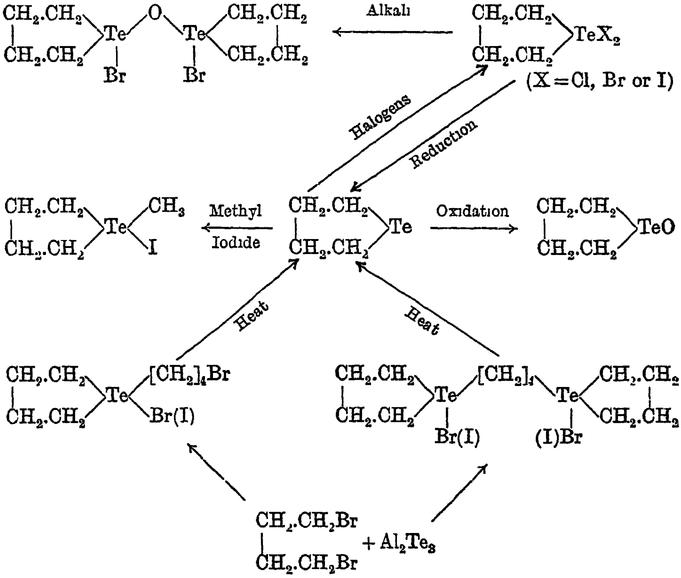
[1] Morgan and Kellett, *J. Chem. Soc.*, 1926, p. 1087.

silver salt, a pale green *copper salt* decomposing at 175° C., and a soluble *potassium salt* crystallising as brick-red plates which decompose at 175° C.

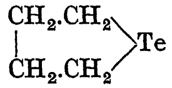
Tribromotelluripropionic acid, $Br_3Te.CH(CH_3).CO_2H$, occurs when the foregoing ditellurodipropionic acid is treated with bromine in chloroform solution. It is a bright yellow solid, M.pt. 139° to 141° C., readily soluble in ether, acetone, warm benzene, chloroform or ethyl acetate. In a sealed tube it changes to a greenish-black decomposition product.[1]

CYCLOTELLUROBUTANE AND ITS DERIVATIVES.[2]

Amorphous tellurium dissolves in αδ-tetramethylene di-iodide at 130° C. to produce *cyclo*telluributane 1 : 1-di-iodide quantitatively, which may be reduced to *cyclo*tellurobutane or tetrahydrotellurophene. The main products obtained from this compound are shown in the following scheme :



cycloTellurobutane (*Tetrahydrotellurophene*),



10 grams of amorphous tellurium are heated at 130° to 140° C. with 63 grams of αδ-tetramethylene di-iodide for five hours with occasional shaking. The solution is filtered hot to remove unchanged tellurium, and on cooling most of the product crystallises. This product is *cyclo*telluributane 1 : 1-di-iodide, and the passage of sulphur dioxide into

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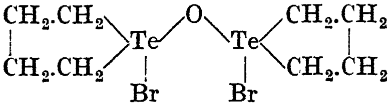
[1] The following are references to the estimation of tellurium in organic compounds: Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831; Morgan and Drew, *Trans. Chem. Soc.*, 1920, 117, 1463; Drew, *J. Chem. Soc.*, 1926, p. 3054. The last-mentioned deals with the estimation of the element in compounds containing tellurium and sulphur.

[2] Morgan and Burstall, *J. Chem. Soc.*, 1931, p. 180.

its boiling aqueous suspension yields *cyclo*tellurobutane, which is extracted with chloroform, dried over calcium chloride, and rectified in carbon dioxide under reduced pressure. It boils at 105° to 106° C. at 122 mm. and at 166° to 167° C. at 761 mm.; $n_D = 1{\cdot}6175$ at 18° C. It possesses a very penetrating and unpleasant odour. Although insoluble in water it is miscible in all proportions with organic solvents. It oxidises readily in air, reacts explosively with concentrated nitric acid, and develops a red coloration with sulphuric acid.

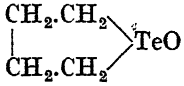
The following derivatives of *cyclo*tellurobutane may be prepared directly from their generators: *mercurichloride*, $C_4H_8 : Te.HgCl_2$, sintering at 140° C. and melting at 146° to 147° C.; *dichloride*, $C_4H_8 : TeCl_2$, M.pt. 111° to 112° C. (may also be prepared from the oxide and concentrated hydrochloric acid); *dibromide*, $C_4H_8 : TeBr_2$, M.pt. 130° C., decomposing at 210° C.; *di-iodide*, $C_4H_8 : TeI_2$, bright red prismatic crystals, M.pt. 149° to 150° C.; *methiodide*, $C_5H_{11}ITe$, crystallising in needles, darkening at 200° C. and vaporising rapidly without melting at 240° C.

Bis-cyclotelluributane 1 : 1′-oxydibromide,



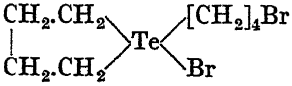
is formed when *cyclo*telluributane 1 : 1-dibromide and the corresponding oxide are warmed together in equimolecular proportions in aqueous solution, or by the addition of sufficient sodium carbonate or sodium hydroxide solution to remove half the bromine from the telluridibromide. The sparingly soluble product separates from warm water as small white prisms melting with decomposition at 207° C. Caustic alkalis convert it into the oxide, and hydrobromic acid regenerates the dibromide.

cycloTelluributane 1-oxide,



arises from the oxidation in air of *cyclo*tellurobutane or the action of caustic or carbonated alkalis on *cyclo*telluributane 1 : 1-dihalides. The crystalline product melts with decomposition at 241° C., and is soluble in water, alcohol or acetone; halogen acids regenerate the corresponding dihalides.

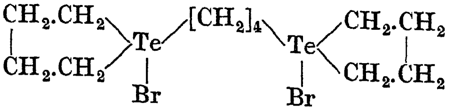
1-δ-Bromobutylcyclotelluributane 1-bromide,



30 grams of aluminium telluride and 67 grams of αδ-tetramethylene dibromide are heated together in a flask fitted with a ground-glass air condenser, a vigorous reaction commencing at 125° C. The flask is then removed and shaken until the reaction subsides, cooling being resorted to if necessary. A little hydrogen bromide is evolved. The heating is then continued at 125° C. for two hours. The cooled semi-solid mixture is extracted successively with carbon tetrachloride,

acetone, alcohol and water. Tetramethylene dibromide (10 grams) is recovered from the carbon tetrachloride extract, and a black insoluble residue (12 grams) remains. The acetone and alcohol extracts crystallise from alcohol as white shining threads, M.pt. 152° to 153° C., dissociating above the melting-point into tetramethylene dibromide and *cyclo*tellurobutane. An aqueous solution of potassium iodide converts the body into the corresponding *1-iodide*, which melts with decomposition at 175° to 176° C.

Tetramethylene-$\alpha\delta$-bis-cyclotelluributane 1 : 1′-dibromide,



separates from the aqueous extract from the preceding reaction between aluminium telluride and $\alpha\delta$-tetramethylene dibromide. It is a white crystalline salt, containing one molecule of water of crystallisation, and at 225° C. it melts with dissociation into tetramethylene dibromide and *cyclo*tellurobutane. Platinic chloride gives a red *chloroplatinate*, M.pt. 135° C. with decomposition. Aqueous potassium iodide converts the dibromide into the corresponding *1 : 1′-di-iodide*, consisting of deep yellow crystals decomposing at 215° C.

CYCLOTELLUROPENTANE AND ITS DERIVATIVES.[1]

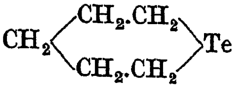
The ring system embodied in these cyclic derivatives is produced by condensing aluminium telluride with $\alpha\epsilon$-pentamethylene dibromide:

$$Al_2Te_3 + 3CH_2Br.[CH_2]_3.CH_2Br = 3C_5H_{10} : Te + 2AlBr_3$$

At this stage, however, addition takes place between the *cyclo*telluropentane and alkylene dihalide, forming two complex telluronium bromides.

Aluminium telluride, 27 grams, and 63·5 grams of $\alpha\epsilon$-pentamethylene dibromide are heated together under reflux and at 165° C. a vigorous reaction ensues. This is moderated by cooling and stirring, and the heating continued for an hour. The semi-solid product is extracted successively with (*a*) carbon tetrachloride to remove unchanged pentamethylene dibromide and most of the *cyclo*telluripentane 1 : 1-dibromide, (*b*) moist acetone to dissolve the remaining 1 : 1-dibromide and 1-ϵ-bromoamyl*cyclo*telluripentane 1-bromide, this solvent also extracting some of the pentamethylene-$\alpha\epsilon$-*bis-cyclo*telluripentane 1 : 1′-dibromide and aluminium bromide, (*c*) water or moist methyl alcohol to extract the remainder of the aluminium bromide and the *bis-cyclo*telluri-compound from a dark grey insoluble residue (6·7 grams). Fractional crystallisation of the three extracts yields 14 grams of 1-ϵ-bromoamyl*cyclo*telluripentane 1-bromide, 23 grams of pentamethylene-$\alpha\epsilon$-*bis-cyclo*telluripentane 1 : 1′-dibromide, and 2 grams of *cyclo*telluripentane 1 : 1-dibromide.

cycloTelluropentane,



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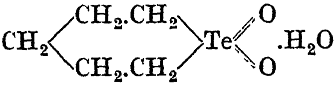
[1] Morgan and Burgess, *J. Chem. Soc.*, 1928, p. 321.

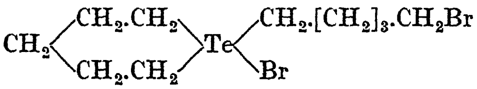
is prepared by reducing the corresponding 1 : 1-dibromide with aqueous potassium metabisulphite. It is a lemon-yellow oil having a very unpleasant alliaceous odour resembling that of trimethylstibine; it boils at 82° to 83° C. at 12 mm., and at 44° to 45° C. at 1 to 2 mm. Exposure to air causes rapid oxidation to a colourless solid, and nitric acid causes a violent reaction to occur. On keeping in a sealed tube for several weeks it becomes reddish-orange in colour, the change being accelerated by light. When its methyl alcohol solution is treated with hydrogen peroxide it gives *cyclotelluripentane 1 : 1-dioxide,*



$$CH_2{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}{>}Te{<}\begin{matrix}O\\ O\end{matrix}.H_2O$$

an insoluble product, darkening on heating and exploding on rapid heating. This has the properties of a tellurone, liberates chlorine from hydrochloric acid, decolorises warm acidified permanganate, and decomposes violently on treatment with concentrated nitric or sulphuric acid.

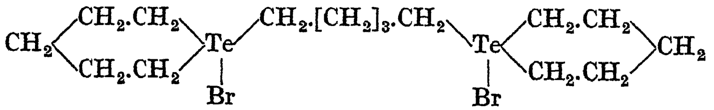
1-ε-Bromoamylcyclotelluripentane 1-bromide,



$$CH_2{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}{>}Te{<}\begin{matrix}CH_2.[CH_2]_3.CH_2Br\\ Br\end{matrix}$$

obtained as already described, crystallises from acetone as colourless, oblong plates, M.pt. 143° to 145° C., resolidifying at 147° C., readily soluble in oxygenated organic solvents, in chloroform and in water. The aqueous solution is faintly acid to litmus and gives an immediate precipitate with silver nitrate.

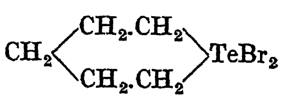
Pentamethylene-$\alpha\epsilon$-bis-cyclotelluripentane 1 : 1′-dibromide,



$$CH_2{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}{>}\underset{Br}{Te}.CH_2.[CH_2]_3.CH_2.\underset{Br}{Te}{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}{>}CH_2$$

isolated from the condensation of aluminium telluride with $\alpha\epsilon$-pentamethylene dibromide, crystallises in colourless needles containing one molecule of water and decomposing at 223° to 224° C. It is readily soluble in water, less soluble in alcohols, and almost insoluble in other organic solvents. The aqueous solution is neutral to litmus and gives with silver nitrate a faint precipitate at first, but which rapidly increases. It adds on bromine forming *pentamethylene-$\alpha\epsilon$-bis-cyclotelluripentane 1 : 1′-bis-perbromide,* $C_5H_{10}[Te(C_5H_{10})Br_3]_2$, M.pt. 102° to 104° C.

cycloTelluripentane 1 : 1-dibromide,



$$CH_2{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}{>}TeBr_2$$

occurs as a by-product in the foregoing condensation, which may be more conveniently carried out by heating the substances to 160°–190° C. under 25 to 30 mm. pressure. It may also be obtained by mixing chloroform solutions of bromine and 1-ε-bromoamyl*cyclo*telluripentane 1-bromide. From carbon tetrachloride it is deposited as pale greenish-yellow prisms and from light petroleum as hexagonal plates, M.pt. 105° to 107° C., soluble in benzene, chloroform or acetone, sparingly soluble in cold alcohol, carbon tetrachloride or light petroleum. Hot water hydrolyses the dibromide, giving an acid solution.

When αε-pentamethylene dichloride or di-iodide replaces the dibromide in the condensation with aluminium telluride, the following chloro- and iodo-derivatives are isolated: 1-ε-*Chloroamylcyclotelluripentane 1-chloride*, M.pt. 149° to 151° C.; *cyclotelluripentane 1 : 1-dichloride*, six-sided prisms, M.pt. 106° to 107° C., isolated by treating the preceding compound with chlorine, and forming a *dichromate* consisting of rosettes of yellow needles; *pentamethylene-αε-bis-cyclotelluripentane 1 : 1′-dichloride*, anhydrous prisms decomposing at 224° to 225° C., and yielding a *1 : 1′-dichromate* as rosettes of daffodil-yellow plates, turning brown at 160° C. and decomposing at 193° C.; 1-ε-*iodoamylcyclotelluripentane 1-iodide*, colourless flakes, M.pt. 135° to 136° C., resolidifying and remelting at 197° to 198° C.; *pentamethylene-αε-bis-cyclotelluripentane 1 : 1′-di-iodide*, brownish-red acicular prisms, melting with decomposition at 216° to 217° C., and *cyclotelluripentane 1 : 1-di-iodide*, forming (*a*) deep red prisms, (*b*) slender orange prisms, the latter changing to the former, both melting at 135° to 136° C., and the red becoming orange at 105° C.

The *monocyclic base*[1] $C_5H_{10}Te(OH)_2$ or $C_5H_{10}TeO$ is prepared by grinding the dibromide with freshly prepared silver oxide, evaporation of the solution in a vacuum giving the base as a colourless solid. Hydriodic acid converts it into a canary-yellow precipitate, M.pt. 136° to 137° C., which is probably the orange form of the *cyclic di-iodide*, M.pt. 135° to 136° C. The *dicyclic base* $(C_5H_{10})_3Te_2(OH)_2$ is isolated in a similar manner to the monocyclic base, but requires six times as long to complete the reaction.

The following tables show the extinction coefficients in alcohol of halogen derivatives of *cyclo*telluropentane and the molecular conductivities ($\Lambda^{25°}$) of these derivatives. The tertiary salts behave as strong electrolytes, like trimethyl tellurium iodide, but the secondary salts resemble dimethyl tellurium di-iodide in losing one molecule of halogen by hydrolysis, giving rise to hydroxyhalides.

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[1] Gilbert and Lowry, *J. Chem. Soc.*, 1928, p. 2658.

[TABLES

EXTINCTION COEFFICIENTS IN ALCOHOL OF HALOGEN DERIVATIVES OF CYCLOTELLUROPENTANE.

(a) Selective absorption.		λ	log ε	λ	log ε
$C_5H_{10}TeI_2$ . . .	Maxima at	3380	3·92	2770	4·05
$C_5H_{10}TeI_4$ . . .	,, ,,	3560	4·28	2880	4·45
$(C_5H_{10})_3Te_2I_6$ (in CH_3OH) .	,, ,,	3560	4·26	2900	4·44
$C_5H_{10}TeBr_2$ . . .	Step-out at λ = 2600 to 2850			log ε = 3·85	

	Wave-lengths for integral values of log ε					
(b) General absorption.	log ε = 1·5	2·0	2·5	3·0	3·5	4·0
$C_5H_{10}TeCl_2$ . . .		2950	2840	2730		
$C_5H_{10}Te(OH)I$ (in water)		2870	2690	2480		
$(C_5H_{10})_2TeI_2$ . . .	3460	3130	2980	2750		
$(C_5H_{10})_2TeBr_2$ . . .		2800	2500	2340		
$(C_5H_{10})_2TeCl_2$ . . .	2680	2520	2340			
$(C_5H_{10})_3Te_2Br_2$ . . .		2900	2580	2420		
$(C_5H_{10})_3Te_2I_2$ . . .				2830	2330	
$(C_5H_{10})_3Te_2Br_6$ (in CH_3OH)				3070	2920	2500

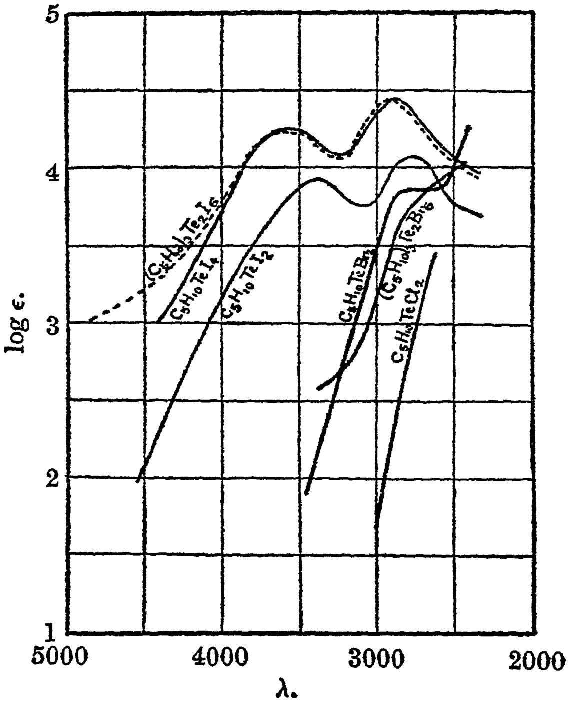


Fig. 1.—Molecular Extinction Coefficients of Cyclic Tellurium Compounds.

MOLECULAR CONDUCTIVITIES ($\Lambda^{25°}$) OF DERIVATIVES OF CYCLOTELLUROPENTANE.

	$v=128$	256	512	1024	2048	4096
Type I.						
$C_5H_{10}TeCl_2$ . . .		475	482	491	482	478
$C_5H_{10}TeBr_2$ . .		481	485	493	492	489
$C_5H_{10}TeI_2$ (orange) .			476	484	484	469
$C_5H_{10}TeI_2$ (purple) .			473	486	493	478
$C_5H_{10}TeI_2$ (purple) 5% alcohol at $v=512$ (corrected values) .			474	479	483	474
$C_5H_{10}TeI_4$ 4·5% alcohol at $v=1024$ (corrected values) .				488	491	493
$C_5H_{10}Te(OH)Cl$ . .	96	98	102	105	107	112
$C_5H_{10}Te(OH)Br$ . .	96	100	104	108	110	112
$C_5H_{10}Te(OH)I$ . .		97	102	107	110	111
$C_5H_{10}Te(OH)_2$ . .	5·5*	6·4	8·0	10·6		
Type II.						
$(C_5H_{10})_2TeCl_2$ . .		92·5	94·4	96·5	98	101
$(C_5H_{10})_2TeBr_2$ . .		90·5	94·4	96·5	99	102
$(C_5H_{10})_2TeI_2$ . .		92	96	98	101·5	104
Type III.						
$(C_5H_{10})_3Te_2Br_2$ . .		199	209	219	225	232
$(C_5H_{10})_3Te_2I_2$ . .		185	197	206	213	219
$(C_5H_{10})_3Te_2Br_6$ . .			1074	1098	1115	1114
$(C_5H_{10})_3Te_2I_6$ . .					965†	986‡

* At $v=42·6$, $\Lambda^{25°}=4·2$, and at $v=64$, $\Lambda^{25°}=4·6$.
† For $v=2260$. ‡ For $v=4520$.

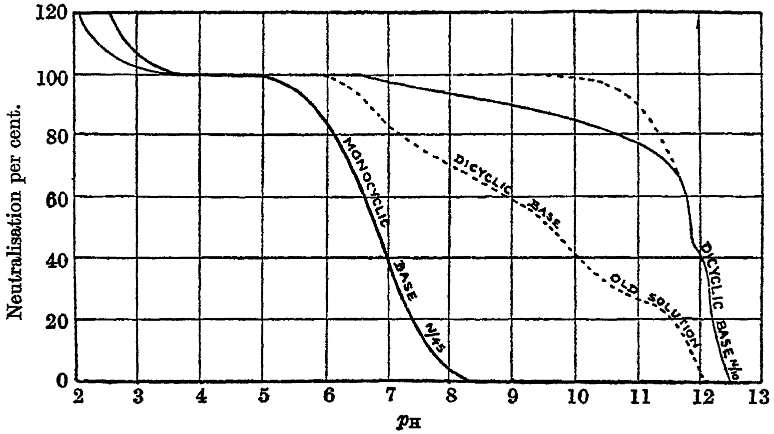
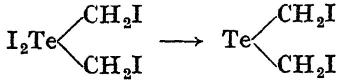


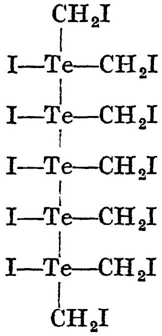
Fig. 2.—Potentiometric Titrations.

TELLURIUM COMPOUNDS OF METHYLENE IODIDE.[1]

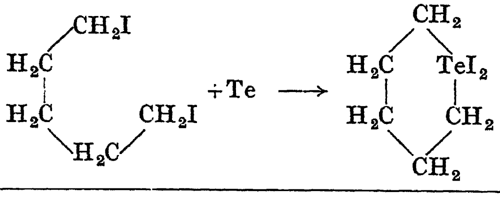
Elemental tellurium and methylene iodide yield *di-iodomethyl tellurium di-iodide,* M.pt. 131° C., which may be reduced by potassium metabisulphite to *di-iodomethyl telluride,* a yellow crystalline substance which changes to an orange polymeride at temperatures above 75° C.



In addition to the foregoing di-iodide, a red amorphous insoluble material results, not reducible by aqueous alkali bisulphites, and which contains a chain of tellurium atoms :



Analysis indicates the probable presence of five tellurium atoms in the chain, but owing to the intractable nature of the product it is unwise to place too much reliance on this conclusion. The substance is accompanied, as is demanded by theory, by the production of a small proportion of tellurium tetra-iodide. It is hoped that an extension of this type of condensation to the cases of higher ω-ω′-di-iodoalkylenes may produce cyclic telluridi-iodides :



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[1] Drew, Private Communication.

CHAPTER V.

ORGANIC COMPOUNDS OF TELLURIUM (*Contd.*).

ARYL TELLURIDES OF THE TYPES R_2Te, R_2Te_2 AND RTeR′.

ARYL tellurides of the type RTeH are unknown at present. The diaryl tellurides are prepared by two methods.

(1) By the interaction of mercury diaryls and elemental tellurium:

$$R_2Hg + 2Te = R_2Te + HgTe$$

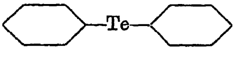
(2) By treating aryl magnesium bromides in ether solution with tellurium dibromide (in the case of diphenyl telluride the by-products consist of diphenyl ditelluride, diphenyl and tellurium).

Only one mixed telluride, RTeR′, is known, namely, phenyl-*p*-tolyl telluride, and this is prepared by the interaction of magnesium phenyl bromide and di-*p*-tolyl tellurium dibromide.

When the preparations are effected by use of the Grignard reagent it is customary to transform the crude diaryl telluride into the diaryl tellurium dibromide, then reduce the latter to obtain the pure diaryl telluride.

The diaryl tellurides combine with halogens to form dihalides, R_2TeX_2, and with mercuric halides mercurihalides are produced, $R_2Te.HgX_2$.

Diphenyl telluride,[1]



This product may be isolated in two ways: (1) Mercury diphenyl (25 grams) and 17·5 grams of tellurium are heated together in a sealed tube for four to five hours at 230° C. and the resulting melt distilled in a vacuum. The product is a yellow oil, B.pt. 174° C. at 10 mm., 182° to 183° C. at 16 mm., and 312° to 320° C. at the ordinary pressure. (2) Phenyl magnesium bromide in ether solution is treated with tellurium dibromide,[2] the mixture boiled for two hours, then decomposed by ice-water. Vacuum distillation of the product gives diphenyl telluride, diphenyl, diphenyl ditelluride, and tellurium is left in the residue. Purification is effected by converting the diphenyl telluride to diphenyl tellurium dichloride or dibromide, the yield of diphenyl telluride in the latter case being 60 per cent. The procedure is as follows: The ditelluride is removed by extraction with hot ether, the sludge digested with ether and treated with dilute hydrochloric acid to dissolve the magnesium hydroxide, the residue containing tellurium. By shaking

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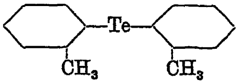
[1] Krafft and Lyons, *Ber.*, 1894, 27, 1768; Krafft and Schuler, *Ber.*, 1895, 28, 1670.
[2] Lederer, *Ber.*, 1915, 48, 1345.

the hydrochloric acid solution with ether the diphenyl tellurium dibromide is dissolved and may be converted to diphenyl telluride by reduction with sodium bisulphite. The resulting product is an oil, B.pt. 182° C. at 14 mm., readily soluble in ether, less soluble in alcohol.

Diphenyl telluride combines directly with halogens giving compounds of the type $(C_6H_5)_2TeX_2$, and with mercuric halides it yields addition products, $(C_6H_5)_2Te.HgX_2$. The *mercurichloride* forms needles from alcohol, sintering at 155° C. and melting at 158° C.; slow crystallisation from alcohol gives a product containing $5C_2H_5OH$, sintering at 115° C. and melting at 130° C. Crystallised from acetic acid the melting-point is 160° to 161° C.[1] The *mercuribromide* crystallises from acetic acid as white needles, M.pt. 148° C.,[2] and the *mercuri-iodide* yields golden-yellow needles sintering at 140° C. and melting at 146° C. *Double salts* are also formed with *basic mercuric cyanide, basic mercuric thiocyanate* and *basic mercuric nitrate.* Near its boiling-point diphenyl telluride gives diphenyl sulphide when treated with sulphur.[3]

Diphenyl ditelluride, $(C_6H_5)_2Te_2$,[4] occurs along with the preceding compound as already mentioned. It separates from ether as long red fibres, M.pt. 53° to 54° C. When its solution in alcohol is treated with sodium it decomposes partly into tellurium and diphenyl telluride, but also gives rise to some *phenyl-telluromercaptan* (phenyl telluride), which is separated as the *mercury chloride derivative,* $C_6H_5.Te.HgCl$, a yellow amorphous product decomposing near 90° C. Oxidation of the ditelluride by nitric acid yields the mixed anhydride of nitric acid and phenyl tellurinic acid, $NO_3.Te(C_6H_5)O$, crystallising in needles which sinter at 229° C. and melt at 232° to 233° C. This anhydride is fairly soluble in alcohol, but insoluble in the usual organic solvents. Careful treatment with sodium hydroxide and hydrochloric acid gives *phenyl tellurinic acid,* $C_6H_5.TeO.OH$, a white powder, sintering at 205° C. and melting at 210° to 211° C. In ordinary organic solvents this acid is insoluble, but it dissolves readily in acids and alkalis.

Di-o-tolyl telluride,[5]



Eight parts of mercury di-*o*-tolyl and 5·6 parts of tellurium are heated together for twelve hours in a sealed tube containing carbon dioxide at a temperature of 225° to 235° C. The product is extracted with ether and the solution distilled *in vacuo.* A crystalline substance results, consisting of small rectangular plates, M.pt. 37° to 38° C., B.pt. 202·5° C. at 16 mm. It may also be obtained by the interaction of *o*-tolyl magnesium bromide and tellurium dibromide.[6] The *mercurichloride*[7] sinters at 209° C. and melts at 212° C.; the *mercuribromide*[8] forms needles or elongated plates, M.pt. 199° to 200° C. with sintering at 195° C., and the *mercuri-iodide* gives sulphur-yellow scales, M.pt. 142° to 143° C. When an aqueous solution of *basic mercuric nitrate* is shaken with an ether solution of di-*o*-tolyl telluride a *compound* $C_{14}H_{15}Te.HgNO_4$ separates as a white precipitate, M.pt. 98° to 99° C.

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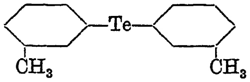
[1] Lederer, *Ber.*, 1914, 47, 277.
[2] Lederer, *Ber.*, 1915, 48, 1422.
[3] Krafft and Steiner, *Ber.*, 1901, 34, 560.
[4] Lederer, *Ber.*, 1915, 48, 1345.
[5] Zeiser, *Ber.*, 1895, 28, 1670.
[6] Lederer, *Ber.*, 1915, 48, 2049.
[7] Lederer, *Ber.*, 1914, 47, 277.
[8] Lederer, *Ber.*, 1915, 48, 1422.

Di-m-tolyl telluride,[1]

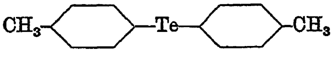


To 143 grams of *m*-bromotoluene and 20·7 grams of magnesium in 500 c.c. of absolute ether, 60 grams of tellurium dibromide are added. The reaction proceeds slowly, and after boiling for three hours the mixture is decomposed with ice-water, being well cooled during the operation. The dark sludge is digested with ether and the ether solution well washed with water. The ether is then removed at the ordinary pressure in a stream of carbon dioxide, the solid residue treated with 20 grams of copper powder and heated to 270° C. in an atmosphere of carbon dioxide, the original red colour disappearing as the ditelluride changes to telluride. Distillation between 190° and 210° C. at 14 mm. gives a yellow oil, which is dissolved in ether and treated with bromine, a pale yellow precipitate of the dibromide (55 grams) separating out. This is reduced to telluride as follows: 66·5 grams of methyl iodide are added to 11·7 grams of magnesium in ether and the dibromide slowly added. The mixture is boiled for 45 minutes, cooled and decomposed by ice-cold water, feebly acidified with dilute hydrochloric acid, the ether layer washed with water and dried over potassium. The solvent is removed in carbon dioxide and the residual oil fractionated, the pure di-*m*-tolyl telluride distilling at 205° to 206° C. at 18 mm. as a pale yellow oil. The yield is 32·5 grams.

The telluride forms a *mercurichloride*, crystallising in needles, sintering at 110° C. and melting at 116° to 117° C., a *mercuribromide*, an oil, solidifying but softening again at 53° C., and a *mercuri-iodide*, isolated only as an oil.

Dibenzyl telluride, $(C_6H_5.CH_2)_2Te$, forms a *compound* with *platinum chloride*, $PtCl_2.2(C_6H_5.CH_2)_2Te$, an orange powder which decomposes in solution with the separation of tellurium, platinum and dibenzyl, but on rapid crystallisation from chloroform is obtained as a microcrystalline powder of greenish-gold colour which darkens and softens at 115° to 120° C.[2]

Di-p-tolyl telluride,[3]



Eight parts of mercury di-*p*-tolyl, 5·6 parts of tellurium and 3 to 4 parts of benzene are heated together in a carbon dioxide atmosphere for fifteen hours at 225° to 230° C. The purification is effected as in the case of the *o*-tolyl compound. Di-*p*-tolyl telluride crystallises as white, flat prisms, M.pt. 63° to 64° C., B.pt. 210° C. at 15 mm. It may also be obtained from *p*-tolyl magnesium bromide and tellurium dibromide, the melting-point then being given as 69° to 70° C.[4] The *mercurichloride* may contain six molecules of alcohol of crystallisation, M.pt. 135° to 136° C., or three molecules of acetic acid, sintering at 128° C., M.pt. 132° to 133° C.[5] The *mercuribromide*[6] sinters at 65° C.

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[1] Lederer, *Ber.*, 1916, 49, 1071.

[2] Fritzmann, *Zeit. anorg. Chem.*, 1924, 133, 119.

[3] Zeiser, *Ber.*, 1895, 28, 1670.

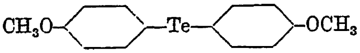
[4] Lederer, *Ber.*, 1915, 48, 2049.

[5] Lederer, *Ber.*, 1914, 47, 277.

[6] Lederer, *Ber.*, 1915, 48, 1422.

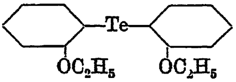
and melts to an oil at 85° C., and the *mercuri-iodide* separates from alcohol as a yellow resin, softening at 50° C. and melting at 65° C.

Di-p-anisyl telluride,[1]



The Grignard solution from 156 grams of *p*-bromoanisole, 20·8 grams of magnesium and 500 c.c. of absolute ether is slowly treated with 60 grams of tellurium dibromide. The reaction is violent, most of the dibromide dissolving; the operation is completed by boiling the mixture for 3 hours on the water-bath. The products are well cooled, decomposed by ice-cold water, the ether layer separated, washed with water and distilled at the ordinary pressure until *p*-bromoanisole is removed. The residue is then heated with 15 grams of copper powder at 275° C. for an hour, and distilled in a vacuum at 210° to 243° C., when the telluride and di-*p*-anisyl are obtained. The distillate is dissolved in ether and the telluride converted to its dibromide by the addition of bromine, about 65 grams of product resulting. The dibromide is then reduced to the telluride as follows: 82 grams of methyl iodide in 250 c.c. of absolute ether are treated with 14·4 grams of magnesium and 70 grams of the dibromide slowly introduced. The latter rapidly dissolves and a mixture of magnesium bromide and iodide separates out as a white powder. After boiling for 30 minutes the whole is decomposed by ice-water and acidified with dilute hydrochloric acid. The ether layer is then washed with water, dried over potassium, the solvent removed in a stream of carbon dioxide and the residue distilled *in vacuo*. Di-*p*-anisyl telluride distils between 237° and 243° C. at 14 mm., and solidifies on standing. From dilute alcohol it separates as glistening plates, sintering at 53° C. and melting between 56° and 57° C. It dissolves in alcohol, benzene or ether. The *mercurichloride* is a yellow amorphous powder, melting towards 90° C.; the *mercuribromide* forms a yellow crystalline powder, softening at 70° C. and melting at 77° to 78° C. to a viscous oil; the *mercuri-iodide* is an amorphous powder, sintering at 55° C. and melting to an oil at 63° C.

Di-o-phenetyl telluride,[2]



The method of preparation is similar to that detailed for di-*p*-anisyl telluride, 105 grams of *o*-bromophenetole, 12·95 grams of magnesium, 500 c.c. of ether and 60 grams of tellurium dibromide giving about 21 grams of di-*o*-phenetyl telluride. The product is a pale yellow viscous oil, B.pt. 244° to 245·5° C., which does not solidify even on cooling in ice. The *mercurichloride* separates from acetic acid as prismatic columns, sintering at 167° C. and melting at 170° to 171° C., whilst when recrystallised from alcohol it sinters at 170° C. and melts at 174° to 175° C.; the *mercuribromide* sinters at 158° C. and melts at 160° to 161° C., and the *mercuri-iodide* sinters at 65° C. and melts to a clear oil towards 90° C.

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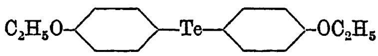
[1] Lederer, *Ber.*, 1916, 49, 1076.

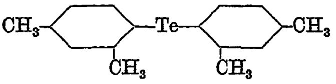
[2] Lederer, *Ber.*, 1916, 49, 2532; compare Rust, *Ber.*, 1897, 30, 2828; Rohrbaech, *Annalen*, 1901, 315, 9; *Ber.*, 1915, 48, 2049.

Di-p-phenetyl telluride,[1]



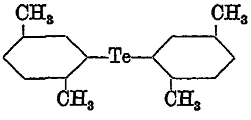
is prepared in the usual manner, but purification is in this case effected through the di-iodide instead of the dibromide. The telluride separates from alcohol as felted needles, sintering at 56° C. and melting at 63° C. to a clear oil, readily dissolving in ether or benzene. The *mercurichloride* forms quadratic plates, sintering at 144° C. and melting at 150° to 151° C.; the *mercuribromide* yields glistening scales, sintering at 150° C. and melting at 155° C., and the *mercuri-iodide* is a yellow powder, softening at 115° C. and melting at 123° to 124° C.

Di-m-xylyl telluride,[2]



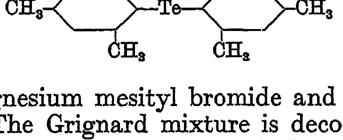
This is prepared from *m*-bromoxylene, magnesium and tellurium dibromide in ether solution, the product being purified through its dibromide, which is reduced by magnesium methyl iodide to the telluride. The telluride is a pale yellow oil, B.pt. 202° to 203° C. at 10 mm., yielding a *mercurichloride*, sintering at 83° C., M.pt. 88° C. when crystallised from alcohol, but sintering at 98° C. and melting at 110° C. from acetic acid; the *mercuribromide* sinters at 95° C. and melts at 99° C.; the *mercuri-iodide* forms plates, sintering at 102° C., M.pt. 107° to 108° C.

Di-p-xylyl telluride,



is prepared in the usual manner, di-*p*-xylyl occurring as a by-product. The telluride crystallises as white glistening needles, M.pt. 72° C., readily soluble in most organic solvents, but sparingly soluble in methyl and ethyl alcohols. The *mercurichloride* softens at 170° C. and melts at 179° to 180° C.; the *mercuribromide* sinters at 165° C. and melts at 169° to 170° C., and the *mercuri-iodide* forms golden-yellow needles, sintering at 164° C., M.pt. 166° to 167° C.

Dimesityl telluride,[3]



is isolated from magnesium mesityl bromide and tellurium dibromide in ether solution. The Grignard mixture is decomposed with copper powder in a stream of carbon dioxide and the products distilled off, dimesityl occurring as a by-product. The telluride softens at 123° C.

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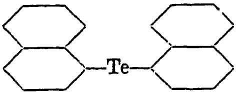
[1] Lederer, *Ber.*, 1917, 50, 283; compare Rust, *loc. cit.*; Rohrbaech, *loc. cit.*
[2] Lederer, *Ber.*, 1916, 49, 334.
[3] Lederer, *Ber.*, 1916, 49, 345.

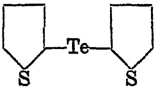
and melts at 129° C., and is readily soluble in most organic solvents with the exception of alcohol and ether.

Di-α-naphthyl telluride,[1]



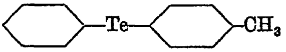
may be prepared by two methods, the earlier one being as follows: 4·5 grams of mercury di-α-naphthyl and 2·5 grams of tellurium are placed in a flask connected to a vacuum pump and the mixture maintained at 190° to 198° C. at 16·5 mm. for eight hours. After cooling, the mixture is steam-distilled and the residue extracted with ether, removal of the solvent giving a 53 per cent. yield of crude product. Excessive or prolonged heating of the reaction mixture brings about a secondary change, yielding a tellurium-free product of melting-point 190° C. The telluride is purified by crystallisation from a large bulk of alcohol, glittering yellowish-brown leaflets being obtained, M.pt. 126·5° C. The more recent preparation consists of treating the Grignard solution from 86·5 grams of α-naphthyl bromide and 10·5 grams of magnesium in ether with 30 grams of tellurium dibromide. The crude product is converted to the dibromide, which is then reduced to the telluride by means of magnesium and ethyl iodide in ether solution. The telluride prepared by this method is identical in all respects with that obtained by the foregoing method. The *mercurichloride* is a yellow crystalline powder, sintering at 183° C. and melting at 187° to 188° C.; the *mercuribromide* softens at 176° C. and melts at 178° to 179° C., and the *mercuri-iodide* sinters at 148° C. and melts with decomposition at 152° to 153° C.

Di-α-thienyl telluride,[2]



is produced by reducing di-α-thienyl tellurium dibromide with stannous chloride in dilute hydrochloric acid at 80° C. The product is an oil of penetrating odour.

Phenyl p-tolyl telluride,[3]



By treating the Grignard solution from 157 grams of bromobenzene, 25 grams of magnesium and 500 c.c. of absolute ether with 90 grams of di-*p*-tolyl tellurium dibromide, crude phenyl *p*-tolyl telluride is obtained in the usual manner. This is converted to the dibromide (68 grams), reduction of which is effected as follows: 50 grams of the dibromide are dissolved in very dilute sodium hydroxide solution and treated with a solution of sodium bisulphite. Reduction takes place immediately and some telluride separates in solid form. The product is extracted with ether, the solution being washed with dilute sodium

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[1] Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 834; Lederer, *Ber.*, 1916, 49, 2663.

[2] Krause and Renwanz, *Ber.*, 1929, 62, [B], 1710.

[3] Lederer, *Ber.*, 1916, 49, 1615.

hydroxide and dried over potassium. The ether is removed by carbon dioxide and the residue fractionated, the yield being about 27 grams. The telluride boils at 207° to 208° C. at 16 mm., and crystallises from alcohol as fine needles, sintering at 59° C. and melting at 63° to 64° C. The *mercurichloride* separates from its components in ether solution as a white amorphous powder, softening at 76° C. and melting at 91° C. From alcohol it is deposited as a yellow amorphous powder sintering at 61° C., whilst warming with acetic acid yields an amorphous product sintering at 64° C. The *mercuribromide* sinters at 40° C. and forms a viscous oil towards 54° C.; the *mercuri-iodide* sinters at 56° C. and melts at about 74° C.

COMPOUNDS OF THE TYPE $Ar_2AlkTeHal$.

These products are formed by the direct combination of diaryl tellurides with alkyl halides.

Diphenyl benzyl tellurium bromide,[1] $(C_6H_5)_2(C_6H_5.CH_2)TeBr$, from diphenyl telluride dissolved in benzyl bromide, forms a crystalline mass, M.pt. 90° to 91° C., converted by silver hydroxide into the corresponding *hydroxide*, a yellow oil, very soluble in water, and yielding a sparingly soluble *picrate* on treatment with picric acid.

Di-o-tolyl methyl tellurium chloride,[2] $(C_7H_7)_2(CH_3)TeCl$, is obtained by boiling the corresponding iodide with silver chloride and water. It separates from water as four-sided plates containing two molecules of water of crystallisation, melting at 93° C. and again at 148° C.; from chloroform it crystallises with half a molecule of chloroform, and melts at 155° to 156° C. The *basic zinc chloride double salt* melts with decomposition at 186° to 187° C.

Di-m-tolyl methyl tellurium iodide,[3] $(C_7H_7)_2(CH_3)TeI$, is obtained in quantitative yield from its components. It crystallises in four-sided columns, soluble in chloroform, insoluble in ether. It melts at 121° to 122° C., splitting up again into its components. When boiled with water and silver oxide and the solution treated with picric acid, a *picrate* is formed; this separates from alcohol with five molecules of solvent of crystallisation, and melts at 114° to 115° C. The *platinichloride* melts with decomposition at 154° to 155° C.

Di-p-anisyl methyl tellurium iodide,[4] $(CH_3O.C_6H_4)_2(CH_3)TeI$, melts at 108° to 109° C., and dissolves in chloroform, but is less soluble in water, from which it separates in a glassy form. The corresponding *picrate* forms yellow needles, sintering at 151° C. and melting at 153° to 154° C.

Di-o-phenetyl methyl tellurium iodide,[5] $(C_2H_5O.C_6H_4)_2(CH_3)TeI$, is obtained by boiling together its components for a short time. It separates from water as monoclinic or triclinic columns, melting at 138° to 140° C., readily soluble in chloroform, sparingly soluble in hot water.

Di-p-phenetyl methyl tellurium iodide,[6] $(C_2H_5O.C_6H_4)_2(CH_3)TeI$.—In order to complete the preparation of this compound it is necessary to allow the di-*p*-phenetyl telluride and methyl iodide to stand together for eight days. The product melts at 69° C., and dissolves in chloroform at the ordinary temperature.

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[1] Lederer, *Ber.*, 1915, 48, 1345.
[2] Lederer, *Ber.*, 1915, 48, 1944.
[3] Lederer, *Ber.*, 1916, 49, 1071.
[4] Lederer, *Ber.*, 1916, 49, 1076.
[5] Lederer, *Ber.*, 1916, 49, 2532.
[6] Lederer, *Ber.*, 1917, 50, 238.

Di-p-xylyl methyl tellurium iodide,[1] $[(CH_3)_2C_6H_3]_2(CH_3)TeI$, melts at 137° C.; it may be converted into a *picrate*, M.pt. 170° C.

Di-α-naphthyl methyl tellurium iodide,[2] $(C_{10}H_7)_2(CH_3)TeI$, crystallises in small needles, melting with decomposition at 146° C., insoluble in chloroform.

Phenyl p-tolyl methyl tellurium iodide, [3]$(C_6H_5)(C_7H_7)(CH_3)TeI$, melts at 73° to 74° C., after sintering at 70° C. It combines with silver *d*-bromocamphor π-sulphonate[4] to give *l-phenyl p-tolyl methyl tellurium d-bromocamphor π-sulphonate*, star-shaped clusters of colourless crystals, M.pt. 180° to 181° C., becoming sticky on exposure to the air. The bromocamphor sulphonate in acetone, when examined in a 2-dcm. polarimeter tube at 18° C., shows the initial rotation $[M]_{5461}^{18^\circ} + 294^\circ$, four minutes after the solvent has been added, and this rises to the steady value $[M]_{5461}^{18^\circ} + 344^\circ$ in 75 minutes. In ethyl acetate the rotation value $[M]_{5461}^{18^\circ} + 275^\circ$ is observed after eight minutes, rising to the value $[M]_{5461}^{18^\circ} + 342$ to 344° in five hours.

l-Phenyl p-tolyl methyl tellurium iodide is precipitated by dissolving the bromocamphor sulphonate in the minimum of acetone and adding a cold dilute aqueous solution of potassium iodide. It is pale yellow and almost insoluble in water, whereas the bromide and chloride are too soluble to be precipitated in the above way. The mutarotation of the *l*-iodide has been measured in ethyl acetate.

d-Phenyl p-tolyl methyl tellurium d-camphor β-sulphonate, from the iodide and Reychler's acid, is obtained only in a solid form. Solutions in acetone gave $[M]_{5461}^{18^\circ} + 119^\circ$, 150°, 123°, 138°. Mutarotation is so slow that a solution with initial rotation $[M]_{5461}^{18^\circ} + 138^\circ$ changed only to $[M]_{5461}^{18^\circ} + 126^\circ$ in a week. A solution having $[M]_{5461}^{18^\circ} + 123^\circ$, when heated in a sealed tube at 100° C., showed no change of rotation in four hours, but a fall to 81° after sixteen hours was observed; the solid separating on evaporation to dryness gave $[M]_{5461}^{18^\circ} + 120^\circ$ again. The dispersion curves for the substance indicate the presence of a cation having a dextrorotation $[M]_{5461}^{18^\circ}$ *ca.* 72°, but this is only regarded as a minimum value, since the camphor sulphonate has not been crystallised. From the sulphonate, *d-phenyl p-tolyl methyl tellurium iodide* has been precipitated by potassium iodide as a pale yellow precipitate, M.pt. 70° to 72° C., but the precipitate is usually inactive. The mutarotation of two active samples has been determined.

Compounds of the Types R_2TeX_2, $R_2Te(OH)X$ and R_2TeO.

It was pointed out on page 187 that the diaryl tellurides combine with halogens to yield dihalides of the type R_2TeX_2. These compounds slowly react with water to give hydroxyhalides, $R_2Te(OH)X$, which at about 150° C. are converted into anhydrides by the elimination of water between the two hydroxyl groups of two molecules of hydroxyhalide,

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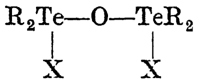
[1] Lederer, *Ber.*, 1916, 49, 334.
[2] Lederer, *Ber.*, 1916, 49, 2663.
[3] Lederer, *Ber.*, 1916, 49, 1615.
[4] Lowry and Gilbert, *J. Chem. Soc.*, 1929, p. 2867.



$$R_2\underset{\underset{\textstyle X}{|}}{Te}-O-\underset{\underset{\textstyle X}{|}}{Te}R_2$$

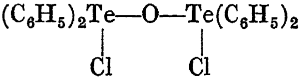
Alkali hydroxides and ammonium hydroxide convert the dihalides to oxides, R_2TeO, aqueous solutions of these products having an alkaline reaction. This may be due to the formation of a hydroxide, $R_2Te(OH)_2$, but such products do not appear to be stable in the solid state.

The interaction of diaryl tellurides and the esters of halogenated fatty acids, *e.g.* methyl bromacetate, gives diaryl-telluretin halide alkyl esters, *e.g.* $(C_6H_5)_2Te(Br).CH_2.COOCH_3$. The halogen present may be chlorine, bromine or iodine, moist silver oxide replacing the bromine by the hydroxyl group.

Diphenyl tellurium dichloride, $(C_6H_5)_2TeCl_2$, may be prepared by the action of chlorine on diphenyl telluride in ether solution,[1] or as follows:[2] 10 grams of diphenyl telluride in 300 c.c. of ether are treated with 100 c.c. of concentrated hydrochloric acid. A stream of oxygen is passed through the two layers of liquid, and the reaction is complete after three to four hours, being favoured by ultra-violet rays. The precipitated solid is recrystallised from absolute alcohol, prisms 2 to 3 cm. long being obtained. The dichloride is very soluble in methyl alcohol or chloroform, sparingly soluble in benzene or ligroin. It melts at 160° to 161° C., and is unchanged after five to six hours' heating at 280° C. in a carbon dioxide atmosphere, but at higher temperatures it is decomposed.

Diphenyl tellurium hydroxychloride, $(C_6H_5)_2Te(OH)Cl$.—The foregoing compound reacts slowly with cold water forming the hydroxychloride, the reaction being more rapid on boiling. The basic chloride melts at 233° to 234° C., and is sparingly soluble in water, alcohol or chloroform, insoluble in ether, benzene, toluene or ligroin. An aqueous solution of the salt gives a yellow precipitate with picric acid.

Diphenyl tellurium chloride anhydride,



$$(C_6H_5)_2\underset{\underset{\textstyle Cl}{|}}{Te}-O-\underset{\underset{\textstyle Cl}{|}}{Te}(C_6H_5)_2$$

The hydroxychloride when heated at 145° to 150° C. until constant in weight is converted into the anhydride. This has the same melting-point as the basic salt, but is much less soluble in chloroform.

Diphenyl tellurium dibromide, $(C_6H_5)_2TeBr_2$, occurs when diphenyl telluride reacts with bromine,[3] or when the bromine is replaced by hydrobromic acid and the process conducted in the manner described for the corresponding dichloride.[4] The dibromide may be crystallised from chloroform, melts at 203·5° C., and when heated to 280° C. the bromine still remains attached to the tellurium atom. It forms crystals belonging to the tetragonal system and a second modification which is triclinic and gives the following values:[5]

$$a : b : c = 1{\cdot}56631 : 1 : 0{\cdot}85954\,;\quad \alpha = 94^\circ\ 31',\ \beta = 114^\circ\ 37',\ \gamma = 112^\circ\ 5'$$

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[1] Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831.

[2] Lederer, *Annalen*, 1912, 391, 326.

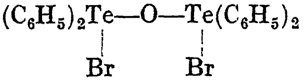
[3] Krafft and Lyons, *Ber.*, 1894, 27, 1770.

[4] Lederer, *loc. cit.*

[5] Billows, *Chem. Zentr.*, 1905, i, 930.

Diphenyl tellurium hydroxybromide, $(C_6H_5)_2Te(OH)Br$, may be obtained by treating the dibromide with water or the corresponding hydroxychloride with sodium or potassium bromide. It melts at 264° to 265° C., is moderately soluble in methyl alcohol but sparingly soluble in boiling water. Treatment with acetic acid yields the dibromide, and the mother-liquors from this give a substance which is probably the diacetate. The latter with 5 per cent. sodium hydroxide gives the oxide.

Diphenyl tellurium bromide anhydride,



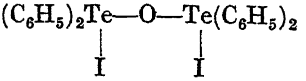
$$(C_6H_5)_2\underset{\substack{|\\ Br}}{Te}-O-\underset{\substack{|\\ Br}}{Te}(C_6H_5)_2$$

The foregoing basic bromide is converted into the anhydride when heated at 160° to 170° C. The anhydride melts at 264° to 265° C., and is sparingly soluble in methyl alcohol.

Diphenyl tellurium di-iodide,[1] $(C_6H_5)_2TeI_2$, separates as a red precipitate when an ether solution of iodine is added to a similar solution of diphenyl telluride. It crystallises from chloroform as small, Bordeaux-red crystals, M.pt. 237° to 238° C. on rapid heating. It is slightly soluble in benzene, toluene, ligroin or alcohols.

Diphenyl tellurium hydroxyiodide, $(C_6H_5)_2Te(OH)I$.—The di-iodide appears to be stable when heated with water, so that the hydroxyiodide is obtained by treating the corresponding basic chloride or bromide with sodium or potassium iodide. In a large excess of the latter, the basic iodide dissolves. From methyl alcohol it crystallises as microscopic canary-yellow columns, sintering at 199° C. and melting at 214° to 215° C. It is soluble in chloroform, but practically insoluble in alcohol or water.

Diphenyl tellurium iodide anhydride,



$$(C_6H_5)_2\underset{\substack{|\\ I}}{Te}-O-\underset{\substack{|\\ I}}{Te}(C_6H_5)_2$$

occurs when the basic iodide is slowly heated to 180° C. It melts at 216° to 217° C.

Diphenyl tellurium dihydroxide, $(C_6H_5)_2Te(OH)_2$, and **Diphenyl tellurium oxide,** $(C_6H_5)_2TeO$.—The latter compound was first isolated by treating the dibromide with 5 per cent. sodium hydroxide.[2] The reactants are warmed to 50° C., when the change is complete. The resulting product melts at 185° C. Aqueous solutions do not contain much oxide, but the addition of hydrochloric acid causes it to separate. Solutions of the oxide have an alkaline reaction and the *dihydroxide* separates out, but this changes to the oxide in air.[3] Recrystallisation of the dihydroxide from water yields crystals, melting at 192° to 193° C.; from xylene the product melts at 187° C. If the hot solution be exposed too long to the air a compound melting at 250° C. is obtained. The oxide is also obtained in small quantities when an ether solution of diphenyl telluride is treated with oxygen, but the oxidation is extremely slow.

Diphenyl tellurium dinitrate, $(C_6H_5)_2Te(NO_3)_2$,[4] is prepared

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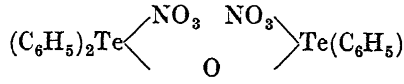
[1] Compare Lederer, *Compt. rend.*, 1910, 151, 611.

[2] Krafft and Lyons, *loc. cit.*

[3] Lederer, *loc. cit.*

[4] Lederer, *Ber.*, 1916, 49, 1082.

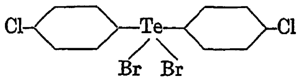
by warming diphenyl telluride with nitric acid or dissolving the oxide in nitric acid. The neutral nitrate appears as prismatic columns, M.pt. 160° C. It dissolves in benzene, toluene, xylene or absolute alcohol, but is insoluble in carbon tetrachloride or ligroin. When treated with water the *anhydride of the basic nitrate* results :



$$(C_6H_5)_2Te\begin{matrix}NO_3 & & NO_3\\ & O & \end{matrix}Te(C_6H_5)_2$$

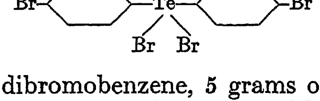
This forms compact prisms, M.pt. 223° to 224° C., soluble in alcohol, chloroform or water, reduction by sulphurous acid giving the telluride.

Di-p-chlorodiphenyl tellurium dibromide,[1]

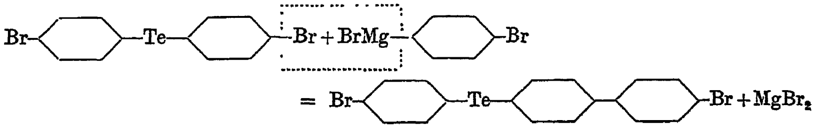


p-Chlorobromobenzene, 40·6 grams, and 5 grams of magnesium are warmed together on a water-bath for thirty minutes, when most of the magnesium disappears. 20 grams of tellurium dibromide are then added slowly and the whole boiled for three hours on the water-bath. Benzene (50 c.c.) is then added and the mixture decomposed with water, being well cooled during the process. The ether and benzene are distilled off in a stream of carbon dioxide, any moisture present removed *in vacuo* and finally *p*-chlorobromobenzene distilled off. The residue is dissolved in 250 c.c. of ether, the solution filtered, cooled and treated with bromine. The dibromide separates as a yellow precipitate, a further quantity being isolated by evaporation of the mother-liquors. The yield is about 19 grams, and the product sinters at 180° C., melting at 184° to 185° C. It is soluble in cold benzene, toluene, xylene, chloroform, carbon disulphide or warm carbon tetrachloride, but sparingly soluble in alcohols.

Di-p-bromodiphenyl tellurium dibromide,



From 50 grams of *p*-dibromobenzene, 5 grams of magnesium, 100 c.c. of absolute ether and 20 grams of tellurium dibromide, worked up in the manner described in the foregoing preparation, two substances (A) and (B) are isolated. The product (B) (7·5 grams) is di-*p*-bromodiphenyl tellurium dibromide, and consists of small needles, M.pt. 195° to 196° C. after repeated crystallisation. It has a similar solubility to the chloro-compound. The substance (A) (6·5 grams) is *p-bromophenyl p'-bromodiphenylyl tellurium dibromide*, an insoluble powder, possibly formed owing to the following reaction taking place :



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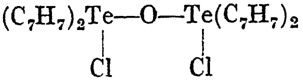
[1] Lederer, *Ber.*, 1916, 49, 2002.

Di-o-tolyl tellurium dichloride, $(CH_3.C_6H_4)_2TeCl_2$, is prepared in a similar manner to the corresponding phenyl compound. It is best recrystallised from absolute alcohol, separating as small monoclinic tablets. M.pt. 183° C., readily soluble in benzene, toluene or xylene, but sparingly soluble in ligroin, methyl or ethyl alcohol.

Di-o-tolyl tellurium chloride anhydride,



$$(C_7H_7)_2\underset{\substack{|\\ Cl}}{Te}—O—\underset{\substack{|\\ Cl}}{Te}(C_7H_7)_2$$

When the foregoing dichloride is treated with water the basic chloride is not isolated, but only the anhydride. It crystallises from water or chloroform-alcohol in thick prisms, M.pt. 220° to 222° C., readily soluble in chloroform, sparingly soluble in water or alcohols.

Di-o-tolyl tellurium dibromide,[1] $(CH_3.C_6H_4)_2TeBr_2$, obtained in the usual way, dissolves in chloroform, benzene or toluene, but is sparingly soluble in alcohols or cold ligroin, more soluble in hot ligroin.

Di-o-tolyl tellurium bromide anhydride, $(C_7H_7)_2Te(Br).O.(Br)Te(C_7H_7)_2$, melts with decomposition at 224° to 225° C. on rapid heating. In addition to the usual method of preparation it may be obtained by dissolving equimolecular quantities of di-*o*-tolyl tellurium oxide and dibromide in toluene. It may be recrystallised from water or chloroform-alcohol.

Di-o-tolyl tellurium di-iodide, $(CH_3.C_6H_4)_2TeI_2$, separates from chloroform as garnet-red, rhombohedral crystals, M.pt. 175° to 176° C., sparingly soluble in ligroin, from which it appears in vermilion crystals. It dissolves in potassium iodide. No positive results have been obtained concerning the existence of a basic iodide.

Di-o-tolyl tellurium oxide, $(CH_3.C_6H_4)_2TeO$, occurs when the dibromide is treated with 5 per cent. sodium hydroxide. It separates from toluene as small monoclinic columns, sintering at 199° C. and melting at 205° to 206° C., readily soluble in alcohols, sparingly soluble in benzene or toluene. Its aqueous solution has an alkaline reaction.

Di-o-tolyl tellurium dinitrate, $(CH_3.C_6H_4)_2Te(NO_3)_2$,[2] forms lancets or rods.

Di-m-tolyl tellurium dichloride, $(CH_3.C_6H_4)_2TeCl_2$,[3] is formed when di-*m*-tolyl telluride in ether solution is chlorinated. The product appears as needles, sintering at 128° C. and melting at 131° to 132° C., readily soluble at the ordinary temperature in benzene, toluene, xylene, carbon disulphide, chloroform or carbon tetrachloride, less soluble in methyl or ethyl alcohol, insoluble in petroleum. When the dichloride is boiled with water a white powder separates on cooling; this melts at 87° C. to a viscous oil which gradually becomes watery. Analysis shows this product to be a *basic salt* and not the anhydride.

Di-m-tolyl tellurium dibromide, $(CH_3.C_6H_4)_2TeBr_2$, forms pale yellow needles, sintering at 163° C. and melting at 165° to 166° C. Its solubility is similar to that of the preceding chloride.

Di-m-tolyl tellurium di-iodide, $(C_6H_3.C_6H_4)_2TeI_2$, appears as

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[1] Compare Zeiser, *Ber.*, 1895, 28, 1670.

[2] Lederer, *Ber.*, 1916, 49, 1082.

[3] Lederer, *Ber.*, 1916, 49, 1071.

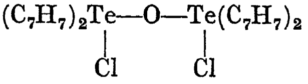
golden-orange plates, sintering at 159° C. and melting without decomposition at 164° C.

Di-m-tolyl tellurium oxide, $(CH_3.C_6H_4)_2TeO$, occurs when the dibromide is heated on the water-bath with ammonium hydroxide. Recrystallised from a mixture of benzene and xylene it sinters at 160° C. and melts at 163° to 164° C., but from xylene alone it sinters at 154° C. and melts at 155° to 156° C. Its solution in water is strongly alkaline.

Di-p-tolyl tellurium dichloride, $(CH_3.C_6H_4)_2TeCl_2$,[1] is obtained in a similar way to the phenyl compound. It separates from absolute alcohol as small needles or plates of the triclinic system, M.pt. 166° to 167° C., soluble in chloroform, benzene, toluene, xylene or ligroin, sparingly soluble in methyl alcohol.

Di-p-tolyl tellurium hydroxychloride, $(CH_3.C_6H_4)_2Te(OH)Cl$, crystallises from water in needles, M.pt. 261° to 263° C., sparingly soluble in water or ethyl alcohol, more soluble in methyl alcohol or chloroform.

Di-p-tolyl tellurium chloride anhydride,



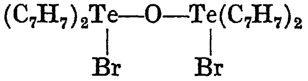
$$(C_7H_7)_2\underset{\underset{\displaystyle Cl}{|}}{Te}—O—\underset{\underset{\displaystyle Cl}{|}}{Te}(C_7H_7)_2$$

occurs when the preceding compound is heated in an air-oven at 145° to 150° C. It is sparingly soluble in chloroform, and melts at 261° to 263° C.

Di-p-tolyl tellurium dibromide,[2] $(CH_3.C_6H_4)_2TeBr_2$, is readily soluble in chloroform, benzene or toluene, practically insoluble in methyl or ethyl alcohol.

Di-p-tolyl tellurium hydroxybromide, $(CH_3.C_6H_4)_2Te(OH)Br$, crystallises in minute prisms, M.pt. 269° to 270° C., sparingly soluble in alcohols, more soluble in chloroform, insoluble in benzene, toluene, ether or carbon disulphide.

Di-p-tolyl tellurium bromide anhydride,



$$(C_7H_7)_2\underset{\underset{\displaystyle Br}{|}}{Te}—O—\underset{\underset{\displaystyle Br}{|}}{Te}(C_7H_7)_2$$

is formed by heating the hydroxybromide at 160° to 170° C., whilst standing over calcium chloride also partially brings about the same change.

Di-p-tolyl tellurium di-iodide, $(CH_3.C_6H_4)_2TeI_2$, crystallises from toluene as deep red prismatic crystals of the monoclinic system, melting at 218° to 219° C. on rapid heating.

Di-p-tolyl tellurium hydroxyiodide, $(CH_3.C_6H_4)_2Te(OH)I$, sinters at 190° C. and melts at 203° to 204° C. It readily dissolves in an excess of potassium iodide, and separates from methyl alcohol as a canary-yellow powder, but warming at 50° C. in this solvent causes decomposition into the di-iodide and oxide. It cannot be converted into an anhydride.

Di-p-tolyl tellurium oxide, $(CH_3.C_6H_4)_2TeO$, is formed when the dibromide is treated with 5 per cent. sodium hydroxide solution. It crystallises in crusts, M.pt. 166° to 167° C., and appears to oxidise further in air giving a product of melting-point 205° to 206° C. It is

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[1] Lederer, *Annalen*, 1912, 391, 326.

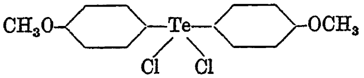
[2] Compare Zeiser, *Ber.*, 1895, 28, 1670.

best recrystallised from benzene-toluene mixture; it readily dissolves in methyl and ethyl alcohols, but is less soluble in ligroin.

Di-p-tolyl tellurium dihydroxide, $(CH_3.C_6H_4)_2Te(OH)_2$, is an unstable product, giving an alkaline solution in water. It is formed by dissolving the oxide in water, and analysis shows that it gradually reverts to the oxide.

Di-p-tolyl tellurium hydroxynitrate, $(CH_3.C_6H_4)_2Te(OH)NO_3$.[1] —Di-*p*-tolyl telluride is heated on the water-bath with nitric acid, the solution treated with an excess of water, the whole boiled and filtered and the precipitated hydroxynitrate collected. The addition of boiling water to the filtrate causes the separation of resinous matter, which is removed, the new filtrate yielding more hydroxynitrate as needles on cooling. The product melts at 237° to 238° C., and dissolves in water with an acid reaction, an amorphous substance being deposited as the solution cools. The latter product sinters at 170° C. and melts at 202° C.

Di-p-anisyl tellurium dichloride,[2]



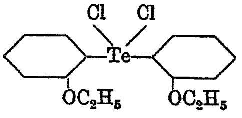
This is isolated in the usual manner from di-*p*-anisyl telluride. It sinters at 180° C. and melts at 183° to 184° C. The crystals consist of four-sided columns, easily soluble in warm benzene, toluene, xylene or chloroform, less soluble in alcohols, carbon disulphide or carbon tetrachloride, insoluble in petroleum ether. Boiling with water for a prolonged period yields a product of which the tellurium content lies between that of the dichloride and that of the oxide.

Di-p-anisyl tellurium dibromide, $(CH_3O.C_6H_4)_2TeBr_2$, is insoluble in methyl alcohol, otherwise it has a similar solubility to the foregoing compound. For purposes of analysis the dibromide is dried at 135° C.

Di-p-anisyl tellurium di-iodide, $(CH_3O.C_6H_4)_2TeI_2$, is prepared from its components in ether solution. It crystallises as dark red needles, sintering at 160° C. and melting between 166° and 167° C. In ether, methyl or ethyl alcohol or petroleum ether the di-iodide is practically insoluble, but it dissolves in the other solvents detailed above.

Di-p-anisyl tellurium oxide, $(CH_3O.C_6H_4)_2TeO$, occurs when 5 grams of the dibromide and 2·5 grams of sodium hydroxide in 50 c.c. of water are heated together for thirty minutes on the water-bath. It separates from benzene as fine needles, sintering at 189° C. and melting at 190° to 191° C. Long standing in air appears to lower the melting-point. The oxide dissolves readily in chloroform and methyl or ethyl alcohol, but is much less soluble in benzene, toluene, xylene, carbon tetrachloride or carbon disulphide. The solution in water has a strongly alkaline reaction.

Di-o-phenetyl tellurium dichloride,[3]



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[1] Lederer, *Ber.*, 1916, 49, 1082.

[2] Lederer, *Ber.*, 1916, 49, 1076; compare Rust, *Ber.*, 1897, 30, 2828.

[3] Lederer, *Ber.*, 1916, 49, 2532; compare Rust, *loc. cit.*

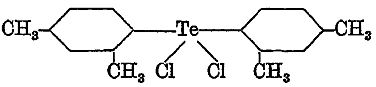
sinters at 160° C. and melts at 163° to 164° C. It is soluble at the ordinary temperature in benzene, toluene, chloroform or carbon disulphide, soluble in warm xylene or carbon tetrachloride, sparingly soluble in methyl or ethyl alcohol. It crystallises from benzene in columns.

Di-o-phenetyl tellurium dibromide, $(C_2H_5O.C_6H_4)_2TeBr_2$, forms small pale yellow needles when an ether solution of di-*o*-phenetyl telluride is treated with bromine. It crystallises as four-sided columns, sintering at 180° C., melting at 183° to 184° C., and having a similar solubility to the dichloride.

Di-o-phenetyl tellurium di-iodide, $(C_2H_5O.C_6H_4)_2TeI_2$, crystallises as four-sided columns or rhombic plates, sintering at 212° C., melting at 214° to 215° C., dissolving readily in cold chloroform or carbon disulphide, also in benzene, toluene or xylene at the ordinary temperature, very slightly soluble in methyl or ethyl alcohol.

Di-o-phenetyl tellurium oxide, $(C_2H_5O.C_6H_4)_2TeO$.—The dibromide in a finely divided state is boiled with concentrated ammonium hydroxide until the colour changes from yellow to white. The product crystallises from toluene as short needles, sintering at 202° C. and melting at 205° to 206° C. The oxide dissolves in chloroform and methyl or ethyl alcohol in the cold, also in warm benzene, toluene, xylene or carbon disulphide; it is very sparingly soluble in carbon tetrachloride.

Di-m-xylyl tellurium dichloride,[1]



is obtained from di-*m*-xylyl telluride by chlorination in ether solution. It forms microscopic columns, soluble in benzene, toluene, xylene, chloroform or carbon disulphide in the cold, very soluble in warm carbon tetrachloride, less soluble in alcohols and insoluble in petroleum ether. It sinters at 185° C. and melts at 187° to 188° C.

Di-m-xylyl tellurium hydroxychloride, $[(CH_3)_2C_6H_3]_2Te(OH)Cl$.—The preceding compound reacts with a large bulk of water to form the hydroxychloride, consisting of small needles, M.pt. 239° to 240° C. An aqueous solution of the product has an acid reaction. When the needles are washed with water and dried in air they fall to a white powder, M.pt. 229° to 230° C., which also forms an acid solution in water.

Di-m-xylyl tellurium dibromide, $[(CH_3)_2C_6H_3]_2TeBr_2$, crystallises from chloroform as microscopic prismatic yellow columns containing solvent of crystallisation, sintering at 197° C. and melting at 200° to 201° C. Its solubility is similar to that of the dichloride.

Di-m-xylyl tellurium di-iodide, $[(CH_3)_2C_6H_3]_2TeI_2$, forms ruby-red columns, sintering at 179° C. and melting at 181° to 182° C. It dissolves in benzene, toluene, xylene, chloroform or carbon disulphide, is sparingly soluble in ether or ethyl alcohol, and insoluble in methyl alcohol or petroleum ether.

Di-m-xylyl tellurium oxide, $[(CH_3)_2C_6H_3]_2TeO$.—The corresponding dibromide is converted to the oxide by warming with sodium hydroxide on the water-bath. The oxide sinters at 212° C., melts at

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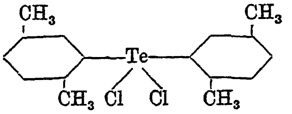
[1] Lederer, *Ber.*, 1916, 49, 334.

216° to 217° C. and is practically insoluble in water, the solution, however, reacting alkaline.

Di-p-xylyl tellurium dichloride,



is prepared in the usual manner using ether as solvent. It forms colourless needles, M.pt. 197° to 198° C., soluble in benzene, toluene, xylene, chloroform or carbon disulphide, less soluble in alcohols, and insoluble in light petroleum.

Di-p-xylyl tellurium hydroxychloride, $[(CH_3)_2C_6H_3]_2Te(OH)Cl$, is the product resulting when the foregoing dichloride is boiled with water. It is a crystalline powder, sintering at 223° C. and melting at 227° C., soluble in water and imparting an acid reaction to the solution.

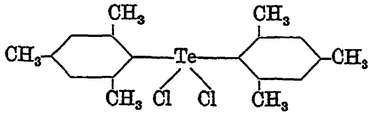
Di-p-xylyl tellurium dibromide, $[(CH_3)_2C_6H_3]_2TeBr_2$, forms yellow needles, M.pt. 189° to 190° C. Its solubility is similar to that of the foregoing dichloride. Prolonged treatment with water does not yield a body giving a neutral solution.

Di-p-xylyl tellurium di-iodide, $[(CH_3)_2C_6H_3]_2TeI_2$, crystallises from alcohol as reddish-brown needles containing alcohol of crystallisation, and from benzene it gives reddish-brown needles, sintering at 156° C. and melting at 161° to 162° C.

Potassium iodide converts the hydroxychloride to *hydroxyiodide*, a reddish-brown powder, sintering at 50° C. and melting at 70° C. when dried in air.

Di-p-xylyl tellurium oxide, $[(CH_3)_2C_6H_3]_2TeO$, occurs when the dibromide is treated with sodium hydroxide solution and the mixture warmed on the water-bath. From hot benzene it separates as a microcrystalline powder, sintering at 223° C. and melting at 225° to 226° C. It dissolves in the usual organic solvents, but is sparingly soluble in water, the solution having an alkaline reaction. The oxide appears to crystallise from water as oxide and not as hydroxide, since the product does not lose weight even when heated to 150° C. for eight hours.

Dimesityl tellurium dichloride,[1]



prepared by passing chlorine into an ether solution of the corresponding telluride, crystallises in needles, sintering at 177° C. and melting at 178° to 179° C. It dissolves readily in benzene, toluene, xylene or chloroform, but is less soluble in alcohol or petroleum ether and practically insoluble in ethyl ether.

Dimesityl tellurium hydroxychloride, $[(CH_3)_3C_6H_2]_2Te(OH)Cl$, is prepared by boiling the preceding compound with water. It is a white powder, M.pt. 220° C.

Dimesityl tellurium dibromide, $[(CH_3)_3C_6H_2]_2TeBr_2$, crystallises in yellow needles, M.pt. 205° to 206° C., having a similar solubility to the dichloride.

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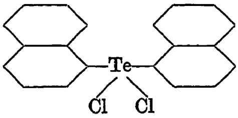
[1] Lederer, *Ber.*, 1916, 49, 345.

Dimesityl tellurium di-iodide, $[(CH_3)_3C_6H_2]_2TeI_2$, when rapidly heated sinters at 108° C. and melts at 111° C. The *hydroxyiodide* is obtained by dissolving the hydroxychloride in a large bulk of water and adding a cooled solution of potassium iodide; it is a yellow precipitate, sintering at 93° C. and melting at 100° C.

Dimesityl tellurium oxide, $[(CH_3)_3C_6H_2]_2TeO$.—The dibromide is quantitatively converted to the oxide by concentrated ammonium hydroxide; if sodium hydroxide is used the reaction is very slow. The oxide crystallises as small columns, sintering at 202° C. and melting at 204° to 205° C. It is soluble in the usual solvents, but dissolves only with difficulty in water, giving a neutral solution.

Di-α-naphthyl tellurium dichloride,[1]



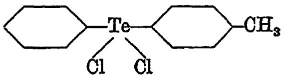
separates from xylene as colourless granules, M.pt. 265° C., soluble in the usual organic solvents.

Di-α-naphthyl tellurium dibromide, $(C_{10}H_7)_2TeBr_2$, forms yellow crystals from carbon disulphide, M.pt. 244° C.

Di-α-naphthyl tellurium di-iodide, $(C_{10}H_7)_2TeI_2$,[2] is obtained in quantitative yield by the usual method. It forms Bordeaux-red needles, M.pt. 184° to 186° C., soluble in benzene, toluene, xylene, chloroform or carbon disulphide, sparingly soluble in petroleum ether or alcohols.

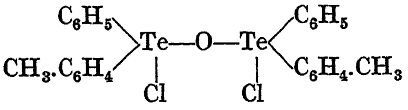
Di-α-naphthyl tellurium oxide, $(C_{10}H_7)_2TeO$, is isolated when the dibromide is treated with sodium hydroxide solution. It is a crystalline powder, melting at 224° to 225° C., soluble in warm benzene, toluene, xylene or carbon disulphide, less soluble in methyl alcohol or carbon tetrachloride.

Phenyl p-tolyl tellurium dichloride,[3]



crystallises from methyl alcohol as needles, sintering at 129° C. and melting at 135° to 136° C. It has the usual solubilities. The *dibromide* forms wide, flat needles, sintering at 169° C. and melting at 175° to 176° C.; the *di-iodide* separates as carmine needles, sintering at 198° C. and melting at 204° C. The *oxide* is deposited from toluene as a white, granular mass.

Phenyl p-tolyl tellurium chloride anhydride,



$$\begin{array}{r} C_6H_5 \\ CH_3.C_6H_4 \end{array}\!>\!\underset{Cl}{\underset{|}{Te}}—O—\underset{Cl}{\underset{|}{Te}}\!<\!\begin{array}{l} C_6H_5 \\ C_6H_4.CH_3 \end{array}$$

is formed by the action of a large bulk of water upon the dichloride. It crystallises from water as microscopic columns of the monoclinic or

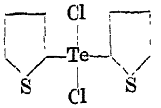
[1] Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 834.

[2] Lederer, *Ber.*, 1916, 49, 2663.

[3] Lederer, *Ber.*, 1916, 49, 1615.

triclinic system, sintering at 238° C. and melting at 243° to 244° C. Treatment with potassium bromide converts it to the *bromide anhydride*, sintering at 256° C. and melting at 259° to 260° C. The *hydroxyiodide*, $(C_6H_5)(CH_3.C_6H_4)Te(OH)I$, is the sole product when the chloride anhydride is treated with potassium iodide; it sinters at 198° C. and melts at 200° to 201° C.

Di-α-thienyl tellurium dichloride,[1]



occurs when di-α-thienyl telluride in ether is treated with the requisite quantity of chlorine dissolved in carbon tetrachloride. It crystallises as minute, colourless needles, M.pt. 189·5° C. (corr.), darkening at 210° C. and decomposing at about 250° C.

Di-α-thienyl tellurium dibromide, $(C_4H_3S)_2TeBr_2$, is prepared from α-thienyl magnesium bromide and tellurium dibromide in cooled ether solution. It forms citron-yellow, highly refractive, six-sided prisms, M.pt. 195° C. (corr.), decomposing towards 220° C. In the light it becomes brownish-yellow. It is soluble in acetone, benzene, chloroform or carbon disulphide, sparingly soluble in hot carbon tetrachloride or alcohol, practically insoluble in ether or petroleum ether. It dissolves in a large bulk of hot water, but is partially hydrolysed.

Di-α-thienyl tellurium di-iodide, $(C_4H_3S)_2TeI_2$, is precipitated as a microcrystalline powder when an ether solution of iodine is added dropwise to a solution of di-α-thienyl telluride in the same solvent. It crystallises from hot benzene as dark violet (permanganate coloured) hexagonal prisms, M.pt. 126·5° C., decomposing at 190° C.

Diphenyl-telluretin bromide methyl ester,[2] $(C_6H_5)_2Te(Br).CH_2.COOCH_3$, is obtained by the interaction of diphenyl telluride and methyl bromacetate. It is a white powder, M.pt. 99° to 100° C., very soluble in hot water and separating on cooling as prismatic crystals, M.pt. 105° to 106° C. Boiling alcohol splits it up into its components. The corresponding *ethyl ester* melts at 63° to 64° C.

Diphenyl-telluretin chloride methyl ester, $(C_6H_5)_2Te(Cl).CH_2.COOCH_3$, occurs when the foregoing bromide in aqueous solution is boiled with a suspension of silver chloride. It crystallises from hot water in prisms, sintering at 109° C. and melting at 115° to 116° C., readily soluble in chloroform. It gives a *mercurichloride*, melting with decomposition at 35° to 36° C., a *platinichloride*, melting and decomposing at 60° C., a *chromate*, sintering at 55° C. and melting at 72° to 73° C., and a *dichromate*, sintering at 60° C. and melting at 115° C.; *compounds* are also formed with *zinc* and *gold chlorides*. Picric acid transforms the chloride to the *picrate*, $(C_6H_5)_2Te(Cl).CH_2.COOCH_3.C_6H_2(NO_2)_3OH$, M.pt. 144° to 145° C.

Diphenyl-telluretin bromide, $(C_6H_5)_2Te(Br).CH_2.COOH$, is the condensation product of diphenyl telluride and bromacetic acid, but has not been isolated in the solid state. The *chloride, picrate* and *platinichloride* have not been obtained in a pure state.

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[1] Krause and Renwanz, *Ber.*, 1929, 62, [B], 1710.

[2] Lederer, *Ber.*, 1913, 46, 1358.

Diphenyl-telluretin, $(C_6H_5)_2Te(OH).CH_2.COOH$.—The preceding bromide, when treated with moist silver oxide, exchanges its bromine for the hydroxyl group. The product sinters at 100° C., melts at 117° to 118° C., dissolves readily in warm chloroform, but is insoluble in benzene, toluene, ligroin or ether. It forms salts with acids.

Diphenyl-telluretin iodide ethyl ester,[1] $(C_6H_5)_2Te(I)CH_2.COOC_2H_5$, is isolated from diphenyl telluride and ethyl iodo-acetate. It forms yellow crystals, readily soluble in chloroform and melting at 110° C.

Diphenyl-α-propionyl-telluretin bromide, $(C_6H_5)_2Te(Br).CH(CH_3)COOH$, from α-bromopropionic acid and diphenyl telluride, is an amorphous powder, sintering at 50° C. and melting at 98° C. The analysis of this product does not give good results.

Diphenyl-α-propionyl-telluretin bromide methyl ester.[2]—The preparation of this compound is carried out at 50° C. The product is a white powder, sintering at 95° C. and melting at 110° C. It is sparingly soluble in cold water, and decomposes on boiling the solution. The corresponding *ethyl ester* sinters at 103° C. and melts at 125° C., and the *propyl ester* softens at about 81° C. and melts at 99° C.; both are soluble in cold chloroform.

Diphenyl-α-butyryl-telluretin bromide methyl ester, $(C_6H_5)_2Te(Br).CH(CH_2.CH_3)COOCH_3$, is a white amorphous powder, readily soluble in chloroform. It sinters at 103° C. and forms an oil at 116° C.

Diphenyl-α-butyryl-telluretin bromide ethyl ester,[3] $(C_6H_5)_2Te(Br).CH(CH_2.CH_3)COOC_2H_5$, is the condensation product formed when diphenyl telluride and ethyl α-bromobutyrate are heated together for ten hours at 60° to 70° C. It is a white amorphous powder, readily soluble in chloroform, sintering at 114° C. and melting at 142° to 143° C. The corresponding *isobutyryl compound*, $(C_6H_5)_2Te(Br).[C(CH_3)_2]COOC_2H_5$, sinters at 95° C. and gives an oil at 130° C.

Diphenyl-α-butyryl-telluretin bromide, $(C_6H_5)_2Te(Br).CH(CH_2.CH_3)COOH$, is obtained only in very small yield; it sinters at 55° C. and melts at 84° to 85° C.

Di-p-tolyl-telluretin bromide methyl ester, $(CH_3.C_6H_4)_2Te(Br).CH_2.COOCH_3$.—When di-*p*-tolyl telluride and methyl bromacetate are allowed to stand together for 24 hours a white crystalline mass separates out. After five days the whole is mixed with absolute ether and the resulting crystals then kept for twenty-four hours over ether. The product is finally purified by dissolving it in chloroform and reprecipitating it by ether, the process being repeated three times. The ester sinters at 88° C. and melts at 92° to 93° C. If recrystallised from methyl bromacetate it contains two molecules of solvent of crystallisation and sinters at 64° C., melting at 68° C. The corresponding *ethyl ester* sinters at 97° C. and melts at 102° to 103° C.

Di-p-tolyl-telluretin bromide, $(CH_3.C_6H_4)_2Te(Br).CH_2.CO_2H$, is mentioned in the literature, but does not appear to have been obtained in a pure state.

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[1] Lederer, *Ber.*, 1915, 48, 1944.

[2] Lederer, *Ber.*, 1913, 46, 1810.

[3] Lederer, *Ber.*, 1915, 48, 1944.

COMPOUNDS OF THE TYPE R_3TeX.

Whilst the interaction of aryl magnesium halides and tellurium dibromide leads to the production of diaryl tellurides, the substitution of tellurium tetrachloride for the dibromide yields derivatives of the type R_3TeX. By working up the Grignard complex in the usual way and treating the aqueous solution of the solid residue with potassium iodide, the compounds are isolated as iodides, R_3TeI. Another method of preparation consists of treating aryl magnesium halides with diaryl tellurium dihalides. Treatment of the iodides with moist silver oxide gives the corresponding hydroxides, which react with acids to form salts. The Grignard reagent transforms the triaryl tellurium halides into diaryl tellurides :

$$R_3TeCl + RMgBr = R_2Te + R.R + MgClBr$$

Triphenyl tellurium iodide, $(C_6H_5)_3TeI$,[1] is obtained by the interaction of phenyl magnesium bromide and tellurium tetrachloride, the solid residue isolated after working up the Grignard mixture in the usual manner being dissolved in water and treated with hot potassium iodide solution. Triphenyl tellurium iodide crystallises from water in needles, softening at 245° C. and melting at 247° to 249° C., soluble in benzene, ether or ligroin, less soluble in alcohol and sparingly soluble in chloroform. When its aqueous solution is boiled with a suspension of silver bromide, *triphenyl tellurium bromide* is obtained, M.pt. 259° to 260° C., and this is very soluble in methyl alcohol or chloroform, less soluble in ethyl alcohol and insoluble in benzene, ether or ligroin. If the silver bromide be replaced by silver chloride, *triphenyl tellurium chloride* is formed. This melts at 244° to 245° C. and has a similar solubility to the foregoing product. With mercuric chloride, auric chloride and stannous chloride it gives precipitates, likewise with picric acid, potassium dichromate and platinic chloride. Phenyl magnesium bromide reacts with the chloride as follows :

$$(C_6H_5)_3TeCl + C_6H_5MgBr = (C_6H_5)_2Te + C_6H_5.C_6H_5 + MgClBr$$

Triphenyl tellurium hydroxide may be isolated from the iodide by boiling with silver oxide and water. It is an alkaline resin, yielding a *picrate*, consisting of broad yellow needles, M.pt. 160° C.[2]

Tri-o-tolyl tellurium iodide,[3] $(CH_3.C_6H_4)_3TeI$, forms needles, M.pt. 195° to 196° C. The *hydroxide* yields a *picrate*, forming long yellow prisms, M.pt. 182° C., a *chloride*, stout columns, M.pt. 175° to 176° C., and a *bromide*, M.pt. 197° to 198° C.[4]

Tri-m-tolyl tellurium iodide[5] separates from water in scales which sinter at 154° C. and melt at 156° to 157° C., and from ether in scales softening at 158° C. and melting at 160° to 161° C. The corresponding *picrate* forms small needles from alcohol, M.pt. 152° to 153° C. The *bromide* is an amorphous powder. The *chloride* yields a *mercurichloride*, $(CH_3.C_6H_4)_3TeCl.HgCl_2$, white plates, M.pt. 159° to 160° C.

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[1] Lederer, *Ber.*, 1911, 44, 2287; *Compt. rend.*, 1910, 151, 611.

[2] Lederer, *Ber.*, 1915, 48, 1944.

[3] Lederer, *Ber.*, 1911, 44, 2287.

[4] Lederer, *Ber.*, 1915, 48, 1944.

[5] Lederer, *Ber.*, 1916, 49, 1385.

Tri-p-tolyl tellurium iodide[1] melts with decomposition at 232° to 233° C., dissolves readily in methyl alcohol or chloroform, less readily in benzene or ether, and is insoluble in water. *Tri-p-tolyl tellurium bromide* occurs when the iodide or chloride is boiled with silver bromide. It melts at 265° to 266° C. with decomposition, and dissolves in alcohols or chloroform, but is insoluble in benzene or ether. *Tri-p-tolyl tellurium chloride* is prepared from the bromide in the usual way. It melts at 260° to 261° C. and gives precipitates with the chlorides of mercury, tin and gold, picric acid and platinic chloride. The *hydroxide* is a resin, melting at about 110° C., and yielding a *picrate*, consisting of long prisms, M.pt. 194° to 195° C.[2]

Tri-o-phenetyl tellurium iodide, $(C_2H_5O.C_6H_4)_3TeI$.[3]—This is isolated in a similar manner to that detailed for the corresponding *para*-compound. It sinters at 224° C., melts at 226° to 227° C., and dissolves readily at the ordinary temperature in chloroform or boiling alcohol, but is sparingly soluble in water. Silver bromide converts it into *tri-o-phenetyl tellurium bromide*, sintering at 200° C. and melting at 202° to 203° C. A *picrate* is also known, crystallising from alcohol in cubes, softening at 161° C. and melting at 164° to 165° C.

Tri-p-phenetyl tellurium iodide.—To the Grignard solution from 37·3 grams of *p*-bromophenetole and 4·6 grams of magnesium, 10 grams of tellurium tetrachloride in 250 c.c. of absolute ether are added with constant agitation. The solution is decomposed by 25 c.c. of ice-water, being well cooled during the process, the precipitate filtered off and extracted first with alcohol and then with ether. The remaining residue is dissolved in water and potassium iodide added to the hot solution, the iodide appearing as a white amorphous precipitate. This is washed with water and dried, the product sintering at 205° C. and melting at 208° to 209° C. The yield is 10·5 grams. The iodide dissolves in cold chloroform or boiling alcohol, from which it separates as microscopic rhombic columns. The *bromide*, obtained in the usual way, sinters at 215° C. and melts at 218° C. It dissolves in warm alcohol, is sparingly soluble in water, insoluble in ether. The *picrate* crystallises from alcohol as rhombic plates, sintering at 173° C. and melting at 178° to 179° C.

Tri-p-anisyl tellurium iodide,[4] $(CH_3O.C_6H_4)_3TeI$, sinters at 156° C. and melts at 160° C. It is moderately soluble in chloroform, but somewhat sparingly soluble in alcohol, from which it separates as a crystalline powder. The corresponding *picrate* forms rhombic crystals, softening at 155° C. and melting at 160° C.

Tri-m-xylyl tellurium iodide, $[(CH_3)_2C_6H_3]_3TeI$, from *m*-bromoxylene, magnesium and tellurium tetrachloride in ether, subsequently treating the product with potassium iodide, crystallises from water as colourless needles, softening at 205° C. and melting at 208° to 209° C., soluble in chloroform or hot alcohol. The *picrate* separates as needles, sintering at 134° C., M.pt. 138° to 139° C.

Tri-p-xylyl tellurium iodide crystallises as quadratic plates, sintering at 182° C., M.pt. 186° to 187° C. When shaken with mercuric bromide the xylyl residue is removed.

Trimesityl tellurium iodide, $[(CH_3)_3C_6H_2]_3TeI$, is deposited from aqueous solution as felted needles, softening at 161° C., M.pt. 164° C.,

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[1] Lederer, *Ber.*, 1911, 44, 2287.

[2] Lederer, *Ber.*, 1915, 48, 1944.

[3] Lederer, *Ber.*, 1916, 49, 2529.

[4] Lederer, *Ber.*, 1916, 49, 1385.

soluble in alcohol or chloroform. The product separating from ether as white needles melts at 169° to 170° C. The *bromide* has a similar crystalline form and solubility to the iodide, softens at 161° C. and melts at 164° C.

Phenyl di-p-tolyl tellurium iodide,[1] $(C_6H_5)(CH_3.C_6H_4)_2TeI$.—To 12·4 grams of bromobenzene and 1·96 grams of magnesium in 60 c.c. of absolute ether, 10 grams of di-*p*-tolyl tellurium dichloride in 250 c.c. of toluene are rapidly added. The reaction is soon complete, and the mixture is decomposed by 25 c.c. of water. The white precipitate is filtered off and extracted first with alcohol, then with chloroform. The residue is dissolved in water and treated with potassium iodide. About 10 grams of iodide are isolated. It crystallises as quadratic columns, sintering at 206° C. and melting at 209° to 210° C. The corresponding *bromide* forms warty crystals, sintering at 227° C. and melting at 230° to 231° C., soluble in alcohol, chloroform or toluene, sparingly soluble in water. The *picrate* crystallises as yellow rhombic plates, sintering at 128° C., M.pt. 132° to 133° C.

Tri-α-thienyl tellurium bromide, $(C_4H_3S)_3TeBr$,[2] occurs when α-thienyl magnesium bromide reacts with di-α-thienyl tellurium dibromide. It is sparingly soluble in most organic solvents and yields microscopic rhomboidal crystals, M.pt. 253° C. with decomposition.

TELLURIUM DERIVATIVES OF DIMETHYLANILINE.[3]

Tellurium tetrachloride and dimethylaniline interact in dry ether solution to give *bis*-dimethylaniline tellurium tetrachloride, a purely additive compound, and a small amount of substitution product, 4 : 4′-tetramethyldiaminodiphenyl telluridichloride. The latter is more conveniently obtained by digesting the tetrachloride in boiling water, and the mother-liquors from this conversion yield on addition of hydrogen chloride *tris*-dimethylaniline hydrochloride tellurium tetrachloride. Reduction of the dichloride by alkali metabisulphite furnishes 4 : 4′-tetramethyldiaminodiphenyl telluride, which is slowly oxidised in the air.

Bis-dimethylaniline tellurium tetrachloride, $[C_6H_5.N(CH_3)_2]_2.TeCl_4$.—When 15·2 grams of tellurium tetrachloride in 160 c.c. of dry ether are added to 21 c.c. of dimethylaniline (3 mols.) in 200 c.c. of the same solvent, a bright red precipitate separates, which rapidly changes to a yellow crystalline solid. This product is washed with ether, a quantitative yield of the tetrachloride resulting. It becomes green at 137° C. and melts to a blue liquid at 144° to 145° C. with elimination of tellurium. In the common organic solvents it is insoluble, with the exception of acetone and alcohols, which, however, decompose it. Exposure to light causes the bright yellow colour to deepen, and the substance slowly decomposes in moist air. It forms a colourless hydrochloride, stable in dry air, but decomposed by alkali with liberation of dimethylaniline.

4 : 4′-Tetramethyldiaminodiphenyl telluridichloride, $[N(CH_3)_2.C_6H_4]_2TeCl_2$, is isolated from the concentrated ether mother-liquor of the preceding preparation, after removing dimethylaniline with

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[1] Lederer, *Ber.*, 1916, 49, 1615.

[2] Krause and Renwanz, *Ber.*, 1929, 62, [B], 1710.

[3] Morgan and Burgess, *J. Chem. Soc.*, 1929, p. 1103.

petroleum, but the best method of preparation is as follows: 28·5 grams of *bis*-dimethylaniline tellurium tetrachloride are added to 200 c.c. of boiling water and the mixture heated for 15 minutes. A yellow precipitate gradually separates, and is extracted with chloroform to separate the organic product from inorganic tellurium compounds. About 8 grams of the dichloride are obtained from the chloroform solution, recrystallisation from acetone yielding well-defined, highly refractive, bright yellow plates or hexagonal prisms, which turn blue at 181° C. and melt to a purple liquid at 188° to 189° C. The compound is readily soluble in chloroform or hot benzene, less soluble in acetone and only sparingly soluble in alcohol, ether or carbon tetrachloride. It dissolves in concentrated sulphuric acid with effervescence, forms a *hydrochloride* (M.pt. 136° to 137° C.), and, although insoluble in hot water, dissolves in warm aqueous alkalis to give colourless solutions which deposit crystals on cooling. Nitration gives a *nitro-derivative*, reducible to a diazotisable *base* without elimination of tellurium. When the dichloride suspended in dilute hydrochloric acid at $-5°$ C. is treated with three molecular equivalents of aqueous sodium nitrite, tellurium dioxide and *p*-nitrosodimethylaniline are produced. If the dichloride in acetone is refluxed with a slight excess of sodium iodide, *4 : 4′-tetramethyldiaminodiphenyl telluridi-iodide*, $[N(CH_3)_2.C_6H_4]_2TeI_2$, is produced. This crystallises from chloroform-acetone as lustrous dark red prisms, melting with decomposition at 158° to 159° C. with gas evolution.

4 : 4′-Tetramethyldiaminodiphenyl telluride, $Te[C_6H_4.N(CH_3)_2]_2$.—A suspension of 0·8 gram of 4 : 4′-tetramethyldiaminodiphenyl telluridichloride in dilute acetone is treated with 2 grams of potassium metabisulphite and after an hour the mixture is extracted with chloroform. After drying and evaporating the extract, methyl alcohol is added, the mixture filtered from tellurium and cooled in ice. Pale olive-green crystals of the telluride separate, these being readily soluble in chloroform, acetone or benzene, sparingly soluble in alcohol and insoluble in water. The telluride slowly oxidises to a colourless insoluble solid. Even in cold solution it tends to deposit tellurium, and it is probably due to this fact that various preparations show differences in colour (orange, orange-red and olive-green).

Tris-dimethylaniline hydrochloride tellurium tetrachloride, $[C_6H_5.N(CH_3)_2.HCl]_3TeCl_4.C_2H_5OH$.—In the foregoing preparation of 4 : 4′-tetramethyldiaminodiphenyl telluridichloride by boiling the tetrachloride compound with water the aqueous mother-liquor on concentration yields a residue which crystallises from alcoholic hydrochloric acid as greenish-yellow flattened needles, M.pt. 119° to 121° C., readily soluble in water to give an acid solution, less soluble in alcohol. The compound is hygroscopic, and decomposed by aqueous alkalis.

4 : 4′ - Diphenyldimethyldiaminodiphenyl telluridichloride, $[C_6H_5.N(CH_3).C_6H_4]_2TeCl_2$, occurs in 5 per cent. yield when tellurium tetrachloride reacts with N-methyldiphenylamine in ether solution. It forms well-defined, transparent, primrose-yellow, rhomboidal plates, M.pt. 170° to 172° C., readily soluble in chloroform or hot acetone and sparingly soluble in alcohol, carbon tetrachloride or light petroleum. In warm sulphuric acid it develops intense violet to blue colorations, and with nitric acid a deep wine-red tint.

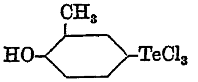
The Interaction of Basic Tellurium Chloride and Cresols.[1]

General Procedure.—The basic tellurium chloride suspended in three times its weight of dry ether is treated with an excess of the cresol (2 to 4 mols.), the solvent distilled off and the residue heated at 120° to 130° C. in the case of *o*- or *m*-cresol and at 110° to 120° C. for *p*-cresol.

o-Cresol Condensation.

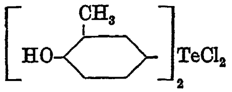
The crude condensation product is extracted successively with (*a*) light petroleum, (*b*) dry benzene and (*c*) dry chloroform, the first solvent removing any unchanged *o*-cresol.

4-Hydroxy-3-methylphenyltellurium trichloride,



The greyish-green insoluble residue from the foregoing extractions, when further extracted in a Soxhlet apparatus with dry chloroform containing 5 per cent. of alcohol, yields olive-green crystals decomposing at 208° to 209° C. The product is insoluble in petroleum, carbon tetrachloride or dry chloroform, but dissolves in the last-named solvent in the presence of a little alcohol. It is decomposed by water or moist alcohol to products soluble in hot water.

Di-4-hydroxydi-3-methyldiphenyl telluridichlorides (Isomeric),



Isomeride (*A*).—The chloroform extract (*c*) of the foregoing crude condensation product on concentration and cooling gives a red solid which after many crystallisations from chloroform yields well-defined, transparent, colourless, oblique prisms, decomposing at 197° to 198° C.

Isomeride (*B*).—The benzene extract (*b*) of the crude product on concentrating and cooling yields a crop of the isomeride (A), but the mother-liquor on the addition of light petroleum gives a grey solid which on repeated crystallisation from benzene forms nodular, colourless, opaque crystals, decomposing at 177° to 178° C. This dichloride, although sparingly soluble in petroleum or carbon tetrachloride, is ten times more soluble in benzene or chloroform than its isomeride (A). It dissolves in water to give an acid solution, from which hydrochloric acid reprecipitates the original dichloride.

Unlike the corresponding *m*-cresol derivatives, these dichlorides are not readily transformed into triarylated tellurium chlorides by prolonged boiling with 95 per cent. alcohol or with aqueous sodium carbonate.

m-Cresol Condensation.

The crude condensation product is a dark semi-solid product which leaves an insoluble green solid after extraction with carbon tetrachloride.

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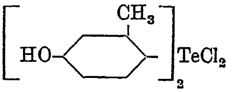
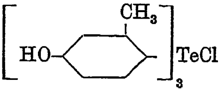
[1] Morgan and Burgess, *J. Chem. Soc.*, 1929, p. 2214.

Di-4-hydroxydi-2-methyldiphenyl telluridichloride,



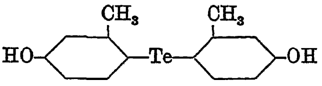
Recrystallisation of the foregoing green solid from absolute alcohol gives the telluridichloride as primrose-yellow crystals, almost insoluble in benzene, chloroform, carbon tetrachloride or ethyl acetate, slightly soluble in acetone and readily soluble in hot absolute alcohol. Boiling with 95 per cent. alcohol precipitates tellurium dioxide and the tellurium dichloride passes into solution, but on boiling with 90 per cent. alcohol more than 90 per cent. of unchanged dichloride is recovered. When a hot aqueous sodium carbonate solution of the dichloride is acidified with hydrochloric acid the telluronium chloride is precipitated quantitatively.

Tri-4-hydroxytri-2-methyltriphenyltellurium chloride,



obtained as just described, crystallises from alcohol-petroleum as colourless, felted, feathery crystals, M.pt. 184° to 185° C., slightly soluble in hot water to give an acid solution, readily soluble in alcohols, but only sparingly soluble in ether, acetone or chloroform. It is insoluble in carbon tetrachloride, benzene or petroleum. When dissolved in 2*N* sodium carbonate or 4*N* sodium hydroxide solution it is converted to the *sodium derivative* $(NaO.C_7H_6)_3TeOH$, which separates on cooling, being washed with 50 per cent. alcohol. The air-dried sodium salt melts sharply at 137° to 138° C. and re-solidifies on further heating. It dissolves sparingly in water to give an alkaline solution.

Di-4-hydroxydi-2-methyldiphenyl telluride,

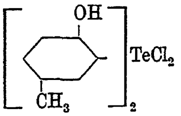


Ether solutions of 6·5 c.c. of *m*-cresol and 5·5 grams of tellurium tetrachloride are mixed and heated for two hours on the water-bath. The resulting greenish-black oil is reduced with an ice-cold solution of 79 per cent. potassium metabisulphite, the product extracted rapidly with chloroform, and the filtered extract concentrated. The addition of light petroleum gives felted, colourless needles, which melt at 143° to 144° C. after recrystallisation from carbon tetrachloride. Only 0·3 gram of telluride is obtained by this method. The product is sparingly soluble in hot water, giving a faintly acid solution which gives a wine-red coloration with alcoholic ferric chloride. It dissolves readily in chloroform, benzene, acetone or alcohol, and is sparingly soluble in carbon tetrachloride or petroleum. Addition of mineral acid to an alkaline solution of this telluride gives a purple coloration which rapidly disappears.

p-Cresol Condensation.

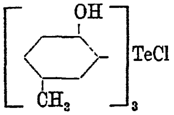
The products arising from the condensation are extracted from the mixture by successive treatment with benzene, chloroform and alcohol, dry solvents being employed in each case. The hot filtered benzene extract deposits a pale sage-coloured crystalline powder, decomposing at 229° to 230° C., and insoluble in the common organic solvents. Its analysis indicates the complex *tri-2-hydroxytri-5-methyltriphenyltelluronium tellurium oxychloride*, $[(HO.C_7H_6)_3Te]TeOCl_3$.

Di-2-hydroxydi-5-methyldiphenyl telluridichloride,



When the benzene mother-liquors from the compound described above are evaporated under 20 mm. pressure, a black viscous tar remains. This is extracted with chloroform and the extract added to the original chloroform extract of the crude condensation product. Concentration of the mixture yields a pink crystalline material, three recrystallisations from chloroform giving colourless compact crystals, decomposing at 213° to 214° C. The complex is slightly more soluble in hot chloroform than in the cold solvent, and dissolves readily in alcohol or acetone.

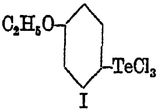
Tri-2-hydroxytri-5-methyltriphenyltellurium chloride,



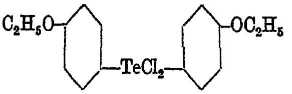
is obtained by precipitating with water both the original alcoholic extract from the crude condensation product and the alcoholic extract of the sage-green complex tellurium oxychloride. The precipitates crystallise from hot dilute alcohol in felted masses of colourless hair-like crystals, melting indefinitely and with decomposition at 244° to 245° C. The product is almost insoluble in benzene, chloroform or carbon tetrachloride.

CONDENSATION PRODUCTS FROM TELLURIUM TETRACHLORIDE AND ARYL ALKYL ETHERS.

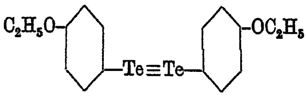
The types of compound obtainable by the condensation of tellurium tetrachloride and mixed ethers may be exemplified by the case of phenetole. The primary product obtained in the reaction is *p*-phenetyl telluritrichloride (I), which on heating with more phenetole gives *bis*-*p*-phenetyl telluridichloride (II). The latter also occurs if an excess of phenetole be used in the initial condensation. Reduction of the trichloride by aqueous potassium metabisulphite at 0° C. produces *bis*-*p*-phenetyl ditelluride (III).



I



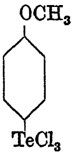
II



III

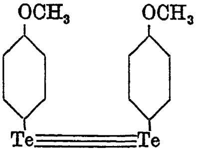
The aromatic ditellurides $RTe{\equiv}TeR$ are intensely coloured substances, often bearing a striking resemblance to the azo-compounds, and the prime cause of the colour is the group $—Te{\equiv}Te—$.

p-Anisyl telluritrichloride,[1]



occurs when one molecular equivalent of tellurium tetrachloride and 1½ to 2 molecular equivalents of anisole are heated together in dry chloroform. The product crystallises from dry chloroform or ether as yellow needles, M.pt. 190° C., almost insoluble in cold chloroform, benzene or light petroleum, but moderately soluble in the warm solvents. Water or moist solvents decompose it to a white hydroxide. The trichloride dissolves completely in hydrochloric acid or aqueous sodium hydroxide.

Bis-p-anisyl ditelluride,



is obtained in quantitative yield when the foregoing compound suspended in ice-water is treated gradually with potassium metabisulphite. It crystallises from dilute alcohol or petroleum as reddish-brown crystals, but from its more highly concentrated solution in benzene it separates as highly lustrous green crystals. It slowly oxidises in air to a yellowish-grey substance, and its alcohol solution is instantly decolorised by hydrogen peroxide, a white amorphous product resulting when the liquid is concentrated. Chlorine converts the ditelluride in chloroform solution into *p*-anisyl telluritrichloride, and bromine gives *p-anisyl telluritribromide*, orange-yellow crystals, M.pt. 187·5° C., hydrolysed by water to the white hydroxide and with metabisulphite regenerating the ditelluride. The ditelluride in ether solution yields a light brown *mercurichloride* when treated with aqueous mercuric chloride.

When the ditelluride is refluxed with methyl iodide it yields *p-anisyl dimethyltelluri-iodide,*[2] $CH_3O.C_6H_4.Te(CH_3)_2I$, as a microcrystalline salmon-coloured precipitate, M.pt. 170° to 172° C., almost insoluble in acetone, benzene and other organic solvents, but hydrolysed by boiling alcohol.

$$RTe \equiv TeR + 3CH_3I = RTe(CH_3)_2I + RTe(CH_3)I_2 \,^{3}$$

The mother-liquor from the monoiodide gives *p-anisyl methyltelluridi-iodide,* $CH_3O.C_6H_4.Te(CH_3)I_2$, a red crystalline substance, M.pt. 109° C., soluble in organic solvents. Reduction of this substance by aqueous potassium metabisulphite in the presence of ether yields *p-anisyl methyl*

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[1] Morgan and Kellett, *J. Chem. Soc.*, 1926, p. 1080.

[2] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 2314.

[3] R = anisyl residue.

telluride, a yellow oil of nauseating odour. Part of the di-iodide is re-transformed to *bis-p*-anisyl ditelluride by partial reduction followed by loss of methyl iodide:

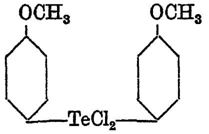
$$CH_3O.C_6H_4.Te(CH_3)I_2 \xrightarrow{2H} 2HI + CH_3O.C_6H_4.TeCH_3$$

$$2CH_3O.C_6H_4.Te(CH_3)I_2 \xrightarrow{2H} 2HI + CH_3O.C_6H_4.Te(CH_3)I.Te(CH_3)I.C_6H_4.OCH_3$$

$$CH_3O.C_6H_4.Te(CH_3)I.Te(CH_3)I.C_6H_4.OCH_3 \longrightarrow 2CH_3I + \begin{array}{c} CH_3O.C_6H_4.Te \\ ||| \\ CH_3O.C_6H_4.Te \end{array}$$

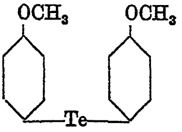
When *p*-anisyl dimethyltelluri-iodide is warmed with aqueous sodium picrate containing free picric acid, two picric acid compounds result, (*a*) a *picrate* $CH_3O.C_6H_4.Te(CH_3)_2O.C_6H_2(NO_2)_3$, forming bright yellow needles from alcohol or water, M.pt. 126° to 127° C., (*b*) a substance forming pale yellow glistening plates, M.pt. 176° C. The latter is probably an additive compound of picric acid and *p*-anisyl methyl telluride, which is formed from the iodide on heating by loss of methyl iodide.

Bis-p-anisyl telluridichloride,[1]



15 grams of tellurium tetrachloride and 30 grams of anisole (5 mols.) are heated together for 24 hours at 150° to 180° C., the solution afterwards being allowed to solidify *in vacuo*. A 95 per cent. yield of dichloride results, the product separating from benzene-petroleum as colourless prisms, M.pt. 181° to 182° C., often retaining a slightly pink tinge. The dichloride is insoluble in, but slightly hydrolysed by, water; complete hydrolysis takes place in aqueous sodium hydroxide, but the compound is not very soluble in the alkali. It is not reduced by potassium metabisulphite and only slowly attacked by zinc dust.

Bis-p-anisyl telluride,



Di-*p*-anisyl telluridichloride, 10 grams, and 5 grams of zinc dust in 150 c.c. of benzene are heated together for 24 hours under reflux. Filtration, followed by concentration, gives white crystals containing chlorine, the product being subjected to the action of more zinc dust until halogen-free. The compound thus obtained separates from dilute alcohol as colourless, nacreous plates, M.pt. 53° to 54° C. On mixing chloroform solutions of the telluride and bromine *bis-p-anisyl telluridibromide* separates as sulphur-yellow crystals, M.pt. 190° C.

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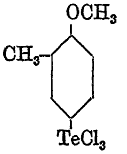
[1] Morgan and Kellett, *loc. cit.*

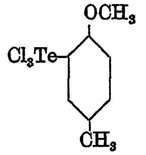
2-Methoxytolyl 5-telluritrichloride,



is the condensation product from tellurium tetrachloride (1 mol.) and *o*-tolyl methyl ether (2 mols.) in dry chloroform. It separates as pale yellow needles, melting at 232° to 233° C. to a red liquid, insoluble in cold water, but hydrolysed on warming to a white *hydroxide*, which dissolves readily in benzene or chloroform.

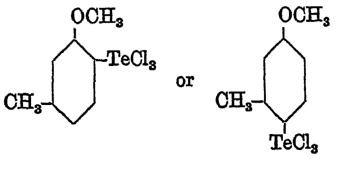
Bis-2-methoxy-m-tolyl ditelluride, $[CH_3O.C_6H_3(CH_3).Te]_2$, occurs when the foregoing compound is reduced with potassium metabisulphite. It separates from petroleum as dark needles having a brownish-green bronzy lustre, M.pt. 77° to 78° C., very soluble in benzene, chloroform, acetone or ether, but sparingly soluble in cold alcohol or petroleum, dissolving more readily on warming. Water precipitates a bright red emulsion from alcohol solution, which solidifies to a dark green crystalline mass. Hydrogen peroxide instantly decolorises the alcohol solution, and when chlorine is passed into the chloroform solution it regenerates 2-methoxytolyl 5-telluritrichloride. Bromine under similar conditions gives orange-yellow *2-methoxytolyl 5-telluritribromide.*

4-Methoxytolyl 3-telluritrichloride,



from *p*-tolyl methyl ether and tellurium tetrachloride, forms well-defined, yellow, rectangular plates, M.pt. 135° C. The condensation requires a higher temperature than is necessary for the foregoing products.

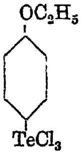
3-Methoxytolyl (4 or 6)-telluritrichloride,



is formed when *m*-tolyl methyl ether is used in the condensation previously described. It is a yellowish-brown crystalline mass, M.pt. 154° C., much more soluble in organic solvents than its isomerides. Exposure to moisture leads to considerable hydrolysis.

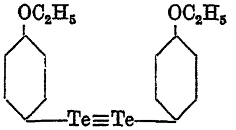
p-Bromoanisole forms a normal *trichloride,* M.pt. 184° C., when condensed with tellurium tetrachloride, this on reduction giving a dark red oily *ditelluride,* which on bromination in chloroform solution yields an orange-yellow *tribromide,* M.pt. 153° C.

p-Phenetyl telluritrichloride,[1]



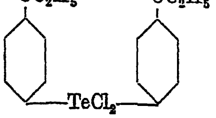
consisting of glistening yellow flakes, M.pt. 182° to 183° C. to a red liquid, is the condensation product of tellurium tetrachloride with phenetole, the yield being 92 per cent. It is moderately soluble in hot chloroform or benzene, giving yellow solutions, and is readily soluble in cold ethyl alcohol, giving a solution which is colourless owing to hydrolysis. Warming with aqueous potassium hydroxide causes development of the odour of phenetole.

Bis-p-phenetyl ditelluride,



The foregoing trichloride affords the ditelluride when reduced at 0° C. with aqueous potassium metabisulphite, the yield being quantitative. The ditelluride separates from petroleum as fluffy masses of brilliant orange-red needles or golden-orange plates, melting at 107° to 108° C. to a deep red liquid, readily soluble in cold benzene or chloroform, less soluble in ethyl alcohol or light petroleum, insoluble in water. It is unaffected by boiling ammonium hydroxide, but decomposed by methyl iodide. When covered with concentrated nitric acid and the liquid allowed to evaporate in an open basin, the ditelluride is decomposed, yielding *p*-nitrophenetole.

Bis-p-phenetyl telluridichloride,



may be prepared in the following ways: (1) *p*-Phenetyl telluritrichloride is heated with four times its weight of phenetole for six hours in an oil-bath at 180° to 190° C. (2) By passing chlorine through a solution of *bis-p*-phenetyl telluride in carbon tetrachloride. (3) By heating tellurium tetrachloride (1 mol.) with phenetole (4 mols.) at 180° to 190° C. The dichloride separates from methyl alcohol as colourless prismatic needles, M.pt. 108° C. to a colourless transparent liquid. The chlorine is only liberated slowly (along with phenetole) even by boiling aqueous potassium hydroxide. When boiled in aqueous suspension the dichloride yields *bis-p-phenetyl tellurioxychloride,*[2]

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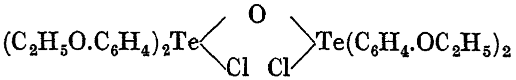
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 2307.

[2] Morgan and Burstall, *J. Chem. Soc.*, 1930, p. 2599.

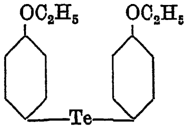


$$(C_2H_5O.C_6H_4)_2Te\genfrac{}{}{0pt}{}{O}{Cl\quad Cl}Te(C_6H_4.OC_2H_5)_2$$

This product separates from benzene, acetone or alcohol as fluffy white crystals, decomposing at 193° C.

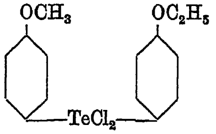
Bis-p-phenetyl telluridibromide forms lemon-yellow crystals, M.pt. 127° C., and the corresponding *di-iodide* affords orange-red needles, M.pt. 144° C. These dihalides on boiling with 2*N* aqueous caustic alkali yield *bis-p-phenetyl telluroxide*, $(C_2H_5O.C_6H_4)_2TeO$, a white microcrystalline substance decomposing at 181° C.

Bis-p-phenetyl telluride,



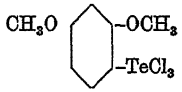
is prepared by the interaction of *p*-phenetyl magnesium bromide and tellurium dibromide in dry ether. It separates from alcohol as white lustrous plates having a faint greenish tinge and melting at 64° C. (see p. 191). It is readily soluble in organic solvents, insoluble in water; cold concentrated sulphuric acid causes the development of a red coloration.

p-Anisyl-p-phenetyl telluridichloride,



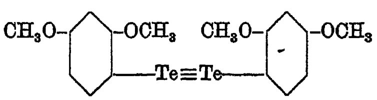
is prepared when *p*-phenetyl telluritrichloride (1 mol.) is heated at 160° C. with anisole (4 mols.) for six hours. After treating the cooled melt with petroleum, it is crystallised repeatedly from alcohol, glistening white needles of the dichloride separating, M.pt. 165° to 166° C. Reduction of this compound in glacial acetic acid by an excess of zinc dust yields *p-anisyl-p-phenetyl telluride*, consisting of white needles having a faint greenish tinge, M.pt. 45° C.

1 : 3-Dimethoxyphenyl 4-telluritrichloride,[1]



obtained when resorcinol dimethyl ether is used in the condensation, forms silky, primrose-yellow, prismatic needles, or transparent golden-yellow prisms, M.pt. 155° to 156° C., which evolve resorcinol dimethyl ether when warmed with aqueous potassium hydroxide.

Bis-1 : 3-dimethoxyphenyl 4 : 4-ditelluride,



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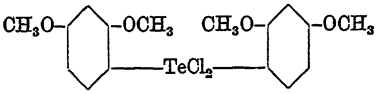
[1] Morgan and Drew, *loc. cit.*

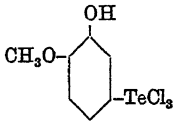
obtained from the preceding compound, separates as orange-brown needles or prisms, M.pt. 134° to 135° C., soluble in benzene, petroleum, ethyl alcohol, ether or ligroin, insoluble in water. It is unaffected by alkalis, but gives an intense reddish-purple coloration with cold concentrated sulphuric acid.

Bis-1 : 3-dimethoxyphenyl 4-telluridichloride,



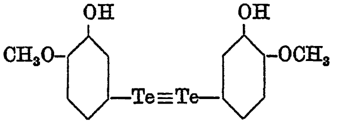
occurs when 6·7 grams of tellurium tetrachloride, 1·8 grams of resorcinol dimethyl ether and 12 c.c. of dry chloroform are heated together on the water-bath for three hours and the resulting product reduced by an excess of aqueous potassium metabisulphite. It separates from alcohol as colourless pearly flakes, which melt at 204° to 205° C., and are resistant to aqueous alkali bisulphite but decomposed by hot potassium hydroxide, liberating resorcinol dimethyl ether.

2-Hydroxy-1-methoxyphenyl 4-telluritrichloride,



is the condensation product of tellurium tetrachloride and guaiacol. It forms deep yellow prisms, melting with decomposition at 157° to 159° C., readily hydrolysed by moist air when in solution.

Bis-2-hydroxy-1-methoxyphenyl 4 : 4-ditelluride,



occurs when the preceding compound is reduced by aqueous potassium metabisulphite at 0° C. It separates from dry benzene as orange-brown prismatic needles, slowly darkening above 114° C. and melting finally at 117° to 118° C. with liberation of tellurium. In benzene, chloroform or ether it is moderately soluble, giving red solutions, but sparingly soluble in petroleum and insoluble in water. Boiling alcohol decomposes it, but solutions in aqueous sodium hydroxide or carbonate yield unchanged ditelluride on addition of mineral acid.

Phenoxtellurine and its Derivatives.[1]

The condensation of tellurium tetrachloride and diphenyl ether in chloroform solution gives rise to *p*-phenoxyphenyl telluritrichloride,

$$TeCl_4 + C_6H_5.O.C_6H_5 = TeCl_3(C_6H_4.OC_6H_5) + HCl$$

Reduction of the telluritrichloride by aqueous potassium metabisulphite gives *pp'*-diphenoxydiphenyl ditelluride,

$$C_6H_5O.C_6H_4.Te \vdots Te.C_6H_4.OC_6H_5$$

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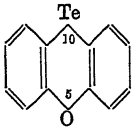
[1] Drew, *J. Chem. Soc.*, 1926, p. 223.

In the foregoing condensation, or when the telluritrichloride is heated with an excess of diphenyl ether at about 160° C., a colourless non-cyclic telluridichloride occurs, *pp'*-diphenoxydiphenyl telluridichloride, $C_6H_5O.C_6H_4.TeCl_2.C_6H_4.OC_6H_5$. This must arise as follows :

$$TeCl_3(C_6H_4.OC_6H_5) + C_6H_5.O.C_6H_5 \xrightarrow{160^\circ \text{ C.}} TeCl_2(C_6H_4.OC_6H_5)_2 + HCl$$

When *p*-phenoxyphenyl telluritrichloride is heated at about 200° C. a further intramolecular condensation takes place, giving 10 : 10-dichlorophenoxtellurine, although this product is best isolated by heating to 200° C. a mixture of tellurium tetrachloride and diphenyl ether in molecular proportions. Reduction of the dichloro-compound gives phenoxtellurine,



which readily adds on bromine or iodine in chloroform, yielding 10 : 10-dibromo- and 10 : 10-di-iodo-phenoxtellurine respectively, while warm nitric acid converts it, through an intense bluish-violet intermediate, into colourless phenoxtellurine 10 : 10-dinitrate. Reduction of the latter by sulphurous acid gives a bluish-violet intermediate product, which finally passes into yellow phenoxtellurine.

An intense violet colour is developed when phenoxtellurine and the dinitrate are merely mixed or rubbed together in the dry state between glass surfaces. An explanation of this phenomenon is given by Drew.[1] He considers it probable that the process involves the migration of an anion from the salt member to the reduced (telluride) member of the pair of generators, accompanied by union of the two residues. The salt member (*i.e.* the dinitrate) would thus become the " donor " of an acid radical, the reduced member (*i.e.* phenoxtellurine) being the " acceptor." The following table shows the types of substances capable of producing coloured complexes by interaction with " acceptors " or " donors " of the phenoxtellurine series:

"*Donors.*"	"*Acceptors.*"
Salts of phenoxtellurine, etc.	Phenoxtellurine, etc.
„ „ *cyclo*telluropentanediones.	*cyclo*Telluropentanediones.
„ „ diethyl sulphide.	Tellurodiacetic acid.
Basic tellurium nitrate or sulphate.	Ditellurodiacetic acid.
Concentrated nitric or sulphuric acid.	Diethyl or Hydrogen sulphide.
	Sulphurous acid.
	Base metals (Fe, Cu, Na, etc.).
	1 : 2-Dihydroxybenzenes and pyrogallol.

The hypothesis is adopted that in every case of interaction between a " donor " and an " acceptor " there occurs an exchange of anions from the former for an equal number of electrons from the latter. This exchange is followed by the union of the two residues with formation of the coloured complex, the extent to which the latter is formed being governed by temperature and concentration as well as by the nature of the interactants. Substances acting as " donors " or " acceptors," but

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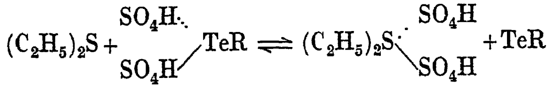
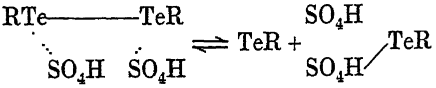
[1] Drew, *J. Chem. Soc.*, 1926, p. 3054.

not entering into the molecule of the resulting complex, are known as "intermediary suppliers" or "receivers of anions," respectively. They create "donors" or "acceptors," respectively, of the phenoxtellurine series. Thus, between diethyl sulphide and phenoxtellurine dibisulphate we have the equilibrium:



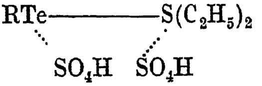
$$(C_2H_5)_2S + \begin{matrix}SO_4H\\ SO_4H\end{matrix}\!>\!TeR \rightleftharpoons (C_2H_5)_2S\!<\!\begin{matrix}SO_4H\\ SO_4H\end{matrix} + TeR$$

where R represents the bivalent carbon grouping of phenoxtellurine. Free phenoxtellurine is therefore present in the system, and unites with its dibisulphate to give the violet complex, which is in turn in equilibrium with its constituents:



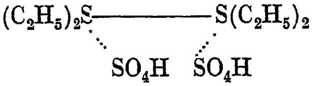
$$\begin{matrix}RTe & \text{———} & TeR\\ \vdots & & \vdots\\ SO_4H & & SO_4H\end{matrix} \rightleftharpoons TeR + \begin{matrix}SO_4H\\ SO_4H\end{matrix}\!>\!TeR$$

The two remaining possible complexes, viz.



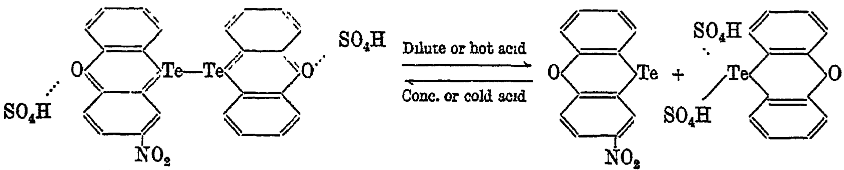
$$\begin{matrix}RTe & \text{———} & S(C_2H_5)_2\\ \vdots & & \vdots\\ SO_4H & & SO_4H\end{matrix}$$

and



$$\begin{matrix}(C_2H_5)_2S & \text{———} & S(C_2H_5)_2\\ \vdots & & \vdots\\ SO_4H & & SO_4H\end{matrix}$$

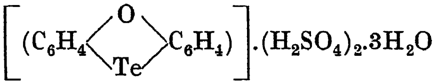
are similarly in equilibrium with their constituents. The tendency towards formation of some of the possible complexes obviously will be small or nil, and depending upon the affinities of the active atoms (tellurium and sulphur in the above case) for anions and by the tendency of these atoms to unite together. The system in dilute solution is equivalent to one in which there are present in equilibrium only the uncharged substances $R:Te$ and $(C_2H_5)_2S$ and the ions $\overset{-}{SO_4H}$, $RT\overset{+}{e}(SO_4H)$ and $(C_2H_5)_2\overset{+}{S}(SO_4H)$. This may be demonstrated in a variety of ways: (1) In the foregoing case, phenoxtellurine dibisulphate becomes violet in gaseous diethyl sulphide; excess of the gas (or the presence of liquid diethyl sulphide) changes the colour to red; the violet solid loses diethyl sulphide and becomes pale yellow when removed from the gas. Crystallisation of the violet solid from glacial acetic acid gives diphenoxtellurylium dibisulphate only in small yield. If phenoxtellurine dibisulphate is exposed on clay to the vapour of diethyl sulphide, a part of it remains permanently violet, showing that a small proportion of $(C_2H_5)_2S(SO_4H)_2$ has been absorbed by the clay, its removal disturbing the normal equilibrium. (2) The combination of a pair $R':Te$ and $R'':Te(SO_4H)_2$ gives the same result as that of the reversed pair, $R'':Te$ and $R':Te(SO_4H)_2$. (3) In glacial acetic acid the following occurs:



(Solution cherry-red) (Solution yellow)

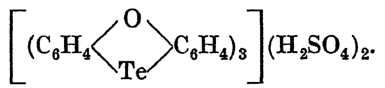
The colour of the hot dilute solutions shows a much more intense yellow, due to the presence of free 2-nitrophenoxtellurine. (4) When a subsidiary reaction can occur to disturb the equilibrium, there is the expected quantitative production of a violet complex, *e.g.* gaseous or dissolved hydrogen sulphide almost completely converts phenoxtellurine dibisulphate into a violet complex, because the "intermediate" compound $H_2S(SO_4H)_2$ changes rapidly to sulphur and sulphuric acid. Diethyl sulphide on the other hand has no permanent action, because the corresponding compound, $(C_2H_5)_2S(SO_4H)_2$, cannot undergo such a change. In the case of nitric and sulphuric acids and phenoxtellurine the reverse phenomenon is noted, the acids supplying anions to tellurium in exchange for electrons, leaving nascent (uncharged) hydrogen, which is removed by its subsidiary reducing action upon the excess of acid.

On rubbing phenoxtellurine dibisulphate upon a porous tile with steel, sodium, aluminium, iron, nickel, copper, tin, zinc, arsenic or antimony, an intense violet colour is developed, but no effect is produced with the noble metals. Another interesting point is that the base metals exhibit selective action towards different anions, *e.g.* iron produces a coloration with both dinitrate and dibisulphate of phenoxtellurine, copper or nickel only with the latter salt. Such reactions afford a rough indication of the relative attractions of different metals for certain anions. The metallic particles remove anions from the salt molecules in exchange for electrons, forming free phenoxtellurine, which then combines with unchanged salt to form substances such as



$$\left[(C_6H_4\begin{smallmatrix}O\\Te\end{smallmatrix}C_6H_4)\right].(H_2SO_4)_2.3H_2O$$

and

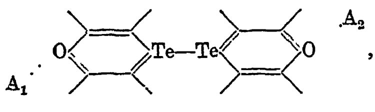


$$\left[(C_6H_4\begin{smallmatrix}O\\Te\end{smallmatrix}C_6H_4)_3\right](H_2SO_4)_2.$$

Salts of the metals are thus present in equilibrium with the violet tellurium compounds, and in the case of the dibisulphate the balance is controlled by the proportion of water present. This is rendered visible in the action of iron upon phenoxtellurine dibisulphate, for the violet mixture becomes red when dried on clay in a desiccator, but the violet colour is restored on exposure to moist air. The method of examining a coloured complex consists in treating it with water, when the "acceptor" is set free and can be extracted by ether; the residual salt can then be reduced by adding potassium bisulphite, and the nucleus of the "donor" again extracted by ether. The products are insoluble in water, so that fresh equilibria cannot presumably be set up.

The addition of a molecular proportion of phenoxtellurine dibisulphate, which is insoluble in ether, to 2 : 4-diethyl*cyclo*telluropentanedione dissolved in ether leads to the separation of blue complexes and the rapid removal of the *cyclo*telluropentanedione from solution, its place being taken by free phenoxtellurine. The tellurium atom of the *cyclo*telluropentanedione has therefore a much greater affinity for bisulphate radicals than has that of phenoxtellurine.

Colour production among the tellurylium compounds is ascribed to the occurrence of the structure (I), in which A_1 and A_2 represent HSO_4, ClO_4, NO_3, H_2PO_4, or the OH radical, but the structures (II) and (III) are possible alternatives :



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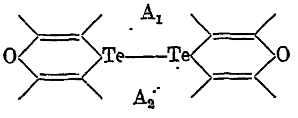
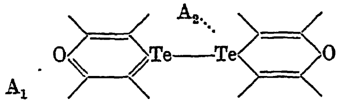


II



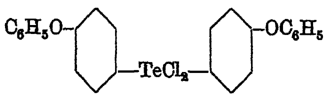
III

Since the radicals Cl, Br or $CH_3.CO.O$ show little tendency to ionise when united to tellurium, they cannot be represented by A_1 and A_2. It should be noted that each of the mobile acid radicals possesses doubly bonded oxygen, and the nitrate ion appears to be mobile even in reaction between dry solids (phenoxtellurine and its anhydrous dinitrate).

The scheme opposite shows the nitro- and dinitro-derivatives obtained from phenoxtellurine.[1] Reduction of the nitro-compounds by tin and hydrochloric acid converts them into the corresponding amino-derivatives.

p-Phenoxyphenyl telluritrichloride,[2] $C_6H_5O.C_6H_4.TeCl_3$.—Tellurium tetrachloride, 23·8 grams, 18·7 grams of diphenyl ether and 15 c.c. of dry chloroform are heated together under reflux for 26 hours, moist air being excluded. Hydrogen chloride is evolved and all the tellurium tetrachloride disappears in about 1·5 hours. The yellow trichloride which separates is recrystallised from boiling dried chloroform, the yield being 31·5 grams, or 90 per cent. The final liquors contain the dichloride (see below). The trichloride separates from chloroform or carbon tetrachloride as opaque nodular rosettes of very small pale yellow needles, which crumble to a yellow crystalline powder on drying. The substance melts at 156° to 157° C. to a transparent yellow liquid. It is almost insoluble in light petroleum, sparingly soluble in hot carbon tetrachloride, but more soluble in hot chloroform or benzene. By water or hydroxylic organic solvents it is readily hydroxylated.

pp′-Diphenoxydiphenyl telluridichloride,



This occurs as a by-product in the foregoing preparation, but is best prepared by heating 3·9 grams (1 mol.) of *p*-phenoxyphenyl telluritrichloride with 1·7 grams (1 mol.) of diphenyl ether at 140° to 165° C. during six hours, moist air being excluded and a slow current of nitrogen maintained in the apparatus. Hydrogen chloride is evolved even at 145° C., and the mass is finally extracted with ether, the solvent removed and the residue triturated successively with light petroleum

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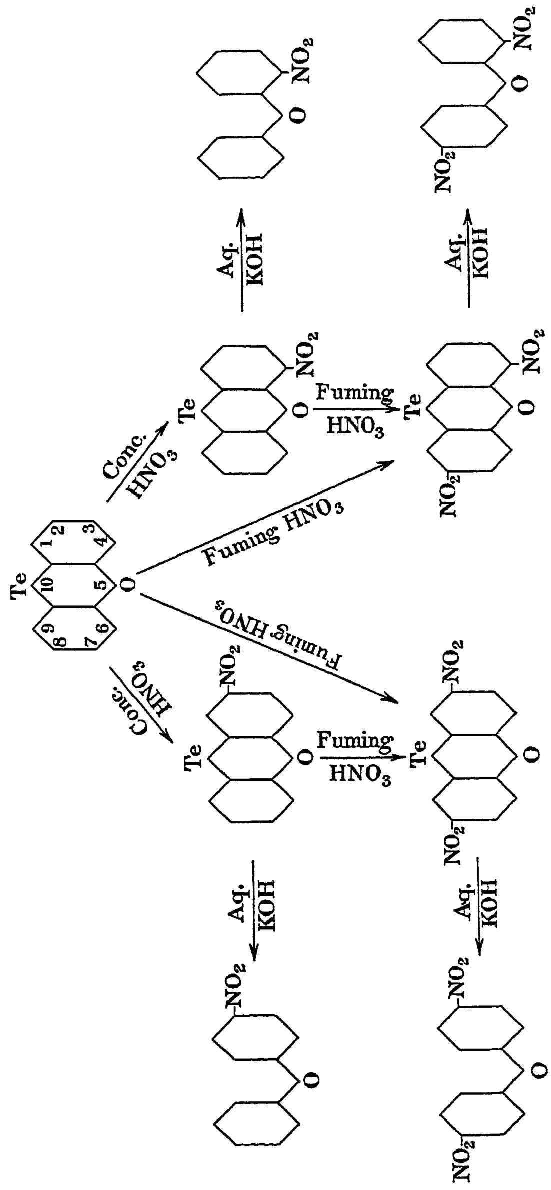
[1] Drew and Thomason, *J. Chem. Soc.*, 1927, p. 116.

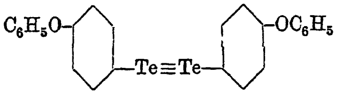
[2] Drew, *J. Chem. Soc.*, 1926, p. 223.

and ethyl alcohol, then filtered. Crude dichloride (2·8 grams) remains, and this is purified by fractional crystallisation from cold benzene,



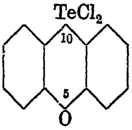
followed by crystallisation of the least soluble fraction from benzene-light petroleum (B.pt. 40° to 60° C.). The dichloride separates from boiling methyl or ethyl alcohol as transparent, colourless, prismatic needles, becoming pink on keeping. It melts at 157° to 158° C., is more soluble in organic solvents than the trichloride, being soluble in cold benzene, chloroform or ether; but it is insoluble in light petroleum, and only moderately easily soluble in hot ethyl alcohol. The halogen is unaffected by cold aqueous potassium hydroxide, although it is removed by the boiling reagent with liberation of diphenyl ether.

pp′-Diphenoxydiphenyl ditelluride,



7 grams of the trichloride are reduced by means of 50 c.c. of ice-cold water and 11·6 grams (3 mols.) of powdered potassium metabisulphite, which is slowly added during 45 minutes, the mixture being mechanically stirred. The reduction is completed by grinding the whole in a glass mortar during a further 30 minutes. The purple crystalline product is filtered off, washed with water and dried in a vacuum (yield, 5·3 grams). Purification is further effected by rapid crystallisation from hot light petroleum (B.pt. 40° to 60° C.) saturated with sulphur dioxide, two such crystallisations giving analytically pure material. The ditelluride separates in clusters of minute, bronzed, brownish-violet or purplish-red needles, which dissolve in organic solvents to give dark red solutions. It sinters at 85° C. and melts to a deep red liquid at 87° to 88° C., is readily soluble in benzene, chloroform, carbon tetrachloride, ether or acetone, only moderately soluble in light petroleum or alcohol, and insoluble in water. With warm concentrated nitric acid it yields ultimately *pp′*-dinitrodiphenyl ether.

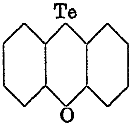
10 : 10-Dichlorophenoxtellurine,



This may be prepared in two ways: (1) The trichloride, 1·4 grams, is heated gradually during 4·75 hours from 150° to 210° C., hydrogen chloride being slowly evolved. The cooled melt is extracted with ether, the residue crystallised from boiling toluene, 0·4 gram (33 per cent.) of cyclic telluridichloride resulting. (2) Tellurium tetrachloride (11·1 grams) and 7 grams of diphenyl ether are heated together in a flask fitted with a long air condenser, carrying a moisture guard-tube, and a slow stream of nitrogen passed through the melt (this does not appear to be essential). The temperature is slowly raised from 100° to 240° C. over a period of thirteen hours, when hydrogen chloride is evolved. The cooled melt is ground, stirred with ether, filtered off, dissolved in acetone and the solution filtered. Removal of the solvent gives 9·4 grams of fairly pure cyclic dichloride (62 per cent.), but further purification with toluene reduces this figure to 48 per cent. The product crystallises from boiling toluene as colourless, nacreous platelets, M.pt. 265° C. to a transparent yellow liquid. At 100° C. the crystalline solid is yellow, but the colourless form reappears on cooling. The tellurine is practically insoluble in ether or petroleum, sparingly soluble in chloroform or ethyl alcohol, rather more soluble in benzene or toluene, and easily soluble in acetone. Boiling water slowly hydrolyses it, giving a white oxide, whilst boiling aqueous potassium hydroxide eliminates tellurium and regenerates diphenyl ether. The solution in cold concentrated sulphuric acid is yellow.

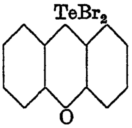
During the second method of preparation a by-product is produced which after reduction consists of a compound of one molecule of phenoxtellurine with one molecule of 2(?)-chloro-8(?)-methylphenoxtellurine. This results from the presence of a small proportion of phenyl *p*(?)-tolyl ether in the diphenyl ether.[1]

Phenoxtellurine,[2]



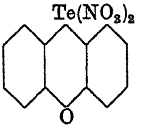
4 grams of the powdered dichloride at 0° C. are treated with 4·8 grams (2 mols.) of potassium metabisulphite and 25 c.c. of water, the potassium salt being added slowly and with stirring. The yellow product is ground beneath the liquid in a glass mortar during one hour to complete the reduction, the solid then filtered off, washed with water and dried. The yield, 3·2 grams, is nearly theoretical. Further purification is effected by recrystallisation from light petroleum (B.pt. 40° to 60° C.). The tellurine separates from the warm solvent as long spear-like needles and from the cold solvent as large transparent prisms, both forms being lemon-yellow to orange in colour, melting without decomposition at 78° to 79° C., and having a delicate floral odour. The product dissolves in alcohol, ether, benzene or carbon tetrachloride, but is insoluble in water. The solution in cold concentrated sulphuric acid is deep purplish-red. The tellurine is stable towards hot concentrated hydrochloric acid or dilute aqueous sodium hydroxide. The compound may be vaporised without decomposition.

10 : 10-Dibromophenoxtellurine,



occurs when the preceding compound in chloroform solution is treated with bromine. It separates as bright yellow spangles from chloroform or primrose-yellow prisms from toluene, melting with decomposition at 290° C. In a similar manner the *10 : 10-di-iodide* is isolated, this forming red spangles, decomposing indefinitely at about 270° C.

Phenoxtellurine 10 : 10-dinitrate,[3]



is formed when warm concentrated nitric acid reacts with phenoxtellurine. It forms large colourless needles or glistening plates, melting

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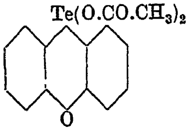
[1] Drew and Thomason, *J. Chem. Soc.*, 1927, p. 116.

[2] Drew, *loc. cit.*

[3] Drew, *J. Chem. Soc.*, 1926, p. 3054.

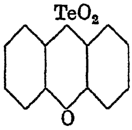
with effervescence at 258° C. In moist air it is stable, but is slowly hydroxylated by water.

Phenoxtellurine 10 : 10-diacetate,

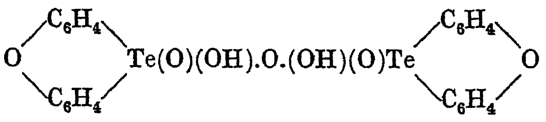


Phenoxtellurine in hot glacial acetic acid is cooled and treated dropwise with aqueous hydrogen peroxide, the mixture being stirred during the addition. When the yellow colour is discharged, the solution is heated to boiling and treated with water until turbid, when the diacetate slowly separates as long needles. The total yield is about 90 per cent., including product recovered from mother-liquors. The substance melts at 205° to 207° C., is soluble in hot water with hydrolysis, sparingly soluble in ether or petroleum, readily soluble in benzene. It gives no coloration when ground with phenoxtellurine or with metals. Aqueous alkali bisulphite readily reduces it to phenoxtellurine.

Phenoxtellurone,

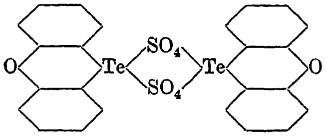


This occurs when an acetone solution of phenoxtellurine is treated with an excess of 30 per cent. hydrogen peroxide, or when an excess of the latter reagent is used in the preparation of the 10 : 10-diacetate. It is soluble in hot glacial acetic acid, insoluble in water or acetone, and reduced to the tellurous state by concentrated hydrochloric or sulphuric acid, chlorine or oxygen being evolved, with the production of a salt of phenoxtellurine. Hydriodic acid causes a similar reduction, with liberation of iodine. The tellurone is insoluble in dilute mineral acids, but dissolves in aqueous sodium hydroxide. Heating in a vacuum at 110° C. for thirty minutes yields a compound having the composition of the half-anhydride of the semi-*ortho*-form of the tellurone :



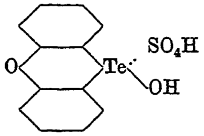
$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle Te(O)(OH).O.(OH)(O)Te\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$$

Sulphates of Phenoxtellurine.—Phenoxtellurine 10 : 10-diacetate (7·1 grams) is heated with 300 c.c. of water, and when most of the solid has dissolved, a mixture of 100 c.c. of water and 100 c.c. of concentrated sulphuric acid is added and the whole heated to boiling-point. On cooling, 6·5 grams of cream-coloured crystals are deposited. This product may yield sulphates of differing composition, according to the method of treatment. (1) If the material be dissolved in a large volume of boiling water and to the cold solution a minimum of sulphuric acid be added to effect separation of crystals, a phenoxtellurine sulphate of the following composition results :



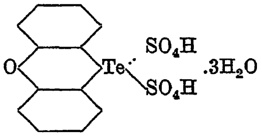
This forms thin, almost colourless, very refractive needles, which develop only a trace of colour when ground with phenoxtellurine.

(2) If the product is dissolved in a boiling mixture of one volume of concentrated sulphuric acid and 1·22 volumes of water, voluminous cream-coloured flakes separate, which, after draining and heating during five hours at about 115° C. in a vacuum, give analytical figures corresponding to a mixture or compound containing two molecular proportions of phenoxtellurine hydroxybisulphate,



and one proportion of phenoxtellurine dibisulphate, together with a molecule of water. This substance gives a violet colour when ground with phenoxtellurine. Its solution in concentrated sulphuric acid is orange-red.

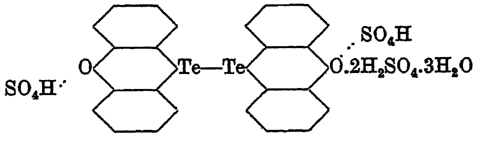
(3) When the product is dissolved by gentle warming in concentrated sulphuric acid (1·7 grams to 10 c.c. of acid) and the clear orange-red solution treated with the minimum of water (about 1 c.c.) to cause a slow separation of crystals, bright yellow glistening plates are obtained. When dried in a vacuum these change to a creamy-yellow powder, *phenoxtellurine dibisulphate trihydrate,*



This derivative gives an intense violet coloration with phenoxtellurine and other tellurides, and with iron or other base metals. Its solution in sulphuric acid becomes intensely red-brown on the addition of hydrogen peroxide.

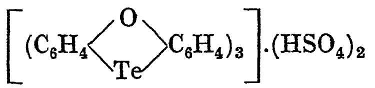
All the foregoing sulphates of phenoxtellurine when reduced by alkali bisulphite give phenoxtellurine as the sole organic product, no evidence of nuclear sulphonation being obtained.

Diphenoxtellurylium dibisulphate disulphuric acid trihydrate,



may be isolated by the following methods: (1) Phenoxtellurine (6 grams) is dissolved in 40 c.c. of concentrated sulphuric acid and the intensely red solution kept for thirty minutes, sulphur dioxide escaping. The whole is then cooled in a freezing mixture and treated gradually with 25 c.c. of water. After standing for an hour, the red crystals are filtered off through sintered glass and kept on a porous tile in a desiccator. The same substance also results when 1·1 grams of phenoxtellurine are treated with 15 c.c. of concentrated sulphuric acid and 10 c.c. of water. The yield is about 94 per cent. The red crystals are hygroscopic, becoming moist with sulphuric acid, and gaining about 30 per cent. of their weight of water when exposed to the air for several days. (2) Phenoxtellurine in glacial acetic acid is treated with a considerable proportion of concentrated sulphuric acid containing a little water, red crystals separating on keeping. (3) Diphenoxtellurylium dibisulphate di- or tri-hydrate, or the hydroxybisulphate monohydrate, is treated with sulphuric acid containing a little water, or with acetic-sulphuric acid, the red crystals separating if the concentration of the sulphuric acid is sufficiently high. (4) The same result is obtained by mixing phenoxtellurine and its hydrated bisulphate (p. 227) in glacial acetic acid and adding a little concentrated sulphuric acid. The phenoxtellurine as "acceptor" in this compound is 28·75 per cent., and as "donor" 27·85 per cent.[1]

Triphenoxtellurylium dibisulphate,



$$\left[(C_6H_4{<}^{O}_{Te}{>}C_6H_4)_3\right].(HSO_4)_2$$

is isolated (1) by dissolving phenoxtellurine in warm glacial acetic acid and adding a few drops of concentrated sulphuric acid, the intensely coloured solution crystallising on cooling; (2) by crystallising the dibisulphate disulphuric acid trihydrate or the dibisulphate di- or tri-hydrate several times from glacial acetic acid; (3) by warming together phenoxtellurine and its hydrated dibisulphate in glacial acetic acid and recrystallising the product from the latter solvent; (4) by carefully adding water to a concentrated sulphuric acid solution of phenoxtellurine until a blue precipitate commences to separate, the precipitate being collected after standing and crystallised from glacial acetic acid; (5) by grinding together phenoxtellurine and its hydroxybisulphate or dibisulphate and recrystallising the product from glacial acetic acid.

The product forms copper-coloured flakes or rosettes of needles, giving a violet-black powder. It has no definite melting-point, but gradually loses colour at 205° to 245° C., forming phenoxtellurine and a whitish solid which remains unmelted at 300° C. Heated at 100° C. *in vacuo* it does not lose its molecule of combined water. The colour change on heating is supposed to be due to decomposition into phenoxtellurine and its hydroxybisulphate, since partial redevelopment of the violet colour occurs on cooling and grinding the whitish mixture. The tellurylium compound is only decomposed slowly by organic solvents, but is quickly disrupted by cold water. When pure it forms a clear transparent solution in hot glacial acetic acid when the solution is dilute, but this becomes intensely cherry-red on concentration, and cold solutions are more coloured than hot solutions of the same concentration. Solutions in glacial acetic acid immediately reduce anhydrous ferric chloride, and in syrupy phosphoric acid the compound

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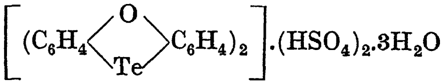
[1] Drew, *J. Chem. Soc.*, 1928, p. 506.

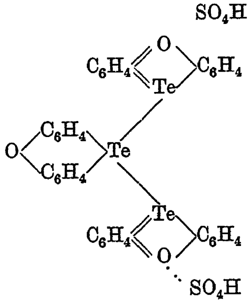
forms an intensely blue solution. The phenoxtellurine as "acceptor" is 53·5 per cent. and as "donor" 27·9 per cent.

The formula assigned to the compound requires some consideration. The third molecule of phenoxtellurine might be regarded as an addendum, substituting $3H_2O$ in the formula[1]

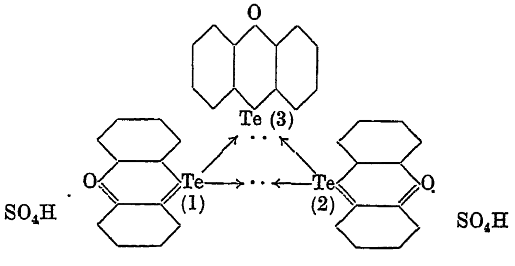


$$\left[(C_6H_4\langle\overset{O}{\underset{Te}{}}\rangle C_6H_4)_2\right].(HSO_4)_2.3H_2O$$

but it is considered probable that the three tellurium atoms are linked together, either in a chain (I) or in a ring (II):



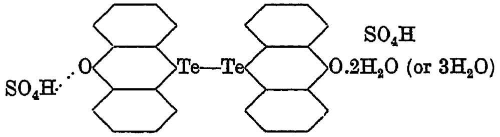
I



II

The second formula is preferred, since in it the three phenoxtellurine residues are equivalently situated if the formula be regarded as potentially dynamic. In the phase represented, the tellurium atoms marked (1) and (2) each supply an electron to affix tellurium atom (3), whilst they are themselves united by means of a non-polar bond (the dots show the binding electrons, and the arrows indicate the atoms whence these electrons originate, the dotted bonds representing polar linkings). At all phases of the formula each of the three tellurium atoms is seen to be associated with 56 electrons, and each oxygen and carbon atom is associated with 10 electrons. The view involves the suggestion that the three atoms may be held together by the sharing of 4 electrons.

Diphenoxtellurylium dibisulphate di- or tri-hydrate,



This derivative occurs when diphenoxtellurylium dibisulphate disulphuric acid trihydrate is exposed to the air for a few days. It is also formed by way of the methods indicated for the preceding hydroxy-compound, if the product be crystallised finally from glacial acetic acid containing a little concentrated sulphuric acid. The dihydrate appears to absorb moisture slowly when exposed to the air. Both hydrates are decomposed by cold water, the final products being phenoxtellurine and its basic sulphate. In diphenoxtellurylium dibisulphate trihydrate the phenoxtellurine as "acceptor" is 34·9 per cent., and as "donor" 35·6 per cent.

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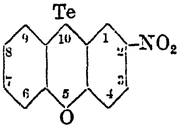
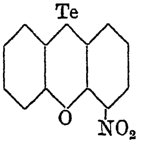
[1] Drew, *J. Chem. Soc.*, 1928, p. 508.

Nitro- and Amino-derivatives of Phenoxtellurine.[1]

2- and 4-Nitrophenoxtellurines,

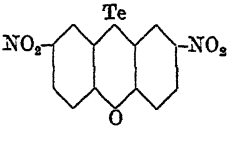


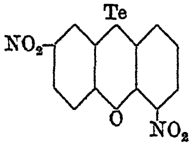


Powdered phenoxtellurine, 4·5 grams, is slowly added to 70 c.c. of nitric acid (density 1·42), and the orange-red solution obtained after ten minutes' boiling yields, after two days, opaque white needles. These are dried over soda-lime, the weight of product being about 5·7 grams. The aqueous mother-liquors on concentration give 0·9 gram of a solid which on reduction yields 2 : 8-dinitrophenoxtellurine. The main product (5·7 grams), when reduced by 30 c.c. of water and 5·7 grams of potassium metabisulphite, yields a dark paste. The yellow ether extract of this, when evaporated using a large surface, leaves yellow needles (A) surrounded by orange-red flakes (B). The mixture is mechanically separated, and (B) is found to consist of 2 : 8 dinitrophenoxtellurine, together with a compound containing two molecular proportions of 2 : 8-dinitrophenoxtellurine and one proportion of 2-nitrophenoxtellurine, which may be separated into its components by fractionation from ethyl alcohol. The complex crystallises unchanged from acetone. The yellow needles (A) give a first crop of crystals from acetone, part of which dissolves more readily in hot ethyl alcohol than the remainder; the more soluble portion separates as silky bright yellow needles of 2-nitrophenoxtellurine, M.pt. 129° C. The less soluble portion separates from the hot solvent as glistening bright yellow spangles, consisting of thin hexagonal prisms; this substance is a complex of 2 : 8-dinitro- and 2-nitro-phenoxtellurines in molecular proportions. This complex can be recrystallised unchanged from alcohol, but is partly disrupted by acetone. It melts slowly between 145° and 185° C. The acetone mother-liquor from (A) on slow evaporation gives impure 2-nitrophenoxtellurine and large lemon-yellow prisms. The latter are removed by hand and recrystallised from ethyl alcohol, lemon-yellow prisms or needles of 4-nitrophenoxtellurine being deposited, M.pt. 104° C.

2-Nitrophenoxtellurine 10 : 10-dinitrate forms colourless needles, M.pt. 196° to 197° C.; *4-nitro-10-hydroxyphenoxtellurine 10-nitrate monohydrate* yields white rods, M.pt. 243° C. with decomposition.[2]

2 : 8- and 4 : 8-Dinitrophenoxtellurines,[3]





Powdered phenoxtellurine, 4·3 grams, is gradually added to 25 c.c. of nitric acid (density 1·50), cooled in ice and salt, and the mixture finally heated for thirty minutes on the water-bath. Addition of water to the

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[1] Drew and Thomason, *J. Chem. Soc.*, 1927, p. 116.

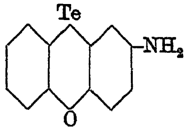
[2] Drew, *J. Chem. Soc.*, 1926, p. 3065.

[3] Drew and Thomason, *loc. cit.*

cooled solution precipitates a white solid, which is recrystallised from boiling nitric acid (density 1·42). The first crop of product (3·9 grams), when again crystallised from nitric acid, yields large, colourless, serrated needles (2·9 grams) which, on reduction with aqueous potassium metabisulphite, give pure 2 : 8-dinitrophenoxtellurine, M.pt. 228° C. This separates from acetone as large hexagonal orange prisms, or from alcohol as smaller yellow prisms, more sparingly soluble in organic solvents than the mononitrophenoxtellurines. The nitric acid mother-liquor from the first crop of product yields a white precipitate (4·2 grams) on dilution with water, and this is boiled for two hours with 20 c.c. of fuming nitric acid. Precipitation by water and recrystallisation of the precipitate from concentrated nitric acid gives a further crop of serrated needles, the mother-liquors slowly depositing minute white rods. The latter, after further crystallisation from concentrated nitric acid, yield on reduction with aqueous potassium metabisulphite pure 4 : 8-dinitrophenoxtellurine, M.pt. 197° to 198° C. The latter occurs also in 60 per cent. yield when 4-nitrophenoxtellurine is nitrated with fuming nitric acid. It crystallises from benzene as long, thin, golden, lath-like needles, containing 0·5 molecule of benzene. The latter is slowly evolved in air, the dinitro-compound remaining as a salmon-red crystalline powder, which separates from ethyl alcohol as minute red crystals. It is only sparingly soluble in organic solvents. The nitration of 2-nitrophenoxtellurine leads to a mixture of 2 : 8-dinitro- and 4 : 8-dinitrophenoxtellurines, the latter being present only in small amount.

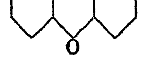
2 : 8-Dinitrophenoxtellurine 10 : 10-dinitrate consists of serrated needles, melting with decomposition at 259° C., and *4 : 8-dinitro-10-hydroxyphenoxtellurine 10-nitrate monohydrate* gives white needles, decomposing violently at 237° to 239° C.

2-Aminophenoxtellurine,



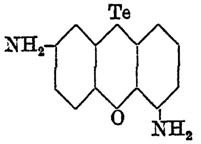
2 grams of the corresponding nitro-compound are heated for several hours on a water-bath with a large excess of tin and concentrated hydrochloric acid, until the yellow colour of the nitro-compound disappears. After filtration, the solid and filtrate are treated separately with cold sodium hydroxide solution and the liberated amine extracted with chloroform in a Soxhlet apparatus. The amine crystallises from aqueous alcohol as pinkish-white needles, M.pt. 157° C.; its *hydrochloride* separates from water as small, very pale yellow needles. If the amine is boiled with aqueous potassium hydroxide it yields 4-aminodiphenyl ether. Diazotisation and coupling with alkaline β-naphthol give an insoluble red *azo-dye*.

2 : 8-Diaminophenoxtellurine,



occurs when the dinitro-compound is reduced by tin and hydrochloric acid. It crystallises from alcohol as lemon-yellow needles, M.pt. 198° C., is slightly soluble in water, and yields a *hydrochloride* which crystallises from hot water as long yellow needles. Tetrazotisation causes the formation of a blood-red solution which yields an insoluble red *azo-dye* with alkaline β-naphthol.

4 : 8-Diaminophenoxtellurine,



forms pale yellow feathery needles or mica-like plates, M.pt. 156° C., soluble in water or aqueous alcohol. On tetrazotisation the diamine yields a bright red diazonium chloride, forming a red *azo-dye* with alkaline β-naphthol.

Molecular Compound of Phenoxtellurine and Chloromethylphenoxtellurine.[1]

When phenoxtellurine is prepared by treating diphenyl ether with tellurium tetrachloride and reducing the 10 : 10-dichlorophenoxtellurine formed, a complex by-product results. This appears to be comprised of a molecule of phenoxtellurine with a molecule of 2(?)-chloro-8(?)-methylphenoxtellurine, the latter resulting from the presence in the diphenyl ether of a small proportion of phenyl *p*(?)-tolyl ether, which is chlorinated by the tellurium tetrachloride. The chlorinated product changes to 2(?)-chloro-8(?)-methylphenoxtellurine, which subsequently unites with phenoxtellurine. The complex separates from alcohols or petroleum in bushes of well-defined light yellow needles with chiselled ends, melting sharply at 59° C. When it is treated in chloroform solution with bromine in the same solvent, phenoxtellurine dibromide separates. The chloroform mother-liquor, when again precipitated by bromine in chloroform, yields a mixture of two dibromides, whilst a further precipitation of the mother-liquor from this mixture yields *chloromethylphenoxtellurine dibromide*, a yellow, crystalline substance, sparingly soluble in chloroform, and melting with decomposition at 315° C. Reduction of this dibromide by potassium metabisulphite solution gives *chloromethylphenoxtellurine*, consisting of prismatic needles from alcohol, M.pt. 46° to 47° C., very soluble in organic solvents, but insoluble in water. This tellurine forms a *dichloride*, consisting of pale yellow prisms from xylene, M.pt. 300° C. (decomp.), a *diacetate*, colourless needles from acetic acid, M.pt. 230° to 232° C. (with frothing), and a *dibisulphate*, cream-coloured scales, which acts as a " donor " towards tellurides, giving deep purplish-black tellurylium compounds. In cold concentrated sulphuric acid chloromethylphenoxtellurine gives a deep maroon-red solution which evolves sulphur dioxide, the addition of a little water precipitating minute dark red crystals which crystallise from acetic acid as a blue-black crystalline powder having a greenish-bronze lustre, the solution in acetic acid being intense reddish-purple, becoming pale yellow on dilution or heating (reversible change).

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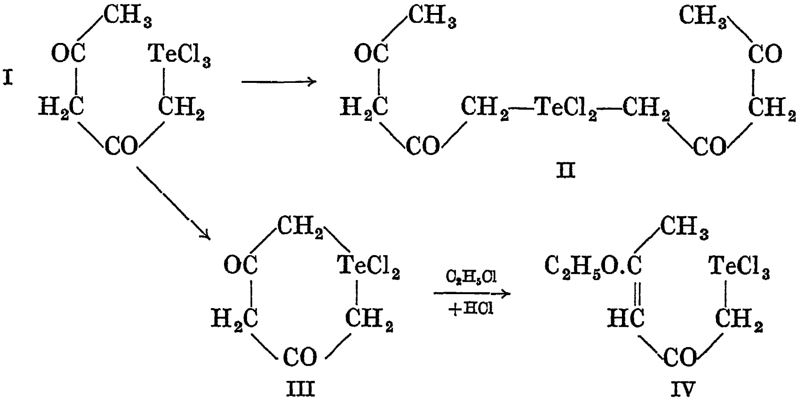
[1] Drew and Thomason, *loc. cit.*; Drew, *J. Chem. Soc.*, 1928, p. 510.

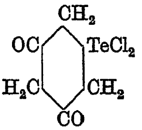
Tellurium Compounds Derived from β-Diketones.

Tellurium Tetrachloride and Acetylacetone.[1]

The condensation of tellurium tetrachloride and acetylacetone in chloroform (B.P.) proceeds with the elimination of hydrogen chloride to a primary product $CH_3.CO.CH_2.CO.CH_2.TeCl_3$ (I), which, although not isolated, may be regarded as the parent substance of the three stable tellurium derivatives subsequently obtained. Interaction of the primary product with more acetylacetone leads to the formation of tellurium *bis*-acetylacetone dichloride (II), whilst loss of hydrogen chloride from (I) yields tellurium acetylacetone dichloride (*cyclo*telluropentanedione dichloride) (III). The presence of ethyl chloride in the solvent causes ethylation of the enolic group, giving tellurium O-ethylacetylacetone trichloride (IV), which is also obtained by the joint action of hydrogen chloride and ethyl chloride on compound III.



Tellurium acetylacetone dichloride (*cycloTelluropentanedione dichloride*),[2]



Sublimed tellurium tetrachloride, 10·3 grams, is mixed with 7·6 grams of acetylacetone in 55 c.c. of dry chloroform, the solution heated for two hours under reflux, filtered and concentrated over lime. The total yield of dichloride is 7 grams, or 62 per cent. The product is sparingly soluble in ether, benzene or chloroform, more soluble in hot alcohol, and very soluble in cold acetone. From alcohol or benzene it is deposited in acicular form, whilst from acetone large transparent hexagonal prisms, often twinned, are isolated. Both forms are colourless, darkening at 155° to 160° C. and melting with decomposition between 169° and 173° C., liberating tellurium and evolving hydrogen chloride and a lachrymatory oil which develops a red coloration with

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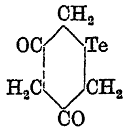
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1922, 121, 922.

[2] Morgan and Drew, *Trans. Chem. Soc.*, 1920, 117, 1456.

aqueous ferric chloride. Crystallisation from methyl alcohol gives prisms, darkening at 140° C. and decomposing at 157° C. The dichloride does not become discoloured on exposure to light, but readily loses chlorine with hot water or aqueous acids or alkalis. Boiling potassium hydroxide solution does not liberate tellurium, and with aqueous ferric chloride a red coloration develops only slowly. When warmed with a large excess of aqueous sulphurous acid the compound is decomposed completely, yielding tellurium and acetylacetone.

Tellurium acetylacetone (*cycloTelluropentanedione*),

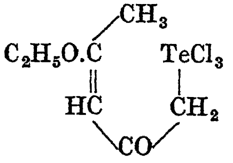


is obtained when the foregoing dichloride is reduced by potassium metabisulphite, or by boiling it with a slight excess of aqueous sulphur dioxide. It forms heavy golden-yellow needles, melting sharply at about 182° C., sparingly soluble in water, ether, chloroform or alcohol. Under reduced pressure it sublimes at about 160° C., giving glistening yellow needles. Cold concentrated hydrochloric acid eliminates the tellurium, whilst cold aqueous potassium hydroxide dissolves the compound, the yellow solution yielding the original compound on immediate neutralisation, but after a few minutes depositing tellurium. Ferric chloride gives a red coloration after long standing; hydrogen peroxide immediately decolorises the yellow aqueous solution; hydrogen sulphide gives a black precipitate, and alcoholic mercuric iodide yields a yellow precipitate. Tellurium acetylacetone is quantitatively decomposed by potassium metabisulphite, warm aqueous sulphur dioxide, aluminium-mercury couple or concentrated hydrochloric acid.

Tellurium acetylacetone dibromide, $C_5H_6O_2 : TeBr_2$,[1] is prepared by reducing the corresponding dichloride and treating the tellurium acetylacetone with bromine in chloroform at 0° C. It forms colourless prisms, darkening at 129° C. and melting at 159° C. when crystallised from chloroform, acetone, ethyl alcohol or glacial acetic acid, but from methyl alcohol darkens at 120° C. and intumesces violently at 124° C.

Tellurium acetylacetone di-iodide, $C_5H_6O_2 : TeI_2$, forms reddish-violet or heliotrope crystals, blackening at 120° C. and decomposing indefinitely at 141° to 143° C. Crystallisation from methyl alcohol gives light red crystals, darkening at 114° C. and decomposing at 121° to 126° C.

Tellurium O-ethylacetylacetone trichloride,



may be prepared in several ways: (1) A solution of 7·8 grams of acetylacetone in 30 c.c. of dry chloroform is added to 10·4 grams of tellurium tetrachloride in 120 c.c. of the same solvent and the mixture allowed to

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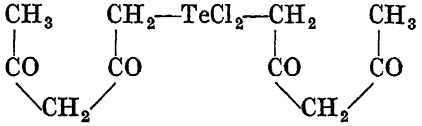
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1921, 119, 610.

stand for fourteen hours. It is then boiled under reflux for one and a half hours and the liquid poured from a small amount of dark heavy oil formed. The chloroform solution is evaporated under reduced pressure, when 2·3 grams of dichloride separate, the mother-liquor yielding an oily product which soon crystallises (5·7 grams). Successive crystallisation from chloroform and benzene-light petroleum yields large, pale yellow, obliquely truncated, tabular prisms, M.pt. 106° to 107° C., $a : b : c = 1{\cdot}182 : 1 : 1{\cdot}198$; $\alpha = 86^\circ\ 29'$, $\beta = 106^\circ\ 4'$, $\gamma = 94^\circ\ 25'$. (2) Tellurium acetylacetone dichloride and ethyl chloride are allowed to react in ice-cold chloroform solution in the presence of hydrogen chloride. (3) Tellurium acetylacetone dichloride is heated under reflux with chloroform saturated with hydrogen chloride, and the resulting solid treated with ethyl chloride. The trichloride is sparingly soluble in cold water, with slow decomposition; it also dissolves sparingly in ether or carbon tetrachloride, more readily in benzene or chloroform, but is practically insoluble in light petroleum. When heated in solvents above 80° C. it decomposes with elimination of tellurium. The pure product has a slightly acid taste and is acid to litmus paper even in dry ether. It is decomposed by cold aqueous potassium bisulphite, alkali carbonate or hydroxide.

Tellurium bis-acetylacetone dichloride,[1]



8 grams of tellurium tetrachloride and 6 grams of acetylacetone in 90 c.c. of "salicylide" chloroform[2] are heated under reflux for forty-five minutes. The orange solution is concentrated to 40 c.c., filtered and evaporated in a vacuum; the yellow syrup obtained is stirred with a small amount of chloroform and allowed to crystallise, when 2·7 grams of tellurium acetylacetone dichloride separate and are removed. The filtrate is shaken with a few cubic centimetres of water, when 0·6 gram of tellurium dioxide is removed. The filtrate is then allowed to evaporate completely, the residue yielding 2 grams of tellurium *bis*-acetylacetone dichloride (18 per cent.). The compound separates from benzene as colourless silvery flakes, melting with decomposition at 115° C., dissolving only sparingly in cold alcohol and decomposing on heating; it remains unchanged in boiling chloroform. Aqueous ferric chloride instantly gives a blood-red coloration with a chloroform solution of the dichloride.

Tellurium Tetrachloride and 3-Alkylacetylacetones.

The condensation between tellurium tetrachloride and C-methylacetylacetone or C-ethylacetylacetone gives rise in either case to only one product, namely, tellurium 3-methylacetylacetone dichloride or tellurium 3-ethylacetylacetone dichloride, respectively. The primary

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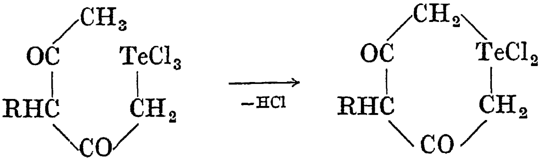
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1922, 121, 922.

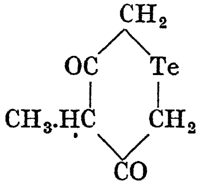
[2] Chloroform purified by the "salicylide process" contains no alcohol or ethyl chloride as impurities.

product, $CH_3.CO.CHR.CO.CH_2.TeCl_3$, loses hydrogen chloride, to give the cyclic compound:



Tellurium 3-methylacetylacetone dichloride (*4-Methylcyclotelluropentanedione dichloride*).—A solution of 8·9 grams of tellurium tetrachloride in 100 c.c. of chloroform (B.P.) is treated with 7·6 grams of redistilled C-methylacetylacetone in 25 c.c. of the same solvent and the mixture heated for one hour under reflux. Hydrogen chloride is evolved and the dichloride separates mixed with 0·2 gram of free tellurium. This mixture is extracted with cold acetone, the dichloride recovered in crystalline form and added to the main chloroform solution, when crystallisation sets in. After standing for several days in a vacuum desiccator, about 6·8 grams (67 per cent.) of dichloride separate out. The product crystallises from acetone as stout hexagonal needles or prisms having obliquely truncated ends. It is colourless when highly purified, but generally has a brownish-grey tint owing to the presence of traces of tellurium. In water or organic solvents other than acetone it is only sparingly soluble. At 180° C. it discolours, and becomes black at 190° C.

Tellurium 3-methylacetylacetone (*4-Methylcyclotelluropentanedione*),

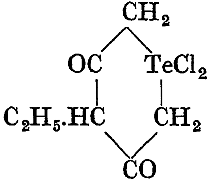


The preceding compound, 4·3 grams, is finely ground and mechanically stirred into 20 c.c. of ice-cold water. Powdered potassium metabisulphite, 6·1 grams, is slowly introduced, sulphur dioxide being evolved, and after thirty minutes the yellow product is removed and crystallised successively from hot water and benzene. The yield is about 2·5 grams, or 76 per cent. The product crystallises as small, hexagonal, pale golden-yellow plates, often acicular in habit, darkening from 155° C. and decomposing sharply at 170° C. with separation of tellurium. On heating it is more stable than tellurium acetylacetone, subliming at 140° C. in a vacuum to small, compact, yellow prisms. Towards ferric and cupric salts it is non-enolic, and it possesses little residual acidity, being comparatively insoluble in cold 5*N* sodium hydroxide, whereas tellurium acetylacetone dissolves at once. The yellow solutions of these two tellurium derivatives are unstable and readily deposit tellurium. Tellurium 3-methylacetylacetone combines additively with bromine or iodine in cold 2 per cent. chloroform solution.

Tellurium 3-methylacetylacetone dibromide, $(C_5H_5O_2.CH_3):TeBr_2$, obtained as described above, separates from alcohol as yellowish-white prisms, decomposing with violent intumescence at 152° to 153° C.

Tellurium 3-methylacetylacetone di-iodide, $(C_5H_5O_2.CH_3):TeI_2$, is a crimson, crystalline powder, sintering sharply at 134° C. to a black core, which intumesces at 175° to 176° C. It separates from alcohol or ethyl acetate as reddish-purple crystals, sintering and intumescing at appreciably lower temperatures, these changes occurring at 131° to 134° C. and 169° to 171° C. respectively.

Tellurium 3-ethylacetylacetone dichloride (*4-Ethylcyclotelluropentanedione dichloride*),



This derivative is prepared in a similar manner to the corresponding 3-methyl compound, and the yield is about 80 per cent. It resembles its lower homologue in solubility, dissolving readily in acetone, but it is more sparingly soluble in other organic media, such as chloroform or the alcohols. When pure it is colourless, but it usually has a brown tinge and separates from acetone or hot methyl alcohol as highly lustrous hexagonal prisms, blackening at 185° to 190° C. It gives no coloration with aquo-alcoholic ferric chloride. It is decomposed by prolonged heating with alcohol. When inhaled in the form of dust it has a very irritating action on the mucous membrane of the nostrils.

Tellurium 3-ethylacetylacetone, $(C_5H_5O_2.C_2H_5):Te$, prepared in a similar manner to the corresponding 3-methyl compound, separates from hot water or alcohol as odourless yellow needles or more compact prisms, and from benzene as lustrous primrose-yellow hexagonal leaflets. It readily dissolves in chloroform and, like its lower methyl homologue, is much more soluble in benzene than is tellurium acetylacetone. It has a neutral reaction in water and shows no enolic properties; it is almost devoid of residual acidity, thus differing from tellurium acetylacetone and tellurium 3-chloroacetylacetone in its sparing solubility in cold 5*N* sodium hydroxide or aqueous sodium carbonate. It exhibits great stability towards moist or dry heat, but is blackened by contact with sodium hydroxide. Unlike tellurium acetylacetone it withstands prolonged boiling with water, and in a vacuum it sublimes slowly but completely at 130° C. giving long needles, which become transformed as the temperature rises to 140° C. into small, yellow, prismatic crystals, melting at 142° C. to a transparent yellow liquid from which black tellurium separates on heating at 160° C. The crystals of this compound represent an orthorhombic combination of *q* (011), *r* (101) and *m* (110). The axial ratios $a:b:c=1:1:0{\cdot}7221$ follow from the annexed values, representing the mean results of measurement on two crystals:

	m (110)	*q* (011)	*r* (101)
Azimuth (ϕ) . .	45° 0′	0° 0′	90° 0′
Polar Distance (ρ) .	90° 0′	*35° 50′	*35° 50′

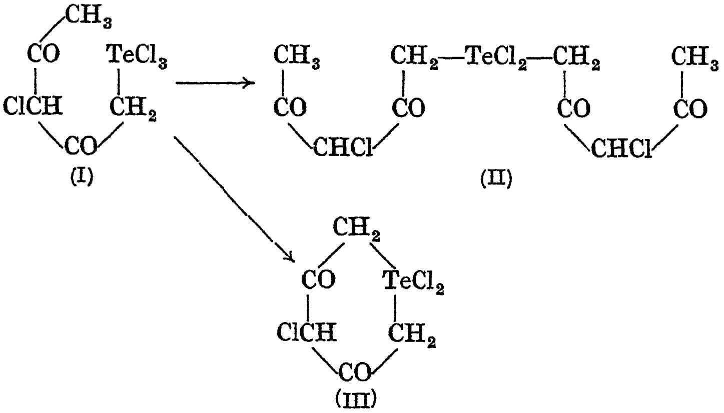
The Fedorov complex symbol is $4\sigma(45° 36')\pm0$. Optically the crystals are biaxial; the acute bisectrix is negative.

Tellurium 3-ethylacetylacetone dibromide, $(C_5H_5O_2.C_2H_5):TeBr_2$, obtained from its generators in chloroform solution at 0° C., separates from methyl or ethyl alcohol as lustrous, very pale yellow crystals, non-enolic towards ferric chloride. Its melting-point ranges from 161° to 170° C.

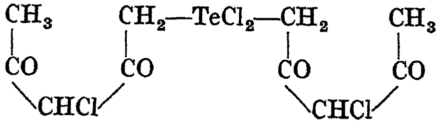
Tellurium 3-ethylacetylacetone di-iodide, $(C_5H_5O_2.C_2H_5):TeI_2$, crystallises from ethyl alcohol as light scarlet crystals. In powdered form and in alcoholic solution it is orange in colour. It gives no coloration with aquo-alcoholic ferric chloride. It sinters and blackens at 149° C., and decomposes with intumescence at 176° C.

Tellurium Tetrachloride and 3-Chloroacetylacetone.

The main product resulting from this condensation is tellurium *bis*-3-chloroacetylacetone dichloride (II), the by-product being tellurium 3-chloroacetylacetone dichloride (III). This result is explained on the assumption that a reactive primary product $CH_3.CO.CHCl.CO.CH_2.TeCl_3$ (I) is first produced, and this condenses with a second molecular proportion of 3-chloroacetylacetone to yield tellurium *bis*-3-chloroacetylacetone dichloride, the retention of two enolic groups being shown by the production of copper tellurium *bis*-3-chloroacetylacetone dichloride, and the fact that this substance is enolic and yields metallic salts is a proof of the general hypothesis that tellurium becomes attached initially to a terminal methyl group. The alternative possibility of replacing the hydrogen of the chloromethylene group would not give rise to an enolic compound. To some extent, however, hydrogen chloride is eliminated from (I), with the formation of tellurium 3-chloroacetylacetone dichloride (III).

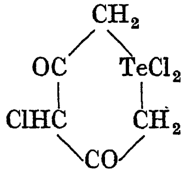

(I) (II) (III)

Tellurium bis-3-chloroacetylacetone dichloride,

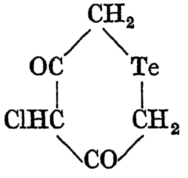


Tellurium tetrachloride, 11 grams, is suspended in 60 c.c. of chloroform (B.P.) and 11 grams of chloroacetylacetone added. After heating under reflux for 1·75 hours the mixture is filtered and the filtrate evaporated to dryness in a vacuum, the gummy residue being dissolved in chloroform and the liquid evaporated under reduced pressure to a syrupy consistency to remove chloroacetylacetone. The syrup, left over solid sodium hydroxide, partly solidifies, and the mixture is stirred with cold chloroform, thus yielding a solid residue (by-product) and a chloroform extract. The latter is evaporated, the semi-solid mass spread on porous tile and the solid (3 grams, or 16 per cent.), consisting of tellurium *bis*-3-chloroacetylacetone dichloride, recrystallised from ligroin or a mixture of carbon tetrachloride and light petroleum. The product separates as colourless, feathery, prismatic needles, melting with decomposition at 131° to 132° C., readily soluble in hot benzene or cold chloroform, less soluble in ether. It is markedly enolic, giving a very intense red coloration with ferric chloride in aquo-alcoholic chloroform. Reduction with potassium hydrogen sulphite yields an unstable, insoluble, yellow product.

Tellurium 3-chloroacetylacetone dichloride, is the residue noted as a by-product in the preceding preparation. This residue is extracted with acetone, filtered and the solution allowed to evaporate, when brownish-white crystals of the dichloride separate; yield 0·6 gram, or 5 per cent. When pure the product melts and decomposes with intumescence at 161° to 162° C.



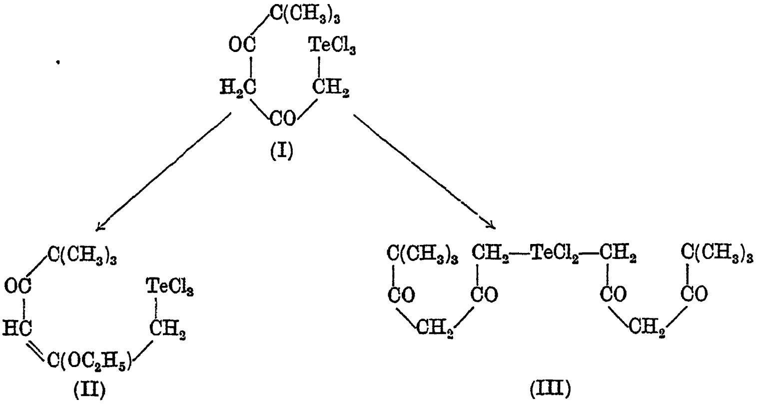
Tellurium 3-chloroacetylacetone (*4-Chlorocyclotelluropentane dione*), occurs in 51 per cent. yield when tellurium 3-chloroacetylacetone dichloride is reduced in the usual manner with powdered potassium metabisulphite. It crystallises from hot benzene in voluminous masses of light yellow needles, blackening and decomposing at 153° to 154° C. It is the least soluble member of this series of tellurium compounds both in water and in organic media. Its aqueous solution is distinctly acid to litmus, but non-enolic towards ferric chloride. In aqueous sodium carbonate it dissolves to give a yellow solution which is stable in the cold but blackens on boiling. It is less soluble in aqueous sodium bicarbonate, but dissolves immediately in cold 5*N* sodium hydroxide, the solution being unstable and liberating tellurium. These properties indicate that tellurium 3-chloroacetylacetone has residual acidity, thus resembling



tellurium acetylacetone, the two compounds differing markedly in this respect from the tellurium 3-alkylacetylacetones.

Tellurium Tetrachloride and Pivalylacetone (*Acetylpinacolin*).

The condensation of the above substances in chloroform solution yields tellurium O-ethylpivalylacetone trichloride (II) as the main product, and tellurium *bis*-pivalylacetone dichloride (III) as a by-product. The enolisation of the primary product (I), $(CH_3)_3C.CO.CH_2.CO.CH_2.TeCl_3$, probably occurs with the CO-group remote from the tertiary group. The compound (I) cannot form a six-membered ring, but tends either to ether formation (II) or to condensation with a second molecule of pivalylacetone to give the dichloride (III).



Tellurium O-ethylpivalylacetone trichloride (*Tellurium O-ethylacetylpinacolin trichloride*) (Formula II).—Acetylpinacolin, 3·4 grams, is added to 3·2 grams of tellurium tetrachloride suspended in 35 c.c. of chloroform (B.P.). Solution takes place and the mixture is heated under reflux for one hour on the water-bath, hydrogen chloride being evolved. The orange-yellow solution is decanted from the dark oil which forms and evaporated *in vacuo*. Pale yellow crystals, 3·8 grams, are obtained. Repeated crystallisation from ligroin, or preferably equal volumes of carbon tetrachloride and light petroleum, yields transparent yellowish-white prismatic needles, sintering at 114° C. and melting at 116° C. to a liquid which rapidly blackens. In all organic solvents except light petroleum the product is very soluble. When pure it is non-enolic towards ferric chloride, thus resembling its acetylacetone and benzoylacetone analogues. Cold aqueous sodium hydroxide or carbonate removes the tellurium, leaving O-ethylpivalylacetone (or O-ethylacetylpinacolin).

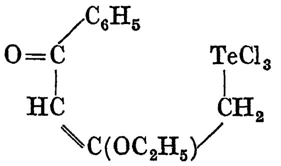
Tellurium bis-pivalylacetone dichloride (*Tellurium bis-acetylpinacolin dichloride*) (Formula III).—A mixture containing 3·9 grams of tellurium tetrachloride, 3·8 grams of acetylpinacolin and 25 c.c. of pure alcohol-free chloroform is heated under reflux for 2·5 hours. Evaporation under reduced pressure then yields a syrup, from which separate 1·6 grams of homogeneous crystals. These are drained on a porous tile, then recrystallised from a mixture of carbon tetrachloride and light petroleum, colourless, glistening flakes separating, M.pt. 133° C.

with decomposition. The product is readily soluble in cold chloroform or ethyl acetate, less soluble in carbon tetrachloride and insoluble in light petroleum. It reacts immediately with copper acetate and gives at once a red coloration with ferric chloride. Treatment with cold 5*N* sodium hydroxide does not yield a fragrant O-ether as in the case of the trichloride.

Tellurium Tetrachloride and Benzoylacetone.[1]

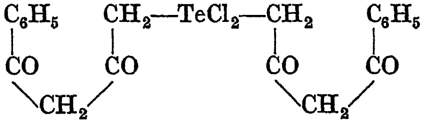
In this condensation only two compounds have been isolated, their formation being explained as in the case of the two compounds in the preceding section.

Tellurium O-ethylbenzoylacetone trichloride,



occurs when molecular proportions of tellurium tetrachloride and benzoylacetone react in B.P. chloroform.[2] It crystallises from hot chloroform, carbon tetrachloride or benzene (light petroleum being used to decrease the solubility) as prismatic tablets, darkening at 138° C. and decomposing at 140° C., $a:b:c=0{\cdot}7288:1:0{\cdot}6600$, $\beta=99°\ 25'$. It does not give an immediate coloration with ferric chloride, the colour developing only slowly. The solubility is somewhat less than that of the corresponding acetylacetone product, and the body is decomposed by prolonged boiling above 80° C. Although very soluble in acetone it is not recoverable unchanged from this solvent. Hydrolytic solvents decompose it, and it is slowly attacked by moisture, alkalis and alkali bisulphite.

Tellurium bis-benzoylacetone dichloride,[3]



formed by carrying out the foregoing condensation in "salicylide" chloroform, is deposited from ethyl acetate as well-defined, flattened, yellowish-white needles, melting and decomposing at 148° C., insoluble in water or light petroleum, sparingly soluble in cold benzene, chloroform or ethyl acetate, more soluble in the hot solvents or in acetone. With aqueous ferric chloride it instantly gives a red coloration.

The Interaction between Acetylpropionylmethane and Tellurium Tetrachloride.[4]

The condensation of the above substances yields tellurium acetylpropionylmethane dichloride, which reacts with ethyl chloride in

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[1] Morgan and Drew, *Trans. Chem. Soc.*, 1922, 121, 922.

[2] Morgan and Drew, *Trans. Chem. Soc.*, 1921, 119, 610.

[3] Morgan and Drew, *Trans. Chem. Soc.*, 1922, 121, 922.

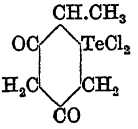
[4] Morgan and Reeves, *Trans. Chem. Soc.*, 1923, 123, 444.

chloroform to give tellurium O-ethylacetylpropionylmethane trichloride, according to the equations

$$C_6H_{10}O_2 + TeCl_4 = (C_6H_8O_2) : TeCl_2 + 2HCl$$
$$(C_6H_8O_2) : TeCl_2 + C_2H_5Cl = (C_2H_5O.C_6H_8O)TeCl_3$$

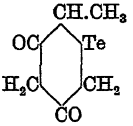
The dichloride, when reduced by sulphurous acid, alkali sulphites or bisulphites, yields tellurium acetylpropionylmethane, from which the dibromide and di-iodide are prepared by the action of the corresponding halogen.

Tellurium acetylpropionylmethane dichloride (*2-Methylcyclotelluropentanedione dichloride*),



Acetylpropionylmethane, 3·54 grams, and 3 grams of sublimed tellurium tetrachloride suspended in 24 c.c. of chloroform (B.P.) are heated together under reflux for one and a half hours and the yellow filtrate concentrated over lime. The yield of dichloride is about 2·2 grams, the product melting with decomposition at 170° to 171° C., dissolving in cold acetone, but only sparingly in ether, benzene or chloroform. On keeping it becomes brownish-grey owing to slight decomposition. It resembles its isomeride, tellurium 3-methylacetylacetone dichloride.

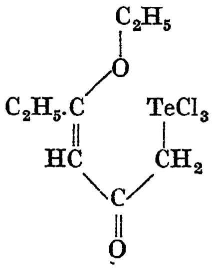
Tellurium acetylpropionylmethane,



2 grams of the foregoing dichloride suspended in 40 c.c. of ice-cold water are treated during ten minutes with 2·8 grams of potassium metabisulphite, the mixture being well stirred. The product which separates after filtration and concentration is recrystallised from hot benzene. Golden-yellow needles are deposited, M.pt. 100° C., more soluble in water than in organic solvents, but moderately soluble in benzene or chloroform. The aqueous solution slowly deposits tellurium.

Tellurium acetylpropionylmethane dibromide, $C_6H_8O_2 : TeBr_2$, occurs when the preceding compound and bromine are mixed in chloroform solution. It crystallises from hot alcohol as white prisms, melting with decomposition at 156° C. The corresponding *di-iodide* is obtained as crimson needles, sintering at 130° C. and melting at 190° C., and as reddish-purple needles, sintering at 135° C. and intumescing at 185° C.

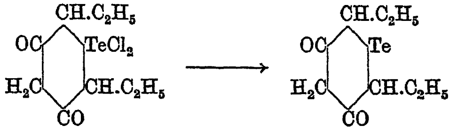
Tellurium O-ethylacetylpropionylmethane trichloride,



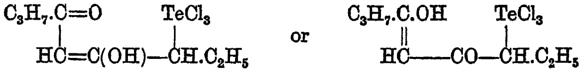
Powdered tellurium acetylpropionylmethane dichloride, 1·5 grams, is added to 25 c.c. of chloroform (B.P.) saturated with hydrogen chloride, 3 c.c. of ethyl chloride are added, and the yellow solution heated under reflux for two hours. Cooling, filtration and concentration *in vacuo* over lime yield an oil which solidifies. This is extracted with cold chloroform, the solution concentrated and the resulting solid redissolved in chloroform and precipitated by light petroleum. It forms pale yellow prismatic needles, decomposing at 120° C., and slowly eliminating tellurium when kept. The chloroform solution develops no immediate red coloration with alcoholic ferric chloride; on boiling and leaving overnight, however, a deep red coloration develops. Aqueous sodium hydroxide causes destructive hydrolysis.

Tellurium Tetrachloride and Dibutyrylmethane.[1]

Di-*n*-butyrylmethane, $C_3H_7.CO.CH_2.CO.C_3H_7$, condenses with tellurium tetrachloride to yield tellurium di-*n*-butyrylmethane dichloride (I), existing in polymorphous forms, each reducible to the same yellow tellurium di-*n*-butyrylmethane (II) (or 2 : 6-diethyl*cyclo*telluropentane), and it also gives rise to tellurium di-*n*-butyrylmethane trichloride (III), a new type of condensation product which makes its appearance at this stage in the homologous series of *β*-diketone derivatives.



(I) (II)



$$\begin{matrix} C_3H_7.C{=}O & & TeCl_3 \\ | & & | \\ HC{=}C(OH){-} & & CH.C_2H_5 \end{matrix} \quad \text{or} \quad \begin{matrix} C_3H_7.C.OH & & TeCl_3 \\ \| & & | \\ HC{-}{-}CO{-} & & CH.C_2H_5 \end{matrix}$$

(III)

Compound (III) is enolic, giving a red ferric chloride coloration, and is readily hydrolysible with water.

Tellurium dibutyrylmethane dichloride (Formula I).—The condensation is carried out in the usual manner, using one molecular equivalent of tetrachloride to two molecular equivalents of diketone in 75 c.c. of chloroform for each gram of tetrachloride, the solution being boiled for three to four hours. Cooling and concentrating gives a crystalline solid (A), the mother-liquor (B) being further concentrated. The product (A) separates from chloroform and light petroleum as white needles, M.pt. 120° C. It possesses the properties of a cyclic dichlorotellurium compound, $R''TeCl_2$, and shows a tendency to exist in different polymorphic forms similar to those noted in the case of the dihalides of tellurium acetylacetone, $C_5H_6O_2 : TeX_2$. When recrystallised from methyl alcohol it separates as vitreous needles, M.pt. 148° C., whereas from ethyl alcohol or chloroform-petroleum (B.pt. 40° to 60° C.) it gives colourless needles, melting indefinitely between 120° and 139° C. The mother-liquor (B) yields another crop

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[1] Morgan and Thomason, *Trans. Chem. Soc.*, 1924, 125, 754.

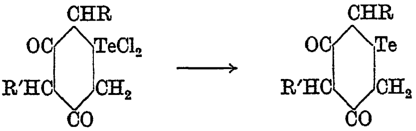
of dichloride separating as woolly needles, M.pt. 138° C., which, when recrystallised from chloroform-petroleum, form colourless short needles, M.pt. 137° to 138° C.

Tellurium dibutyrylmethane (Formula II) occurs when any of the foregoing forms of the dichloride is reduced by alkaline bisulphite. It crystallises from alcohol as golden-yellow needles, M.pt. 97° C.

Tellurium dibutyrylmethane trichloride (Formula III).—This is isolated when the final mother-liquors from the dichloride are concentrated and cooled to 0° C. It yields large tabular crystals, melting and blackening at 87° to 88° C. Unlike the dichloride it develops a blood-red coloration with aquo-alcoholic ferric chloride. It is decomposed by moisture, and is very soluble in chloroform.

Tellurium Tetrachloride and C_8-Diketones Alkylated in the Methylene Group.[1]

3-Ethylpropionylacetone, 3-*n*-propyl- and 3-*iso*propyl-acetylacetone each condense with tellurium tetrachloride to yield dichlorotellurium compounds which are reducible in the usual manner :



(where R $=CH_3$ or H, and R′ $=C_2H_5$ or C_3H_7)

Tellurium 3-ethylpropionylacetone dichloride ($R=CH_3$, $R'=C_2H_5$) is obtained in 63 per cent. yield when the condensation is conducted in the usual manner. It separates from cold acetone or hot alcohol as acicular prisms, melting with blackening at 167° C.

Tellurium 3-ethylpropionylacetone (*2-Methyl-4-ethylcyclotelluropentanedione*), formed by reducing the dichloride (1 mol.) with aqueous potassium metabisulphite (2 mols.), crystallises from alcohol as pale yellow needles, M.pt. 109° C., sparingly soluble in water.

Tellurium 3-n-propylacetylacetone dichloride crystallises from acetone-light petroleum as colourless acicular prisms, melting indefinitely at 180° C., reduction yielding *tellurium 3-n-propylacetylacetone* (*4-n-propylcyclotelluropentanedione*), very pale yellow needles from alcohol or benzene, M.pt. 106° to 107° C.

Tellurium 3-isopropylacetylacetone dichloride forms lustrous, colourless, acicular prisms from cold acetone, M.pt. about 150° C., and yields on reduction *tellurium 3-isopropylacetylacetone*, yellow needles from alcohol, M.pt. 152° to 153° C.

Tellurium Tetrachloride and Higher β-Diketones.[2]

The β-diketones dealt with in this section react smoothly with tellurium tetrachloride, forming derivatives similar to those in the preceding section.

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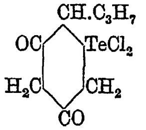
[1] Morgan and Thomason, *loc. cit.*

[2] Morgan and Holmes, *Trans. Chem. Soc.*, 1924, 125, 760.

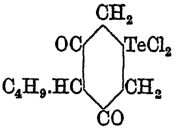
Tellurium n-valerylacetone dichloride,



occurs in 50 per cent. yield when *n*-valerylacetone (2 mols.) and tellurium tetrachloride (1 mol.) are heated together under reflux in chloroform, using 7·5 grams of the solvent for each gram of tetrachloride. It crystallises from benzene-petroleum (B.pt. 80° to 100° C.) or from acetone as colourless needles, M.pt. 125° C. Reduction gives *tellurium n-valerylacetone* (*2-n-propylcyclotelluropentanedione*) in 70 per cent. yield, the product separating from hot alcohol as yellow needles, M.pt. 80° C.

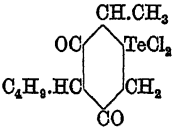
Tellurium n-hexoylacetone dichloride crystallises from acetone as colourless needles, M.pt. 102° C., yielding on reduction *tellurium n-hexoylacetone* (*2-butylcyclotelluropentanedione*), brilliant yellow needles from warm water or alcohol, M.pt. 86° C.

Tellurium 3-n-butylacetylacetone dichloride,



separates from cold acetone as lustrous, colourless crystals, M.pt. 155° C., and may be reduced to *tellurium 3-n-butylacetylacetone* (*4-n-butylcyclotelluropentanedione*), consisting of well-defined primrose-yellow needles, M.pt. 129° C., sufficiently stable to undergo sublimation under reduced pressure.

Tellurium 3-n-butylpropionylacetone dichloride,



is obtained in 30 per cent. yield, very difficult to free from oil. From boiling carbon tetrachloride it separates as colourless leaflets, M.pt. 103° C. *Tellurium 3-n-butylpropionylacetone* (*2-methyl-4-n-butylcyclotelluropentanedione*) crystallises from alcohol as golden-yellow needles, M.pt. 93° C.

Tellurium n-decoylacetone dichloride, $C_{13}H_{22}O_2TeCl_2$, from *n*-decoylacetone and tellurium tetrachloride, forms grey crystals, M.pt. 49° C., and may be reduced to *tellurium n-decoylacetone* (*2-n-octylcyclotelluropentanedione*), yellow needles from warm alcohol, M.pt. 64° C.

Other Cyclotelluropentanedione Derivatives.[1]

Condensation of tellurium tetrachloride and dimethylacetylacetone leads to the formation of tellurium 3 : 3-dimethylacetylacetone di-

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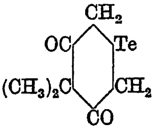
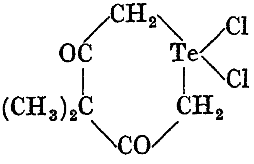
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1924, 125, 1601.

chloride, which may be reduced to tellurium 3 : 3-dimethylacetylacetone (4 : 4-dimethyl*cyclo*telluropentanedione). The latter is represented by the formula



The compound forms a mono-oxime and a di-oxime, and therefore the presence of two ketonic groups is proved.

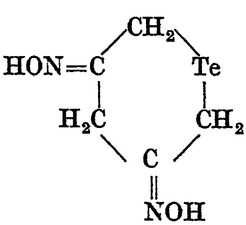
cycloTelluri-4 : 4-dimethylpentane-3 : 5-dione 1 : 1-dichloride,



10 grams of tellurium tetrachloride and 11 grams of dimethylacetylacetone (from sodium 3-methylacetylacetone and methyl iodide) in 100 c.c. of pure chloroform are refluxed for 2¾ hours, hydrogen chloride being evolved. The pale yellow filtrate from tellurium is concentrated in a desiccator and the crystals washed with cold carbon tetrachloride and chloroform. A further yield obtained by concentration of the filtrates brings the total to 60 per cent. The product forms colourless, transparent, brittle, prismatic needles from acetone, M.pt. 194° C. with decomposition.

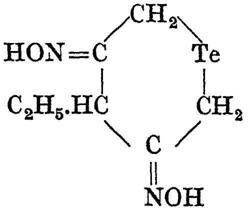
Reduction of the dichloride (8·7 grams) by 12·2 grams of potassium metabisulphite in 70 c.c. of cold water gives a quantitative yield of *cyclotelluro-4 : 4-dimethylpentane-3 : 5-dione* as transparent lemon-yellow refractive prisms from benzene, golden-yellow needles from alcohol or serrated needles from water, melting at 124° to 125° C. and subliming in a vacuum at 105° C. The dione is moderately soluble in cold chloroform, alcohol, or other organic solvents when warm, and moderately soluble in cold water.

cycloTelluropentane-3 : 5-dione dioxime,



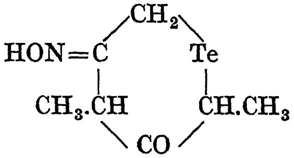
occurs when 0·5 gram of tellurium acetylacetone in 45 c.c. of boiling water is treated with 1 gram of hydroxylamine sulphate in 45 c.c. of water containing sodium acetate. It separates from hot water or glacial acetic acid in voluminous masses of pale yellow needles, blackening at 180° to 190° C. and eliminating tellurium at 207° C.

cycloTelluro-4-ethylpentane-3 : 5-dione dioxime,



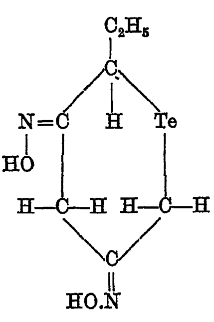
is the result of treating tellurium ethylacetylacetone with a large excess of hydroxylamine sulphate in boiling water, neutralising the solution with sodium hydroxide and allowing it to cool after ten minutes. It separates from acetylacetone as golden-yellow platelets, and from hot water as shortened needles ; it is sparingly soluble in volatile organic solvents, darkens at 173° C. and decomposes violently at 192° C.

cycloTelluro-2 : 4-dimethylpentane-3 : 5-dione 5-monoxime,

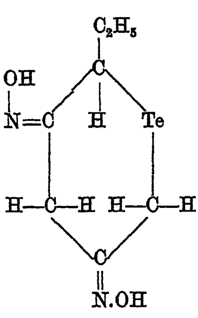


from tellurium 3-methylpropionylacetone and hydroxylamine sulphate, is obtained as minute yellow needles from hot water or benzene, darkening at 140° C., blackening at 164° C. and disrupting at 168° C. The preparation is carried out in a solution nearly neutral to litmus ; if a slightly alkaline solution be used the *dioxime* is obtained. The latter separates from hot acetylacetone as a yellow crystalline powder, sparingly soluble in hot water, insoluble in volatile organic solvents, darkening at 173° C. and decomposing with violence at 198° C.

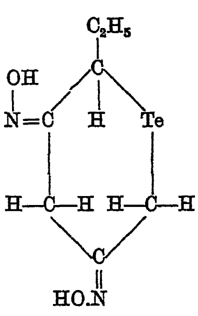
α- and **β-cycloTelluro-2-ethylpentane-3 : 5-dione dioximes,**



syn.



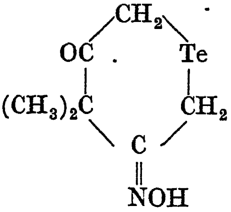
anti.



amphi.
(Two forms possible)

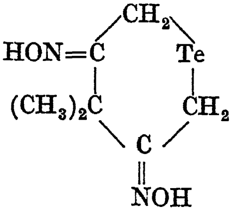
A slightly alkaline solution of 10 grams of hydroxylamine sulphate in aqueous sodium hydroxide is added to 3·5 grams of tellurium *n*-butyrylacetone in 100 c.c. of warm alcohol, water being added until the two layers mix. After boiling for ten minutes the solution is cooled for twelve hours, the first crops of product to separate being the α-dioxime (*syn.* form), the intermediate crops being mixtures, and finally the β-isomeride (*anti.* form) is deposited. The α- and β-oximes are separated by means of boiling benzene, the proportions obtained being α : β = 5 : 1. The *α-dioxime* forms canary-yellow needles in nacreous masses, is readily soluble in hot benzene, and melts with decomposition at 149° C. It is more soluble in organic solvents than the β-isomeride. The *β-dioxime* forms yellow needles similar to the preceding but lighter in colour. It is practically insoluble in boiling benzene, crystallises from boiling alcohol, darkens at 173° C. and melts at 183° C. Both isomerides are slightly soluble in hot water and dissolve in cold aqueous sodium hydroxide to give yellow solutions which blacken on warming.

cycloTelluro-4 : 4-dimethylpentane-3 : 5-dione 5-monoxime,



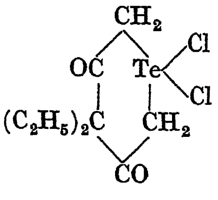
is the condensation product of tellurium 3 : 3-dimethylacetylacetone and hydroxylamine sulphate. From hot benzene it is deposited as orange-yellow needles, melting with decomposition at 183° to 184° C., and from alcohol as pale yellow needles or orange prisms, M.pt. 180° C., sublimable in a vacuum.

cycloTelluro-4 : 4-dimethylpentane-3 : 5-dione dioxime,



forms minute golden-yellow needles from acetylacetone, but is practically insoluble in water, benzene and other volatile solvents ; it decomposes at 235° C.

cycloTelluri-4 : 4-diethylpentane-3 : 5-dione 1 : 1-dichloride,[1]



prepared from 3 : 3-diethylacetylacetone (2 mols.) and tellurium

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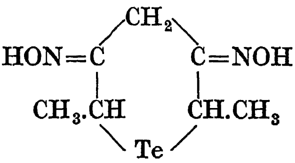
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1924, 125, 749.

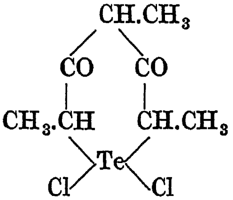
tetrachloride (1 mol.) in chloroform solution, crystallises from chloroform, benzene or benzene-light petroleum as colourless, nacreous flakes or prisms, softening at 177° C. and melting with decomposition at 178° to 180° C. It is very soluble in organic solvents excepting light petroleum, and gives no trace of ferric chloride coloration. Reduction by aqueous potassium metabisulphite yields *cyclotelluro-4 : 4-diethylpentane-3 : 5-dione*, consisting of acicular prisms or needles, M.pt. 85° to 86° C., soluble in benzene or alcohol, sparingly soluble in petroleum. The aqueous solution of the dione is neutral to litmus. The dione is decomposed by cold aqueous sodium hydroxide. It may be sublimed *in vacuo*.

2 : 6-Dimethylcyclotelluropentane-3 : 5-dione dioxime,[1]



The 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione required for this preparation is obtained from the corresponding dichloride by reduction with sodium metabisulphite. Condensation with hydroxylamine sulphate then gives the dioxime, which separates from hot dilute alcohol as pale yellow needles, decomposing at 168° to 170° C., insoluble in water, but freely dissolving in aqueous sodium hydroxide.

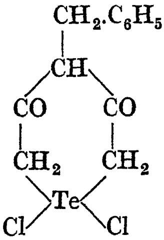
2 : 4 : 6 - Trimethylcyclotelluripentane - 3 : 5-dione 1 : 1 - dichloride,



10 grams of 3-methyldipropionylmethane, 9·5 grams of tellurium tetrachloride and 70 c.c. of pure chloroform are heated together on the water-bath for two and a half hours. The liquid is then concentrated *in vacuo*, and after a few days several crops of crystals are obtained. These when recrystallised from warm acetone give needles darkening at 180° C. The yield is 68 per cent. The product is sparingly soluble in the ordinary organic solvents, except acetone. Reduction of the dichloride with aqueous potassium metabisulphite (2 mols.) in the cold gives a quantitative yield of *2 : 4 : 6-trimethylcyclotelluropentane-3 : 5-dione*, consisting of bright yellow needles, darkening at 133° C., melting with decomposition at 135° C., and slightly soluble in cold water to give a yellow neutral solution. This dione in the usual manner yields *2 : 4 : 6-trimethylcyclotelluropentane-3 : 5-dione dioxime*, yellow flakes, decomposing at 170° C.

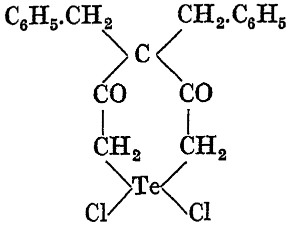
Morgan and Taylor, *Trans. Chem. Soc.*, 1925, 127, 797.

4-Benzylcyclotelluripentane-3 : 5-dione 1 : 1-dichloride,



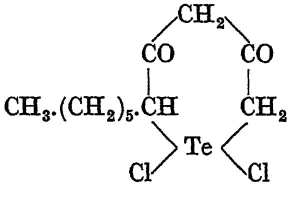
crystallises from benzene on the addition of light petroleum as white flakes, decomposing at 180° C., reduction yielding *4-benzylcyclotelluropentane-3 : 5-dione,* pale yellow glistening flakes or large prismatic crystals, melting with decomposition at 153° C. The *dioxime* of the dione is a yellowish-green powder, decomposing at 168° to 170° C.

4 : 4-Dibenzylcyclotelluripentane-3 : 5-dione 1 : 1-dichloride,



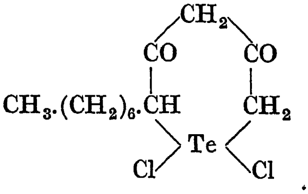
is the condensation product of dibenzylacetylacetone and tellurium tetrachloride. It yields white flakes, melting with decomposition at 189° to 190° C., reduction giving *4 : 4-dibenzylcyclotelluropentane-3 : 5-dione,* separating from dilute alcohol as yellow needles, M.pt. 128° C. with previous softening at 123° C. The dichloride dissolves in benzene, but not in water or aqueous caustic alkalis, thus showing no residual affinity ; it is quite stable to boiling alkali.

2-n-Hexylcyclotelluripentane-3 : 5-dione 1 : 1-dichloride,



occurs when *n*-octoylacetone is condensed in the usual manner with tellurium tetrachloride. The isolation of this dichloride is more difficult than in the case of those previously described owing to the greater solubility and fusibility as the series is ascended ; the yield is about 25 per cent. The product is precipitated from warm benzene by *n*-hexane as colourless glistening flakes, M.pt. 80° C., readily soluble in alcohol, chloroform or benzene, less soluble in carbon tetrachloride, and sparingly soluble in petroleum or water. Reduction yields *2-n-hexylcyclotelluropentane-3 : 5-dione,* bright yellow scales, M.pt. 74° to 75° C. from dilute alcohol. This dissolves readily in organic solvents, but is sparingly soluble in water; it possesses residual acidity, dissolving in cold aqueous sodium hydroxide, but gives no ferric chloride coloration.

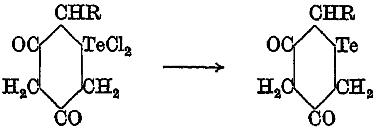
2-n-Heptylcyclotelluripentane-3 : 5-dione 1 : 1-dichloride,



results when *n*-nonoylacetone replaces the *n*-octoylacetone in the foregoing preparation. It forms colourless plates, M.pt. 89° C., reduction giving *2-n-heptylcyclotelluropentane-3 : 5-dione,* bright yellow woolly masses, M.pt. 89° C., sparingly soluble in water, but exhibiting residual acidity by dissolving more readily in dilute aqueous sodium hydroxide to a solution depositing tellurium on boiling. In the condensation, in addition to the cyclic dichloride, a considerable proportion of *tellurium n-nonoylacetone trichloride* is isolated, $CH_3.[CH_2]_6.CH_2.CO.CH : C(OH).CH_2.TeCl_3$; this forms colourless glistening flakes, M.pt. 114° to 115° C., slowly decomposed by moisture.

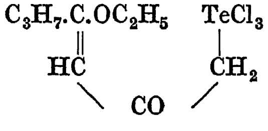
Tellurium Tetrachloride and β-Diketones of the Type $R.CO.CH_2.CO.CH_3$.[1]

The case of propionylacetone has been dealt with already, and the higher homologues, *n*-butyrylacetone, *n*-valerylacetone and *n*-hexoylacetone behave in a similar manner. The chief product of the reaction has the general formula (I) and yields on reduction compound (II):

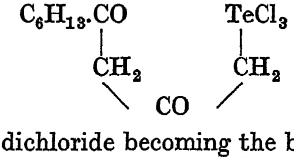


(I) (II)

n-Butyrylacetone gives, in addition to the cyclic dichloride, a small amount of tellurium O-ethyl-*n*-butyrylacetone trichloride as by-product:



In the case of *n*-heptoylacetone, tellurium *n*-heptoylacetone trichloride,



is isolated, the cyclic dichloride becoming the by-product.

As the homologous series is ascended the melting-points of the dichlorides fall and the solubility in organic solvents increases.

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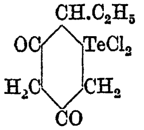
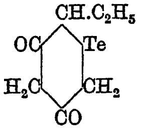
[1] Morgan and Drew, *Trans. Chem. Soc.*, 1924, 125, 731.

Tellurium n-butyrylacetone dichloride,



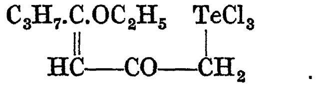
A mixture containing 5·5 grams of tellurium tetrachloride, 5·2 grams of *n*-butyrylacetone and 40 c.c. of purified chloroform is boiled for 1·5 hours, then filtered and the orange filtrate concentrated in a vacuum desiccator. About 3·8 grams (58 per cent.) of product separates, and recrystallisation from hot alcohol gives transparent, colourless prisms, darkening above 144° C. and melting at 153° to 154° C. Prolonged heating in alcohol or acetone causes hydrolysis. The dichloride does not react with ferric chloride.

Tellurium n-butyrylacetone (*2-Ethylcyclotelluropentanedione*),



This is prepared by the general method of reduction of the dichloride using aqueous potassium metabisulphite. It crystallises from hot water or benzene-petroleum as yellow needles, melting without decomposition at 110° to 112° C., very soluble in cold acetone or hot benzene. It possesses residual acidity, dissolving in cold 5*N* sodium hydroxide to give an intensely yellow solution which blackens rapidly and then has an odour of methyl *n*-propyl ketone.

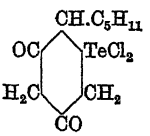
Tellurium O-ethyl-n-butyrylacetone trichloride,



$$\begin{array}{lcl} C_3H_7.\overset{}{C}.OC_2H_5 & & TeCl_3 \\ \| & & | \\ HC—CO—CH_2 & & \end{array}.$$

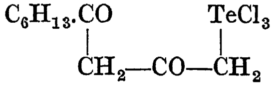
This occurs when the condensation is carried out as for the preceding dichloride, but in ordinary chloroform (B.P.). After separation of the dichloride, concentration of the mother-liquor gives a 28 per cent. yield of trichloride. Crystallisation from benzene-petroleum (B.pt. 40° to 60° C.) yields golden-yellow needles, M.pt. 105·5° to 106·5° C. with slight decomposition, and giving no coloration with ferric chloride.

Tellurium n-heptoylacetone dichloride,



The condensation between the tellurium tetrachloride and *n*-heptoylacetone is carried out in purified chloroform, the solution being heated for four hours. The yield is about 15 per cent., and the product crystallises from benzene-petroleum in rosettes of nacreous, compact or acicular prisms, M.pt. 87° C., readily soluble in cold chloroform or benzene, less soluble in carbon tetrachloride or light petroleum. It yields no coloration with ferric chloride; boiling aqueous caustic alkali causes hydrolysis, methyl *n*-hexyl ketone being one of the ultimate products.

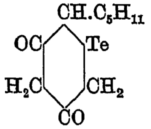
Tellurium n-heptoylacetone trichloride,



$$\begin{matrix} C_6H_{13}.CO & & TeCl_3 \\ | & & | \\ CH_2 & —CO— & CH_2 \end{matrix}$$

occurs when 3·2 grams of tellurium tetrachloride, 3·2 grams of *n*-heptoylacetone and 20 c.c. of alcohol-free chloroform are heated together under reflux for two hours. Filtration and evaporation of the reaction mixture gives 1·4 grams, or 30 per cent., of product. It separates as colourless, nacreous, six-sided plates, melting with blackening at 117° C., very soluble in cold chloroform or benzene, less soluble in carbon tetrachloride or ether, and almost insoluble in petroleum (B.pt. 40° to 60° C.). With aquo-alcoholic ferric chloride it develops instantly a blood-red coloration; its ether-chloroform solution gives a pale green precipitate of copper salt with aqueous copper acetate. Both the compound itself and its copper salt soon hydrolyse in contact with moist air or water. With aqueous alkalis, alkali tellurite and *n*-heptoylacetone are produced unaccompanied by any earthy odour of O-ether of heptoylacetone. The trichloride when boiled in pure chloroform in the presence of anhydrous aluminium chloride evolves hydrogen chloride and a crystalline *aluminium compound*, $C_6H_{13}.CO.CH : C(OAl\frac{1}{3}).CH_2.TeCl_3$, is formed.

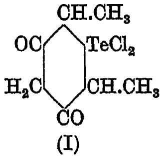
Tellurium n-heptoylacetone (*2-n-amylcyclotelluropentanedione*),



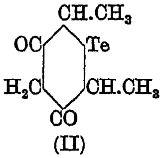
is obtained from the corresponding dichloride by reduction with aqueous potassium metabisulphite. It crystallises from hot water or aqueous alcohol as yellow needles, or from alcohol as golden scales, M.pt. 86° C., readily soluble in alcohol, benzene or acetone, sparingly soluble in cold water or petroleum. With ferric chloride it gives no coloration, but it shows residual acidity, dissolving more readily in dilute alkali than in water alone; the yellow alkaline solution slowly blackens.

Tellurium Tetrachloride with β-Diketones of the Type $R.CO.CH_2.CO.R'$.

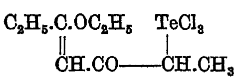
Dipropionylmethane condenses with tellurium tetrachloride yielding tellurium dipropionylmethane dichloride (I) and tellurium O-ethyldipropionylmethane trichloride (III), the latter being the by-product. The cyclic dichloride may be quantitatively reduced to tellurium dipropionylmethane (II). Similarly propionyl-*n*-butyrylmethane condenses to tellurium propionyl-*n*-butyrylmethane dichloride, which may be reduced to tellurium propionyl-*n*-butyrylmethane.



(I)



(II)



$$\begin{matrix} C_2H_5.C.OC_2H_5 & & TeCl_3 \\ \| & & | \\ CH.CO & —— & CH.CH_3 \end{matrix}$$

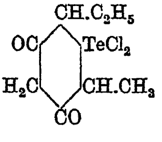
(III)

Tellurium dipropionylmethane dichloride (Formula I).—The condensation is carried out in the usual manner in rectified chloroform, using slightly more than two molecular equivalents of dipropionylmethane to each equivalent of tellurium tetrachloride. The mixture is heated for 1·5 hours, about 78 per cent. of dichloride resulting. The residual oil from the latter contains tellurium O-ethyldipropionylmethane trichloride mixed with dichloride. The dichloride crystallises from acetone, benzene or benzene-light petroleum as thin, colourless, transparent, six-sided plates, darkening at 157° C. and melting and intumescing at 162° C. From methyl alcohol it crystallises as glistening prisms, darkening at 150° C. and intumescing at 170° C.

Tellurium dipropionylmethane (*2 : 6-Dimethylcyclotelluropentanedione*) (Formula II), obtained from the dichloride by bisulphite reduction, crystallises from methyl alcohol, benzene or aqueous ethyl alcohol as well-defined golden-yellow needles, M.pt. 151° C. with slight decomposition. Under diminished pressure it sublimes at 110° C. as slender needles, which slowly pass at this temperature into compact prisms. It readily dissolves in organic solvents, except light petroleum ; in water it is sparingly soluble, the solution giving no enolic reactions.

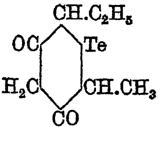
Tellurium O-ethyldipropionylmethane trichloride (Formula III), isolated as indicated above, crystallises from a mixture of chloroform and petroleum (B.pt. 40° to 60° C.) as transparent lemon-yellow prisms, M.pt. 110° to 111° C. with blackening and decomposition. It yields pale yellow solutions in cold organic solvents, and gives no enolic reaction with ferric chloride in aquo-alcoholic chloroform solution, but decomposes rapidly, giving a yellow turbidity. With aqueous alkalis it develops the earthy odour of the free O-ether of dipropionylmethane.

Tellurium propionyl-n-butyrylmethane dichloride,



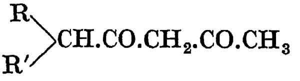
The condensation is conducted in the usual manner, the heating being continued for three hours. The yield is about 19 per cent. The dichloride crystallises in silvery flakes from boiling chloroform or chloroform-petroleum mixture, darkening at 150° C. and melting with decomposition at 156° C. It is very soluble in acetone. It gives no coloration even on boiling chloroformic ferric chloride with its solution in alcohol.

Tellurium propionyl-n-butyrylmethane (*2-Methyl-6-ethylcyclotelluropentanedione*),



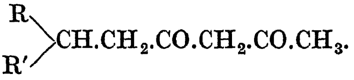
the reduction product of the preceding derivative, crystallises from water, petroleum or dilute alcohol as yellow needles, M.pt. 101° to 102° C. to a yellow liquid showing traces of decomposition. Under reduced pressure it sublimes below 100° C. without decomposition, giving short microscopic needles. Its aqueous solution is feebly acid to litmus; the solid dissolves much more readily in 0·3*N* sodium hydroxide than in water, but it is not enolic towards ferric or copper salts.

Tellurium Tetrachloride and β-Diketones of the Types



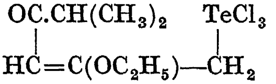
$$\begin{matrix}R\\R'\end{matrix}\!\!>CH.CO.CH_2.CO.CH_3$$

and



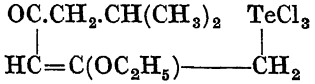
$$\begin{matrix}R\\R'\end{matrix}\!\!>CH.CH_2.CO.CH_2.CO.CH_3.$$

*iso*Butyrylacetone behaves differently from *n*-butyrylacetone when condensed with tellurium tetrachloride, giving exclusively tellurium O-ethyl*iso*butyrylacetone trichloride (I); *iso*valerylacetone yields tellurium O-ethyl*iso*valerylacetone trichloride (II) and tellurium *bis*-*iso*valerylacetone dichloride (III):



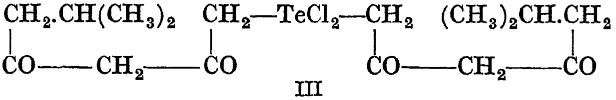
$$\begin{array}{lcl} OC.CH(CH_3)_2 & & TeCl_3 \\ | & & | \\ HC{=}C(OC_2H_5) & — & CH_2 \end{array}$$

(I)



$$\begin{array}{lcl} OC.CH_2.CH(CH_3)_2 & & TeCl_3 \\ | & & | \\ HC{=}C(OC_2H_5) & —— & CH_2 \end{array}$$

(II)



$$\begin{array}{ccccccc} CH_2.CH(CH_3)_2 & & CH_2 & —TeCl_2— & CH_2 & & (CH_3)_2CH.CH_2 \\ | & & | & & | & & | \\ CO & —CH_2— & CO & & CO & —CH_2— & CO \end{array}$$

III

In the first two formulæ products are represented in which the alcohol present in the chloroform used as a condensing medium takes part in the reaction.

It is evident from the foregoing condensations that a branched chain inhibits the formation of a cyclic dichloro-tellurium derivative containing the bivalent diketone radical. Hence β-diketones with terminal branched chains ($RR'CH.CO.$ and $RR'CH.CH_2.CO.$) cannot be employed in the production of yellow cyclic tellurium derivatives such as are obtained from *n*-butyrylacetone.

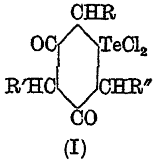
Tellurium O-ethylisobutyrylacetone trichloride (Formula I).—Tellurium tetrachloride (1 mol.) is heated with *iso*butyrylacetone (B.pt. 95° C.) (2 mols.) in chloroform solution for one hour, the reaction mixture filtered from free tellurium and evaporated in a vacuum. The trichloride thus obtained in about 30 per cent. yield crystallises from benzene-petroleum mixture as pale yellow flakes or needles, M.pt. 103° C. with decomposition. It gives no coloration with ferric chloride, and is decomposed by 5*N* sodium hydroxide, the odour of the O-ethyl ether of the β-diketone being noticed.

Tellurium O-ethylisovalerylacetone trichloride (Formula II).—The condensation is carried out as before, using *iso*valerylacetone, but the final product is more difficult to purify. Some dichloride is formed during the reaction, this showing itself in the later crops of crystals. Crystallisation from benzene-light petroleum yields crystals of the two substances, and they may then be separated by hand-picking. The trichloride forms small, compact, lemon-yellow, gem-like crystals, producing a yellow glass at 88° to 92° C., this melting suddenly at 100° to 101° C. to a liquid from which tellurium soon separates. The compound is very soluble in cold benzene or chloroform, less soluble in cold carbon tetrachloride, and almost insoluble in cold light petroleum. With ferric chloride it gives no immediate enolic reaction, but a yellow cloud slowly separates, this decomposing and becoming red after ten minutes. Cold aqueous caustic alkali decomposes the body in the usual manner.

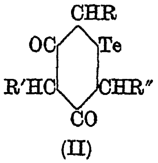
Tellurium bis-isovalerylacetone dichloride (Formula III).—A solution containing 3·3 grams of tellurium tetrachloride, 3·4 grams of *iso*valerylacetone and 30 c.c. of chloroform freed from alcohol is heated for thirty minutes. Concentration of the filtrate leaves a red glue, from which cold carbon tetrachloride removes 0·5 gram of the dichloride. The residue, dissolved in chloroform, is exposed to the air to decompose tellurium tetrachloride and other tellurium compounds sensitive to moisture and then filtered and evaporated to crystallising point. A further 0·2 gram of dichloride results, bringing the total yield to 12 per cent. The compound separates from carbon tetrachloride or benzene-light petroleum as transparent, colourless, acicular prisms or nacreous leaflets, M.pt. 97° to 98° C. with rapid elimination of tellurium. With the exception of light petroleum it readily dissolves in organic solvents. It is decidedly enolic, giving with aquo-alcoholic-chloroformic ferric chloride an immediate blood-red coloration. With hot aqueous potassium hydroxide it gives no trace of spongy tellurium. Reduction with cold aqueous metabisulphite gives a yellow viscous oil, sparingly soluble in water but readily dissolving in chloroform.

Tellurium Tetrachloride and β-Diketones Alkylated in the Methylene Group.

3-Methylpropionylacetone yields a cyclic dichlorotellurium derivative (I), and replacement of the methyl group by the ethyl or *n*-butyl group gives rise to a similar product, reduction in each case forming a yellow product (II). 3-Ethyl-*n*-butyrylacetone and dipropionylethylmethane both behave in a similar manner.



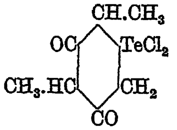
(I)



(II)

(R = H, CH_3 or C_2H_5, R′ = CH_3, C_2H_5, *n*- or *iso*-C_3H_7 or *n*-C_4H_9, and R″ = H or CH_3)

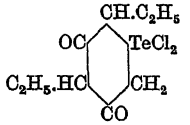
Tellurium 3-methylpropionylacetone dichloride,



The condensation between tellurium tetrachloride (1 mol.) and 3-methylpropionylacetone in purified chloroform gives an 80 per cent. yield of this dichloride. It crystallises from boiling benzene as colourless glistening prisms, sintering at 164° C. and melting at 166° to 167° C. with decomposition.

Tellurium 3-methylpropionylacetone (*2 : 4-Dimethylcyclotelluropentanedione*) occurs when the preceding compound is reduced with potassium metabisulphite. The product readily dissolves in organic solvents or hot water, whilst in cold water it is more soluble than its alkylated homologues ; it is devoid of residual acidity, its aqueous solution being neutral to litmus. It crystallises from water or methyl alcohol as long, soft, pale golden needles or elongated prisms, M.pt. 125° to 126° C. with decomposition, and sublimes in a vacuum at 100° C. as short needles or prisms.

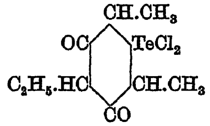
Tellurium 3-ethyl-n-butyrylacetone dichloride,



separates from hot benzene as nacreous rosettes of colourless prismatic needles, M.pt. 140° C. with decomposition ; it is sparingly soluble in chloroform, carbon tetrachloride or light petroleum, readily soluble in cold acetone. It develops no coloration with ferric chloride.

Tellurium 3-ethyl-n-butyrylacetone (*2 : 4-Diethylcyclotelluropentanedione*), when crystallised successively from water and petroleum, separates as yellow needles sintering at 110° C. and melting with blackening at 113° C. Its aqueous solution is very stable on boiling, but devoid of enolic or acidic properties.

Tellurium dipropionylethylmethane dichloride,

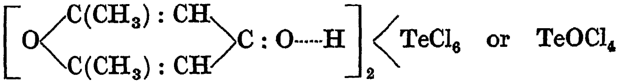


from tellurium tetrachloride (1 mol.) and dipropionylmethane in chloroform (B.P.), crystallises from benzene or acetone as colourless, transparent, six-sided prisms, very sparingly soluble in chloroform, darkening above 172° C. and melting with decomposition at 182° C.

Tellurium dipropionylethylmethane (*2 : 6-Dimethyl-4-ethylcyclotelluropentanedione*) separates from boiling methyl alcohol or dry benzene as tough golden needles, melting with decomposition at 137° to 138° C. From hot water it separates either as needles or shorter gem-like forms, the latter when sublimed at 110° C. in a vacuum passing into one or other of the preceding forms.

Tellurium Tetrachloride and Complex Ketones.[1]

When tellurium tetrachloride is condensed with diacetylacetone, $CH_3.CO.CH_2.CO.CH_2.CO.CH_3$, the triketone is transformed to dimethylpyrone, and the cyclic compound combines with tellurium tetrachloride and hydrogen chloride to form the oxonium salt dimethylpyrone tellurichloride,



$$\left[O\left\langle \begin{matrix} C(CH_3):CH \\ C(CH_3):CH \end{matrix} \right\rangle C:O\cdots H \right]_2 \left\langle TeCl_6 \quad \text{or} \quad TeOCl_4 \right.$$

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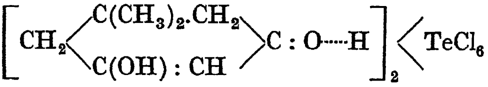
[1] Morgan and Drew, *loc. cit.*

During the process some of the tellurium tetrachloride becomes hydrolysed to oxychloride and a portion of the dimethylpyrone appears as dimethylpyrone tellurioxychloride which has the above structure.

Dimethylpyrone tellurichloride.—When 5·2 grams of tellurium tetrachloride, 2·8 grams of diacetylacetone and 50 c.c. of rectified chloroform are heated together under reflux for one hour, a trace of tellurium is eliminated but no hydrogen chloride is evolved. The chloroform is decanted from the solid which has separated and evaporated to a syrup, which contains the tellurioxychloride. The solid contains the tellurichloride and is hydrolysed by moist air and dissolved in concentrated hydrochloric acid, from which the tellurichloride separates as spear-like aggregates of golden-yellow needles; yield, about 2·5 grams. Its solution in hot water is colourless and contains ionised chlorine and hydrogen, spontaneous evaporation yielding a white residue which changes to the yellow tellurichloride on drying in a vacuum. When reduced with aqueous metabisulphite, sulphur dioxide, tellurium and dimethylpyrone are produced.

Dimethylpyrone tellurioxychloride is obtained as noted above. About 0·3 gram of colourless crystals, M.pt. 115° C., is isolated. The product is soluble in chloroform, insoluble in benzene and light petroleum. It gives no enolic reaction with ferric chloride, no odour with aqueous alkali, and is hydrolysed by water, but not so rapidly as the tellurichloride.

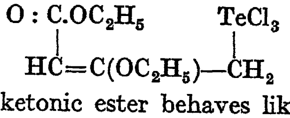
Dimethyldihydroresorcinol tellurichloride,



As in the preceding preparation, no hydrogen chloride is evolved in the condensation between tellurium tetrachloride and dimethyldihydroresorcinol, but a tellurichloride of the above structure is formed. This separates from hot concentrated hydrochloric acid as large, transparent, pale yellow prisms, not crystallisable from organic solvents, although sparingly soluble in chloroform. In moist air the tellurichloride readily undergoes hydrolysis into hydrogen chloride, tellurium dioxide and dimethyldihydroresorcinol. At 130° C. it commences to resinify, and it melts with blackening and gas evolution at 160° to 165° C.

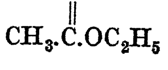
Tellurium Tetrachloride and Ethyl Acetoacetate.

This condensation is only satisfactory when the chloroform contains alcohol, and the only product obtained is *tellurium ethyl-β-ethoxycrotonate trichloride,*



$$\begin{array}{lcl} O:C.OC_2H_5 & & TeCl_3 \\ \quad | & & \;| \\ HC{=}C(OC_2H_5){-}CH_2 & & \end{array}$$

showing that this β-diketonic ester behaves like the β-diketones containing branched chains. Hydrolysis with aqueous alkali yields ethyl β-ethoxycrotonate, an ester which on further hydrolysis with alcoholic potassium hydroxide gives the *cis*-form of β-ethoxycrotonic acid,



$$\begin{array}{l} HC.CO_2H \\ \quad \| \\ CH_3.C.OC_2H_5 \end{array}$$

Tellurium ethyl O-ethylacetoacetate trichloride (*Tellurium ethyl-β-ethoxycrotonate trichloride*) is best obtained by heating 4·4 grams of tellurium tetrachloride and 4·3 grams of ethyl acetoacetate in 50 c.c. of chloroform (B.P.) for 30 minutes under reflux. Hydrogen chloride is evolved and traces of tellurium eliminated during the reaction. Decantation and evaporation of the solution yields 2·1 grams, or 32 per cent., of crystals. These recrystallise from benzene or light petroleum as colourless plates often showing octagonal lines, softening at 88° C., melting to a turbid liquid at 90° to 92° C., and decomposing at about 140° C. The product dissolves readily in chloroform, but is less soluble in carbon tetrachloride; water readily hydrolyses it, and with alkalis it yields tellurium dioxide, alkali chloride and a pale yellow oil having a powerful liquorice odour. The trichloride is non-enolic towards ferric chloride.

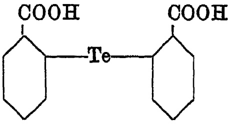
ARSENIC-TELLURIUM COMPOUND.[1]

4-Aminophenylarsenotelluride hydrochloride,

is formed by the interaction of hydrogen telluride and 4-aminophenyldichloroarsine in alcohol solution. It is an orange powder, sparingly soluble in dilute hydrochloric acid.

ATTEMPTED SYNTHESIS OF TELLUROINDIGO.

Diphenyltellurodi-o-carboxylic acid,[2]



6 grams of anthranilic acid in 11 c.c. of concentrated hydrochloric acid are diazotised by 3 grams of sodium nitrite dissolved in the smallest possible quantity of water. The diazo-solution is ice-cooled and shaken in a hydrogen atmosphere with a solution of sodium telluride (from 6 grams tellurium and 3 grams sodium) in air-free water treated with the calculated amount of air-free sodium carbonate solution. Nitrogen is evolved and the carboxylic acid separates as yellow crystals, M.pt. 215° C. The *disodium salt* forms white prisms.

Phenyltelluroglycollic-o-carboxylic acid, $HOOC.C_6H_4.Te.CH_2.COOH$, is isolated by reducing the foregoing acid with hot 10 per cent. potassium hydroxide and zinc dust, filtering the product into the requisite amount of sodium chloracetate, boiling for fifteen minutes and acidifying with sulphuric acid. The product melts at 195° C.

3 - Hydroxytelluronaphthene (*Telluro - 2 - hydroxybenzofuran*),

$\overline{C_6H_4TeCH{=}C}OH$.—The foregoing glycollic acid derivative is refluxed

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[1] German Patent, 269699.

[2] Mazza and Melchionna, *Rend. Accad. Sci. Napoli*, 1928, [3], 34, 54.

for two hours with its own weight of sodium acetate and 8 parts of acetic anhydride. The anhydride is then removed, the residue boiled with 10 per cent. sodium hydroxide, the liquid filtered, cooled, and acidified with hydrochloric acid. A yellowish-white powder separates, which decomposes at 160° C. and is soluble in alkali hydroxides. It yields an *acetyl derivative*, but could not be oxidised to telluroindigo.

CHAPTER VI.

ORGANIC COMPOUNDS OF CHROMIUM AND PLATINUM.

ORGANIC CHROMIUM COMPOUNDS.

Chromium pentaphenyl bromide,[1] $(C_6H_5)_5CrBr$, is obtained by the action of phenyl magnesium bromide on anhydrous chromic chloride or chromyl chloride, the reaction in the former case probably taking the following course:

$$5C_6H_5MgBr + 4CrCl_3 = (C_6H_5)_5CrBr + 2MgBr_2 + 3MgCl_2 + 3CrCl_2$$

In the case of chromic chloride the operation is carried out in ether solution, and for chromyl chloride the solvent is benzene, efficient cooling being necessary in each case.

The bromide is an orange-brown amorphous substance, and is probably a mixture. The yields are not good, and purification is difficult owing to the sensitiveness of the compound towards air, light, rise of temperature and acids, also to its persistently amorphous nature. The body is soluble in ethyl alcohol or large volumes of methyl alcohol, acetone, ethylene bromide, acetonitrile, nitrobenzene or acetic acid. In pyridine and many organic solvents it is bright orange. It is only sparingly soluble in benzene, ethyl acetate or trichlorethylene, very slightly soluble in water or concentrated ammonium hydroxide, and insoluble in ether, thioether, carbon disulphide, ligroin, toluene and carbon tetrachloride. Alcoholic mercuric chloride yields a *mercurichloride*, $(C_6H_5)_5CrBr.HgCl_2$, which is purified by several crystallisations from alcohol. This treatment yields a product resembling sealing-wax; it is less stable than the crude bromide and insoluble in many organic solvents. With difficulty the bromide may be converted into the *ether compound* $2(C_6H_5)_5CrBr.(C_2H_5)_2O$, an amorphous powder, sintering at 80° C. and melting with decomposition at about 100° C.

Chromium pentaphenyl hydroxide, $[(C_6H_5)_5Cr(OH)_2]OH.2H_2O$, is isolated from the crude bromide by dissolving the latter in alcohol and adding potassium hydroxide solution, followed by ether. After one or two hours the potassium bromide is filtered off and the solution concentrated *in vacuo* over concentrated sulphuric acid. The dark brown residue is freed from alkali by treating it with cool, dry chloroform, or, better, anisole. The clear filtrate is shaken with ice-cold water, into which the chromium phenyl bases gradually pass, the operation requiring three to four hours. The hydroxide separates from the solution as golden-yellow plates or prismatic needles, best preserved over 30 per cent. potassium hydroxide solution under diminished pressure. When

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[1] Hein, *Ber.*, 1919, 52, [B], 195; 1921, 54, [B], 1905.

thus prepared the substance loses two molecules of water when placed over calcium chloride, and a further similar quantity of water in the presence of phosphoric oxide, the hydroxide in the latter case changing from orange-brown to dark olive-brown. The completely dehydrated hydroxide decomposes somewhat readily at the ordinary temperature, yielding diphenyl; the dihydrate tends to follow the same course of decomposition, but the process is slower. The anhydrous form and the dihydrate may be hydrated again to yield the *tetrahydrate,* which loses 2 per cent. of water and gives an orange-coloured product when dried over concentrated sulphuric acid, this being the *dihydrate* according to analytical results; the latter cannot be further dehydrated over phosphoric oxide, and is termed the *β-base.*

Comparison of the electrical conductivities of chromium pentaphenyl hydroxide, sodium hydroxide and ammonia in absolute methyl alcohol and in methyl alcohol-water solution, shows that the former is a very strong base. In aqueous methyl alcohol solution the chromium compound does not appear to approach the limiting value with increasing dilution. The ultra-violet absorption spectrum examined in absolute ethyl alcohol solution resembles that of chromic acid and the dichromates, but the absorption is noticeably greater in the case of the organic compound.

The bromine atom of chromium pentaphenyl bromide is also replaced by the hydroxyl group when the compound is shaken in chloroform solution with an aqueous suspension of silver oxide. The other products present in the crude bromide remain dissolved in the chloroform, but since silver oxide seems to exert an oxidising action a mixture of bases results, and not pure chromium pentaphenyl hydroxide as might be anticipated.

The hydroxide is usually converted by acids and salts into chromium tetraphenyl salts,[1] the fifth phenyl group being split off as phenol or diphenyl. The amount of phenol formed varies apparently with the previous history of the base, homogeneous chromium pentaphenyl hydroxide in its hydrated form giving a 100 per cent. yield of phenol and only traces of diphenyl when treated with a salt such as potassium bromide in the presence of chloroform. The hydrate in absolute alcohol in the complete absence of air affords one molecule of phenol from each molecule of base when acted upon by potassium iodide. The production of phenol probably occurs according to the scheme

$$(C_6H_5)_5CrOH + KX + H_2O \rightarrow (C_6H_5)_4CrX + C_6H_5OH + KOH + (H)$$

In the complete absence of water the anhydrous base does not yield more than 50 per cent. of phenol, as might be expected:

$$2(C_6H_5)_5CrOH + 2CH_3X \rightarrow 2(C_6H_5)_4CrX + (CH_3)_2O + C_6H_5OH + (H) + C_6H_5.C_6H_5$$

The anhydrous base does not react with gaseous or liquid ammonia, but potassium iodide or ammonium bromide reacts with a suspension of the base in liquid ammonia yielding chromium tetraphenyl salts and phenol, but no aniline is isolated. This shows that the fifth phenyl group can only react with a similar group or with a molecule of solvent, which becomes united to the base by solvation. The intramolecular activity of the group explains its inability to form tetraphenylmethane

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[1] Hein, *Ber.*, 1929, 62, [B], 1151.

when treated with triphenylmethyl. The fact that hydrogen is produced as indicated in the foregoing equations is shown by decomposing the base with ammonium chloride in the presence of Methylene Blue, when the latter is decolorised. The change is accelerated by the addition of palladised calcium carbonate or barium sulphate or slight rise of temperature. Under the most favourable circumstances (illumination of the solutions, and the presence of an excess of dyestuff), about 33 per cent. of the theoretical quantity of Methylene Blue is hydrogenated in three days.

Certain acids transform the hydroxide into pentaphenyl salts, and by using the various acids and phenols, the following salts have been isolated:

Chromium pentaphenyl carbonate,[1] $[(C_6H_5)_5Cr]_2CO_3.6H_2O$, occurs when the concentrated aqueous mother-liquors from the preparation of the base are exposed to the air in an ice-chest. It forms orange-coloured plates, sintering at about 108° C. and melting indefinitely at 118° to 119° C. A *mono-* and a *di-hydrate* are also known.

Chromium pentaphenyl hydrogen carbonate,[2] $(C_6H_5)_5Cr.HCO_3.3H_2O$, is formed when a methyl alcohol solution of the base is saturated with carbon dioxide. The crystals are orange-red and melt at 120° C. in a bath previously heated to 100° C. By suitably drying the product *mono-* and *di-hydrates* are isolated. The crystals are readily soluble in alcohols, sparingly soluble in water, insoluble in ether or benzene.

Chromium pentaphenyl acetate tetrahydrate, $(C_6H_5)_5Cr.O.CO.CH_3.4H_2O$, is obtained by shaking the base with the requisite quantity of $N/10$ acetic acid. The product is orange-yellow and melts at 118° C.; by drying it may be converted into the *dihydrate.* From the mother-liquors of the foregoing hydrates, an *acid acetate* is isolated, $(C_6H_5)_5Cr.O.CO.CH_3.CH_3.COOH$, M.pt. 108° to 111° C. Rapid cooling of the solution in the preparation of the tetrahydrate gives a *basic salt* which sinters at 45° C. and melts at 51° to 53° C.

Chromium pentaphenyl chloroacetate trihydrate, $(C_6H_5)_5Cr(O.CO.CH_2Cl)_2H.3H_2O$, from monochloracetic acid and the chromium base, forms hygroscopic, intensely red plates, M.pt. 103° C. The anhydrous salt is also known. The products dissolve readily in alcohol, pyridine or ethyl acetate.

Chromium pentaphenyl acid anthranilate, $(C_6H_5)_5Cr.O.CO.C_6H_4.NH_2.NH_2.C_6H_4.COOH$, is formed by the action of anthranilic acid in chloroform on the hydroxide, the temperature of the reaction being 50° C. The salt melts at 141° to 142° C., is readily soluble in methyl alcohol, sparingly soluble in chloroform, insoluble in ether or benzene. Microscopic examination reveals the compound as bright reddish-orange columns.

Chromium pentaphenyl sulphate tetrahydrate, $[(C_6H_5)_5Cr]_2SO_4.4H_2O$, obtained from the base and the acid in alcohol solution, when dehydrated melts at 130° C., and is very soluble in alcohol or chloroform. If the amorphous product in methyl alcohol be treated with *acetone,* bright orange prisms are deposited, M.pt. 143° to 144° C.; this *product* has the composition $[(C_6H_5)_5Cr]_2SO_4.3CH_3.CO.CH_3$.

Compounds from Phenol.—An absolute alcohol solution of the base reacts with phenol to give a substance having the composition

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[1] Hein, *Ber.*, 1921, 54, [B], 2708.

[2] Hein, *Ber.*, 1928, 61, [B], 730.

$(C_6H_5)_5Cr.O.C_6H_5.C_6H_5OH$. This forms glistening plates, M.pt. 129·5° C., somewhat hygroscopic, soluble in alcohol or pyridine, sparingly soluble in acetone or chloroform, insoluble in carbon disulphide, benzene or ligroin. If the reaction be conducted in aqueous alcohol the resulting product has the formula $(C_6H_5)_4Cr.O.C_6H_5.2C_6H_5.OH$, and melts at 144° C.

Compounds from m-Chlorophenol.—Chromium pentaphenyl hydroxide and *m*-chlorophenol in absolute alcohol react to give the compound $(C_6H_5)_5Cr.O.C_6H_4Cl.HO.C_6H_4.Cl$, M.pt. 112·5° to 113° C., which, on crystallisation from alcohol-acetone or submitted to protracted washing with ether, yields the tetraphenyl derivative, $(C_6H_5)_4Cr.O.C_6H_4Cl.HO.C_6H_4.Cl$, M.pt. 130° C.

Compound from p-Cyanophenol.—*p*-Cyanophenol and the base in absolute alcohol give $2(C_6H_5)_5Cr.O.C_6H_4.CN.HO.C_6H_4.CN$, crystallising in columns, M.pt. 123·5° C. This body readily dissolves in alcohol, acetone, pyridine or chloroform, but is insoluble in benzene or ether.

Compound from m-Nitrophenol.—The base and the phenol yield the product $(C_6H_5)_5Cr.O.C_6H_4.NO_2.HO.C_6H_4.NO_2$, M.pt. 86° C., readily soluble in alcohol, pyridine or chloroform, less soluble in benzene or carbon disulphide, insoluble in ether or ligroin.

Compound from Dibromogallic Acid.—The chloroform layer obtained during the preparation of chromium pentaphenyl hydroxide is repeatedly shaken with water, dried over potassium carbonate and then over paraffin in a vacuum. The residue is treated with ether and extracted with alcohol. After removing the ionic halogen by silver hydroxide, a stable alcoholic solution remains, which is treated with dibromogallic acid in alcohol. From the resulting solution a compound $(C_6H_5)_5Cr.O.CO.C_6Br_2(OH)_3$ is isolated.

Compound from Reinecke's Salt.—A solution of Reinecke's salt gives an orange-yellow amorphous salt with the chromium base in ether solution, $(C_6H_5)_5Cr[(SCN)_4Cr(NH_3)_2].C_2H_5.O.C_2H_5$.

Chromium tetraphenyl, $(C_6H_5)_4Cr$, may be obtained in two ways: (1) By the electrolysis of a solution of chromium tetraphenyl iodide in liquid ammonia at $-40°$ to $-50°$ C.[1] The cathode consists of a platinum plate, and the anode is made of graphite and contained in a porous cell. (2) By the electrolysis of chromium pentaphenyl hydroxide in liquid ammonia.[2] The compound forms a smooth or crystalline deposit, possessing the colour of chromium tetraphenyl salts. It readily decomposes, giving diphenyl, and is converted quantitatively by alcohol into chromium tetraphenyl hydroxide. Solutions of the compound in pyridine are stable if kept in the dark in an atmosphere of nitrogen. The compound is unimolecular at concentrations 0·062 to 0·086*N*, according to results by Rast's capillary method. Measurements of the decomposition tension and the cathodic polarisation potential of chromium tetraphenyl hydroxide in methyl alcohol do not indicate metallic properties of the radical. Chromium tetraphenyl is deposited on the mercury as a compact precipitate which shows no tendency to penetrate into the metal and does not possess the characteristic metallic conductivity. The cathodic potential curve shows no similarity to that of the metals. The ion $Cr(C_6H_5)_4'$ does not appear to be formed during the transformation of the tetraphenyl compound

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[1] Hein and Eissner, *Ber.*, 1926, 59, [B], 362.

[2] Hein and Markert, *Ber.*, 1928, 61, [B], 2255.

into its hydroxide, and the change is represented in one of the following ways :

$$r(C_6H_5)_4 + H.OH \longrightarrow (C_6H_5)_4CrH.OH \quad \text{or} \quad Cr(C_6H_5)_4 + H' \longrightarrow (C_6H_5)_4CrH'$$

Hydrogen is not evolved, but remains attached to the basic molecule.

Chromium tetraphenyl salts are the outcome of attempts to prepare pentaphenyl salts, acids or salts converting chromium pentaphenyl hydroxide into tetraphenyl salts, with loss of a phenyl group. The salts dissolve in aqueous alcohol, yielding neutral solutions, and appear to have the ability to combine with hydrogen. Chromium tetraphenyl chloride absorbs 8·5 to 11·5 per cent. of hydrogen, and after being dehydrogenated with Methylene Blue absorbs more active hydrogen than otherwise. This addition of hydrogen does not appreciably affect the melting-points of the salts, nor their colour or analytical behaviour, so that an unusual form of union must be in existence. The union is so feeble that a portion of the hydrogen disappears during the isolation of the salts ; the gas seems to be present in a form similar to that in certain metallic hydrides, *e.g.* palladium hydride. The salts are not hydrolysed in solution ; the halides give immediate precipitates with silver nitrate, and with suitable acids sparingly soluble chromium tetraphenyl salts are obtained.

Chromium tetraphenyl iodide, $(C_6H_5)_4CrI$.[1]—Chromium pentaphenyl hydroxide is shaken with an excess of hydriodic acid or aqueous potassium iodide solution. The liquid is extracted with chloroform, from which the *chloroform double compound,* $(C_6H_5)_4CrI.CHCl_3$, is isolated as dark brownish-red rhombic leaflets. Washing with ether gives $2(C_6H_5)_4CrI.CHCl_3$, and gentle heating removes all the chloroform, leaving the iodide, M.pt. 178° C. after being placed in a bath at 165° to 170° C. The iodide dissolves in chloroform, alcohol, acetone, ethyl acetate, pyridine or phenol, is less soluble in benzene and completely insoluble in ether or ligroin. The stability of the product differs in various solvents ; in boiling chloroform some association takes place, but dissociation occurs in freezing phenol. With *silver iodide* or *mercuric chloride* the iodide forms *complex salts,* which are unstable orange substances. The addition of an alcohol or chloroform solution of the iodide to iodine in alcohol yields glistening chocolate-brown prisms of the *periodide,* $(C_6H_5)_4CrI_5$.

Chromium tetraphenyl bromide, $(C_6H_5)_4CrBr$, is prepared in a similar manner to the foregoing iodide. The product initially isolated contains half a molecule of chloroform of crystallisation and separates as bright orange rectangular plates. These on warming lose chloroform and give the bromide, which melts at 138° to 139° C., and is less stable than the iodide. The bromide dissolves in absolute alcohol, aqueous alcohol or chloroform.

Chromium tetraphenyl perchlorate, $(C_6H_5)_4CrClO_4$, from an alcohol solution of the pentaphenyl base and an excess of $N/10$ perchloric acid, is very unstable in the dry state, exploding when gently warmed or on percussion. It is practically insoluble in water, but somewhat more soluble in alcohols.

Chromium tetraphenyl dichromate, $[(C_6H_5)_4Cr]_2Cr_2O_7$, is obtained by allowing ammonium dichromate in methyl alcohol to

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[1] Hein, *Ber.*, 1921, 54, [B], 2708.

react with an aqueous alcohol solution of the pentaphenyl base. It decomposes in a few days in air or over calcium chloride, and very readily in the presence of phosphoric oxide. It crystallises as golden-yellow plates which explode on heating.

Chromium tetraphenylchromitetrathiocyanatodiammine, $(C_6H_5)_4Cr\left[Cr\begin{matrix}(CNS)_4\\(NH_3)_2\end{matrix}\right]$, occurs when a very dilute alcohol solution of the base reacts with a dilute alcohol solution of Reinecke's salt. It crystallises as thin golden-yellow leaflets, melting with decomposition at 175° C. when placed in a bath at 165° C., and is sensitive to heat and prolonged desiccation over concentrated sulphuric acid. It is very stable when preserved beneath alcohol or mixtures of alcohol and water. Determinations of the molecular weight in freezing nitrobenzene point to extensive dissociation, apparently ionic in character.

Chromium tetraphenyl hydroxide,[1] $(C_6H_5)_4CrOH.3H_2O$.—Chromium tetraphenyl iodide in methyl alcohol or moist chloroform is treated with silver oxide, or the iodide is subjected to electrolysis, using an alcohol solution with a platinum or mercury cathode and a rotating silver anode. One molecule of water is removed by drying over calcium chloride. The base forms orange-coloured plates, M.pt. 104° to 105° C. when placed in a bath previously heated to 95° C. It dissolves readily in water or alcohols, is sparingly soluble in chloroform, insoluble in benzene or ether. Measurements of its conductivity in aqueous solution show that it is comparable in strength with the alkali hydroxides, whilst comparative tests in methyl alcohol solution show that it is a stronger base than chromium pentaphenyl hydroxide. It may readily be converted into the chloride, bromide and iodide.

Chromium tetraphenyl chloride, $[(C_6H_5)_4CrCl]_2.CHCl_3$, occurs when the corresponding chloroform-iodide compound is treated with sodium chloride in aqueous solution. It forms shining crystals, M.pt. 118° C. in a bath previously warmed to 112° C.

Chromium tetraphenyl hydrogen carbonate, $(C_6H_5)_4Cr.HCO_3.2H_2O$.—An aqueous solution of the tetraphenyl base is saturated with carbon dioxide and concentrated over sulphuric acid *in vacuo*. The residue is treated with alcohol and the product precipitated by ether. Orange crystals separate, M.pt. 110° to 111° C., prolonged desiccation over phosphorus pentoxide causing decomposition and formation of diphenyl.

Chromium tetraphenyl dianthranilate, $(C_6H_5)_4Cr.H(O.CO.C_6H_4.NH_2)_2$.—An aqueous solution ($N/50$) of the tetraphenyl base is treated with twice the requisite quantity of anthranilic acid in chloroform solution. The product crystallises as orange needles, M.pt. 145° to 146° C. An *acid salt* is also known, $[(C_6H_5)_4Cr.CO_2.C_6H_4.NH_2]_2.NH_2.C_6H_4.COOH$, M.pt. 130° C., soluble in alcohols, sparingly soluble in chloroform, and insoluble in water.

Chromium tetraphenyl hydrogen dibromomalonate, $(C_6H_5)_4Cr.O_2C.CBr_2.CO_2H$,[2] is prepared from chromium pentaphenyl hydroxide and dibromomalonic acid. It is an orange product, decomposing at 88·5° C., moderately soluble in alcohol, acetone, pyridine or nitrobenzene, insoluble in ethyl acetate, benzene, carbon disulphide or ligroin. It decomposes when kept for three weeks in a vacuum, becoming green.

[1] Hein and Schwartzkopff, *Ber.*, 1924, 57, [B], 8.

[2] Hein, *Ber.*, 1928, 61, [B], 730.

Chromium tetraphenyl hydrogen oxanilate,[1] $(C_6H_5)_4Cr.O_2C.CO.NH.C_6H_5.C_6H_5.NH.CO.CO_2H$, from the pentaphenyl base and oxanilic acid, yields orange-red needles, M.pt. 141° C., very soluble in methyl alcohol, pyridine or chloroform, sparingly soluble in ethyl alcohol, insoluble in benzene.

Chromium tetraphenyl acid r-α-chlorophenylacetate, $2(C_6H_5)_4Cr.O_2C.CH(Cl).C_6H_5.C_6H_5.CH(Cl).CO_2H$, prepared from the pentaphenyl base and two equivalents of phenylchloracetic acid, melts at 118° C., is soluble in alcohols, less soluble in chloroform, and insoluble in ether.

Chromium tetraphenyl acid α-bromocinnamate, $(C_6H_5)_4Cr.O_2C.C(Br):CH.C_6H_5.C_6H_5.CH:C(Br).CO_2H$, forms orange-red crystals, M.pt. 127° C., giving a yellow solution in methyl alcohol and an orange-red solution in ethyl alcohol. It is only sparingly soluble in ethyl acetate and insoluble in benzene or carbon disulphide.

Chromium tetraphenyl benzoate trihydrate, $(C_6H_5)_4Cr.O_2C.C_6H_5.3H_2O$, is isolated when the pentaphenyl base in chloroform solution is treated with the calculated quantity of $N/10$ benzoic acid in the same solvent. It crystallises as yellowish-orange prisms, M.pt. 99° C. When twice the quantity of benzoic acid is used the *acid benzoate dihydrate* results, $(C_6H_5)_4Cr.O_2C.C_6H_5.C_6H_5.CO_2H.2H_2O$, M.pt. 84° C.

Chromium tetraphenyl acid m-aminobenzoate, $2(C_6H_5)_4Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, from *m*-aminobenzoic acid and the pentaphenyl base, melts at 130° C. *p*-Aminobenzoic acid yields $3(C_6H_5)_4Cr.O_2C.C_6H_4.NH_2.2NH_2.C_6H_4.CO_2H$, M.pt. 141° C.

Chromium tetraphenyl acid N-phenylanthranilate, $2(C_6H_5)_4Cr.O_2C.C_6H_4.NH.C_6H_5.C_6H_5.NH.C_6H_4.CO_2H$, isolated from N-phenylanthranilic acid, forms orange-red columns, M.pt. 105° C., soluble in alcohols or chloroform, insoluble in ether.

Chromium tetraphenyl o-chlorobenzoate, $(C_6H_5)_4Cr.O_2C.C_6H_4.Cl$, yields dark orange-red crystals, blackening at 104° C., melting at 107° C., dissolving in alcohol or chloroform, sparingly soluble in acetone, the solution decomposing on heating, and insoluble in ether or benzene. The *m-bromobenzoate*, $2(C_6H_5)_4Cr.O_2C.C_6H_4.Br.Br.C_6H_4.CO_2H$, forms microscopic quadratic prisms, M.pt. 97° C., the *m-nitrobenzoate*, $(C_6H_5)_4Cr.O_2C.C_6H_4.NO_2$, is a hygroscopic salt melting at 90° C., and the *3 : 5-dinitrobenzoate*, $(C_6H_5)_4Cr.O_2C.C_6H_3(NO_2)_2.(NO_2)_2.C_6H_3.CO_2H$, separates as orange-red quadratic plates, blackening at 149° C.

Chromium tetraphenyl acid 5-nitrosalicylate, $(C_6H_5)_4Cr.O_2C.C_6H_3(OH)(NO_2).CO_2H.C_6H_3(OH)(NO_2)$, is isolated from the pentaphenyl base and two equivalents of 5-nitrosalicylic acid. It crystallises in rosettes of needles, M.pt. 132° C.

Chromium tetraphenyl 1 : 2 : 3 : 4-tetrahydronaphthalene-2-sulphonate, $(C_6H_5)_4Cr.O_3S.C_{10}H_{11}$, forms orange-coloured crystals, melting with decomposition at 131° C.

Chromium tetraphenyl azobenzene-p-sulphonate monohydrate, $(C_6H_5)_4Cr.O_3S.C_6H_4.N_2.C_6H_5.H_2O$, separates as pale orange columns, M.pt. 167° C. with decomposition.

Chromium tetraphenyl sulphanilate, $(C_6H_5)_4Cr.O_3S.C_6H_4.NH_2$, forms reddish-orange needles, M.pt. 90° C.

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[1] Hein, *loc. cit.*

Compound from Phenol.—Whereas phenol in absolute alcohol reacts with chromium pentaphenyl hydroxide to give a pentaphenyl salt, in aqueous alcohol a tetraphenyl derivative is produced, $(C_6H_5)_4Cr.O.C_6H_5.2C_6H_5OH$, M.pt. 144° C., identical with the product formed by the interaction of an excess of phenol with chromium tetraphenyl hydroxide.

Compound from m-Chlorophenol.—Repeated washing of the compound $(C_6H_5)_5Cr.O.C_6H_4Cl.HO.C_6H_4.Cl$ (p. 264) with ether yields a tetraphenyl derivative, $(C_6H_5)_4Cr.O.C_6H_4.Cl.HO.C_6H_4.Cl$, M.pt. 130° C.

Compound from o-Nitrophenol.—This nitrophenol reacts with the pentaphenyl base in alcohol to give the substance $(C_6H_5)_4Cr.O.C_6H_4.NO_2$, consisting of orange needles, M.pt. 130° C., whilst *p-nitrophenol* yields $(C_6H_5)_4Cr.O.C_6H_4.NO_2.HO.C_6H_4.NO_2$, long prisms, M.pt. 134° C.

Compound from p-Bromophenol.—In this case the product has the structure $(C_6H_5)_4Cr.O.C_6H_4.Br.HO.C_6H_4.Br$, and separates as glistening orange plates, M.pt. 121° C., soluble in alcohol, pyridine or ethyl acetate, less soluble in chloroform, sparingly soluble in benzene, ligroin, carbon disulphide, ether or water.

Compounds from Pyrocatechol, Resorcinol and Quinol.—These three phenols yield compounds of the type $(C_6H_5)_4Cr.O.C_6H_4OH.C_6H_4(OH)_2$; the pyrocatechol derivative consists of orange columns, M.pt. 153·5° C., the resorcinol compound is a microcrystalline product, M.pt. 180° to 181° C., and the quinol compound forms yellow needles, decomposing at 206° C.

Compounds from 3-Nitropyrocatechol and 2-Nitroquinol.—The general formula for the derivatives from these products is $(C_6H_5)_4Cr.O.C_6H_3(NO_2)(OH)$, and the melting-points are 157° C. and 175° C. (decomp.) respectively.

Compound from 2-Nitroresorcinol.—This nitrophenol yields the substance $(C_6H_5)_4Cr.O.C_6H_3(NO_2).O.Cr(C_6H_5)_4.2(HO)_2C_6H_3.NO_2$, consisting of olive-coloured crystals, melting with decomposition at 162·5° C.

Compounds from o-Nitro-p-cresol and 2 : 6-Dinitrophenol.—These phenols yield respectively $(C_6H_5)_4Cr.O.C_6H_3(NO_2)CH_3$, red needles, M.pt. 135° C. with explosion, and $(C_6H_5)_4Cr.O.C_6H_3(NO_2)_2$, orange-red plates, melting and violently exploding at 160° C.

Compounds from 2 : 5-Dibromoquinol, 2 : 4 : 6-Tribromophenol and Picrolonic Acid.—These three derivatives have the compositions $(C_6H_5)_4Cr.O.C_6H_2Br_2.O.Cr(C_6H_5)_4.2C_6H_2Br_2(OH)_2$, golden-yellow crystals, M.pt. 184° to 185° C., $(C_6H_5)_4Cr.O.C_6H_2Br_3$, glittering needles, M.pt. 153° C., and $(C_6H_5)_4Cr.O.C_3N_2(CH_3)(NO_2)(C_6H_4.NO_2)$, large shining needles, M.pt. 176° C.

Compound from Dibromogallic Acid.—This product has the formula $(C_6H_5)_4Cr.O_2C.C_6Br_2(OH)_3$ (see p. 264).

Chromium triphenyl, $(C_6H_5)_3Cr$,[1] is formed when chromium triphenyl iodide in liquid ammonia is electrolysed using a platinum cathode, or a solution of the iodide in liquid ammonia is treated with sodium in the same solvent. The product isolated by the former process often contains chemically combined or adsorbed ammonia.

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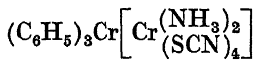
[1] Hein and Markert, *Ber.*, 1928, 61, [B], 2255.

It is a brownish-yellow friable unstable powder, diphenyl being easily eliminated, and may be converted to the hydroxide by the action of alcohol and water. Since the production of the hydroxide takes place with ease, it is assumed that the metal is not normally tervalent, but that the operative valency electrons are derived from groups other than the usual and that the 4_{11} electron ("potassium electron") is not involved, thus causing the similarity of chromium triphenyl to the alkali metals, as shown by its ready conversion into the base.

Chromium triphenyl hydroxide, $(C_6H_5)_3CrOH$.[1]—Crude chromium pentaphenyl bromide (p. 261) is in reality a mixture of chromium polyphenyl bromides, which are converted into the corresponding hydroxides by treating their solution with silver oxide. Of these hydroxides the triphenyl compound remains in solution after the removal of the pentaphenyl hydroxide. The triphenyl base appears to predominate when the original action is prolonged or when the temperature is allowed to rise; both bromides, however, appear to be primary products. The triphenyl base is very soluble in water, and concentration of the solution yields a strongly alkaline, syrupy, transparent, reddish-black mass. This is unstable, but in dilute solution in the absence of light and air it may be preserved indefinitely. With many mineral acids or their alkali salts characteristic precipitates, usually of an amorphous nature, are produced, the colours of these deposits resembling that with the corresponding tetra- and pentaphenyl bases.

Chromium triphenylchromitetrathiocyanatodiammine,



$$(C_6H_5)_3Cr\left[Cr\begin{matrix}(NH_3)_2\\(SCN)_4\end{matrix}\right]$$

is the most characteristic salt of chromium triphenyl obtained and is produced by treating an aqueous alcohol solution of the base with a similar solution of Reinecke's salt. It is isolated as a *dihydrate,* which loses a molecule of water on dehydration over sulphuric acid; prolonged dehydration in this manner again causes loss of water, but decomposition also occurs. The freshly prepared dihydrate when exposed to the air in the absence of light and warmth for one to one and a half days and then placed in a vacuum over concentrated sulphuric acid rapidly loses its water, yielding a salt which can be preserved for a few hours in the absence of air, but rapidly decomposes on exposure to air. The mono- and di-hydrates melt at 168° C. when placed in a bath pre-heated to 155° C. Molecular weight determinations in nitrobenzene by the cryoscopic method give abnormally low results, and the monohydrate appears to be extensively dissociated electrolytically.

Chromium triphenyl iodide, $(C_6H_5)_3CrI.C_2H_5.O.C_2H_5$, is obtained by the interaction of potassium iodide or hydriodic acid and an aqueous solution of the base in the presence of chloroform. The aqueous layer is discarded, the chloroform solution dried, the bulk of the solvent removed at 40° to 50° C. *in vacuo* and the residue added dropwise to eight or ten volumes of dry ether. The iodide separates as an oil which gradually solidifies. The salt is hygroscopic, can be preserved for some time over concentrated sulphuric acid in a vacuum, but is unstable in air. It dissolves more readily in hot than cold water, and is also soluble

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[1] Hein, *Ber.*, 1921, 54, [B], 2727.

in chloroform or alcohol, but insoluble in ether, ethylene dibromide or methylene iodide. With mercuric chloride in alcohol solution it yields an orange-red precipitate, and a *periodide* is also known.

Chromium triphenyl perchlorate, $(C_6H_5)_3CrClO_4$, is prepared by the fractional precipitation of a solution of chromium triphenyl hydroxide with dilute perchloric acid. The salt is microcrystalline; it is best preserved under a mixture of alcohol and ether in an ice-chest; in the dry state it is more labile and explosive than the corresponding tetraphenyl compound.

Chromium tetra-p-bromophenyl bromide,[1] $(BrC_6H_4)_4CrBr$.—When magnesium *p*-bromophenyl bromide, prepared from *p*-dibromobenzene and magnesium in dry ether, reacts with anhydrous chromium chloride, a semi-solid product is obtained. This is orange in colour and requires washing with dilute ammonium hydroxide and repeatedly with water before a perfectly solid product results. The product is then extracted with alcohol, the extract dried by means of potassium hydroxide, concentrated in a vacuum at 40° C. and treated with ether. The precipitate is dissolved in absolute alcohol, the solution filtered, concentrated *in vacuo*, and the product reprecipitated with ether. After washing the deposit several times with ether it is dried over sulphuric acid. When slowly heated it melts at 90° C., but in a bath pre-heated to 110° C. it melts with decomposition at 115° C. Its alcohol solution gives a yellow precipitate with mercuric chloride, a brown precipitate with iodine and a pale yellow precipitate with silver nitrate.

Chromium penta-p-bromotriphenylene bromide, $(C_6H_4Br.C_6H_4.C_6H_4)_5CrBr$, is obtained by extracting the residue from the foregoing preparation with chloroform. Concentration of the solution and treatment with ether yields an orange-red amorphous product. After purification a dark red compound results, decomposing at about 120° C. after darkening. It is readily soluble in chloroform, ethylene dibromide, ethyl bromide, bromobenzene or nitrobenzene, quickly decomposing in warm benzene, insoluble in alcohol or ether.

Chromium di-p-bromotetraphenylene hydroxide, $[Br(C_6H_4)_4]_2CrOH$, appears to be present in the residues insoluble in alcohol and chloroform from the two preceding preparations. It is isolated with one molecule of carbon disulphide of crystallisation, and melts between 220° and 260° C., dissolving in carbon disulphide or benzene, insoluble in ether or alcohol.

Chromium Tolyl Compounds.[2]

p-Tolyl magnesium bromide reacts with chromium chloride in ether solution to give a mixture of chromium polytolyl bromides, this feature having already been noted in the case of the corresponding phenyl compounds. The following products have been derived from this crude mixture.

Chromium penta-p-tolyl bromide mercurichloride, $(C_7H_7)_5CrBr.HgCl_2$, obtained from an alcohol solution of the crude bromides and mercuric chloride, is stable only for a few days, moisture and sunlight causing it to change from bright yellow to green.

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[1] Hein and Späte, *Ber.*, 1926, 59, [B], 751.

[2] Hein and Späte, *Ber.*, 1924, 57, [B], 899.

Chromium penta-p-tolyl carbonate, $[(C_7H_7)_5Cr]_2CO_3.6H_2O$.—When the crude bromides are treated with caustic alkali a solution of chromium penta-*p*-tolyl hydroxide is obtained, which passes into the carbonate. This salt forms orange crystals, M.pt. 139° to 140° C., soluble in alcohols, chloroform or nitrobenzene, sparingly soluble in water or *cyclo*hexanol, insoluble in ether.

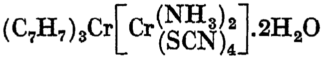
Chromium penta-p-tolyl hydrogen anthranilate, $2(C_7H_7)_5Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, occurs when a solution of the base is treated with an excess of anthranilic acid. It melts at 170° C. after previously sintering, dissolves in alcohols, is sparingly soluble in chloroform and insoluble in carbon disulphide.

Chromium tetra-p-tolyl hydrogen anthranilate, $(C_7H_7)_4Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, is isolated during the preparation of the corresponding tri-*p*-tolyl compound. It is a red substance, M.pt. 176° C., sparingly soluble in cold chloroform or methyl alcohol, but readily soluble on heating, difficultly soluble in cold nitrobenzene, the solution decomposing on warming, and insoluble in carbon disulphide or ethylene dibromide.

Chromium tri-p-tolyl iodide, $2(C_7H_7)_3CrI.C_2H_5.O.C_2H_5$.—Chromium tri-*p*-tolyl hydroxide is isolated by a similar method to that used for the corresponding phenyl compound, and by means of an excess of aqueous potassium iodide is converted into the iodide. This melts with decomposition at 115° to 119° C., is soluble in alcohol, nitrobenzene or chloroform, insoluble in cold benzene, ethyl acetate or ether.

Chromium tri-p-tolyl hydrogen anthranilate, $(C_7H_7)_3Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, is an orange-yellow amorphous product, M.pt. 145° to 149° C. It is soluble in pyridine, and sparingly soluble in chloroform; its solution in nitrobenzene decomposes on warming.

Chromium tri-p-tolylchromitetrathiocyanatodiammine,



$$(C_7H_7)_3Cr\left[Cr\begin{matrix}(NH_3)_2\\(SCN)_4\end{matrix}\right].2H_2O$$

is an unstable amorphous substance.

Chromium tri-p-tolyl picrolonate is also known.

The *p*-tolyl compounds are less stable than the corresponding phenyl derivatives, and this difference is more marked with the *o*-tolyl compounds, of which the following have been isolated: *Chromium tetra-o-tolyl hydrogen anthranilate,* $(C_7H_7)_4Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, a reddish-brown product, M.pt. 75° to 110° C., and *chromium penta-o-tolyl hydrogen anthranilate,* $2(C_7H_7)_5Cr.O_2C.C_6H_4.NH_2.NH_2.C_6H_4.CO_2H$, melting with decomposition at 151° C.

ORGANIC COMPOUNDS OF PLATINUM.[1]

Trimethylplatinic iodide, $(CH_3)_3PtI$.—Chloroplatinic acid is used in the preparation, and in order that the method may be successful the acid must be pure. It is heated at 200° C. at atmospheric pressure in a distilling flask placed in a metal-bath; the water and hydrochloric acid evolved are absorbed by suction through a Woulfe's bottle containing solid caustic potash. After several hours the acid remaining is nearly pure. It is further treated with anhydrous ether until part

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[1] Pope and Peachey, *Trans. Chem. Soc.*, 1909, 95, 571.

is in solution and the remainder becomes a dark red syrup. The solution and syrup are then slowly added to a solution of magnesium methyl iodide in ether, with careful cooling and shaking during the addition. Excess of Grignard reagent is required, and the reagent is made using the minimum amount of ether, then diluting with five volumes of anhydrous benzene.

$$PtCl_4 + 3CH_3MgI = (CH_3)_3PtI + 2MgCl_2 + MgI_2$$

The magnesium methyl iodide is used in twice the quantity given by the above equation. The reaction mixture after standing an hour is poured into ice-water. The benzene solution having been separated, the aqueous portion is extracted several times with benzene. On distilling off the benzene under diminished pressure a sandy powder remains which easily dissolves in boiling benzene, and after filtration deposits a bright yellow crystalline powder consisting of trimethyl platinic iodide.

The compound is explosive when heated, thus making analysis rather difficult. A weighed amount is treated with solid iodine and a few drops of chloroform in a porcelain crucible and very carefully heated to redness. The iodine is estimated by heating with lime, then titrating with silver nitrate and thiocyanate in the usual way. The compound is easily soluble in hot benzene or chloroform, also in cold ethyl bromide or methyl iodide. From benzene it takes the form of square doubly refracting plates of an amber-yellow colour, whilst from ethyl bromide it crystallises as hexagonal plates which appear to belong to the cubic system. The compound is very sparingly soluble in ether, alcohol, acetone or light petroleum, and insoluble in water. It is completely decomposed below 250° C.

Trimethylplatinic hydroxide, $(CH_3)_3Pt(OH)$, is formed when trimethylplatinic iodide in moist acetone solution is boiled with freshly precipitated silver oxide. The reaction is considerably accelerated by the presence of benzene, which dissolves the iodide and hydroxide. The compound forms colourless transparent plates which become opaque in the air. When recrystallised from benzene large rectangular tablets are formed which are doubly refracting and show straight extinction and a perfect cleavage parallel to their longer edges. They contain benzene of crystallisation, but the proportion is not known, as efflorescence quickly occurs. The hydroxide is explosive on heating ; it is moderately soluble in ether, alcohol, acetone, ethyl acetate or chloroform.

Trimethylplatinic sulphate, $[(CH_3)_3Pt]_2SO_4.2H_2O$, occurs when equivalent quantities of the iodide and silver sulphate in moist acetone or benzene are boiled together for several hours. The compound consists of colourless rectangular plates.

Trimethylplatinic nitrate, $(CH_3)_3PtNO_3$, consisting of colourless deliquescent plates, is produced by boiling the hydroxide with dilute nitric acid, or, better, by treating an aqueous solution of the sulphate with an equivalent quantity of barium nitrate.

Trimethylplatinic chloride, $(CH_3)_3PtCl$, is obtained from the nitrate or sulphate in aqueous solution by adding potassium chloride, or by adding hydrochloric acid to an alcoholic solution of the hydroxide. It crystallises from chloroform as colourless dodecahedra of the cubic system.

Trimethylplatinic cyanide, $(CH_3)_3PtCN$, is formed only as a flocculent precipitate from the nitrate or sulphate using potassium cyanide.

Potassium trimethylplatinic platinocyanide, $K[(CH_3)_3Pt]Pt(CN)_4$, is isolated from an aqueous solution of the nitrate by adding potassium platinocyanide. A slimy yellow precipitate is formed, insoluble in water and the usual organic solvents except acetone and alcohol. On evaporation from one of these solvents an amorphous resinous greenish-yellow compound is produced which, from determination of the platinum, appears to correspond to $K_2Pt(CN)_4[(CH_3)_3Pt]_2Pt(CN)_4$.

Diamminotrimethylplatinic iodide, $(CH_3)_3PtI(NH_3)_2$, consisting of white crystalline scales, occurs when trimethylplatinic iodide is heated with a mixture of benzene, alcohol and concentrated ammonia on a water-bath, then evaporated to dryness. It yields free ammonia on heating with potassium hydroxide, is slightly soluble in water, moderately soluble in benzene or ether, and easily soluble in alcohol, ethyl acetate or acetone.

NAME INDEX.

SUBJECT INDEX.

N.B.—Index is arranged under headings of elements placed in their order of appearing in the Periodic Classification. References in italics indicate where the preparation and properties of the compound in question may be found.

Chromium.

PATENT INDEX.

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