

THE WAR GASES

CHEMISTRY AND ANALYSIS

BY

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Preface by

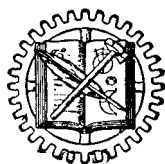
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PREFACE TO THE FIRST ITALIAN EDITION

THE world conflict of 1914-18 opened a new field of study in the Chemistry of War : that of the war gases. Thus the Chemistry of War, which had for its cradle the chemical laboratory in Turin where Ascanio Sobrero discovered nitroglycerine and which for 60 years was confined to the study of explosives, underwent a new development and a new orientation when substances which had an offensive action on the human and animal organism were first used on the field of battle. Then commenced the study of war gases which has become one of the most complex and important departments of chemistry.

Our present knowledge of most of these asphyxiating gases is very superficial and even inexact, which is the reason that while some merit the importance given to them, others tend to be overvalued. Books are therefore necessary to give information as to what has been published of the constitution, the methods of preparation and the properties of these substances.

While many German, American and Russian treatises elucidate this subject, which is of such great and present interest, in a wide and complete manner, few publications exist on the subject in the Italian language. Dr. Sartori's book therefore fills a lacuna in our scientific bibliography.

This book by my pupil, which I present to the Italian public, is a complete account of the information and facts obtained with scrupulous diligence from very various sources, explained with clarity and scientific precision, so that it constitutes a trustworthy and practical work of reference for chemists and of information for students of this subject.

PROFESSOR GUIDO BARGELLINI.

INTRODUCTION

THE date of the commencement of scientifically organised chemical warfare is universally fixed at April 22nd, 1915, when the Germans launched the first cloud of chlorine gas in the region of Ypres.

It may be said that on the same date the study of the war gases commenced. In the literature of the pre-war period, occasional notes appear concerning the physical, chemical and biological properties of most of the substances which were employed in the European War as war gases. These notes, however, were not the result of systematic researches, at any rate from the biological side, but of inquiries into accidents.

A complete study of only a few substances was in existence, but these were more properly poisons, such as the alkaloids and the arsenic-containing pharmaceuticals, etc., and cannot be included among the war gases.

The employment of noxious substances as munitions of war imposed on chemists of all nations the necessity of co-ordinating and adding to the existing data concerning substances which were both toxic and also had the necessary physical, chemical and technical properties. These researches were concerned both with the manufacturing processes best suited to the national resources and with the most efficient methods of employing substances already known to be toxic. Furthermore, the biological properties of known substances were defined so as to correlate offensive action with chemical structure, and finally, especially at the end of the war and in the post-war period, new war gases were synthesised whose employment would surprise the enemy and which would also be superior in some respects to those already in use.

In these researches several thousand substances were examined during the war, and Edgewood Arsenal, U.S.A., alone examined some 4,000. But, of all these, only 54, according to American data, were tried in the field, and only 12 were being actually used at the end of the war.

This selection, which was made on the basis of the actual conditions in which the substances were employed, shows how rigorous are the physical, chemical and technical requirements

of a substance for it to be utilisable in the field. Substances which are satisfactory from the biological point of view must also

(1) Be capable of being manufactured by practicable and economical methods with due regard to national resources.

And (2) possess physical and chemical properties which render them utilisable in the field.

Studies carried out during and since the war have shown that

(a) Not all substances harmful to the human organism can be used as war gases.

(b) The most efficient war gases are organic compounds, the inorganic compounds which have great toxicity being unsuitable for use owing to their physical and chemical properties.

The war of 1914-18 thus initiated a new branch of chemistry, predominantly organic, which only to a limited extent borders on toxicological chemistry.

Work in this new field of study is characterised both by experimental difficulty and by the necessity of co-ordinating chemical facts with physiopathological data and techno-military requirements.

It is with the confidence of being able to contribute modestly to a wider knowledge of the war gases and in the hope of satisfying requests for a book which should contain all the purely chemical data, at present published in the various manuals of chemical warfare in fragmentary or summary form, that I have collected in this volume all the best and most recent work published up to the present on the chemistry of the war gases.

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2 PRINCIPAL PROPERTIES OF THE WAR GASES

The degree of toxicity is usually expressed by the following characteristics: ¹

- (1) The lower limit of irritation.
- (2) The limit of insupportability.
- (3) The mortality-product.

1. The Lower Limit of Irritation

The lower limit of irritation of a gas, also termed "the threshold value of pathological sensitivity," ² is the minimum concentration provoking a painful sensation at those surfaces on which it acts in its characteristic manner. The surfaces are the conjunctiva, the nasal mucosa and the pharynx, the skin, etc. Experiments are made on human subjects and are continued until the appearance of signs of the specific action of the gas, generally lachrymation or sneezing, on all or nearly all the persons taking part in the experiment.

The lower limit of irritation is generally expressed in mgm. of substance per cubic metre of air.

In Table I the values of the lower limit of irritation are given for several substances.

TABLE I. *Lower Limits of Irritation*

WAR GAS	MGM./CU. M.
Diphenyl chloroarsine	0.1
Chloro acetophenone	0.3
Ethyl dichloroarsine	1
Chloropicrin	2
Phosgene	5
Trichloromethyl chloroformate	5
Dichloromethyl ether	14

It will be seen from this table that the lower limit of irritation of the war gases may vary between fairly wide limits. The substance with the greatest irritant power known to the present is diphenyl chloroarsine.

2. The Limit of Insupportability

The limit of insupportability is the maximum concentration which a normal man can support for 1 minute without injury. This characteristic can only be determined for those war gases which have a predominantly irritant action. In the case of

¹ Detailed accounts of the methods of determining these characteristics are given in LUSTIG, *Patologia e clinica delle malattie da gas di guerra*, Milan, 1937, and in AKSENOV, *Metodika Toksikologii boevikh otravljajuscich vescestv*, Moscow, 1931.

² FERRI and MADESINI, *Giornale di Medicina Militare*, January, 1936, 36.

lachrymatories, it is usual after abundant lachrymation to arrive at a condition of photophobia, burning of the eyes and inability to keep the eyes open, and this stage is considered that of the limit of insupportability. In the case of sternutators, insupportability is taken to be the stage when, after the production of sneezing, other symptoms such as coughing, retrosternal pain, headache, etc., appear and produce the sensation of having reached a limit beyond which it would be unwise to proceed.

In Table II the values of the limits of insupportability are given for several substances :

TABLE II. *Limits of Insupportability*

WAR GAS	MGM./CU. M.
Diphenyl chloroarsine	1
Chloroacetophenone	4.5
Ethyl dichloroarsine	10
Dichloromethyl ether	40
Trichloromethyl chloroformate	40
Chloropicrin	50

The substance having the lowest limit of insupportability is diphenyl chloroarsine, and that having the highest is chloropicrin.

3. The Mortality-product

The mortality-product, also termed the *Lethal Index*, or the *Haber Product*, W , is given by the product of the concentration, C , of the substance in air (expressed in mgm. per cu. m.), by the duration, t , of its action (expressed in minutes) sufficient to cause death. It is normally expressed by the following equation :

$$C \times t = W$$

The mortality-product gives the toxic power of the asphyxiants and of those poisons absorbed through the skin. It cannot be experimentally determined on the human subject, and experiments are normally made on animals, cats, rabbits, cavies or dogs.

It is inversely proportional to the toxicity of a substance : the lower the value of the index, the greater is the toxic power.

According to Flury,¹ the formula quoted above gives values sufficiently accurate for practical purposes when working with concentrations insufficient to cause the death of the animals in a few minutes and not so low as to need less than several mgm. of the substance.

American workers have generally determined the mortality-

¹ FLURY, *Z. ges. expt. Med.*, 1921, 13, 1, and *Gasschutz und Luftschutz*, 1932, 149.

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product at two different durations: at an exposure time of 10 minutes (short exposure) and at an exposure time of 30 minutes (long exposure).

The values of the mortality-products are referred to the species of animal used in the experiments and are valid only under the same experimental conditions. They are thus not applicable to man. However, they give comparative data of great importance for the evaluation of the relative toxic power of substances.

Table III gives values of the mortality-product for several substances.

TABLE III. *Mortality-product*

WAR GAS	GERMAN DATA ON CATS ¹	AMERICAN DATA ON DOGS AND MICE ²
Phosgene	450	5,000
Trichloromethyl chloroformate	500	5,000
Dichloromethyl ether	500	4,700
Chloropicrin	2,000	20,000
Ethyl dichloroarsine	3,000	5,000
Diphenyl chloroarsine	4,000	15,000
Chloroacetophenone	4,000	8,500

The difference between the German and the American results in Table III is attributable to various causes ³: the German values were obtained with cats, and the American with dogs and mice; cats are more sensitive to some toxic substances and less to others; the German values were obtained during the war, when the cats used in the experiments were suffering from malnutrition.

(B) PHYSICAL PROPERTIES

The principal physical properties to be considered in evaluating the practical utility of a substance for use as a war gas are as follows:

1. Vapour Tension

All liquid and solid substances possess a definite tendency to pass into the gaseous condition. Because of this tendency, a layer of vapour forms above each substance and exercises a certain

¹ MEYER, *Die Grundlagen des Luftschutzes*, Leipzig, 1935.

² PRENTISS, *Chemicals in War*, New York, 1937. The values quoted refer to an exposure period of 10 minutes.

³ FLURY, *loc. cit.*, and WIRTH, *Gasschutz und Luftschutz*, 1936, 250.

pressure whose magnitude depends on the temperature. This pressure, termed the vapour tension or vapour pressure, is expressed in mm. of mercury.

In the case of the war gases, this physical constant has an especial interest. In order to be of use in warfare, at least as a toxic agent on the respiratory tract, a gas must have a vapour pressure high enough at ordinary temperatures to supply enough gas to the atmosphere to produce useful physiopathological effects. However, this property has only a minor value in the case of substances such as diphenyl dichloroarsine, which are used in the form of aerosols.

There are various methods (static, dynamic, etc.) of determining the vapour tension of a substance, but it is not proposed to describe these here, as they may be found in special treatises.¹ Moreover, various formulæ may be employed to calculate the vapour tension of a substance at different temperatures. That in most general use is the empirical formula of Regnault²:

$$\log p = a + b \beta^t + c \gamma^t$$

This may also be used in the following shorter form³:

$$\log_{10} p = A + \frac{B}{273 + t}$$

In this formula A and B are two constants which vary from substance to substance and whose values may be calculated from the boiling points of the substance, t_1 and t_2 , at two different pressures, p_1 and p_2 . Two equations are thus obtained with two unknowns:

$$\log_{10} p_1 = A + \frac{B}{273 + t_1}$$

$$\log_{10} p_2 = A + \frac{B}{273 + t_2}$$

from which the values of A and B may be obtained.

Research carried out by various workers has demonstrated that this formula gives values sufficiently concordant with those obtained experimentally by the dynamic method. In calculating

¹ OSTWALD-LUTHER, *Physico-chemischen Messungen*, Leipzig, 1925.

² WINKELMANN, *Handbuch der Physik*, III, 1906, 950.

³ BAXTER and BEZZENBERGER, *J. Am. Chem. Soc.*, 1920, **42**, 1386; HERBST, *Kolloidchem. Beihefte*, 1926, **23**, 323; MUMFORD and coll., *J. Chem. Soc.*, **1932**, 589; LIBERMANN, *Khimiya i Teknologiya Otravljajuscikh Vescestv*, Moscow, 1931.

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the values of the two constants it is necessary, however, to employ two boiling points at temperatures at least 70° C. apart.

Baxter, Mumford and others,¹ applying this formula to the determination of the vapour tension of war gases, have determined the values of *A* and *B* for various substances as follows :

TABLE IV. *Values of Constants A and B*

	A.	B.
Phosgene	7·5595	— 1,326
Chloropicrin	8·2424	— 2,045·1
Cyanogen bromide	10·3282	— 2,457·5
Dichloromethyl sulphide	8·3937	— 2,734·5
Methyl dichloroarsine	8·6944	— 2,281·7
Diphenyl chloroarsine	7·8930	— 3,288

By substituting the values of Table IV in the formula already given, the vapour tensions of the various substances may be found at different temperatures.

In Table V the values of the vapour tensions of several substances are given in mm. of mercury at 20° C.

TABLE V. *Vapour Tension at 20° C.*

	MM. MERCURY
Bromobenzyl cyanide	0·012
Dichloroethyl sulphide	0·115
Chlorovinyl dichloroarsine	0·395
Trichloromethyl chloroformate	10·3
Chloropicrin	16·9
Cyanogen chloride	1,001·0
Phosgene	1,173·4

It is seen from this table that the variation in the vapour tensions of the war gases is very great. For example, some of these substances have a vapour tension greater than one atmosphere (phosgene, cyanogen chloride), while others (dichloroethyl sulphide, bromobenzyl cyanide) have an extremely low vapour tension, and for this reason special methods are necessary in order to obtain efficient results in using them in warfare.

2. Volatility

By the term volatility is meant the weight of the substance contained in 1 cu. m. of saturated vapour at a certain temperature.

¹ See the preceding note.

The volatility is usually expressed in mgm. of the substance per cu. m. of air, though occasionally also in cu. mm. per cu. m. of air. From the latter value the weight per unit volume may be calculated from the formula :

$$\text{mgm.} = \text{cu. mm.} \times d$$

in which d is the density of the substance.

The volatility is one of the most important factors in the selection and evaluation of war gases.

The volatility V of a substance at a certain temperature t may be easily calculated from the following relation :

$$V^t = \frac{M \cdot 273 \cdot p \cdot 10^6}{22.4 (273 + t) 760}$$

in which M = molecular weight of the substance, in gm.

P = vapour tension in mm. of mercury of the substance at the temperature t .

In the following table, values of the volatility are given in mgm. of substance per cu. m. of air of some war gases at 20° C.

TABLE VI. *Volatility at 20° C.*

	MGM./CU. M.
Diphenyl cyanoarsine	0.17
Diphenyl chloroarsine	0.68
Dichloroethyl sulphide	625.00
Benzyl bromide	2,400.00
Trichloromethyl chloroformate	26,000.00
Methyl dichloroarsine	74,400.00
Chloropicrin	184,000.00

As is seen from Table VI, the values vary over a wide range ; while diphenyl chloroarsine at 20° C. has a volatility of only 0.68 mgm. per cu. m. of air, at the same temperature the volatility of chloropicrin is 184,000 mgm. per cu. m. of air. Because of these differences in volatility, the various war gases are used for different types of objective and applied by different methods.

As already noted, the volatility of the war gases varies with temperature. Herbst ¹ has established the following approximate relationship between temperature and volatility :

Between 10° and 30° C. an increase in temperature of 1° C. causes an increase in volatility of about 10%.

Experimental values of the volatility of dichloroethyl sulphide

¹ HERBST, *Kolloidchem. Beihefte*, 1926, **23**, 340.

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between 15° and 25° C. are compared in the following table with values calculated from Herbst's rule :

TABLE VII. *Volatility of Dichloroethyl Sulphide*

TEMPERATURE °C.	VOLATILITY IN MGM./CU. M.	
	FOUND	CALCULATED
15	401	401
16	439	441
17	480	482
18	525	528
19	573	577
20	625	630
21	682	687
22	743	750
23	810	817
24	881	891
25	958	969

The increase in volatility caused by increase in temperature is very effective in bringing about useful effects from the offensive point of view, especially in the case of relatively involatile substances.

3. Boiling Point

The boiling point of a substance is that temperature at which its vapour tension attains the value of the atmospheric pressure. The lower the boiling point of a substance, the higher is its vapour tension and its volatility.

TABLE VIII. *Boiling Points of some War Gases at a Pressure of 760 mm. of Mercury*

	° c.
Chlorine	— 33·5
Phosgene	8·2
Hydrocyanic acid	26·5
Cyanogen bromide	61
Monochloromethyl chloroformate	107
Chloropicrin	112
Dichloroethyl sulphide	217
Chloroacetophenone	245

The war gases have very varied boiling points, as is seen from Table VIII. This variation in the boiling points, together with the differences in physiopathological action, explains the variation between the types of employment which the war gases find in

warfare. Thus substances with a relatively low boiling point are employed in the field when a high gas concentration is required for a short time, while those with a rather high boiling point are used when a prolonged action is desired.

According to Herbst, a knowledge of the boiling point of a substance enables deductions to be made regarding its volatility. In the following table volatilities at 20° C. are given corresponding with a series of boiling points.

TABLE IX. *Relation between Boiling Point and Volatility*

B.P. AT 760 MM. ° C.	VOLATILITY AT 20° MGM./CU.M.	B.P. AT 760 MM. ° C.	VOLATILITY AT 20° MGM./CU.M.
300	3	190	2,000
290	6	180	4,500
280	12	170	9,000
270	25	160	14,000
260	50	150	21,000
250	100	140	31,000
240	200	130	46,000
230	380	120	68,000
220	630	110	100,000
210	1,000	100	155,000
200	1,550		

From these values, Herbst ¹ deduces the following rule concerning the relation between boiling point and the volatility at 20° C.

(a) For boiling points between 300° and 230° C., a diminution in boiling point of 10° C. corresponds to a doubling of the volatility.

(b) For boiling points below 230° C., a diminution in boiling point of 10° C. corresponds to an increase in volatility of 1.5 to 1.6 times.

The boiling point is an important characteristic of a war gas, not only because of its connection with vapour tension and therefore with the tactical aims attainable in warfare, but also because of its influence on the ease of storage and transport of the substance. A war gas whose boiling point is lower than ordinary temperatures, as, for example, phosgene, is difficult to pack and necessitates the use of refrigerating apparatus during transport in order to keep it below its boiling point.

The preference of the Germans during the war of 1914-18 for employing trichloromethyl chloroformate (diphosgene) rather than

¹ HERBST, *loc. cit.*

phosgene was due to the difficulties of manipulating the latter gas, owing to its low boiling point.

4. Melting Point

The melting point of a substance is the temperature at which the solid and the liquid phases of the substance are in equilibrium.

TABLE X. *Melting Points of some War Gases*

	° c.
Chlorine	— 102
Chloropicrin	— 69
Trichloromethyl chloroformate	— 57
Hydrocyanic acid	— 15
Dichloroethyl sulphide	+ 14.4
Chloroacetophenone	+ 58

The melting point is an important factor in the use of a gas in warfare, for on it depends the practicability of its employment. It is easily understood that substances which are quite suitable for use with respect to their action in the vapour state cannot be efficiently employed in cold regions if they have a high melting point, without having recourse to special methods such as admixture with other substances so as to reduce the melting point. Thus in the case of dichloroethyl sulphide, which in the pure state melts at about 14° C., a solution of this substance in chlorobenzene was widely used during the war. The melting points of mixtures of dichloroethyl sulphide (of 94–95% purity ; m.p. 13.4° C.) with chlorobenzene and with carbon tetrachloride in various proportions are given in the following table :

% Solvent	<i>Chlorobenzene</i>	<i>Carbon tetrachloride</i>
	<i>m.p.</i>	<i>m.p.</i>
0	13.4°	13.4°
10	8.4°	9.8°
20	6.4°	6.6°
30	—1.0°	3.1°

As will be seen, chlorobenzene, which was more commonly employed for this purpose, forms mixtures whose melting points are lower than the corresponding mixtures containing carbon tetrachloride.

5. Persistence

The persistence is the time during which a substance can continue to exercise its action in an open space.

Among the numerous factors which influence the persistence of a gas, the most important are the speed of evaporation of the substance, the temperature of the air and the chemical and physical nature of the ground.

Leitner ¹ has proposed the following formula for calculating the persistence of a war gas :

$$S = \frac{C_1}{C} = \frac{p_1}{p} \sqrt{\frac{M_1 T}{M T_1}}$$

in which :

- S is the persistence of the substance.
 C is the velocity of evaporation of the substance at absolute temperature T .
 C_1 is the velocity of evaporation of water at 15°C .
 p is the vapour tension of the substance at T .
 p_1 is the vapour tension of water at 15°C . = 12.7 mm.
 M is the molecular weight of the substance.
 M_1 is the molecular weight of water = 18.
 T is the absolute temperature of the air.
 T_1 is the absolute temperature corresponding to 15°C .

This formula gives accurate values for the time which a substance takes to evaporate compared with the time taken by the same quantity of water at 15°C . in the same conditions.

In the following table the values of the persistences of several war gases are given at various temperatures (persistence of water at 15°C . = 1) calculated according to Leitner's formula :

TABLE XI. *Persistences of some War Gases*

	Temperature ° C.								
	- 10	- 5	0	+ 5	+ 10	+ 15	+ 20	+ 25	+ 30
Phosgene . . .	0.014	0.012	0.01	0.008	—	—	—	—	—
Chloropicrin . .	1.36	0.98	0.72	0.54	0.4	0.3	0.23	0.18	0.14
Trichloromethyl chloroformate . .	2.7	1.9	1.4	1.0	0.7	0.5	0.4	0.3	0.2
Lewisite . . .	96	63.1	42.1	28.5	19.6	13.6	9.6	6.9	5
Dichloroethyl sulphide (liquid).	—	—	—	—	—	103	67	44	29
Dichloroethyl sulphide (solid) .	2,400	1,210	630	333	181	—	—	—	—
Bromobenzyl cyanide . . .	6,930	4,110	2,490	1,530	960	610	395	260	173

¹ LEITNER, *Militärwissensch. u. Techn. Mitteil*, 1926, 662.

However, Nielson's work ¹ shows that these data have only an approximate value and indicate merely the order of magnitude of the persistence. Nielson observed, *inter alia*, that in Leitner's formula the time of evaporation of a substance is compared with that of water into a *dry* atmosphere, whereas in practice the atmosphere always contains a certain amount of water which retards the velocity of evaporation. Nevertheless, the data for persistence obtained from Leitner's formula, though they have only an approximate value, are of interest from the practical point of view, for they allow values of the persistences of different gases to be compared. For example, from Table XI it is seen that the relative persistences of dichloroethyl sulphide and lewisite at 25° C. are as 44 is to 6.9, and this signifies that at this temperature dichloroethyl sulphide is about six times as persistent as lewisite.

These values, it will be understood, indicate only the persistences independently of the atmospheric conditions, and of the stability of the substances to humidity, and to the physical structure and condition of the ground.

With regard to the last factor, Leitner has specified that the values of the persistences given above refer to substances spread on "open flat land in dry weather." They may be doubled if the substance lies on "broken ground" and tripled if it is in "wooded country."

(C) CHEMICAL PROPERTIES

The most important chemical properties to be considered in evaluating the practical possibilities of a substance for warfare are :

1. Stability to Atmospheric and Chemical Agencies

From the chemical point of view a war gas must be sufficiently resistant to the various agents into which it may come into contact in practice. It is especially important that it should be indifferent to atmospheric agencies. In the first place, all these substances must be indifferent to atmospheric oxygen. However, a large number are decomposed more or less rapidly by the action of atmospheric humidity, and almost all are decomposed in time by rain.

Rona ² has made some experiments on the decomposition of war gases by water. He has demonstrated experimentally that some substances are rapidly decomposed by water (phosgene,

¹ B. NEILSEN, *Z. ges. Schiess.-Sprengstoffw.*, 1931, **26**, 420.

² RONA, *Z. ges. expt. Med.*, 1921, **13**, 16.

dichloromethyl ether, etc.), others decompose slowly (dichloroethyl sulphide), others only very slowly (benzyl bromide, benzyl iodide, xylyl bromide, etc.), while some are practically unattacked (chloropicrin, chloroacetone, iodoacetone, etc.).

Chlorovinyl dichloroarsine is rapidly hydrolysed by water. According to Vedder¹ this substance, though powerfully toxic, could not be efficiently used in open country because of its high velocity of hydrolysis.

In general, oxygen-containing compounds are more stable than the corresponding sulphur-containing ones, according to Meyer,² who adds that the stability increases with an increase in the length of a chain of carbon atoms.

With respect to their employment in war a knowledge of the behaviour of substances towards water is of great importance, particularly by rendering it possible to define the conditions of humidity in which a certain substance may be employed, especially in considering the length of time during which it is desired to maintain an area in the gassed condition.

The sensitivity to water seriously complicates both the storage of war gases and their filling into projectiles. Those which are readily hydrolysed need the employment of special precautions when they come into contact with air, which always contains water vapour, and when they are being filled into projectiles or storage containers, which must be quite dry internally.

War gases must further possess a certain indifference towards the common chemical agents, as alkalis, acids, oxidants, etc. Chemical resistance contributes greatly to the aggressive value of a gas by making its destruction difficult.

2. Stability on Storage

Another type of stability required of a war gas is that it shall not undergo decomposition or polymerisation during storage. The decomposition which takes place in some substances, such as bromoacetone, hydrocyanic acid, etc., may be so inconvenient that the storage of such compounds is impossible.

Polymerisation usually results in the formation of substances of little or no toxicity, as happens, for example, in the case of acrolein.

This form of alteration has raised the problem of stabilisers, that is, substances which when added in quite small quantity, preserve the aggressive properties of the gas. For some of these gases, as acrolein, hydrocyanic acid, etc., efficient stabilisers are

¹ VEDDER, *Medical Aspects of Chemical Warfare*, Baltimore, 1925, 158.

² MEYER, *Der Gaskampf u. die chemischen Kampfstoffe*, Leipzig, 1938, 72.

known, while for others the problem is still being studied, and at present it is still impracticable to employ some substances which in other ways present great interest as potential war gases.

3. Stability to Explosion

From the tactical point of view a substance which is to be employed in projectiles must be stable to the heat and pressure generated by the explosion of the bursting charge. With regard to the stability to heating, the substance must be able to resist the rise in temperature resulting from the explosion of the charge in the projectile. This is of great importance and limits the number of useful war gases. Among the substances hitherto considered, bromobenzyl cyanide shows some sensitivity to a rise in temperature. Many others, including diphenyl chloroarsine, chloroacetophenone, etc., resist even high temperatures fairly well, while some, as chloropicrin, trichloromethyl chloroformate, etc., though decomposing with heat, have the advantage of producing equally toxic compounds in doing so.

With regard to the resistance to the explosion pressure the insensitivity of war gases is another condition essential to their use in projectiles. Chloroacetophenone is practically completely insensitive.

4. Absence of Attack on Metals

The last requisite of a war gas is comparatively important : the absence of any attack on the material in which it is to be stored or used. Some war gases strongly attack the iron which commonly forms the storage containers and projectiles ; such are xylyl bromide, the incompletely chlorinated formates, bromobenzyl cyanide and a few others.

This corrosive action necessitates the employment of special expedients, such as :

(a) Protection of the metal walls of the container with layers of a substance which is not attacked, such as shellac, enamel, tin, etc.

(b) Employment of a supplementary container which isolates the war gas from the walls of the container. (Containers of glass, lead, etc., are used.)

CHAPTER II

RELATION BETWEEN CHEMICAL STRUCTURE AND AGGRESSIVE ACTION

THE employment of toxic substances as a military arm has added interest to the study of the relation between physio-pathological action and chemical constitution, which started some years ago.

This study, particularly important in the case of the war gases because of the guidance afforded in the discovery of new gases, has centred around the relation between their chemical structure and the type of action which they exert (lachrymatory, asphyxiant, sternutatory, etc.).

The problem has always attracted intensive study and experiment, but owing to the short period during which this has been prosecuted, as well as the secrecy which has surrounded the results, it is not yet possible to state the general laws with any certainty. However, it will be of interest to give an account of the observations and hypotheses published on the influence of the structure of these substances, and in particular of the introduction of certain atoms or radicles, on the nature of the action exerted.

The majority of the substances employed as war gases during the war of 1914-18 were organic. Among the inorganic compounds employed were chlorine, bromine, arsenic trichloride, etc. These, though having relatively little aggressive power, were used at the commencement of gas warfare chiefly because of the ease of their manufacture and the simplicity of their application. Various other inorganic substances, such as phosphine, arsine and stibine, although very toxic, have not been used as war gases because of their unsuitable physical properties.

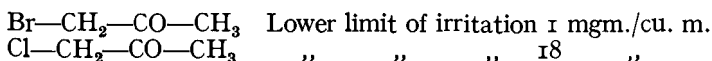
The organic compounds having aggressive action usually contain atoms of halogen, sulphur or arsenic or radicles such as $-\text{NO}_2$, $-\text{CN}$, etc., in their molecules. It is to these atoms or radicles as well as to the molecular structure that the physio-pathological action is nowadays attributed.

1. Influence of Halogen Atoms

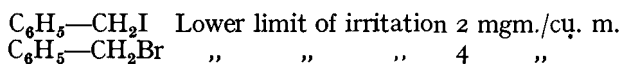
The halogens themselves have a noxious action on the animal organism and this diminishes in intensity in passing from fluorine

to iodine, that is, it is less the greater the atomic weight of the halogen ; the tendency to combine with hydrogen also diminishes with increase in atomic weight.

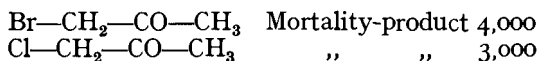
The introduction of halogen into the molecule confers aggressive properties which vary according to the nature of the halogen and the number of halogen atoms introduced. With regard to the influence of the nature of the halogen, it has been observed that the lachrymatory power of halogenated substances increases with increase of the atomic weight of the halogen present. Thus, bromoacetone is a more powerful lachrymatory than chloroacetone :



Benzyl iodide has a lachrymatory action superior to that of the bromide :



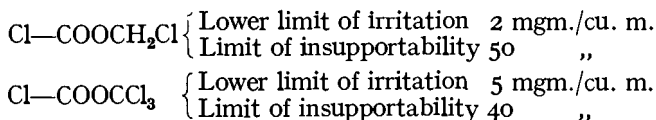
However, the truly *toxic* action varies inversely as the atomic weight of the halogen. Bromoacetone is less toxic than chloroacetone ¹ :



Dibromoethyl sulphide is less toxic than dichloroethyl sulphide :



In considering the influence of the number of halogen atoms present it is found that while one halogen atom confers predominantly lachrymatory properties on the molecule, an increase in the number of the halogen atoms diminishes the lachrymatory but increases the asphyxiant action. A typical example of this observation is the series of halogenated esters of formic acid. In this the first member, monochloromethyl chloroformate, has a predominantly lachrymatory action, while the last, trichloromethyl chloroformate, has an essentially asphyxiant action and practically no lachrymatory property.

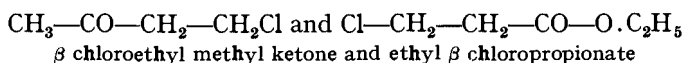


¹ The mortality products quoted in this chapter are those of German authorities (*cp.* p. 4).

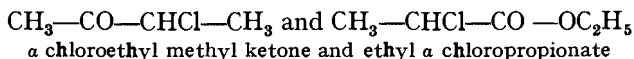
Other examples occur in the series of chlorinated nitromethanes, in which it is found that the dichloro-derivative is less toxic than the trichloro-compound.

This law is not, however, always applicable. With some substances, as dichloroethyl sulphide, diphenyl chloroarsine, etc., it is found that the introduction of further halogen atoms first diminishes and then destroys the aggressive properties of the original compound.

The position occupied by the halogens in the molecule also has a notable influence on the aggressive properties. In the aliphatic series, it is found that compounds with the halogen atom in the β position,



are more powerful lachrymatories than their isomers which have the halogen in the α position,



In the aromatic series it is observed that the introduction of a halogen atom into the side chain of a substance confers lachrymatory properties, while if it replaces a hydrogen atom from the benzene nucleus, a substance results which has no physiopathological properties. Thus, from toluene, benzyl bromide, $\text{C}_6\text{H}_5\text{—CH}_2\text{Br}$, is obtained in the first case. This has energetic lachrymatory properties, while bromotoluene, $\text{C}_6\text{H}_4\text{Br—CH}_3$, has no toxic action.

This difference in physiopathological properties is probably connected with a difference in the mobility of the halogen atom. It is noteworthy that if this is in the nucleus it is less easily removed than if it is in the side chain.

The degree of mobility of the halogen atom has a great influence on the aggressivity of the substance. The halogen must not be bound in too labile a manner to the molecule, otherwise it will be attacked by atmospheric agencies or by the surface of the organism before the entire molecule has penetrated the cells. Neither may it be bound to the molecule in too stable a manner, otherwise the substance will be practically inert, for the atom will not even be detached in the interior of the organism.

2. Influence of the Sulphur Atom

Sulphur is not generally considered as a toxic element in the same way as are the halogens. Nevertheless, its presence seems to confer on a substance the capability of penetrating the

epidermis, which explains the actual aggressive properties of such compounds.

An example of this observation is found in a comparison of substances containing a sulphur atom with their analogues which contain oxygen. For example, dichloroethyl sulphide

(mustard gas) $\text{S} \begin{cases} \text{CH}_2-\text{CH}_2\text{Cl} \\ \text{CH}_2-\text{CH}_2\text{Cl} \end{cases}$ is a powerful vesicant, while the corresponding oxide, dichloroethyl ether, $\text{O} \begin{cases} \text{CH}_2-\text{CH}_2\text{Cl} \\ \text{CH}_2-\text{CH}_2\text{Cl} \end{cases}$ has

no such properties.

Comparatively few war gases contain sulphur in their molecules. It is generally observed that the degree of toxicity of the sulphur compounds varies with the valency of the sulphur atom and with the nature of the radicles with which the sulphur is united. Among the sulphur compounds those of the type R_2S (divalent sulphur) are more toxic than those of the type R_2SO (tetravalent sulphur) and far more than those of the type R_2SO_2 (hexavalent sulphur). That is, the higher the valency of the sulphur atom, the lower the toxicity of the substance. Some studies have been carried out showing the relation between the decrease in toxicity observed when the sulphur atom in the molecule passes from the divalent to the hexavalent state, and the variation in physical properties, more especially the diminished solubility in lipoids. Those compounds in which the sulphur has a specific function also contain halogen atoms. Such are, for instance, dichloroethyl sulphide, dibromoethyl sulphide, etc.

Little is known regarding the influence on the aggressive properties of a substance of the introduction of a sulphur atom. In the particular case of the derivatives of dichloroethyl sulphide, it has been observed that an increase in the number of sulphur atoms in the molecule does not notably diminish the vesicatory

properties. Dichloroethyl disulphide, *e.g.*, $\begin{array}{c} \text{S}-\text{CH}_2-\text{CH}_2\text{Cl} \\ | \\ \text{S}-\text{CH}_2-\text{CH}_2\text{Cl} \end{array}$ has a vesicatory power only one-third less than that of dichloroethyl sulphide.¹

3. Influence of the Arsenic Atom

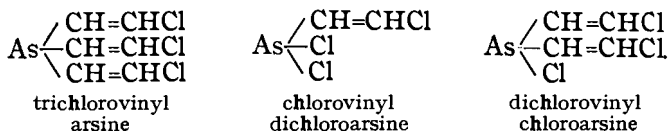
The arsenic atom also imparts toxic properties to a higher degree than the sulphur atom. It is a general rule that substances containing a trivalent arsenic atom have a considerably greater

¹ BENNETT, *J. Chem. Soc.*, 1921, 119, 418.

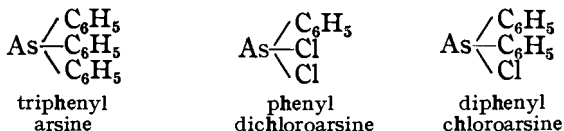
physiopathological action than those containing a pentavalent arsenic atom.

The arsenical war gases contain halogen atoms or organic radicles such as —CN, —SCN, etc., besides the arsenic atom. The nature of the aggressive action depends on the number and the nature of the organic radicles with which the arsenic atom is linked.

In general, arsenical compounds have an aggressive action when two of the three valences of the arsenic atom are linked to like atoms or groups and the third to a different atom or radicle. If all the three valences of the arsenic atom are linked to similar atoms or radicles the compound has practically no aggressive action. Thus in the series of chlorovinyl arsines, it has been found that trichlorovinyl arsine has practically no aggressive action compared with chlorovinylchloroarsine or dichlorovinyl chloroarsine :



In the series of aromatic arsines there is a great difference in aggressive action between triphenyl arsine, phenyl dichloroarsine and diphenyl chloroarsine.



In particular it may be observed that :

(a) When the arsenic atom is linked to an unsaturated radicle, the substance has a predominantly vesicatory action, as in the vinyl chloroarsines, the styryl chloroarsines, etc. This physiopathological action decreases with increase in the number of organic radicles linked to the arsenic atom. Thus, substances with a single organic radicle have a more powerful vesicatory action than those with two or more organic radicles. A typical example of this observation is found in the chlorovinyl arsine series, for chlorovinyl dichloroarsine has a greater vesicatory action than dichlorovinyl chloroarsine.

(b) When the arsenic atom is linked to an alkyl or phenyl group, substances with a predominantly irritant action are obtained. This physiopathological action is accentuated in

compounds containing two such radicles linked to the arsenic atom :

$(C_6H_5)_2AsCl$ Diphenyl chloroarsine : Limit of insupportability,
1 mgm./cu. m.

$C_6H_5AsCl_2$ Phenyl dichloroarsine : Limit of insupportability,
16 mgm./cu. m.

and in compounds containing the phenyl radicle rather than an alkyl radicle :

$C_6H_5AsCl_2$ Phenyl dichloroarsine : Limit of insupportability,
16 mgm./cu. m.

CH_3AsCl_2 Methyl dichloroarsine : Limit of insupportability,
25 mgm./cu. m.

(c) Arsenic compounds containing ethyl radicles are more toxic than the corresponding compounds containing methyl radicles. Thus the derivatives of ethyl arsine (the oxide, chloride, etc.) have a greater toxic action than the corresponding compounds of methyl arsine :

$C_2H_5AsCl_2$ Ethyl dichloroarsine : Limit of insupportability,
10 mgm./cu. m.

CH_3AsCl_2 Methyl dichloroarsine : Limit of insupportability,
25 mgm./cu. m.

(d) The substitution of the phenyl radicle by one of its higher homologues reduces the aggressive action of the resulting compound. For example, ditolyl chloroarsine is less irritant in its action than diphenyl chloroarsine.

The presence of halogen atoms in the molecules of organic arsenicals usually confers irritant properties. Among these halogen compounds, those containing chlorine have a superior irritant power to the analogous bromine and iodine compounds, *e.g.*, diphenyl chloroarsine has a greater irritant power than diphenyl iodoarsine.

An increase in toxic power is also found in organic compounds whose molecules contain a cyanide radicle ; thus diphenyl cyanoarsine is more irritant than diphenyl chloroarsine :

$(C_6H_5)_2AsCN$ Limit of insupportability, 0.25 mgm./cu. m.

$(C_6H_5)_2AsCl$ „ „ I „

4. Influence of the Nitro Group

The aggressive properties conferred on a substance by the introduction of the $-NO_2$ group depend on whether the group combines through an oxygen or a carbon atom, that is, whether

a nitrate or a nitro compound is produced. The nitrates have not been used as war gases, but very efficient agents are included among the nitro derivatives, *e.g.*, trichloro nitromethane (chloropicrin), tribromo nitromethane, etc.

In particular the introduction of the NO₂ group confers lachrymatory properties or increases any such tendency if it is originally present in the molecule.

Typical examples of this are found among the nitro derivatives of the benzene halides: *o*-nitro benzyl chloride has a much more powerful lachrymatory action than benzyl chloride or than the corresponding bromide or iodide.

C ₆ H ₅ CH ₂ Cl	Benzyl chloride: Lower limit of irritation, 77 mgm./cu. m.
C ₆ H ₅ CH ₂ Br	Benzyl bromide: Lower limit of irritation, 4 mgm./cu. m.
C ₆ H ₄ (NO ₂)CH ₂ Cl	<i>o</i> -Nitro benzyl chloride: Lower limit of irritation, 1.8 mgm./cu. m.

With an increase in the number of NO₂ groups the augmentation of the lachrymatory properties is sometimes found to be very great. Such is the case with tetrachloro dinitroethane, which is eight times as powerful a lachrymator as trichloro nitromethane.

According to Nekrassov, and Hackmann,¹ the introduction of the NO₂ group into the molecule of an aromatic compound confers vesicatory properties, or increases any which the substance already possesses.

The influence of the NOH group on the toxic properties of substances has only recently been studied, derivatives of carbonyl chloride such as dichloro- and dibromo-formoxime being examined. It seems that the NOH group causes accentuation of aggressive properties, in particular conferring "orticant" action (*i.e.*, causing skin irritation).

5. Influence of the —CN Group

To the CN group two different structures are attributed: one, —C≡N, the nitrile, the other —N = C, the isonitrile grouping. It has been observed that compounds containing the isonitrile group have more powerful toxic properties than those containing the nitrile. This difference in biological properties can be compared with the greater facility with which compounds containing the isonitrile radicle liberate hydrocyanic acid.

The presence of a second CN group generally diminishes the aggressive properties of a substance, and the presence in the

¹ NEKRASSOV, *Khimija Otravljajuscik Vescestv*, Leningrad, 1929; and HACKMANN, *Chem. Weekblad*, 1934, **31**, 366.

same molecule of the $-\text{CN}$ group and of other atoms such as halogens, while reducing the toxic action of the substance, confers highly lachrymatory properties. For example, cyanogen bromide and iodide are much less toxic than hydrocyanic acid but are powerful lachrymators. The same rule applies in the case of such aromatic derivatives as bromobenzyl cyanide, chlorobenzyl cyanide, etc.

6. Influence of Molecular Structure

According to various observations, the aggressive action of a substance depends not only on the presence of particular atoms or radicles in the molecule, but also on the molecular structure, and in particular on

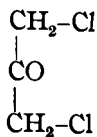
- (a) The presence of unsaturated bonds, and
- (b) The molecular symmetry.

Influence of Unsaturated Bonds. The presence of unsaturated bonds in the molecule usually involves an increase in the physiopathological properties. This observation was made by Loew in 1893.

Among the war gases various examples occur of the influence of the unsaturated bond. Thus, acrolein $\text{CH}_2 = \text{CH}-\text{CHO}$, has strongly irritant properties, while the corresponding saturated aldehyde, propionaldehyde, $\text{CH}_3-\text{CH}_2-\text{CHO}$ is innocuous. Similarly, β chlorovinyl dichloroarsine, $\text{Cl}-\text{CH} = \text{CH}-\text{AsCl}_2$, is a powerful vesicant, while the corresponding saturated compound, β chloroethyl dichloroarsine, $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{AsCl}_2$, has only weak vesicatory properties.¹

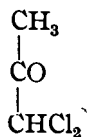
Other examples may be found among the mono- and di-halogenated acetylenes, such as diiodo- and dibromo-acetylene, $\text{Cl}_2 = \text{C}$ and $\text{CBr}_2 = \text{C}$, which have more interesting physiopathological properties than the halogenated paraffin hydrocarbons.

Influence of Molecular Symmetry. The spatial arrangement of the functional groups in a molecule has a definite influence on the degree of its toxicity. It has been observed that substances with symmetrical molecules generally have a more powerful aggressive action than asymmetrical substances. Thus, symmetrical-dichloroacetone,



¹ FERRAROLO, *Minerva Medica*, 1935, 27, II, 30.

has great irritant powers, while asymmetrical dichloroacetone



is almost completely lacking in irritant properties.

Another example occurs in the series of halogenated methyl ethers. When the halogens occupy a symmetrical position, as

in sym. dichloromethyl ether, $\text{O} \begin{array}{l} \text{CH}_2\text{-Cl} \\ \text{CH}_2\text{-Cl} \end{array}$ the substance has a

much more energetic lachrymatory action than that in which the chlorine atoms are asymmetrically placed, *i.e.*, in asym.

dichloromethyl ether $\text{O} \begin{array}{l} \text{CH}_3 \\ \text{CH-Cl}_2 \end{array}$.

7. Theories of General Nature

General theories concerning the relation between chemical structure and physiopathological action have been elaborated with especial reference to the war gases. From among the many published, an account is given here of two : Meyer's Theory and the "Toxophor-Auxotox" Theory.

Meyer's Theory. According to this theory,¹ the physiopathological action of war gases is attributed to certain atoms or radicles which have a tendency to react easily with other substances by addition. This classification on the basis of their ease of reaction should be determined by their combination with the various biological entities or tissues (as the blood, the nerve cells, the respiratory epithelia, etc.) which undergo specific and characteristic alterations.

To one group belong, for example, the halogen atoms, as the chlorine in phosgene, cyanogen chloride and the chlorovinyl chloroarsines ; the bromine in ethyl bromoacetate, cyanogen bromide, etc. These atoms are linked in a very labile manner to the remainder of the molecule and react easily with water and other substances. Also the oxygen atom is highly reactive when in the vicinity of a halogen in the halogenated aldehydes, esters and ethers, such as dichloromethyl ether, trichloromethyl chloroformate, etc.

The radicles which react most easily are the NO_2 — group in *o*-nitro benzyl chloride and bromide, the CO — group in the

¹ J. MEYER, *Der Gaskampf u. die chemischen Kampfstoffe*, Leipzig, 1926, 90.

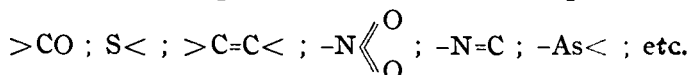
halogenated ketones and the CN— group in bromobenzyl cyanide and diphenyl cyanoarsine, etc. All these radicles, which are notable for their reactivity with water or other substances, confer a certain degree of toxicity by their presence in the molecule. However, on considering the structure of the molecules of the war gases, it is seen that while some of these contain atoms or radicles of great reactivity, others are distinguished by an unusual resistance to chemical reagents yet possess a high degree of aggressiveness.

In such cases, Meyer suggests, the aggressive action may be attributed to the capacity of the entire molecule of forming additive compounds with vital constituents of the organism.

Toxophor-Auxotox Theory. The theory of toxophors and auxotoxes, first elaborated by Ehrlich¹ for toxic substances and later applied by Nekrassov² to the war gases, attributes the physiopathological properties of these substances to special atoms or radicles in a similar manner to Witt's theory regarding the colour of organic substances.

Witt's theory of coloured substances may be summarised as follows: the presence of colour in a substance depends on the presence of certain atomic groupings called "chromophores." For instance, the —N = N— group characteristic of the azoic colours, the —NO₂ group, the = C = O group, etc. It is to the presence of these groups that the more or less intense colouration of a compound is due. But in order that a coloured substance may be capable of being fixed on animal or vegetable fibres, it must have in the molecule not only chromophoric groups, but also contain other groups, called "auxochromes" which give it the capability of combining intimately with the fibre. Typical auxochromic groups are: NH₂, OH, etc.

The war gases, according to Nekrassov, have structures analogous to those of coloured substances. By examining the chemical structures of the war gases, certain atomic groups are found which confer on substances the potentiality of becoming war gases, in the same way as Witt found certain groupings common to coloured substances. The groupings found in war gases are called "toxophors." Such are, for example:



There also exist other groups capable of communicating the characteristic toxic functions of the toxophoric group, that is, of

¹ P. EHRLICH, *Deut. med. Wochschr.*, 1898, 1052.

² NEKRASSOV, *Khimiya Otravliajuscikh Vescestv*, Leningrad, 1929, 30

transforming into actuality the latent capacity of the toxophor group. These groups are named "auxotoxes," and may be either :

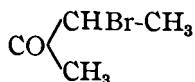
atoms : halogens, oxygen, etc.

or

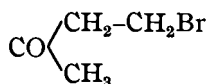
atomic groups : $-\text{NH}_2$, benzyl, phenyl, methyl, ethyl radicles, etc.

With the aid of this theory it is explained that just as in coloured substances the introduction of some auxochromic groups changes the colour of the substances, so in the war gases the presence of certain autotoxes can alter the type of biological action. Thus, for example, halogen introduced into the hydrocyanic acid molecule reduces the toxicity of the toxophor, $-\text{CN}$, and confers on the product lachrymatory properties.

Also, the auxotoxic groups in the war gases, like the auxochromes in coloured substances, differ in their effect according to their positions in the molecules. Thus the halogens differ in their influence according to whether they are in a methyl or an ethyl group, at the end or the beginning of a side-chain. It is easily seen that a halogen atom distant from the end of a side-chain has little influence on the aggressive power.



α bromoethyl methyl ketone is less lachrymatory in action than



β bromoethyl methyl ketone.

Similarly, $\alpha\alpha'$ dichloroethyl sulphide $\text{S} \begin{cases} \text{CHCl-CH}_3 \\ \text{CHCl-CH}_3 \end{cases}$ has only slight aggressive power, while $\beta\beta'$ dichloroethyl sulphide (mustard gas) $\text{S} \begin{cases} \text{CH}_2\text{-CH}_2\text{Cl} \\ \text{CH}_2\text{-CH}_2\text{Cl} \end{cases}$ has an aggressive action which is well known.

However, Nekrassov's theory cannot be applied so generally to the war gases as Witt's to coloured substances.

In some cases there are actually strongly marked differences. Thus in the coloured substances the auxochrome group brings out the latent colour-potentiality of the chromophore group and so makes colouration possible, while in the war gases the auxotox group merely develops the characteristic property of the toxophor

group. On the other hand, the merest glance at the chemical structures of the war gases will show that the auxo group may function either positively or negatively. That is, on its presence depends the increase or the decrease, or sometimes even the destruction of the toxicity of the substance (*e.g.*, the introduction of alcoholic, sulphonic groups, etc.).

In coloured substances, increase in molecular complexity leads not to a decrease of the colour, but to its strengthening, while it is observed that an increase in the number of toxophors or auxotoxes in the molecule does not increase the toxicity. Typical is the case of $\beta\beta'$ dichloroethyl sulphide in which the introduction of more chlorine atoms into the molecule produces the tetra- and hexachloro- compounds whose aggressive action is practically nil.

Furthermore, this theory, like that of Meyer already described, though having many interesting aspects, does not sufficiently explain the behaviour of some of the war gases.

Many gaps still exist in this field of study. The many discussions and the various theories put forward show merely the efforts which have been made to solve this important problem.

It must be concluded that only after a long series of studies and experiments will it be possible to enunciate general and precise laws on the relation between chemical constitution and the aggressive action of the war gases. These laws, besides supplying a profound knowledge of the science of war gases, will be invaluable in preparing new substances of greater value in warfare.

CHAPTER III

CLASSIFICATION OF THE WAR GASES

THE classification of the war gases is particularly difficult because of the many aspects which these substances, some similar to one another, some completely different, present. The number of methods of classification which have been proposed are an indication of this difficulty.

Without entering into unnecessary detail, a few of the more important classifications in use at present will be given, with especial emphasis on the chemical nature of the gases.

1. Physical Classification

The physical classification of the war gases has often been proposed by taking as criterion either their state of aggregation, or their boiling point.

The method of classification most used to-day is based on their state of aggregation at ordinary temperatures. According to this classification the war gases are divided as follows into three groups :

Gaseous. Chlorine, phosgene, etc.

Liquid. Bromine, chloropicrin, dichloroethyl sulphide (mustard gas), etc.

Solid. Diphenyl chloroarsine, diphenyl cyanoarsine, chloroacetophenone, etc.

This classification is altogether too crude, uniting in one and the same group very varied substances which have only a single quality in common—one which is not generally considered to be the most important. Moreover, the one criterion of the classification is influenced by temperature, so that by normal temperature changes of the air a substance may pass from one group to the other, for example, dichloroethyl sulphide from liquid to solid, phosgene from gas to liquid.

2. Tactical Classification

This classification is based on the criterion of the tactical employment of the war gases. From this view-point they are divided into two groups :

Non-persistent Gases. Including substances which diffuse into the air in a short time, losing some of their toxic concentration : chlorine, phosgene, hydrocyanic acid, etc.

Persistent Gases. Including substances which vaporise only slowly and remain on the ground for long periods in the liquid or solid state, still retaining their aggressive power : dichloroethyl sulphide, etc.

This classification also lacks neatness and precision, for the place of some substances in it is doubtful. It is proposed nowadays to add a third intermediate group, to include substances whose vapour tension lies between the gases of the first group and those of the second. This third group has been termed that of the "*Semi-persistent Gases.*"

Another tactical classification which may be mentioned is one largely employed in text-books on chemical warfare and was in use in Germany during the war. In this classification the gases are divided into the following four classes :

Green Cross Gases. This includes substances with a high vapour tension and great toxic power on the respiratory tract : phosgene, trichloromethyl chloroformate (diphosgene), chloropicrin, etc.

Yellow Cross Gases. This includes substances with a low vapour tension and high toxic and vesicatory power : dichloroethyl sulphide (mustard gas), chlorovinyl dichloroarsine (lewisite), etc.

Blue Cross Gases. This includes solid substances with low volatility and great irritant power : diphenyl chloroarsine, diphenyl cyanoarsine, etc.

White Cross Gases. This includes the powerful lachrymators : bromoacetone, chloroacetophenone, etc.

3. Physiopathological Classification

This classification is based on the most characteristic action of each war gas on the living organism. Various classifications have been made on this basis (German, English, American, etc.). The usual method is to divide the gases into the following classes :

(A) THE TOXIC SUFFOCANTS (OR LUNG IRRITANTS). These include those gases which act principally on the respiratory tract : chlorine, phosgene, chloropicrin, etc.

(B) THE VESICANTS. These include those substances whose characteristic action is to produce blisters on the skin : dichloroethyl sulphide, chlorovinyl dichloroarsine, etc.

(C) THE IRRITANTS. These include substances having lachryma-

tory power: benzyl chloride and bromide, and those causing sneezing (the sternutatories): diphenyl chloroarsine, etc.

(D) THE TOXIC GASES. These include those gases acting particularly on the blood, as carbon monoxide, or on the nervous system, like hydrocyanic acid, etc.

The physiopathological classification of the war gases, though used very widely, is even less exact than the others mentioned. In point of fact the biological action of these substances is extremely complex and in certain concentrations a gas may change its action to that of another group.

In order to classify these substances accurately on this basis the new tendency to-day is to regroup them according to the actual mechanism of their action on the human organism. In this, however, there is still so much work to be done that with regard to a great many substances practically nothing is known.

4. Chemical Classification

Classification of the war gases according to the characteristic chemical groups in their molecules has been almost completely neglected. It is only by taking the chemical characteristics of the substances as the sole criterion that it will be possible to elaborate a precise and complete classification of the war gases, and these chemical characteristics must be quite definite both as to the nature and the number of atoms in the molecule.

The first attempts at a chemical classification of the war gases were those of Chugaev¹ in 1918 and of Zitovic.² These classifications are, however, merely schematic and are particularly lacking in precise and distinctive characteristics.

Later, other chemical classifications were proposed, and two of these will be outlined here—that of Jankovsky and that of Engel.

(a) *Jankovsky's Classification.* In 1925 Jankovsky³ proposed a completely new classification, founding it on a study, then in its infancy, of the relationship between the chemical constitution and the aggressive action of the war gases. It was based on the theory of toxophoric and auxotoxic groups which has been described in the preceding chapter. In this classification the war gases are grouped according to the toxophoric group present in their molecules, being divided in this way into the following six classes:

¹ CHUGAEV, *Khimiceski Osmovi gas i protivogas diela*, 1918.

² ZITOVIC, *Khimiceskaja Promiscelnost*, 1924, **11**, 295.

³ JANKOVSKY, *Voina i Tecnica*, 1925, nn. **220-221**, 23.

CLASS I

Toxophoric Group. Chlorine, bromine, iodine, etc.

Auxotoxic Group. Phenyl, benzyl, etc.

Includes :	Benzyl chloride	$C_6H_5-CH_2Cl$
	Benzyl bromide	$C_6H_5-CH_2Br$
	Benzyl iodide	$C_6H_5-CH_2I$
	<i>o</i> -Nitrobenzyl chloride	$C_6H_4-(NO_2)CH_2Cl$
	Dichloromethyl ether	$ClCH_2-O-CH_2Cl$
	Dibromomethyl ether	$BrCH_2-O-CH_2Br$

CLASS II

Group. Unsaturated oxides.

Includes :	Carbon monoxide	CO
	Sulphur dioxide	SO ₂
	Nitrogen oxides	NO ; NO ₂ ; N ₂ O ₃

CLASS III

Toxophoric Group. CO.

Auxotoxic Group. Halogens, or double bonds.

Includes :	Chloroacetone	$CH_3-CO-CH_2Cl$
	Bromoacetone	$CH_3-CO-CH_2Br$
	Bromomethyl ethyl ketone	$C_2H_5-CO-CH_2Br$
	Chloroacetophenone	$C_6H_5-CO-CH_2Cl$
	Ethyl chloroacetate	$ClCH_2-COO-C_2H_5$
	Phosgene	COCl ₂
	Acrolein	$CH_2=CH-CHO$

CLASS IV

Toxophoric Group. S ; S = O ; O = S = O.

Auxotoxic Group. Halogens, methyl, etc.

Includes :	Perchloromethyl mercaptan	CCl_3-S-Cl
	Dichloroethyl sulphide	$S(CH_2-CH_2-Cl)_2$
	Dibromoethyl sulphide	$S(CH_2-CH_2-Br)_2$
	Sulphoxides	O=SR ₂
	Sulphones	O=SR ₂ =O
	Esters of sulphuric acid	O=S(OR) ₂ =O

CLASS V

Toxophoric Group. —C≡N ; —N = C ; —NO₂.

Auxotoxic Group. Halogens, benzyl, etc.

Includes :	Hydrocyanic acid	HCN
	Cyanogen chloride	CNCl
	Bromobenzyl cyanide	$C_6H_5-CH(CN)Br$
	Chloropicrin	CCl_3-NO_2
	Tetrachloro dinitroethane	$(CCl_2-NO_2)_2$

CLASS VI

Toxophoric Group. —As =.

Auxotoxic Group. Methyl, ethyl, vinyl, phenyl.

Includes :	Methyl dichloroarsine	CH_3AsCl_2
	Ethyl dichloroarsine	$C_2H_5AsCl_2$
	Diphenyl chloroarsine	$(C_6H_5)_2AsCl$
	Diphenyl cyanoarsine	$(C_6H_5)_2AsCN$
	Phenarsazine chloride	$NH(C_6H_4)_2AsCl$

TABLE XII

GROUP								
Series	1	2	3	4	5	6	7	8
	Hydrocarbons	Alcohols	Ethers	Aldehydes and Ketones	Acids	Esters	Amines	Arsines
I	CCl_2NO_2 Chloropicrin		$\begin{array}{l} \text{CH}_2\text{Cl} \\ \diagdown \text{O} \diagup \\ \text{CH}_2\text{Cl} \end{array}$ Dichloromethyl ether		COCl_2 Phosgene \angle	$\text{Cl}-\text{COOCCl}_3$ Diphosgene \times		$\text{CH}_3-\text{AsCl}_2$ Methyl dichloroarsine \cdot
II			$\begin{array}{l} \text{CH}_2\text{CH}_2\text{Cl} \\ \diagdown \text{S} \diagup \\ \text{CH}_2\text{CH}_2\text{Cl} \end{array}$ Dichloroethyl sulphide			$\text{CH}_2\text{Br}-\text{COOC}_2\text{H}_5$ Ethyl bromoacetate		$\text{C}_2\text{H}_5-\text{AsCl}_2$ Ethyl dichloroarsine \times
III				$\begin{array}{l} \text{CH}_2\text{Br} \\ \diagdown \text{CO} \diagup \\ \text{CH}_3 \end{array}$ Bromoacetone				
IV	$\text{C}_6\text{H}_5-\text{CH}_2\text{Br}$ Benzyl bromide			$\begin{array}{l} \text{CH}_2\text{Cl} \\ \diagdown \text{CO} \diagup \\ \text{C}_6\text{H}_5 \end{array}$ Chloroacetophenone			$\text{C}_6\text{H}_5\text{N} = \text{CCl}_2$ Phenyl carbylamine chloride	$(\text{C}_6\text{H}_5)_2\text{AsCl}$ Diphenyl chloroarsine \times

(b) *Engel's Classification.* Another chemical classification of war gases is that proposed recently by Engel.¹ It is an improved version of that published by him in 1928,² and divides the war gases into eight groups (see Table XII). These correspond to eight of the simplest organic types of compounds, arranged according to their differing oxygen-content: hydrocarbons, alcohols, ethers, aldehydes and ketones, acids, esters, amines, arsines. The two last types—the amines and the arsines—may be considered as hydrocarbons in which a hydrogen atom is substituted by an NH_2 group or an AsH_2 group respectively.

Each of these groups of substances may be sub-divided into four series: The first three of these comprise the aliphatic compounds derived from methane (series I), ethane (series II) and propane (series III). The fourth series comprises the aromatic compounds derived from benzene and its homologues.

All the war gases have not been included in Table XII, but only the most important. Those not included may be easily classified into their proper groups. Acrolein, for instance, in the aldehyde group, lewisite and diphenyl cyanoarsine in that of the arsines, methyl cyanofornate and methyl chlorofornate in that of the esters.

According to Engel this classification allows for the allocation of gases which have never yet been employed in warfare. Stibine and phosphine, for example, may be considered as arsines in which the arsenic atom has been substituted by that of antimony or phosphorus; similarly dichloroethyl selenide and telluride may be considered as ethers in which the oxygen atom has been replaced by that of selenium or tellurium.

This and other classifications of war gases will not be considered further.

It is possible to arrange the war gases in the chronological order in which they were first used in the war of 1914–18. This is the order employed in Table XIV at the end of this book, where the physical, chemical and physiopathological properties of the principal war gases are summarised. In the text, however, it is considered more convenient to catalogue them according to chemical relationships and similarity of structure.

¹ ENGEL, *Gasschutz und Luftschutz*, 1935, 239.

² ENGEL, *Z. ges. Scheiss.-Sprengstoffw.*, 1928, **23**, 321.

PART II

CHAPTER IV

THE HALOGENS

1. Chlorine. Cl_2 .

(M.Wt.70.9)

CHLORINE may be considered as the only substance which has been used in the elementary state as a war gas.

Its asphyxiating properties have been recognised ever since it was discovered in 1774 by Karl Wilhelm Scheele.

Its use in war was due to its conforming to the principles of gas warfare: its ease of production, its low cost and also its high specific gravity, an important characteristic in the forcing of gases by the wind into the zone to be gassed. It is more useful than other agents for employment in wave-attacks. Later it lost much of its offensive importance, especially when very simple defensive means were found against it and when the method of wave-attack was replaced by the use of gas projectiles. However, this element still retains much interest as it forms the most important raw material for the preparation of other war gases.

As the various methods of preparing this element are generally known and will be found in the inorganic chemistry text-books, it is considered unnecessary to spend time describing them here. Those physical and chemical properties which have considerable interest in chemical warfare will be considered instead.

PHYSICAL AND CHEMICAL PROPERTIES

Chlorine is a yellowish-green gas with an irritating and characteristic odour.

Under normal conditions of temperature and pressure (0°C . and 760 mm.) a litre of chlorine weighs 3.22 gm.,¹ and its density compared with that of air is therefore 2.49 (= 3.22 : 1.293). Because of this high density a cloud of chlorine rises slowly,

¹ At other temperatures and pressures, the weight of a litre of chlorine varies according to the Boyle-Gay-Lussac law. From the following formula the weight of 1 litre of any gas may be calculated at temperature t and pressure h , from a knowledge of the value at 0°C . and 760 mm.:

$$\text{gr. } \begin{matrix} t \& h \end{matrix} = \text{gr. } \begin{matrix} 0^\circ \& 760 \end{matrix} \times \frac{h \times 273}{760 (273 + t)}$$

clinging to the earth until an air current blows it away or dilutes it.

Chlorine is fairly easily liquefiable ; at ordinary temperatures it can be liquefied by a pressure of 6–8 atmospheres, while at normal pressure it liquefies at -40°C .

The critical temperature of chlorine, *i.e.*, the temperature above which it cannot be liquefied whatever pressure is applied, is 146°C . The critical pressure, *i.e.*, the pressure necessary to liquefy chlorine at the critical temperature, is 93.5 atmospheres.

Liquid chlorine is green with a tinge of yellow and is very mobile. It boils at ordinary pressure at -33.6°C . The value of the vapour tension of liquid chlorine at different temperatures is given in the following table :

TEMPERATURE $^{\circ}\text{C}$.	VAPOUR TENSION ATMOSPHERES
— 20	1.8
— 10	2.63
0	3.66
10	4.95
20	6.62
30	8.75
40	11.5
100	41.7

From this table it is seen that the pressure in a cylinder of liquid chlorine at 20°C . is 6.62 atmospheres.

Liquid chlorine has a somewhat high coefficient of expansion : at 0°C . it is 0.00187 ; at 20°C ., 0.00212, and at 50°C ., 0.00259.

From this it may be calculated that while 1 kg. of liquid chlorine at -35°C . occupies 641.5 ml., at 60°C . it has a volume of 782 ml., that is, it increases 21.9% in volume.

The specific gravity of liquid chlorine at various temperatures is as follows :

TEMPERATURE $^{\circ}\text{C}$.	S.G.
— 35	1.5589
0	1.4685
20	1.4108
30	1.3799
60	1.2789

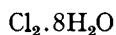
One litre of liquid chlorine gives 463.8 litres of gaseous chlorine at 0°C . and 760 mm. The latent heat of vaporisation of liquid chlorine at 0°C . is 62.7 calories.

Chlorine on cooling to -102° C. solidifies to a yellow crystalline solid.

It is soluble in water ; at 760 mm. and the temperature stated, 1 litre of water dissolves the following quantities of chlorine ¹ :

TEMPERATURE ° C.	ML. CHLORINE AT 0° AND 760 MM.	GM. CHLORINE
10	3,095	9.97
15	2,635	8.48
20	2,260	7.27
25	1,985	6.39
30	1,769	5.69

The solution obtained has a yellowish-green colour and is termed chlorine water. By cooling this solution to -8° C. a crystalline hydrate of the following composition



separates ; on heating, it again decomposes.

Chlorine also dissolves easily in carbon tetrachloride (at 13° C. to the extent of 10% by weight), in sulphuryl chloride, in tetrachloroethane and in pentachloroethane.²

Chemically, chlorine is one of the most active elements and combines directly with almost all simple bodies.

It combines with hydrogen under the influence of light and heat, and reacts energetically with most of the non-metals forming the respective chlorides. By this method arsenic trichloride may be prepared and this is employed in the preparation of the chlorovinyl arsines (Perkins's method) and diphenyl chloroarsine (Michaelis's method). Sulphur chloride is prepared similarly, and this is employed in the preparation of dichloroethyl sulphide by Guthrie's method.

Chlorine combines also with almost all metals. Potassium placed in chlorine gas inflames with evolution of heat. Mercury combines at ordinary temperature. Chlorine has no action on other metals if it is perfectly dry, but reacts vigorously in the presence of moisture or on heating with sodium, calcium, magnesium, aluminium and tin (especially if finely divided), but only slowly with silver, gold and platinum. Among these compounds of chlorine with metals, aluminium trichloride is

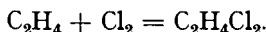
¹ L. WINKLER, *Die Chemische Analyse*, Vol. XXXV. (*Ausgewählte Untersuchungsverfahren für das chemische Laboratorium*), Part II, 1936, p. 27.

² PERKINS, *J. Chem. Soc.*, 1894, 65, 20.

important for its use in the syntheses, in industry as well as in the laboratory, of many substances of application in war, as chloroacetophenone, the chlorovinyl arsines, etc.

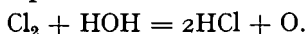
Chlorine can also combine directly with certain compounds, such as the addition to sulphur dioxide and to carbon monoxide to form sulphuryl chloride and carbonyl chloride (phosgene) respectively. The latter has wide application as a war gas.

Other additive reactions take place with the unsaturated hydrocarbons, such as that with ethylene to form ethylene dichloride :



Chlorine does not usually react in this manner however. More frequently the mode of reaction is of a different type. Thus with binary hydrogen compounds it reacts combining with the hydrogen and freeing the other element. For example, bromine and iodine are respectively liberated from hydrobromic and hydriodic acids.

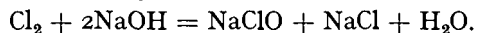
Water is also decomposed with liberation of oxygen :



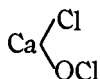
This reaction is reversible and arrives at a state of equilibrium. In this condition decomposition is very slow, becoming almost instantaneous, however, in the presence of easily oxidisable bodies.

Chlorine reacts similarly with a large number of metallic oxides, forming the metal chloride and evolving oxygen. In presence of water and of soluble metallic oxides, oxygen is not formed, but unites with the chlorine to form salts of the oxygenated acids of chlorine (hypochlorites or chlorates).

If chlorine is bubbled through a cold, dilute solution of an alkali hydroxide, chloride and hypochlorite are formed, as, for example, with sodium hydroxide :



This mixture is known as "*Labarraque Water*." The corresponding product obtained from potash is "*Javel Water*." With lime, however, there results a compound to which the following formula is generally given :



which is the familiar "chloride of lime." This compound is somewhat unstable and has an oxidising and chlorinating action. Because of this property, chloride of lime is used as a disinfectant, and especially for the destruction of several of the war gases.

Chlorine irritates the respiratory tract in a concentration¹ of 3.6 parts per million of air (= 10 mgm./cu. m.). The limit of insupportability, *i.e.*, the highest concentration which a normal man can breathe for 1 minute is 100 mgm. per cu. m. of air.² Haber's product of mortality, or lethal index, *i.e.*, the product of the concentration of chlorine in the inhaled air (expressed in mgm. per cu. m.) by the duration of its action (expressed in minutes) to cause the death of animals, is 7,500 for cats according to Flury,³ and 56,000 for dogs according to Prentiss.⁴

2. Bromine. Br₂. (M.Wt. 159.84)

In the war of 1914-18 this element had a very limited use as a war gas. It was only used together with chlorine in order to increase the persistence of the latter, but according to some authorities⁵ could be used alone if carried in special bombs.

Bromine was discovered in 1826 by Balard, who extracted it from saline mother-liquors. It has since been obtained also from the ash of algæ, but nowadays is obtained almost exclusively from the Stassfurt salt deposits and from saline mother-liquors.

PREPARATION

Only the more important methods of preparation of this element will be given. In the laboratory bromine may be

¹ *Method of Expressing Concentrations.* The following methods are in common use to express concentrations of gases and vapours in air :

(a) Parts by volume.

(b) Weight per volume of air.

The expression as parts by volume, that is, parts per cent., per thousand, per hundred thousand or per million, is employed particularly in toxicology. Though often convenient, it forms a true basis of comparison of the toxicity of substances only when these have approximately equal molecular weights.

Of more practical use for war gases is the expression of concentrations in weight of substance per unit volume of air, usually in mgm. per cu. m.

To convert mgm. per cu. m. to parts per million, the following formula may be used :

$$\frac{\text{mgm./cu. m.} \times 22.4}{M} = \text{ppm. (M = molecular weight)}$$

while to convert parts per million into mgm./cu. m., the following may be employed :

$$\frac{\text{ppm.} \times M}{22.4} = \text{mgm./cu. m.}$$

By means of Table XIII, at the end of this volume, values of concentrations in parts per million may be converted into mgm. per cu. m., and *vice versa*.

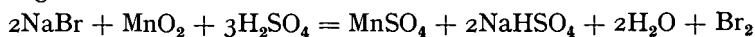
² U. MÜLLER, *Die Chemische Waffe*, Berlin, 1932, 57.

³ F. FLURY, *Z. ges. expt. Med.*, 1921, 13, and *Gasschutz und Luftschutz*, 1932, 149. The values for mortality-products reported by Flury are considered as minimum values.

⁴ PRENTISS, *Chemicals in War*, New York, 1937, 16.

⁵ CHLOPIN, *Grundlagen des Gasschutzes*. Extract in *Z. ges. Schiess-Sprengstoffw.*, 1927 and 1928.

prepared by heating sodium bromide with sulphuric acid and manganese dioxide :



But more usually it is preferable to purify commercial bromine for use. This is carried out by washing the bromine repeatedly with water,¹ then dissolving it in a concentrated solution of calcium bromide and reprecipitating it from this with excess of water. Bromine is thus obtained free from chlorine and may be dried over calcium bromide and oxide, shaken with phosphoric anhydride and then distilled in a current of carbon dioxide.

INDUSTRIAL MANUFACTURE

The bromine industry has grown considerably in recent years with the utilisation of that in the mother-liquors from the Stassfurt salts in Germany and of that in saline mother-liquors in America.

The method used in Germany (Pfeiffer process) is based essentially on the following :

The mother-liquors from washing the salts, in which bromine exists in the form of bromides, is sprayed in the form of a fine rain from the top of a tower filled with fragments of a refractory material, while into the bottom of the tower is led a current of chlorine and water vapour. By this means bromine is displaced from the bromide. The liquid which collects at the bottom of the tower is rich in bromine and passes into another vessel where it is distilled by means of superheated steam. The bromine which is vaporised passes from the top of the tower into a lead vessel where it is purified from the chlorine it contains by heating.

In America bromine is obtained by treating the saline mother-liquors with dilute sulphuric acid and then adding to the previously concentrated liquid, manganese dioxide and sulphuric acid. The mixture is then distilled, when the bromine passes over together with water and a little bromine chloride.

According to a recent American patent of the Dow Chemical Co. bromine is prepared by the electrolysis of saline mother-liquors ; by this means chlorine liberated in a nascent condition displaces the bromine which is recovered by a current of hot air.

PHYSICAL AND CHEMICAL PROPERTIES

Bromine is a heavy liquid of a dark red colour and an irritating and repugnant odour, from which it derives its name.

It boils at 59° C. and has a specific gravity of 3.18 at 0°. Its

¹ B. BRAUNER, *Monatsh.*, 1889, **10**, 411.

vapour also has a high specific gravity (about 5.5 times that of air) and is reddish-brown in colour.

The vapour tension of bromine varies with temperature as follows (Landolt) :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
0.13	62
4	77.3
20.6	172
30.6	378
45.6	487
59.5	768

From this table it will be seen that bromine has a high vapour pressure at ordinary temperatures.

On cooling to -7.3°C . it is converted into a crystalline mass of a lead-grey colour and a metallic glint. At 0°C . it forms a red crystalline hydrate with water of the formula $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ which on heating to 15° decomposes into bromine and water.

It is soluble in water ; the solubility at various temperatures is given in the following table (Dancer) :

TEMPERATURE ° C.	PARTS OF BROMINE IN 100 PARTS BROMINE WATER
5	3.600
10	3.327
15	3.226
20	3.208
25	3.167
30	3.126

A saturated solution of bromine in water has a yellow colour, an acid taste and irritates like bromine. In the air, particularly on heating, it loses bromine without becoming acid. In sunlight, however, hydrobromic acid is formed.

Bromine is soluble in alcohol, ether, chloroform and carbon disulphide, but alcoholic and ethereal solutions rapidly decompose. It dissolves more readily in aqueous solutions of hydrobromic acid, potassium bromide and hydrochloric acid. Solutions in the last may be obtained containing 13% bromine.

The latent heat of volatilisation of bromine at 58°C . is 45.6 calories.

The chemical properties of bromine are similar to those of chlorine, but it is less active. Thus, for example, in order to bring about the reaction with hydrogen it is not sufficient to expose the mixture to light, but it is also necessary to heat it.

With alkaline reagents it reacts in a similar manner to chlorine.

With non-metals of the fourth and fifth groups it reacts so vigorously that they inflame.

Bromine in a dry condition either reacts not at all or only partially with the common metals, though it attacks aluminium violently. Magnesium is the most resistant metal. Mercury reacts directly with bromine to form insoluble mercurous bromide. The presence of moisture always increases the corrosive action of this substance on metals.

Commercial bromine usually contains chlorine, iodine and some organic bromine compounds.

It has a vigorous toxic action on the organism and provokes irritation of the eyes. The fatal concentration is 220 mgm./cu. m. for 30–60 minutes' breathing.

Analysis of the Halogens

DETECTION OF CHLORINE

Chlorine may be simply recognised by means of its characteristic pungent odour. According to experiments carried out by Smolczyk,¹ chlorine can be detected by means of its odour at a dilution of 5 parts per million of air (= 14 mgm./cu. m. of air at 20° C.). Confirmation of the presence of chlorine by chemical methods may be carried out by one of the following reactions :

Flame Method. Detection of chlorine by this method is based on the reaction noticed by Beilstein,² according to which chlorine burnt at the base of a spiral of copper wire suspended in the flame of a spirit lamp produces volatile copper chloride which colours the flame a bright green.

The apparatus usually employed for this test consists of an ordinary spirit lamp or gas burner carrying in the flame a small copper spiral. The gaseous mixture to be tested is introduced into the base and interior of the flame, not merely at the spiral. In presence of chlorine a change of colour from bluish-violet to bright greenish-yellow is seen. The limit of sensitivity is 1 in 20,000.³

This reaction is given also by bromine and iodine, as well as by all substances containing halogen atoms in the molecule. The sensitivity in these cases depends only on the quantity of halogen present in the substance under test.

Decolorisation of Indigo Solution. By passing a gaseous

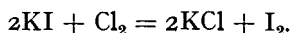
¹ SMOLCZYK, *Die Gas-maske*, 1930, 27.

² BEILSTEIN, *Ber.*, 1872, 5, 620.

³ LAMB, *J. Am. Chem. Soc.*, 1920, 42, 78.

mixture containing chlorine through a solution of indigo, the blue of the latter is discharged by the oxidation of the indigo to isatin.

Method with Potassium Iodide. Chlorine may also be detected by its property of liberating iodine from potassium iodide :

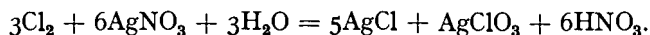


The iodine which separates may be recognised either by the reddish-violet colouration which it imparts to chloroform or to carbon disulphide, or by the blue colouration which is produced with starch solution. This latter reaction can be adapted in practice by employing starch-iodide paper,¹ which when exposed even for a short period to an atmosphere containing chlorine assumes a blue colour more or less intense according to the concentration of chlorine present. According to the experiments of Smolczyk² a content of 14 mgm. chlorine per cu. m. of air produces a change in the colour of starch-iodide paper within 3-5 seconds.

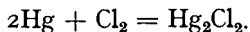
Aniline Method. Chlorine brought into contact with a solution of aniline hydrochloride produces a wine-red colouration which becomes blue.³ The aniline hydrochloride solution is prepared by dissolving 2 ml. aniline in 8 ml. hydrochloric acid and 40 ml. water.

Reactions of Chlorine Water. Chlorine in gas mixtures can also be detected by bubbling the gas to be tested through water ; chlorine water is formed and the presence of chlorine can be confirmed in this :

(a) With silver nitrate by the formation of a white precipitate of silver chloride :



(b) With metallic mercury by the formation of a grey precipitate of mercurous chloride :



This last reaction allows chlorine to be recognised in presence of hydrochloric acid or phosgene as these substances do not react with mercury.

¹ *Preparation of the Test Papers.* One part of starch is boiled with 100 parts of water and the solution filtered. To the filtrate 5 parts of potassium iodide are added and the strips of filter paper are immersed in this. They are then allowed to dry in the air and kept in a closed vessel. The period during which they may be stored depends upon the method by which they have been prepared and the care with which they have been stored. When the papers are prepared according to the instructions of Storm (*J. Ind. Eng. Chem.*, 1909, 1, 802, or *Chem. Zentr.*, 1910, 1, 1806) and stored in a glass-stoppered bottle they may be kept for 8 years.

² SMOLCZYK, *Die Gas-maske*, 1930, 29.

³ GANASSINI, *Boll. chim. farm.*, 1904, 43, 153.

DETECTION OF BROMINE

Bromine may be detected by the bluish-violet colour which it imparts to a paper impregnated with Schiff's reagent. This paper may be prepared by soaking a narrow strip of filter paper in an aqueous solution containing 0.025% fuchsine decolorised with sulphur dioxide, and allowing to dry.

The presence of bromine vapour may also be recognised by bubbling the gaseous mixture to be tested through water and testing the solution obtained by one of the following methods:

(a) Addition of a solution of potassium iodide and recognition of the iodine freed by means of starch paste.

(b) Addition of a solution of phenol, which in the presence of bromine produces a white or faintly yellowish flocculent precipitate of tribromophenol, $C_6H_2Br_3.OH$ (m.p. 93° to $94^\circ C.$). If the bromine is in excess, however, a whitish-yellow crystalline precipitate of tribromophenol bromide (m.p. 132° to $134^\circ C.$) is formed.¹

Finally, bromine may be recognised either by the red colouration which is produced with fluorescein, due to the formation of tetrabromofluorescein or eosin, or by the fluorescence produced by passing it through a dilute solution of resorufin in alkali carbonate. This reaction of bromine also forms the basis of a method of quantitative determination of the element in air.²

QUANTITATIVE DETERMINATION OF CHLORINE

The quantitative determination of chlorine may be carried out either by a volumetric or a gravimetric method.

Volumetric Method (Bunsen). This method depends on the determination of the quantity of iodine freed by chlorine when brought into contact with a solution of potassium iodide.

In proceeding to analyse a sample of gas, if the concentration of chlorine is not too great, it is advisable to draw the gas by means of a pump or an aspirator through an aqueous solution of potassium iodide³ contained in an ordinary bubble absorber large enough to ensure the complete reaction of the chlorine with the potassium iodide. If, however, the gas contains a large proportion of chlorine it is preferable to introduce it into a glass globe fitted with a tap and previously evacuated. The volume of this should be known. A solution of potassium iodide is then

¹ KOBERT, *Compendio di tossicologia pratica*, Milan, 1915, 146; BENEDICT, *Ann.*, 1879, 199, 127.

² H. EICHLER, *Z. anal. Chem.*, 1934, 99, 272.

³ In order to prepare this solution, 1 part by weight of potassium iodide (free from iodine) is dissolved in 10 parts of water. The solution should be colourless and remain so when a few drops of dilute sulphuric or hydrochloric acid are added.

introduced into the globe, which is allowed to stand. By this method one equivalent of chlorine sets free one equivalent of iodine, which remains dissolved in the excess potassium iodide. Then the amount of iodine in this solution is determined by the usual method of analysis with sodium thiosulphate.

$$\begin{aligned} 1 \text{ ml. } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 &= 0.00354 \text{ gm. Cl} \\ &= 1.1228 \text{ ml. gaseous chlorine} \end{aligned}$$

at 20° and 760 mm.

*Gravimetric Method.*¹ This method is based on the determination of the quantity of sulphuric acid formed by the action of chlorine on sodium thiosulphate.

In carrying out this analysis a measured quantity of the liquid in which chlorine is to be estimated is taken. It should contain no sulphuric acid. A slight excess of sodium thiosulphate is added and the whole warmed for a short time in a vessel closed with a tightly fitting stopper. The odour of chlorine completely disappears. A slight excess of hydrochloric acid is then added and the whole heated to boiling to decompose the excess thiosulphate. The liquid is then filtered and the sulphuric acid precipitated in the filtrate with barium chloride in the usual way.

For the rapid determination of the percentage of chlorine and carbon dioxide in air, the following method is recommended²:

Two 100-ml. burettes are filled with the gas to be examined; in one the chlorine is absorbed with a solution of potassium iodide and the iodine liberated is determined by titration with a decinormal solution of sodium thiosulphate; in the second burette both the chlorine and the carbon dioxide are absorbed by sodium hydroxide solution, and the difference in the diminutions of volume in the two burettes gives the volume of the carbon dioxide.

For the determination of chlorine in presence of phosgene see p. 88.

QUANTITATIVE DETERMINATION OF BROMINE

To determine bromine quantitatively in air a measured quantity of the gas to be examined is passed through 15–20 ml. of a freshly prepared potassium iodide solution (10%). By this means one equivalent weight of bromine liberates one equivalent weight of iodine, which may then be estimated by titration with a standard solution of sodium thiosulphate according to the method described above for chlorine.

$$1 \text{ ml. } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 = 0.00799 \text{ gm. bromine.}$$

¹ WICKE, *Ann.*, 1856, **99**, 99.

² OFFERHAUS, *Z. angew. Chem.*, 1903, **16**, 1033.

CHAPTER V

COMPOUNDS OF DIVALENT CARBON

CARBON, like several other elements, exhibits a variable valency in its compounds. Thus it is tetravalent in the greater number of organic compounds, trivalent in triphenylmethyl, and pentaphenylethyl, etc., and divalent in carbon monoxide, fulminic acid and its derivatives, in the halogenated compounds of acetylene, etc.

Substances containing a divalent carbon atom have in general the following properties :

(1) They react with halogens, hydrogen acids of the halogens, oxygen, etc., forming addition products.

(2) They have powerful and disagreeable odours (with the exception of carbon monoxide).

(3) They are toxic.

Among these substances, carbon monoxide merits special attention. According to some authorities it will play a great part in future warfare.

Several possible methods of using it are at present in the suggestion stage, but the methods suggested do not seem to have found practical application.¹

The method of applying carbon monoxide which was first thought of, was in the form of the metal carbonyls—iron-pentacarbonyl and nickel tetracarbonyl—which in the presence of catalysts such as the activated carbon used in anti-gas filters evolve carbon monoxide.

These compounds are unstable, however, and easily decompose, even by simple exposure to light. For this reason it does not seem that in practice it will be possible to obtain a sufficient concentration in the anti-gas filter of these substances to develop by contact with the activated carbon a dangerous concentration of carbon monoxide in the respirator.

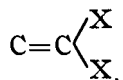
Another possible mode of using carbon monoxide which has been suggested is in the form of a solution in a suitable liquid. Carbon monoxide dissolves to a considerable extent in liquid gases such as ammonia and can be liberated from these solutions

¹ HANSLIAN, *Der chemische Krieg*, Berlin, 1937, Part I, 327.

by evaporation. Suitable solvents according to Hanne belong to the class of amines.¹

The last suggestion for applying carbon monoxide is in admixture with hydrocyanic acid. Such a mixture would be capable of passing through the anti-gas filters in actual use.²

Among the compounds containing divalent carbon atoms the acetylene mono- and di- halides may be mentioned. These have a certain interest from the point of view of the chemistry of the war gases. The following structural formula is given to these compounds³ :



The halogen derivatives of acetylene differ from the halogen derivatives of the paraffin series in being more toxic, and in being unstable and spontaneously inflammable. The instability and inflammability diminish considerably on passing from the chlorine to the bromine derivatives and are less still in the iodine derivatives.⁴

So far as the physiopathological properties have been studied it has been observed that the iodo- derivatives are more toxic than the bromo-compounds and are also more poisonous than hydrocyanic acid. The toxic action exhibited by substances of this class has been attributed to the presence of the divalent carbon atom which, as already mentioned, has a greater chemical affinity than tetravalent carbon.

In spite of the high toxicity, these compounds have not yet found application as war gases, above all because of their instability and the difficulty of preparing them on the industrial scale.

Compounds containing a divalent carbon atom united to a nitrogen atom are described in Chapter XIII.

1. Carbon Monoxide. CO. (M.Wt. 28)

Carbon monoxide was not employed during the war of 1914-18 as a war gas, but its toxic action has been established on several occasions in the field.

Carbon monoxide is formed whenever the combustion of carbon is incomplete, and from the military point of view is, in particular, developed during the deflagration of explosive

¹ HANNE, *Industrie Chimique*, 1935, **22**, 322.

² *Instructions sur la défense passive*, Lavauzelle, Paris, 1934.

³ J. LAWRIE, *J. Am. Chem. Soc.*, 1906, **36**, 487; INGOLD, *J. Chem. Soc.*, **1924**, 1528.

⁴ STRAUS and coll., *Ber.*, 1930, **63**, 1872.

substances both at the time of firing and on explosion of the projectile, also in the detonation of mines, etc.

The amount of carbon monoxide formed during these processes varies notably with the explosive substance, the density of the charge, the temperature, pressure, etc. The usually accepted data for explosives of different types are as follows :

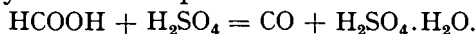
1 kg. black powder yields	279 litres gas at 0° C.
1 kg. nitroglycerine yields	713 " "
1 kg picric acid yields	828 " "
1 kg. guncotton yields	859 " "

In normal deflagration the following percentages of carbon monoxide are formed :

Black powder	. . .	about 10%
Powder B	. . .	" 33%
Dynamite	. . .	" 35%
Guncotton	. . .	" 40%
Trinitrotoluol	. . .	" 55%

LABORATORY PREPARATION

Carbon monoxide is usually prepared by the dehydration of formic acid by means of sulphuric acid ¹ :



Concentrated sulphuric acid is placed in a flask closed with a three-holed stopper. One of the holes carries a tap-funnel, another a thermometer and the third a gas delivery tube. The flask is heated to 100° C. and then industrial formic acid (about 98%) is allowed to flow in slowly while the temperature of the liquid is maintained at 100° C. From 175 gm. formic acid, 100 gm. carbon monoxide are obtained.

INDUSTRIAL MANUFACTURE

See the usual treatises on inorganic chemistry and the section " Phosgene " in the present volume (p. 62).

PHYSICAL AND CHEMICAL PROPERTIES

A colourless, odourless gas. B.p., -190° C. Critical temperature, -135.9° C. Critical pressure, 35.5 atmospheres. Density, 0.967.

It is only very slightly soluble in water : at 0° C., 1 litre of water dissolves 32 ml. ; at 20° C., 23 ml. It dissolves readily in alcohol and other organic solvents.

It is absorbed by aqueous ammonia and also by ammoniacal or hydrochloric acid solutions of cuprous salts.

¹ A. KLEMENC, *Die Behandlung und Reindarstellung von Gasen*, Leipzig, 1938, 122.

It burns with a violet flame. Mixtures of carbon monoxide and air in certain proportions are inflammable. The upper and lower explosive limits at room temperature are respectively 73·4% and 16·2% of CO.¹

The chemical behaviour of carbon monoxide depends on the presence of the divalent carbon atom in the molecule: the addition of oxygen to form carbon dioxide, the addition of chlorine to form phosgene, etc.

By heating under pressure with sodium hydroxide sodium formate is produced :



Highly reducing metals like aluminium and (powdered) magnesium react on heating with carbon monoxide, forming the corresponding oxide and freeing carbon.

Some metals, as nickel, iron and cobalt, form additive compounds of the formulæ $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Co}(\text{CO})_4$.

Platinum chloride forms several additive compounds with carbon monoxide: $\text{PtCl}_2 \cdot \text{CO}$; $\text{PtCl}_2 \cdot 2\text{CO}$; $\text{PtCl}_2 \cdot 3\text{CO}$, which are all yellow and which decompose easily by the action of water, separating platinum in a finely divided state and giving carbon dioxide and hydrochloric acid.

Oxygen, ozone and hydrogen peroxide do not oxidise carbon monoxide at ordinary temperatures, but in presence of catalysts, as, for instance, "Hopcalite" (a mixture of 60% MnO_2 and 40% CuO), even atmospheric oxygen will convert carbon monoxide to carbon dioxide. Because of this behaviour, "Hopcalite" is employed in filters for defence against carbon monoxide.

The conversion of carbon monoxide to carbon dioxide is also brought about by the action of other oxidising agents as silver oxide, potassium permanganate, iodic acid, chromic acid, mercuric chromate, etc.

Carbon monoxide easily reacts with hæmoglobin forming carboxy-hæmoglobin. The affinity of carbon monoxide for hæmoglobin is some 200 times as great as that of oxygen.

2. Iron Pentacarbonyl. $\text{Fe}(\text{CO})_5$ (M.Wt. 195·8)

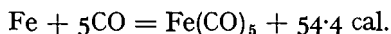
Iron pentacarbonyl was obtained in 1891 by Ludwig Mond² by the action of carbon monoxide on iron, prepared from ferrous oxalate. The yield obtained was about 1% of the theoretical from the iron employed.³

¹ J. SCHMIDT, *Das Kohlenoxyd*, Leipzig, 1935, 229.

² L. MOND and LANGER, *J. Chem. Soc.*, 1891, 59, 1090.

³ BERTHELOT, *Compt. rend.*, 1891, 112, 1343; R. MOND, *Chim. et Ind.*, 1929, 21, 681.

The reaction for the formation is as follows :



and this takes place more easily at low temperatures and high pressures.

Carbon monoxide may be prepared by the action of dehydrating agents on formic acid (see p. 46). The iron may be prepared from other compounds besides ferrous oxalate, but it must have as large a reactive area as possible and be of high purity.

Iron pentacarbonyl is formed at a pressure of 100–200 atmospheres in a tube heated externally to a temperature of 150° to 200° C.

The iron pentacarbonyl formed is drawn as vapour with the current of carbon monoxide out of the reaction tube into a refrigerant where it condenses. The excess carbon monoxide is collected in a gas holder and may be returned in cycle.¹

The industrial preparation of iron pentacarbonyl has presented much difficulty from the beginning. The difficulties have been due to ² :

(1) The presence of oxygen even in minute quantity, either in the iron or in the carbon monoxide.

(2) The precipitation of the pentacarbonyl on the iron during the reaction.

(3) The presence of impurities in the iron.

PHYSICAL AND CHEMICAL PROPERTIES

Iron pentacarbonyl is a liquid boiling at 102.7° C. at 767 mm. of mercury and having a melting point of – 20° C. (Dewar). Density, 1.4665 at 18° C. Coefficient of thermal expansion between 0° and 21° C., 0.00121; between 20° and 40° C., 0.00128, and between 40° and 60° C., 0.00142. Latent heat of evaporation, 39.45 gm. cal.

In the following table, the vapour tension and the volatility at various temperatures are given ³ :

TEMPERATURE	VAPOUR TENSION	VOLATILITY
° C.	MM. MERCURY	MGM./LITRE
–7	14	160
0	16	180
18.4	28	310
35.0	52	580
57.0	135	—
78.0	311	—

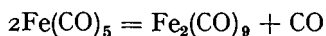
¹ D.R.P., 428,042 ; 436,369 ; 440,770, etc.

² A. MITTASCH, *Z. angew. Chem.*, 1928, **41**, 827.

³ J. DEWAR and H. JONES, *Proc. Roy. Soc. (Lond.)*, 1905, **76**, 558.

It is insoluble in water which slowly decomposes it in the cold. It is soluble in most organic solvents (acetone, benzene, etc.). The solutions are generally brown in colour and slowly decompose in the air forming a precipitate of iron hydroxide.

Iron pentacarbonyl when exposed to the action of light decomposes to form carbon monoxide and a solid crystalline substance of a golden-yellow colour and the formula $\text{Fe}_2(\text{CO})_9$, diferro-nonacarbonyl¹ :



This decomposition does not take place if a solution of iron pentacarbonyl in nickel carbonyl is exposed to light, perhaps because of the formation of a stable compound of the formula $\text{NiFe}(\text{CO})_9$ (Dewar).

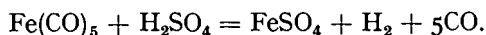
When mixed with air, iron pentacarbonyl decomposes on exposure to sunlight in a very few minutes with formation of carbon monoxide and iron oxide.

It is very sensitive to the action of heat ; on warming to about 200° C. under ordinary pressure it decomposes completely to iron and carbon monoxide.² This decomposition, however, takes place at a much lower temperature in the presence of substances having a porous structure. Thus in the presence of iron, about 60° C. is sufficient and in the presence of activated carbon, magnesium oxide, etc., it takes place even at ordinary temperatures.³

The vapour of iron pentacarbonyl burns in the air with a brilliant flame and a characteristic spectrum (Mittasch). By directing this flame against a porcelain capsule, a black deposit of partly oxidised iron forms.

Alcoholic solutions of sodium or potassium hydroxide easily absorb iron pentacarbonyl⁴ ; the resulting solution has vigorous reducing properties.

Concentrated nitric and sulphuric acids react with iron pentacarbonyl according to the equation :



On shaking iron pentacarbonyl with a dilute solution of hydrogen peroxide, colloidal ferrous hydroxide separates.

With chlorine it reacts easily, forming ferric chloride and carbon dioxide. With bromine it reacts similarly ; with iodine the reaction is much slower (Dewar).

¹ SPEYER, *Ber.*, 1927, **60**, 1424.

² DEWAR and JONES, *Proc. Roy. Soc. (Lond.)*, 1907, **79**, 66.

³ HLOCH, *Gasschutz und Luftschutz*, 1933, 180.

⁴ FREUNDLICH, *Ber.*, 1923, **56**, 2264 ; *Z. anorg. Chem.*, 1924, **141**, 317.

According to recent researches, by allowing bromine to drop into a solution of iron pentacarbonyl in pentane, a yellow precipitate of $\text{Fe}(\text{CO})_4 \cdot \text{Br}_2$ is formed.¹

Iron pentacarbonyl reacts with mercuric chloride with separation of a white substance according to the equation² :



It possesses reducing properties, especially in alkaline solution. Nitrobenzene is reduced to aniline, ketones to alcohols,³ etc.

It also has a dehalogenating action, reacting with carbon tetrachloride to form carbon monoxide, phosgene and hexachloroethane, while the iron is converted to ferric chloride (Mittasch).

It does not react with ammonia, but the basic amines, like pyridine, react to produce carbon monoxide. With hydrazine it reacts vigorously, forming a syrupy substance with an intense red colour; for each molecule of hydrazine, four molecules of carbon monoxide are set free.⁴

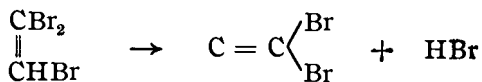
The vapour of iron pentacarbonyl is absorbed by activated carbon, which catalytically decomposes it with formation of carbon monoxide.

Alumina also absorbs iron pentacarbonyl vapour to the extent of about 2.5% by weight. If the alumina containing the absorbed pentacarbonyl is exposed to sunlight, it becomes red in colour and the theoretical quantity of carbon monoxide in the absorbed iron pentacarbonyl is evolved (Dewar).

According to Mittasch, the toxicity of iron pentacarbonyl is relatively slight. It is necessary, however, to take into account the carbon monoxide formed by its decomposition.

3. Dibromoacetylene. $\text{CBr}_2 = \text{C}$. (M.Wt. 183.8)

Dibromoacetylene was prepared in 1903 by Lemoult⁵ by the action of alcoholic potash on tribromoethylene :



Later, Lawrie⁶ also obtained it by the same method, but did not establish the structure with the divalent carbon atom.

Recently, this compound has been prepared by Nekrassov⁷ by

¹ W. HIEBER and G. BADER, *Ber.*, 1928, **61**, 1717.

² HOCK, *Ber.*, 1928, **61**, 2097.

³ *D.R.P.*, 441,179/1925.

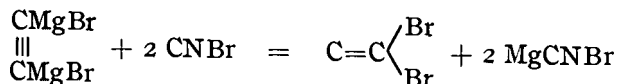
⁴ W. HIEBER and coll., *Ber.*, 1928, **61**, 558.

⁵ LEMOULT, *Compt. rend.*, 1903, **136**, 1333.

⁶ LAWRIE, *J. Am. Chem. Soc.*, 1906, **36**, 490.

⁷ NEKRASSOV, *Ber.*, 1927, **60**, 1757.

the action of an ethereal solution of cyanogen bromide on magnesium dibromoacetylene :



LABORATORY PREPARATION

26.5 gm. tribromoethylene and 10.5 gm. 82% potass. hydroxide are placed in a separatory funnel of about 1 litre capacity. The stopper of the funnel has two holes, through one of which passes a small tap-funnel and through the other a simple tap. The contents are treated in an atmosphere of nitrogen with 35–50 gm. alcohol (95%), cooling meanwhile in a stream of water. After 2 hours, 400–500 ml. air-free water are added. At the bottom of the separatory funnel an oily layer of dibromoacetylene collects ; this is run off into a flask filled with carbon dioxide and distilled in an atmosphere of carbon dioxide by heating in an oil bath to 100° to 120° C. (Lawrie).

PHYSICAL AND CHEMICAL PROPERTIES

Dibromoacetylene is a colourless heavy liquid which boils at 76° to 76.5° C.,¹ has an unpleasant odour and a density of about 2. It is soluble in most organic solvents.

It is a very unstable substance. It inflames in the air, burning with a red flame. On heating it decomposes with explosive force and deposits carbon. In absence of oxygen it is not a dangerous substance.

With damp oxygen it reacts to form hydrobromic acid, oxalic acid and a bromine-compound which has strongly irritating properties (Lemoult).

It reacts with bromine to form tetrabromoethylene, colourless crystals melting at 55° to 56° C. It reacts with iodine to form diiodo-dibromoethylene, crystals with m.p. 95° to 96° C.

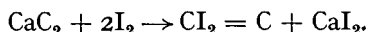
At ordinary temperatures, hydriodic acid adds on to the molecule forming dibromiodoethylene, Br₂C = CHI, a liquid boiling at 91° C. at 15 mm. pressure. Density, 2.952 at 24° C. (Lawrie).

Dibromoacetylene is a substance of highly toxic properties. Inspiration of its vapour causes violent and prolonged headaches and general debility (Lawrie).

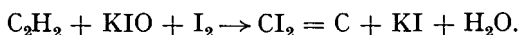
¹ LEMOULT, *Compt. rend.*, 1903, **137**, 55.

4. Diiodoacetylene. $\text{Cl}_2 = \text{C}$. (M.Wt. 277.8)

Diiodoacetylene was obtained in 1865 by Berend,¹ together with other substances, by the action of an ethereal solution of iodine on silver acetylide. But it was only in 1885 that Bayer² recognised it as an individual substance. He prepared it together with tetraiodoethylene by the action of iodine on calcium carbide³:



According to Biltz⁴ a more practicable method is by the action of acetylene on an alkaline solution of iodine in potassium iodide:



Recently⁵ a new method has been elaborated, which consists in bubbling acetylene through a solution of iodine in liquid ammonia. The yield in this reaction is 90–97%.

LABORATORY PREPARATION

300 ml. of a seminormal solution of potassium hydroxide are introduced into a flask furnished with a tap-funnel, an electric agitator and a tube for the introduction of gas. A rapid current of acetylene, previously washed with a solution of basic lead acetate, is passed in, meanwhile stirring and cooling strongly and dropping in from the tap-funnel a solution of 32 gm. iodine and 35 gm. potassium iodide in 25 ml. water until the colour of the iodine persists in the reaction mixture. This operation lasts 30–40 minutes.

The precipitate obtained is filtered off, washed with water, dried in a desiccator, and, if necessary, crystallised from ligroin. Yield almost theoretical (Biltz).

PHYSICAL AND CHEMICAL PROPERTIES

Diiodoacetylene forms white crystals melting at 78.5°C . which have a strong, disagreeable odour very similar to that of phenyl isocyanide. It has a high volatility and is insoluble in water, but soluble in alcohol, ether, etc. Exposed to light it slowly becomes red with separation of iodine.

When heated in either a closed or an open tube, diiodoacetylene decomposes explosively, forming carbon and iodine. The temperature of decomposition is about 125°C . (Vaughn). It also explodes on rubbing in a mortar.

¹ BEREND, *Ann.*, 1865, **135**, 257.

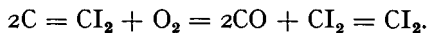
² BAYER, *Ber.*, 1885, **18**, 2275.

³ BIESALSKY, *Z. angew. Chem.*, 1928, **41**, 720.

⁴ BILTZ, *Ber.*, 1904, **37**, 4415.

⁵ VAUGHN and NIEUWLAND, *J. Am. Chem. Soc.*, 1932, **54**, 788.

It oxidises slowly in air, especially in neutral solution, forming carbon monoxide and tetraiodoethylene :



This oxidation also takes place if sodium hydroxide is added to an alcoholic solution of diiodoacetylene.¹

By passing a current of dry chlorine into diiodoacetylene or into its solution in chloroform, white needles of hexachloroethane (m.p. 186.5° C.) are obtained after removing the excess chlorine.

By the prolonged action of bromine on diiodoacetylene hexabromoethane is similarly obtained in the form of white crystals, which melt at 210° to 215° C. with separation of bromine. Under suitable conditions several compounds of bromine and iodine may be obtained, as dibromodiiodoethylene, triiodobromoethylene, etc. (Berend and Nef).

Concentrated nitric acid or chromic acid in acetic acid solution reacts to form carbon dioxide and iodoethylene.

With fuming nitric acid a very violent reaction takes place with evolution of carbon dioxide and separation of iodine and of triiodovinyl nitrate, which has the formula



and forms yellow crystals (Nef).

It has powerfully toxic properties, the vapour strongly irritating the mucous membranes and particularly the eyes (Nef). Iodine separates as it acts on the organism, though it partly penetrates the tissues without decomposition.²

Analysis of Divalent Carbon Compounds

DETECTION OF CARBON MONOXIDE

The various reactions that have been proposed for the detection of carbon monoxide depend on its reducing properties and its power of reaction with hæmoglobin.

The following are the principal :

(1) *Silver Nitrate.* (A solution of silver nitrate to which sufficient ammonia has been added to redissolve the precipitate which first forms.) By shaking the gas containing carbon monoxide with this solution, a black precipitate is produced.³ Sensitivity : 0.04%.

¹ NEF, *Ann.*, 1898, **298**, 341.

² BILTZ, *Ber.*, 1897, **30**, 1201.

³ KAST and SELLE, *Gas- und Wasserfach.*, 1927, **69**, 812.

(2) *Palladium Chloride*. This employs 0.2% aqueous solution of palladium chloride, or palladium chloride paper.¹ The latter is prepared just before use by immersing a strip of filter paper in a freshly prepared mixture of equal volumes of a 0.5% solution of palladium chloride and a 5% solution of sodium acetate.²

Sensitivity³ : 0.05% CO, in a few minutes.

0.02% CO, in 2-4 hours.

0.005% CO, in 24 hours.

These two reactions, with silver nitrate and palladium chloride, can only be used to detect carbon monoxide in air which does not contain hydrogen sulphide, ammonia or unsaturated hydrocarbons.

Spectroscopic Method. This is the most certain and specific method of detecting carbon monoxide. The gas to be tested is passed into a dilute solution (1 in 10, or 1 in 100) of blood which is then examined spectroscopically. Pure blood gives the spectrum of hæmoglobin with its two absorption bands of which one is narrow and yellow, near the D line, while the other is less intense but wider in the green, near to the E line. Carboxyhæmoglobin also gives two bands in D and E but of equal width and intensity, somewhat closer together and also displaced towards the violet.

This test is simplified by adding ammonium sulphide to the solution to be tested, when the spectrum of oxyhæmoglobin is substituted for that of hæmoglobin, and the two bands in D and E disappear and give place to a single band, less intense and narrower. The spectrum of carboxyhæmoglobin remains unaltered. Sensitivity : 0.05%.

DETECTION OF IRON PENTACARBONYL

(1) *Method of Pyrogenic Decomposition*. The gas to be examined is passed through a glass tube, similar to that usually employed in carrying out the Marsh test, and heated by means of a gas flame. In the presence of iron pentacarbonyl a ring of iron oxide is deposited on the cold part of the tube. Carbon monoxide may be detected in the gas issuing from the tube by one of the methods given above.

(2) *Griffith's Method*.⁴ The gas to be tested is bubbled through a wash bottle containing concentrated sulphuric acid. By

¹ WINKLER, *Lehrbuch d. Techn. Gasanal.*, Leipzig, 1927 ; BRUNCK, *Z. angew. Chem.*, 1912, **25**, 2479.

² LJUNGREEN, *Eng. Pat.*, 341269/1930.

³ V. ITALIEN, *Toxicologie*, 1928, 183.

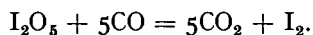
⁴ GRIFFITH, *J. Soc. Chem. Ind.*, 1928, **47**, 311.

evaporating to dryness and taking up the residue with water, iron may be detected by the well-known Prussian blue reaction.

QUANTITATIVE DETERMINATION OF CARBON MONOXIDE

Of the various methods suggested, the two described here enable very small quantities of carbon monoxide to be determined in air. Other methods (gas-volumetric, gravimetric, by combustion, etc.) may be found in the usual books on chemical analysis.

(1) *Iodine Pentoxide Method.* This method is based on the determination of the iodine liberated in the reaction between carbon monoxide and iodic anhydride according to the equation ¹ :



Three U-tubes are connected in series, the first filled with granular potassium hydroxide, the second with pumice impregnated with sulphuric acid, and the third with pure anhydrous iodic acid which should not liberate iodine when pure air is passed through.² This last U-tube is connected by glass-to-glass connections with a boiling-tube containing sufficient concentrated potassium iodide solution to ensure complete absorption of the iodine.

The iodic acid is heated in an oil-bath to about 150° C., and a measured volume of the gas mixture to be examined is passed through at a velocity of about 10 ml. per minute. The iodine liberated by the carbon monoxide is carried over by the gas stream and bubbles into the potassium iodide solution. After the measured volume of gas has been passed, pure air is drawn through for some minutes to ensure complete absorption of the iodine which remains in the connecting tubes.

The liberated iodine is titrated with sodium thiosulphate by the usual method of analysis.

According to Froboese,³ it is preferable to determine, either gravimetrically or volumetrically, the carbon dioxide formed in the above reaction rather than to titrate the iodine.

An apparatus utilising the reaction between carbon monoxide and iodic acid has been produced by the Mines Safety Appliances.⁴ This permits the determination of the amount of carbon monoxide in air in a few seconds with sufficient accuracy for practical purposes. A measured volume of gas is passed first through a

¹ M. NICLOUX, *Compt. rend.*, 1898, **126**, 746; GAUTIER, *Compt. rend.*, 1898, **126**, 793.

² It is best not to use the iodic acid of commerce, but to prepare it by the action of nitric acid on iodine, as described by NICLOUX, *Compt. rend.*, 1912, 1166.

³ FROBOESE, *Z. anal. Chem.*, 1915, **54**, 1.

⁴ "Safety in Mines Apparatus," *Jour. Sci. Instrum.*, 1932, **9**, 327.

layer of activated carbon and then through a tube containing pumice saturated with iodic anhydride and oleum, known as "Hoolamite."¹ In the presence of carbon monoxide the tube assumes a colour varying from greyish-blue to greenish-blue according to the amount of carbon monoxide. By comparison with a standard reference-tube the quantity present in the air under examination can be determined.

(2) "Hopcalite" Method. This is based on the catalytic oxidation of carbon monoxide when passed through the oxidising mixture of manganese dioxide and copper oxide known as "Hopcalite."² Determination of the percentage of carbon monoxide present is carried out by measuring either the quantity of carbon dioxide formed³ or the heat of oxidation.

The "Draeger-CO-Messer" apparatus measures the rise in temperature of the oxidising mixture mentioned above. This rise in temperature may be measured either by means of an ordinary thermometer or registered on a thermograph. From the increase in temperature the percentage of carbon monoxide may be obtained from suitable tables.⁴

QUANTITATIVE DETERMINATION OF IRON PENTACARBONYL

The method of Griffith, already described, may be applied to the determination of iron pentacarbonyl by colorimetric determination of the Prussian blue formed.

If the sample has been dissolved in benzine, methyl alcohol, etc., it is treated with perhydrol and the iron precipitated with ammonia and determined in the usual way as oxide.⁵

¹ HOOVER, *J. Ind. Eng. Chem.*, 1921, **13**, 770; KATZ, *J. Ind. Eng. Chem.*, 1925, **17**, 555.

² LAMB and coll., *J. Am. Chem. Soc.*, 1922, **44**, 738. For the composition of Hopcalite, see p. 47.

³ GRICE, *Eng. Pat.*, 343724/1930.

⁴ STAMPE, *Von der Kohlen und Mineralölen*, 1931, **3**, 227.

⁵ MITTASCH, *Z. angew. Chem.*, 1928, **41**, 827.

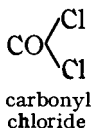
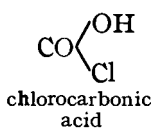
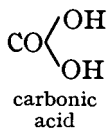
CHAPTER VI

ACYL HALOGEN COMPOUNDS

THE substitution of carboxylic-hydroxyl in the molecules of organic acids by halogen atoms or by the CN group, generally confers toxic properties.

Among the halogen derivatives of acid radicles especial interest attaches to phosgene or carbonyl chloride because of its great toxic properties, and it was used in the war of 1914-18.

From its structure it will be seen that phosgene may be considered as carbonic acid in which both the hydroxyl groups are substituted by chlorine atoms.

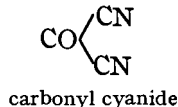
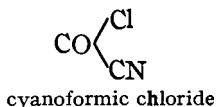


Analogues of phosgene, such as carbonyl bromide have been studied at various times,¹ but experiments on the chemical and particularly toxicological properties have only been carried out in the last few years.²

Carbonyl bromide, because of its boiling point (64° C.) and its comparative stability to the action of water would be preferred as a war gas to phosgene were it not for its lower stability to light and its lesser toxicity.

Recently *carbonyl fluoride* has also been prepared and studied. It is a colourless gas obtained by the action of silver fluoride on carbon monoxide.³ Because of its great sensitivity to water and its low boiling point (-83° C.) it appears improbable that it would give satisfactory service as a war gas.

By the substitution of the halogen atoms in the phosgene molecule by CN groups it is possible to obtain the following two compounds :



¹ EMMERLING, *Ber.*, 1880, **13**, 874; BARTAL, *Z. anorg. Chem.*, 1907, **56**, 49.

² H. SCHUMACHER and S. LENHER, *Ber.*, 1928, **61**, 1671.

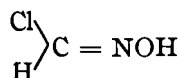
³ O. RUFF, *Z. anorg. Chem.*, 1934, **221**, 154.

The *chloride of cyanoformic acid* is obtained by the action of the amide of ethyl oxalate on phthalyl chloride.¹ It is an oily substance with b.p. 126° to 128° C. at 750 mm. of mercury.

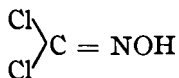
Carbonyl cyanide has been obtained² from diisonitrosoacetone. It is a colourless liquid with a boiling point of 65.5° C. at 740 mm. Density, 1.124 at 20° C. By hydrolysis it decomposes forming carbon dioxide and hydrocyanic acid.

In recent years compounds of the same general type, but having the carbonyl group C:O substituted by the oximic group C:NOH, have attracted attention as possible war gases.

(1) *Chloroformoxime*³



and (2) *Dichloroformoxime*, the oxime of carbonyl chloride,⁴



The vapours of these substances even in low concentration are strongly lachrymatory and produce very painful lesions of the eyes which may result in blindness. Both in the solid state and in solution they also cause irritation and blistering of the skin. This vesicant action results from actual contact of the substances with the skin and the blisters heal only very slowly. According to Hackmann,⁵ very few substances known in the whole of organic chemistry are capable of exerting on the human organism physiopathological action that is as violent as that produced by these oximes. However, their physical and chemical properties render them of little use as war gases.

Recently other compounds analogous with dichloroformoxime have been prepared.⁶

(1) *Dibromoformoxime*, crystals with a melting point of 68° to 69° C. (Birckenback) or 70° to 71° C.⁷ Distils between 75° and 85° C. at a pressure of 3 mm.

(2) *Diiodoformoxime*, crystals with m.p. 69° C.

These two substances have a less powerful toxic action than

¹ E. OTT, *Chem. Ztg.*, 1926, **50**, 448.

² MALACHOVSKY and coll., *Ber.*, 1937, **70**, 1012.

³ NEF, *Ann.*, 1894, **280**, 307.

⁴ PRANDTL, *Ber.*, 1929, **62**, 1766; M. SLUNESKO, *Vojenské Technické Zpravy*, 1927, **14**, 155.

⁵ HACKMANN, *Chem. Weekblad.*, 1934, **31**, 366.

⁶ BIRCKENBACH and SENNEWALD, *Ann.*, 1931, **489**, 9.

⁷ J. DE PAOLINI, *Gazz. chim. ital.*, 1930, **60**, 703.

the analogous chlorinated derivatives and especially as vesicants, provoke irritation of minor intensity.

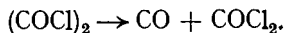
Finally, among the various acyl halogen compounds, formyl fluoride, oxalyl chloride, oxalyl bromide, etc., are interesting possibilities as war gases.

Formyl fluoride, $\text{H}\cdot\text{COF}$, has been prepared only recently by Nesmejanov¹ by the action of benzoyl chloride on a solution of potassium fluoride in formic acid. It is a mobile, colourless liquid, b.p. -26°C . It dissolves in water, slowly hydrolysing. At room temperature either in the liquid or gaseous state, it decomposes in a few hours with the formation of carbon monoxide and hydrofluoric acid.



Considered from the physiopathological point of view, formyl fluoride is about three times as toxic as acetyl fluoride or chloropicrin.

Oxalyl chloride, $(\text{COCl})_2$, has been obtained by the action of phosphorus pentachloride on oxalic acid.² On heating, it decomposes, forming carbon monoxide and phosgene according to the equation :



Oxalyl bromide, $(\text{COBr})_2$, has been obtained by the action of hydrobromic acid on oxalyl chloride.³ Heat decomposes it with production of carbon monoxide and carbonyl bromide. It reacts easily with water forming carbon monoxide, carbon dioxide and hydrobromic acid.

The vapours of these two substances violently attack the respiratory organs.

It has been demonstrated that the stability of the oxalic acid halides diminishes in passing from the chlorides to the iodides.

	$(\text{COCl})_2$	$(\text{COBr})_2$	$(\text{COI})_2$
Temperature of decomposition	350°	150°	-80°

This is analogous to the behaviour of the carbonic acid halides :

	COCl_2	COBr_2	COI_2
Temperature of decomposition	400°	100°	-80°

1. Phosgene. COCl_2 . (M.Wt. 98.9)

Phosgene, or carbonyl chloride, was obtained in 1812 by Davy⁴

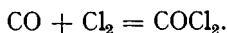
¹ A NESMEJANOV and E. KAHN, *Ber.*, 1934, **67**, 370.

² STAUDINGER, *Ber.*, 1908, **41**, 3558.

³ STAUDINGER, *Ber.*, 1912, **45**, 1595, and 1913, **46**, 1431.

⁴ DAVY, *Phil. Trans. Roy. Soc.*, 1812, **102**, 144.

by exposing a mixture of chlorine and carbon monoxide to the action of sunlight.



This reaction can also be brought about without the influence of solar radiation by means of catalysts such as platinum sponge, vegetable carbon, animal charcoal,¹ etc.

Phosgene was employed for the first time as a war gas in December, 1915. It was used throughout the war alone or mixed with chlorine by emission from containers, while shells were also used which contained the same mixture or one including metallic chlorides as stannic chloride or other war gases such as chloropicrin, diphosgene, diphenylchloroarsine, etc.²

LABORATORY PREPARATION

In the laboratory, phosgene may be easily prepared by treating chloroform with chromic acid mixture³:



but by this method the product is impure with chlorine and chloroform (5% about).

Either Erdmann's method, based on the reaction between

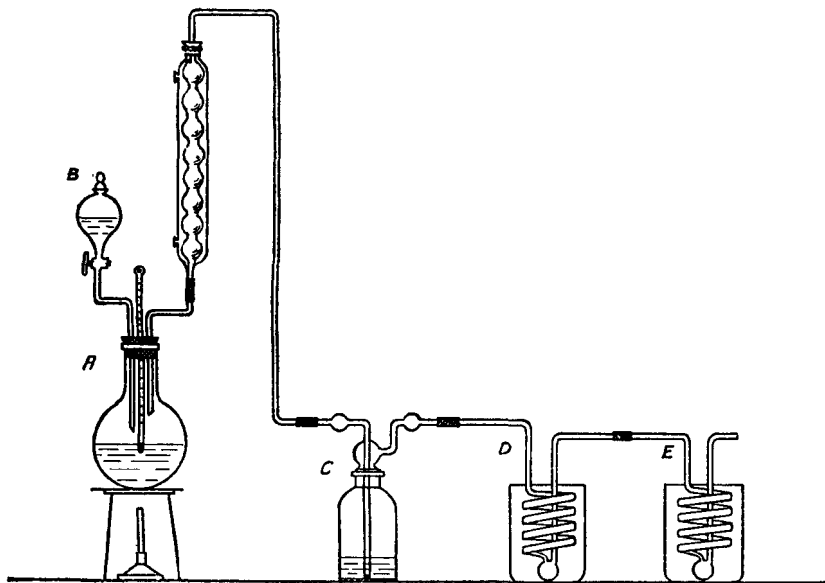


FIG. 1.

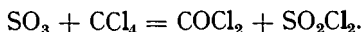
¹ PATERNÒ, *Gazz. chim. ital.*, 1878, **8**, 233, and 1920, **50**, 30.

² MAMELI, *Chimica tossicologica*, Turin, 1927, 527.

³ EMMERLING, *Ber.*, 1869, **2**, 547.

fuming sulphuric acid and carbon tetrachloride, or the synthetic method from carbon monoxide and chloride in presence of activated carbon is generally used.

*Preparation from Oleum and Carbon Tetrachloride.*¹ 100 ml. carbon tetrachloride are placed in a flask, *A* (Fig. 1), fitted with a stopper through one of whose three holes passes a tap-funnel, *B*, containing 120 ml. oleum (80% free SO₃), while a thermometer and a reflux condenser pass through the other two holes. The flask *A* is gently heated, while fuming sulphuric acid is allowed to enter drop by drop from the tap-funnel, and when this comes into contact with the carbon tetrachloride it reacts according to the equation :



The phosgene formed is first passed through the wash bottle *C*, containing concentrated sulphuric acid which absorbs sulphur trioxide and sulphuryl chloride vapours, and then through two condensation receivers, *D* and *E*, externally cooled with a freezing mixture of ice and calcium chloride.

After all the oleum has been added, the flask is heated strongly for about 5 minutes in order to eliminate all the phosgene.

In this way phosgene impure with carbon tetrachloride and sulphuryl chloride is obtained. According to Popescu² it can be purified by first heating it to its boiling point (+ 8° C.) and then condensing the vapour again after passing it through strongly cooled concentrated sulphuric acid.

Preparation by Synthesis from Chlorine and Carbon Monoxide. A wide-mouthed vessel (*A*, see Fig. 2) is closed with a stopper

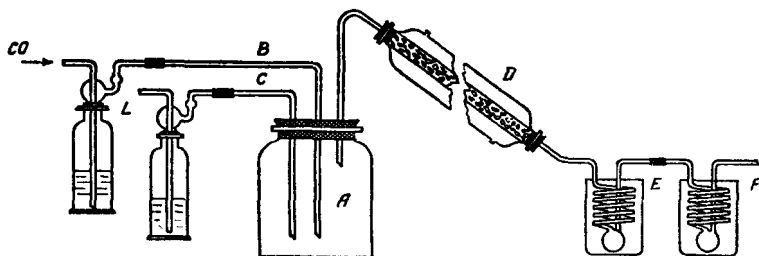


FIG. 2.

pierced with three holes. Through two of these holes glass tubes (*B* and *C*) pass to the bottom of the vessel, while through the third a very short tube passes and connects with a condenser

¹ H. ERDMANN, *Ber.*, 1893, 26, 1993. This method was used in the " *Serviciul de oparare contra gazelor* " of Rumania. *Antigaz*, 1927, 7, 9.

² POPESCU, *Antigaz*, 1927, 7, 11.

(D) filled with granules of activated carbon. The other end of the condenser is connected with two receivers, *E*, *F*, externally cooled with a freezing mixture of ice and calcium chloride.

Carbon monoxide from a gas holder is passed through a wash bottle *L* containing sulphuric acid, and then by means of tube *B* into the vessel *A* where it mixes with chlorine introduced through the other tube *C*. The chlorine is passed in at the rate of five or six bubbles a second and the carbon monoxide at eight or nine bubbles a second. As the two gases pass through the charcoal, the latter becomes heated, and water is therefore circulated through the outer tube of the condenser to cool it. The phosgene as it forms gradually condenses in the two externally cooled receivers.¹

INDUSTRIAL PREPARATION

In Italy and France phosgene was prepared during the first years of the war of 1914-18 from carbon tetrachloride and fuming sulphuric acid according to the method of Schüttzenberger² modified by Grignard.³

This method, though giving a high yield of phosgene (about 90% of theoretical), consumes much chlorine. For this reason, the method was later abandoned in favour of the synthesis from carbon monoxide and chlorine which had been used in Germany from the beginning. Until a few years ago the synthesis from carbon monoxide and chlorine was carried out in presence of animal charcoal exclusively, this being conveniently prepared from bones and washed first with hot hydrochloric acid, then with water, and finally dried. Later it was discovered that vegetable carbon prepared from birch wood, lime wood, coconut, etc., had greater catalytic activity.

The synthetic method is nowadays the most widely used for the industrial manufacture of phosgene.

The preparation of the chlorine for use in this process involves no points calling for special mention, except that the chlorine should be as dry as possible in order to prevent the formation of hydrochloric acid during the synthesis. Special care is necessary, however, in preparing the carbon monoxide. The most generally used process employs the reduction of carbon dioxide obtained by the combustion of coke and is carried out in the following manner :

Coke is burned in a special furnace, and the carbon dioxide

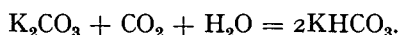
¹ PATERNÓ and MAZZUCHELLI, *Gazz. chim. ital.*, 1920, **50**, 30.

² SCHÜTTZENBERGER, *Bull. soc. chim.*, 1869, **12**, 198.

³ GRIGNARD, *Compt. rend.*, 1919, **169**, 17.

formed is purified by first washing with water and then passing it through a series of tubes containing a solution of potassium carbonate.

The carbon dioxide reacts with this solution to form potassium bicarbonate according to the equation :



The solution thus obtained is pumped into a still and heated in absence of air, so as to liberate the carbon dioxide again together with water vapour. The latter is removed by cooling and then passing through concentrated sulphuric acid.

Carbon dioxide alone is left and this is reduced to carbon monoxide by passage through red-hot coke. In order to prevent the coke being cooled by the endothermic nature of the reaction to a temperature at which the combination no longer takes place or occurs only incompletely and very slowly, the carbon dioxide is mixed with a definite quantity of oxygen.

In this way carbon monoxide is obtained impure with carbon dioxide which is removed by absorption in caustic soda :



After drying, the carbon monoxide is ready for the synthesis.

The plant for the manufacture of phosgene by the synthetic method is shown diagrammatically in Fig. 3. The carbon

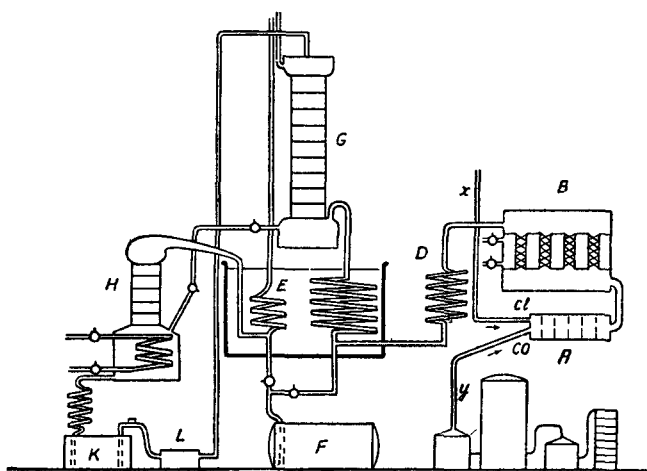


FIG. 3.

monoxide and chlorine are passed into a mixer *A*, suitably arranging the proportions to correspond with the synthetic process which follows. These mixers are simple lead cylinders

containing perforated diaphragms. The gases enter tangentially at one end of the mixer by two separate tubes, x , y , then are mixed in passing through the holes in the diaphragms and leave from the other end of the mixer to pass directly into the catalyst chamber, B . This may take various forms, but generally consists of lead tubes 5–6 m. in height and 1 m. in diameter filled with active carbon. The gases enter at the bottom of the chamber at a temperature of about 20° C. As the reaction between chlorine and carbon monoxide takes place with development of a considerable quantity of heat, the temperature is moderated by external cooling. The optimum temperature for the reaction is about 125° C. and should not exceed 150° C.¹

The gas mixture containing the phosgene formed is passed next through the cooling coils, D , where the greater part condenses and is collected in the receiver F . The uncondensed portion then enters at the bottom of the absorption tower G , into the top of which a fine spray of tetrachloroethane drops, this liquid being a solvent for phosgene. The solution obtained passes into the still H , in which the phosgene is recovered by heating and condenses in the cooler E and collects in the reservoir F , while the tetrachloroethane freed from phosgene passes into K and by means of the montejus L is carried again to the top of the column G . The phosgene obtained in this manner contains about 1.5–2% free chlorine and traces of carbon dioxide.

American Method. At Edgewood the Americans carried out the synthesis of phosgene by a method similar to that described above, employing, however, a special carbon known as "*Filtchar*" as catalyst. What is particularly interesting about this method is the means by which the synthesis from the carbon monoxide and chlorine is carried out.

The catalyst is placed in special boxes of iron covered with graphite sheets to protect the iron from the action of the chlorine and the temperature during the synthesis allowed to rise of its own accord to at least 250° C. However, as in these conditions the combination of the two gases is incomplete, in order to prevent chlorine and carbon monoxide from escaping uncombined, the gases issuing from the catalyst chambers, containing about 85% phosgene, are passed into a second series of reaction chambers. These are constructed like the first and also contain "*Filtchar*." They are known as the cold catalysts and are kept at a temperature of about 95° C.

The resulting gas mixture containing approximately 93–94% of phosgene is dried by means of sulphuric acid and then cooled

¹ CHAPMAN, *J. Chem. Soc.*, 1911, **99**, 1726.

by passing through coils immersed in calcium chloride brine at -20°C . At this temperature the phosgene is liquefied, while the remaining gas which still contains gaseous phosgene is absorbed in linseed oil in a recovery plant.

PHYSICAL AND CHEMICAL PROPERTIES

At ordinary temperatures phosgene is a colourless gas with a characteristic odour described as that of mouldy hay. On cooling to below 8°C . it becomes a colourless, mobile liquid boiling at 8.2°C . It solidifies at -118°C .¹ to a white crystalline mass. The technical product is, however, pale yellow or orange owing to the presence of coloured impurities, such as chlorine, ferric chloride, etc.

The critical temperature of phosgene is 181.7°C . and the critical pressure 55.3 atmospheres. A litre of gaseous phosgene at 0°C . and 760 mm. weighs 4.4 gm., *i.e.*, three and a half times (3.505 to be exact) that of air (1.293). In the following table the values of the specific gravity of liquid phosgene are given at various temperatures, as well as the values of the specific volume (volume of unit weight of liquid phosgene).

TEMPERATURE ° C.	SPECIFIC WEIGHT	SPECIFIC VOLUME
- 40	1.5011	0.6662
- 20	1.4615	0.6842
- 10	1.4411	0.6939
0	1.4203	0.7041
10	1.3987	0.7150
20	1.3760	0.7260
40	1.3262	0.7541
60	1.2734	0.7853

The vapour tension of liquid phosgene at temperatures between -15°C . and $+23^{\circ}\text{C}$. can be calculated from the formula :

$$\log p = 7.5595 - \frac{1326}{273 + t}$$

For temperatures between -13°C . and $+25^{\circ}\text{C}$. the vapour tension is as follows :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
- 13.7	335
- 10	365
- 5	452
0	555
8.2	760
10	839.8
20	1,173.4
25	1,379

¹ ERDMANN, *Ann.*, 1908, **362**, 148.

From these data it will be seen that even at ordinary temperatures phosgene has a high vapour pressure which makes it of low persistence as a war gas, although its vapour density is much greater than that of air.

The evaporation of phosgene is also favoured by its low specific heat (0.243 calorie) and its low latent heat of evaporation (about 60 calories). The coefficient of expansion of phosgene is 0.001225 at 0° C.

Phosgene dissolves readily in many organic solvents, such as benzene, toluene, xylene,¹ etc., as well as in fats and oils. From these solutions it can be easily removed by a current of dry air. Use is made of this property in marketing phosgene as a 30% solution in toluene.

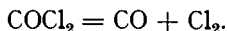
According to Baskerville and Cohen ² the solubility of phosgene in some organic solvents at a temperature of 20° C. is as follows :

1 gm. phosgene dissolves in 1.0 gm. benzene	
" " " " 1.5 " toluene	
" " " " 1.2 " petrol	
" " " " 1.7 " chloroform	
" " " " 3.6 " carbon tetrachloride	
" " " " 1.6 " glacial acetic acid	

Phosgene is also easily soluble in arsenic trichloride (1 part AsCl₃ dissolves 100 parts COCl₂) and in sulphur monochloride.

In the liquid state phosgene dissolves various substances, as, for example, chlorine in the following proportions: at 0° C., 6.63%; at -15° C., 20.5%, as well as several of the war gases, such as dichloroethyl sulphide, chloropicrin, diphenylchloroarsine, etc.

Phosgene is a stable compound at ordinary temperatures and in absence of humidity. At somewhat elevated temperatures, however, it dissociates fairly easily into carbon monoxide and chlorine :



Bodenstein and others ³ have observed that this dissociation has the following values at ordinary pressure :

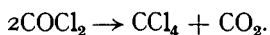
At 101° C. 0.45%	At 503° C. 67%
At 208° C. 0.83%	At 553° C. 80%
At 309° C. 5.61%	At 603° C. 91%
At 400° C. 21.26%	At 800° C. 100%

¹ W. KIREEV and coll. have determined the boiling points at ordinary pressure and the composition of the vapour from solutions of phosgene in xylene and in ethylene dichloride containing amounts of phosgene varying from zero to 35% by weight (*J. Prikl. Khim.*, 1935, 949).

² C. BASKERVILLE and P. COHEN, *J. Ind. Eng. Chem.*, 1921, **13**, 333.

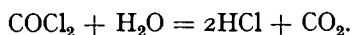
³ BODENSTEIN and DUNANT, *Z. physik. Chem.*, 1908, **61**, 437; BODENSTEIN and PLAUT, *Z. physik. Chem.*, 1924, **110**, 399.

When phosgene is passed through incandescent carbon, it decomposes according to the equation ¹ :



By exposure to the light from a mercury vapour lamp in presence of oxygen and chlorine, decomposition takes place, and as an intermediate product, a compound of the formula COCl^2 is formed. By exposure to ultra-violet light chlorine and carbon monoxide are formed.³

Phosgene in contact with water is hydrolysed even at the ordinary temperature according to the equation :



Very divergent values are reported in the literature for the velocity of this reaction ; according to some workers the hydrolysis of phosgene is instantaneous ; according to others it has a measurable velocity.⁴ The reaction is strongly influenced by the physical state of the phosgene when it is brought into contact with the water and also whether the water is in the vapour state or the liquid state. Thus, according to Delepine,⁵ the reaction velocity is not very rapid if the phosgene comes into contact with the water vapour normally present in the atmosphere. Experiments carried out on this have demonstrated that 1 ml. of gaseous phosgene, placed in a 500-ml. stoppered flask with ordinary air, still retains the odour of phosgene after 15 days. The normal humidity of the air, therefore, does not completely decompose phosgene, though there is present in the air more water than that necessary for complete hydrolysis. By addition to the flask of a drop of water, which is more than sufficient to saturate the air, the odour of phosgene is still perceptible after 4 days, but not after 12 days. With 2 drops of water the odour disappears in 2 days.

The hydrolysis of phosgene actually in contact with water is, however, very rapid.⁶ Paternò and Mazzucchelli ⁷ have found that by placing 100 ml. water together with a small glass bulb containing about 1 gm. phosgene inside a closed vessel, and after cooling to 0° C., breaking the bottle and shaking, decomposition of the phosgene is complete in barely 20 seconds.

¹ MELNIKOV, *J. Khim. Promisl.*, 1932, **9**, 20.

² G. ROLLEFSON and C. MONTGOMERY, *J. Am. Chem. Soc.*, 1933, **55**, 142.

³ COHEN and BECKER, *Ber.*, 1910, **43**, 131.

⁴ FRIES and WEST, *Chemical Warfare*, 1921, 131 ; MEYER, *Der Gaskampf und die chemischen Kampfstoffe*, 1925, 318 ; *Handleiding in de Chemische Oorlogsvoe Ring, Uitgave Mavors*, 1927, 63.

⁵ DELEPINE, *Bull. soc. chim.*, 1920, [4], **27**, 286.

⁶ S. VLES, *Rec. trav. Chim.*, 1934, **53**, 961.

⁷ PATERNÒ and MAZZUCHELLI, *Gazz. chim. Ital.*, 1920, **50**, 30.

Although the hydrolytic reaction is irreversible, the products formed in the reaction retard further decomposition of the phosgene.

Thus in the case of gaseous phosgene, the carbon dioxide formed, being sparingly soluble, immediately saturates the surface layer of the water with which it is in contact and the greater part remaining in the gaseous state forms an inert layer over the liquid preventing further attack of the phosgene. In the case of liquid phosgene, it is the hydrochloric acid which slows down further decomposition by saturating the water in immediate contact.

It seems, therefore, that such retarding action depends principally on the diffusion in the water of the products of hydrolysis, which by not diffusing rapidly form a sort of protective layer against further decomposition of the phosgene. As soon as the products diffuse away into the water, further hydrolysis becomes possible.

The property of retarding the reaction between phosgene and water is not specific for hydrochloric acid, but is common to all acids.

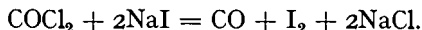
Phosgene, which, as stated on p. 57, may be considered as carbonic acid chloride, is very reactive, like all acid chlorides. It reacts easily with bases; for instance, with sodium hydroxide it forms sodium chloride and sodium carbonate.



It reacts with calcium hydroxide similarly. Soda-lime is also a good neutralising agent for phosgene and has been employed for this purpose in the antigas filters of respirators.

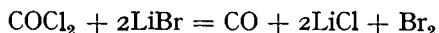
Phosgene does not react with hydrobromic acid even when heated to 200° C., but hydriodic acid when passed together with phosgene through a glass tube 6 m. long, reacts at ordinary temperatures with separation of iodine derived from the decomposition of iodophosgene.¹

In the absence of water, phosgene reacts quantitatively with sodium iodide in acetone solution according to the equation ² :



This reaction is rapid and makes possible the determination of small quantities of phosgene in mixed gases (see p. 86).

Phosgene reacts similarly in contact with an acetone solution of lithium bromide :



¹ STAUDINGER, *Ber.*, 1913, **46**, 1426.

² *Jahresb. der Chem. Tech. Reichsanstalt*, 1927, **6**, 57.

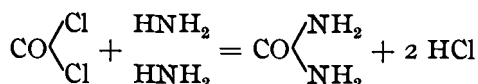
and, according to Perret,¹ this reaction can be employed for the quantitative determination of phosgene by measuring the volume of carbon monoxide formed. In this determination, the bromine does not interfere as it gradually combines to form bromoacetone

Chlorobromophosgene is formed by the action of aluminium bromide or boron bromide on phosgene at 140° C. :

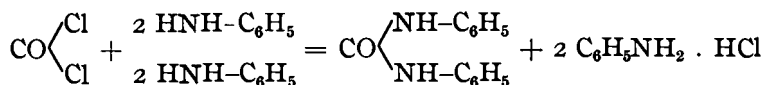


This is a liquid with a boiling point of 25° C. and specific gravity 1.82 at 15° C.²

Phosgene also reacts with ammonia, aniline, dimethyl aniline, etc. With ammonia it forms urea.³

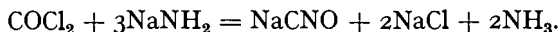


With aniline, diphenyl urea is formed⁴ :

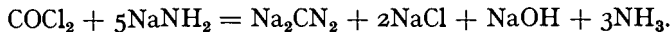


The reaction of phosgene with aniline, according to Kling and Schmutz⁵ takes place more rapidly than that with water, and, according to Vles,⁶ phosgene in contact with a saturated aqueous solution of aniline at 0° C. reacts almost only with the aniline. A method of analysis of phosgene (see p. 84) has been based on this reaction.

Phosgene reacts with sodamide even at the ordinary temperature, according to the equation.⁷



At a higher temperature, about 250° C., the reaction follows a different course :



Phosgene acts on dimethyl aniline at ordinary temperatures

¹ PERRET, *Bull. soc. chim.*, 1936, 349.

² BARTAL, *Ann.*, 1906, **345**, 334.

³ R. FOSSE and coll., *Compt. rend.*, 1936, **202**, 1544.

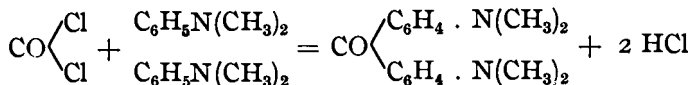
⁴ HOFMANN, *Ann.*, 1849, **70**, 139.

⁵ KLING and SCHMUTZ, *Compt. rend.*, 1919, **168**, 773.

⁶ S. VLES, *Rec. trav. Chim.*, 1934, **53**, 961.

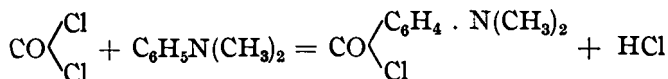
⁷ A. PERRET and PERROT, *Compt. rend.*, 1934, **199**, 955.

to give tetramethyl diamino benzophenone, or Michler's ketone¹:



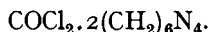
This is a crystalline substance, melting at 173° C., insoluble in water but soluble in the common organic solvents.

In presence of excess phosgene and heating to 50° C., *p*-dimethyl amino benzoyl chloride is formed:

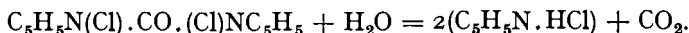


The reaction of phosgene with dimethylaniline when carried out in the presence of aluminium trichloride or zinc chloride² gives Crystal Violet.

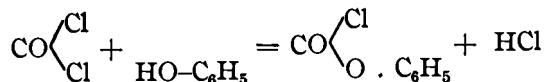
With hexamethylene tetramine, or urotropine, an addition compound of the following formula is obtained³:



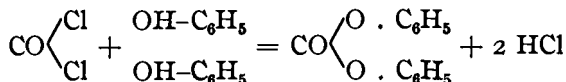
Phosgene reacts with pyridine forming a yellow crystalline substance of the formula⁴ $\text{C}_5\text{H}_5\text{N}(\text{Cl}) \cdot \text{CO} \cdot (\text{Cl})\text{NC}_5\text{H}_5$, which is decomposed by water with formation of carbon dioxide according to the equation:



The course of the reaction of phosgene with alcohols and phenols is also interesting. With phenols it can react in two ways, according to the proportions of the two substances present. With one molecule of phenol and one of phosgene, phenyl chloroformate is formed:



and with two molecules of phenol, phenyl carbonate:



Because of this peculiar behaviour, sodium phenate is used as neutralising agent for phosgene in filters. Alcohols react with

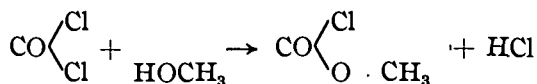
¹ MICHLER, *Ber.*, 1876, **9**, 400.

² HOFFMANN, *Ber.*, 1885, **18**, 769.

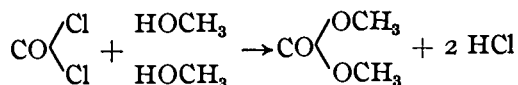
³ PUSCHIN and MITIC, *Ann.*, 1937, **532**, 300.

⁴ *D.R.P.*, 109933/1898; *Chem. Zentr.*, 1900, **II**, 460.

phosgene in a similar manner to phenols¹; for example, with one molecule of methyl alcohol, methyl chloroformate is formed (see p. 102) :

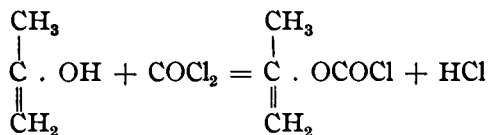


and with two molecules, methyl carbonate :



The latter is a colourless liquid of agreeable odour, boiling at 90.6° C. and with a density of 1.065 at 17° C. It melts after freezing at - 0.5° C. It is stable to water and is miscible with acids and alkalis. Though insoluble in water, it is soluble in most organic solvents. It is transformed into hexachloromethyl carbonate or triphosgene by chlorinating agents (see p. 115).

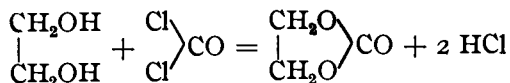
Phosgene, when left in contact with acetone for about half an hour and then distilled, forms isopropenyl chloroformate according to the following equation, in which acetone is represented by its enolic formula² :



Isopropenyl chloroformate is a liquid, b.p. 93° C. at 746 mm. density 1.103 at 20° C., having an irritating odour and powerful lachrymatory properties.

In presence of aluminium trichloride, phosgene reacts with ethylene dissolved in carbon disulphide, forming β -chloropropionic chloride as well as polymerisation products of ethylene.³

By the action of phosgene on ethylene glycol at ordinary temperatures, glycol carbonate is formed according to the equation :



Glycol carbonate is a liquid boiling at 238° C. at a pressure of 759 mm. and at 152° C. at 30 mm. It is soluble in hot water and volatile in steam, soluble in benzol, but in alcohol only with

¹ DUMAS, *Ann.*, 1835, **15**, 39; BÖSE, *Ann.*, 1880, **205**, 229.

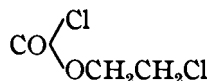
² M. MATUSZAK, *J. Am. Chem. Soc.*, 1934, **56**, 2007.

³ A. KLEBANSKY, *J. Obscei Khim.*, Ser. A., 1935, **5**, 535.

difficulty, soluble in petroleum ether and also in carbon disulphide.¹

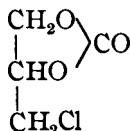
In the presence of substances like pyridine, which are capable of absorbing the hydrochloric acid formed in the reaction, phosgene reacts with glycerol to form glycerol carbonate.²

By bubbling gaseous phosgene through ethylene monochlorohydrin at 0° C., β -chloroethyl chloroformate is formed



a colourless, irritating liquid, b.p. 152.5° C. at 752 mm. Its density at 20° C. is 1.3825. Insoluble in cold water; hot water and alkaline solutions hydrolyse it.³

At ordinary temperatures gaseous phosgene reacts with α -monochlorohydrin, forming the corresponding carbonate⁴:



a colourless, heavy liquid, b.p. 156–157° C. at 10–12 mm. Density 1.55 at 20° C. Sparingly soluble in water.

In the dry state phosgene has little or no action on most of the metals,⁵ but in the presence of moisture it has a powerfully corrosive action because of the formation of hydrochloric acid. It is interesting to note Germann's⁶ findings with regard to its action on aluminium. According to this worker, phosgene reacts with aluminium because the aluminium trichloride which is formed is soluble in phosgene. Germann was also able to demonstrate that in the presence of aluminium trichloride those metals whose chlorides form soluble double salts with aluminium trichloride also react with phosgene.

At temperatures between 350° and 650° C. phosgene reacts with metallic oxides, forming carbon dioxide and the corresponding chlorides.⁷

Rubber is rapidly attacked by phosgene.

Phosgene is stored in cylinders like liquid chlorine. Iron containers which have been used for long periods for the storage

¹ VORLAENDER, *Ann.*, 1894, **280**, 186.

² *D.R.P.*, 252758.

³ NEKRASSOV and KOMISSAROV, *J. prakt. Chem.*, 1929, **123**, 160.

⁴ CONTARDI and ERCOLI, *Gazz. Chim. Ital.*, 1934, **64**, 522.

⁵ MELNIKOV, *J. Khim. Promiscl.*, 1932, **9**, 20.

⁶ A. GERMANN, *J. Phys. Chem.*, 1924, **28**, 879.

⁷ CHAUVENET, *Compt. rend.*, 1911, **152**, 89.

or transport of phosgene often contain a small quantity of a yellowish-red, heavy liquid which has been found to be iron pentacarbonyl (Paternò).

Activated carbon has a high sorptive capacity for phosgene.¹ Its capacity for absorbing such substances from their mixtures with air depends on various factors : the quality and the quantity of the carbon, the humidity, the concentration of the gas mixture, the velocity of the gas through the carbon, etc.

Concerning the influence of the humidity in the air and the carbon, the following results have been obtained² :

Phosgene in contact with carbon is hydrolysed by moisture with formation of hydrochloric acid.

The capacity for sorption at various phosgene concentrations, with dry carbon and dry air, follows Freundlich's equation.

With dry carbon and air containing an excessive humidity it is found that the carbon contains a hydrolysing layer, a hydrochloric-acid-absorbing layer and a phosgene-absorbing layer.

The time of resistance of the carbon increases up to a certain point with the moisture content of the carbon, since it dissolves the hydrochloric acid which forms. For small amounts of moisture the carbon layer first absorbs the hydrochloric acid, with high moisture content the phosgene first.

Dry active carbon has protracted resistance if the air is high in humidity and low in phosgene concentration.

The values of the sorptive powers for phosgene of activated carbon of various moisture-contents have been determined by Engelhardt.³

Materials which have been exposed to phosgene may be decontaminated by exposure to air and, if necessary, washing with a 10% solution of soda.⁴

The action of phosgene on foodstuffs differs according to whether foods of high water-content, like fresh meat, milk, beer, wine, etc., are being considered, or those poor in water like wheat, flour, coffee, etc. Those foodstuffs which are high in water-content absorb phosgene in large quantities and decompose it into hydrochloric acid and carbon dioxide. Fresh meat may remain edible according to the quantity of hydrochloric acid it contains. The drier foodstuffs can be made wholesome by exposure to a current of dry, warm air.⁵

¹ H. BUNBURY, *J. Chem. Soc.*, 1922, **121**, 1525.

² I. NIELSEN, *Z. ges. Schiess-Sprengstoffw.*, 1932, **27**, 134-284.

³ ENGELHARDT, *Z. Elektrochem.*, 1934, **40**, 833.

⁴ J. THOMANN, *Antigaz*, 1935, **9**, n. 3-4, 49.

⁵ W. PLÜCKER, *Z. Untersuch. Lebensmitt.*, 1934, **68**, 317.

The absorption of phosgene by fats and its energetic action on the membranes of the lungs is attributed by Kling¹ to a possible reaction between the gas and the sterol existing in the fat of the lungs. In fact, phosgene reacts with cholesterol forming the chloroformic acid ester, which forms crystals melting at 108° to 110° C.

According to the researches of Laqueur and Magnus,² the irritating power of phosgene on the mucous membranes and on the respiratory tract is very small, but the suffocating power great.

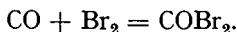
The mortality-product, according to Meyer,³ Hofmann⁴ and others is 450. This value is, however, considered to be too low; recent experiments⁵ have demonstrated that it ranges for cats from 900 (Flury) to the figure (obtained by exposure to low concentrations of 5-7 mg. per cu. m.) of 3,000 (Wirth). This fact demonstrates, according to Wirth, that phosgene at very low concentrations behaves like substances of the hydrocyanic acid type with regard to mortality-product. According to American experiments, the mortality-product of phosgene is higher even than those already cited, and for dogs actually reaches 5,000 for an exposure time of 10 minutes.⁶

2. Carbonyl Bromide. COBr₂. (M.Wt. 187.8)

Carbonyl bromide, or bromophosgene, was prepared for the first time by Emmerling⁷ by the oxidation of bromoform with potassium dichromate and sulphuric acid. Later it was also obtained by heating boron bromide to 150° C. with phosgene,⁸ but by this method a mixture with other compounds is obtained :



It is formed in small quantity also from carbon monoxide and bromine, in the presence of aluminium trichloride or by the action of the dark electric discharge⁹ :



The most suitable method for the preparation of carbonyl bromide consists in treating carbon tetrabromide with sulphuric

¹ A. KLING, *Compt. rend.*, 1933, **197**, 1782.

² LAQUEUR and MAGNUS, *Z. ges. exp. Med.*, 1921, **13**, 31.

³ MEYER, *Grundlagen des Luftschutzes*, Leipzig, 1935, 61.

⁴ HOFMANN, *Sitzb. preuss. Akad. Wiss.*, 1934, 447.

⁵ FLURY, *Gasschutz und Luftschutz*, 1932, 149; WIRTH, *ibid.*, 1936, 250.

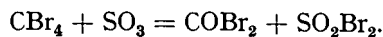
⁶ PRENTISS, *Chemicals in War*, New York, 1937.

⁷ EMMERLING, *Ber.*, 1880, **13**, 873.

⁸ BESSON, *Compt. rend.*, 1895, **120**, 191.

⁹ BARTAL, *Ann.*, 1906, **345**, 334.

acid in a similar manner to Erdmann's preparation of phosgene (see p. 60).



LABORATORY PREPARATION ¹

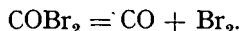
100 gm. carbon tetrabromide ² are placed in a small flask fitted with a reflux condenser and warmed until it is completely melted. Then 90 ml. concentrated sulphuric acid (S.G. 1.83) are allowed to enter very slowly in drops, and the whole heated to 150° to 170° C. At the end of the reaction the mass is distilled, and the distillate, which is brown in colour because of the presence of bromine, is purified by addition of mercury in small portions, shaking and freezing. A further purification is effected by adding powdered antimony in small portions. It is distilled under reduced pressure in an all-glass apparatus with glass-to-glass connections. The product obtained is kept over antimony or silver powder in a sealed vessel. Yield 44%.

PHYSICAL AND CHEMICAL PROPERTIES

A colourless, heavy liquid of characteristic odour perceptible at great dilutions. It boils at ordinary pressure at 64° to 65° C., with incipient decomposition.

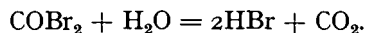
Specific gravity about 2.5 at 15° C.

Carbonyl bromide easily decomposes under the influence of light and heat, liberating bromine, according to the equation :



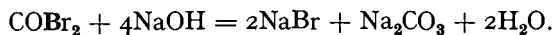
This decomposition is accelerated by the presence of extraneous organic substances.

It is hydrolysed by water :



This reaction, according to Schumacher, takes place more slowly than in the case of phosgene.

It reacts easily with bases, as, for example, with sodium hydroxide, to form sodium bromide and carbonate :



With dimethylaniline in presence of aluminium tribromide, a coloured substance of the Crystal Violet type is formed.

The vapour of carbonyl bromide attacks rubber, rendering it hard and brittle.

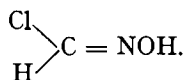
Its physiopathological action is very similar to that of phosgene.

¹SCHUMACHER, *Ber.*, 1928, **61**, 1671.

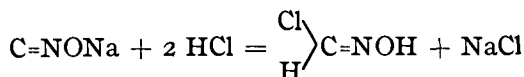
²A. BARTAL, *Chem. Ztg.*, 1905, **28**, 377.

3. Chloroformoxime.

(M.Wt. 79.4)



This substance was obtained for the first time by Nef ¹ in 1894 by the action of sodium fulminate on hydrochloric acid. It was prepared by Scholl ² in a similar manner :



LABORATORY PREPARATION

A solution of sodium fulminate cooled to 0° C. is allowed to drop into 150 ml. of an aqueous solution of hydrochloric acid (1 part water and 1 of conc. hydrochloric acid) also at 0° C. It is immediately extracted three times with ether and distilled (Nef).

PHYSICAL AND CHEMICAL PROPERTIES

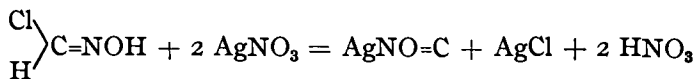
It is obtained in the form of crystalline needles. Its odour is similar to that of hydrocyanic acid.

It is stable at 0° C., almost insoluble in petroleum ether, slightly soluble in carbon disulphide and easily soluble in other organic solvents and in water. The aqueous solution decomposes in time.

Small quantities completely volatilise at the ordinary temperature. Large quantities decompose spontaneously with evolution of heat forming carbon monoxide and hydroxylamine hydrochloride (Nef).

Treated for an hour with concentrated hydrochloric acid, it decomposes with quantitative formation of hydroxylamine.

With silver nitrate it reacts according to the equation :



An aqueous solution of chloroformoxime reacts with sodium hydrate and with ammonia, forming metafulminuric acid ³; treated with ferric chloride it gives an intense red coloration.

It possesses lachrymatory and vesicant properties.

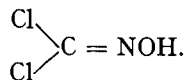
¹ NEF, *Ann.*, 1894, **280**, 307.

² SCHOLL, *Ber.*, 1894, **27**, 2819.

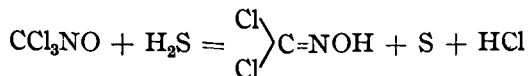
³ WIELAND, *Ber.*, 1909, **42**, 1350.

4. Dichloroformoxime.

(M.Wt. 113.9)



Dichloroformoxime, the oxime of carbonyl chloride, was prepared in 1929 by Prandtl and Sennewald¹ by the reduction of trichloro nitroso methane (see p. 164), with hydrogen sulphide according to the equation :



Instead of hydrogen sulphide, aluminium amalgam may be employed as reducing agent.

Dichloroformoxime, like the corresponding dibromoformoxime, can also be prepared by treating fulminic acid with chlorine in the cold.²

PREPARATION FROM TRICHLORONITROSOMETHANE (PRANDTL)

To a known quantity of trichloronitrosomethane is added a solution, saturated at ordinary temperature, of hydrogen sulphide in methyl alcohol (0.25 gm. H₂S in 10 ml. alcohol at 15° C.), 10 ml. being added for each gramme of trichloronitrosomethane. The mixture is allowed to stand for several hours in a closed vessel until the blue colour of the nitroso compound disappears. If excessive heating takes place during this time, the vessel should be occasionally cooled by immersion in cold water. At the end of the reaction the product is treated with water and filtered from sulphur. It is then extracted with ether, dried over calcium chloride and distilled under reduced pressure. The oxime distils between 50° and 70° C. at 20 mm. of mercury.

PREPARATION FROM MERCURY FULMINATE³

A current of chlorine is bubbled through a suspension of 38 gm. mercury fulminate in 500 ml. semi-normal hydrochloric acid which is meanwhile stirred for 1 to 2 hours. The product is twice extracted with ether, the solvent evaporated and the oily residue distilled under reduced pressure. At a pressure of 15 mm. the distillation commences at 23° C., and after the first fraction has come over, the thermometer rises to 30° C. and dichloroformoxime begins to crystallise in the condenser. This is then replaced by a receiver cooled in ice. Dichloroformoxime distils between 32° and 35° C. at 15 mm. Yield about 65%.

¹ PRANDTL and SENNEWALD, *Ber.*, 1929, **62**, 1766.

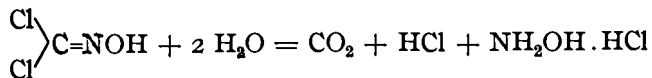
² BIRCKENBACH and SENNEWALD, *Ann.*, 1931, **489**, 18.

³ G. ENDRES, *Ber.*, 1932, **65**, 67.

PHYSICAL AND CHEMICAL PROPERTIES

Dichloroformoxime forms colourless, prismatic crystals melting at 39° to 40° C. Even at ordinary temperatures it has a high vapour pressure. It boils at normal pressure at 129° C. and at 28 mm. of mercury at 53° to 54° C. It has a penetrating, unpleasant odour.

It is a relatively stable substance, soluble in water and in the common organic solvents. Slow hydrolysis takes place in aqueous solution, according to the equation :

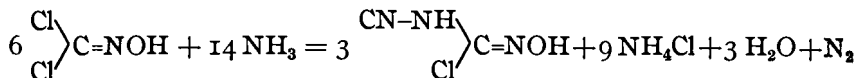


This hydrolysis is accelerated and becomes quantitative in presence of dilute acids.

On raising to its boiling point under reflux, dichloroformoxime gradually decomposes to give brown vapours ; cyanogen chloride and hypochlorous acid are formed in the decomposition.

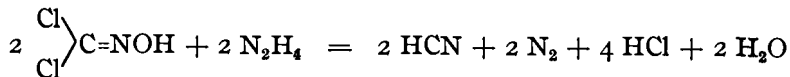
The alkaline hydroxides and carbonates react energetically with an aqueous solution of dichloroformoxime, and heat is evolved, while the solution turns yellow.

It reacts with ammonia even at the temperature of liquid air, forming ammonium chloride. By the action of aqueous ammonia on an ethereal solution of dichloroformoxime, cyanamide chloroformoxime is formed together with other products, according to the equation ¹ :

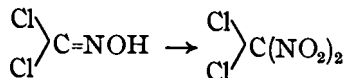


This substance forms colourless crystals melting at 168° C. ; it has no vesicant power.

By the action of hydrazine on an aqueous solution of dichloroformoxime, hydrocyanic acid is formed by the following equation :



With fuming nitric acid it is transformed into dichlorodinitromethane ² :



a liquid boiling at 40° C. at a pressure of 12 mm.³

¹ PRANDTL and DOLLFUS, *Ber.*, 1932, **65**, 755.

² BIRCKENBACH and SENNEWALD, *Ann.*, 1931, **489**, 21.

³ R. GOTTS and coll., *J. Chem. Soc.*, 1924, **125**, 442.

On treatment with copper acetate a small quantity of a tarry precipitate forms. Ferric chloride gives no colouration with dichloroformoxime, unlike chloroformoxime.

Dichloroformoxime, even when stored in sealed vessels of glass or quartz, decomposes at ordinary temperatures with formation of phosgene and separation of a liquid compound. The decomposition is practically complete in 3-4 weeks, but is influenced by humidity and temperature.¹ The vapour of dichloroformoxime attacks rubber and cork.

It has a violently irritant action on the mucous membrane of the nose and on the eyes. The vapour of this substance, even in very low concentrations, provokes lachrymation.

When it comes into contact with the skin it produces inflammation and blisters, which can be prevented by treating the affected part immediately with plenty of aqueous ammonia (Prandtl).

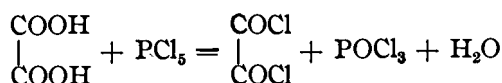
5. Oxalyl Chloride.

(M.Wt. 126.9)



Oxalyl chloride was prepared by Fauconnier² in 1892 by heating ethyl oxalate with phosphorus pentachloride. The product obtained in this way, however, is impure with phosphorus oxychloride.

It is obtained in better yield and greater purity by the action of phosphorus pentachloride on oxalic acid :



PREPARATION³

90 gm. anhydrous powdered oxalic acid are mixed with 400 gm. pulverised phosphorus pentachloride, cooling in ice. The mixture is allowed to stand for 2 or 3 days at the ordinary temperature until the mass is completely liquefied. It is then fractionally distilled; the portion distilling between 60° and 100° C. contains the oxalyl chloride. By repeated rectification it is obtained completely free from phosphorus oxychloride. Yield about 50%.

¹ PRANDTL and DOLLFUS, *Ber.*, 1932, **65**, 758.

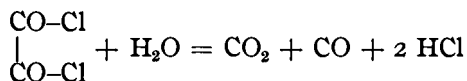
² FAUCCONNIER, *Compt. rend.*, 1892, **114**, 122.

³ STAUDINGER, *Ber.*, 1908, **41**, 3558.

PHYSICAL AND CHEMICAL PROPERTIES

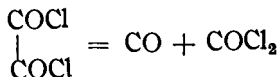
A colourless liquid, boiling at 64° C. It solidifies on cooling to -12° C. to a white crystalline mass, soluble in ether, chloroform, etc.

In contact with water or alkaline solutions it decomposes quantitatively according to the equation :



This reaction can be used for the quantitative determination of oxalyl chloride by measuring the volume of the carbon monoxide or by titrating the hydrochloric acid formed.

Like other derivatives of oxalic acid, heating splits off carbon monoxide. By passing oxalyl chloride vapour through a tube 1 m. long heated to 600° C. quantitative decomposition takes place :



Oxalyl chloride decomposes in a similar manner when exposed to ultra-violet radiation¹ or when heated in carbon disulphide solution with aluminium chloride.

It is stable to fuming sulphuric acid even when heated.

Oxalyl chloride reacts with organic compounds in various ways :

As an *acid chloride*, that is, retaining the grouping —CO—CO—, to form the corresponding ethers² from alcohols and the oxamides³ from amines.

Like *phosgene*, as in the decomposition by heat or in presence of aluminium chloride; thus it reacts with dimethylaniline forming Crystal Violet.⁴

As *chlorinating agent*, it chlorinates aldehydes and ketones⁵ and reacts with acids in the cold, though better on heating, to form the acid chlorides,⁶ etc.

By passing oxalyl chloride vapour through a solution of aniline, oxanilide is obtained in quantitative yield (Staudinger).

It does not react with zinc, mercury, silver or magnesium.

Oxalyl chloride vapours strongly attack the respiratory organs.

¹ K. KRAUSKOPF, *J. Am. Chem. Soc.*, 1936, **58**, 443.

² STAUDINGER, *Ber.*, 1908, **41**, 3565.

³ STOLLÉ, *Ber.*, 1913, **46**, 3915.

⁴ POSTOVSKY, *J. Khim. Promscl.*, 1927, **4**, 552.

⁵ STAUDINGER, *Ber.*, 1909, **42**, 3966.

⁶ ULICH, *J. Am. Chem. Soc.*, 1920, **42**, 604.

Analysis of the Acyl Halogen Compounds

DETECTION OF PHOSGENE

Phosgene may be recognised by its odour. The minimum concentration detectable by odour is 4 mgm. per cu. m. of air, according to Suchier.¹

By the use of chemical methods phosgene can also be detected by one of the usual tests for the hydrochloric acid formed by hydrolysis of the vapour.

Following are the methods usually adopted for detecting phosgene :

Method using Dimethyl Amino Benzaldehyde—Diphenylamine Paper. Phosgene, even if present in traces in the air, can be detected by means of papers prepared with dimethyl amino benzaldehyde and diphenylamine.

These papers are prepared by immersing strips of filter paper in a solution of 5 gm. *p*-dimethyl-amino-benzaldehyde and 5 gm. diphenylamine in 100 ml. ethyl alcohol and allowing them to dry in a dark place, or better still, according to Suchier, in an atmosphere of carbon dioxide. By exposing these papers, which are originally white or pale straw-yellow, to an atmosphere containing phosgene, an orange-yellow colouration is produced in a few seconds, the intensity of the colour varying with the concentration of phosgene. This change of colour is also observed in presence of chlorine or hydrochloric acid.

It is possible to detect phosgene at a concentration of 4 mgm. per cu. m. of air.²

The test-papers should be kept in a closed container filled with carbon dioxide and protected from light, as it seems that the colour changes merely by the action of sunlight.³

Method using Nitroso-dimethylaminophenol Paper. Two solutions are prepared in xylene :

(a) 0.1 gm. 1.3.6-nitroso-dimethylaminophenol in 50 ml. xylene.

(b) 0.25 gm. *m*-diethyl-aminophenol in 50 ml. xylene.

5 ml. solution (a) are mixed with 2 ml. solution (b) and strips of filter paper immersed in the mixture and allowed to dry.⁴ The paper should be damped with 50% alcohol just before use as the dry paper does not give the test. In the presence of phosgene the colour changes from white to green.

¹ SUCHIER, *Z. anal. Chem.*, 1929, **79**, 183.

² This test-paper was employed by Dubinin (*J. Prikl. Khim.*, 1931, 1109) to determine the duration of protection afforded by anti-gas filters against mixtures of air and phosgene.

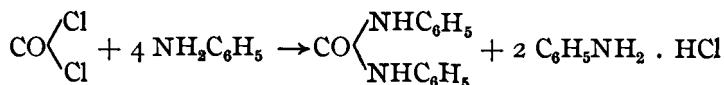
³ N. KOLOBAIEV, *Khimiya e Oborona.*, 1934, **10**, 12.

⁴ KRETOV, *J. Prikl. Khim.*, 1929, **2**, 483.

These papers are specific for phosgene¹ and are more sensitive than the dimethyl amino benzaldehyde papers. Sensitivity: 0.8 mgm. of phosgene per cu. m. of air.²

The two solutions (a) and (b) may be kept mixed for not more than 4 days.

*Kling and Schmutz's Method.*³ This method of detection depends on the ease with which the two chlorine atoms in phosgene react with the amino group of aniline:



This leads to the formation of symmetrical diphenylurea in the form of rhombic prisms,⁴ with a m.p. 236° C. This is insoluble in water. The reaction has the advantage of being specific for the CO group united to two chlorine atoms.

In practice, in order to detect phosgene mixed with air or other inert gas by this method, it is sufficient to bubble the gas mixture under test through a few ml. of water saturated with aniline in the cold (3 gm. aniline in 100 ml. water). A white crystalline precipitate forms which can be easily seen, and, if necessary, confirmed by microscopic examination (rhombic prisms) or by a determination of the melting point (236° C.).

According to Kling, by passing 5 litres of a gas mixture (phosgene and air) through aniline solution at a velocity of about 200 ml. a minute, it is possible to detect phosgene at a concentration of 40 mgm. per cu. m. of air.⁵

The sensitivity of this method of detection can be increased, according to Olsen,⁶ by employing an aqueous solution of aniline saturated with diphenylurea.

DETECTION OF PHOSGENE IN PRESENCE OF HALOGENS

If the phosgene is mixed with halogens, *e.g.*, chlorine or bromine, the latter may oxidise the aniline and so render the diphenylurea crystals impure. In this case it is necessary to pass the gas through a reagent which will remove them. This is carried out by inserting before the vessel containing the aniline a tube containing cotton wool soaked in a concentrated solution

¹ PANCENKO, *Metodi Issliedovanija i Khimiceskie Svoistva Otravljajuscik Vescestv*, MOSCOW, 1934, 91; STUDINGER, *Mitt. Lebensm. Hyg.*, 1936, 27, 12.

² J. THOMANN, *Schweiz. Apoth. Ztg.*, 1937, 75, 41.

³ KLING and SCHMUTZ, *Compt. rend.*, 1919, 168, 773.

⁴ MEZ, *Zeit. Krist.*, 35, 254.

⁵ This method was also recommended by GLASER and FRISCH, *Z. angew. Chem.*, 1928, 41, 264.

⁶ OLSEN and coll., *Ind. Eng. Chem. Anal. Ed.*, 1931, 3, 189.

of potassium iodide and allowed to dry. In this way the chlorine and bromine deposit iodine which remains in the cotton wool, while the phosgene passes on unaltered.

QUANTITATIVE DETERMINATION OF PHOSGENE IN AIR

*Kling and Schmutz's Method.*¹ This method depends on the reaction between phosgene and aniline, which has already been described.

In order to carry out this determination, a volume of 1–5 litres of the gas mixture to be examined is passed through a bubbler containing water saturated with aniline. With gas mixtures containing more than 2% phosgene it is necessary to use a second bubbler to absorb any slight traces of phosgene which may escape the first. The precipitate which forms is collected on a small disc of filter paper supported on a spiral of platinum wire in the neck of a funnel. It is washed four or five times with the smallest possible amount of water in order to remove the aniline and then dried in an oven at 50° to 60° C. for 2 hours so that the last traces of aniline are removed.

If the precipitate is large enough to be weighed (more than 10 mgm.), it is dissolved from the filter with boiling alcohol, collecting the filtrate in a tared platinum capsule. After evaporating the filtrate on a water bath, the residue is dried at 50° to 60° C. for 2 hours and weighed. The quantity of phosgene present in the volume of air taken is obtained by multiplying the weight of the precipitate by 0.467.

If, however, the precipitate of diphenylurea is too small to weigh accurately, it is converted to ammonia and determined colorimetrically by the Nessler method. In this procedure, the filter paper is removed from the funnel and placed in a small beaker ; 4 ml. pure sulphuric acid (66° Bé) are added, allowing this to flow slowly over the platinum spiral and through the funnel so as to wash off all traces of adherent precipitate. To the mixture obtained in this way 10 mgm. mercuric sulphate are added and the whole is then kept near boiling temperature for 2 hours. After allowing to cool, 20 ml. distilled water are added and the mixture is transferred to a 200-ml. flask containing 0.25 gm. sodium thiosulphate dissolved in 100 ml. water to remove the mercury. The beaker is washed with water which is added to the contents of the flask until the total volume is about 150 ml. and the ammonia determined in this.

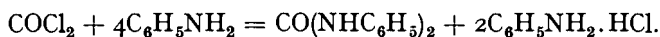
The authors recommend carrying out this determination in a

¹ A. KLING and R. SCHMUTZ, *Compt. rend.*, 1919, 168, 891.

small distillation apparatus (Aubin type) and liberating the ammonia by means of magnesium oxide. About 70 ml. liquid is distilled into 25 ml. water containing 1 ml. decinormal hydrochloric acid. The distillate is then made up to 100 ml. and the ammonia determined in it by adding a few drops of recently prepared Nessler reagent. A solution of ammonium chloride containing 0.324 gm. NH_4Cl per litre is used for comparison. 1 ml. of this solution corresponds to 0.3 mgm. COCl_2 .

This method of determination of phosgene with aniline gives results which are slightly low because the precipitate of diphenylurea is slightly soluble in water (5 mgm. in 100 ml. saturated aqueous aniline solution). According to Olsen,¹ more accurate results may be obtained by employing an aniline solution saturated with diphenylurea, prepared by passing phosgene into water saturated with aniline until a slight precipitate forms and filtering this off so as to obtain a clear liquid.

According to Vles,² instead of determining the diphenylurea gravimetrically, the aniline hydrochloride formed in the filtrate may be titrated :



*Kling and Schmutz's Method, Modified by Yant.*³ A known volume of the gas mixture to be examined is passed through a solution of aniline prepared in the following manner : an excess of aniline is placed in water contained in a flask which is then stoppered, and, after shaking, allowed to stand for about a week, shaking two or three times a day. Then phosgene is bubbled through the solution until a permanent precipitate of diphenylurea is obtained. A portion of the reagent is filtered through a Gooch crucible just before the test when the filtrate is ready for use.

Analytical procedure : After passing the desired volume of the gas mixture through two absorption bottles in series containing the aniline solution, the latter is allowed to stand for 2 hours and then filtered through a weighed Gooch. The precipitate which remains in the bubbler tubes is washed out with hot alcohol. The alcoholic solution obtained is evaporated almost to dryness in a small beaker on the water bath, then a few ml. of water added and the evaporation continued until at last there is no longer any odour of alcohol. This solution is filtered through the same Gooch and the entire precipitate washed with normal hydrochloric acid saturated with pure diphenylurea. Air is

¹ OLSEN, *loc. cit.*

² S. VLES, *Rec. trav. Chim.*, 1934, **53**, 961.

³ YANT and coll., *Ind. Eng. Chem.*, 1936, **28**, 20.

drawn through the precipitate for a few minutes and then it is dried at 70° to 80° C. to constant weight. The precipitate is then dissolved from the crucible by washing several times with boiling ethyl alcohol, the alcoholic solution being evaporated and then dried in an oven at 70° to 80° to constant weight. From this weight the quantity of phosgene in the gas mixture may be calculated.

For determining phosgene in the atmosphere after extinction of a fire by means of an extinguisher of the carbon tetrachloride type, Yant¹ has proposed the apparatus shown in Fig. 4. The

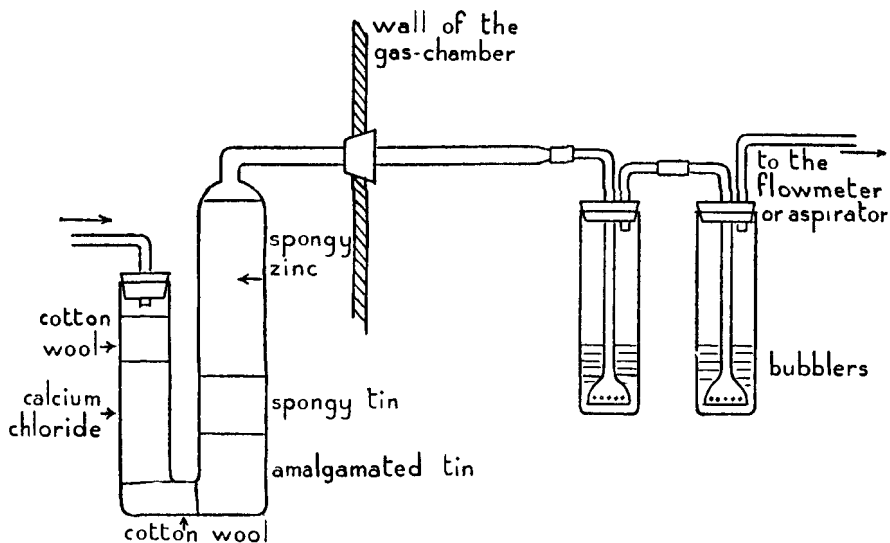


FIG. 4.

sample to be examined is passed first through a purifier consisting of a U tube of 5 cm. diameter with one arm 22 cm. long and the other 30 cm. This tube is filled as follows : in the more constricted part between the two arms a little cotton wool is placed, and over this, in the short arm of the tube, a layer 12 cm. thick of calcium chloride in small granules while over this again is 6 cm. cotton wool. In the long arm first a layer of spongy tin amalgam 10 cm. thick, then a layer 3 cm. thick of spongy tin, and finally a 15 cm. layer of zinc sponge, are introduced.

The gas mixture is passed at a velocity of 1 litre a minute through two bubblers containing 25 ml. of an aqueous solution of aniline prepared as described on p. 84.

Hydrochloric acid and chlorine do not interfere with the determination of phosgene by this method.

¹ YANT and coll., *loc. cit.*

*Delepine, Douris and Ville's Method.*¹ This method depends on the hydrolysis of phosgene by sodium hydroxide and the titration with silver nitrate of the hydrochloric acid formed.

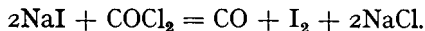
By means of an aspirator, a known volume of the gas mixture to be tested (2–5 litres in 4–10 minutes) is passed through 10 ml. of an aqueous alcoholic solution of soda prepared in the following way :

Sodium hydroxide, normal solution	10 ml.
95% alcohol	50 ml.
Made up with water to 100 ml.	

After the passage of the gas the liquid is evaporated in a platinum (or porcelain) capsule on the water bath to a volume of 2–3 ml. and then 2 drops of acetic acid are added and the evaporation continued almost to dryness. The residue is redissolved in 2–3 ml. water and again evaporated to dryness to decompose the sodium bicarbonate which is formed. The residue is once more dissolved in 2 ml. water, a drop of potassium chromate solution added and then titrated with N/40 silver nitrate. It is advisable to carry out a blank determination. The amount of phosgene present in the sample is calculated from the number of ml. of N/40 silver nitrate solution employed in titration.

This method can be improved, according to Matuszak,² by acidifying the alkaline solution with nitric acid and boiling in order to remove the carbon dioxide before neutralising and titrating. Also, according to the same author, in the case of the analysis of a gas mixture containing halogenated hydrocarbons, it is advisable to substitute an aqueous solution of sodium hydroxide. This absorbs the phosgene completely, is more stable and has the advantage of absorbing less of the halogenated hydrocarbons than the alcoholic solution.

The Sodium Iodide Method. The determination of phosgene by this method, due to the Chemisch-Technischen Reichsanstalt,³ is carried out by titrating the iodine liberated when a gas mixture containing phosgene but free from acid gases, reacts with a solution of sodium iodide in acetone. The reaction is as follows :



The gas mixture to be examined is passed through a gas pipette (see Fig. 5) of about 500 ml. capacity until the air in bulb *E* is completely replaced by gas. Taps *B* and *C* are closed, the bulb *D* is completely freed from the gas mixture and 25 ml. of a 2%

¹ DELEPINE, *Bull. soc. chim.*, 1920, [4] 27, 288.

² M. MATUSZAK, *Ind. Eng. Chem. Anal. Ed.*, 1934, 374.

³ *Jahresb. der Chem. Tech. Reichsanstalt.*, 5, 1926, 11, 20.

solution of sodium iodide in acetone are introduced into it. The tap *A* is then closed and the sodium iodide solution allowed to run down into the bulb *E* after which the liberated iodine is titrated with N/10 or N/100 sodium thiosulphate solution in presence of starch paste.

As the reaction between sodium iodide and phosgene proceeds quantitatively only in absence of water, the sodium iodide should be dissolved in acetone which has been dried for several days over calcium chloride.

According to Matuszak ¹ it is preferable to use potassium iodide rather than sodium iodide. (A saturated solution in acetone contains about 1.9% of potassium iodide.)

In order to determine phosgene in a gas mixture containing chlorine and hydrochloric acid by this method it is necessary to pass the gas mixture first through three U tubes. The first of these (that is, the one which the gas mixture first enters) contains calcium chloride, the second metallic antimony, and the third zinc dust.²

If Kölliker's ³ apparatus is used to determine phosgene in presence of hydrochloric acid, zinc dust cannot be used as it has too great a resistance. In this case the gas mixture to be tested is first passed through a wash bottle containing a sulphuric acid solution of silver sulphate (3 gm. in 100 ml. sulphuric acid of S.G. 1.84) and then through the acetone solution of sodium iodide.



FIG. 5.

DETERMINATION OF PHOSGENE IN INDUSTRIAL PRODUCTS

About 0.2 to 0.3 gm. phosgene is accurately weighed ⁴ in a glass bulb sealed in the flame. This bulb is then introduced into a bottle of 250 ml. capacity in which 150 ml. of an aqueous solution of aniline have previously been placed (26 gm. aniline in 1 litre of water).

The bottle is tightly closed and shaken so as to break the bulb. A flocculent white precipitate of diphenylurea forms immediately. After allowing to stand for 2 hours, the liquid is

¹ M. MATUSZAK, *Ind. Eng. Chem. Anal. Ed.*, 1934, 457.

² BIELASKY, *Z. angew. Chem.*, 1934, 47, 149.

³ KÖLLIKER, *Die Chemische Fabrik.*, 1932, 5, 1; 1933, 6, 299.

⁴ KLING and SCHMUTZ, *Compt. rend.*, 1919, 168, 774.

filtered through a Gooch crucible, preventing the broken pieces of the bulb from entering the crucible as far as possible, washed with 50–60 ml. cold water, dried at 70° C. and weighed.

As this precipitate always contains some fragments of glass it is advisable to redissolve the diphenylurea from the crucible with boiling acetone, then drying the crucible in an oven, heating it to 400° C. and reweighing. The difference between the two weights, multiplied by 0.467, gives the weight of phosgene contained in the gas sample employed.

It should be noted that the reaction between phosgene and aniline takes place only in presence of an excess of the latter.

DETERMINATION OF FREE CHLORINE IN PHOSGENE

In the synthetic preparation of phosgene from chlorine and carbon monoxide, some free chlorine may remain dissolved in the phosgene.

Various methods have been suggested for the determination of free chlorine in phosgene. The most commonly used method is that of Delepine,¹ in which 500 ml. dilute sodium hydroxide solution are placed in a vessel closed with a ground-glass stopper, and a glass bulb containing a weighed quantity of the phosgene to be tested is dropped in. The bulb is broken, and after a few minutes an alkaline solution of sodium iodide is added and the liquid acidified. If the phosgene contains any free chlorine, this liberates an equivalent quantity of iodine which is titrated with thiosulphate solution.²

Recently Nenitzescu³ has described another method which allows the simultaneous determination of chlorine and phosgene. It is based on the separation of chlorine from phosgene by passage of the mixed gas through metallic antimony and absorption of the phosgene by an alcoholic potash solution.

The mixture to be examined is passed through a U tube filled with metallic antimony and previously weighed (about 20 gm.). The antimony absorbs the chlorine quantitatively without reacting with the phosgene. The residual gas is passed into a Fresenius potash bulb containing 20 ml. 10% alcoholic potash, and connected by glass to glass joints with the U tube. The bulb tube of the Fresenius potash bulb is connected with a tube filled with silica gel to catch solvent vapour. The absorption of phosgene in the alcoholic solution of potash is complete. In order

¹ DELEPINE, *Bull. soc. chim., loc. cit.*

² This method was also recommended by A. E. KRETOV, *J. Prikl. Khim.*, 1929, **2**, 483.

³ NENITZESCU and PANA, *Bull. soc. chim. Rom.*, 1933, **15**, 45.

to displace all the phosgene from the apparatus a current of dry air is passed through at the end of the test.

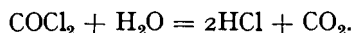
The difference in the weights of the antimony U tube before and after the absorption gives the amount of chlorine present in the gas mixture.

The difference in the weights of the potash bulb and the silica gel before and after the absorption gives the amount of phosgene in the sample.

DETERMINATION OF HYDROCHLORIC ACID IN PHOSGENE

In the synthetic preparation of phosgene, if the carbon monoxide is not perfectly dry or contains a trace of hydrogen, hydrochloric acid will be formed and will remain dissolved in the phosgene.

If this acid is present in considerable quantity, it may be determined quantitatively by the gas-volumetric method of Berthelot,¹ which consists in absorbing the hydrochloric acid in a small quantity of water. Measurement of the volume of the phosgene before and after the treatment with water gives the quantity of hydrochloric acid present in the sample. In this determination the hydrolysing action of the water on the phosgene may be neglected, for the small quantity of phosgene hydrolysed produces an equal volume of carbon dioxide.



It is, of course, obvious that this method cannot be employed for the determination of small amounts of hydrochloric acid in phosgene.

In this case, use is made of the property of very dilute, gaseous hydrochloric acid of reacting with mercuric cyanide, liberating an equivalent quantity of hydrocyanic acid, while phosgene does not do this.²

Delepine and Monnot³ have worked out the following method from this difference in behaviour⁴ :

5 gm. powdered mercuric cyanide and a glass bulb containing the phosgene are placed in a perfectly dry flask of 500-1,000 ml. capacity which is closed by a ground-glass stopper carrying two tubes, one leading to the bottom of the flask and the other projecting only a few cm. inside. The flask is evacuated by means of a mercury pump, the glass bulb is broken and the whole allowed to stand for 12-14 hours. At the end of this period, a

¹ BERTHELOT, *Bull. soc. chim.*, 1870, [2] **13**, 15.

² BERTHELOT and GAUDECHON, *Compt. rend.*, 1913, **156**, 1990.

³ DELEPINE and MONNOT, *Bull. soc. chim.*, 1920, [4] **27**, 292.

⁴ This method was also recommended by KRETOV, *loc. cit.*

vessel containing about 50 ml. 2 N. sodium hydroxide solution is connected between the pump and the flask, while the other tube from the flask is connected with a wash-bottle containing concentrated sulphuric acid. Dry air is slowly allowed to enter the flask to bring the pressure to atmospheric and then a current of air drawn through the whole apparatus at a speed of about twenty-five bubbles a minute for 8-9 hours. In this way the hydrocyanic acid and the phosgene are swept out in the air stream and bubbled through the alkaline solution which completely absorbs them.

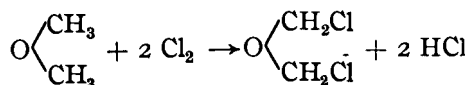
At the end of the operation, 5 ml. of ammonia are added to the alkaline solution and 1 ml. 10% sodium iodide solution, after which the hydrocyanic acid present is titrated with N/20 silver nitrate solution. The number of ml. of silver nitrate employed, multiplied by 0.00365 gives the amount of hydrochloric acid present in the sample of phosgene employed.

CHAPTER VII

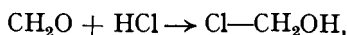
HALOGENATED ETHERS

THE war gases belonging to this group may be considered as true ethers whose alkyl groups have a hydrogen substituted by a halogen atom.

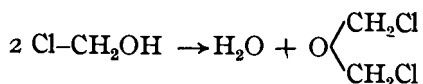
These compounds are usually prepared by the direct action of the halogens on the corresponding ethers. For example, from methyl ether and chlorine, dichloromethyl ether is obtained¹:



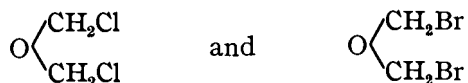
However, in the particular case of the halogenated methyl ethers it is preferable, especially in their industrial manufacture, to commence with formaldehyde (or its polymers) and the hydrogen halide. In this case the reaction takes place in two stages; for instance, in the preparation of dichloromethyl ether, chloromethyl alcohol is formed first:



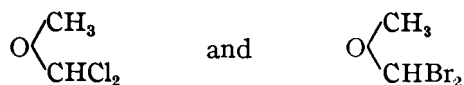
and then this in the presence of dehydrating agents is transformed into symmetrical dichloromethyl ether:



The compounds of this group furnish a typical example of the influence exercised by the symmetry of the molecular structure on the aggressive power of the substances. It has been found experimentally that while the symmetrical ethers



have a powerful irritant effect, the asymmetric ethers, which contain the same number of halogen atoms in the molecule

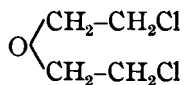


¹ MORESCHI, *Atti accad. Lincei.*, **28** (I), 277.

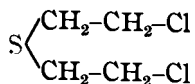
have no offensive properties whatever. Dichloromethyl and dibromomethyl ethers were used as war gases in the war of 1914-18, especially by the Germans.

These substances have a high mortality-product, but very low irritant power. According to some workers, they act on the semicircular canals and produce staggering and vertigo; they have been, therefore, named "*labyrinthic gases*." They have had little success, however, more particularly because of their great sensitivity to the hydrolysing action of water.

Since the war various higher homologues of dichloromethyl ether have been prepared and studied from the point of view of their offensive power. Among these, symmetrical dichloroethyl ether¹ may be mentioned:



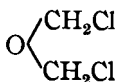
This has a structure analogous to dichloroethyl thioether, or mustard gas, which has the formula:



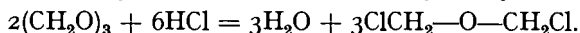
Dichloroethyl ether, though very similar in its chemical properties to the sulphur derivative, has very different physio-pathological properties, being destitute of vesicant power.² According to Hofmann³ this lack of vesicant power must be attributed to the fact that dichloroethyl ether, unlike dichloroethyl sulphide, cannot penetrate the epidermis.

1. Dichloromethyl Ether

(M.Wt. 114.76)



Dichloromethyl ether is employed in war both as a war gas and as a solvent for other war gases (ethyl dichloroarsine, dichloroethyl sulphide, etc.). It was obtained for the first time by Regnault⁴ who brought about the reaction between methyl ether and chlorine by means of diffused sunlight. It is better prepared, however, by the action of hydrochloric acid on trioxymethylene⁵:



¹ KAMM and VALDO, *J. Am. Chem. Soc.*, 1921, **43**, 2223.

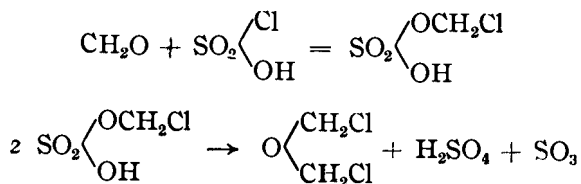
² CRETCHER and PITTENGER, *J. Am. Chem. Soc.*, 1925, **47**, 1173.

³ HOFMANN, *Sitzb. preuss. Akad. Wiss.*, 1934, 447.

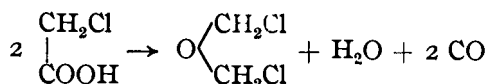
⁴ REGNAULT, *Ann.*, **1**, 292 (3rd edn.).

⁵ TISCENKO, *J. Rusk. Fis. Khim. Ob.*, 1887, **19**, 473; GRASSI and MASELLI, *Gazz. Chim. Ital.*, 1898, **28** (II), 477; LITTELSCHIED, *Ann.*, 1904, **334**, I.

The water produced in this reaction causes the gradual decomposition of the ether as it is formed, and for this reason, chlorosulphonic acid¹ is used to replace the hydrochloric acid. The reaction is then as follows :



It is also obtained by passing the vapour of monochloroacetic acid through a red-hot tube² :



and also by the action of phosphorus trichloride on trioxymethylene in presence of zinc chloride.³

LABORATORY PREPARATION⁴

30 gm. paraformaldehyde and 40 gm. 80% sulphuric acid (S.G. 1.73) are weighed accurately into a flask of about 200 ml. capacity, which is closed by a two-holed stopper. Through one of the holes in the stopper a tap-funnel passes, and through the other a glass tube to lead the gas formed in the reaction to an aspirator. While agitating and cooling to 0° C. by means of a freezing mixture, 175 gm. chlorosulphonic acid are added drop by drop from the tap-funnel, care being taken that the temperature does not rise above 10° C. At the end of the reaction (1-2 hours) the product is poured into a dry separatory funnel, the upper oily layer separated and washed with dilute sodium carbonate, and finally distilled at normal pressure. Yield 80-90%.

INDUSTRIAL MANUFACTURE

In Germany,⁵ this ether was manufactured by the same method as that described above for the laboratory preparation : by the action of chlorosulphonic acid on formaldehyde. The reaction is carried out in iron vessels of 5 cu. m. capacity (about 1,100 gals.), coated internally with acid-resistant material and fitted with stirring apparatus and lead cooling coils.

¹ FUCHS and KATSCHER, *Ber.*, 1927, **60**, 2288.

² GRASSI and CRISTALDI, *Gazz. Chim. Ital.*, 1897, **27** (II), 502.

³ DESCUDÉ, *Bull. soc. chim.*, 1906, **35**, 198.

⁴ STEPHEN, *J. Chem. Soc.*, 1920, **117**, 510.

⁵ NORRIS, *J. Ind. Eng. Chem.*, 1919, **11**, 819.

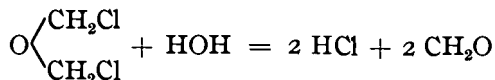
1,200 kg. 70% sulphuric acid are first placed in the vessel and then 600 kg. paraformaldehyde added, continuous agitation being maintained and the temperature being kept at 5° to 10° C. The operation takes between 3 and 4 hours. Then 2,400 kg. chlorosulphonic acid are added very slowly (in about 48 hours), the agitation being continued and the temperature kept between 10° and 15° C. At the end of the reaction the liquid forms two layers, the lower consisting of sulphuric acid and the upper the ether. Yield 90–95%.

PHYSICAL AND CHEMICAL PROPERTIES

Dichloromethyl ether is a colourless liquid, boiling at 105° C. at ordinary pressure, and at 46° C. at 100 mm. mercury. The specific gravity is 1.315 at 20° C. The volatility is fairly high; at 20° C. it is 180,000 mgm. per cu. m. The density in the gaseous state is 3.9.

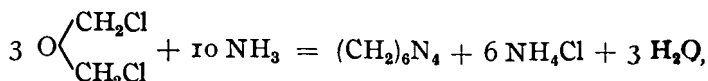
It is insoluble in water, but dissolves in methyl and ethyl alcohols with evolution of heat. It is also soluble in acetone and in benzene (Tiscenko).

Heat decomposes it into hydrochloric acid and trioxymethylene. With water it forms formaldehyde and hydrochloric acid, even at ordinary temperatures¹:



The hydrolysis of 1 gm. of dichloromethyl ether, dissolved in ethyl ether in contact with 250 ml. water and agitated, is complete in 95 minutes.²

Even atmospheric humidity causes this decomposition. Alkalies and carbonates react with dichloromethyl ether forming the chloride of the metal and formaldehyde. Ammonia, however, forms hexamethylene tetramine,³



identifiable by its reaction with bromine water to give a yellow, crystalline substance which is a bromo-derivative of hexamethylene tetramine.

Dichloromethyl ether is converted by chlorine under the action of sunlight⁴ into:

¹ SONAY, *Bull. acad. roy. belg.*, 1894, [3] **26**, 629; *Ber.*, 1894, **27**, 336; LITTSCHNEID, *Ann.*, 1901, **316**, 177.

² STRAUS, *Ber.*, 1909, **42**, 2168; STRAUS and THIEL, *Ann.*, 1936, **525**, 161.

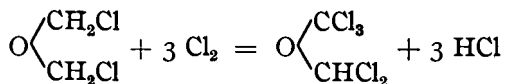
³ BROCHET, *Ann. chim. phys.*, 1897, [7] **10**, 299.

⁴ SONAY, *Bull. acad. roy. belg.*, 1894, [3] **26**, 629.

(1) *Trichloromethyl ether*: a lachrymatory liquid with a pungent odour, boiling at 130° to 132° C. Density, 1.5066 at 10° C. Insoluble in water, soluble in alcohol, ether, benzene, carbon disulphide.

(2) *Tetrachloromethyl ether*: a liquid which fumes in air and has a more pungent odour than the preceding compound. B.p. 145° C. and density 1.6537 at 18° C. Unlike trichloromethyl ether, it is insoluble in alcohol, ether, benzene and carbon disulphide. By long boiling with water it decomposes into formic acid and crystals of hexachloroethane.

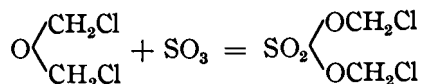
When exposed to ultra-violet rays and heated to about 80° C., the chlorination of dichloromethyl ether proceeds differently and pentachloromethyl ether is formed.¹



This is a colourless liquid with an odour of phosgene and b.p. 158.5° to 159.5° C. Density 1.64 at 20° C. It is stable to cold water, but on heating with water it decomposes to form hexachloroethane, hydrochloric acid, carbon monoxide and carbon dioxide. With an aqueous solution of aniline it forms diphenyl urea.

Further chlorination causes the substitution of all the six hydrogen atoms by chlorine and hexachloromethyl ether is obtained. This is a liquid with an odour of phosgene, having a boiling point of 98° C., at which temperature it partially decomposes into phosgene and carbon tetrachloride. Density 1.538 at 18° C.

By bubbling a current of sulphur trioxide through dichloromethyl ether cooled in ice and salt, besides monochloromethyl chlorosulphonate, dichloromethyl sulphate is formed as follows²:

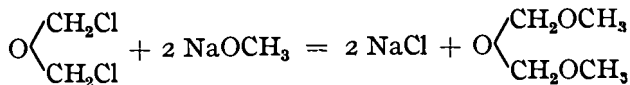


Dichloromethyl sulphate is a colourless, odourless liquid with b.p. 96° to 97° C. at 14 mm. of mercury and density 1.60 at ordinary temperatures. It is readily soluble in the common organic solvents, though only slightly in petroleum ether. Unlike dimethyl sulphate, it has no physiopathological action.

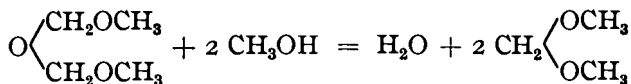
¹ RABCEWICZ and CHWALINSKY, *Roczniki Chem.*, 1930, **10**, 686.

² FUCHS and KATSCHEK, *Ber.*, 1927, **60**, 2295.

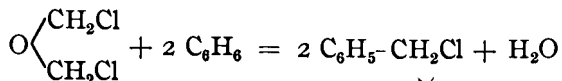
Boiling with sodium methylate converts dichloromethyl ether into dimethyl methylal.¹ The reaction apparently takes place in two phases : dimethoxy methyl ether is first formed,



and then this in presence of excess alcohol is decomposed into water and dimethyl methylal :



In the presence of dehydrating agents such as zinc chloride, dichloromethyl ether reacts with benzene to form benzyl chloride :



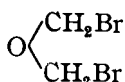
In the absence of moisture most metals are unattacked by dichloromethyl ether.

It finds application in the refining of lubricating oils.²

The lower limit of irritation, that is, the minimum concentration which produces lachrymation, is 14 mgm. per cu. m. The limit of insupportability is 40 mgm. per cu. m. The product of mortality is 500 (Müller).

2. Dibromomethyl Ether

(M.Wt. 204)



Like the preceding substance, dibromomethyl ether found a very limited application in the war of 1914-18. It was used both as a war gas and as a solvent for the chloroarsines.

It is easily obtained by the reaction of trioxymethylene with hydrobromic acid.³

LABORATORY PREPARATION⁴

30 gm. paraformaldehyde are mixed with 80 gm. sulphuric acid (S.G. 1.84) in a 300-ml. flask. The mixture is cooled in ice and

¹ SONAY, *loc. cit.* ; LITTELSCHIED and THIMME, *Ann.*, 1904, **334**, 13.

² *French Pat.* 748925/1933.

³ TISCHENKO, *J. Rusk. Fis. Khim. Ob.*, 1914, **46**, 705.

⁴ STEPHEN, *J. Chem. Soc.*, 1920, **117**, 510.

agitated continuously while 155 gm. finely powdered sodium bromide are added in small portions. By heating at the boiling point for 10 minutes, the paraformaldehyde dissolves and an oily layer of dibromomethyl ether floats to the top. This is separated and purified by distillation.

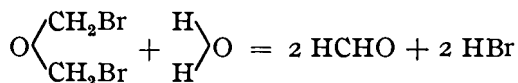
INDUSTRIAL MANUFACTURE ¹

Six parts by weight of 70% sulphuric acid and 1 part of paraformaldehyde are placed in an acid-resistant vessel, the mixture stirred and cooled so as to keep the internal temperature at 15° to 20° C., and then ammonium bromide added slowly in amount about 10% in excess of that calculated. At the end of this operation, which requires about 48 hours, the mass is stirred for a further 5-10 hours at 30° C. and then the dichloromethyl ether separated. Yield 70-80%.

PHYSICAL AND CHEMICAL PROPERTIES

Dibromomethyl ether is a colourless liquid boiling at 154° to 155° C. and solidifying at - 34° C.² Its specific gravity is very high (2.2) and its volatility at 20° C. is 21,100 mgm. per cu. m. It has a coefficient of expansion of 0.0009. Though insoluble in cold water, it dissolves easily in ether, benzene and acetone.

Water decomposes dibromomethyl ether with formation of hydrobromic acid and formaldehyde, according to the equation ³ :



This decomposition takes place more rapidly in the presence of alkaline solutions (Tiscenko).

By heating with trioxymethylene and water to 140°, methyl bromide and formic acid are formed. It reacts energetically with alcohols and phenols, but is not attacked at ordinary temperatures by concentrated sulphuric acid (Henry).

The minimum concentration capable of provoking lachrymation is 20 mgm. per cu. m. of air. The limit of insupportability is 50 mgm. per cu. m., and the product of mortality is 400, which is greater than that of phosgene (Müller).

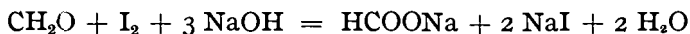
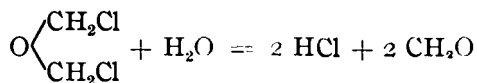
¹ NORRIS, *loc. cit.*

² HENRY, *Bull. acad. roy. belg.* 1894, [3] 26, 615; *Ber.*, 1894, 27, 336.

³ P. RONA, *Z. ges. exp. Med.*, 1921, 13, 16.

Analysis of the Halogenated Ethers**QUANTITATIVE DETERMINATION OF DICHLOROMETHYL ETHER**

The ether is decomposed by water and the formaldehyde obtained is titrated iodometrically :



0.1-0.15 gm. of the substance to be examined is weighed into a glass bulb which is then placed in a flask containing 100 ml. water. After closing the flask with a stopper the bulb is broken, and the whole allowed to stand for 2-3 hours. 40 ml. N/10 iodine solution are added from a burette and then an aqueous solution of sodium hydroxide until the liquid is a clear yellow in colour. After allowing to stand for 15-20 minutes, 2 N hydrochloric acid is added to acidify and to liberate the iodine, and excess of the latter is then titrated with decinormal sodium thiosulphate in presence of starch.

1 ml. N/10 iodine solution corresponds to 0.002874 gm. dichloromethyl ether.

CHAPTER VIII

HALOGENATED ESTERS OF ORGANIC ACIDS

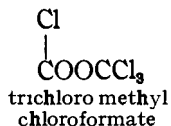
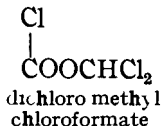
(A) THE METHYL FORMATE GROUP

THESE compounds form an important group of war gases. They were employed alone and also mixed with other war gases : phosgene, chloropicrin, diphenyl-chloroarsine, etc.

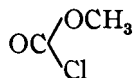
Structurally, these compounds may be considered as derivatives of methyl chloroformate :



by the substitution of successive hydrogen atoms of the methyl group by chlorine atoms :



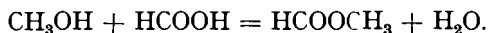
or else as derivatives of the methyl ester of monochlorocarbonic acid :



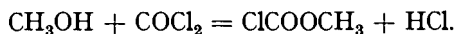
by the progressive substitution of the hydrogen atoms of the methyl group by chlorine atoms.

They may be prepared by two different methods :

(1) *From Methyl Formate.*¹ By chlorination of methyl formate, obtained from methyl alcohol and formic acid according to the equation :



(2) *From Methyl Chloroformate.*² By chlorination of methyl chloroformate, obtained from methyl alcohol and phosgene.



The compounds of this group have a characteristic penetrating

¹ HENTSCHEL, *J. prakt. Chem.*, 1887, **36**, 99.

² KLING and coll., *Compt. rend.*, 1919, **169**, 1046.

odour and also lachrymatory and asphyxiating properties. It is noteworthy that as the number of chlorine atoms in the methyl group increases, the lachrymatory power diminishes and the toxic and asphyxiating power increases. For example, while the first member of the series, monochloromethyl chloroformate, has an essentially irritant action, the last member, trichloromethyl chloroformate, is essentially toxic and asphyxiating, its lachrymatory action being weak.

Since the war other analogous compounds have been studied, especially from the physiopathological point of view. Such are methyl cyanoformate¹ and ethyl cyanoformate, which are powerful lachrymators but are easily decomposed by the action of water.

Recently some fluorine derivatives have also been prepared² :

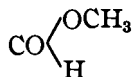
Methyl fluoroformate, obtained by the action of thallium fluoride on methyl chloroformate, is a liquid boiling at 40° C. Density 1.06 at 33° C.

Ethyl fluoroformate, obtained by the action of thallium fluoride on ethyl chloroformate, is a liquid with b.p. 57° C. and density 1.11 at 33° C.

Both of these compounds are powerful lachrymators.

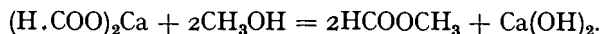
1. Methyl Formate

(M.Wt. 60)



Methyl formate was prepared in 1835 by Dumas³ by the action of dimethyl sulphate on sodium formate. Later, it was obtained in better yield by the reaction between magnesium or aluminium methylate and trioxymethylene.⁴

It is usually prepared, however, by the action of methyl alcohol saturated with hydrochloric acid on calcium formate⁵ :



LABORATORY PREPARATION⁵

100 gm. calcium formate are placed in a flask fitted with a tap-funnel and a reflux condenser, the latter being connected with a well-cooled descending condenser. 130 ml. methyl alcohol recently saturated with hydrochloric acid (that is, containing

¹ WEDDIGE, *J. prakt. Chem.*, 1874, **10**, 197.

² H. GOSWAMI and SARKAR, *J. Indian Chem. Soc.*, 1933, **10**, 537.

³ DUMAS, *Ann.*, 1835, **15**, 35.

⁴ TISCHENKO, *J. Rusk. Fis. Khim. Ob.*, 1906, **38**, 355; *Chem. Zentr.*, 1906 (II), 1309.

⁵ VOLHARD, *Ann.*, 1875, **176**, 133.

about 40% HCl) are placed in the tap-funnel and allowed to flow slowly on to the calcium formate, shaking at intervals. When all the alcohol has been added, the mixture is allowed to stand for a short time and then distilled from a water-bath. The distillate is washed many times in a tap-funnel with a little saturated sodium chloride solution, neutralising with sodium carbonate. In order to separate water formed in the reaction and the excess methyl alcohol, the product is placed in a flask fitted with a reflux condenser and allowed to stand with a large quantity of fused and finely ground calcium chloride for 24 hours. The methyl formate and calcium chloride form a crystalline compound, and when this is distilled on a water-bath pure methyl formate comes over.

INDUSTRIAL MANUFACTURE

95% formic acid and methyl alcohol without any condensing agent are placed in an iron still, coated internally with acid-resistant material and fitted with copper coils, and heated. The product obtained is distilled and the distillate then redistilled.

PHYSICAL AND CHEMICAL PROPERTIES

Methyl formate is a liquid boiling at 31.7°C . at 760 mm. pressure. It has a S.G. of 0.9745 at 20°C . and on cooling in liquid air solidifies at -100°C .

Water or alkaline solutions saponify it. The velocity of this decomposition has been determined in the presence of various saponifying agents.¹

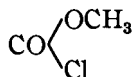
By exposure to ultra-violet light it decomposes, forming carbon dioxide, hydrogen and methane.²

Chlorine aided by sunlight transforms it into various chlorine derivatives: mono-, di and trichloromethyl chloroformates (see p. 104).

It has been used as a solvent for cellulose acetate. In chemical warfare it is interesting as an intermediate for the manufacture of its chloro- derivatives.

2. Methyl Chloroformate

(M.Wt. 94.5)

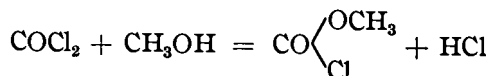


This compound may be obtained by directly chlorinating

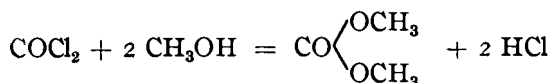
¹ HOLMES, *J. Am. Chem. Soc.*, 1916, **38**, 110; SKRABAL, *Monatsh.*, 1917, **38**, 191.

² BERTHELOT, *Compt. rend.*, 1911, **153**, 384.

methyl formate, but it is more commonly prepared from the reaction between phosgene and methyl alcohol ¹ :



During this reaction it is necessary to keep the temperature rather low and to be careful to maintain the phosgene always in excess. This is in order to prevent the following reaction from taking place and methyl carbonate from being formed :



This is a colourless liquid, boiling at normal pressure at 90.6° C. M.p. 0.5° C. Density at 17° C. is 1.065. Insoluble in water ; soluble in alcohol, ether, etc. Its aggressive power is less than that of methyl chloroformate. By chlorination, hexachloromethyl carbonate is formed, also known as "triphosgene" (see p. 115).

LABORATORY PREPARATION ²

A small quantity, about 10 ml., of methyl chloroformate is placed in a flask fitted with a tap-funnel, a tube to introduce the phosgene and an exit tube, and after cooling to 0° C. a current of chlorine-free phosgene is bubbled in. Methyl alcohol is added from the tap-funnel, after a time, in volume about one-third of that of the liquid in the flask, this addition being made all at once. The addition of a fresh quantity of methyl alcohol is made when it is obvious that the phosgene is no longer being absorbed. The total quantity of methanol used should preferably not exceed 150 ml.

As soon as the reaction is complete, the product is transferred to a separatory funnel containing cold water. The oily, colourless, heavy layer which separates from the aqueous layer is washed twice with cold water, dried over calcium chloride and fractionally distilled from a water-bath. The fraction passing over between 69° and 72° C. is collected. Yield about 70% of theory.³

INDUSTRIAL MANUFACTURE

In the French method the reaction between methanol and phosgene takes place in large vessels fitted with agitators and cooled externally. The hydrochloric acid which forms is rapidly

¹ DUMAS, *Ann.*, 1835, **15**, 39.

² KLEPL, *J. prakt. Chem.*, 1882, **26**, 448 ; HENTSCHEL, *Ber.*, 1885, **18**, 1177.

³ STOLZENBERG, *Darstellungsvorschriften für Ultrazifite*, Hamburg, 1930, 42.

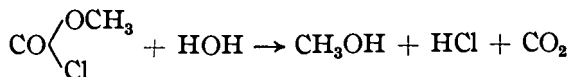
removed either by bubbling a stream of indifferent gas through the liquid, or by adding calcium carbonate.

In the German plants, however, methyl chloroformate was made by first introducing into the reaction vessels, which were of cast iron lined internally with lead and of about 3 cu. m. capacity (about 660 gallons), a small quantity of the ester and then liquid phosgene and anhydrous methanol in small portions, with stirring. The temperature was regulated during the reaction so that it did not rise above 0° C. Yield about 80% of theory.

PHYSICAL AND CHEMICAL PROPERTIES

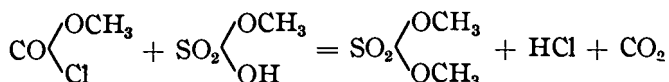
Methyl chloroformate is a clear liquid which boils at ordinary pressure at 71.4° C. The specific gravity at 15° C. is 1.23; the vapour density is 3.9 (air = 1).

It is fairly stable to cold water,¹ but is decomposed by hot water to form methanol, hydrochloric acid and carbon dioxide²:



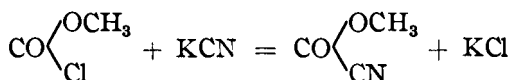
Methyl chloroformate does not liberate iodine from sodium iodide, nor bromine from lithium bromide.³

By the action of methyl chloroformate on methyl sulphuric acid, dimethyl sulphate is formed in good yield⁴:



Chlorosulphonic acid also reacts with methyl chloroformate⁵ to give a good yield of methyl chlorosulphonate (see p. 266).

Methyl chloroformate, when dissolved in methanol and treated with hot potassium or sodium cyanide, reacts according to the following equation⁶:



forming methyl cyanoformate. This is a colourless liquid with an ethereal odour boiling at 100° C. at ordinary pressure. S.G. about 1. Soluble in alcohol, ether and other organic solvents.

¹ VLES, *Rec. trav. chim.*, 1934, **53**, 964.

² RÖSE, *Ann.*, 1880, **205**, 229.

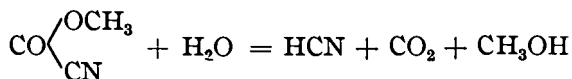
³ A. PERRET, *Bull. soc. chim.*, 1936, 958.

⁴ M. KRAFT and LJUTKINA, *J. Obscei Khim.*, Ser. A., 1931, **63**, 190.

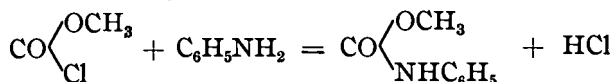
⁵ M. KRAFT and ALEXEJEV, *J. Obscei Khim.*, Ser. A., 1932, **64**, 726.

⁶ WEDDIGE, *J. prakt. Chem.*, 1874, **10**, 197.

Water and alkalis decompose it, forming hydrocyanic acid, carbon dioxide and methyl alcohol ¹ :



With aniline, methyl chloroformate reacts as follows ² :



This reaction forms the basis of a method for the quantitative determination of methyl chloroformate which consists essentially in treating the substance to be tested with aniline solution and titrating the hydrochloric acid formed. In this case it is not possible to determine the carbamic ester formed gravimetrically (as in the phosgene estimation), for it is very soluble in water.³

Though methyl chloroformate is a powerful lachrymator, it was not used alone as a war gas.

Because of its strongly irritant properties, it has been used in insecticidal preparations: "Zyklon A," which is a mixture of 90% of methyl cyanoformate and 10% of methyl chloroformate, and "Zyklon B," a mixture of liquid hydrocyanic acid and irritant chlorinated and brominated compounds.⁴

3. Mono-, di- and tri-chloromethyl Chloroformates

These compounds were prepared by Hentschel in 1887 ⁵ by the action of chlorine on methyl chloroformate.

During the war of 1914-18 they were employed as war gases, especially :

The mixture of monochloromethyl chloroformate with dichloromethyl chloroformate, used in 1915 by the Germans under the name of "*K-Stoff*," and later also by the Allies, especially the French, by whom it was called "*Palite*."

Trichloromethyl chloroformate, used almost exclusively by the Germans, under the name of "*Perstoff*" (Meyer).

The manufacture of these substances was carried out by the formate method or the chloroformate method, as mentioned on p. 99. The method of chlorination in each of these is similar and requires a suitable source of light. Many experiments on this subject have indicated that the Osram $\frac{1}{2}$ -watt arc lamp and the mercury vapour lamp are suitable light sources, and the

¹ NEF, *Ann.*, 1897, **287**, 290.

² WILM and WISCHIN, *Ann.*, 1868, **147**, 157.

³ VLES, *Rec. trav. chim.*, 1934, **53**, 964.

⁴ FRICKINGER, *Gase in der Schädlingsbekämpfung*, Berlin, 1933, 27.

⁵ HENTSCHEL, *J. prakt. Chem.*, 1887, **36**, 99.

latter is to be preferred owing to its light being rich in ultraviolet radiation.¹

By this means a mixture of the three chloro-derivatives is generally obtained, and these may be separated by fractional distillation :

Monochloro-derivative	.	b.p. 106.5° to 107° C.
Dichloro-derivative	. .	b.p. 110° to 111° C.
Trichloro-derivative	. .	b.p. 127.5° to 128° C.

Separation of the mono- and dichloro-derivatives is difficult because of the closeness of their boiling points, but the trichloro-compound is very easily separated from the mono- and dichloro-compounds.

LABORATORY PREPARATION

*Various Chloro-derivatives.*² 100 gm. methyl formate are placed in a 250 ml. flask fitted with a reflux condenser and a glass inlet tube for chlorine, and the whole weighed. The contents of the flask are heated to boiling and then a current of chlorine introduced, exposing the reacting substances to direct sunlight as far as possible, or to the light from a 500-watt lamp. By properly regulating the temperature and the addition of the chlorine and occasionally weighing the flask and its contents it is possible to obtain any of the chloro-derivatives. The reaction-product is fractionally distilled under reduced pressure.

*Trichloromethyl Chloroformate.*³ 100 ml. of methyl formate are placed in a flask connected by a ground-glass joint with a condenser containing ice and salt. From the commencement the flask is exposed to a 500-watt lamp, and the current of chlorine then started and maintained at a very low speed in the early phase, so that the temperature is maintained at 30° C. As the reaction proceeds the rate of addition of the chlorine is gradually increased, so that the temperature finally reaches about 90° C. The chlorination is complete after about 30 hours.

The product obtained is distilled under reduced pressure in an all-glass apparatus provided with a fractionating column and a condenser. The middle fraction, boiling between 50.0° and 50.4° C. at 48 mm., is collected in a receiver containing calcium chloride. In order to purify the product it is redistilled. Yield about 70% of theoretical.⁴

¹ GRIGNARD, *Compt. rend.*, 1919, **169**, 1074; A. KLING and coll., *Compt. rend.*, 1919, **169**, 1046.

² HENTSCHEL, *J. prakt. Chem.*, 1887, **36**, 213-305; FLORENTIN, *Bull. soc. chim.*, 1920, **27**, 97; BARTHELEMY, *Rev. prod. chim.*, 1922, **25**, 685.

³ RAMSPERGER and WADDINGTON, *J. Am. Chem. Soc.*, 1933, **55**, 214.

⁴ STOLZENBERG, *op. cit.*

INDUSTRIAL MANUFACTURE

During the war of 1914-18 both of the methods described were used—the formate method and the chloroformate method.

The Formate Method. This method was used in the Bayer plants in Germany. It was very costly, chiefly because concentrated formic acid was needed for the preparation of the formate.

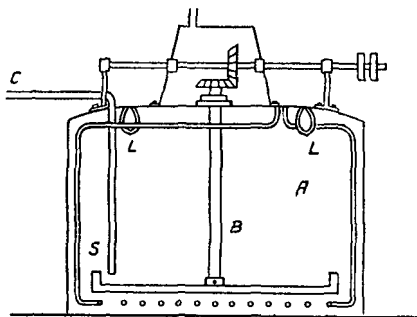


FIG. 6.

The methyl formate was obtained as described on page 101, and was chlorinated in special vessels *A* (Fig. 6), 2-3 m. in diameter and 1.5 m. in height, fitted with an agitator *B*. These vessels were of cast iron, lined with lead, or often enamelled. The gaseous chlorine was led

in at the bottom of the vessel through the pipe *C* and the reaction accelerated by employing eight Osram lamps (*L*) of 4,000 candle-power, placed in the upper part of the vessel. The heating of the reaction-mass is carried out by means of steam coils or by the electrical resistances, *S*.

In order to obtain the less highly chlorinated products the reaction is suitably regulated and lamps of a lower intensity employed. By chlorinating more vigorously, however, and using a mercury-vapour lamp it is very easy to obtain the trichloro-compound.

After the chlorination the product is distilled in special vessels

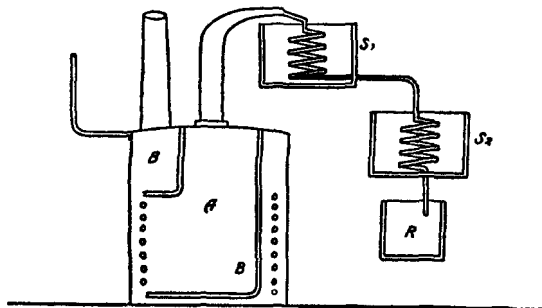


FIG. 7.

lined with porcelain (Fig. 7) heated by the coils *B*. The fraction boiling at lower temperatures is condensed in *S*₁ (cooled by

water) and S_2 (cooled by ice), and then collected in the receiver *R*. The more highly chlorinated product remains in *A*.

The Chloroformate Method. This method is less expensive and more suited to large-scale manufacture than the preceding. It was used in Germany by the Hoechst works and later also in France.

The chlorination of the chloroformate, obtained by the method given on p. 102, was carried out like that of methyl formate, in lead-lined or enamelled vessels. The lids of these vessels were also enamelled and carried eight Osram lamps protected by glass bells. The chlorine was introduced through eight pipes.

According to Grignard, the chlorination must commence in the gaseous phase, and so the methyl chloroformate is first heated in such a way as to produce a slight pressure, then the lamps switched on and the chlorine then introduced at such a rate as to prevent the reaction from being violent. The product may be rectified as described in the preceding method.

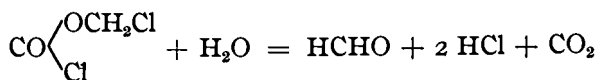
PHYSICAL AND CHEMICAL PROPERTIES

The chloro-derivatives of methyl chloroformate are all colourless liquids at ordinary temperatures, have boiling points close together and dissolve easily in organic solvents. All are hydrolysed by water even at ordinary temperatures and react readily with various compounds.

(a) MONOCHLOROMETHYL CHLOROFORMATE (M.Wt. 128.9) ClCOOCH₂Cl.

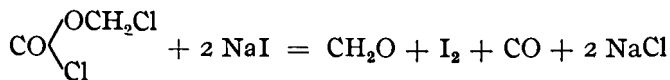
This is a mobile, colourless liquid with an irritating odour, which boils at 106.5° to 107° C. at ordinary pressure and at 52.5° to 53° C. at 100 mm. of mercury. It has a S.G. of 1.465 at 15° C., while its vapour density is 4.5 (air = 1). The vapour tension at 10° C. is 3.6 mm. and at 20° C. 5.6 mm.

Monochloromethyl chloroformate is hydrolysed by water at ordinary temperatures; this decomposition takes place more rapidly and completely by the action of hot water or in the presence of alkali. Formaldehyde, hydrochloric acid and carbon dioxide are formed:



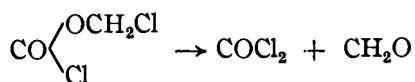
This behaviour of the monochloro-derivative is applied in the identification and quantitative determination in air of the industrial product (see pp. 123, 124).

Monochloromethyl chloroformate, like phosgene, liberates iodine from sodium iodide, but the reaction is not quantitative, proceeding only to about 70% completion.¹

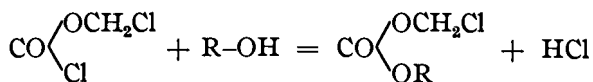


Like methyl chloroformate, but unlike the di- and tri-chloro-derivatives, it does not liberate bromine from lithium bromide.

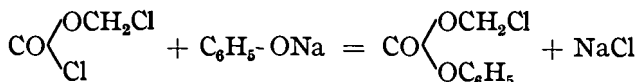
Ferric chloride and anhydrous aluminium chloride decompose chloromethyl chloroformate even in the cold, while on heating to about 70° C. the reaction is more rapid,² phosgene being formed.



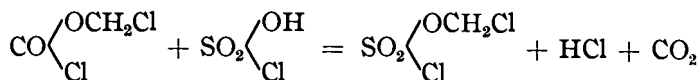
Alcohols react energetically, giving hydrochloric acid and the corresponding monochloromethyl carbonate :



With sodium phenate, reaction takes place at the ordinary temperature with formation of sodium chloride and phenyl monochloromethyl carbonate :



Monochloromethyl chloroformate, unlike methyl chloroformate, reacts with difficulty with chlorosulphonic acid, forming monochloromethyl chlorosulphonate only after boiling on the water bath for 4 hours³ :



This is a colourless liquid, boiling at 49° to 50° C. at a pressure of 14 mm. of mercury ; its S.G. is 1.63 at room temperature. It has powerful irritant properties.⁴

By the action of methyl sulphuric acid on monochloromethyl

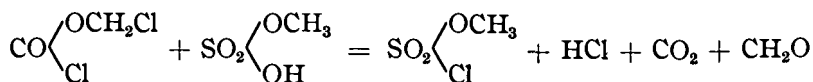
¹ A. PERRET, *Bull. soc. chim.*, 1936, 957.

² A. KLING and D. FLORENTIN, *Compt. rend.*, 1919, 169, 1166.

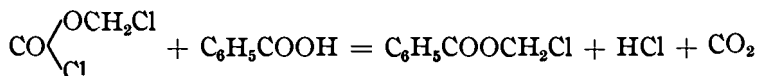
³ M. KRAFT and ALEXEJEV, *J. Obscei Khim.*, Ser. A., 1932, 64, 726.

⁴ FUCHS and KATSCHER, *Ber.*, 1927, 60, 2292.

chloroformate, methyl chlorosulphonate is formed (see p. 266), according to the following (Kraft) :



Monochloromethyl chloroformate also reacts with benzoic acid, forming monochloromethyl benzoate (Kraft) :



The toxicity of monochloromethyl monochloroformate is relatively slight. Its lachrymatory power is, however, considerable ; the minimum concentration capable of producing lachrymation is 2 mgm. per cu. m. of air. The limit of insupportability is 50 mgm. per cu. m. of air (Flury).¹

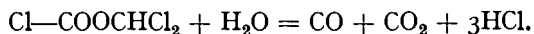
(b) DICHLOROMETHYL CHLOROFORMATE (M.Wt. 163.4)
Cl.CO.OCHCl₂.

Colourless liquid, boiling at 110° to 111° C. at 760 mm., and at 54° to 55° C. at a pressure of 100 mm. of mercury. Its S.G. is 1.56 at 15° C., and its vapour density is 5.7 (air = 1).

The vapour tension varies with the temperature as shown in the following table :

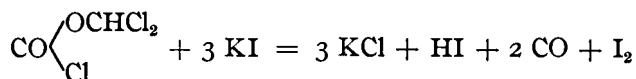
TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
10	3.6
20	5
30	6

This compound in contact with water decomposes as follows :



The hydrolysis proceeds fairly rapidly, even in the cold, but is much accelerated by heating and even more so by addition of alkali.

Dichloromethyl chloroformate reacts with cold potassium iodide, liberating iodine :

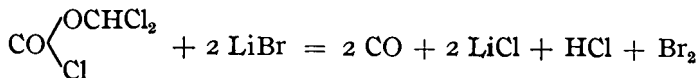


In this reaction carbon monoxide is evolved quantitatively.²

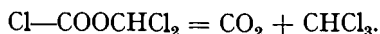
¹ FLURY, *Z. ges. exp. Med.*, 1921, **13**, 567.

² A. PERRET and J. BIECHLER, *Compt. rend.*, 1936, 86.

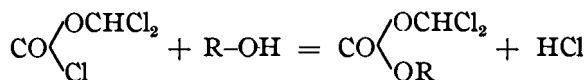
The dichloro-compound reacts with lithium bromide (unlike the monochloro-derivative) ¹ :



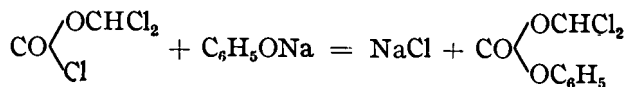
Ferric chloride and anhydrous aluminium chloride decompose dichloromethyl chloroformate slowly at ordinary temperatures and rapidly at 80° C., forming a mixture of carbon dioxide and chloroform ² :



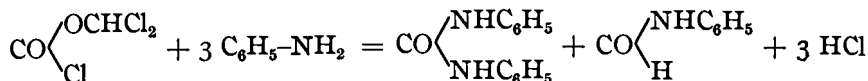
Like the preceding compound, it reacts with alcohols, forming hydrochloric acid and the corresponding dichloromethyl carbonate :



and with sodium phenate forming sodium chloride and phenyl dichloromethyl carbonate :



Aniline in aqueous or benzene solution reacts with dichloromethyl chloroformate to give diphenylurea and formanilide according to the equation :



Dichloromethyl chloroformate is less irritant than the preceding compound, but more toxic. Its limit of insupportability is 75 cu. mm. per cu. m. (Flury).

(c) TRICHLOROMETHYL CHLOROFORMATE (M.Wt. 197.85)
Cl.CO.OCCl₃.

Colourless mobile liquid with an irritating odour slightly reminiscent of phosgene. It is also known as "*Diphosgene*."

At ordinary pressure it boils at 127.5° to 128° C. and at a pressure of 18 mm. at 41° C. It solidifies at -57° C. Its S.G. is 1.65 at 15° C. and its vapour density 6.9 (air = 1). Its refractive index at 22° C. is 1.45664.

¹ A. PERRET, *Bull. soc. chim.*, 1936, 350.

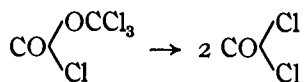
² A. KLING and D. FLORENTIN, *loc. cit.*; GRIGNARD, RIVAT, etc., *Compt. rend.*, 1919, 169, 1074, 1143.

The variation of vapour tension with temperature is as follows (Herbst) :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
0	3
10	5
20	10.3
30	16.3

It dissolves in benzene and in many other organic solvents. At the ordinary temperature it dissolves in 24 parts by weight of phosgene.

On heating this compound it decomposes, forming phosgene according to the equation ¹ :



This decomposition takes place also at ordinary temperatures when trichloromethyl chloroformate comes into contact with substances having a porous structure such as activated carbon, or with iron oxide,² etc.

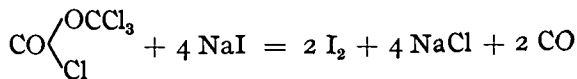
Trichloromethyl chloroformate reacts with cold water very slowly, but hot water or alkalis accelerate this, hydrochloric acid and carbon dioxide being formed :



By heating to boiling with alkali carbonates it decomposes to form sodium chloride and carbon dioxide :

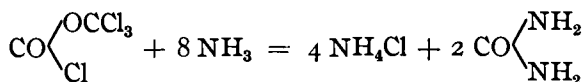


With sodium iodide in acetone solution it reacts rapidly and quantitatively as follows :



The reaction with lithium bromide is similar.³

Ammonia reacts vigorously, forming urea and ammonium chloride :

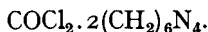


¹ CAHOURS, *Ann. chim. phys.*, 1847, 352 ; HENTSCHEL, *J. prakt. Chem.*, 1887, 36, 99, 209 ; RAMSPERGER, *J. Am. Chem. Soc.*, 1933, 55, 214.

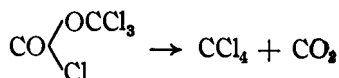
² H. P. HOOD and H. MURDOCH, *J. Phys. Chem.*, 1919, 23, 498.

³ A. PERRET, *Bull. soc. chim.*, 1936, 350.

With hexamethylene tetramine it reacts, like phosgene, to form an addition product of the formula ¹ :

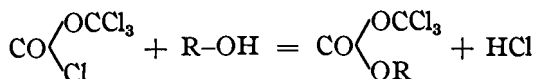


Ferric chloride and anhydrous aluminium chloride decompose trichloromethyl chloroformate into carbon tetrachloride and carbon dioxide ² :

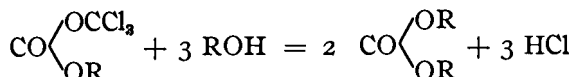


Trichloromethyl chloroformate does not react with concentrated hydrochloric acid.

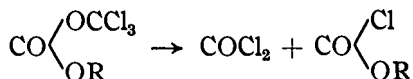
With alcohols it reacts similarly to the other members of this group to form the corresponding trichloromethyl carbonate :



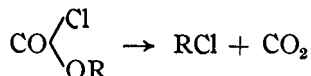
However, if the alcohol is in excess and the reaction proceeds in the cold, its course is different ³ :



The nature of the alcohol also affects the nature of the products formed. Thus with most primary alcohols the reaction described above takes place, but if there are present in the molecule of the primary alcohol radicles of high molecular weight, partial decomposition of the carbonate takes place with formation of phosgene and the corresponding chlorocarbonic ester, as follows ⁴ :



With secondary alcohols the reaction proceeds similarly, but with tertiary alcohols a further decomposition of the chlorocarbonic ester formed takes place and carbon dioxide is evolved and the corresponding alkyl chloride is formed :



With excess of aniline in aqueous or benzene solution trichloromethyl chloroformate reacts like phosgene, being

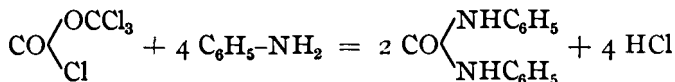
¹ PUSCHIN and MITIC, *Ann.*, 1937, **532**, 300.

² KLING and coll., *loc. cit.*

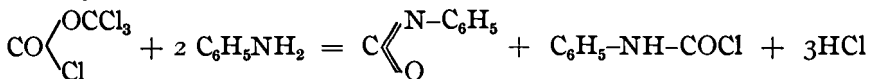
³ NEKRASSOV and MELNIKOV, *J. prakt. Chem.*, 1930, **126**, 81.

⁴ NEKRASSOV and MELNIKOV, *J. Rusk. Fis. Khim. Obsc.*, 1930, **62**, 631, 1545.

quantitatively transformed into symmetrical diphenylurea or carbanilide ¹ :

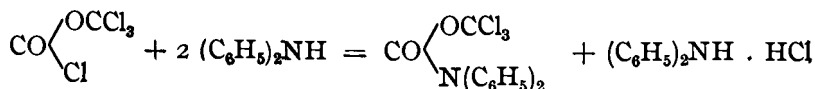


If, however, there is insufficient aniline, a mixture of phenyl isocyanate and anilido-formyl chloride is formed :



With dimethyl aniline in presence of aluminium trichloride or zinc chloride, Crystal Violet is formed.²

By the action of trichloromethyl chloroformate on diphenylamine, trichloromethyl N-diphenyl urethane results, together with a small quantity of tetraphenylurea ³ :

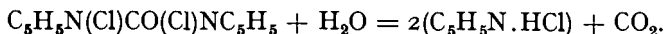


This urethane forms white crystals, melting at 61° C., which on heating to 200° to 250° C. decompose forming phosgene and diphenyl carbamic chloride. Cold water decomposes it into diphenylamine, hydrochloric acid and carbon dioxide.

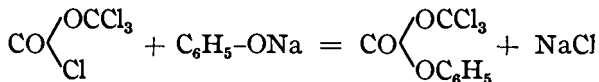
Trichloromethyl chloroformate reacts with pyridine, forming a yellow crystalline substance of the formula ⁴ :



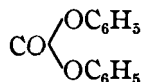
which decomposes by the action of water with evolution of carbon dioxide :



Like the preceding compound, trichloro methyl chloroformate reacts with sodium phenate, forming sodium chloride and phenyl trichloromethyl carbonate :



In presence of an excess of the phenate the reaction proceeds further, diphenyl carbonate being formed ⁵ :



¹ HENTSCHEL, *J. prakt. Chem.*, 1887, **36**, 310.

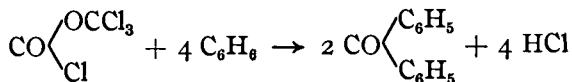
² HÖCHST FARB. W., *D.R.P.* 34607.

³ N. MELNIKOV and VINOKUROV, *J. Obscei Khim.*, Ser. A., 1932, **64**, 484.

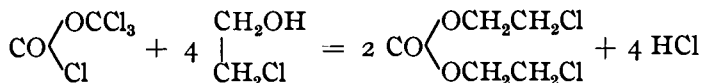
⁴ *D.R.P.* 109933/1898.

⁵ N. MELNIKOV, *J. prakt. Chem.*, 1930, **128**, 233.

It also reacts with benzene to form benzophenone :



By heating under reflux with ethylene chlorohydrin, dichloroethyl carbonate is formed ¹ :



This is a colourless liquid, boiling at ordinary pressure at 240° C. with partial decomposition and at a pressure of 8 mm. at 115° C. Its specific gravity at 20° C. is 1.3506. It is insoluble in water, volatile in steam, and is slowly hydrolysed by alkalis.

Trichloromethyl chloroformate in the pure state has no corrosive action on iron, and so may be loaded directly into projectiles of this material.

It is completely retained by filters of activated carbon.²

The action of trichloromethyl chloroformate on foodstuffs varies according to whether these are high in water content, like fresh meat, milk, wine, or beer, or low in water content, like grain, flour, coffee, etc. The water-rich foods absorb large quantities of trichloromethyl chloroformate, which then decomposes into hydrochloric acid and carbon dioxide, so that their edibility depends upon the quantity of hydrochloric acid which they have absorbed. The drier foods can be purified,³ as in the case of phosgene, by exposure to a current of warm, dry air.

Trichloromethyl chloroformate is less irritant than the other members of this group. The minimum concentration causing irritation is 5 mgm. per cu. m. of air (Müller). The limit of insupportability is 40 mgm. per cu. m. The toxicity is about equal to that of phosgene, and, according to Prentiss, it is probable that this is not a specific property of trichloromethyl chloroformate, but is due to the phosgene into which it decomposes in contact with the tissues of the human body.

The mortality-product is 500 according to Flury, but this value must be considered too low, as in the case of phosgene. According to American experiments on dogs,⁴ the mortality-product of trichloromethyl chloroformate for 10 minutes' exposure is ten times as great—about 5,000.

¹ NEKRASSOV, *J. prakt. Chem.*, 1929, **123**, 160.

² M. DUBININ and coll., *J. Prikl. Khim.*, 1931, **4**, 1100.

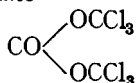
³ W. PLÜCKER, *Z. Untersuch. Lebensmitt.*, 1934, **68**, 317.

⁴ PRENTISS, *Chemicals in War*, New York, 1937.

Statistics based on data obtained during the war of 1914-18 show that trichloromethyl chloroformate is a war gas which when used in projectiles produces a large number of deaths.

4. Hexachloromethyl Carbonate

(M.Wt. 296.7)



This compound, also known as "*Triphosgene*," was prepared for the first time by Councler ¹ in 1880, by the chlorination of methyl carbonate.

It is obtained as a by-product in the preparation of trichloromethyl chloroformate when methyl chloroformate which is impure with dimethyl carbonate is employed.

LABORATORY PREPARATION

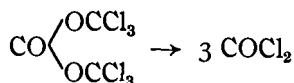
Hexachloromethyl carbonate is prepared, according to Councler, by passing dry chlorine through dimethyl carbonate exposed to direct sunlight. After some days' chlorination colourless crystals separate. When the whole mass has become solid, a current of dry carbon dioxide is passed through to remove the chlorine and hydrochloric acid present.

The product obtained is dried on filter paper, washed many times with a little absolute ether and dried *in vacuo* over sulphuric acid.

PHYSICAL AND CHEMICAL PROPERTIES

White crystals, melting at 78° to 79° C. It has an odour of phosgene and boils at ordinary pressure at 205° to 206° C. with partial decomposition. S.G. about 2. Soluble in benzene, carbon tetrachloride, ether, etc.

On heating near its boiling point at ordinary pressures, it decomposes to form phosgene and diphosgene, which further decomposes into phosgene. The reaction of decomposition is thus ²:



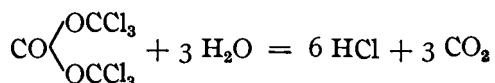
The presence of catalysts such as ferric chloride facilitates this decomposition.

Cold water reacts very slowly with hexachloromethyl carbonate,

¹ COUNCLER, *Ber.*, 1880, **13**, 1698.

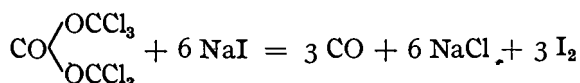
² HOOD and MURDOCH, *J. Phys. Chem.*, 1919, **23**, 509.

though hot water decomposes it rapidly with formation of carbon dioxide and hydrochloric acid :



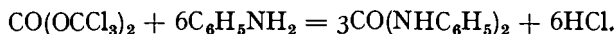
Aqueous solutions of the alkali hydroxides decompose hexachloromethyl carbonate, forming the corresponding carbonates and chlorides.

It reacts with sodium iodide and with lithium bromide in the same manner as trichloromethyl chloroformate, liberating iodine and bromine respectively. All the six chlorine atoms take part in this reaction,¹ which is as follows :



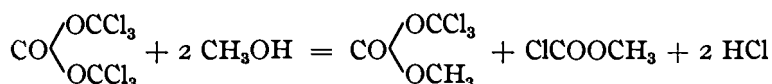
About 80% of the theoretical iodine is actually liberated.²

It reacts with aqueous aniline forming diphenyl urea³ :



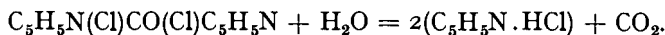
With sodium phenate, phenyl carbonate is formed (Grignard).

Methanol forms trichloromethyl carbonate and methyl chloroformate⁴ :



In presence of excess methanol, the trichloromethyl carbonate is converted into methyl carbonate and methyl chloroformate, so that the final product of the reaction with excess methanol present is methyl carbonate.

It reacts with pyridine in the same manner as phosgene, forming a yellow crystalline substance of the formula⁵ $\text{C}_5\text{H}_5\text{N}(\text{Cl})\text{CO}(\text{Cl})\text{C}_5\text{H}_5\text{N}$, which decomposes by the action of water according to the equation :



It has no corrosive action on metals.

The physiopathological action of this compound is similar to that of phosgene.

¹ A. PERRET and coll., *Bull. soc. chim.*, 1936, 958.

² PERRET, *Compt. rend.*, 1936, 203, 84.

³ GRIGNARD and coll., *Ann. chim.*, 1919, 12, 229.

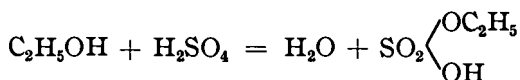
⁴ W. NEKRASSOV and MELNIKOV, *J. prakt. Chem.*, 1930, 126, 81.

⁵ V. HEYDEN, *D.R.P.* 109933; *Chem. Zentr.*, 1900 (II), 460.

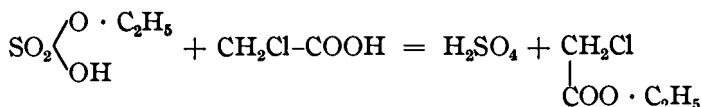
(B) THE ETHYL ACETATE GROUP

The halogen derivatives of ethyl acetate are compounds which have been known for some time and are used nowadays for organic syntheses both in the laboratory and in industry. They have a powerful action on the eyes and were used as war gases in the war of 1914-18.

They are commonly prepared by the esterification of ethyl alcohol by the corresponding acids: monochloroacetic, bromoacetic, etc., using sulphuric acid as dehydrating agent. This acid first reacts with alcohol to form ethyl hydrogen sulphate:



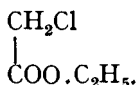
which then condenses with the monohalogenated acid forming the ester:



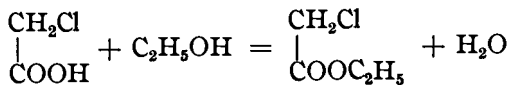
The compounds of this type have the halogen atom bound very unstably to the remainder of the molecule. It is easily split off by the action of water, alkaline solutions and ammonia. This instability considerably reduces the value of these substances as war gases.

1. Ethyl Chloroacetate

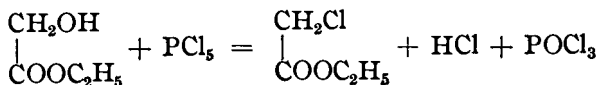
(M.Wt. 122)



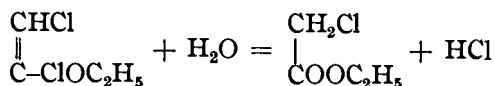
Ethyl chloroacetate may easily be prepared by the reaction of chloroacetyl chloride with alcohol,¹ or by means of the action of ethyl alcohol on monochloroacetic acid in presence of sulphuric acid:



It is also prepared by the action of phosphorus pentachloride on ethyl glycollate²:

¹ WILLM, *Ann.*, 1857, **102**, 109.² A. HENRY, *Ann.*, 1870, **156**, 176.

or by the action of water on dichlorovinyl ethyl ether.



LABORATORY PREPARATION ¹

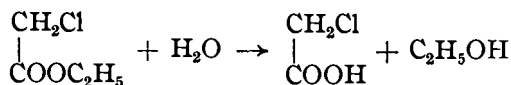
Into a flask of about 200 ml. capacity fitted with a reflux condenser, 75 gm. monochloroacetic acid, 45 gm. 95% alcohol and 10 gm. sulphuric acid (S.G. 1.84) are introduced. These are stirred and heated on the water-bath at 100° C. for about 5-6 hours. At the end of the heating the mass is allowed to cool and then poured into a separatory funnel containing about 150 ml. cold water. The ethyl chloroacetate layer is separated, washed once more with water and then fractionally distilled.

PHYSICAL AND CHEMICAL PROPERTIES

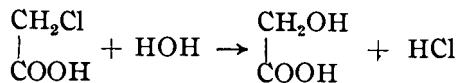
Ethyl chloroacetate is a colourless, mobile liquid with an odour of fruit, boiling at 143.5° C. at a pressure of 758 mm. of mercury (Willm) and decomposing by long heating at the boiling point.² Its specific gravity is 1.1585 at 20° C., and its vapour density has been experimentally found to be 4.46 (Willm), while the calculated value is 4.23.

It is insoluble in water, but easily soluble in the common organic solvents.

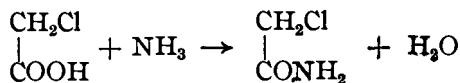
It is easily decomposed by alkalis and also by hot water. In this decomposition, besides the saponification of the ester :



the halogen atom of the CH₂Cl group is also substituted by a hydroxyl with formation of the corresponding hydroxy-acid :



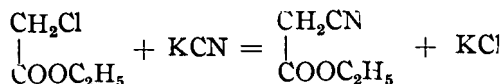
It reacts with ammonia to form chloroacetamide :



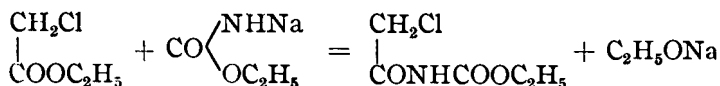
¹ CONRAD, *Ann.*, 1877, **188**, 218.

² VANDERVELDE, *Bull. acad. roy. belg.*, 1897, [3] **34**, 894.

With potassium cyanide, ethyl cyanoacetate is formed ¹ :



By the action of sodium urethane on ethyl chloroacetate, N-chloroacetyl urethane is formed ² :

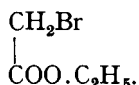


This forms crystals melting at 129° C., sparingly soluble in cold water, but soluble in alcohol.

Ethyl chloroacetate was used only to a limited extent in the last war. It was manufactured in large quantities, however, for the preparation of two other substances whose aggressive action was much more efficacious : ethyl bromo- and iodo-acetates.

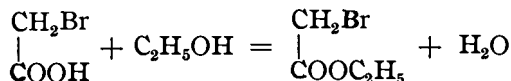
2. Ethyl Bromoacetate

(M.Wt. 167)

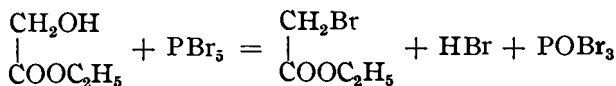


Ethyl bromoacetate, according to Meyer,³ was the first substance employed in warfare as gas (at the end of 1914). At the beginning it was used in hand grenades, but later the French preferred to use it in shells.

It was prepared for the first time by Perkin and Duppa⁴ by treating bromoacetic acid with ethyl alcohol in a closed tube for 1 hour in the cold :



It may also be obtained by the action of phosphorus pentabromide on ethyl glycolate ⁵ :



¹ MUELLER, *Ann.*, 1865, **131**, 351.

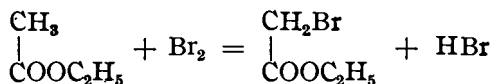
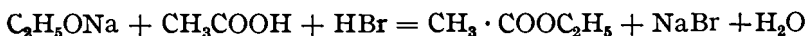
² DIELS, *Ber.*, 1903, **36**, 745.

³ MEYER, *op. cit.*

⁴ PERKIN and DUPPA, *Ann.*, 1858, **108**, 106.

⁵ HENRY, *Ann.*, 1870, **156**, 174.

or by the action of bromine on sodium ethylate ¹ :



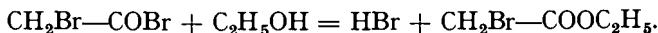
It is generally prepared by the action of bromine on acetic acid in presence of red phosphorus.² Phosphorus pentabromide is formed first, and this reacts with the acetic acid, forming acetyl bromide, as follows :



This reacts with more bromine, forming bromoacetyl bromide



which with alcohol forms the ester :



LABORATORY PREPARATION ³

30 gm. glacial acetic acid with 3.9 gm. red phosphorus are placed in a flask fitted with a stopper containing two holes. Through one of the holes passes a tap-funnel ; through the other a condenser which is joined at its upper end, by means of a glass tube, to a small flask containing water, in such a manner that the tube does not dip into the water. While stirring vigorously and cooling with water, 50 gm. bromine are slowly added from the tap-funnel and the flask warmed on the water-bath to 60° to 65° C. while a further 85 gm. bromine are added a little at a time. When all the bromine has been added, the flask is heated on a boiling water-bath until no more hydrobromic acid is evolved. The flask is then cooled to about 0° C., and 35 gm. absolute alcohol added from the tap-funnel in small portions with constant stirring. 6 gm. sulphuric acid are also added and the flask stirred and heated on the boiling water-bath for about 2 hours. At the end of this time the flask is again cooled and the reaction-product poured into water. The oily layer is separated, washed with water, dried over calcium chloride and distilled, collecting the fraction boiling between 155° and 175° C. The yield is about 80% of theoretical.

¹ SELL and SALZMANN, *Ber.*, 1874, **7**, 496.

² SELINSKI, *Ber.*, 1887, **20**, 2026.

³ AUWERS and BERNHARDI, *Ber.*, 1891, **24**, 2216 ; NAUMANN, *Ann.*, 1864, **129**, 268.

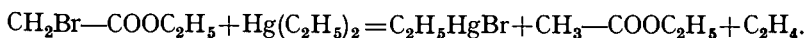
PHYSICAL AND CHEMICAL PROPERTIES

Ethyl bromoacetate is a clear, colourless liquid boiling at ordinary pressure at 168°C .¹ On cooling by means of a mixture of carbon dioxide and ether, it solidifies in colourless needles which melt at -13.8°C . Its specific gravity is 1.53 at 4°C . In the vapour state it has a density of 5.8. It is insoluble in water but soluble in most of the organic solvents. Its volatility at 20°C . is 21,000 mgm. per cu. m. of air.

Chemically it is not a very stable compound, and is partially decomposed even by water and completely by sodium or potassium hydroxide solutions on boiling. The hydrolysis is as follows :



Ethyl bromoacetate on treatment with mercury ethyl at 150°C . decomposes according to the equation ² :



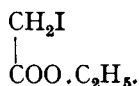
Ethyl bromoacetate, because of its relatively high boiling point and its low volatility can be used in shells without causing a visible cloud on bursting.

It has no corrosive action on iron.

The limit of insupportability for man is 40 mgm. per cu. m. of air (Flury). The minimum concentration capable of provoking irritation of the eyes is 10 mgm. per cu. m. The product of mortality is 3,000 (Müller).

3. Ethyl Iodoacetate

(M.Wt. 214)



Ethyl iodoacetate was used by the Allies in shells, especially in mixtures with chloropicrin (10%).

This substance cannot be prepared, like the two preceding, by esterification of iodoacetic acid with ethyl alcohol. It is necessary to start with ethyl chloroacetate or bromoacetate, both of which react with potassium iodide to form the iodo-compound.

Perkin and Duppa,³ commencing with ethyl bromoacetate and potassium iodide, prepared ethyl iodoacetate for the first time.

LABORATORY PREPARATION

25 gm. ethyl chloroacetate are dissolved in 150 ml. alcohol in a flask fitted with a reflux condenser, then 35 gm. potassium iodide

¹ PERKIN, *J. Chem. Soc.*, 1894, **65**, 427.

² SELL and LIPMANN, *Z. f. Chem.*, 1886, 724.

³ PERKIN and DUPPA, *Ann.*, 1859, **112**, 125.

are added and 25 ml. water. The mixture is heated on a water-bath at 40° to 50° C., stirring frequently. After heating for 1-2 hours, the mixture is transferred to a separatory funnel containing about 200 ml. water. The oily layer is separated, dried over calcium chloride and distilled.

The ethyl iodoacetate should be stored in a dark place in order to prevent decomposition.

PHYSICAL AND CHEMICAL PROPERTIES

Ethyl iodoacetate is a colourless, dense liquid boiling at ordinary pressure at 179° C. and at a pressure of 16 mm. at 76° to 78° C.¹ Its specific gravity is 1.8.

The vapour tension varies with temperature as follows :

° C.	MM. MERCURY
10	0.28
20	0.54
30	0.87

The vapour density is 7.4 and the volatility at 20° C. is 3,100 mgm. per cu. m. (Müller). Like most organic compounds containing iodine, it decomposes easily in the air and light, becoming brown by separation of iodine.

It is very slowly decomposed by water and alkaline solutions in the cold² but more rapidly on warming.³ The reaction is as follows :



Ethyl iodoacetate also reacts easily with sodium thiosulphate. The velocity of this reaction has been studied by Slator.⁴

It is completely decomposed by heating with nitric acid.⁵

Owing to their low volatility these esters are rarely employed in warfare in the pure state. They are generally diluted with either alcohol or ethyl acetate.

It is particularly as an eye irritant that ethyl iodoacetate functions, and it seems that this is due to iodoacetic acid and not hydriodic acid.

The minimum concentration capable of producing irritation of the eyes is 1.4 mgm. per cu. m. of air, according to Fries. The limit of insupportability is 15 mgm. per cu. m. and the product of mortality is 1,500 (Müller).

¹ TIEMANN, *Ber.*, 1898, **31**, 825.

² RONA, *Z. ges. exp. Med.*, 1921, **13**, 16.

³ BUTLEROV, *Ber.*, 1872, **5**, 479.

⁴ SLATOR, *J. Chem. Soc.*, 1905, **87**, 482.

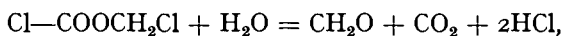
⁵ NEF, *Ann.*, 1897, **298**, 353.

Analysis of the Halogenated Esters

IDENTIFICATION

The various chlorinated methyl chloroformates are identified by the diverse manners in which they react with alkali. The method described dates from Hentschel in 1887 and is still used to-day.¹

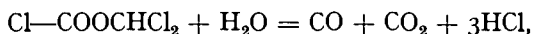
Identification of Monochloromethyl Chloroformate. Monochloromethyl chloroformate when treated with water or aqueous sodium hydroxide is decomposed even in the cold according to the equation :



producing formaldehyde which may be easily identified by one of the common reagents for an aldehyde, such as the Schiff reagent, a 0.025% aqueous solution of fuchsin decolorised with sulphur dioxide.

As the other chlorinated methyl chloroformates when they react with alkaline solutions form no formaldehyde, this method may be used for the identification of the monochloro derivative even in the presence of di- and tri- methyl chloroformates.

Identification of Dichloromethyl Chloroformate. On treating dichloromethyl chloroformate with water or an alkaline solution it decomposes according to the following equation :



thus forming carbon monoxide, unlike the other derivatives. By applying one of the usual methods for the identification of this carbon monoxide, evolved when the substance being examined is treated with an alkaline solution, the presence of dichloromethyl chloroformate may be confirmed.

Identification of Trichloromethyl Chloroformate. This substance may be identified by its reaction with an aqueous solution of aniline (3 : 100). Like phosgene and dichloromethyl chloroformate, a white crystalline precipitate of diphenyl urea forms, which may be confirmed by microscopic examination (rhombic prisms) or by a determination of its melting point (236° C.).

Identification of trichloromethyl chloroformate may also be made by using dimethyl amino benzaldehyde and diphenylamine paper, prepared as described on p. 81. In presence of trichloromethyl chloroformate this turns yellow as in the presence of phosgene.

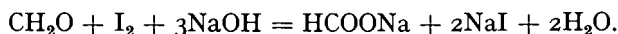
¹ HENTSCHEL, *J. prakt. Chem.*, 1887, **36**, 99, 305.

QUANTITATIVE DETERMINATION

The quantitative determination of the chloromethyl chloroformates is carried out by making use of the same reactions as those described above for their identification.¹

Determination of Monochloromethyl Chloroformate. The substance under examination is treated with sodium hydroxide and the amount of formaldehyde formed is then determined.

In practice, about 0.4 ml. of the substance is accurately weighed into a graduated 125 ml. flask containing 50 ml. normal sodium hydroxide solution. After stoppering, this is then shaken, then allowed to stand for $\frac{1}{2}$ hour and made up to volume. 25 ml. of the alkaline liquid obtained are placed in a burette and allowed to drop into an excess of a decinormal iodine solution, shaken and allowed to stand for about 20 minutes. The following reaction then takes place :

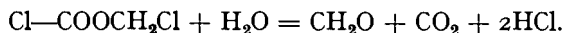


The solution is slightly acidified with dilute sulphuric acid and the excess of iodine titrated with thiosulphate. A blank should be carried out.²

Then the quantity of formaldehyde is given by the following, as a percentage :

$$\text{CH}_2\text{O}\% = \frac{N \times 0.0015 \times 5 \times 100}{P} = \frac{0.75 N}{P}$$

in which N is the number of ml. of iodine used and P the weight of substance taken. From this value the content of $\text{Cl}-\text{COOCH}_2\text{Cl}$ in the sample may be calculated from the knowledge that 1 gramme-molecule of formaldehyde corresponds to one of monochloromethyl chloroformate :



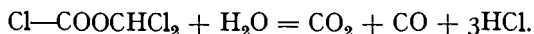
Determination of Dichloromethyl Chloroformate. The sample to be examined is treated with sodium hydroxide and the volume of carbon monoxide evolved is measured.

0.3–0.5 gm. of the substance is introduced into a Lunge nitrometer over mercury and 10 ml. of a 4 N solution of sodium or potassium hydroxide added. The carbon monoxide which is formed is collected and its volume measured. From the knowledge that 1 gramme-molecule of carbon monoxide is obtained from

¹ M. DELEPINE, *Bull. soc. chim.*, 1920, [4] 27, 39.

² Method suggested by ROMIJIN, *Z. anal. Chem.*, 1897, 36, 18.

1 gramme-molecule of dichloromethyl chloroformate, the amount of the latter present in the sample may be calculated :

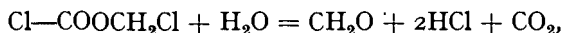


Determination of Trichloromethyl Chloroformate. The quantitative determination of trichloromethyl chloroformate may be carried out by the aniline method according to Pancenko.¹ unless mono- or dichloromethyl chloroformate is present. These both react with aniline in the same way as the trichloro derivative (see p. 110).

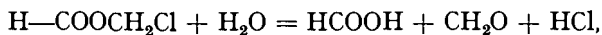
0.3–0.4 gm. of the substance to be examined is weighed into a small glass bulb which is then sealed and placed in a cylinder containing an aqueous solution of aniline as in the determination of phosgene. The bulb is broken and shaken in the cylinder for a few minutes, allowed to stand and then the diphenylurea determined as in the method described on p. 83.

Quantitative Determination of Monochloromethyl Formate in presence of Monochloromethyl Chloroformate. In controlling the manufacture by analysis it is frequently necessary to determine the quantity of chloroformate present in the chlorination product of methyl formate ; that is, to determine if the product obtained from the methyl formate still contains some hydrogen in the form of HCO— group which is not substituted by chlorine.

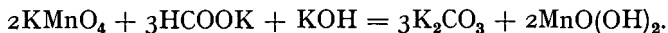
The method proposed by Delepine² for carrying out this determination depends on the differences between the behaviour of the chloromethyl chloroformates when treated with alkaline solutions. As already described, monochloromethyl chloroformate on treatment with alkali gives formaldehyde, carbon dioxide and hydrochloric acid according to the equation :



while the chlorinated methyl formates hydrolyse to form formic acid, formaldehyde and hydrochloric acid :



so that the amount of formic acid found after hydrolysing a sample is proportional to the chloromethyl formate present. The determination of the formic acid may be made by titration with potassium permanganate³ :



¹ PANCENKO, *Metodi Issliedovaniya i chimiceskie Svoista Otravljajuscix Vescectv*, Moscow, 1934, 105.

² DELEPINE, *loc. cit.*

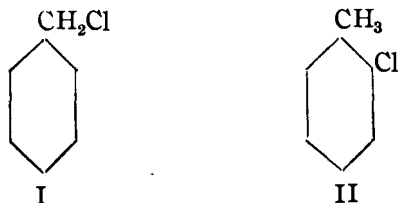
³ SMITH, *Analyst*, 1896, 21, 148.

However, as the formaldehyde formed by the hydrolysis of monochloromethyl chloroformate is also oxidised by potassium permanganate it must be first determined by titration with iodine solution. Then, by subtracting from the number of ml. permanganate solution decolorised, twice the number of ml. of iodine solution used (for formaldehyde needs twice as much oxygen as formic acid for its oxidation), the result is the number of ml. permanganate corresponding to the quantity of formic acid present and from this the chloromethyl formate in the sample may be calculated.

CHAPTER IX

AROMATIC ESTERS

ON halogenating the homologues of benzene, two series of compounds with very different physical and chemical, but especially physiopathological, properties may be formed, according to whether the halogen atom enters the side chain or the benzene nucleus. While the compounds with a halogen atom in the side chain, like benzyl chloride (I), are efficient lachrymators, those with a halogen atom in the nucleus, like *o*-chlorotoluene (II), have no lachrymatory action at all.



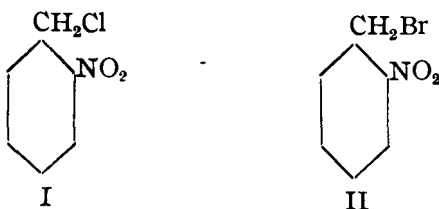
In preparing the war gases of this group it is therefore necessary to employ methods which will ensure the halogen entering the side chain rather than the nucleus. In general it is advisable to carry out the halogenation at the boiling point of the hydrocarbon or under the influence of a light-source rich in ultra-violet radiations, such as diffused sunlight, the mercury-vapour lamp, etc. Attempts to use catalysts have not been successful, for catalysts, though accelerating the halogenation, orient the halogen into the nucleus, even when the operation is carried out at the boiling point of the hydrocarbon.

Examination of the physiopathological properties of these halogen compounds has shown that the lachrymatory power is increased by an increase in the atomic weight of the halogen present, that is, the iodo-compounds are biologically more efficient than the bromo-compounds and these more efficient than the chloro-compounds.

In the war of 1914-18 these substances had a limited use. On the one hand, the raw material for their preparation (toluol) was too costly, and on the other their lachrymatory power was soon surpassed by that of other substances.

Research carried out in the latter part of the war and continued in the post-war period has shown that the introduction of certain radicles into the molecules of these substances considerably increases their aggressive power. The entry of the NO_2 -group into the benzene nucleus in the ortho-position to the side chain containing the halogen, and the introduction of the CN-group into the halogenated side chain itself are particularly efficacious.

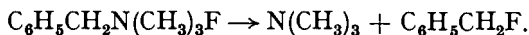
Thus among the halogen-compounds containing the NO_2 -group, *o*-nitrobenzyl chloride (I) and bromide (II) are superior to the corresponding simple halogenated derivatives.



These may be easily obtained by halogenation of nitrotoluene or nitration of the corresponding halogenated toluene.¹ Moreover, it appears that the introduction of the NO_2 -group confers vesicant power on these substances.²

A study of those compounds in which the CN-group is in the side chain containing the halogen atom has indicated that chlorobenzyl cyanide,³ and bromobenzyl cyanide to an even greater degree, have an increased lachrymatory power. These compounds are described in the chapter on "Cyanogen Compounds" (see p. 196).

Later benzyl fluoride was prepared by the decomposition of benzyl trimethylammonium fluoride⁴:



This is a colourless liquid boiling at 139.8°C . at a pressure of 753 mm. and at 40° to 40.5°C . at 14 mm. pressure. Density, 1.022 at 25°C . On cooling strongly, it solidifies to acicular crystals, melting at -35°C . It does not fume in air and has no lachrymatory properties. Treatment with nitric acid converts it into nitrobenzyl fluoride. The *p*-compound was isolated as acicular crystals melting at 38.5°C .

¹ MOUREU, *Bull. soc. chim.*, 1921, **29**, 1006.

² NEKRASSOV, *loc. cit.*

³ MICHAEL, *Ber.*, 1892, **25**, 1679; CHRZASZCZEVSKA and POPIEL, *Roczniki Chem.*, 1927, **7**, 74.

⁴ C. INGOLD, *J. Chem. Soc.*, 1928, 2249.

with a lid, and then a current of chlorine is introduced from a cylinder mounted on a weighing machine, so that the weight of chlorine used may be controlled. The mixture is then heated with steam generated in the boiler *C*; it may be illuminated by means of the apparatus *D*. Above the reaction vessel a reflux condenser *E* is arranged, and this is connected to the receivers *F* and *F*¹, in which the evolved hydrochloric acid is collected. As the chlorination proceeds the product passes from the vessel *A* into the receiver *G*, and thence into the apparatus *H*, where it is distilled. The distillate containing the benzyl chloride is collected in the special receivers *M*, *N*.

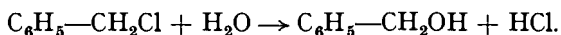
PHYSICAL AND CHEMICAL PROPERTIES

Benzyl chloride is a colourless liquid which boils at ordinary pressure at 179° C.¹ (Perkin), while at a pressure of 40 mm. mercury it boils at 89.9° C. The specific gravity is 1.113 at 20° C., and the vapour density is 4.4.

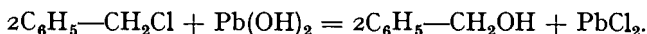
On cooling, a crystalline mass melting at - 39° C. is obtained.

It is insoluble in water, but soluble in most of the organic solvents.

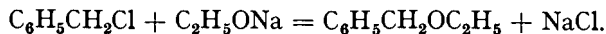
Benzyl chloride is fairly stable to water, and only by prolonged boiling with an excess is it decomposed into benzyl alcohol and hydrochloric acid :



By heating for 2 hours with 10 parts of water and 3 parts of freshly-precipitated lead hydroxide, benzyl alcohol is also obtained according to the equation ² :



On boiling benzyl chloride with alcoholic potassium hydroxide solution or with sodium ethylate, benzyl ethyl ether is formed :



This is a liquid boiling at 185° C. and volatile in steam.³ This reaction with boiling alcoholic sodium ethylate is quantitative.⁴

Benzyl chloride reacts similarly with other alcoholates and with phenates.

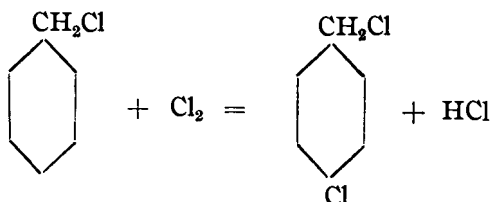
¹ PERKIN, *J. Chem. Soc.*, 1896, **69**, 1203.

² LAUTH, *Ann.*, 1867, **143**, 81.

³ CANNIZZARO, *Jahresber. fortschr. Chemie*, 1856, 581.

⁴ INGOLD, *J. Chem. Soc.*, 1928, 2249.

By the action of chlorine on benzyl chloride, in presence of iodine as catalyst, *p*-chlorobenzyl chloride is formed :

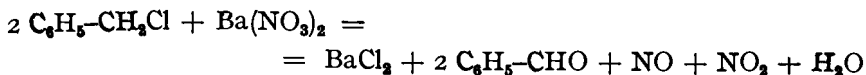


This is a crystalline substance melting at 29° C., soluble in alcohol, ether, benzene and acetic acid, but insoluble in water. It boils at ordinary pressure at 214° C.¹

By the action of bromine in the presence of iodine, *p*-bromobenzyl chloride and *p*-bromobenzyl bromide are formed.²

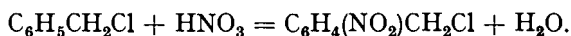
On passing the vapour of benzyl chloride over a platinum wire heated to redness, stilbene and hydrochloric acid are formed.³

By the action of mild oxidising agents like calcium nitrate, barium nitrate, etc., benzyl chloride is converted into benzaldehyde :



When strong oxidising agents like chromic acid mixture are employed, benzoic acid is formed.

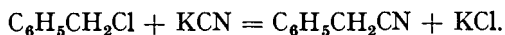
The action of fuming nitric acid introduces a nitro-group into the benzene nucleus and *o*-nitrobenzyl chloride is formed⁴ :



This compound is more powerfully lachrymatory than benzyl chloride (see p. 135).

With alcoholic ammonia, a mixture of mono-, di- and tri-benzylamines is formed. With hexamethylene tetramine an addition product results.⁵

On boiling an alcoholic solution of benzyl chloride with an aqueous solution of potassium cyanide, benzyl cyanide is formed⁶ :



This is a colourless liquid, S.G. 1.0125 at 25° C., boiling at 233° C. at normal pressure and at 107° C. at a pressure of 12 mm. On cooling it solidifies to a crystalline mass, melting at - 24.6° C.

¹ KUHLEBERG, *Ann.*, 1868, 146, 320.

² ERRERA, *Gazz. Chim. Ital.*, 1887, 17, 198.

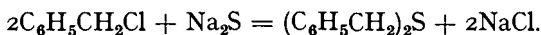
³ LOB, *Ber.*, 1903, 36, 3060.

⁴ NOELTING, *Ber.*, 1884, 17, 385.

⁵ SAMMELT, *Compt. rend.*, 1913, 157, 852.

⁶ CANNIZZARO, *Ann.*, 1855, 96, 247.

By heating alcoholic solutions of sodium sulphide and benzyl chloride together on the water-bath, benzyl sulphide is formed¹:



This is white and crystalline, insoluble in water and soluble in alcohol and ether. On heating to about 120° C. it decomposes into hydrogen sulphide, sulphur, toluene, triphenyl butane and triphenyl thiophene.

Sodium sulphide and benzyl chloride also react in aqueous solution, but in this case the reaction is much slower.

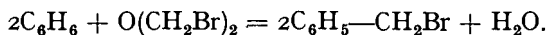
Benzyl chloride attacks iron, tin and copper vigorously and polymerises in contact with these metals.

The animal fibres absorb the vapour of benzyl chloride in greater quantities than do the vegetable fibres. Following this absorption, the resistance of the vegetable fibres is notably lowered, while that of the animal fibres is practically unchanged. The benzyl chloride vapour is only partly removed by a current of air.² The limit of insupportability is 85 mgm. per cu. m. of air, according to Flury.

2. Benzyl Bromide. $\text{C}_6\text{H}_5\text{—CH}_2\text{Br}$. (M.Wt. 171.01)

Benzyl bromide was used by the Germans as a war gas in March, 1915, but only for a short time owing to the cost and the scarcity of the raw material (toluol). Later it was completely abandoned, being superseded by other substances with greater irritant power.

Benzyl bromide may be prepared by the action of hydrobromic acid on benzyl alcohol³ or by the action of bromine on toluene.⁴ Stephen⁵ has worked out a method which consists in treating dibromomethyl ether with benzene:



LABORATORY PREPARATION

The method of Schramm⁶ is usually employed; this is based on the action of bromine on toluene.

50 gm. toluene are placed in a perfectly dry flask of 250 ml. capacity which is fitted with a tap-funnel and a reflux condenser. The flask is exposed to direct sunlight and then 75 gm. bromine are allowed to enter drop by drop, agitating at the same time.

¹ MAERCKER, *Ann.*, 1865, **136**, 86.

² ALEXEJEVSKY, *J. Prikl. Khim.*, 1929, **1**, 184.

³ KEKULÉ, *Ann.*, 1866, **137**, 190.

⁴ BEILSTEIN, *Ann.*, 1867, **143**, 369.

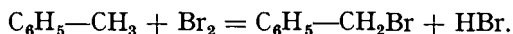
⁵ STEPHEN and SHORT, *J. Chem. Soc.*, 1920, **117**, 510.

⁶ SCHRAMM, *Ber.*, 1885, **18**, 608.

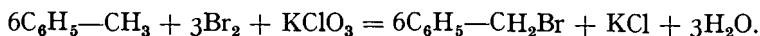
The solution, which is first coloured reddish-brown, becomes colourless as the reaction proceeds. When all the bromine has been added, the reaction product is fractionally distilled and the fraction boiling between 190° and 205° C. collected separately. This is refractionated through a dephlegmator.

INDUSTRIAL MANUFACTURE

Benzyl bromide is prepared on the large scale as in the laboratory by the action of bromine on toluene. In this reaction half of the bromine is converted into hydrobromic acid :



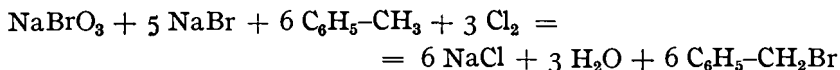
In order to utilise this bromine, potassium chlorate is added to the reaction mixture so as to regenerate the bromine, which re-enters the reaction cycle :



The bromine may also be treated with sodium hydroxide in order to prevent the loss of bromine as hydrobromic acid :



The mixture of sodium bromide and bromate obtained is then agitated with the toluene while a current of chlorine¹ is passed into the mixture.



PHYSICAL AND CHEMICAL PROPERTIES

Benzyl bromide is a clear, refractive liquid with an aromatic odour which boils at 198° to 199° C. at ordinary pressure, and at 127° C.² at 80 mm. pressure. It solidifies at - 3.9° C.

Its specific gravity is 1.438 at 16° C. and its vapour density is 5.8. The volatility at 20° C. is 2,440 mgm. per cu. m. (Müller).

It is insoluble in water, but soluble in the common organic solvents.

Benzyl bromide, like the chloride, is decomposed by water with difficulty.³ Only after prolonged boiling (30 hours) of an aqueous solution of benzyl bromide is it saponified into hydrobromic acid and benzyl alcohol.

Concentrated nitric acid forms, besides benzoic acid, tribromoaniline and tribromoaminobenzoic acid.⁴

¹ LIBERMANN, *op. cit.*

² VAN DER LAAN, *Chem. Weekblad.*, 1906, **3**, 15.

³ P. RONA, *Z. ges. exp. Med.*, 1921, **13**, 16.

⁴ FLUERSCHEIM and HOLMES, *J. Chem. Soc.*, 1928, 1607.

Alcoholic ammonia reacts with benzyl bromide, even in the cold, to form tribenzylamine¹ $(C_6H_5CH_2)_3N$.

Benzyl bromide, when treated with an alcoholic solution of silver acetate, separates silver bromide rapidly, even in the cold (Kekulé).

In contact with iron it decomposes in a short time. Because of this decomposition it must be placed in lead containers if it is to be used in projectiles.²

During the war a mixture of benzyl bromide, castor oil, alcohol, sodium thiosulphate and glycerol was employed.³

The minimum concentration of benzyl bromide causing irritation is 4 mgm. per cu. m. air. The limit of insupportability is 60 mgm. per cu. m. and the mortality product 6,000 (Müller).

3. Benzyl Iodide. $C_6H_5-CH_2I$ (M.Wt. 218.01)

This substance, which has well-known lachrymatory properties, may be obtained according to Cannizzaro⁴ by the action of phosphorus iodide with benzyl alcohol or by the action of potassium iodide on benzyl chloride or bromide.

According to some authors, benzyl iodide was used as a war gas by the French in March, 1915.

LABORATORY PREPARATION⁵

150 ml. 95% ethyl alcohol, 20 gm. benzyl bromide and 25 gm. potassium iodide are placed in a flask of 250–300 ml. capacity fitted with a reflux condenser. This is then warmed on the water-bath to 50° to 60° C. with continual agitation. After heating for half an hour, the product is poured into 150 ml. water, the oily layer separated, washed with water and crystallised by means of a freezing mixture. The crystals are collected and purified by crystallisation from alcohol.

PHYSICAL AND CHEMICAL PROPERTIES

Benzyl iodide forms colourless crystals melting at 24.1° C. The liquid has a specific gravity of 1.7735 at 25° C. and boils with decomposition at 226° C. (Lieben).⁶ The vapour density is 7.5. It is insoluble in water, soluble in alcohol, ether and benzene and slightly soluble in carbon disulphide (Kumpf).

Benzyl iodide has a volatility of 1,200 mgm. per cu. m. of air.

¹ KERULÉ, *Ann.*, 1866, **137**, 190.

² ALEXEJEVSKY and coll., *J. Prikl. Khim.*, 1928, **1**, 194.

³ S. DE STACKELBERG, *Le péril chimique et la croix violette*, Lucerne, 1929.

⁴ CANNIZZARO, *Gmelins Handbuch*, **6**, 38.

⁵ MEYER, *Ber.*, 1877, **10**, 311; KUMPF, *Ann.*, 1884, **224**, 126.

⁶ LIEBEN, *Jahresber. Fortschr. Chem.*, 1869, 425.

Like the two previous compounds, it is decomposed by water with difficulty.¹

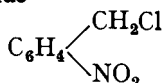
Crystals of benzyl iodide when gently heated become red in colour owing to incipient decomposition. By the action of silver acetate in presence of acetic acid, silver iodide and benzyl acetate are formed (Lieben).

It reacts easily with tertiary amines, forming quaternary ammonium iodides.²

It may be classed among the strongest lachrymators. The lower limit of irritation is 2 mgm. per cu. m. of air (Müller). The maximum concentration which a normal man can support for a period of not more than 1 minute is 25-30 mgm. per cu. m. Mortality-product : 3,000 (Müller).

4. Ortho-nitrobenzyl Chloride

(M.Wt. 171.55)



Ortho-nitrobenzyl chloride was prepared in 1883 by Abelli,³ together with the meta-compound, by the reaction of concentrated nitric acid on benzyl chloride. It may also be obtained, according to Häussermann and Beek,⁴ by the action of chlorine at 130° to 140° C. on a mixture of 2 parts of o-nitrotoluene and 1 part sulphur.

According to Lindemann,⁵ it was used by the French during the war mixed with p-nitro benzyl chloride under the name of "Cedenite."

PHYSICAL AND CHEMICAL PROPERTIES

o-Nitrobenzyl chloride forms crystals with a melting point of 48° to 49° C. It is purified by crystallisation from ligroin. Its vapour density is 5.9. It is insoluble in water, but easily soluble in cold benzene and in ether and alcohol on warming.

With potassium iodide it is easily converted into o-nitrobenzyl iodide,⁶ and an alcoholic solution of potassium cyanide converts it into o-nitrobenzyl cyanide.⁷ Potassium permanganate oxidises it to o-nitrobenzoic acid.

The lower limit of irritation is 1.8 mgm. per cu. m. of air (Lindemann). It has a vesicant action.

¹ P. RONA, *Z. ges. exp. Med.*, 1921, **13**, 16.

² VEDEKIND, *Ann.*, 1901, **318**, 92.

³ ABELLI, *Gazz. chim. Ital.*, 1883, **13**, 97.

⁴ HÄUSSERMANN and BEEK, *Ber.*, 1892, **25**, 2445.

⁵ LINDEMANN, *Toxikologiya chem. sredkov bojowych*, Warsaw, 1925

⁶ KUMPF, *Ann.*, 1848, **224**, 103.

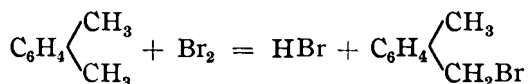
⁷ BAMBERGER, *Ber.*, 1886, **19**, 2635.

5. **Xylyl Bromide.** $C_6H_4(CH_3)CH_2Br$. (M.Wt. 185)

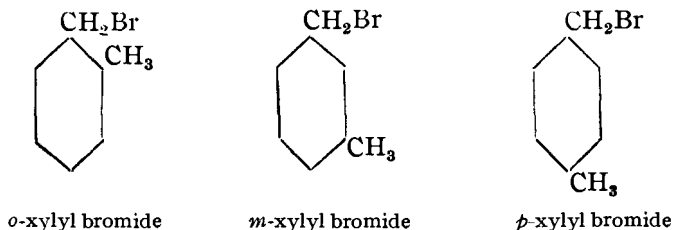
Xylyl bromide was prepared in 1882 by Radziszewsky.¹ It was used for the first time as a war gas in January, 1915, but its use was abandoned towards the end of the war because of the ease with which it was dealt with by the ordinary carbon filters and of the inconvenience caused by its attack on iron containers. It is also known as "*T-Staff*."

Xylyl bromide may be easily prepared by the reaction of bromine on commercial xylyl.² This reaction is carried out either by heating the xylyl to 115° C. or by exposing the reaction-mass to the action of a light source rich in ultra-violet radiations and keeping the temperature at 50° to 60° C.³

In both cases the following reaction takes place :

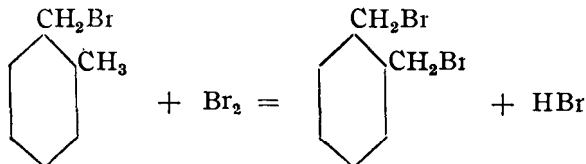


Since commercial xylyl is a mixture of the three isomeric xylenes, ortho, meta and para, the method of bromination mentioned above produces a mixture of the three derivatives :



All these three compounds have lachrymatory properties.

In the bromination of xylyl a secondary reaction also takes place ; this is the conversion of xylyl bromide into xylylene bromide, due to the tendency of bromine to react with xylyl bromide as well as with the xylyl also present.



¹ RADZISZEWSKY and WISPEK, *Ber.*, 1882, **15**, 1747.

² ATKINSON and THORPE, *J. Chem. Soc.*, 1907, **91**, 1695.

³ SCHRAMM, *Ber.*, 1885, **18**, 1278 ; FARBENFABR. F. BAYER, *D.R.P.*, 297933 ; *Chem. Zentr.*, 1921 (II), 803.

LABORATORY PREPARATION

It is prepared by the action of bromine on xylol. 500 gm. commercial xylol are placed in a 1-litre flask which is closed with a stopper carrying three holes. Through one of these passes a thermometer whose bulb is immersed in the reacting liquid, through the second the stem of a tap-funnel, and through the third a reflux condenser which leads by means of a tube bent at right angles to a dish containing water.

The flask is heated so as to raise the temperature of the liquid to about 115° C. and to keep it as near this temperature as possible while bromine is dropped in slowly (about 4 drops a second) from the tap-funnel, into which 500 gm. bromine have been previously measured. This quantity of bromine is about a quarter less than the theoretical.

Each drop of bromine reacts immediately it enters the xylol, which becomes slightly coloured, while the hydrobromic acid which is formed bubbles out and passes through the condenser to the water in the dish, where it dissolves.

When all the bromine has been dissolved (about 2 hours), the heating to 115° to 120° C. is continued until all the hydrobromic acid has been driven off from the reaction mixture. At the end of this evolution of gas, the flask is cooled and its contents transferred to a distillation flask. On distillation, the first fraction between 140° and 200° C. is collected separately. This contains the xylol which has not reacted and any hydrobromic acid which remained behind. At 210° C. the mixture of the three xylyl bromides begins to distil. When the thermometer reaches 230° C. the distillation is stopped; the flask contains a black oily residue. In order to obtain a purer product, the fraction collected between 210° and 230° C. may be redistilled. The yield is about 75%.

INDUSTRIAL MANUFACTURE

In the manufacture of xylyl bromide in Germany, enamelled vessels fitted with agitators and cooling coils were employed, according to Norris.¹

The required quantity of xylol was poured into these vessels, heated to 115° C. and then about three-quarters of the theoretical bromine added in small quantities so that at the end of the reaction some unchanged xylol still remained. The hydrobromic acid evolved was absorbed in special towers.

At the end of the operation the product was distilled under

¹ NORRIS, *J. Ind. Eng. Chem.*, 1919, 11, 828.

reduced pressure. After the xylol had been recovered, the residue was employed without rectification or purification.

PHYSICAL AND CHEMICAL PROPERTIES

In the pure state it is a colourless liquid boiling between 210° and 220° C., with a density of 1.4, and has an aromatic odour, which when much diluted is reminiscent of elder blossom.

The volatility at 0° C. is 140 mgm. per cu. m. of air, and at 20° C. is 600 mgm. per cu. m.

It is slowly decomposed by water, like benzyl iodide.¹ The crude product energetically attacks iron and so must be stored in lead-lined containers.

The minimum concentration capable of provoking irritation is 1.8 mgm. per cu. m. The limit of insupportability is 15 mgm. per cu. m. The mortality-product is 6,000 according to Müller. However, according to Prentiss it is 56,000.

Analysis of the Aromatic Esters

DETECTION

The aromatic esters are identified by saponifying them with alcoholic potash and then examining the product for the halogen hydroacids with silver nitrate solution.²

Detection of Benzyl Chloride. Benzyl chloride, on heating under reflux with a solution of lead nitrate, forms benzaldehyde which is easily recognised by its almond-like odour.

Another method of detecting benzyl chloride, according to Lob,³ consists in passing the vapour of the substance to be examined over a platinum wire heated to redness and then testing for hydrochloric acid in the product with silver nitrate.

Detection of Benzyl Bromide. According to Kekulé,⁴ when benzyl bromide is treated with an alcoholic solution of silver acetate, a yellow precipitate of silver bromide rapidly separates even in the cold.

QUANTITATIVE DETERMINATION

The quantitative determination of the aromatic esters is best carried out by the same reactions given above for their detection.

Determination of Benzyl Chloride. Benzyl chloride may be determined, according to Schulze, in the following manner⁵:

¹ RONA, *Z. ges. exp. Med.*, 1921, **13**, 16.

² WESTON, *Carbon Compounds*, London, 1927, 21.

³ LOB, *Ber.*, 1903, **36**, 3060.

⁴ KEKULÉ, *Ann.*, 1866, **137**, 191.

⁵ K. SCHULZE, *Ber.*, 1884, **17**, 1675.

about 2 gm. of the substance to be examined are accurately weighed into a flask fitted with a reflux condenser, excess of an alcoholic solution of silver nitrate, saturated in the cold, is added and then the whole is heated to boiling for about 5 minutes. At the end of the reaction, the precipitate formed is filtered on a weighed Gooch crucible, washed first with alcohol, then with hot water slightly acidified with nitric acid and then again with alcohol. The crucible is heated, first gently, then to red heat and reweighed. From the gain in weight the quantity of benzyl chloride in the sample may be calculated.

Determination of Benzyl Bromide. The determination of this substance may be carried out by the method already described for benzyl chloride. However, according to Van der Laan,¹ it is sometimes more convenient to decompose the substance directly with a measured volume of standardised alcoholic silver nitrate solution and to titrate the excess of the latter with ammonium thiocyanate solution by the Volhard method.

Determination of Benzyl Iodide. The following method may be employed for the quantitative determination of benzyl iodide :

About 2 gm. benzyl iodide are weighed into a flask and then 50 ml. 20% alcoholic potash solution are added and the mixture refluxed for about an hour. At the completion of the saponification the contents of the flask are allowed to cool and then transferred to a 500-ml. flask and made up to volume with water. 100 ml. of the resulting solution are placed in a distillation flask and distilled in steam after adding 10 gm. ferric ammonium alum and acidifying with sulphuric acid. By this treatment, the ferric salt is converted to the ferrous condition, liberating iodine which is distilled over into 5% potassium iodide solution. At the end of the distillation, the free iodine in the potassium iodide solution is titrated with a decinormal solution of sodium thiosulphate. From this, the amount of iodine and so the quantity of benzyl iodide in the sample may be calculated.

¹ VAN DER LAAN, *Rec. trav. Chim.*, **26**, 54.

CHAPTER X

ALDEHYDES

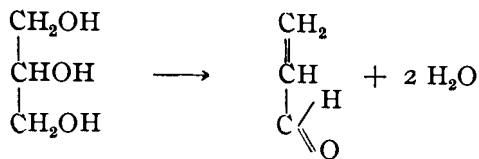
ACROLEIN was the only aldehyde used as a war gas during the war of 1914-18, and its use was very limited as it was soon superseded by other substances having superior offensive properties.

In the post-war period several halogenated derivatives of acrolein have been examined; for example, *monochloroacrolein*,¹ $\text{CH}_2 = \text{CCl} \cdot \text{CHO}$, a colourless liquid, boiling at 29° to 31°C . at a pressure of 17 mm. of mercury and having S.G. 1.205 at 15°C ., is both lachrymatory and vesicant in its action. Also some of the homologues of acrolein, like *crotonic aldehyde*, and its *monochloroderivative*, $\text{CH}_3 - \text{CH} = \text{CCl} - \text{CHO}$, a colourless liquid, boiling at 146°C ., and having a specific gravity of 1.422 at 15°C . This has toxic and lachrymatory properties inferior to those of chloropicrin, however.²

Acrolein. $\text{CH}_2 = \text{CH} - \text{CHO}$. (M.Wt. 56)

Acrolein, or acrylic aldehyde, was prepared by Redtenbacher in 1843,³ and was first used as a war gas by the French in 1916, being suggested by Le Pape, whence its name of "*Papite*." However, it was not very efficient, chiefly because of its tendency to polymerise into substances having no irritant action.

Acrolein is usually obtained from glycerol by abstraction of 2 molecules of water :



The following may be employed as dehydrating agents: phosphoric acid, boric acid, potassium bisulphate, sodium sulphate, etc. However, the preparation of acrolein is not very satisfactory when these substances are used, the yield being not above 30-40% of the theoretical. It was only as a result of the

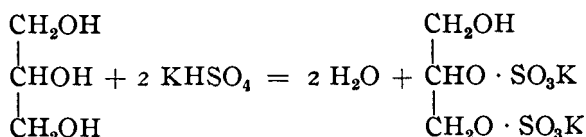
¹ MOUREU and coll., *Ann. chim.*, 1921, **15**, 158.

² MOUREU and coll., *Bull. soc. chim.*, 1921, [4] **29**, 29.

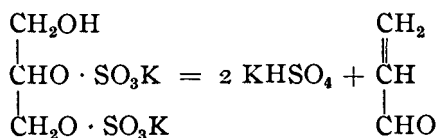
³ REDTENBACHER, *Ann.*, 1843, **47**, 114.

studies of Moureu ¹ on this subject that it was possible to obtain higher yields. In his method a mixture of 5 parts potassium bisulphate and 1 part potassium or sodium sulphate is used.

Little is known concerning the action of the acid sulphates on glycerol. A recent theory suggests that salts of glycerol-sulphuric acid are first formed :



On heating, these are thought to decompose forming sulphuric acid again and acrolein :



LABORATORY PREPARATION ²

100 gm. glycerol, 80 gm. potassium bisulphate and 20 gm. anhydrous sodium sulphate are placed in a flask *A* of about 1 litre capacity, which is fitted with a tap-funnel and connected by means of a glass tube (see Fig. 9) with another flask *B* of the

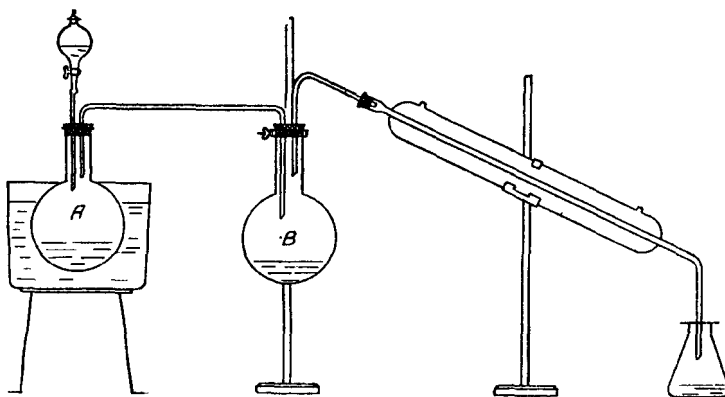


FIG. 9.

same size, this being also connected to a Liebig condenser. The first flask is immersed in an oil bath and heated to 160° to 180° C. The products of the reaction—water, acrolein, etc.—pass over

¹ MOUREU, *Compt. rend.*, 1919, **169**, 621, 705, 885 and 1068; *Bull. soc. chim.*, 1920, **27**, 297.

² NEKRASSOV, *op cit.*; E. ZAPPI, *Anales Assoc. Quim. Argentina*, 1930, **18**, 243.

into the flask *B* in which 1 gm. hydroquinone has been placed. When the acrolein commences to distil, a further 100 gm. glycerol are slowly run into *A* from the tap-funnel and the reaction continued for 4–5 hours by heating to about 250° C. at the end. In the receiver *B* a liquid collects which separates into two layers; the lower of these is an aqueous solution of acrolein and the upper a solution of water in acrolein. The upper layer is separated off, washed with soda solution, dried over fused calcium chloride and distilled.

It is advisable to add 0.1–0.2 gm. hydroquinone in order to retard polymerisation.

INDUSTRIAL MANUFACTURE

The industrial manufacture of acrolein is carried out in cylindrical iron vessels of about 30 cm. diameter fitted with agitators and closed by a lid having three holes, through one of which the glycerol is introduced, through the second passes a thermometer and through the third a condenser leading to a large flask heated on a water-bath. This flask is also fitted with a thermometer and may be connected to another condenser, cooled by water.

In the iron vessel 2 kgm. potassium bisulphate and 400 gm. potassium sulphate are placed, while 600 gm. glycerol of 28° Bé. are run in. The whole is then heated in an air-bath until the temperature inside the vessel reaches 100° C., when the reaction commences and a mixture of water and acrolein begins to distil. The temperatures in the first condenser and in the flask are then so regulated that the mixture of vapours enters the second condenser at a temperature of about 70° C. A considerable proportion of the water and compounds with higher boiling points is thus condensed in the flask while the acrolein, together with the remaining water vapour condenses in the second condenser and is collected in the appropriate receiver.

When only a little glycerol remains in the iron vessel, more is added at such a rate that the speed of distillation is not diminished.

The internal temperature should be maintained throughout the reaction at 195° C.

The crude acrolein obtained is dried over calcium chloride and redistilled. The yield is 60–65% of theoretical (Moureu).

PHYSICAL AND CHEMICAL PROPERTIES

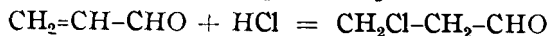
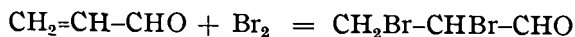
In the pure state acrolein is a clear liquid boiling at 52° C. and solidifying at – 88° C. Its specific gravity is 0.86 at 15° C., and its vapour density is 1.94. Its volatility at 20° C. is 407,000 mgm.

per cu. m. It is somewhat miscible with water (1 part of acrolein is miscible with 2-3 parts water)¹ and with most of the organic solvents.

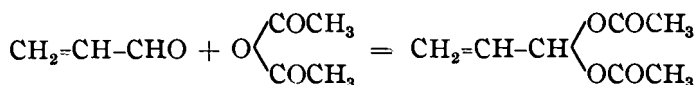
Acrolein is a substance which alters easily and in it the characteristic properties of the aldehydes—the tendencies to polymerisation and oxidation—are very pronounced. Polymerisation transforms acrolein into an amorphous white mass, insoluble in water and alcohol, which no longer has the irritating properties of acrolein and is known as “*disacryl.*” In order to prevent, or rather retard, this polymerisation the acrolein should be left in a somewhat impure condition, as it seems that the impurities have the property of inhibiting the change. Substances which have been found to be especially good stabilisers for acrolein are phenol, hydroquinone, benzoic acid, etc., which even if present to the extent of 1-2% check the polymerisation for many months (Moureu).

Among the reactions of acrolein which are important in determining its structural formula are those in which it is reduced to allyl alcohol and to propionaldehyde or oxidised to acrylic acid. Reduction is most conveniently carried out by means of aluminium amalgam,² while atmospheric oxygen is sufficient to oxidise it. More powerful oxidants cause profound breakdown of the molecule; thus nitric acid forms oxalic and glycolic acids and chromic acid mixture formic acid and carbon dioxide.

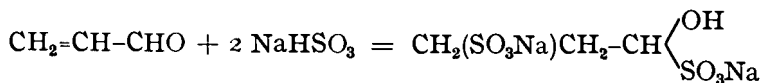
Because of the presence of a double link and an aldehyde group in its molecule, acrolein forms two different types of compounds, according to whether the double link or the aldehyde-oxygen takes part in the reaction. Thus, with the halogens or the halogen hydroacids, the following take place:



while with acetic anhydride



With sodium bisulphite, reaction takes place both with the unsaturated carbon atoms and with the aldehyde group³:

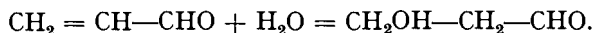


¹ GEUTHER, *Ann.*, 1859, **112**, 10.

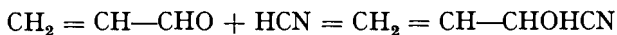
² HARRIES and HAGA, *Ann.*, 1904, **330**, 226.

³ M. MÜLLER, *Ber.*, 1873, **6**, 1445.

Water reacts with acrolein only at 100°, forming the corresponding hydroxy-aldehyde :



Alkalies rapidly polymerise acrolein.¹ An ethereal solution of potassium cyanide in presence of acetic acid forms the nitrile of α hydroxy vinylacetic acid² :



This is a colourless liquid, boiling at 93° to 94° C. at 16 mm. of mercury. Its density at 15° C. is 1.009, and it is miscible in all proportions with alcohol, ether and water, but sparingly soluble in petroleum ether.

Pure acrolein does not attack metals.

The minimum concentration of acrolein which causes lachrymation is 7 mgm. per cu. m. of air. The limit of insupportability is 50 mgm. per cu. m. The mortality-product is 2,000 according to Müller, and 7,000 according to Meyer.

DETECTION

*Lewin's Reactions.*³ On treatment of acrolein with a solution of sodium nitroprusside in piperidine, an intense blue coloration is produced which passes to violet with ammonia and to brown with mineral acids. The same colour changes are produced by bubbling air containing acrolein vapour through the reagent. Sensitivity : 25 mgm. acrolein per cu. m. of air.⁴ Instead of piperidine, dimethylamine may be employed, but the sensitivity of the reaction is then less.

*Nierenstein's Reaction.*⁵ This reaction is based on the change of colour of a solution of phloroglucinol in presence of acrolein. On treatment of the solution to be tested with 2-3 ml. 5% phloroglucinol and addition of 5-10 drops of alkali, and then boiling rapidly, the presence of acrolein is detected by a bluish-green colour.

*p-Nitro Phenylhydrazine Reaction.*⁶ An aqueous solution of *p*-nitro phenylhydrazine hydrochloride, which should remain colourless on addition of a few drops of acetic acid, produces an orange-yellow precipitate with acrolein. This precipitate consists of small stellar crystals, easily visible under the microscope.

¹ NEF, *Ann.*, 1904, **335**, 220.

² LOBRY DE BRUYN, *Rec. trav. chim.*, 1885, **4**, 223 ; V. DER SLEEN, *Rec. trav. chim.*, 1902, **21**, 211.

³ LEWIN, *Ber.*, 1899, **32**, 3388.

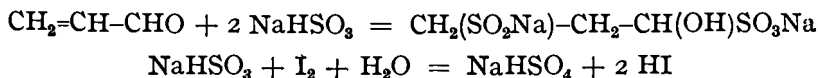
⁴ GRODPOVSKY, *Analisis Vozduxu*, Moscow, 1931, 206.

⁵ NIERNSTEIN, *Collegium*, 1905, 158 ; *Chem. Zentr.*, 1905 (II), 169.

⁶ H. BEHRENS, *Chem. Ztg.*, 1905, **27**, 1105.

QUANTITATIVE DETERMINATION

*Ivanov's Method.*¹ This is founded on the reaction of acrolein with sodium bisulphite already mentioned. The excess bisulphite is titrated with iodine according to the following equations :



0.1-0.15 gm. of the substance to be analysed is placed in a small glass bulb which is then sealed in the blowpipe and weighed. The bulb is placed in a bottle together with 100 ml. water. The bulb is then broken and a standardised solution of sodium bisulphite added, sufficient being employed to react with 50% more acrolein than is actually present in the sample. The mixture is allowed to stand for about 6 hours and then the excess of bisulphite is titrated with iodine solution in presence of starch, to a blue coloration stable for 15 minutes.

The bisulphite and iodine solutions are standardised so that 1 ml. of each is equivalent to 1 mgm. acrolein.

This method has also been suggested by Zappi.²

¹ N. IVANOV, *Arch. Hyg.*, 1911, **74**, 307.

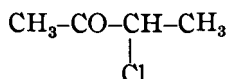
² E. ZAPPI and LABRIOLA, *Anales Asoc. Quim. Argentina*, 1930, **18**, 243.

CHAPTER XI
 HALOGENATED KETONES
 (A) ALIPHATIC

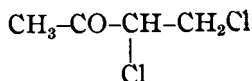
IN the ketone group, the halogenated derivatives are of great interest as war gases.

They are usually prepared by the direct action of the halogens on the corresponding ketones. The introduction of a halogen atom into the molecule of a ketone usually takes place according to a definite rule: The first halogen atom entering substitutes a hydrogen of the least hydrogenated alkyl group, whether secondary or tertiary, and it is only the second halogen atom which can enter a different group.

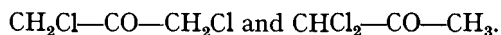
For example, in chlorinating methyl ethyl ketone, $\text{CH}_3\text{—CO—CH}_2\text{—CH}_3$, methyl- α -chloroethyl ketone is first obtained:



and then on further chlorination, methyl- α - β -dichloroethyl ketone:



The introduction of a second halogen atom into the molecule of these substances affects their properties differently according to the position it occupies. It is found that the symmetric dihalogenated ketones have higher specific gravities, higher boiling points and, in particular, more powerful toxic properties than the asymmetric dihalogenated ketones. Thus in chlorinating acetone, chloroacetone is first obtained, $\text{CH}_2\text{Cl—CO—CH}_3$, and then by further chlorination a mixture of the symmetric and asymmetric dichloro-derivatives is obtained:

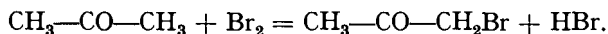


On examining these two compounds,¹ it is found that the symmetric compound (S.G. 1.383 and b.p. 171° C.) is more toxic

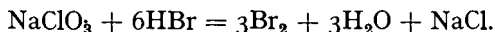
¹ T. POSNER and K. ROHDE, *Ber.*, 1909, **42**, 3233.

than the asymmetric derivative (S.G. 1·236 and b.p. 120° C.).¹ Symmetric dichloroacetone, besides its normal irritant action on the eyes and the respiratory organs, has, even in low concentrations, an irritant action on the skin which is more precisely termed "ortificant" action.²

In the preparation of the halogenated ketones by direct halogenation only half the halogen reacting enters the ketone molecule, the other half forming the halogen hydracid :



In order to prevent this loss of halogen, especially in the industrial manufacture of the bromo- and iodo- derivatives, the halogen of the hydracid is regenerated by adding to the reaction mixture an oxidising agent, usually sodium chlorate. By reaction with the hydracid this liberates the halogen which can re-enter the reaction :



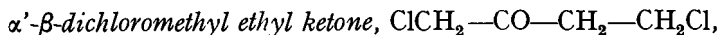
The halogenated aliphatic ketones are, in general, somewhat unstable compounds. In time, decomposition or resinification takes place. These processes are partly prevented by the addition of stabilising substances which impede the changes for some time.

Because of the presence of the carbonyl group in the molecule, they react with sodium bisulphite to form well-crystallised additive products. This behaviour is employed in practice to separate the halogenated ketones from the secondary products of the reaction.

The halogenated ketones have powerful lachrymatory properties. The iodine compounds are the most irritant, then following the bromine and lastly the chlorine.

During the war of 1914-18, bromoacetone and bromomethyl ethyl ketone were especially used. Chloroacetone was employed only for a short time, being soon superseded by other substances having a more powerful aggressive action.

Since the war several other halogenated ketones have been prepared and examined, such as



obtained by the action of ethylene on chloroacetyl chloride in presence of aluminium chloride, or, in better yield, by the action of diazomethane on β -chloropropionyl chloride and then treat-

¹ LINDEMANN, *Toxikologiya chem. sredkow bojowch*, Warsaw, 1925, 381.

² HACKMANN, *Chem. Weekblad.*, 1934, 31, 366.

ment with hydrochloric acid. It is a liquid boiling at 65° C. at a pressure of 3 mm. and has strong lachrymatory properties.¹

Fluoroacetone, obtained by the action of thallium fluoride on bromoacetone,² is a yellow liquid boiling at 72.5° C. It has a density of 0.967 at 20° C. It is described as having a pungent odour, but nothing has been reported concerning its aggressive action.

1. Chloroacetone. $\text{ClCH}_2\text{—CO—CH}_3$ (M.Wt. 92.5)

Chloroacetone was obtained by Riche in 1859³ in electrolysing a mixture of hydrochloric acid and acetone. It was used in the last war, especially by the French, to replace bromoacetone during the period of bromine shortage (1914–15).

LABORATORY PREPARATION⁴

It is prepared by the action of chlorine on acetone.

80 gm. acetone and 20 gm. calcium carbonate in lumps are placed in a wide-necked flask fitted with a three-holed stopper. Through one of the holes in the stopper a reflux condenser passes, through the second a tap-funnel and through the third a delivery tube for the chlorine. The calcium carbonate is added in order to neutralise the hydrochloric acid liberated in the reaction. A current of chlorine is passed in from a cylinder, and 30–40 ml. water are gradually added from the tap-funnel. The temperature is raised to 60° C. on a water-bath. When the calcium carbonate in the flask is almost exhausted, the current of gas is stopped and the mixture allowed to stand overnight. The liquid then settles into two layers; the top layer is separated and fractionally distilled.

PHYSICAL AND CHEMICAL PROPERTIES

Chloroacetone is a clear liquid boiling at 119° C. It is sparingly soluble in water, but easily in alcohol, ether, chloroform and other organic solvents. Its specific gravity is 1.162 at 16° C., and its vapour density is 3.2. It is relatively slightly volatile: its volatility at 20° C. is about 61,000 mgm. per cu. m. (Libermann).

On exposure to light in sealed glass containers it is converted in about 1 year into a solid carbonaceous substance which fumes in air giving off hydrochloric acid, and does not react with phenylhydrazine, hydroxylamine or oleum, but dissolves in fuming nitric acid.⁵

¹ R. CARROLL and SMITH, *J. Am. Chem. Soc.*, 1933, **55**, 370.

² P. RAY and coll., *J. Indian Chem. Soc.*, 1935, **12**, 93.

³ RICHE, *Ann.*, 1859, **112**, 321.

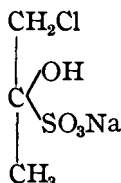
⁴ P. FRITSCH, *Ber.*, 1893, **26**, 597.

⁵ GIUA and ROCCIU, *Atti accad. sci. Torino*, 1932, **67**, 409.

When the vapour of chloroacetone is passed through a tube heated to 450°C ., acetone, acetaldehyde and crotonaldehyde are formed.¹

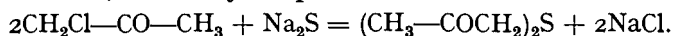
Chloroacetone does not react with water.² Chlorine even in the cold converts it into more highly chlorinated compounds; treatment at 100°C . in sunlight converts it into pentachloroacetone of the formula³ $\text{CHCl}_2\text{—CO—CCl}_3$. Bromine is almost without action in the cold, but on heating to about 100°C . it reacts vigorously forming chlorotribromoacetone.⁴ Potash decomposes chloroacetone, forming potassium chloride and red or brown products whose composition has not yet been determined.⁵

The manner in which chloroacetone reacts with other compounds is also interesting. With gaseous ammonia, for example, aminoacetone is formed,⁶ and with nascent hydrogen (from zinc and acetic acid) it is converted into acetone.⁷ Damp silver oxide oxidises it to glycollic, formic and acetic acids. On combination with sodium bisulphite, acicular crystals are formed, probably of an additive compound of the formula⁸ :



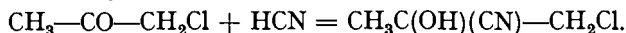
An additive compound is also formed with hexamethylene tetramine; this consists of crystals melting at 122°C . (Nef).

By the action of sulphuretted hydrogen or sodium sulphide on chloroacetone, diacetyl sulphide is formed :



This forms crystals melting at 47°C . and boiling at 136° to 137°C . at 15 mm. mercury pressure.

Chloroacetone reacts with hydrocyanic acid, forming chloroacetone chlorohydrin⁹ :



With potassium cyanide, cyanoacetone is not formed, but various polymerisation products are produced.

¹ NEF, *Ann.*, 1904, **335**, 278.

² LINNEMANN, *Ann.*, 1865, **134**, 171.

³ FRITSCH, *Ber.*, 1893, **26**, 597.

⁴ CLOEZ, *Ann. chim. phys.*, 1886, [6] **9**, 207.

⁵ MULDER, *Ber.*, 1872, **5**, 1009.

⁶ G. PINKUS, *Ber.*, 1893, **26**, 2197.

⁷ LINNEMANN, *loc. cit.*

⁸ NEKRASSOV, *op. cit.*

⁹ BISCHOF, *Ber.*, 1872, **5**, 864.

Chloroacetone decomposes in contact with iron and cannot be loaded directly into projectiles.

The lowest concentration producing irritation of the eyes is 18 mgm. per cu. m. of air. The limit of insupportability is 100 mgm. per cu. m. and the mortality-product is 3,000 (Müller).

2. Bromoacetone. $\text{BrCH}_2\text{—CO—CH}_3$ (M.Wt. 136.5)

Bromoacetone was prepared by Linnemann¹ in 1863, and because of its powerful lachrymatory properties was used by the Germans in 1915 in shells and hand-bombs.

LABORATORY PREPARATION

This compound is obtained in a similar manner to chloroacetone, by the action of bromine on acetone.

30 gm. acetone, 30 gm. acetic acid and 120 ml. water are placed in a flask of 250–300 ml. capacity which is fitted with a reflux condenser and a tap-funnel (Fig. 10). The whole is heated on a water-bath to 70° C. and then 91 gm. bromine are added from the tap-funnel, the flask being exposed to the direct light from a 750-watt lamp. When the liquid is decolourised 60 ml. of water are added, the flask cooled and a saturated solution of soda added. An oil separates and this is dried and distilled *in vacuo*.

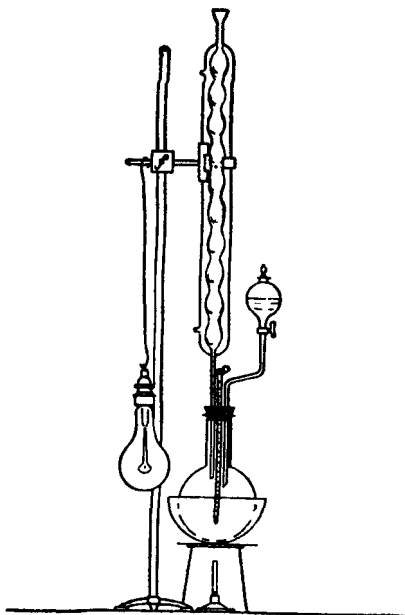
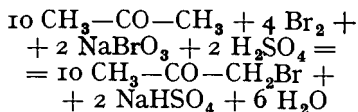


FIG. 10.

Bromoacetone may be also obtained in the laboratory by

the action of bromine dissolved in acetone on an aqueous solution of sodium bromate and sulphuric acid at 30° to 35° C.² The following reaction then takes place :

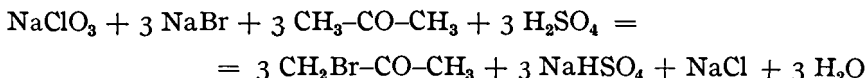


¹ LINNEMANN, *Ann.*, 1863, 125, 307.

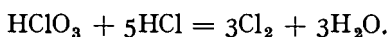
² A. CHRZASZCZEWSKA and W. SOBIERANSKY, *Roczniki Chem.*, 1927, 7, 79.

INDUSTRIAL MANUFACTURE

French Method. Because of the limited availability of bromine the manufacture of bromoacetone was carried out in France during the war by treating acetone with sodium bromate and sodium chlorate in presence of sulphuric acid instead of by the direct action of bromine on acetone. The following reaction takes place :



In this method, if the solution remains acid, hydrochloric acid is formed and this reacts with the sodium chlorate, liberating chlorine :



Hence there is simultaneous chlorination and bromination of the acetone, with the formation of a mixture of bromoacetone and chloroacetone.

German Method. The manufacture of bromoacetone in Germany¹ was carried out by treating an aqueous solution of sodium or potassium chlorate with acetone and then adding in small quantities the proper quantity of bromine.

The reaction is carried out in iron vessels *A* (Fig. II) of 4-5 cu. m. capacity (900-1,100 gallons) coated internally with resistant tiles and fitted with an agitator *D*. These are set in a wooden framework *E*.

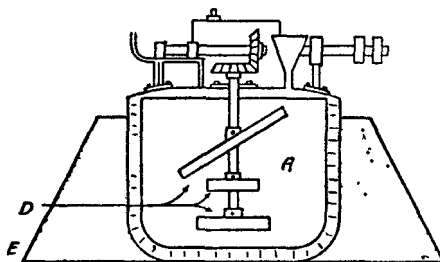


FIG. II.

The aqueous solution of sodium chlorate is first prepared, the acetone is added, and then the bromine introduced slowly,

stirring and maintaining the internal temperature at 30° to 40° C. At the end of the reaction the oily layer is separated and transferred to a vessel where it is treated with magnesium oxide to neutralise the excess of free acid.

In order to determine the quantity of bromoacetone formed, a part of the product is dried with calcium chloride and distilled. If more than 10% of the product distils below 136° C. the product is brominated further, if less than 10% then the operation is considered satisfactory. The product is stored with the addition

¹ NORRIS, *J. Ind. Eng. Chem.*, 1919, 11, 828.

of about 1 part of magnesium oxide to 1,000 parts of bromoacetone in order to neutralise the hydrobromic acid slowly formed on storage.

PHYSICAL AND CHEMICAL PROPERTIES

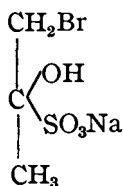
Pure bromoacetone is a colourless liquid with a pungent odour and a boiling point of 23.5° C. to 24.5° C. at 3.5 mm. mercury and 31.4° C. at 8 mm. mercury pressure. At ordinary pressure it boils at 136° C. with partial decomposition, hydrobromic acid and a resinous residue slightly soluble in water and alcohol being formed. On cooling strongly it solidifies to a mass which melts at -54° C. Its specific gravity at 0° C. is 1.631, its vapour tension at 10° C. is 1 mm. and at 20° C., 9 mm. The vapour density is 4.75 and its volatility at 20° C. is 75,000 mgm. per cu. m. (Müller).

The commercial product is yellow or brown.

Bromoacetone is only slightly soluble in water, but very soluble in alcohol, ether, acetone and other organic solvents. It is not very stable, even in the pure state.¹ It polymerises in time, especially under the influence of light and heat,² though this process may be impeded by the addition of stabilising substances. During the war a small quantity of magnesium oxide was added to bromoacetone and this checked the polymerisation for several months (Meyer).

Bromoacetone when distilled with steam partly passes over unaltered and partly decomposes to give an oily product containing little bromine, while the water is coloured brown.

It combines readily with a variety of substances. With sodium bisulphite it forms a crystalline substance of the formula :



On passing well-dried ammonia into bromoacetone in ethereal solution, acicular crystals separate, probably due to the formation of an additive compound.³

By the action of hydrocyanic acid on bromoacetone⁴ in the cold (*i.e.*, at about 0° C.) bromoacetone cyanohydrin is formed.

¹ EMMERLING and WAGNER, *Ann.*, 1880, **204**, 29.

² GIUA and ROCCIU, *Atti accad. sci. Torino*, 1932, **67**, 409.

³ SOKOLOVSKY, *Ber.*, 1876, **9**, 1687.

⁴ A. CHRZASZCZEVSKA and W. SOBIERANSKY, *loc. cit.*

This is a colourless liquid with a boiling point of 94.5°C . at a pressure of 5 mm. of mercury. Its specific gravity is 1.584 at 13°C ., and it is soluble in water, alcohol and ether.

The bromine atom of bromoacetone is easily separated from the molecule and substituted by other atoms or radicles. Thus on treating bromoacetone with alcoholic potash, hydroxyacetone and potassium bromide are obtained; with sodium iodide iodoacetone is formed, this being a substance with strongly lachrymatory properties, but of little importance as a war gas because of its high cost.

Bromoacetone reacts with iron, but does not attack lead, so it is essential to store it in lead-lined containers.

The animal fibres absorb more bromoacetone than do the vegetable fibres. The absorption capacity is fairly high and textiles are discoloured. It is found that textiles which are merely air-dried absorb more bromoacetone than those which have been completely freed from all water.¹

For the purification of places contaminated with bromoacetone, spraying with a solution of 240 gm. "liver of sulphur" in 140 ml. of a soap solution diluted with 10 litres of water is recommended.

The lower limit of irritation is 1 mgm. per cu. m. of air. The maximum concentration which a normal man can support for not more than 1 minute is 10 mgm. per cu. m. The mortality-product is 4,000 (Müller) or 32,000 (Prentiss).

During the war of 1914-18 the French used a mixture of bromoacetone and chloroacetone (80 : 20) known as "*Martonite*." The reasons for the employment of this mixture are of a technical nature (see p. 151).

3. Bromomethyl Ethyl Ketone. $\text{BrCH}_2\text{—CO—C}_2\text{H}_5$ (M.Wt. 151)

This substance was employed in place of bromoacetone, whose production during the war period was impeded by the necessity of reserving acetone for the needs of the explosives industry.

On the other hand, methyl ethyl ketone, the primary material in the preparation of this war gas, is easily obtainable even in wartime, for it is a by-product in the manufacture of acetone from pyroligneous acid. The monobromo- derivative of methyl ethyl ketone has similar aggressive properties to bromoacetone and was used by both the French and the Germans in the war of 1914-18.

PREPARATION

This compound is prepared both in the laboratory and on the plant scale by a method similar to that already described for

¹ ALEXEJEVSKY, *J. Prikl. Khimii.*, 1929, 1, 184.

bromoacetone. That is, by brominating methyl ethyl ketone with sodium bromide in presence of sodium chlorate. In this preparation bromomethyl ethyl ketone is not the only product, a mixture with the isomeric methyl- α -bromoethyl ketone always being obtained.¹

PHYSICAL AND CHEMICAL PROPERTIES

Bromomethyl ethyl ketone is a colourless or pale yellowish liquid which boils at ordinary pressure at 145° to 146° C. with decomposition. Its specific gravity is 1.43. It is insoluble in water; alteration on exposure to light is rapid. It is not decomposed by the action of water, and in general its chemical behaviour is very similar to that of bromoacetone. It is easily absorbed by active carbon. Places contaminated with bromomethyl ethyl ketone can be decontaminated by spraying with a soapy solution of "liver of sulphur."

Bromomethyl ethyl ketone is an irritant especially to the eyes. The minimum concentration capable of causing irritation of the eyes is 1.6 mgm. per cu. m., according to Müller. The limit of insupportability is 11 mgm. per cu. m. of air (Fries), and the mortality-product is 6,000.

(B) AROMATIC

The halogenated ketones of the aromatic series may be prepared, like those of the aliphatic series, by the action of the halogens on the corresponding ketones. Some may be obtained by the Friedel and Craft synthesis, that is, by condensing an aromatic hydrocarbon with an aliphatic halogen acid in presence of anhydrous aluminium chloride.

In the preparation of these war gases by direct halogenation it is necessary to follow the exact procedure given so as to introduce the halogen only into the side-chain, as compounds with a nuclear halogen atom have no lachrymatory properties.

In order to ensure this, according to Graebe² and Staedel,³ the halogenation should be carried out at the boiling point of the ketone, or, according to Gautier⁴ and Hunnius,⁵ by operating in presence of special solvents such as carbon disulphide, acetic acid or carbon tetrachloride,⁶ which seem to have the function of directing the halogen atom into the side-chain.

¹ L. V. REYMENTANT, *Bull. acad. roy. Belg.*, 1900, 724.

² GRAEBE, *Ber.*, 1871, 4, 35.

³ STAEDEL, *Ber.*, 1877, 10, 1830.

⁴ GAUTIER, *Ann. chim. phys.*, 1888, 14, 377.

⁵ HUNNIUS, *Ber.*, 1877, 10, 2006.

⁶ WARD, *J. Chem. Soc.*, 1923, 123, 2207.

The aromatic halogenated ketones, unlike those of the aliphatic series, are quite stable compounds. Another difference is that the aromatic derivatives, although they contain a carbonyl group, form no additive compounds with bisulphite.¹

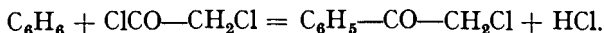
Recently, some fluorinated members of this group have been prepared, such as *fluoroacetophenone*,² a brown liquid with a pungent odour, which boils at 98° C. at 8 mm. pressure. It is described as having lachrymatory properties, but the magnitude of these is not reported.

An interesting fact concerning these compounds from the aggressive point of view is that the halogenated aromatic ketones have superior lachrymatory properties to the corresponding aliphatic compounds. Thus chloroacetophenone has a much more powerful lachrymatory action than the chloro- and even the bromo- derivative of acetone. This fact, besides having great advantages on the economic side—and being by no means negligible from the purely offensive point of view—indicates that it is not only the halogen to which the lachrymatory properties of these compounds is due, but also to the rest of the molecule to which the halogen is united.

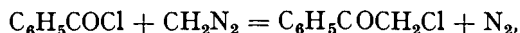
With regard to the biological properties, it has been found that several substances of this group, like α -chloroacetophenone and α -3:4 trichloroacetophenone, cause,³ besides lachrymation, a painful sensation of itching when they penetrate the pores of the skin in the form of a vapour or a cloud. This action, as previously mentioned, is termed "*orticant action*."

1. Chloroacetophenone. $C_6H_5-CO-CH_2Cl$ (M.Wt. 154.5)

α -Chloroacetophenone—also termed *ω -chloroacetophenone*, *phenacyl chloride* or *phenyl chloromethyl ketone*—was prepared in 1871 by Graebe⁴ by absorbing chlorine in acetophenone. Later, in 1884, Friedel and Craft⁵ succeeded in obtaining it by the action of chloroacetyl chloride on benzene in presence of aluminium chloride :



It may also be prepared by the action of diazomethane on benzoyl chloride in ethereal solution⁶ :



¹ NEKRASSOV, *op. cit.*

² P. RAY, *J. Indian Chem. Soc.*, 1935, **12**, 93.

³ M. JASTRZEBSKY and SUSZKO, *Roczniki Chem.*, 1933, **13**, 293.

⁴ GRAEBE, *Ber.*, 1871, **4**, 35.

⁵ FRIEDEL and CRAFT, *Ann. chim. phys.*, 1886, [6] **1**, 507.

⁶ CLIBBENS and NIERENSTEIN, *J. Chem. Soc.*, 1915, **107**, 1492.

or by the action of chloroacetyl chloride and aluminium trichloride on a solution of phenyl dichloroarsine in carbon disulphide.¹

This compound, because of its lachrymatory properties was tested during the last war (1918) in Edgewood Arsenal and considered to be a useful and practicable war gas.

It is designated in the Chemical Warfare Service of America as "CN."

LABORATORY PREPARATION

It is prepared by the action of chlorine on acetophenone according to Korten and Scholl's method.²

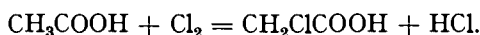
20 gm. acetophenone and 100 gm. acetic acid are placed in a flask fitted with a stopper carrying two holes, through one of which passes a delivery tube for the chlorine and through the other an air-condenser. The mixture is agitated to facilitate the solution of the acetophenone and then the whole is weighed. A rapid stream of chlorine is passed through the solution, cooling externally if necessary until the necessary amount of chlorine has been absorbed.

The product is allowed to stand at ordinary temperature until the liquid becomes colourless. It is then poured into ice-water; the chloroacetophenone separates as an oily liquid which rapidly solidifies. The crystals are separated and crystallised from dilute alcohol.

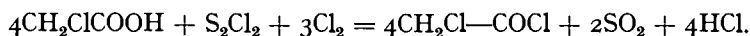
INDUSTRIAL MANUFACTURE

The manufacture of chloroacetophenone commencing with acetic acid comprises the following steps:

(1) *Preparation of Monochloroacetic acid*:

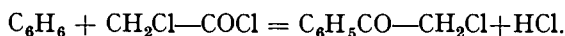


(2) *Chlorination of Monochloroacetic Acid* to obtain chloroacetyl chloride:



This chlorination may be carried out either by means of chlorine and sulphur monochloride or by the action of phosphorus trichloride.

(3) *Condensation of Chloroacetyl Chloride with Benzene*:



Operating Details. The glacial acetic acid is placed in a lead-

¹ GIBSON and coll., *Rec. trav. chim.*, 1930, **49**, 1006.

² KORTEN and SCHOLL, *Ber.*, 1901, **34**, 1902.

lined vessel fitted with a thermometer and a fractionating column connected with an absorption tower, which is filled with coke and serves to absorb the hydrochloric acid. The vessel is heated to about 98° C., while the calculated quantity of dry chlorine gas is slowly passed in.

Monochloroacetic acid is thus obtained and this is transferred without further purification to another similar vessel. Sulphur monochloride is added, and chlorine is introduced, while heating to 45° C., to complete the chlorination. The chlorinated product is then transferred to a third vessel in which fractional distillation separates the chloroacetyl chloride from the other products (sulphur chloride, excess monochloroacetic acid, etc.).

The calculated quantities of benzene and aluminium chloride are placed in an enamelled vessel and maintained at 25° C. The chloroacetyl chloride is then added in small quantities while the mixture is agitated. At the end of this addition, the mass is warmed to 60° to 70° C. for 2 hours and then poured into cold water. The layer containing the chloroacetophenone is freed from benzene by distillation and the chloroacetophenone finally purified by steam distillation.

PHYSICAL AND CHEMICAL PROPERTIES

Chloroacetophenone forms colourless or slightly yellowish crystals which melt at 58° to 59° C. (Staedel).

It boils at ordinary pressure at 244° to 245° C. and may be distilled without any decomposition. At 14 mm. mercury pressure it boils at 139° to 141° C. Its specific gravity at various temperatures is as follows :

TEMPERATURE ° C.	S.G.
0	1.334
15	1.324
25	1.313
55	1.263

The vapour tension of chloroacetophenone at ordinary temperatures is very low. It is given as a function of temperature in the following table :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
0	0.0017
15	0.0078
25	0.0198
35	0.0473
55	0.158

The volatility is 30 mgm. per cu. m. of air at 0° C., and 105 mgm. per cu. m. at 20° C.

The specific heat of chloroacetophenone is 0.264 calorie and the latent heat of evaporation 89 calories.

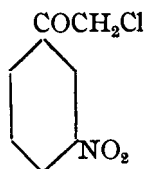
Chloroacetophenone is soluble in alcohol, benzene (40% by weight), ether and carbon disulphide,¹ as well as in many of the other war gases. For instance, phosgene dissolves 9.5% by weight, and cyanogen chloride 63% by weight. It is, however, very slightly soluble in titanium tetrachloride, silicon tetrachloride or water (1 gm. in 1,000 ml.).

The solubility of chloroacetophenone in the readily volatile solvents is utilised in diffusing it in air. For this purpose benzene is the best solvent, carbon tetrachloride also being occasionally employed. When a solution in one of these solvents is sprayed into the air the solvent evaporates rapidly, leaving the chloroacetophenone dispersed in a state of fine subdivision.

Chloroacetophenone is quite stable. It is not hydrolysed by water even on boiling and it is unaffected by humidity. It is completely decomposed by 60% oleum. Hot aqueous solutions of sodium carbonate convert it into hydroxymethyl phenyl ketone of the formula (Graebe), $C_6H_5-CO-CH_2OH$, which forms crystals melting at 86° C. and boiling at 118° C. at 11 mm. mercury pressure. It is soluble in alcohol, ether and chloroform.

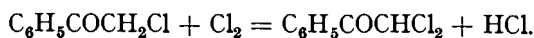
Chloroacetophenone is oxidised in benzene solution by such oxidising agents as chromic acid or potassium permanganate to benzoic acid.

By adding it in small quantities to a mixture of fuming nitric acid and sulphuric acid, shaking after each addition, it is converted into benzoic acid and *m*-nitro- α -chloroacetophenone² :



This forms crystals melting at 100.5° to 102° C.

By bubbling gaseous chlorine through chloroacetophenone in presence of aluminium iodide or chloride, $\alpha\alpha$ -dichloroacetophenone³ is formed :



This is obtained as crystals melting at 20° to 21.5° C. Its density

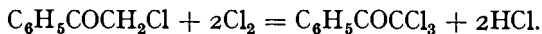
¹ STAEDEL, *Ber.*, 1877, **10**, 1830.

² BARKENBUS and CLEMENTS, *J. Am. Chem. Soc.*, 1934, **56**, 1369.

³ H. GAUTIER, *Ann. chim. phys.*, 1888, [6] **14**, 345-385.

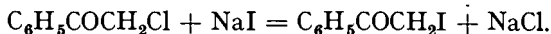
is 1.34 at 15° C., and it boils at ordinary pressure at 247° C. with decomposition. At 25 mm. pressure it distils unaltered at 143° C. It has inferior lachrymatory properties to chloroacetophenone.

With more vigorous chlorination, at a temperature of 200° C. aided by sunlight, $\alpha\alpha\alpha$ -trichloroacetophenone¹ is formed :



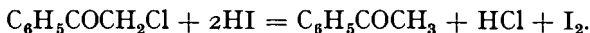
This is a liquid boiling at 145° C. at 25 mm. pressure and having a density of 1.425 at 16° C.

Chloroacetophenone reacts with sodium iodide in solution in aqueous alcohol, forming α -iodoacetophenone² :

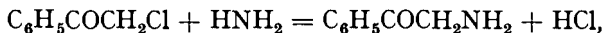


This is a crystalline substance melting at 29.5° to 30° C., which boils at 170° C. at 30 mm. pressure and is insoluble in water, but soluble in alcohol, ether and benzene.

With hydriodic acid or, better, by boiling with an acetic acid solution of potassium iodide, chloroacetophenone separates iodine and forms acetophenone³ :

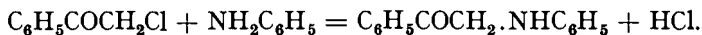


Alcoholic ammonia converts chloroacetophenone in the cold to α -aminoacetophenone⁴ :



which is partly converted into iso-indole.

With aniline, phenacyl aniline is formed⁵ :

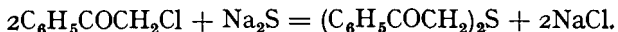


Urotropine forms an additive product of the formula⁶



which forms crystals melting at 145° C.

Chloroacetophenone dissolved in alcohol reacts at 60° C. with an alcoholic solution of sodium sulphide to form phenacyl sulphide, as follows⁷ :



This is a colourless crystalline compound, melting at 76.5° to 77.2° C., odourless, insoluble in water, but soluble in alcohol,

¹ H. GAUTIER, *Ann. chim. phys.*, 1888, [6] **14**, 396.

² A. COLLET, *Compt. rend.*, 1899, **128**, 312; MATHESON, *J. Chem. Soc.*, **1931**, 2515.

³ PANCENKO, *loc. cit.*

⁴ W. STAEDEL and coll., *Ber.*, 1876, **9**, 563.

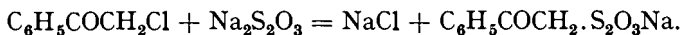
⁵ MÖHLAU, *Ber.*, 1882, **15**, 2466; MATHESON, *J. Chem. Soc.*, **1931**, 2514.

⁶ MANNICH and HAHN, *Ber.*, 1911, **44**, 1542.

⁷ TAFEL, *Ber.*, 1890, **23**, 3474; A. CHRZASZCZEWSKA and CHVALINSKY, *Roczniki Chem.*, 1927, **7**, 67.

ether and acetic acid. On heating to 100° C. it decomposes, forming hydrogen sulphide, acetophenone and products whose nature has not yet been defined.

By boiling an alcoholic solution of chloroacetophenone with an aqueous solution of sodium thiosulphate, the sodium salt of phenacyl thiosulphuric acid is formed :

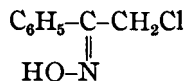


On refluxing equimolecular amounts of chloroacetophenone and potassium thiocyanate together, needle-shaped crystals are formed of the following formula :



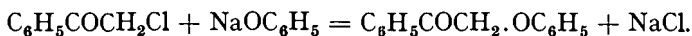
which melt at 72° to 73° C. and are soluble in alcohol, ether and chloroform.¹

1 mol. chloroacetophenone reacts with 3 mols. hydroxylamine hydrochloride in dilute methanol solution at ordinary temperatures, with formation of α -chloroacetophenone oxime, of the formula ² :



This forms crystals melting at 88.5° to 89° C. whose vapours have a powerful lachrymatory action. This substance causes persistent and strong irritation when applied to the skin in the solid state or in solution.

Chloroacetophenone, on treatment in the cold with sodium phenate in aqueous or alcoholic solutions, reacts as follows ³ :



Chloroacetophenone does not attack iron containers. It is resistant to heat and insensitive to detonation, so that it can be loaded into projectiles without fear of its suffering change.

It was used, melted with magnesium oxide and mixed with nitrocellulose, for the preparation of irritant candles.⁴

Graebe noted that the vapours of chloroacetophenone irritated the eyes, and the Americans (Fries) have found that a concentration of 0.3 mgm. per cu. m. of air is sufficient to provoke lachrymation. According to Müller,⁵ the lachrymatory action commences at a concentration of 0.5 mgm. per cu. m., while it

¹ DYCKERHOF, *Ber.*, 1877, **10**, 119.

² KORTEN and SCHOLL, *Ber.*, 1901, **34**, 1901.

³ LELLMANN, *Ber.*, 1890, **23**, 172.

⁴ Federal Laboratory, *U.S. Pat.* 1,864,754.

⁵ MÜLLER, *Militär-Wochenblatt.*, 1931, **116**, 754.

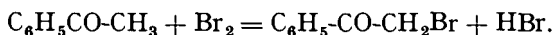
irritates the nose at 1 mgm. per cu. m. At a concentration of 2 mgm. per cu. m. it causes irritation of the skin of the face.

Besides its lachrymatory action, this substance has an "ortieant" action on the skin if diffused in the air in sufficient concentration (100 mg. per cu. m. according to Müller).

The limit of insupportability is 4.5 mgm. per cu. m. The mortality-product is 4,000 according to Müller and 8,500 according to American experiments (Prentiss).

2. Bromoacetophenone. $C_6H_5-CO-CH_2Br$ (M.Wt. 199)

Bromoacetophenone was obtained by Emmerling and Engler¹ by the reaction of bromine on acetophenone.



PREPARATION

In the laboratory it is usually prepared by Möhlau's² modification of Emmerling's original method, that is, by the action of bromine on acetophenone.

25 gm. acetophenone and 125 gm. acetic acid are placed in a flask through whose stopper passes a reflux condenser, a tap-funnel and a delivery-tube for carbon dioxide. While agitating the contents of the flask, 30 gm. bromine³ are added little by little from the tap-funnel, meanwhile passing a current of carbon dioxide through the liquid to remove the hydrobromic acid formed in the reaction. When all the bromine has been added, the current of carbon dioxide is continued for 5-10 minutes and then the whole allowed to stand for about 1 hour before heating on the water-bath to remove the carbon dioxide completely. When the liquid in the flask is colourless it is poured into much water. The bromoacetophenone separates for the most part as a yellow oil which forms a crystalline mass on cooling. The crystals are collected and purified by alcohol.

PHYSICAL AND CHEMICAL PROPERTIES

Bromoacetophenone forms white rhombic prisms which become greenish on exposure to light, owing to incipient decomposition. It melts at 50° C. and boils at ordinary pressure at 260° C. with decomposition, and at 12 mm. mercury pressure at 133° to 135° C. with partial decomposition. It is insoluble in water, but soluble in the common organic solvents (alcohol, ether, benzene, etc.).

Bromoacetophenone is not decomposed by water even on

¹ EMMERLING and ENGLER, *Ber.*, 1871, 4, 147.

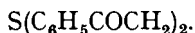
² MÖHLAU, *Ber.*, 1882, 15, 2465.

³ WARD, *J. Chem. Soc.*, 1923, 123, 2207.

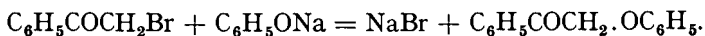
boiling. With potassium permanganate it reacts to form benzoic acid.¹ With cold fuming nitric acid it gives bromotrinitroacetophenone.

Treated in the cold with alcoholic ammonia, it forms iso-indole. The reaction with aniline is more vigorous than in the case of chloroacetophenone.²

Bromoacetophenone³ in alcoholic solution when treated with an alcoholic solution of sodium sulphide reacts vigorously, evolving hydrogen sulphide and forming a crystalline mass of phenacyl sulphide (see p. 159).



On treatment in the cold with sodium phenate in aqueous or alcoholic solution, bromoacetophenone reacts according to the equation⁴:



It combines with hexamethylene tetramine to form an additive product of the formula:



which forms crystals melting at 165° C.⁵

The lachrymatory power of bromoacetophenone is less than that of chloroacetophenone.

¹ HUNNIUS and ENGLER, *Ber.*, 1878, **11**, 932.

² MATHESON and coll., *J. Chem. Soc.*, **1931**, 2514.

³ TAFEL and MAURITZ, *Ber.*, 1890, **23**, 3474.

⁴ R. MÖHLAU, *Ber.*, 1882, **15**, 2498.

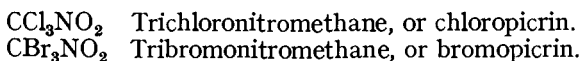
⁵ MANNICH, *Ber.*, 1911, **44**, 1545.

CHAPTER XII

HALOGENATED NITRO- COMPOUNDS

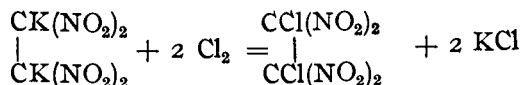
THE presence in a molecule of a nitrogen atom united by a double link to an oxygen almost always involves a certain degree of toxicity. Moreover, this toxicity is increased and lachrymatory action is added if halogen atoms are also present.

During the last war much interest was taken in the trihalogen derivatives of nitromethane as war gases :



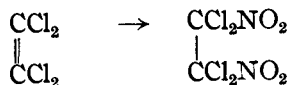
Since the war, research on the halogenated nitro- compounds has been continued, especially on the corresponding compounds of the higher homologues of methane. The following results have been obtained :

(1) *Symmetrical dichlorotetranitro ethane*,¹ obtained by the action of chlorine on the potassium salt of symmetrical tetranitro ethane :



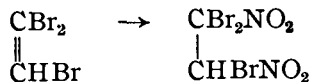
forms crystals melting at 105° C.²

(2) *Symmetrical tetrachlorodinitro ethane*, obtained by the action of fuming nitric acid on tetrachloro ethylene³ :



forms crystals melting at 142° to 143° C.

(3) *α α β Tribromo α β dinitro ethane*,⁴ obtained by the action of oxides of nitrogen on tribromo ethylene in a closed tube at 40° C.



forms colourless crystals melting at 133° to 134° C.

¹ HUNTER, *J. Chem. Soc.*, 1924, **125**, 1480.

² BURROWS, *J. Chem. Soc.*, **1932**, 1360.

³ BILTZ, *Ber.*, 1902, **35**, 1529; ARGO and JAMES, *J. Phys. Chem.*, 1919, **23**, 578.

⁴ BURROWS, *J. Chem. Soc.*, **1932**, 1357.

These compounds all have lachrymatory power, especially tetrachloro dinitro ethane, which is much more powerful in this respect than chloropicrin.

Some of the halogenated derivatives of unsaturated nitro-compounds have also been examined, e.g., *chloronitro ethylene* ($\text{CH}_2 = \text{CClNO}_2$) and various of its homologues.¹ These compounds, though having powerful lachrymatory properties, cannot be considered for use as war gases for owing to the presence of the unsaturated linkage in their molecules they tend to polymerise forming substances without lachrymatory properties.

Recently other substances having a certain amount of interest in war gas chemistry have been prepared :

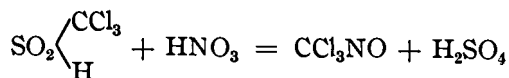
(1) *Trifluoronitroso methane*,² obtained by the action of fluorine on silver cyanide in the presence of silver nitrate, is a bright blue gas, fairly stable chemically. It melts at -150°C ., boils at -80°C . and has an unpleasant odour.

(2) *Trichloronitroso methane*,³ obtained by the action of nitric acid on the sodium salt of trichloromethyl sulphinic acid, is a liquid boiling at 5°C . at 70 mm. pressure.

Both these substances have an irritant action.

1. Trichloro Nitroso Methane. CCl_3NO (M.Wt. 148)

Trichloronitroso methane has been prepared recently by Prandtl and Sennewald⁴ by the action of nitric acid on the sodium salt of trichloromethyl sulphinic acid :



A very violent reaction takes place and the yield of trichloro nitroso methane is low. This compound is more conveniently obtained by the action of an aqueous solution of sodium trichloro methyl sulphinate, potassium nitrate and sodium nitrite on sulphuric acid.⁵

LABORATORY PREPARATION

250 ml. 20% sulphuric acid are placed in a round-bottomed flask fitted with a tap-funnel and a well-cooled coil-condenser. The flask is heated to 70°C . and a cold solution of 94 gm. sodium trichloromethyl sulphinate, 50 gm. potassium nitrate and 25 gm. sodium nitrate in 300 ml. water is dropped in from the tap-funnel,

¹ WILKENDORF, *Ber.*, 1924, **57**, 308 ; SCHMIDT and RUTZ, *Ber.*, 1928, **61**, 2142.

² O. RUFF, *Ber.*, 1936, **69**, 598, 684.

³ PRANDTL and SENNEWALD, *Ber.*, 1929, **62**, 1754.

⁴ PRANDTL and SENNEWALD, *loc. cit.*

⁵ PRANDTL and DOLLFUS, *Ber.*, 1932, **65**, 756.

regulating the rate of addition so that the internal temperature is maintained at 70° C. by the heat of reaction. The contents of the flask suddenly turn blue and the trichloronitroso methane commences to distil, collecting in the receiver, which is cooled by ice, as a blue liquid. The yield is 75–80%.

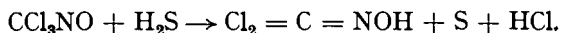
PHYSICAL AND CHEMICAL PROPERTIES

It is a dark blue liquid which when boiled at ordinary pressures partially decomposes. It boils undecomposed at 5° C. at a pressure of 70 mm. Its specific gravity is 1.5 at 20° C.

It is insoluble in water, but dissolves in the common organic solvents. On storing at ordinary temperature in a sealed glass container, it decomposes in 2–3 months with formation of nitrosyl chloride, oxides of nitrogen and chloropicrin. It is much more stable in solution.

It reacts slowly with aqueous alkaline solutions and rapidly in presence of ether.

Oxygen and oxidising agents transform it into various compounds, among which chloropicrin has been identified. On reduction with hydrogen sulphide, dichloro formoxime (see p. 77) is formed :



The vapour of trichloronitroso methane strongly attacks rubber.

Both in the liquid and the vapour states it has a disagreeable odour ; irritation is caused to the eyes and to the respiratory tract, lachrymation and coughing being produced.

2. Chloropicrin. CCl_3NO_2 (M.Wt. 164.5)

Chloropicrin, or trichloronitromethane, was prepared in 1848 by Stenhouse.¹ In the war of 1914–18 it was largely employed as a war gas, more particularly as it combined a simple and economic manufacture with many of the characteristic desiderata of a war gas.

It was first employed by the Russians in 1916 in hand-grenades, dissolved in sulphuryl chloride (50%).

Chloropicrin is also known as “ *Klop* ” (Germany), “ *Aquinite* ” (France), and “ *PS* ” (America).

It has found application as an insecticide and fungicide² and has been used for eradicating rats from ships.³

¹ STENHOUSE, *Ann.*, 1848, **66**, 241.

² G. BERTRAND, *Compt. rend.*, 1919, **168**, 742 ; *Chim. et Ind.*, 1937, **37**, 419.

³ A. PIUTTI, *Rend. accad. sci. Napoli*, 1918, **26**, para. iii.

PREPARATION

Various methods have been proposed for the preparation of chloropicrin. For example :

- (1) By the action of picric acid on calcium hypochlorite.¹
- (2) By the action of chlorine on nitromethane or mercury fulminate.²
- (3) By the action of nitric acid on certain chlorinated organic compounds, as chloroform,³ chloral,⁴ trichloroethylene,⁵ etc.
- (4) By the action of a mixture of nitric and hydrochloric acids on the by-products of acetone manufacture.⁶

The method which was most used during the war of 1914-18 was that of the action of picric acid on calcium hypochlorite. This method was not very suitable in practice, for it required as raw material a substance not easily spared during the war, when it was needed for the explosive industry. The other methods of production referred to above have been studied since the war, showing the interest of chemists in working out a method which does not require the use of a raw material of limited accessibility.

LABORATORY PREPARATION

Chloropicrin may be prepared in the laboratory by the method proposed by Hoffmann.⁷

550 gm. chloride of lime made into a paste with about 1 litre water are placed in a 5-litre flask. A paste of sodium picrate, made by mixing 50 gm. picric acid with 10 gm. sodium hydroxide and 250 ml. water, is added with continuous stirring. The flask is then fitted with a stopper carrying a long condenser and the contents steam-distilled until no more oily droplets come over.

The reaction takes place very rapidly and is completed in about $\frac{1}{2}$ hour. The oily distillate is separated from the water in a separatory funnel, dried over calcium chloride and redistilled.

Yield 70% of the theoretical.

INDUSTRIAL MANUFACTURE

The various methods used during the war for the manufacture of chloropicrin do not differ greatly from Hoffmann's method given above.

¹ STENHOUSE, *Ann.*, 1848, **66**, 241 ; HOFFMANN, *Ann.*, 1866, **139**, 111.

² KEKULÉ, *Ann.*, 1857, **101**, 204.

³ MILLS, *Ann.*, 1871, **160**, 117.

⁴ KEKULÉ, *Ann.*, 1857, **101**, 212 ; N. DANAILA and SOARE, *Bul. chim. soc. română științe*, 1932, **35**, 53.

⁵ R. BURROWS and HUNTER, *J. Chem. Soc.*, **1932**, 1357.

⁶ G. SANNA, *Rend. sem. fac. sci. Cagliari*, 1933, **2**, 87.

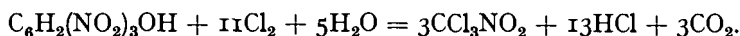
⁷ HOFFMANN, *Ann.*, 1866, **139**, 111.

In the German plants a paste of chloride of lime and water was treated in large vessels of 2-3 m. diameter and 4-5 m. depth with picric acid added in small amounts at a time, the temperature being maintained at about 30° C. The mixture was then distilled in a current of steam, the distillate being collected in large receivers where the chloropicrin was separated from water.

The Americans preferred to use calcium picrate instead of the sparingly soluble picric acid, proceeding in the following manner¹ :

A paste of chloride of lime was first prepared and pumped into a vertical vessel of enamelled iron where it was mixed with calcium picrate prepared previously by mixing picric acid with water and an excess of lime. The mixture was allowed to react at ordinary temperatures for about 2 hours and then a current of steam was introduced at the bottom of the vessel. In these conditions the rise in temperature accelerated the reaction and at 85° C. the chloropicrin began to distil. Distillation was continued until no more chloropicrin came over.

According to a patent by Orton and Pope,² chloropicrin may also be obtained by the direct action of chlorine on picric acid, or other nitro-derivative of phenol or of naphthol :



The reaction is carried out in alkaline solution (sodium or potassium hydroxide, or a mixture of the corresponding carbonates) so as to dissolve the nitro-compound and to neutralise the hydrochloric acid which otherwise impedes the chlorination of the picric acid. The reaction takes place very readily at a low temperature (between 0 and 5° C.).

Recently a new method of preparation of chloropicrin has been worked out in Rumania.³ This uses petroleum as raw material. The principal stages of the preparation of chloropicrin by this process are as follows :

- (a) Nitration of hydrocarbons present in the petroleum.
- (b) Chlorination of the nitro-compounds obtained with chloride of lime.
- (c) Distillation of the chloropicrin in a current of steam.

PHYSICAL AND CHEMICAL PROPERTIES

Chloropicrin in the pure state is a slightly oily, colourless, refractive liquid with a characteristic odour. The crude product is yellow due to impurities.

¹ TRUMBULL and coll., *J. Ind. Eng. Chem.*, 1920, **12**, 1068.

² ORTON and POPE, *Brit. Pat.*, 142,878/1918.

³ RADULESCU and SECAREANU, *Antigaz*, 1927, No. 6, 3.

It boils at 112° C. at 760 mm. pressure and at 49° C. at 40 mm. of mercury.¹ It solidifies at - 69.2° C.

It may be distilled in a current of steam without decomposition.

The specific gravity of chloropicrin between 0° and 50° C. is as follows :

TEMPERATURE (° C.)	S.G.	TEMPERATURE (° C.)	S.G.
0	1.6930	30	1.6400
10	1.6755	40	1.6219
20	1.6579	50	1.6037

The coefficient of expansion at various temperatures is as follows :

At 0° C. .	0.00102	At 30° C. .	0.00106
At 10° C. .	0.00103	At 50° C. .	0.00110

Its specific heat between 15° and 35° C. is 0.235 ; its latent heat of evaporation is 59 calories. Its vapour density compared with that of air is 5.69. The vapour tension of chloropicrin at any temperature t may be calculated empirically² by employing the formula (see p. 5) :

$$\log p = 8.2424 - \frac{2045.2}{273 + t}$$

In the following table the values of the vapour tension are reported together with the corresponding volatilities at various temperatures³ :

TEMPERATURE ° C.	VAPOUR TENSION MM. HG.	VOLATILITY MG./LITRE
0	5.91	57.4
10	10.87	104
15	14.12	136
20	16.91	184
25	23.81	—
30	30.50	295
35	40.14	—
50	80.7	748

¹ COSSA, *Gazz. chim. Ital.*, 1872, **2**, 181.

² BAXTER and BEZZENBERGER, *J. Am. Chem. Soc.*, 1920, **42**, 1386.

³ KRCZIL, *Untersuchung und Bewertung Techn. Adsorptionsstoffe*, Leipzig, 1931, 422.

The solubility of chloropicrin in water is very low ; according to Thompson and Black¹ 100 gm. water dissolve the following amounts of chloropicrin :

° c.	GM.
0	0·22
10	0·19
20	0·17
30	0·15
40	0·14
75	0·11

The solubility of water in chloropicrin is also very low :

° c.	GM. IN 100 GM. WATER
32	0·1003
36	0·1185
48	0·1647
55	0·2265

These low mutual solubilities facilitate their separation in the preparation and render drying of the chloropicrin unnecessary, unless it is to be employed for some special purpose, as, for example, in " NC " mixture (80% chloropicrin and 20% stannic chloride).

Chloropicrin dissolves easily in benzine, carbon disulphide and ethyl alcohol (1 part dissolves 3·7 parts chloropicrin at water-bath temperature). In ether it is, however, relatively sparingly soluble. (At 11°C., 5 volumes ether dissolve 1·5 volumes chloropicrin—Cossa.)

Chloropicrin is a fairly stable compound. It is not hydrolysed by water² and not attacked by mineral acids like hydrochloric, nitric and sulphuric, either cold or hot. Only 20% oleum decomposes it with formation of phosgene and nitrosyl sulphuric acid.³

On heating to 112° C., according to some authorities (Stenhouse, Cossa, etc.), it distils unchanged, while, according to others,⁴ when maintained gently boiling it partially decomposes into phosgene and nitrosyl chloride :



The presence of some metals like copper, tin, zinc, aluminium, iron and lead only slightly influences the velocity of decomposition even at boiling point.⁵

¹ T. THOMPSON and BLACK, *J. Ind. Eng. Chem.*, 1920, **12**, 1066.

² P. RONA, *Z. ges. expt. med.*, 1921, **13**, 16.

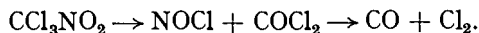
³ SECAREANU, *Bull. soc. chim.*, 1927, **41**, 630.

⁴ I. A. GARDEN and F. FOX, *J. Chem. Soc.*, 1919, **115**, 1188.

⁵ A. PETROV and coll., *J. Prikl. Khim.*, 1929, **2**, 629.

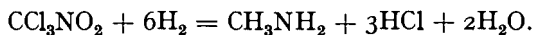
By passing chloropicrin in the vapour state through a red-hot tube of quartz or porcelain, it decomposes with formation of chlorine and nitric oxide, while hexachloroethane deposits on the cold part of the tube.¹

According to the researches of Piutti,² chloropicrin decomposes as follows when exposed to ultra-violet rays :



A similar decomposition takes place when an aqueous solution of chloropicrin is shaken with wood-charcoal, previously activated by treatment with sodium hydroxide and heating to 450° C.³

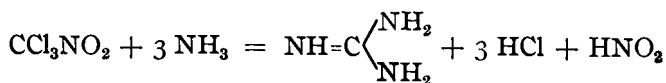
Reducing agents convert it into various products according to the nature of the reductant and the conditions of reduction. Thus Raschig⁴ obtained cyanogen chloride with stannous chloride and hydrochloric acid ; Geisse,⁵ with iron filings and acetic acid, obtained methylamine :



Frankland⁶ observed that the best results are obtained in this reaction by adding the chloropicrin in small portions to a mixture of iron filings and acidified water.

On treatment of chloropicrin with an aqueous solution of sodium or potassium hydroxide there is no reaction, but if alcoholic soda or potash is employed, a gradual decomposition takes place and after a time crystals of potassium chloride separate.

Aqueous ammonia does not react with chloropicrin. However, if the latter is saturated with ammonia gas, or even brought into reaction with an alcoholic solution of ammonia, ammonium chloride and nitrate are formed (Stenhouse). According to Hoffmann,⁷ on heating chloropicrin in an autoclave to 100°C. with an alcoholic solution of ammonia, guanidine is formed according to the following equation :



By the action of alcoholic sodium sulphide⁸ on chloropicrin also dissolved in alcohol, a violent reaction takes place, heat is

¹ STENHOUSE, *Ann.*, 1848, **66**, 244.

² A. PIUTTI and MAZZA, *Atti accad. sci. Napoli*, 1926, **32**, 97.

³ ALEXEJEVSKY, *J. Obscei Khim.*, Ser. A., 1932, **2**, 341.

⁴ RASCHIG, *Ber.*, 1885, **18**, 3326.

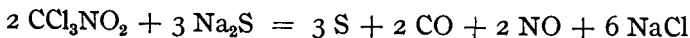
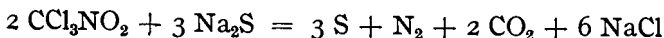
⁵ GEISSE, *Ann.*, 1859, **109**, 284.

⁶ FRANKLAND, *J. Chem. Soc.*, 1919, **115**, 159.

⁷ HOFFMANN, *Ber.*, 1868, **1**, 145.

⁸ KRETOV and MELNIKOV, *J. Obscei Khim.*, Ser. A., 1932, **2**, 202.

developed and a tarry material separates. According to the conditions of the reaction there are formed carbon monoxide, nitric oxide, nitrogen, carbon dioxide, sodium chloride, sulphur, etc.



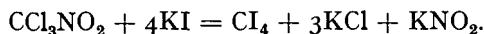
Chloropicrin reacts with sodium or potassium sulphite, forming the corresponding salt of nitromethane disulphonic acid ¹ :



This reaction must be brought about by heating to 90° to 100° C., and takes place very rapidly in alcoholic as well as aqueous solution. The product of the reaction, sodium nitromethane disulphonate, forms small spheroidal plates, soluble with difficulty in cold water but easily in hot water. According to Rathke,² if the reactants are heated excessively a salt is obtained which no longer contains the NO₂— group and to which he attributes the formula CH(SO₃Na)₃.

By the action of potassium bromide on chloropicrin, tribromo nitromethane or bromopicrin is obtained, together with carbon tetrabromide, nitromethane, etc.

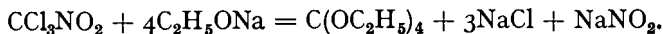
Potassium iodide reacts with chloropicrin, giving no triiodo nitromethane, but completely decomposing the molecule with formation of carbon tetraiodide, as follows ³ :



Even in the presence of insufficient potassium iodide, no triiodo nitromethane is formed.

Sodium cyanide in aqueous-alcoholic solution reacts energetically with chloropicrin to form various compounds : sodium chloride, nitrite, carbonate and oxalate, cyanogen chloride, etc.⁴

Chloropicrin reacts even at ordinary temperature with sodium ethylate, forming sodium nitrite and chloride and the tetra ethyl ester of orthocarbonic acid ⁵ :



Sodium methylate reacts similarly.⁶ This reaction also takes place when sodium reacts with an alcoholic solution of chloropicrin.⁷

¹ RATHKE, *Ann.*, 1872, **161**, 153 ; BACKER, *Rec. trav. chim.*, 1930, **49**, 1107.

² RATHKE, *Ann.*, 1873, **167**, 219.

³ G. D. SSYCHEV, *J. Khim. Promiscl.*, 1930, **7**, 1168.

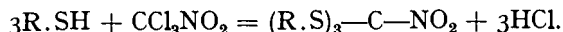
⁴ BASSETT, *Jahresb. fortschr. Chem.*, 1866, 495 ; NEKRASSOV, *op. cit.*

⁵ H. BASSETT, *Ann.*, 1864, **132**, 54 ; RÖSE, *Ann.*, 1880, **205**, 249.

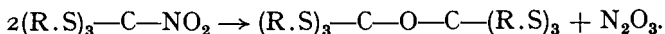
⁶ H. HARTEL, *Ber.*, 1927, **60**, 1841.

⁷ ALEXEJEVSKY, *J. Khim. Promiscl.*, 1931, **8**, 50.

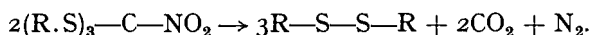
Chloropicrin reacts with mercaptans at the ordinary temperature, forming hydrochloric acid and the ester of orthonitro trithioformic acid :



The researches of Ray and Das¹ show that on heating, the reaction takes place very rapidly and nitrous gases are evolved :



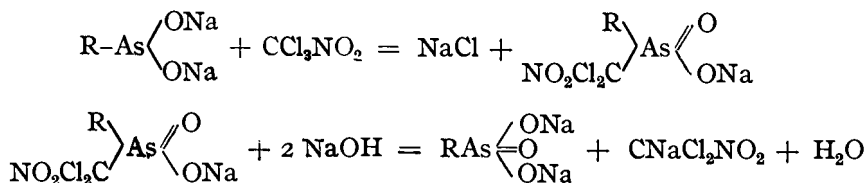
Later researches by Nekrassov,² however, have demonstrated that chloropicrin in these conditions behaves as an oxidising agent on the mercaptan, so that a disulphide of the formula R.S.S.R and also carbon monoxide and nitrogen are formed.



In this reaction between chloropicrin and mercaptans, an intense yellowish-red colouration is produced, which appears as readily in presence of potassium mercaptide as with the free mercaptan. As an insoluble substance is formed, this reaction may be employed for the detection of chloropicrin (see p. 178).

Chloropicrin oxidises hydrazine³ even at the ordinary temperature, evolving nitrogen. Tronov and Gershevich⁴ have studied the velocity of the reaction between chloropicrin and hydrazine in various solvents (alcohol, ether, carbon disulphide, etc.).

By the action of the sodium salts of the arylarsenious or alkylarsenious acids on chloropicrin in alcoholic solution, a reaction takes place which is first gentle and then very violent and leads to the formation of the following compounds⁵ :



Much data has been accumulated on the behaviour of chloropicrin in contact with metals. According to Ireland,⁶ chloropicrin attacks steel slightly and copper and lead very energetically. American publications, however, assert that chloropicrin attacks all metals. The corrosion of metals is confined to superficial

¹ RAY and DAS, *J. Chem. Soc.*, 1919, **115**, 1308 ; 1922, **121**, 323.

² NEKRASSOV and MELNIKOV, *Ber.*, 1929, **62**, 2091.

³ A. K. MACBETH and J. D. PRATT, *J. Chem. Soc.*, 1921, **119**, 1356.

⁴ TRONOV and GERSHEVICH, *J. Rusk. fis. khim. obsc.*, 1928, **60**, 171.

⁵ JAXUBOVICH, *J. prakt. Chem.* (N.F.), 1933, **138**, 159.

⁶ IRELAND, *Medical Aspects of Gas Warfare*, Washington, 1926, 298.

staining, a layer being formed which protects the metal from further corrosion.

Chloropicrin is one of the war gases most easily held back by active carbon.¹

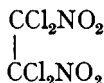
Fibrous materials absorb relatively little chloropicrin vapour and are not changed in resistance or colour. The absorbed chloropicrin may usually be removed by a current of dry air.²

Chloropicrin in vapour form strongly irritates the eyes. According to American observations (Fries), a man's eyes are closed after 3-30 seconds' exposure to an atmosphere containing 2-25 mgm. chloropicrin per cu. m. of air. At a concentration of 19 mgm. per cu. m. the eyes commence to lachrymate³ and the limit of insupportability is about 50 mgm. per cu. m.

Besides its irritant action, chloropicrin has a toxic and asphyxiating action. The mortality-product is 20,000 according to Prentiss,⁴ and according to Ferri is 12,000 for dogs and cavies.⁵

3. Tetrachloro dinitroethane

(M.Wt. 258)



This substance was first prepared by Kolbe,⁶ who did not, however, succeed in determining its physical and chemical characteristics. It was later obtained by Biltz,⁷ by the action of fuming nitric acid, or a mixture of nitric acid and concentrated sulphuric acid, on tetrachloroethylene.

It may also be obtained by the action of anhydrous nitrogen peroxide on tetrachloroethylene at 10-12 atmospheres and 60° to 80° C. for 3-6 hours (Biltz).

LABORATORY PREPARATION (BILTZ)

5 gm. tetrachloroethylene and about 8 gm. nitrogen peroxide are placed in a glass tube which is sealed off in the blowpipe and then heated at 100° C. for about 3 hours. After cooling, the tube is opened, the contents poured into a basin and the excess nitrogen peroxide allowed to evaporate off at room temperature. The solid white residue is then redissolved in warm

¹ H. S. HARNED, *J. Am. Chem. Soc.*, 1920, **42**, 372; HERBST, *Biochem. Z.*, 1921, **115**, 204.

² ALEXEJEVSKY, *J. Prikl. Khim.*, 1929, **1**, 184.

³ D. KISS, *Z. ges. Schiess-Sprengstoffw.*, 1930, **25**, 260, 300.

⁴ A. PRENTISS, *Chemicals in War*, New York, 1937, 16.

⁵ FERRI and MADESINI, *Giorn. di Medicina Militare*, 1936.

⁶ H. KOLBE, *Ber.*, 1869, **2**, 326.

⁷ H. BILTZ, *Ber.*, 1902, **35**, 1529.

ligroin (not over 60° C.) and the tetrachlorodinitroethane crystallised out as plates.

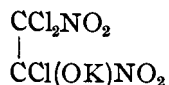
The nitrogen peroxide is prepared by drying the product obtained by the action of nitric acid on arsenious oxide by means of calcium nitrate and saturating it with oxygen.

PHYSICAL AND CHEMICAL PROPERTIES

It occurs as crystals which are decomposed by heating to 130° C. with evolution of nitrogen peroxide. In a closed tube it melts at 142° to 143° C.

It is volatile in steam and insoluble in water, but easily soluble in benzene and ether. It dissolves also in alcohol and in acetic acid. From these two solvents it may be reprecipitated by addition of water.

It is not decomposed, even at the boiling point, by aqueous alkali solutions. With alcoholic potash it is converted into a crystalline substance of the formula ¹ :



Potassium cyanide causes complete breakdown of the molecule, and potassium carbonate, cyanogen chloride and carbon are formed.

Heat is developed on adding an alcoholic solution of tetrachlorodinitroethane to an aqueous solution of potassium iodide, and iodine separates as well as a crystalline substance : potassium tetranitroethane.²

Tetrachlorodinitroethane has powerful irritant³ properties, and besides being about six times⁴ as toxic as chloropicrin, has about eight times the lachrymatory power of the latter, according to Nekrassov.

4. Bromopicrin. CBr_3NO_2 (M.Wt. 298)

Bromopicrin, or tribromonitromethane, was prepared in 1854 by Stenhouse⁵ while studying the action of bromine on picric acid. It was never employed as a war gas in the war of 1914-18.

PREPARATION

This compound may be obtained in various ways :

(a) By the action of picric acid on " bromide of lime." ⁶

¹ HOCH and KOLBE, *J prakt Chem*, 1871, [2] 4, 60

² R BURROWS and coll, *J Chem Soc*, 1932, 1360

³ HANZLIK, *J pharm exp Med*, 1919, 14, 221.

⁴ A HOOGVEEN, *Chemische Strijdmiddelen*, The Hague, 1936.

⁵ STENHOUSE, *Ann*, 1854, 91, 307.

⁶ GROVES and BOLAS, *Ber*, 1870, 3, 370.

(b) By the action of bromine and potash on nitromethane.¹

(c) By the action of bromine on nitranilic acid (*i.e.*, *p*-dinitro dihydroxy quinone).²

The most practical method of preparing bromopicrin in the laboratory is the following, according to Bolas and Groves³ :

Four parts of calcium oxide and 50 parts of water are mixed in a flask. Six parts of bromine are then added in small portions while the flask is shaken and externally cooled to prevent an excessive rise in temperature. One part of picric acid is then added and the mixture distilled under reduced pressure. The bromopicrin passes over in the first fractions of the distillate. It is separated from the water and dried over calcium chloride.

PHYSICAL AND CHEMICAL PROPERTIES

Bromopicrin forms prismatic crystals which melt at 10.25° C. and boil at 127° C. at 118 mm. pressure.

Its specific gravity is 2.811 at 12.5° C. and 2.79 at 18° C.⁴

It is only slightly soluble in water, but dissolves easily in benzene, carbon tetrachloride, chloroform, alcohol and ether. Bromopicrin is precipitated from its alcoholic solution by the addition of water.

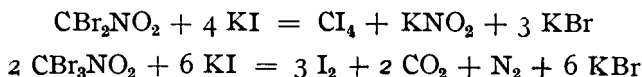
It dissolves small quantities of iodine to form a violet solution.

When heated rapidly at the ordinary pressure it decomposes with explosion. On heating to 130° C. it forms carbonyl bromide and nitrosyl bromide according to the equation :

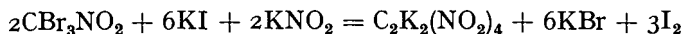


In general, bromopicrin behaves chemically like chloropicrin, but is less stable to chemical reagents. By the action of brominating agents it is converted into carbon tetrabromide (Bolas and Groves).

It reacts with potassium iodide variously according to the conditions of the reaction :



With potassium iodide and nitrite, iodine separates⁵ :



An alcoholic solution of potassium cyanide reacts with

¹ MEYER and CHERNIAK, *Ann.*, 1875, **180**, 122.

² LEVY and JEDLICKA, *Ann.*, 1888, **249**, 85.

³ BOLAS and GROVES, *Ann.*, 1870, **155**, 253.

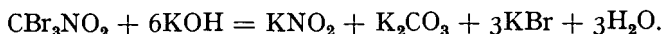
⁴ NEKRASSOV, *Khimija Otravljajuscikh Vescestv*, Leningrad, 1929, 125.

⁵ L. HUNTER, *J. Chem. Soc.*, 1922, **123**, 543.

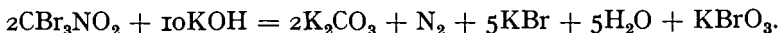
bromopicrin in the cold to give, as final products of reaction, the potassium salt of symmetrical tetranitroethane and cyanogen bromide.¹

Alcoholic solutions of bromopicrin precipitate silver bromide by the action of silver nitrate, slowly in the cold and rapidly on warming (Stenhouse).

When bromopicrin is treated with a solution of potassium hydroxide (1 part KOH and 1.5 parts H₂O) it first dissolves slowly and then decomposes as follows² :



or else,



It is not decomposed by cold sulphuric acid.

Like chloropicrin, it reacts with hydrazine to evolve nitrogen.³

It also reacts with sodium ethylate, but very slowly.⁴ Sodium or potassium sulphide react differently with bromopicrin, according to the conditions of the reaction.⁵

Bromopicrin vapour irritates the eyes : the minimum concentration which causes irritation is 30 mgm. per cu. m. of air, according to Lindemann.⁶ According to Mayer's researches,⁷ bromopicrin has a toxic power only one-eighth to one-tenth of that of chloropicrin.

Analysis of the Halogenated Nitro-compounds

DETECTION OF CHLOROPICRIN

The detection of chloropicrin is most simply carried out by direct sensory perception.

Various methods have been suggested for the detection of chloropicrin by chemical means. None of these is as sensitive as perception by odour, according to Deckert.⁸

*Method of Pyrogenic Decomposition.*⁹ One of the most widely used methods for the detection of chloropicrin in air consists in decomposing it by heat and then testing for chlorine in the products.

¹ SCHOLL and BRENNISEN, *Ber.*, 1898, **31**, 642.

² WOLFF and RUEDEL, *Ann.*, 1897, **294**, 202 ; N. MELNIKOV, *J. Obscei Khim.*, Ser. A., 1936, **4**, 1061.

³ A. K. MACBETH and J. D. PRATT, *J. Chem. Soc.*, 1921, **119**, 1356.

⁴ L. HUNTER, *loc. cit.*

⁵ KRETOV, *J. Obscei Khim.*, Ser. A, 1932, **2**, 202.

⁶ LINDEMANN, *Toxsykologia chemicznych srodkow bojowych*, Warsaw, 1925, 379.

⁷ A. MAYER, *Compt. rend.*, 1920, **171**, 1396.

⁸ W. DECKERT, *Z. Hyg. Infektionskrankh.*, 1929, **109**, 485.

⁹ A. C. FIELDNER, OBERFELL, etc., *J. Ind. Eng. Chem.*, 1919, **11**, 519.

The gas mixture is passed through a tube of quartz or porcelain heated almost to redness and the products of the decomposition are then bubbled through a solution containing potassium iodide and starch paste. If chloropicrin is present in the mixture under examination, chlorine will be liberated and this will liberate iodine from the potassium iodide and so colour the starch blue.¹

Engel's "*Indicator Apparatus*" is based on a similar principle.² It consists of a glass tube (see Fig. 12) through which passes a

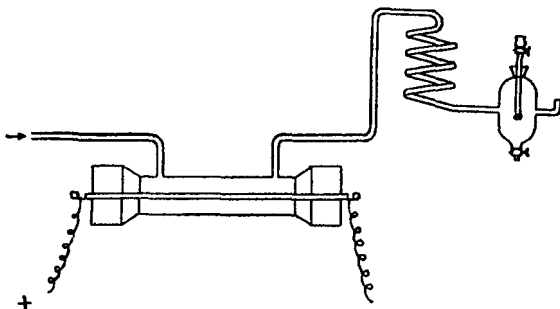


FIG. 12.

silica rod which can be electrically heated to redness. The tube is connected with a special glass receiver inside which the stem of a tap-funnel projects so as to hold in suspension a drop of starch-iodide solution. The detection of chloropicrin in air is carried out by passing the gas to be examined through the apparatus. If chloropicrin is present, the hanging drop of starch-iodide solution will be coloured blue.

The sensitivity of this reaction depends very much on the age of the starch solution and it is advisable to use a recently prepared solution.³

The Flame Test. Another method of detection, also based on the pyrogenic decomposition of chloropicrin, consists in passing the gas mixture to be examined into a gas jet, the flame of which maintains a copper spiral at red heat.⁴

This flame, in presence of even 0.25 mgm. chloropicrin per litre of air, is coloured green (Krczil).

*Ray and Das's Method.*⁵ This method of detection is based on

¹ This method of detecting chloropicrin was employed to determine the duration of the protection afforded by anti gas filters against mixtures of air and chloropicrin. DUBININ, *J. Prikl. Khim.* 1931, 1109.

² ENGEL, *Z. ges. Schuess Sprengstoffw.*, 1929, 24, 451.

³ F. KRCZIL, *Untersuchung und Bewertung Technischer Adsorptionsstoffe*, Leipzig, 1931, 422.

⁴ See p. 40 of the present book, and LAMB, *J. Am. Chem. Soc.*, 1920, 42, 78.

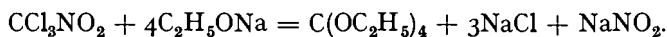
⁵ RAY and DAS, *J. Chem. Soc.*, 1919, 115, 1308; 1922, 121, 393.

a reaction recently discovered by Ray and Das, according to which chloropicrin, in reacting with the potassium salts of mercaptans, forms insoluble condensation products.

According to Nekrassov,¹ in this method the gas to be tested is passed through an alcoholic solution of the potassium salt of dithioethylene glycol. In the presence of chloropicrin a yellow precipitate, m.p. 123° C., separates.

This method may also be conveniently applied to the quantitative determination of chloropicrin, since the chlorine in the chloropicrin molecule is quantitatively converted into potassium chloride.

Sodium Ethylate Method. This method consists in decomposing chloropicrin with sodium ethylate (see p. 171) and then proceeding to the detection of the sodium nitrite or chloride formed in the reaction :



By means of this reaction chloropicrin may be detected at a concentration of about 6 mgm. per cu. m. of air, according to Ireland.²

Dimethylaniline Paper. The detection of chloropicrin by means of this paper depends on the change in colour from white to yellow or maroon which takes place in presence of this gas.

The dimethylaniline papers are prepared by soaking strips of filter paper in a 10% solution of dimethylaniline in benzene.³

If the concentration of chloropicrin is low, the colour change may be seen when the paper is moved about in the gaseous atmosphere. Chlorine, bromine and nitrous gases also produce a colour-change with this paper, but of a different shade from that with chloropicrin.⁴

Thiophenol Method. This method consists in passing the gas mixture to be tested through an alcoholic solution of thiophenol. In the presence of chloropicrin a white precipitate or opalescence forms.⁵ A turbidity appears in 3-4 minutes with 1-2 litres of the gas containing about 60 mgm. chloropicrin per cu. m.⁶

Alexejevsky's Method. This depends on the reduction of chloropicrin by metallic calcium to form nitrous acid, which is detectable by the Griess reaction.⁷

¹ NEKRASSOV, *Voina i Tecnica*, 1926, **275**, 32.

² IRELAND, *op. cit.*, 298.

³ DECKERT, *Z. Hyg. Infektionskrankh.*, 1929, **109**, 485; *Z. anal. Chem.*, 1938, **113**, 183.

⁴ HENNIG, *Gasschutz und Luftschutz*, 1937, 19.

⁵ NEKRASSOV, *Ber.*, 1929, **62**, 2091.

⁶ PANCENKO, *op. cit.*

⁷ ALEXEJEVSKY, *J. Khim. Promiscl.*, 1931, **8**, 50.

The gas mixture under examination is passed through a wash-bottle containing ethyl alcohol and the solution obtained then treated with metallic calcium. The nitrous acid which is formed is then identified with sulphanilic acid and α naphthylamine. In the presence of chloropicrin a red precipitate is produced. Sensitivity, 2 mgm. of chloropicrin.

This reaction cannot be used for the quantitative determination of chloropicrin.

Other Colour Reactions. On boiling the substance to be tested with an alcoholic solution of potassium hydroxide and then adding a few ml. of thymol, a yellow colouration appears in the presence of chloropicrin and this changes to reddish-violet on addition of sulphuric acid.

Substitution of resorcinol for thymol gives a red colouration.¹

Quantitative Determination

GAS VOLUMETRIC METHOD OF DUMAS. The quantitative determination of chloropicrin may be carried out by decomposing the sample to be examined and measuring the volume of the nitrogen formed by the volumetric method of Dumas. In employing this method it is advisable² to use a very long combustion tube with its front part filled for 8-10 cm. with a mixture of copper turnings and reduced copper. It is also best to carry out the combustion as slowly as possible so as to prevent the nitrogen peroxide from escaping decomposition.

SODIUM SULPHITE METHOD.³ This method is based on the reaction between sodium sulphite and chloropicrin already mentioned :



In practice this determination is carried out by adding to a weighed quantity of the chloropicrin in a small flask fitted with a condenser, an excess of an aqueous-alcoholic solution of sodium sulphite, prepared by dissolving 10 gm. sodium sulphite in 250 ml. water and diluting with an equal volume of ethyl alcohol. The liquid in the flask is then carefully heated so as to distil off all but about 10 ml. This is then diluted with water to 100 ml. and 10 ml. of nitric acid and an excess of a standardised solution of silver nitrate are added. The solution is then warmed to drive off the nitrous gases and to coagulate the silver chloride, and then cooled and the excess silver nitrate titrated with a solution of ammonium thiocyanate (ferric alum indicator).

¹ GUILLEMARD and LABAT, *Bull. soc. pharm. Bordeaux*, 1919.

² STENHOUSE, *Ann.*, 1848, **66**, 245.

³ THOMPSON and BLACK, *J. Ind. Eng. Chem.*, 1920, **12**, 1067.

This method, according to Aksenov,¹ may be applied to the determination of chloropicrin vapour in air. A measured volume of the air is passed through an aqueous alcoholic solution of potassium sulphite, the latter then boiled and the amount of chloride determined by Volhard's method.

SODIUM PEROXIDE METHOD. This method consists in decomposing the chloropicrin with sodium peroxide and then volumetrically determining the chlorine liberated in the reaction.²

A measured volume of the gas mixture to be examined is passed through a wash-bottle containing 50 ml. of a 1% solution of sodium peroxide in 50% ethyl alcohol prepared in the following manner: 2 gm. sodium peroxide is dissolved in 100 ml. iced water and just before using 25 ml. of this solution is diluted with 25 ml. 95% alcohol.

The chloropicrin, on coming into contact with the alcoholic solution of sodium peroxide, decomposes, forming sodium chloride, which may be determined volumetrically with a N/100 solution of silver nitrate (using potassium chromate as indicator), after neutralising the alcoholic solution with sulphuric acid (to the phenolphthalein end-point).

The number of ml. of silver nitrate solution used multiplied by 0.546 gives the quantity of chloropicrin in mgm. present in the volume of air passed through the sodium peroxide solution.

This method of analysis was also used by Dubinin³ for the determination of chloropicrin in the gas mixtures prepared for the testing of activated carbons.

¹ AKSENOV, *Metodica Toksikologii boevikh otravljajuscikh Vescestv*, Moscow, 1931, 95.

² FIELDNER and coll., *J. Ind. Eng. Chem.*, 1919, **11**, 519.

³ DUBININ, *J. Prikl. Khim.*, 1931, 1100.

CHAPTER XIII

CYANOGEN DERIVATIVES

THE war gases belonging to the class of cyanogen derivatives are characterised by the presence of the CN— radicle in their molecules. It has been found that this radicle may have one of the following two formulæ :



The first of these formulæ seems less suitable than the second for these war gases, which like the mono- and di-halogenated derivatives of acetylene (see p. 45), have properties more in keeping with the presence of a divalent carbon atom. It may be concluded that it is the presence of this divalent carbon atom rather than that of the nitrogen atom which accounts for the toxicity of this radicle. The bivalent carbon atom has in fact great chemical reactivity and is the point of attack in all chemical and biochemical reactions.

Among the various compounds containing the CN group which were employed in the war of 1914-18, hydrocyanic acid, phenyl carbylamine chloride and the cyanogen halides, particularly cyanogen bromide, were most widely used.

The cyanogen halides may be considered as derivatives of hydrocyanic acid in which the hydrogen atom is substituted by a halogen atom. According to some authorities the aggressive power of these compounds is greater than that of hydrocyanic acid, for besides their toxic properties, due to the presence of the CN— group, they have an irritant action due to the presence of the halogen.

Various other compounds containing the CN— radicle were studied towards the end of the war and since that period. Of these, chlorobenzyl cyanide, bromobenzyl cyanide, diphenyl cyanoarsine, phenarsazine cyanide, etc., were used to a considerable extent as war gases. Recently cyanogen fluoride has also been prepared and studied. It is a colourless gas with powerful lachrymatory properties.

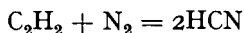
1. Hydrocyanic Acid. HCN (M.Wt. 27)

Hydrocyanic acid was discovered by Scheele in 1782. He noted that it was extremely toxic, but it was scarcely used as a war gas

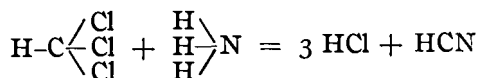
during the war of 1914-18 because of its high vapour tension and its rapid diffusion.

Only the French used it, and not more than 4,000 tons were employed during the whole war period.

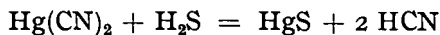
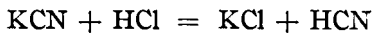
Hydrocyanic acid may be prepared in various ways: by passing electric sparks through a mixture of acetylene and nitrogen,



or by heating chloroform with ammonia,



The method most commonly used, especially if it is desired to prepare anhydrous hydrocyanic acid, consists in decomposing a cyanide with an acid (hydrochloric, sulphuric, hydrosulphuric, carbonic, etc.).



LABORATORY PREPARATION ¹

100 gm. potassium cyanide, as free as possible from carbonate and in pellet form, are placed in a flask fitted with a tap-funnel and a delivery tube. The delivery tube leads to two U tubes in series which are filled with a mixture of fused and granular calcium chloride, and immersed in a water-bath at 35° C. The second of these tubes may be connected to two more U tubes, the first of which is maintained at about -10° C.² in a freezing mixture and the second at +20° C. Each of these tubes, which are designed to receive the condensate of hydrocyanic acid formed in the reaction, is fitted at the bottom with a glass lead-off tube. This is connected through a glass cock to a cooled flask in which the liquid hydrocyanic acid collects.

Before the preparation is commenced it is advisable to pass a current of dry air through the whole of the apparatus. Cooled aqueous sulphuric acid (1 : 1) is allowed to drop slowly through the tap-funnel on to the potassium cyanide, regulating the rate of addition so that 1 drop of hydrocyanic acid condenses in the first receiver every second minute. Towards the end of the operation it may be necessary to heat the contents of the flask

¹ MADE and PANTING, *J. Chem. Soc.*, 1898, **73**, 256.

² It is advisable not to cool below -10°, otherwise the hydrocyanic acid solidifies and prevents the gas passing.

almost to boiling in order to maintain the evolution of hydrocyanic acid.

The greater part of the hydrocyanic acid produced in the reaction condenses in the first U tube and is collected in the corresponding flask.

According to Slotta,¹ in order to maintain a regular evolution of hydrocyanic acid it is advisable to add about 40% ferrous sulphate to the sulphuric acid and to run a recently prepared solution of potassium cyanide on to the sulphuric acid (1 : 1) which is meanwhile maintained at 50° C., rather than to add the sulphuric acid to the potassium cyanide. The evolution tube for the hydrocyanic acid should also be connected to the following apparatus :

(a) A condenser, in which water vapour and part of the hydrocyanic is condensed.

(b) A wash-bottle containing 20 ml. 2 N. sulphuric acid maintained at 50° C. in a bath.

(c) A wash-bottle containing glass-wool and 200 gm. calcium chloride, maintained at 50° C. in a bath.

(d) A receiver, cooled externally with ice and salt, in which the hydrocyanic acid collects.

In storing liquid hydrocyanic acid it is advisable to add 2 drops of concentrated sulphuric acid and to wire on the stopper of the bottle.

In order to prepare hydrocyanic acid for producing a definite concentration of the gas in the air,² for example 1% by volume in a space of 100 cu. m. capacity, 2.6 litres of 60° Bé. sulphuric acid are added to 4.4 litres of water at 50° to 60° C., then, while still hot, 2.75 kgm. sodium cyanide are added as rapidly as possible.

INDUSTRIAL PREPARATION

Until a few years ago, hydrocyanic acid was always prepared by heating potassium ferrocyanide with dilute sulphuric acid. Nowadays, it is preferred to employ the alkali cyanides, either sodium or potassium, as these are manufactured synthetically on a large scale and very cheaply. Usually 50% aqueous sulphuric acid is run on to sodium cyanide either in concentrated solution or in lumps, and then the mixture heated in order to drive off the hydrocyanic acid. As it is evolved, the acid is dried by passing through calcium chloride and then liquefied by passing it first

¹ K. SLOTTA, *Ber.*, 1934, **67**, 1030.

² SIEVERTS and HERMSDORF, *Z. angew. Chem.*, 1921, **34**, 5.

through a coil immersed in water at 15° C. and then through a coil in brine at 0° C.

Several other methods are now employed industrially for the preparation of hydrocyanic acid. Synthesis from the elements is widely used. In this a mixture of hydrogen, carbon monoxide and nitrogen is passed through an electric arc, mixtures of nitrogen and hydrocarbons being sometimes employed, *e.g.*, 20% methane, 10% hydrogen and 70% nitrogen.

Also the formation of hydrocyanic acid from spent fermentation wash may be mentioned. This material is obtained from molasses, which, after fermenting and distilling, leaves a residue which still contains about 4% nitrogen as betaine. On further distilling this spent wash to about 40° Bé. the evolved gas, after separating from the tar by cooling, is passed through a superheater consisting of a quartz tube heated to about 1,000° C. In this way the nitrogenous compounds are converted to ammonia and hydrocyanic acid. The gas issuing from the superheater is washed with sulphuric acid to remove ammonia, while the hydrocyanic acid is taken out in an alkaline absorbent. By this means about 50% of the nitrogen of the spent wash is converted into ammonia and hydrocyanic acid, while the other half is lost as elementary nitrogen.

PHYSICAL AND CHEMICAL PROPERTIES

Pure anhydrous hydrocyanic acid is a clear colourless liquid with a peculiar odour which is usually compared with that of bitter almonds. It has been observed, however, that this substance has an indefinite odour which varies with the degree of its dilution with air and the period of exposure to it.¹

The vapour from the pure liquid or concentrated aqueous solution causes an irritation at the back of the throat and a bitter taste in a short time. Diluted with air it is not very irritant, but has a less disagreeable odour which is somewhat aromatic. It is a peculiar property of this substance that even in minute quantity it paralyses the nerves of odour and taste, and after a few seconds the first sensitivity to the odour is lost.

It boils at 26.5° C., and solidifies on cooling at -13.4° C., forming a crystalline mass which melts at -15° C.

If liquid hydrocyanic acid is coloured yellow or brown, it may be considered as being less dangerous, because it is in process of alteration. The commercial product should be colourless and contain 96-98% of hydrocyanic acid, the balance being water.

In the gaseous state it is colourless with a vapour density of

¹ ANON., *Die Gasmasken*, 1935, Nos. 4-5.

0.948 ; that is, 1 litre of gaseous hydrocyanic acid weighs 1.21 gm. at 0° C. and 760 mm. The specific gravity of liquid hydrocyanic acid is 0.7058 at 7° C. and 0.6969 at 18° C. The coefficient of thermal expansion between 0° C. and 15° C. is 0.0019. The critical temperature is 138.5° C. and the critical pressure 53.3 atmospheres. The heat of vaporisation is 210.7 cal. per gm. By spontaneous evaporation the current of air produced passes over the surface of the hydrocyanic acid, lowering the temperature to that of freezing (— 13.4° C.).

The vapour tension at various temperatures is as follows ¹ :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
— 10	165
0	256
4	380
10.8	427
14.8	504
18.0	567
25.6	757

Its volatility at 20° C. is 873,000 mgm. per cu. m.

Because of its high vapour tension as well as its low density it is difficult to maintain a high concentration of hydrocyanic acid in an open place. As the toxic action is considerably reduced by dilution, numerous artifices were used during the war to render this gas more persistent. Lebeau, in France, suggested mixing it with the smoke-producing chlorides, as stannic, titanium or arsenic chloride. The result was that the already low stability of the hydrocyanic acid was still further reduced. Then it was proposed to add a proportion of chloroform to the mixture, this forming the mixture termed "*Vincennite*" by the French. It consisted of 50% hydrocyanic acid, 30% arsenic trichloride, 15% stannic chloride and 5% chloroform.

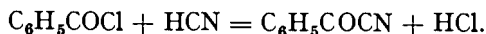
Hydrocyanic acid is miscible in all proportions with alcohol, ether, glycerol, chloroform, benzene, tricresyl phosphate, etc. It does not dissolve nitro-cellulose, but cellulose acetate and the other cellulose esters are soluble. Gums, rubber and gelatin are not dissolved. Carbon dioxide and hydrogen sulphide are slightly soluble and sulphur dioxide is soluble in all proportions.²

It dissolves in water to form a solution which has a weak acid reaction and is unstable in time. The dissolved hydrocyanic acid partly forms a brown flocculent substance and partly

¹ BREDIG and TEICHMANN, *Z. Elektrochem.*, 1925, **31**, 449 ; M. LINHARD, *Z. anorg. Chem.*, 1938, **236**, 207.

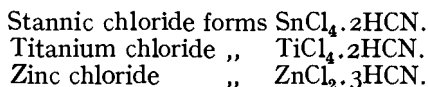
² BUCHANAN, *Chim. et Ind.*, 1932, **28**, 1026.

Hydrocyanic acid reacts with benzoyl chloride in presence of pyridine, benzoyl cyanide being formed¹ :



Benzoyl cyanide forms crystals melting at 33° C. and boiling at 206° to 208° C. It is decomposed by water.

Hydrocyanic acid forms additive compounds with several inorganic salts, such as the following :



It can be transported in the liquid condition in metal containers, for example, in tinned-iron cans, which are cooled with ice in summer, or in iron cylinders, like the compressed gases (Buchanan).

The lower limit of sensitivity to the odour is about 1 mgm. per cu. m. of air.²

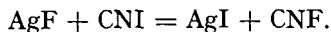
It is a powerful poison, but the human body is capable of neutralising the effects of the gas within certain limits. Thus in a concentration of about 30 mgm. per cu. m. hydrocyanic acid is eliminated from the human organism as rapidly as it is absorbed and so no dangerous consequences follow. At higher concentrations, however, poisoning is rapid.

The lethal concentration, according to Flury, is 120–150 mgm. per cu. m. of air for $\frac{1}{2}$ –1 hour's exposure, while, according to Prentiss, it is 200 mgm. per cu. m. for 10 minutes' exposure and 150 mgm. per cu. m. for 30 minutes' exposure.

2. Cyanogen Fluoride. CNF (M.Wt. 45)

Moissan attempted to prepare this substance by acting on cyanogen with fluorine.³ A very violent reaction took place without any deposition of carbon.

Recently cyanogen fluoride has been prepared by Cosslett⁴ by the action of silver fluoride on cyanogen iodide :



It may also be prepared in lower yield by the action of silver fluoride on cyanogen bromide, but in this case it is always impure with brominated products.

¹ CLAISEN, *Ber.*, 1898, **31**, 1024.

² SMOLCZYK, *Die Gas-Maske*, 1930, 32.

³ H. MOISSAN, *Le Fluor et ses composés*, 1900, 138.

⁴ V. COSSLETT, *Z. anorg. Chem.*, 1931, **201**, 75.

PREPARATION

1.3 gm. silver fluoride is powdered in a mortar with 1.5 gm. cyanogen iodide and transferred to a Jena glass tube about 50 cm. long and 2.5 cm. diameter. After evacuating the tube it is sealed off in the blowpipe and then heated in a furnace to 220° C. for 2½ hours. After cooling, the tube is immersed in liquid air and the products allowed to condense. The tube is then opened and the contents distilled at -70° C. in a freezing mixture of acetone and carbon dioxide. Yield 20-25% (Cosslett).

PROPERTIES

Cyanogen fluoride is a colourless gas at normal temperature, and on cooling to a low temperature it forms a white pulverent mass which sublimes at -72° C. at atmospheric pressure.

It is insoluble in water. In glass vessels it is stable and does not attack mercury. However, after storing for about a week in glass containers it attacks the surface; this is attributed to the action of light.

3. Cyanogen Chloride. CNCl (M.Wt. 61.47)

Cyanogen was discovered by Würtz and prepared for the first time by Berthollet.¹ It was used during the war by the French (October, 1916) both alone and in admixture with arsenic trichloride ("Vivrite").

LABORATORY PREPARATION ²

It is prepared by the action of chlorine on potassium cyanide.

About 100 ml. of a solution of chlorine saturated at 0° C. are placed in a 300-ml. flask and cooled while a solution of potassium cyanide is allowed to flow in slowly from a tap-funnel until the yellow colour of the chlorine disappears. The liquid is again saturated with chlorine and further potassium cyanide added still slowly, taking care not to add an excess, which causes decomposition of the cyanogen chloride. The latter is then liberated from the aqueous solution by warming on the water-bath to 60° to 70° C.

According to Held,³ in order to prevent the formation of paracyanogen, a secondary product in the reaction between chlorine and potassium cyanide, it is advisable to add to the latter 1 molecule of zinc sulphate per 4 molecules of the cyanide.

¹ BERTHOLLET, *Ann. chim. phys.*, 1802, [1] 35, 1789.

² HANTZSCH and MAI, *Ber.*, 1895, 28, 2471; ZAPPI, *Bull. soc. chim.*, 1930, [4] 47, 453; JONESCU, *Antigaz*, 1932, 6, Nos. 1-2, 17.

³ HELD, *Bull. soc. chim.*, 1897, [3] 17, 287.

INDUSTRIAL MANUFACTURE

Cyanogen chloride is also prepared industrially by the reaction of chlorine on sodium cyanide.¹

Two solutions are added to a large iron vessel fitted with cooling coils, one of sulphuric acid and the other of sodium cyanide. After cooling, chlorine is bubbled in. At the end of the reaction, the cyanogen chloride is distilled off and purified from the gaseous reaction products by passing it through a series of purification towers, two containing calcium chloride to remove traces of moisture and one containing pumice and arsenic to remove the chlorine still present. Yield 80%.

PHYSICAL AND CHEMICAL PROPERTIES

Cyanogen chloride is a colourless, very volatile liquid, which boils at 12.5°C. and solidifies at -6.5°C. (Mauguin). Its specific gravity is 1.2 and its vapour density 2.1. It is very soluble in water (1 volume water at 20°C. dissolves 25 volumes cyanogen chloride) and in the organic solvents such as alcohol, ether, etc.² The alcoholic solution easily decomposes.

The vapour tension of cyanogen chloride at various temperatures is given in the following table³:

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
-10	270.51
0	444.11
10	681.92
20	1,001.87
30	1,427.43

Its volatility at 15°C. is 2,600,000 mgm. per cu. m. and at 20°C. is 3,300,000 mgm. per cu. m.

The heat of volatilisation at 0°C. is 109 cals., while at 12.5°C. it is 135. The coefficient of thermal expansion at 0°C. is 0.0015.

It has a low stability and is gradually transformed into its trimer, cyanuryl chloride, (CNCl)₃, a crystalline substance melting at 190°C. and having a specific gravity of 1.32. It is soluble in ether, chloroform, etc.⁴ Biologically, it is almost inactive. In order to impede this transformation, the French mixed cyanogen chloride with arsenic chloride. Water, chlorine and hydrochloric acid tend to favour the polymerisation.⁵

¹ MAUGUIN and SIMON, *Compt. rend.*, 1919, **169**, 383; *Ann. chim.* 1921, **15**, 18.

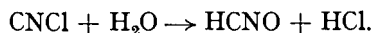
² SERULLAS, *Ann. chim. phys.*, [2] **35**, 342.

³ REGNAULT, *Jahresber. u. fortschr. Chem.*, 1863, 65; KLEMENC, *Z. anorg. Chem.*, 1938, **235**, 429.

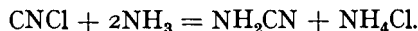
⁴ NEF, *Ann.*, 1895, **287**, 358.

⁵ WÜRTZ, *Ann.*, 1851, **79**, 284; NAUMANN, *Ann.*, 1870, **155**, 175.

Water slowly hydrolyses cyanogen chloride, forming cyanic acid and hydrochloric acid :

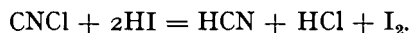


This reaction is accelerated by the alkali hydroxides.¹ Cyanogen chloride reacts quantitatively with an alcoholic solution of ammonia to form cyanamide² :



By the action of alkaline reducing agents, like sodium sulphite with sodium hydroxide, sodium cyanide, sodium chloride and sodium sulphate are formed.

When hydriodic acid is added to an aqueous solution of cyanogen chloride at ordinary temperatures, iodine is liberated. The amount set free increases slightly on standing, but more rapidly on heating to about 100° C., reaching a maximum at 80% of that required by the equation (Chattaway) :



On heating an aqueous solution of hydrogen sulphide with a solution of cyanogen chloride to about 100° C., sulphur separates, while the hydrocyanic acid which is formed is partly hydrolysed and partly combines with the sulphur, forming thiocyanic acid.

Aqueous solutions of cyanogen chloride do not react with silver nitrate,³ but aqueous-alcoholic solutions form silver chloride.⁴ Unlike cyanogen bromide, the Prussian blue reaction does not take place with cyanogen chloride.⁵

It has practically no corrosive action on iron, lead, aluminium, tin or silver. It does attack copper and brass slightly, however, a protective coating being formed which prevents further corrosion.

Commercial cyanogen chloride contains 2-5% of hydrocyanic acid.

It may be mixed with chloropicrin and with dichloroethyl sulphide without change.

It is added to "Zyklon B" (see p. 104) both to prevent the polymerisation of the hydrocyanic acid present and also to act as a warning substance.⁶

Concentrations of 2.5 mgm. per cu. m. of air produce abundant

¹ CHATTAWAY and WADMORE, *J. Chem. Soc.*, 1902, **81**, 191.

² CLOEZ and CANNIZZARO, *Ann.*, 1851, **78**, 229.

³ SERULLAS, *Berzelius Jahresber.*, **8**, 90.

⁴ E. ZAPPI, *Rev. de Ciencias Químicas. Univ. La Plata*, 1930, 7.

⁵ E. ZAPPI, *Bull. soc. chim.*, 1930, [4] **47**, 453.

⁶ RIMARSKY and coll., *Jahresber. Chem. Techn. Reichsanstalt.*, 1930, **8**, 71.

lachrymation in a few minutes. The maximum concentration which a normal man can support without damage for 1 minute is 50 mgm. per cu. m. of air (Flury).

The lethal concentration for 10 minutes' exposure is 400 mgm. per cu. m. (Prentiss).

4. Cyanogen Bromide. CNBr (M.Wt. 105.93)

Cyanogen bromide was first employed by the Austrians in September, 1917, both in benzol solution and in admixture with bromoacetone and benzol.

It was first prepared by Serullas in 1827.¹ It is obtained by the action of bromine on potassium cyanide, similarly to cyanogen chloride.

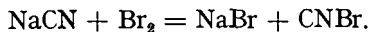
LABORATORY PREPARATION ²

150 gm. bromine and 50 ml. water are placed in a flask fitted by means of a three-holed stopper with a tap-funnel, a condenser and a thermometer. A solution of 65 gm. potassium cyanide in 120 ml. water, cooled to 0° C., is introduced through the tap-funnel gradually (about 1 drop per second), into the flask which is also cooled to about 0° C. and agitated. As soon as the red colour of the bromine commences to pale, the cyanide solution remaining in the tap-funnel is diluted to about double its volume and added carefully, avoiding an excess, which would cause the decomposition of the cyanogen bromide with formation of azulmic products, darkening the colour of the mass.

At the end of the reaction the contents of the flask are transferred to a retort, which is partly filled with calcium chloride and stoppered, and then warmed on the water-bath at 65–70° C. The cyanogen bromide distils over and condenses in white needles, which may be purified further by redistilling over calcium chloride. The yield is about 90%.³

INDUSTRIAL MANUFACTURE

In the preparation of cyanogen bromide from bromine and sodium cyanide there is a loss of half of the bromine as sodium bromide ⁴ :



In order to avoid this loss, sodium chlorate is generally added,

¹ SERULLAS, *Ann. chim. phys.*, 1827, [2] 34, 100.

² SCHOLL, *Ber.*, 1896, 29, 1822 ; GRIGNARD, *Bull. soc. chim.*, 1921, 29, 214.

³ K. SLOTTA, *Ber.*, 1934, 67, 1029.

⁴ V. GRIGNARD and P. CROUZIER, *Bull. soc. chim.*, 1921, 29, 214.

as in the preparation of the halogenated ketones (see p. 147). The following reaction takes place :



The manufacture of cyanogen bromide is carried out in large metal vessels in which a solution of the three salts is first prepared. 30% sulphuric acid at a temperature of 30°C. is then slowly run in. At the end of the reaction the product is separated by distillation. Yield 75%.¹

PHYSICAL AND CHEMICAL PROPERTIES.

Cyanogen bromide forms transparent crystals which are either acicular or prismatic. It has a penetrating odour and melts at 52° C. Its boiling point at 750 mm. is 61.3° C. Its specific gravity is 1.92 and its vapour density 3.6. The vapour tension at any temperature may be calculated by means of the following formula (see p. 5) :

$$\log p = 10.3282 - \frac{2457.5}{273 + t}$$

Baxter and Wilson ² give the following experimental values :

TEMPERATURE ° C.	VAPOUR PRESSURE MM. MERCURY
-15	6.3
0	21.2
15	63.3
25	119.5
35	223.5

The volatility at 16° C. is about 155,000 mgm. per cu. m. and at 20° C. about 200,000 mgm. per cu. m.

It is only sparingly soluble in water, but more readily in alcohol, ether, carbon disulphide, acetone, benzene and carbon tetrachloride.

The chemical behaviour of cyanogen bromide is very similar to that of cyanogen chloride. For instance, like the chloride it polymerises in time to the trimer, (CNBr)₃.³ This polymer is reconverted to cyanogen bromide by heat, so that in order to purify polymerised cyanogen bromide it is merely necessary to distil it.

It is decomposed by water, slowly at ordinary temperatures,

¹ For more detailed descriptions of the industrial manufacture of cyanogen bromide, see *Chem. Zentr.*, 1907 (I), 591, and 1908 (I), 1807.

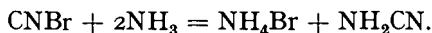
² BAXTER and WILSON, *J. Amer. Chem. Soc.*, 1920, **42**, 1389.

³ PONOMAREV, *Ber.*, 1885, **18**, 3261.

but more rapidly at 100° C. The products of hydrolysis are similar to those formed from cyanogen chloride. It reacts with sodium or potassium hydroxide forming sodium or potassium bromide and cyanate¹ :

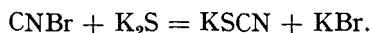


With an aqueous solution of ammonia it is quantitatively converted to ammonium bromide and cyanamide, as follows :

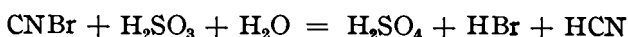
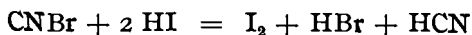


This reaction may be used for the quantitative determination of cyanogen bromide, according to Oberhauser² (see p. 209).

By the action of the alkali sulphides on cyanogen bromide, the corresponding thiocyanates are formed according to the following equation³ :

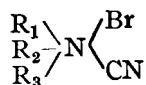


With various other substances cyanogen bromide reacts as vigorously as does cyanogen chloride. For instance, even at ordinary temperatures iodine is liberated from hydriodic acid and sulphur from hydrogen sulphide, while sulphurous acid is oxidised to sulphuric acid :

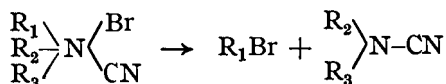


All these reactions take place quantitatively, but that with hydriodic acid is somewhat slow.⁴

On treatment of cyanogen bromide with tertiary amines, additive products of the following general formula are produced :



These are not stable and decompose with formation of alkyl bromide and dialkyl cyanamides, as follows :



A similar reaction takes place with the tertiary arsines.⁵

¹ SERULLAS, *Ann. chim. phys.* 1827, [2] **35**, 345 ; NEF, *Ann.*, 1895, **287**, 316.

² F. OBERHAUSER and J. SCHORMULLER, *Ber.*, 1929, **62**, 1439.

³ GUTMANN, *Ber.*, 1909, **42**, 3627.

⁴ R. MOONEY, *J. Chem. Soc.*, **1933**, 1319.

⁵ STEINKOPF, *Ber.*, 1921, **54**, 2791.

By the action of cyanogen bromide on pyridine in alcoholic solution in the cold, a reddish-brown colouration is formed and white crystals separate ¹

Cyanogen bromide has a powerfully corrosive effect on metals, attacking copper, iron, zinc, aluminium, and in time even lead and brass ²

Unlike cyanogen chloride, the bromide is not miscible with dichloroethyl sulphide, but reacts with it. It is, however, miscible with chloropicrin.

During the war of 1914-18 it was employed in solution in benzene and bromoacetone in the following proportions: cyanogen bromide 25%, bromoacetone 25%, benzene 50%. This mixture was known as "*Campbellite*."

Concentrations of 6 mgm. per cu. m. cause strong irritation of the conjunctiva and of the mucous membranes of the respiratory system. The limit of insupportability, that is, the maximum concentration which a normal man can support for a period of not over 1 minute, is 85 mgm. per cu. m., according to Flury, and 40-45 mgm. per cu. m., according to Ferrarolo.³ The mortality-product is 2,000 according to Müller, and 4,000 for 10 minute's exposure according to Prentiss.

5. Cyanogen Iodide. CNI (M.Wt. 153)

Cyanogen iodide has a powerful lachrymatory action. It was prepared by Serullas in 1824.⁴ It was not used as a war gas in the war of 1914-18 however.

PREPARATION

It is prepared by the action of iodine on mercuric cyanide ⁵ or sodium cyanide ⁶

12 gm. iodine and 20 gm. water are placed in a flask of about 200 ml. capacity fitted with (1) a tap-funnel containing 100 ml. of a 5% aqueous solution of sodium cyanide, (2) an inlet tube for gas, and (3) an outlet tube. The contents of the flask are stirred and 50 ml. of the sodium cyanide solution are run in little by little with continued agitation. The sodium iodide formed in the reaction dissolves the iodine and the liquid in the flask is continuously decolourised. When the 50 ml. sodium cyanide solution have been added, a slow current of chlorine is passed into

¹ T SHIMIDZU, *J Pharm Soc Japan*, 1926, **538**, 107

² PANCENKO, *op cit*

³ FERRAROLO, *Policlunico* (pract sect), 1936, 1435

⁴ SERULLAS, *Ann chim phys*, 1824, [2] **27**, 188

⁵ SEUBERT, *Ber*, 1890, **23**, 1063, R COOK, *J Chem Soc*, **1935**, 1001

⁶ NEKRASSOV, *op cit*.

the flask, and while continuing to agitate the liquid the other 50 ml. cyanide solution are added from the tap-funnel at such a rate that there is always an excess of iodine present. The current of chlorine is then stopped and a little more sodium cyanide is added. The reaction product is then extracted with ether, the ethereal extract dried over calcium chloride and the ether distilled off. A crystalline residue of cyanogen iodide remains.

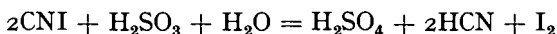
Yield 80–85% of theoretical.

PHYSICAL AND CHEMICAL PROPERTIES

Cyanogen iodide forms white crystals which gradually decompose, liberating iodine.¹ It melts at 146° C., according to Cook,² and in a closed tube at 140° C. according to Zappi.³ It dissolves sparingly in cold water but with ease in hot. It is more soluble in alcohol and ether. The vapour density is 5.3 (air = 1).

Cyanogen iodide reacts with hydriodic acid much more readily than the chloride and bromide, iodine being liberated.

Sulphurous acid is oxidised to sulphuric acid :

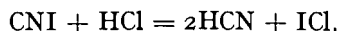


and sulphur is liberated from sulphides.⁴

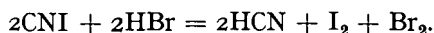
It reacts quantitatively with sodium arsenite according to the equation⁵ :



It also reacts with hydrochloric acid, forming iodine monochloride :



and with hydrobromic acid liberating bromine and iodine :



It does not react with silver nitrate. On treatment of an aqueous solution of cyanogen iodide with potassium hydroxide and subsequent addition of ferrous and ferric salts and hydrochloric acid, a precipitate of Prussian blue is obtained.⁶

The reactions of cyanogen iodide with many other substances have been studied.⁷ From these it has been found that when treated with reducing agents its iodine is completely removed, while other reagents which normally remove iodine from iodides do not affect it.

¹ SEUBERT, *Ber.*, 1890, **23**, 1063.

² R. COOK, *loc. cit.*

³ ZAPPI, *Bull. soc. chim.*, 1930, [4] **47**, 453.

⁴ A. GUTMANN, *Z. anal. Chem.*, 1925, 246.

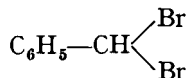
⁵ G. ALSTERBERG, *Biochem. Z.*, 1926, **172**, 223.

⁶ E. ZAPPI, *Rev. fac. cienc. quim. Univ. La Plata*, 1930, **7**.

⁷ MEYER, *J. prakt. Chem.*, 1887, **35**, 292.

6. Bromobenzyl Cyanide.

(M.Wt. 196)



Bromobenzyl cyanide was prepared by Reimer¹ in 1881, but it was not isolated in the pure state until 1914. It was employed as a war gas by the French in the last years of the war, usually in solution in chloropicrin.

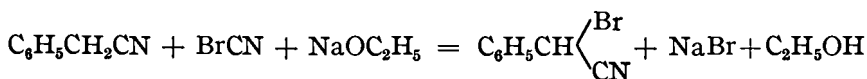
According to American experiments made since the war, this compound is to be considered as one of the most efficient of the war gases because of its great persistence and its high lachrymatory power.

It is also known as “*Camite*” (France), and by the symbol “*CA*” (America).

PREPARATION

Bromobenzyl cyanide was prepared by Reimer by the action of bromine on benzyl cyanide heated to 120° to 130° C.

This compound may be prepared either by the action of cyanogen bromide on an alcoholic solution of benzyl cyanide in presence of sodium ethylate, according to the equation²:



or else, by a method similar to that used by Reimer, by the action of bromine vapour on benzyl cyanide heated simply to 105° C., or to 120° C. while the gas mixture is exposed to the light of a 1,000 c.p. Osram lamp. By this method a much higher yield of bromobenzyl cyanide is obtained.³

LABORATORY PREPARATION⁴

In preparing this substance, it is advisable to start with benzyl bromide and first convert this into the cyanide, which is afterwards brominated.

60 gm. benzyl bromide, 27 gm. potassium cyanide, 45 gm. ethyl alcohol and 25 gm. water are placed in a flask fitted with a reflux condenser and boiled for 4 hours. The mixture is then extracted with ether, the ether extract separated and dried over calcium chloride, the ether distilled off and the residue itself then

¹ REIMER, *Ber*, 1881, **14**, 1797, STEINKOPF, *Ber*, 1920, **53**, 1146, NEKRASSOV, *J prakt Chem*, 1928, **119**, 108

² VON BRAUN, *Ber*, 1903, **36**, 2651

³ STEINKOPF and coll., *Ber*, 1920, **53**, 1144

⁴ NEKRASSOV, *op cit*

distilled, the fraction boiling between 210° and 240° C. being collected. This may then be fractionally redistilled, when the portion boiling between 228° and 233° C. is collected.

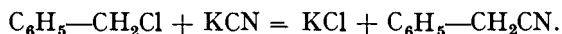
36 gm. benzyl cyanide are placed in a flask of 100–150 ml. capacity, fitted with a two-holed stopper. Through one of the holes a reflux condenser passes and through the other a tap-funnel. The top of the condenser is connected by means of a tube bent at right angles with a flask containing water which serves to absorb the hydrobromic acid evolved during the reaction.

60 gm. bromine are added slowly from the tap-funnel during $\frac{1}{2}$ hour while the benzyl cyanide is heated to about 120° C. After allowing to cool, the product is washed with 5% soda solution, extracted with ether and the ether removed by distillation, after filtering. The residue is then distilled in steam or at reduced pressure (25 mm.).

INDUSTRIAL MANUFACTURE ¹

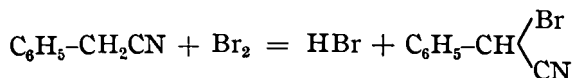
In the industrial manufacture of bromobenzyl cyanide it is preferable to commence with benzyl chloride rather than benzyl bromide. This is easily obtained by the chlorination of toluene under the influence of sunlight (see p. 129) or by the aid of a mercury vapour lamp.²

An alcoholic solution of benzyl chloride is heated at 80° C. for 3–4 hours with the corresponding quantity of potassium or sodium cyanide dissolved in water :



When the reaction is complete the alcohol is first distilled off and then the residue is distilled in a current of steam until no more oily distillate comes over. Crude benzyl cyanide is thus obtained. As the yield of bromobenzyl cyanide is greatly dependent on the purity of the benzyl cyanide, it is advisable to purify the latter by fractional distillation under reduced pressure.

The benzyl cyanide obtained may be converted into bromobenzyl cyanide by treatment with a mixture of air and bromine vapour in sunlight or under the influence of ultra-violet rays ³ :



The amount of air should be carefully regulated so that bromine is neither carried forward nor remains in the benzyl cyanide as hydrobromic acid, this latter eventuality causing the formation

¹ KNOLL, *Synthetische und Isolierte Riechstoffe*, Halle, 1928, 194.

² MARK and WALD, *D.R.P.* 142,939.

³ STEINKOPF, *Ber.*, 1920, 53, 1146.

of a dibrominated derivative which has no aggressive properties. The reaction temperature is about 60° C.

After the bromine has been completely absorbed, dry air is passed through the reaction-product to drive off any traces of hydrobromic acid. This is absorbed in sodium hydroxide and may be recovered. The bromobenzyl cyanide is stored in containers coated internally with lead, or enamelled.

PHYSICAL AND CHEMICAL PROPERTIES

Pure bromobenzyl cyanide forms yellowish-white crystals melting at 25.4° C.¹ In time these crystals become pink by incipient decomposition.

The technical product is an oily liquid, brown with the impurities, usually liquids, which it contains. In order to purify it, it is necessary to recrystallise repeatedly from alcohol. It has a pungent but not disagreeable odour.

The pure product boils at ordinary pressure at 242° C. with decomposition, distilling unaltered at 132° to 134° C. at 12 mm. mercury pressure.

The specific gravity of bromobenzyl cyanide between 0° C. and 50° C. is as follows :

TEMPERATURE ° C.	S.G.
0	1.5360
5	1.5312
10	1.5262
20	1.5160
30	1.5000
50	1.4840

The vapour tension of bromobenzyl cyanide is given in the following table at various temperatures :

TEMPERATURE ° C.	VAPOUR TENSION MM. MERCURY
0	0.0019
10	0.0050
20	0.0120
30	0.0281
50	0.1280

The vapour density is 6.8 (air = 1). The latent heat of volatilisation is 58.7 cal. The volatility at 20° C. is 130 mgm.

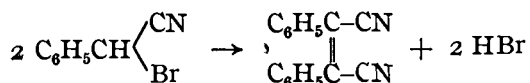
¹ Because of its high melting point, it has been proposed to employ bromobenzyl cyanide in solution in chloropicrin. The melting points of such mixtures are as follows (Liebermann) :

100 parts bromobenzyl cyanide and	10 parts of chloropicrin,	9° C.
"	"	6° C.
"	"	3° C.
"	"	1° C.

per cu. m. (Prentiss), and at 30° C. is 420 mgm. per cu. m.¹ Müller² reports a volatility of 750 mgm. per cu. m., which possibly refers to the technical product.

It is insoluble in water, though it easily dissolves in many organic solvents (alcohol, benzene, carbon disulphide, acetic acid, acetone, ether, chloroform, carbon tetrachloride, etc.). It is also soluble in several of the other war gases, such as phosgene, chloropicrin, etc. Because of this property, it may be used together with these war gases so as to attain a more complete range of effects.

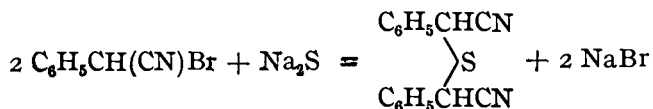
Bromobenzyl cyanide decomposes on heating : at 160° C. the decomposition commences with the formation of dicyanostilbene and hydrobromic acid :



It is highly resistant to chemical and atmospheric agencies. Water and humidity decompose it only very slowly. Cold sodium hydroxide solution acts similarly, though on prolonged boiling almost quantitative decomposition takes place with an aqueous solution of sodium hydroxide. A 20% solution of sodium hydroxide decomposes two and a half times its own weight of the cyanide. Alcoholic potash decomposes it even in the cold.

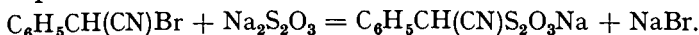
When treated with some of the most vigorous oxidising agents, such as potassium or sodium chlorate, potassium permanganate, peroxides, etc., it is attacked only slowly. Owing to this stability to humidity and to chemical reagents, as well as its low vapour pressure, this substance has a high persistence, especially in suitable meteorological conditions such as cold, dry weather.³

Bromobenzyl cyanide in alcoholic solution reacts with sodium sulphide to form dicyanobenzyl sulphide :



which forms yellow crystals with m.p. 150° to 152° C. It is insoluble in water, but soluble in the common organic solvents.

On boiling bromobenzyl cyanide with an aqueous-alcoholic solution of sodium thiosulphate, the sodium salt of cyanobenzyl thiosulphuric acid is formed :

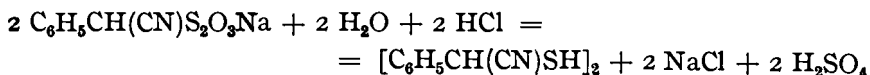


¹ FERRI and MADESANI, *Giornale Medicina Militare*, 1936, Part I.

² MÜLLER, *Militär Wochenblatt*, 1931, 116, 113.

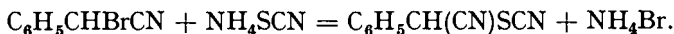
³ MÜLLER, *loc. cit.*, p. 754.

This, on treatment with hydrochloric acid, gives cyanobenzyl mercaptan :



which forms crystals melting at 101°C . It is insoluble in water, but soluble in alkalis and in the common organic solvents.¹

On mixing an alcoholic solution of bromobenzyl cyanide with ammonium thiocyanate, cyanobenzyl thiocyanate is formed :



This forms white crystals with m.p. 63° to 65°C ., insoluble in water, but soluble in all the usual organic solvents with the exception of ligroin. It decomposes on heating to 100°C .²

From the practical point of view, bromobenzyl cyanide has a great limitation in application because of its low stability to the shock of the bursting of the projectile. It can only be employed in bombs with a comparatively small bursting charge.

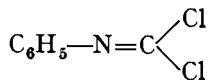
It also has the inconvenient property of vigorously attacking all the common metals except lead, and in doing so its lachrymatory properties are destroyed. Containers which are to be used for holding bromobenzyl cyanide must therefore be coated internally with lead or glass.

It does not attack rubber.

It is highly irritant. The minimum concentration which causes lachrymation is 0.3 mgm. per cu. m. of air according to Müller, and 0.2 mgm. per cu. m. of air according to Ferri.³ The limit of insupportability is 30 mgm. per cu. m. (Müller) ; 5 mgm. per cu. m. (Ferri). Haber's toxicity product is 7,500. This value is considered too low by Ferri and Madessani, from experiments carried out on dogs and cavies. According to these observers, the toxic-suffocating power of bromobenzyl cyanide is insufficient to be of practical use.

7. Phenyl Carbylamine Chloride

(M.Wt. 175)



This substance was prepared in 1874 by Sell and Zierold, and was employed as a war gas towards the middle of 1917 (in May) by the Germans. It was principally used in projectiles together

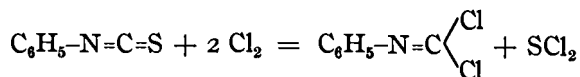
¹ KRETOV, *J. Rusk. Fis. Khim. Obsc.*, 1929, **61**, 1975.

² KRETOV, *loc. cit.*

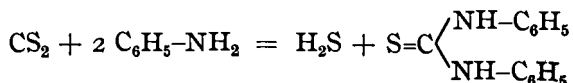
³ FERRI and MADESANI, *loc. cit.*

with dichloroethyl sulphide in order to mask the odour of the latter.

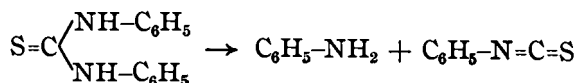
Phenyl carbylamine chloride is usually prepared by the chlorination of phenyl isothiocyanate ¹ :



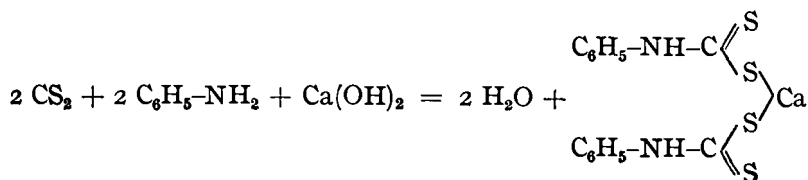
Various methods have been employed for preparing phenyl isothiocyanate. It may be obtained, for instance, from carbon disulphide and aniline, which react to form thiocarbanilide in presence of alkali hydroxides :



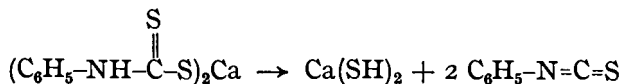
and this on heating with acid decomposes into aniline and phenyl isothiocyanate :



Another rather similar method is to treat carbon disulphide with aniline in presence of lime. Calcium phenyl dithiocarbamate is first formed, according to the equation :



On treating this with an alkaline zinc chloride solution it decomposes with production of phenyl isothiocyanate :



This second method of preparation was employed by the Germans during the war.

LABORATORY PREPARATION ²

In the laboratory, phenyl isothiocyanate is first prepared from aniline and carbon disulphide and the product then chlorinated.

¹ SELL and ZIEROLD, *Ber.*, 1874, **7**, 1228.

² NEKRASSOV, *op. cit.* ; NEF, *Ann.*, 1892, **270**, 274.

40 gm. aniline, 50 gm. carbon disulphide, 50 gm. alcohol and 10 gm. potassium hydroxide are heated to boiling on a water-bath for 2-3 hours in a flask of about 300-400 ml. capacity fitted with a reflux condenser. The condenser is then altered so as to make distillation possible, and the excess of carbon disulphide and alcohol removed by distillation. The residue is taken up with water, when crystals of thiocarbanilide separate. These are filtered off and washed with water. After drying, 30 gm. are weighed into a round-bottomed flask of 350-400 ml. capacity which is connected with a Liebig's condenser. 120 ml. hydrochloric acid (S.G. 1.19) are added and the mixture rapidly distilled almost to dryness. The distillate is collected in a separatory funnel and then diluted with an equal volume of water. The oily layer of phenyl isothiocyanate which separates is dried with calcium chloride and distilled under reduced pressure.

15 gm. of the phenyl isothiocyanate obtained are placed in a flask of 50-100 ml. capacity and dissolved in 20 gm. chloroform. The solution obtained is cooled with ice and water and saturated with chlorine for about 2 hours. The current of chlorine is stopped when the space over the liquid is coloured greenish-yellow. The chloroform is distilled off and the residue fractionally distilled by heating the flask with a naked flame. The fraction which passes over between 200° and 215° C. is collected and purified further by distillation under reduced pressure. The yield is 80-90% of the theoretical.

INDUSTRIAL MANUFACTURE

The method used by the Germans consisted in preparing the phenyl isothiocyanate first from carbon disulphide, milk of lime and aniline and then chlorinating this.

450 kgm. carbon disulphide are mixed with an excess of a 30% milk of lime in a large iron vessel and then about 560 kgm. aniline are added in small quantities during 1 hour. The mixture is agitated for about 24 hours at 25° C. Meanwhile 840 kgm. zinc chloride are dissolved in sufficient water to give a 50% solution and this mixed with 550 kgm. of a sodium hydroxide solution of 40° Bè. The products of the reaction are added to this and the whole is then maintained at 30° to 40° C. By the action of the sodium zincate, phenyl isothiocyanate is formed and this may be separated from the other products of the reaction by steam distillation.

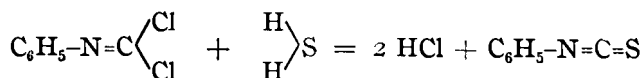
600 kgm. of the phenyl isothiocyanate are placed in a vessel and a current of chlorine bubbled through it, maintaining the temperature at 0° C., until the specific gravity of the reaction

product reaches the value of 1.45 (about 24 hours). The sulphur chloride is separated by distillation, when the phenyl carbylamine chloride remains as a residue ; it is transferred to containers for storage. Yield 90%.

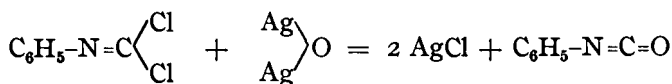
PHYSICAL AND CHEMICAL PROPERTIES

Phenyl carbylamine chloride is an oily liquid which is only slightly volatile. It is pale yellow in colour and has an onion-like odour. At ordinary pressure it boils at 208° to 210° C.,¹ and at 15 mm. pressure at 95° C. The specific gravity is 1.30 at 15° C., and the vapour density is 6.03. The coefficient of thermal expansion is 0.000895. The volatility at 20° C. is 2,100 mgm. per cu. m. It is insoluble in water, but soluble in chloroform, carbon tetrachloride and other organic solvents.

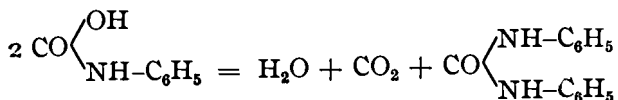
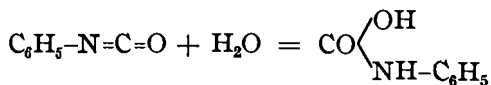
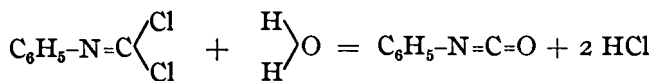
Like the isonitriles, it has a strong tendency to react with various substances. For instance, it reacts quantitatively with hydrogen sulphide even at ordinary temperature, forming phenyl isothiocyanate :



In contact with mild oxidising agents like mercuric oxide, silver oxide, etc., phenyl isocyanate is formed :



It is not hydrolysed by water at ordinary temperatures, but on heating to 100° C. in a closed tube it is decomposed with formation of diphenyl urea :



On heating with aniline it reacts vigorously, forming triphenyl guanidine (Nef).

¹ BLY and coll., *J. Am. Chem. Soc.*, 1922, 44, 2896.

Phenyl carbylamine chloride, even when diffused in the air in the vapour state (at concentrations above 4%), produces with the Grignard reagent (see p. 248) a turbidity like that obtained with dichloroethyl sulphide (Hanslian).

In contact with steel it decomposes slowly.

Owing to its high boiling point it is classed as a very persistent war gas, but found only limited employment in the last war.

The irritant power of phenyl carbylamine chloride is very great; according to Müller 3 mgm. are sufficient to produce irritation. The limit of insupportability is 30 mgm. per cu. m. of air. The mortality-product is 3,000 according to Müller and 5,000 for 10 minutes' exposure according to Prentiss.

Analysis of the Cyanogen Compounds

DETECTION OF HYDROCYANIC ACID

Of the various methods proposed for the detection of hydrocyanic acid, the following are recommended:

The Prussian Blue Reaction. On addition to an alkaline solution of hydrocyanic acid of a few ml. of ferrous sulphate solution and of ferric chloride solution, then shaking and warming, a blue precipitate of ferric ferrocyanide appears on acidification with hydrochloric acid. In presence of only a trace of hydrocyanic acid, only a greenish-blue colouration appears, due to the formation of a colloidal suspension of the ferric ferrocyanide. On standing (sometimes for as long as 12 hours) the suspension settles to blue flocs, leaving the supernatant solution colourless.

This reaction is specific for hydrocyanic acid and is quite sensitive, detecting 5 mgm. per cu. m. of air according to Kolthoff.¹

The Prussian blue reaction may be rendered more convenient in use by employing a reaction paper. For this purpose Ganassini's² paper is strongly recommended. It is prepared by immersing a strip of filter paper, just before use, in a mixture of 10 ml. 10% ferrous sulphate solution (containing a trace of ferric salt) and 20 ml. of an alkaline solution of Rochelle salt (30 gm. Rochelle salt, 10 gm. potassium hydroxide and 100 ml. water). This paper should be exposed first to the atmosphere containing hydrocyanic acid and then to hydrochloric vapour, when it becomes greenish-blue.

The Ferric Thiocyanate Reaction. This test is carried out on a solution of the material to be examined; if the sample is gaseous, a solution may be obtained by bubbling it through an alkaline

¹ KOLTHOFF, *Z. anal. Chem.*, 1918, **57**, 1.

² GANASSINI, *Bull. soc. Medico chirurg. di Pavia*, 1910.

solution. The solution is evaporated on the water-bath with a little ammonium sulphide and the residue is taken up in dilute hydrochloric acid, filtered, and the filtrate then treated with a few drops of a very dilute solution of ferric chloride. In the presence of hydrocyanic acid the liquid is coloured blood-red, or merely pink if only traces of hydrocyanic acid are present, owing to the formation of ferric thiocyanate. When a weak colouration is obtained, it may be rendered more distinct by adding a little ethyl ether to the solution ; the ferric thiocyanate then passes into the ether, producing a more intense colouration.¹

*Guignard's Sodium Picrate Paper.*² Sodium picrate paper on exposure to gaseous hydrocyanic acid assumes a blood-red colour by the formation of sodium isopurpurate.³

These papers are prepared by immersing strips of filter paper first in a 0.1% aqueous solution of sodium carbonate, allowing them to dry, and then immersing them in a 0.1% aqueous picric acid solution. The Guignard reaction is sensitive (0.05 mgm. hydrocyanic acid gives a colouration in 12 hours), but not specific, for various reducing substances, as aldehydes, acetone, hydrogen sulphide and sulphur dioxide also respond to it.

Benzidine Acetate Reaction. If a solution of benzidine acetate is added to a dilute solution of hydrocyanic acid in presence of copper acetate, an intense blue colouration is produced. This reaction, which was suggested by Pertusi and Gastaldi,⁴ is more conveniently applied by means of papers prepared as follows⁵ :

Two separate solutions are prepared :

(a) 2.86 gm. copper acetate in 1 litre of water.

(b) 475 ml. of a solution of benzidine acetate, saturated at ordinary temperature, together with 525 ml. water.

The two solutions are mixed in equal parts just before use and strips of filter paper are immersed in the mixture. The two solutions may be kept separately for a long period if stored in a dark place, but the mixture undergoes alteration in the course of about a fortnight.⁶

According to Smolczyk,⁷ on exposing a benzidine acetate paper in an atmosphere containing 0.0001% by volume of hydrocyanic acid (1.1 mgm. per cu. m. at 20° C.), the change of colour to blue takes place in 1 minute.

¹ JOFINOVA, *J. Obscei Khim.*, Ser. A., 1935, 5, 34.

² GUIGNARD, *Compt. rend.*, 1906, 142, 552 ; JOFINOVA, *J. Obscei Khim.*, Ser. A., 1935, 5, 34.

³ WALLER, *Proc. Roy. Soc. Lond.*, 1910, 82, 574.

⁴ PERTUSI and GASTALDI, *Chem. Zeitung.*, 1913, 37, 609.

⁵ SIEVERT and HERMSDORF, *Z. angew. Chem.*, 1921, 34, 3.

⁶ D. KISS, *Z. ges. Schiess-Sprengstoffw.*, 1930, 6, 262.

⁷ SMOLCZYK, *Die Gas-Maske*, 1930, 32.

Wieland's Method. This method of detecting hydrocyanic acid depends on the decolourisation of starch iodide by the substance :



This reaction was employed by the Americans during the war and was carried out by passing the gas to be examined through a 2% solution of sodium bicarbonate containing starch solution and iodine. In the presence of hydrocyanic acid the solution is completely decolourised. The reaction is quite sensitive (8 mgm. per cu. m. of air), but is not specific for hydrocyanic acid (Guareschi).

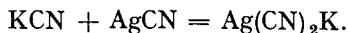
QUANTITATIVE DETERMINATION OF HYDROCYANIC ACID

Hydrocyanic acid may be determined gravimetrically, volumetrically or colorimetrically.

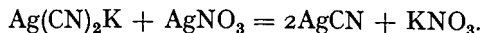
Gravimetric Methods. These methods are seldom employed because of their laborious nature. In any case, their use is advisable only when the quantity of hydrocyanic acid to be determined is not too small. Of these methods, the procedure of Rose is the most generally employed.¹

In this the hydrocyanic acid is precipitated by silver nitrate from solutions slightly acidified with nitric acid (not more than 2% nitric acid). The precipitate is filtered on a tared filter, washed, dried at 100° C. and reweighed. Rose also described the alternative procedure of heating the precipitate to redness for about $\frac{1}{4}$ hour and weighing it as metallic silver.

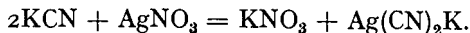
Volumetric Methods. (1) *Liebig's Method.*² This depends on the fact that when a neutral or alkaline solution of an alkaline cyanide is treated with silver nitrate solution drop by drop, a white precipitate of silver cyanide forms as each drop enters the solution. This disappears on shaking because the silver cyanide dissolves in the excess of alkali cyanide to form an argento-cyanide :



When all the cyanide has been transformed into argento-cyanide, however, the first drop of silver solution in excess produces a turbidity caused by the decomposition of the double cyanide and formation of insoluble silver cyanide :



The total reaction is as follows :



¹ ROSE, *Z. anal. Chem.*, 1862, 199 ; or GREGOR, *Z. anal. Chem.*, 1894, 33, 30.

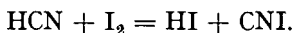
² LIEBIG, *Ann.*, 1851, 77, 102.

In order to carry out this determination, not more than 0.1 gm. free hydrocyanic acid is treated with a few ml. of sodium hydroxide solution and 0.5 gm. sodium bicarbonate and made up to a volume of 50 ml. with water. The titration is carried out with decinormal silver nitrate solution, shaking until finally a slight permanent opalescence remains.

$$1 \text{ ml. N/10 AgNO}_3 = 0.005404 \text{ gm. HCN.}$$

In order to detect the end-point with greater ease it is better to add a little sodium iodide to the solution. This reacts with the silver nitrate only when all the hydrocyanic acid has been converted into the double cyanide.

(2) *Fordos and Gelis's Method.* The method suggested by Fordos and Gelis¹ depends on the reaction between hydrocyanic acid and iodine in presence of alkali bicarbonate, which has been mentioned already :



The solution for examination should not contain more than 0.05 gm. hydrocyanic acid. It is treated with a few ml. of sodium hydroxide solution and 0.5 gm. sodium bicarbonate, and is then titrated with a decinormal solution of iodine until a yellow colour persists. In this case it is unnecessary to use starch as indicator :

$$1 \text{ ml. N/10 iodine solution} = 0.001351 \text{ gm. HCN.}$$

Several analytical procedures have been based on this reaction, *e.g.*, those of Seil,² Page,³ etc. The following is especially suitable for the analysis of hydrocyanic acid used in the mixtures of gases used for disinfection.

About 200 ml. distilled water are placed in a 1-litre Woulfe's bottle having two necks. One of these necks is fitted with a delivery tube reaching almost to the bottom of the bottle for the entry of the gas mixture, while the other is connected with an aspirator. 5 ml. 5% sodium bicarbonate solution, 5 ml. 1% starch solution and 10 ml. standard iodine solution are added to the water in the bottle, the concentration of the iodine solution being chosen according to the amount of hydrocyanic acid presumed to be present in the gas. Usually, in analysing disinfection mixtures, an iodine solution containing 0.94014 gm. of iodine per litre is employed, 10 ml. of this solution corresponding to 0.001 gm. hydrocyanic acid.

¹ FORDOS and GELIS, *J. prakt. Chem.*, 1853, **59**, 255.

² G. SEIL, *Ind. Eng. Chem.*, 1926, **18**, 142.

³ PAGE and GLOYNS, *J. Soc. Chem. Ind.*, 1936, **55**, 209.

By means of the aspirator, which is of about 5 litres capacity, the gas sample is drawn slowly through the Woulfe's bottle. The absorbing liquid is continually agitated. The water flowing out of the aspirator is accurately measured in a graduated cylinder. When the iodine solution is decolourised the gas-flow is immediately stopped and the water volume measured, this corresponding to the volume of gas examined.

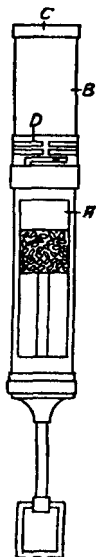


FIG. 13.

(3) *Colorimetric Method.* For the approximate estimation of hydrocyanic acid in air, W. Deckert's¹ apparatus may be employed. This is based on the intensity of the blue colour produced by hydrocyanic acid on benzidine acetate paper (see p. 205).

The apparatus consists of an aspirator *A* (see Fig. 13), one stroke of whose piston aspirates 25 ml. air through the aperture *C*. This air passes first through the cylinder *B* and then over the reaction paper which rests on the disc *D*. The disc is divided into three sectors coloured pale blue, blue and deep blue respectively.

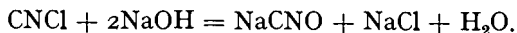
In carrying out an analysis with this apparatus, a sufficient number of inspirations of air are made to obtain a colouration of the reaction paper to match one of the three sectors. The amount of HCN in the air may then be obtained from the following :

Pale blue	corresponds to	0.004	mgm. HCN.
Blue	"	0.008	"
Deep blue	"	0.012	"

This is accurate to $\pm 25\%$.

QUANTITATIVE DETERMINATION OF CYANOGEN CHLORIDE

Cyanogen chloride may be estimated by utilising its reaction with alkalis.² The substance to be examined is treated with an excess of a standard solution of sodium hydroxide and the excess then determined by titration with sulphuric acid. Phenolphthalein should be used as the indicator, as it does not react with sodium cyanate :



¹ W. DECKERT, *Z. Desinfekt. Gesundh.*, 1930, **22**, 81.

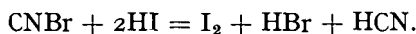
² MAUGUIN and SIMON, *Compt. rend.*, 1919, **169**, 383.

From this equation it is seen that each molecule of cyanogen chloride reacts with two molecules of sodium hydroxide. If, for instance, N ml. normal sodium hydroxide were used and n ml. normal sulphuric acid were necessary to neutralise the excess, the quantity of cyanogen chloride present in the sample is given by the following :

$$\text{CNCl} = (N - n) 0.0306.$$

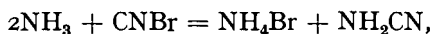
QUANTITATIVE DETERMINATION OF CYANOGEN BROMIDE

(1) *The Hydriodic Acid Method.* The determination of cyanogen bromide by this method depends on the estimation of the iodine liberated in the reaction between hydriodic acid and cyanogen bromide ¹ :



In carrying out this determination, a weighed quantity of cyanogen bromide is treated with an excess of hydriodic acid solution, which is prepared by dissolving 10 gm. potassium iodide in 100 ml. of a 5% solution of acetic acid. The iodine liberated is titrated with a decinormal solution of sodium thiosulphate.

(2) *The Ammonia Method.* This method depends on the decomposition of cyanogen bromide by ammonia :



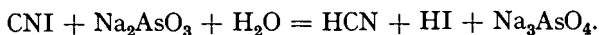
and the titration of the ammonium bromide formed with silver nitrate. ²

The sample to be analysed is weighed accurately into a flask, about 100 ml. aqueous ammonia are added and the flask stoppered and allowed to stand in the cold for about 20 minutes. After warming for a short time on the water-bath, the solution is diluted with 300 ml. water and brought to the boil to free it from the excess of ammonia. It is then slightly acidified with nitric acid and titrated with silver nitrate solution.

The decomposition of cyanogen bromide may be carried out with sodium or potassium hydroxide instead of ammonia.

QUANTITATIVE DETERMINATION OF CYANOGEN IODIDE

The determination of cyanogen iodide may be carried out by utilising its reaction with sodium arsenite ³ :



¹ CHATTAWAY, *J. Chem. Soc.*, 1902, **81**, 196.

² F. OBERHAUSER and I. SCHORMÜLLER, *Ber.*, 1929, **62**, 1439.

³ GUTMANN, *Ber.*, 1909, **42**, 3624 ; *Z. anal. Chem.*, 1925, 246.

The sample is treated with an exactly measured quantity of standard arsenious acid solution in excess and an excess of a 15% solution of sodium hydroxide. The liquid is warmed on the water-bath, and while still hot a slow current of carbon dioxide is passed through until the hydrocyanic acid is completely eliminated. The solution is then allowed to cool and made up to a convenient volume. The excess of arsenious acid is then determined in an aliquot of this by addition of sodium bicarbonate and titration with a standard solution of iodine.

CHAPTER XIV

SULPHUR COMPOUNDS

(A) MERCAPTANS AND THEIR DERIVATIVES

THE mercaptans may be considered as derivatives of hydrogen sulphide, with one hydrogen atom substituted by an alkyl radical.

These compounds, unlike hydrogen sulphide itself, have a comparatively low toxicity, confirming what has already been indicated regarding the influence of alkyl groups on the toxicity of substances. It also follows that the introduction of one or more halogen atoms into the molecule does not generally increase the toxicity, but decreases the chemical stability.

Of the chloro-compounds, perchloromethyl mercaptan and its less chlorinated derivative, thiophosgene, have been used as war gases. Although the latter cannot be considered as a mercaptan, it is described in this chapter because of its close relationship to perchloromethyl mercaptan.

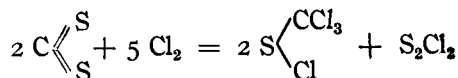
1. Perchloromethyl Mercaptan

(M.Wt. 185.91)



This substance was employed by the French in September, 1915, but with little success owing to its low offensive powers.

It was prepared in 1873 by Rathke¹ and later by others, by the action of chlorine on carbon disulphide :



The temperature of the reaction should not be allowed to rise above 50° C., otherwise more highly chlorinated compounds will be formed, especially in the presence of an excess of chlorine.

Perchloromethyl mercaptan may also be obtained by the action of chlorine on methyl thiocyanate² or on thiophosgene.³

¹ RATHKE, *Ann.*, 1873, **167**, 195.

² JAMES, *J. Chem. Soc.*, 1887, **51**, 268.

³ KLASON, *Ber.*, 1887, **20**, 2381.

LABORATORY PREPARATION

In the laboratory, perchloromethyl mercaptan is easily prepared by the method recommended by Helfrich,¹ based on the reaction of chlorine with carbon disulphide.

75 gm. carbon disulphide and 0.3 gm. iodine are placed in a flask of 200–300 ml. capacity fitted with a reflux condenser. While the flask is being externally cooled with water, a current of dry chlorine is passed in for several hours. In order to accelerate the reaction, it is as well to expose the contents of the flask to diffused daylight. When the volume of the liquid has been approximately doubled (and its weight has reached about 150–160 gm.) the current of chlorine is stopped and the mixture allowed to stand overnight. It is then warmed on the water-bath to drive off the excess of carbon disulphide and also the carbon tetrachloride, which is formed as a secondary product of the reaction. The sulphur chloride is decomposed by adding an equal volume of water to the residue and shaking vigorously. This is then distilled first in steam and then under reduced pressure (50 mm.).

PHYSICAL AND CHEMICAL PROPERTIES

Perchloromethyl mercaptan is an oily, clear yellow liquid with an unpleasant odour, which boils at ordinary pressure at 148° to 149° C. with decomposition. At 50 mm. pressure it distils unaltered at 73° C. Its specific gravity is 1.722 at 0° C., its vapour density is 6.414, and its volatility is 18,000 mgm. per cu. m. at 20° C.

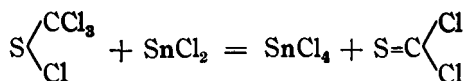
When perchloromethyl mercaptan is heated with water in a closed tube to 160° C., it decomposes into carbon dioxide, hydrochloric acid and sulphur.² This decomposition also takes place to a very limited extent by the action of atmospheric humidity.

In the presence of oxidising agents, the sulphur atom is oxidised and the perchloromethyl mercaptan is converted into trichloromethyl sulphonic chloride, $\text{CCl}_3\text{—SO}_2\text{—Cl}$.

Reducing agents act on perchloromethyl mercaptan in various ways. For instance, nascent hydrogen (from zinc and hydrochloric acid) reduces it to methane, iron and hydrochloric acid converts it into carbon tetrachloride (Helfrich), while with stannous chloride, thiophosgene is obtained.

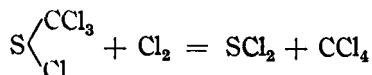
¹ HELFRICH, *J. Am. Chem. Soc.*, 1921, **43**, 591; AUTENRIETH, *Ber.*, 1925, **58**, 2152.

² RATHKE, *Ann.*, 1873, **167**, 201.



This last reaction also takes place with some other reducing agents, such as copper and silver powder.

When treated in the cold with chlorine, perchloromethyl mercaptan is converted into sulphur chloride and carbon tetrachloride ¹ :

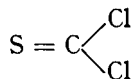


In contact with iron, perchloromethyl mercaptan decomposes even at ordinary temperatures. ²

Perchloromethyl mercaptan has an irritant action on the eyes. The minimum concentration capable of causing this irritation is 10 mgm. per cu. m. of air. The limit of insupportability is 70 mgm. per cu. m. and the mortality-product is 3,000 (Müller).

2. Thiophosgene

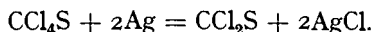
(M.Wt. 114.98)



Thiophosgene was prepared by Kolbe in 1843, ³ and was employed as a war gas by the Austrians and the French in the war of 1914-18 (" *Lacrimite* ").

PREPARATION

It may be obtained by passing a mixture of carbon tetrachloride and hydrogen sulphide through a red-hot tube, or by passing perchloromethyl mercaptan over silver powder ⁴ :



In the laboratory, it is preferable to prepare thiophosgene by the reduction of perchloromethyl mercaptan with tin and hydrochloric acid. ⁵

60 gm. of granulated tin and 200 ml. hydrochloric acid (density 1.19) are placed in a round-bottomed flask of about 1 litre capacity fitted with a tap-funnel and a reflux condenser. It is warmed gently to accelerate solution of the tin and meanwhile 60-70 gm. perchloromethyl mercaptan are added gradually

¹ JAMES, *J. Chem. Soc.*, 1887, **51**, 273.

² FRANKLAND and coll., *J. Soc. Chem. Ind.*, 1920, **39**, 256.

³ KOLBE, *Ann.*, 1843, **45**, 44.

⁴ RATHKE, *Ann.*, 1873, **167**, 204.

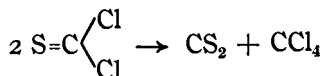
⁵ KLASON, *Ber.*, 1887, **20**, 2380.

from the tap-funnel. When it has all been added the contents of the flask are heated and the thiophosgene distilled off. In order to obtain a purer product it is redistilled.

In France during the war, thiophosgene was prepared by acting on carbon disulphide with chlorine at ordinary temperatures and then reducing the perchloromethyl mercaptan formed as intermediate product with stannous chloride.

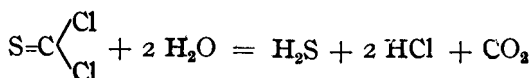
PHYSICAL AND CHEMICAL PROPERTIES

Thiophosgene is an oily liquid with an orange-yellow colour and a pungent odour. It fumes in the air and boils at 73.5° C. Its specific gravity at 15° C. is 1.508 and its vapour density 4. It is insoluble in water. On heating even to 200° C., it decomposes to a slight extent (Klason), but on heating with dry ammonium chloride it is quantitatively decomposed into carbon disulphide and carbon tetrachloride ¹ :

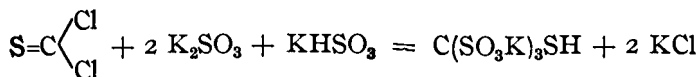


Exposure to light, even for a short time, converts it into a polymer of the formula C₂Cl₄S₂. This is termed "dithiophosgene" and forms colourless crystals melting at 116° C.²

Water slowly decomposes thiophosgene in the cold and rapidly hot (Bergreen) :



A similar decomposition is produced by the action of alkalis. With ammonia, ammonium thiocyanate is formed. The alkali sulphites react vigorously as follows (Rathke) :



Chlorine is rapidly absorbed even in the cold, perchloromethyl mercaptan being formed (Klason).

Strong acids, even fuming nitric acid, do not decompose it (Kolbe).

The lethal concentration for 30 minutes' exposure is 4,000 mgm. per cu. m. of air (Lindemann).

(B) SULPHIDES (THIOETHERS) AND THEIR DERIVATIVES

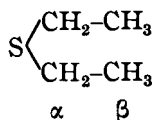
The sulphides, or thioethers, whose general formula is R—S—R, may be considered as derivatives of hydrogen sulphide in which

¹ BERGREEN, *Ber.*, 1888, 21, 339.

² G. CARRARA, *Atti accad. Lincei.*, 1893, 1, 421 ; RATHKE, *Ber.*, 1888, 21, 2539.

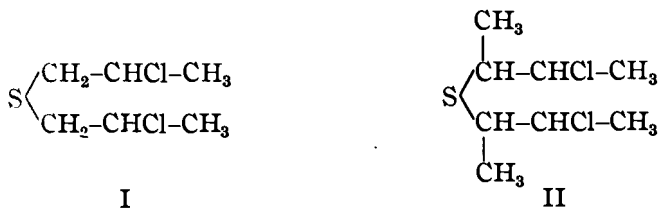
both the hydrogen atoms have been substituted by alkyl groups.

These compounds have no toxic action on the human organism, but, like the sulphur derivatives already described, a certain degree of toxicity and in some cases powerful vesicant power are acquired when one or more of the hydrogen atoms in the alkyl radicals are substituted by one or more halogen atoms. Thus from methyl sulphide, chloromethyl sulphide is obtained, this having a toxic power on the respiratory system. From ethyl sulphide, derivatives are obtained which have differing toxic actions according to whether the halogen atom is attached at position α or β :



The monosubstituted derivatives, ethyl β chloroethyl sulphide and ethyl β bromoethyl sulphide,¹ are weak in toxicity, as is also the disubstituted compound $\alpha\alpha'$ dichloroethyl sulphide.² The disubstituted derivative with both the halogen atoms in the β position, $\beta\beta'$ dichloroethyl sulphide, however, is powerfully toxic and vesicant : it is more commonly known as "*Mustard Gas*."

Other derivatives analogous to $\beta\beta'$ dichloroethyl sulphide have been prepared, such as $\beta\beta'$ dibromoethyl sulphide³ and $\beta\beta'$ diiodoethyl sulphide,⁴ which have similar physiopathological properties, as well as homologues of $\beta\beta'$ dichloroethyl sulphide such as $\beta\beta'$ dichloropropyl sulphide (I) and $\beta\beta'$ dichlorobutyl sulphide (II) :



These two substances resemble $\beta\beta'$ dichloroethyl sulphide in odour, but show some differences in offensive action, for it has been found that only $\beta\beta'$ dichlorobutyl sulphide possesses vesicant action and that to a much milder degree than the ethyl compound.⁵

¹ STEINKOPF, *Ber.*, 1920, **53**, 1007.

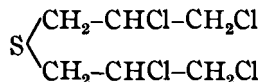
² BALES, *J. Chem. Soc.*, 1922, **121**, 2137.

³ STEINKOPF, *Ber.*, 1920, **53**, 1011.

⁴ HELFRICH and REID, *J. Am. Chem. Soc.*, 1920, **42**, 1219.

⁵ POPE, *J. Chem. Soc.*, 1921, **119**, 396 ; COFFEY, *J. Chem. Soc.*, 1921, **119**, 94.

Derivatives have also been prepared with the chlorine atom in the γ position, like $\gamma\gamma'$ dichloropropyl sulphide, whose toxic properties are, however, as yet unknown,¹ and also derivatives with chlorine atoms in the β and γ positions, such as $\beta\beta'\gamma\gamma'$ tetrachloropropyl sulphide :



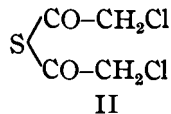
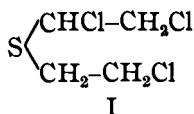
whose physiopathological properties are similar to those of $\beta\beta'$ dichloroethyl sulphide, but not so vigorous.²

Attempts made to prepare substances like $\delta\delta'$ dichlorobutyl sulphide with chlorine atoms in the δ position have not been successful up to the present.

With regard to the relations between the chemical structure of these substances and their vesicant power, the following observations may be made :

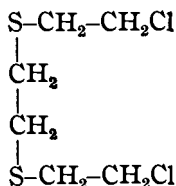
(a) Of the halogenated sulphides prepared and studied only those with the halogen atoms at the end of the carbon chain have vesicant properties.

(b) The CH_2 -group in the α position should remain unsubstituted. It has been shown that on substituting a hydrogen atom in this group with a halogen atom, as in $\alpha\beta\beta'$ trichloroethyl sulphide (I), or replacing each pair of hydrogen atoms in the two CH_2 -groups with oxygen, as in monochloroacetic thioanhydride (II) :



the products are completely or almost completely deprived of vesicant properties.

(c) The introduction of one or more sulphur atoms linked with one or more CH_2 -groups, between the chloroethyl groups, as in dichloroethyl ethylene dithioglycol³ :



¹ BENNETT, *J. Chem. Soc.*, 1925, 127, 2671.

² E. BOGGIO-LERA, *Chim. e Industria*, 1935, 334.

³ BENNETT, *J. Chem. Soc.*, 1921, 119, 1860 ; ROSEN, *J. Am. Chem. Soc.*, 1922, 44, 634.

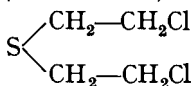
diminishes the vesicant power, but confers orticant properties (see p. 147).

Of the analogues of dichloroethyl sulphide, the following have a place in the chemistry of the war gases :

(a) $\beta\beta'$ dichloroethyl selenide,¹ crystals melting at $24.2^\circ\text{C}.$,² which have a vesicant action on the skin like that of the corresponding sulphide but to a less degree. This action is produced by a benzene solution of dichloroethyl selenide containing more than 2% as selenium.³

(b) Dichloroethyl telluride, which, according to American experiments, does not possess the interesting offensive properties expected of it (Hanslian).

1. Dichloroethyl Sulphide (Mustard Gas) (M.Wt. 159)



The discovery of this war gas, more commonly known as "*Iprite*" from the locality (Ypres in Flanders) where it was first used, is due to Despretz,⁴ who obtained it in 1822 by the reaction of ethylene on sulphur chloride.

It is also known as "*Senfgas*," "*Mustard Gas*" (England), "*Ypérite*" (France) and "*Lost*" (Germany). This last name is derived by joining the first letters of the names of the two Germans, Lommel and Steinkopf, who proposed and studied the use of this gas in warfare. In America, it is referred to in the Chemical Warfare Service as "*HS*."

The application of this substance as a war gas, which commenced in July 1917 by the Germans, marked the beginning of a new period of chemical warfare and constituted a great surprise for the Allied armies. It was identified a few days after it was first used, but its preparation on an industrial scale required several months of study and research by the Allies. By the end of the war, however, the potential production of the Allied plants was greater than that of the German.

PREPARATION

After Despretz, this substance was prepared by Riche⁵ in 1854, and later by Guthrie⁶ in 1860, while studying the condensa-

¹ H. BAUSOR and coll., *J. Chem. Soc.*, 1920, **117**, 1453; C. BOORD, *J. Am. Chem. Soc.*, 1922, **44**, 395; POGGI, *Gazz. chim. Ital.*, 1934, **64**, 497.

² H. BELL and coll., *J. Chem. Soc.*, 1925, **127**, 1877.

³ G. FERRAROLO, *Pensiero Medico*, 1936, No. 5.

⁴ DESPRETZ, *Ann. chim. phys.*, 1822, [2] **21**, 428.

⁵ RICHE, *Ann. chim. phys.*, 1854, [3] **42**, 283.

⁶ GUTHRIE, *Quart. Jour. Chem. Soc.*, 1860, **12**, 116.

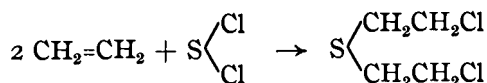
tion products of the halogens and of the halogenated sulphur compounds with the olefines. Guthrie, to whom many accounts have erroneously attributed the discovery of dichloroethyl sulphide, prepared it like Despretz by bubbling ethylene through sulphur chloride and noticed its peculiar vesicant properties.

At the same time, but independently of Guthrie's work, Niemann,¹ in 1860, employing the same method as Despretz, obtained dichloroethyl sulphide, but was not able to determine its chemical constitution.

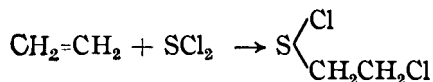
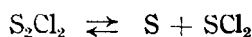
Later, in 1886, Meyer² made a special study of the compound and succeeded in preparing it in the pure state by a completely new process depending on the chlorination of thiodiglycol with phosphorus trichloride, and described its physical, chemical and biological properties.

More recently, in 1912, Clarke³ prepared this compound by a method similar to that of Meyer, that is, by chlorination of thiodiglycol, but used hydrochloric acid instead of phosphorus trichloride.

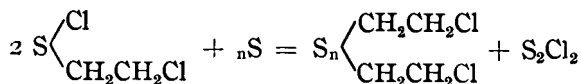
In 1920, Gibson and Pope⁴ perfected Guthrie's method by bubbling dry and completely alcohol-free ethylene through sulphur dichloride maintained in agitation at 40° to 45° C. :



By employing sulphur monochloride instead of the dichloride, the reaction passes through the following phases, according to Conant⁵ :



Furthermore, the following secondary reaction takes place :



¹ NIEMANN, *Ann.*, 1860, **113**, 288.

² V. MEYER, *Ber.*, 1886, **19**, 632, 3259.

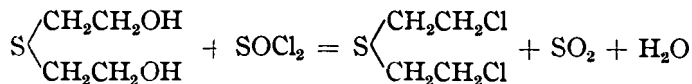
³ CLARKE, *J. Chem. Soc.*, 1912, **101**, 1583.

⁴ GIBSON and POPE, *J. Chem. Soc.*, 1920, **117**, 271.

⁵ CONANT and coll., *J. Am. Chem. Soc.*, 1920, **42**, 585.

Other methods of preparing dichloroethyl sulphide of minor importance have been proposed :

Steinkopf's method,¹ which consists in reacting on a solution of thiodiglycol in chloroform with thionyl chloride also dissolved in chloroform :



Myers and Stephen's method,² in which a mixture of 75 parts of sulphur dichloride and 25 parts of sulphur monochloride is sprayed in an atmosphere of ethylene. According to the authors, this method permits the rapid and continuous preparation of dichloroethyl sulphide in 93% yield, without over-chlorination.

LABORATORY PREPARATION

Dichloroethyl sulphide may be easily prepared in the laboratory by following Guthrie's original method: bubbling ethylene through sulphur chloride.

An apparatus like that shown in Fig. 14 is set up. The reaction

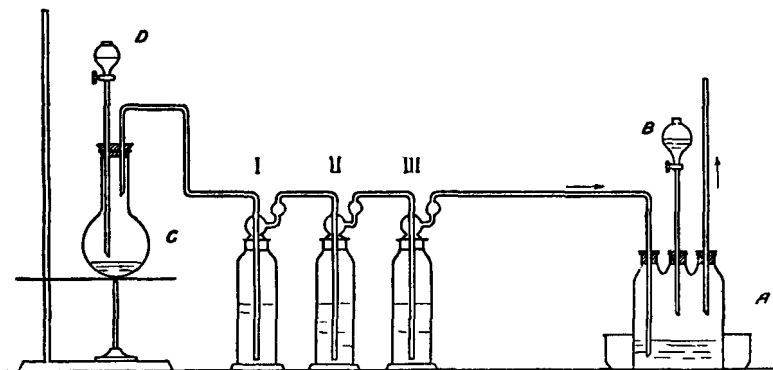


FIG. 14.

between the ethylene and the sulphur chloride takes place in the Woulfe's bottle *A* (capacity 100–200 ml.) which has three necks, one of which serves to carry off excess gas, another is fitted with a tap-funnel *B* in which the sulphur chloride is placed, while ethylene, made in the flask *C*, is introduced through the third. The three wash-bottles contain respectively (*I*) concentrated sulphuric acid, (*II*) 10% sodium hydroxide and (*III*) concentrated

¹ STEINKOPF, *Ber.*, 1920, **53**, 1007.

² MYERS and STEPHEN, *J. Soc. Chem. Ind.*, 1920, **39**, 656T.

sulphuric acid, and serve to dry the ethylene. It is advisable not to connect the wash-bottle *III* to the Woulfe's bottle until the evolution of the ethylene has become regular.

25 gm. alum and a mixture of 25 gm. ethyl alcohol and 150 gm. concentrated sulphuric acid (density 1.84) are placed in the flask *C*, which is then heated cautiously. As soon as the current of ethylene becomes steady, wash-bottle *III* is connected with the Woulfe's bottle, in which 20 gm. sulphur chloride have been previously placed. At the same time a mixture of 150 gm. ethyl alcohol and 300 gm. concentrated sulphuric acid is introduced drop by drop into *C* from the tap-funnel *D*.

During the passage of the ethylene, a further 30 gm. sulphur chloride are added from the tap-funnel *B* in three portions and the Woulfe's bottle is immersed in a vessel containing water so that the temperature of the reaction mixture does not exceed 35° C. The passage of the ethylene through the Woulfe's bottle is continued until all the sulphur chloride has been used up. This stage is determined by treating a little of the product with sodium iodide solution.

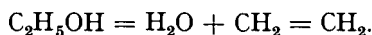
At the end of the reaction the product is distilled under reduced pressure, the fraction passing over between 106° and 108° C. at 15 mm. pressure being collected.

INDUSTRIAL MANUFACTURE

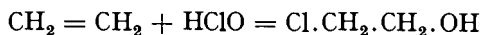
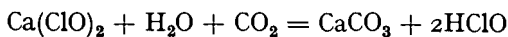
Dichloroethyl sulphide may be prepared industrially by several processes, all of which are based on one of the two methods described above: Meyer's and Guthrie's.

The various stages of manufacture by *Meyer's process*, which is referred to as "*the German process*," as it was largely employed during the war of 1914-18 by Germany, may be schematically expressed as follows:

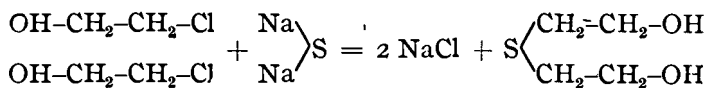
(a) Preparation of Ethylene:



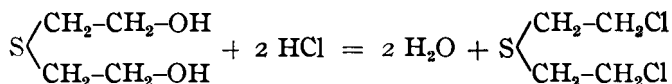
(b) Preparation of Ethylene Chlorohydrin:



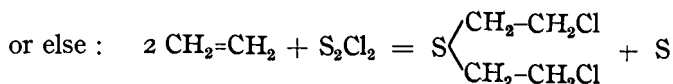
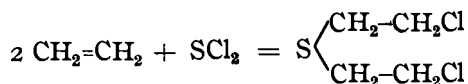
(c) Preparation of Thiodiglycol:



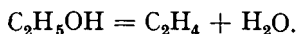
(d) Preparation of Dichloroethyl Sulphide :



Guthrie's method, which was used by the Allies, and is, therefore, referred to as "the *Allied process*," consists simply in acting on sulphur chloride with ethylene :



Meyer's Method : Preparation of Ethylene. Ethylene is prepared by passing ethyl alcohol in the vapour state over aluminium oxide heated to 350° to 400° C. The dehydration reaction is as follows :



The alcohol is first vaporized by passing it through coils heated to 80° to 90° C. and through a copper tube containing the catalyst and heated in a bath of fused potassium nitrate. The reaction products then pass through coolers where the water and alcohol are condensed while the ethylene is washed and led into storage vessels.

*Preparation of Ethylene Chlorohydrin.*¹ This reaction is carried out in large cylindrical iron pans, lined with lead and coated externally with cork. 5 cu. m. (1,100 gallons) of water and bleaching powder equivalent to 500 kgm. active chlorine are placed in this vessel and while stirring well a current of carbon dioxide is introduced in order to liberate part of the hypochlorous acid. After about 20 minutes, ethylene instead of carbon dioxide is introduced to saturation point and finally carbon dioxide and ethylene simultaneously until all the hypochlorite has reacted. The reaction should be carried out at as low a temperature as possible, between 5° and 10° C., the reaction mixture being cooled by circulating a cooling mixture through coils.

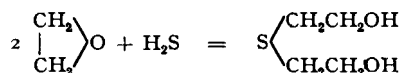
After the ethylene has been absorbed, the reaction products are pumped through a filter-press to remove the calcium carbonate and the filtrate, which contains from 10 to 12% ethylene

¹ G. BOZZA and MAMOLI, *Giorn. chim. ind. applicata.*, 1930, 283.

chlorohydrin, is distilled in steam so as to obtain a solution containing 18–20% of the chlorohydrin.¹

Preparation of Thiodiglycol. The theoretical quantity of sodium sulphide is added to the chlorohydrin solution, prepared as already described, and the mixture heated to about 90° to 100° C., the product being drawn over into an evaporator and again heated to remove all the water. The thiodiglycol formed is filtered, and distilled *in vacuo*.

NOTE. According to Nenitzescu,² the preparation of thiodiglycol may be carried out by acting on ethylene oxide with hydrogen sulphide at 40° to 60° C. in presence of a small quantity of thiodiglycol which acts as a solvent for the two gases.



This method gives a yield of 90%.

Preparation of Dichloroethyl Sulphide. The chlorination of thiodiglycol is carried out in cylindrical cast-iron pans, 2.5 m. in height and 2.8 m. in diameter, lead-lined and jacketed so that the reaction mass may be heated and cooled. The hydrochloric acid necessary for the chlorination is first passed through sulphuric acid and then introduced into the thiodiglycol as slowly as possible so as to obtain complete absorption. During the reaction the temperature is held at about 50° C. Two layers form in the pan, a heavy oily one consisting of a solution of dichloroethyl sulphide in thiodiglycol and an upper one consisting of an aqueous solution of hydrochloric acid. At the end of the reaction, the oily layer is drawn over into a lead-lined iron vessel fitted with lead coils for heating and a condenser, also constructed of lead, connected to a vacuum pump. The water is removed by distillation under reduced pressure (60–70 mm.) and the residual liquid then treated in a mixer with suitable solvents.

Guthrie's Method (the Allied Process). This method, comparatively simple for preparing small quantities of dichloroethyl sulphide in the laboratory, presented considerable technical difficulties when first used on the industrial scale. These were later overcome by the efforts of English and American chemists.³

Compared with the Meyer process, the Guthrie method allows

¹ M. GOMBERG, *J. Am. Chem. Soc.*, 1919, **41**, 1414.

² NENITZESCU, *Antigaz*, 1935, **9**, No. 9, 12; No. 11, 3.

³ A. GREEN, *J. Soc. Chem. Ind.*, 1919, **38**, 363, 469; GIBSON and POPE, *J. Chem. Soc.*, 1920, **117**, 271.

the product to be prepared more rapidly and in better yield, but it requires careful control during the course of the reaction.¹

Several systems of manufacture were proposed and actually employed during the war for the preparation of dichloroethyl sulphide by this process.² The most successful procedure in practice was that of Levinstein which was first used in America and then later by the Allies.

The preparation of dichloroethyl sulphide by this method was carried out in a cylindrical vessel of sheet steel or cast-iron, lead-lined and jacketed, of about 100 cm. diameter and 130 cm. in height, fitted with an agitator. This vessel has a lid through which a pipe passes to within a short distance of the bottom in order to introduce the ethylene.

Sufficient sulphur monochloride to cover the end of the tube is first placed in the vessel and then ethylene is bubbled in, so arranging the speed of its introduction and the cooling that the temperature of the reaction mixture remains at 30° to 35° C. Meanwhile more sulphur monochloride is added in small portions. Employing 430 kgm. of ethylene, which needs 750 kgm. sulphur chloride, the reaction is completed in about 20 hours. At the end of the reaction the product is siphoned into a settling vessel where the sulphur is removed.

PHYSICAL PROPERTIES

In the pure state, dichloroethyl sulphide is an oily, colourless liquid which boils at 760 mm. pressure at 217.5° C.³ and melts at 14.4° C.⁴ In the crude state, it is brown and has a characteristic odour which is reminiscent of mustard. The melting point of the crude product is lower than that of the pure substance and varies with the impurities present.

The latent heat of fusion is 25 calories, the refractive index n_D is 1.53125 (Pope and Gibson), and the coefficient of thermal

¹ Report of the Chemical Warfare Service of January 16th, 1918 (JACKSON, *Chem. Rev.*, 1934, 426).

² For detailed descriptions of the French method (Pascal), see GIUA, *Chimica degli aggressivi chimici*, Turin, 1931, 68 ff.

³ This value is that quoted by Meyer; other authors, like Vedder and Hanslian, however, give the boiling point of dichloroethyl sulphide as 219.5° C. This discordance may be attributed to the fact that this substance decomposes at its boiling point at ordinary pressure. According to Flury and Wieland the boiling point at 15 mm. mercury pressure is 108° to 109° C., and according to Clarke (*J. Chem. Soc.*, 1912, 101, 1583) 97° to 98° C. at a pressure of 10 mm.

⁴ In the literature many different values are quoted for the melting point of dichloroethyl sulphide: Meyer (1887), 12° C.; Gibson and Pope (1919), 13° to 13.5° C.; Gombert (1919), 14.5° C.; Delepine and Flury (1920), 14° to 14.5° C.; Fries (1921), 13° to 14° C. The most dependable value is 14.4° C. for the pure substance.

expansion 0.000881. The specific gravity of the solid is 1.362 at 9° C. (Vedder) and 1.338 at 13° C. (Fries).

The specific gravity of liquid dichloroethyl sulphide and the corresponding specific volume are given in the following table at various temperatures ¹ :

TEMPERATURE (° C.)	SPECIFIC GRAVITY	SPECIFIC VOLUME
15	1.2790	0.781
20	1.2741	0.785
25	1.2686	0.788
30	1.2635	0.791
35	1.2584	0.795
40	1.2531	0.798
50	1.2426	—
75	1.2158	—
90	1.1996	—

The vapour density of dichloroethyl sulphide in the gaseous state, calculated by dividing the weight of a litre of the vapour (7.09 gm.) by the weight of a litre of air (1.293 gm.), is 5.4.

The vapour pressure of dichloroethyl sulphide at various temperatures may be calculated from the formula (see p. 11) :

$$\log p = 8.3937 - \frac{2734.5}{T}$$

The values of the vapour pressure determined experimentally and calculated from the formula already quoted ² are given in the following table, as well as the corresponding values for the volatility ³ at various temperatures :

TEMPERATURE ° C.	VAPOUR TENSION (<i>mm. mercury</i>)		VOLATILITY <i>mgm./litre</i>
	<i>Obs.</i>	<i>Calc.</i>	
0	0.035	0.024	0.28
10	0.055	0.054	—
15	0.075	0.079	0.401
20	0.115	0.115	0.625
25	—	—	0.958
30	0.225	0.23	1.443
35	—	—	2.135
40	0.45	0.45	3.66
50	0.83	0.85	—
60	1.55	1.52	—

¹ WILKINSON and WERNLUND, *J. Am. Chem. Soc.*, 1920, **42**, 1382.

² MUMFORD and coll., *J. Chem. Soc.*, 1932, 589.

³ VEDDER, *loc. cit.*

The values of the vapour tension and of the corresponding volatilities of dichloroethyl sulphide in the solid state are, according to Vedder :

TEMPERATURE ° C.	VAPOUR TENSION mm. mercury	VOLATILITY mgm./litre
— 17·8	0·0045	0·045
0	0·031	0·28

Because of its low vapour tension, dichloroethyl sulphide evaporates very slowly, in spite of its low specific heat (0·330 calories) and low latent heat of volatilisation (80 calories). It is thus highly persistent, especially on terrain covered with bushes and shrubs (see p. 12).

Dichloroethyl sulphide is very sparingly soluble in water, its solubility increasing to a certain limit with increase in temperature. According to Hopkins ¹ the solubility in water is 0·033% at 0·6° C., and 0·07% at 10° C. According to French data,² the solubility at 25° C. is 0·047%, and according to American data ³ 0·069%.

It is, however, very soluble in various hydrocarbons ⁴ and organic solvents, such as kerosene (in which it is soluble in all proportions at 26° C.), petrol, carbon tetrachloride, monochlorobenzene, ethyl alcohol (in absolute alcohol it is soluble in all proportions above 15·6° C., and above 38·6° C. in 92·5% alcohol),⁵ ethyl ether, carbon disulphide, thiodiglycol, glycerol, as well as in the animal and vegetable oils and fats. It is only slightly soluble in vaseline and paraffin wax.⁶

Dichloroethyl sulphide also dissolves in chloropicrin.⁷ It is absorbed by rubber and penetrates leather and the ordinary textile fabrics.

The following observations have been made on the degree of penetration of dichloroethyl sulphide into various materials ⁸ :

Into *ordinary brickwork*, very little penetration; increased if the material is very porous.

¹ HOPKINS, *J. Pharmacol.*, 1919, **12**, 393.

² BOULIN and SIMON, *Compt. rend.*, 1920, **170**, 845.

³ WILSON, *J. Am. Chem. Soc.*, 1922, **44**, 2867.

⁴ THOMPSON and H. ODEEN, *J. Ind. Eng. Chem.*, 1920, **12**, 1057.

⁵ THOMPSON and BLACK, *J. Am. Chem. Soc.*, 1921, **43**, 877.

⁶ SCHRÖTER, *Dräger-Hefte*, 1936, No. **186**, 3309.

⁷ LINDEMANN, *Yperit*, Warsaw, 1929, 74.

⁸ THEMME, *Gasschutz und Luftschutz*, 1936, 189, also considers the penetration of dichloroethyl sulphide into bitumen, tar, linoleum, road-making materials, etc

Into *glazed brickwork and porcelain* it does not penetrate, but spreads out slightly, remaining thus until it has completely evaporated.

Oil paints applied to house walls offer protection to penetration provided that the paint coating is homogeneous and free from cracks.

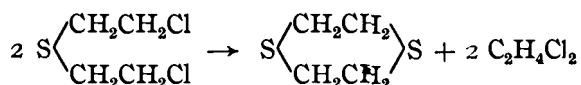
Unpainted woodwork easily absorbs dichloroethyl sulphide, penetration into the fibres taking place very easily along the grain.

The action of dichloroethyl sulphide on parchment, documents, seals, deed papers, handwriting, etc., has also been studied. On these objects dichloroethyl sulphide in the vapour form has been applied without having any noticeable action, though in the liquid state it penetrates paper, shellac, wax, etc.¹

CHEMICAL PROPERTIES

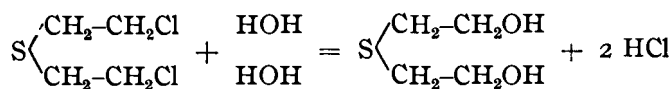
At ordinary temperature, dichloroethyl sulphide is a stable compound, but on heating it decomposes into hydrochloric acid and toxic and lachrymatory gases whose composition has not yet been defined. This decomposition commences at about 150° C. and is complete at 500° C.

According to Bell,² on heating dichloroethyl sulphide at 180° C. for 18 hours, dithiane and ethylene dichloride are formed :



This reaction is reversible, so that on heating dithiane with ethylene dichloride to 180° C. dichloroethyl sulphide is formed.

Dichloroethyl sulphide in contact with water undergoes hydrolysis even at ordinary temperatures to form thiodiglycol and hydrochloric acid :



Thiodiglycol³ is a colourless, syrupy liquid with a characteristic odour, soluble in water, ethyl alcohol, acetone and chloroform, but sparingly soluble in ether, benzene and carbon tetrachloride. On heating at ordinary pressure it decomposes without distilling. At 12 mm. of mercury pressure it distils at 161° to 165° C., and

¹ ZERNICK, *Archiv. Zeitschr.*, 1936, **44**, 185.

² BELL and coll., *J. Chem. Soc.*, 1927, 1803.

³ GOMBERG, *J. Am. Chem. Soc.*, 1919, **41**, 1414.

at 2 mm. of mercury it distils at 130° C. Its specific gravity at 20° C. is 1.1821.

As to the velocity of hydrolysis of dichloroethyl sulphide, a subject not without a certain interest, especially from the military point of view, there is not the least information in pre-war literature. The first studies commenced in 1918-19 with Hopkins's¹ work, and were continued with those of Rona² and of Wilson.³

These have shown that complete hydrolysis of dichloroethyl sulphide takes place by an irreversible reaction⁴ except in the presence of a considerable quantity of hydrochloric acid. The velocity of the hydrolysis may be determined either by measuring the development of acidity or of the quantity of ionised chlorine present (Hopkins), or from the decrease in electrical resistance. This velocity is influenced by various factors, such as the time of contact, the temperature, the water/dichloroethyl sulphide ratio, the quantities of acid, alkali and hydrolysis products present, as well as the degree of dispersion of the dichloroethyl sulphide in the water.

In the following table, due to Hopkins, the degree of hydrolysis at the ordinary temperature (20° to 21°C.) is given as a function of the time of contact of the dichloroethyl sulphide with water :

TIME <i>minutes</i>	% DICHLOROETHYL SULPHIDE HYDROLYSED COMPARED WITH THAT DISSOLVED
10	50
20	70
30	79
40	84
50	85
60	85

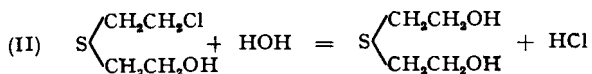
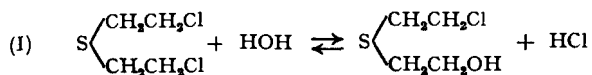
Regarding the influence of the ratio of water to dichloroethyl sulphide, it has been found that in presence of a large excess of

¹ HOPKINS, *J Pharmacol*, 1919, **12**, 393, 403

² RONA, *Z ges expt Med*, 1921, **13**, 16, also gives the velocity of hydrolysis of substances similar to dichloroethyl sulphide, like tetrachloroethyl sulphide, dibromoethyl sulphide, etc

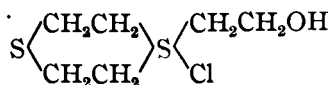
³ WILSON, *J Am. Chem Soc*, 1922, **44**, 2867-2878

⁴ According to the experiments of Wilson (*loc cit*) and Peters and Walker (*Biochem J*, 1923, **17**, 260) the hydrolysis of dichloroethyl sulphide takes place in two distinct steps, one reversible and the other irreversible



water the conversion into thiodiglycol is practically quantitative according to the equation already given.¹

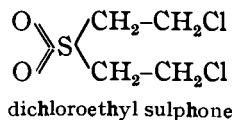
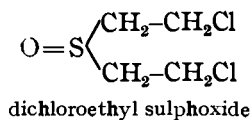
If, however, the amount of water is small compared with that of the dichloroethyl sulphide, for instance three times the volume of the sulphide, only a little thiodiglycol is formed, together with hydrochloric acid and a complex mixture of sulphonium chlorides, some of which form dichloroethyl sulphide with concentrated hydrochloric acid, while others do not. These latter compounds are formed principally when the ratio of water to the sulphide is very small. The only one which has been isolated is the following compound¹:



As to the influence on the hydrolysis of the degree of dispersion of the dichloroethyl sulphide, Wilson's² experiments have shown that the hydrolysis is considerably accelerated by adding alkaline solutions of sulphonated vegetable or animal oils, for example, solutions containing 3% of sulphonated corn oil and 2% sodium carbonate. These have the effect of increasing the degree of dispersion of the substance.

REACTIONS OF DICHLOROETHYL SULPHIDE IN WHICH THE SULPHUR ATOM TAKES PART

With Oxidising Agents. Like all thioethers, dichloroethyl sulphide tends to add one or two oxygen atoms and be converted into the corresponding sulphoxide or sulphone by oxidising agents like nitric acid, hydrogen peroxide, potassium permanganate, chromic acid, etc.



Dichloroethyl sulphoxide may be obtained, according to Gibson and Pope,³ by placing a drop of dichloroethyl sulphide in concentrated nitric acid (d. 1.40) at ordinary temperature. The reaction is violent, heat is evolved and a bright green liquid is formed. When this liquid is diluted with water, a white

¹ DAVIES and OXFORD, *J. Chem. Soc.*, **1931**, 224.

² WILSON, *J. Am. Chem. Soc.*, **1922**, **44**, 2762.

³ GIBSON and POPE, *J. Chem. Soc.*, **1920**, **117**, 271.

precipitate of the sulphoxide separates. On crystallising this from 60% alcohol, colourless scales are formed which melt at 110° C. This substance is soluble in water (1.2 gm. in 100 ml. at 20° C.), in alcohol (4.3 gm. in 100 ml. at 20° C.), in ether, benzene, carbon disulphide, acetone, chloroform and mineral acids.¹ On distilling even at reduced pressure it partly decomposes and the principal product of the decomposition is dichloroethyl sulphide.

Dichloroethyl sulphoxide has also been prepared by Steinkopf² from the reaction of hydrogen peroxide on dichloroethyl sulphide.

According to Marshall and Williams,³ this substance has no vesicant action on the skin.

Dichloroethyl sulphone may be obtained by the oxidation of dichloroethyl sulphoxide or sulphide. Thus by the action of potassium permanganate on dichloroethyl sulphide, Steinkopf⁴ obtained the sulphone as colourless crystals melting at 52° C.⁵ and boiling at 179° to 181° C. at 14–15 mm. of mercury pressure. This compound is sparingly soluble in water (0.6 gm. in 100 ml. at 20° C., and 2.4 gm. in 100 ml. at 100° C.) and is only slightly hydrolysed. It is soluble in alcohol (7.1 gm. in 100 ml. at 20° C.), ether, chloroform, etc. Helfrich and Reid obtained the sulphone by treating the sulphoxide in the cold with a solution of chromic acid in sulphuric acid.

According to Marshall, the sulphone in contact with the skin produces vesicles and persistent ulcers. Its vapour has a lachrymatory and sometimes even a sternutatory action. This physiopathological action is not observed when working with the substance at ordinary temperatures because of its low vapour pressure.

By the action of the strongest oxidising agents,⁶ such as fuming

¹ HELFRICH and REID, *J. Am. Chem. Soc.*, 1920, **42**, 1208.

² Dichloroethyl sulphoxide may be prepared as follows, according to STEINKOPF (*Ber.*, 1920, **53**, 1007): 23 gm. 30% hydrogen peroxide are added slowly to a cooled solution of 32 gm. dichloroethyl sulphide in 100 ml. acetic acid. The reaction is violent and heat is developed. After cooling and allowing to stand, the sulphoxide deposits when the solution is diluted with water.

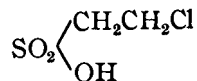
³ MARSHALL and WILLIAMS, *J. Am. Chem. Soc.*, 1920, **42**, 1298.

⁴ Preparation of the sulphone, according to STEINKOPF (*Ber.*, 1920, **53**, 1007): 20 gm. dichloroethyl sulphide, dissolved in 100 ml. of an aqueous solution of acetic acid (1:1), are shaken with a saturated aqueous solution of 30 gm. potassium permanganate in presence of 20 ml. dilute sulphuric acid, and then allowed to stand. After reduction of the excess permanganate with sulphur dioxide, crystals of the sulphone separate.

⁵ According to HELFRICH (*loc. cit.*), the melting point of this substance is 56° C. and its boiling point 183° C. at 20 mm. pressure.

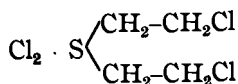
⁶ BENNETT, *J. Chem. Soc.*, 1921, **119**, 418; 1922, **121**, 2139; MANN and POPE, *J. Chem. Soc.*, 1922, **121**, 594.

nitric acid, on heating or in a closed tube at 100° C., dichloroethyl sulphide is converted into β chloroethane sulphonic acid :



and by the action of *aqua regia* it is converted into sulphuric acid and carbon dioxide.

With Chlorine. Lawson and Dawson¹ obtained a compound of the following structure :

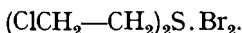


by bubbling a current of chlorine through a solution of dichloroethyl sulphide in carbon tetrachloride cooled to - 5° C. This forms white needles, unstable at ordinary temperatures (see p. 234).

With Bromine. Bromine also reacts easily with dichloroethyl sulphide. According to Gibson and Pope,² on treating a cold solution of dichloroethyl sulphide in chloroform with bromine an unstable addition compound is obtained. This is orange-yellow and has the following structure :

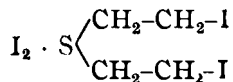


It decomposes to form a less highly brominated substance :



which is obtained as a yellow powder, m.p. 43° to 44° C. Sodium hydroxide solution converts it into dichloroethyl sulphoxide.

With Iodine. According to Lindemann³ a tetraiodo derivative is obtained, " tetraiodo-iprite " :



With Fluorine. No additive compounds of fluorine and dichloroethyl sulphide have been mentioned in the literature.

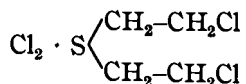
With Sulphur Chloride. From the reaction between sulphur

¹ LAWSON and DAWSON, *J. Am. Chem. Soc.*, 1927, **49**, 3119.

² GIBSON and POPE, *J. Chem. Soc.*, 1920, **117**, 271.

³ LINDEMANN, *Yperit*, Warsaw, 1929, 47.

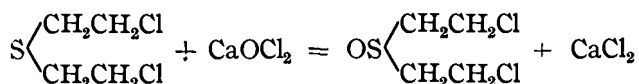
monochloride and dichloroethyl sulphide, a compound of the following formula is obtained ¹ :



that is, the same substance which is obtained from the action of chlorine on dichloroethyl sulphide. It forms white needles and is unstable at ordinary temperatures (see p. 234).

With Bleaching Powder. Dry chloride of lime reacts with dichloroethyl sulphide, acting as oxidant and chlorinating agent.² A very violent reaction, with evolution of heat, flame and white vapours, takes place. Numerous compounds are formed : carbon dioxide, hydrochloric acid, chloroform, chloral and chlorinated substances which are not yet defined.³

According to some workers, dichloroethyl sulphoxide is also formed in this reaction ⁴ :



The temperature of the reaction rises to such a point that combustible material (hay, paper, etc.) is inflamed.

By the action of chloride of lime mixed with water the action is less violent.

Bleaching powder is used to decontaminate objects which have been contaminated with mustard gas. For this purpose it is recommended that the bleaching powder be mixed to a porridge with water, or with some other powdered substance, so as to prevent the inconvenient results already mentioned, which would be caused by the violence of the reaction. In the reaction with undiluted bleaching powder, a zone of contact forms, consisting of a layer of decomposition products which protects the sulphide from further attack.⁵

Chloride of lime may also be employed for decontamination of the skin. In this case the violence of the reaction should be reduced by mixing the bleaching powder with water (1 part of water to 1 part of chloride of lime) or with magnesium oxide.⁶

¹ LIBERMANN, *op. cit.*

² WIRTH, *Gasschutz und Luftschutz*, 1932, 2, 60.

³ DESGREZ and coll., *Chim. et Ind.*, 1921, 6, 842. With regard to the practical aspects of decontamination with chloride of lime, see DRÄGER, *Gasschutz im Luftschutz*, Lubeck, 1934, 98.

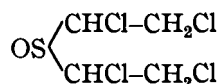
⁴ MEYER, *Der Gaskampf und die chemischen Kampfstoffe*, Leipzig, 1925, 406.

⁵ RENWANZ, *Die Gasmaske*, 1935, 1.

⁶ MUNTSCHE, *Pathologie und Therapie der Kampfgaserkrankungen*, Leipzig, 1935.

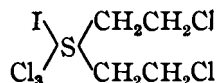
The decontaminating power of the bleaching powder depends on the content of active chlorine. According to Weidner,¹ in order to obtain sufficient decontaminating action, the bleaching powder should contain at least 15% active chlorine.

With Sodium Hypochlorite. On bubbling a current of carbon dioxide through a mixture of dichloroethyl sulphide and sodium hypochlorite solution, $\alpha\alpha'\beta\beta'$ tetrachloroethyl sulphoxide² is formed :

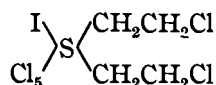


This is a crystalline substance melting at 121° C.

With Iodine Trichloride. On adding a carbon tetrachloride solution of dichloroethyl sulphide to a solution of iodine trichloride also in carbon tetrachloride, an addition compound of the following formula is immediately formed³ :

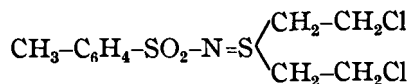


In the presence of an excess of iodine trichloride or of iodine trichloride and free chlorine, dissolved in carbon tetrachloride, dichloroethyl sulphide is converted into a yellow crystalline substance of the formula :



This reaction may be used for the detection of dichloroethyl sulphide.

With Chloramine-T. Dichloroethyl sulphide reacts readily with chloramine-T (the sodium salt of *p*-toluene sulphochloroamide, $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-N}=\text{NCl}$) to form an additive compound of the formula :



which contains a tetravalent sulphur atom. The $=\text{S}=\text{N}$ — according to Mann and Pope⁴ may be termed the “ sulphilimine ” group. The condensation of dichloroethyl sulphide with

¹ WEIDNER, *Gasschutz und Luftschutz*, 1936, 133.

² MÜLLER, *J. prakt. Chem.*, 1926, 114, 123.

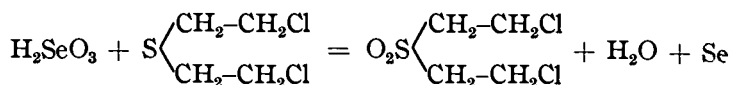
³ E. BOGGIO-LERA, *Chim. e Industria*, 1935, 334.

⁴ MANN and POPE, *J. Chem. Soc.*, 1922, 121, 1052.

chloramine-T takes place even in the cold ; on adding 17.1 gm. dichloroethyl sulphide to an aqueous solution of 28 gm. chloramine-T, small white crystals separate after about an hour. They melt at 144.6° C.

Chloramine-T is employed as decontaminating agent for dichloroethyl sulphide and has the advantage over bleaching powder of not producing too violent a reaction. Moreover, it is not toxic, non-irritant and keeps for a long time. It is recommended for the decontamination of clothing of linen, cambric, cotton and mixed fabrics. In decontaminating woollen materials it is necessary to avoid boiling.¹

With Selenious Acid. Dichloroethyl sulphide reacts with selenious acid, reducing it to selenium :



The selenium separates in the form of an orange-yellow suspension. Selenious acid in sulphuric acid solution has been proposed by Yablich as a reaction for the detection of dichloroethyl sulphide (see p. 247).

REACTIONS OF DICHLOROETHYL SULPHIDE INVOLVING THE WHOLE MOLECULE

With Chlorine. The behaviour of dichloroethyl sulphide with chlorine was studied by Mann and Pope² in 1922, by Lawson and Dawson³ in 1927, by Mumford⁴ in 1928, and by Phillips⁵ in 1929.

By the action of chlorine on dichloroethyl sulphide at ordinary temperatures, the following compounds are obtained, according to Mann and Pope :

		S.G.	B.P. 15 mm. mercury
Trichloro-compound	$\text{S} \begin{cases} \text{CHCl}-\text{CH}_2\text{Cl} \\ \text{CH}_2-\text{CH}_2\text{Cl} \end{cases}$	1.4219	106° to 108° C.
Tetrachloro-compound	$\text{S} \begin{cases} \text{CHCl}-\text{CHCl}_2 \\ \text{CH}_2-\text{CH}_2\text{Cl} \end{cases}$	1.5441	123° to 125° C.
Hexachloro-compound	$\text{S} \begin{cases} \text{CCl}_2-\text{CCl}_3 \\ \text{CH}_2\text{CH}_2\text{Cl} \end{cases}$	1.6944	160° to 161° C.

¹ WEIDNER, *loc. cit.*

² MANN and POPE, *J. Chem. Soc.*, 1922, 121, 594.

³ LAWSON and DAWSON, *J. Am. Chem. Soc.* 1927, 49, 3119.

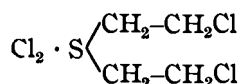
⁴ MUMFORD and COLE-PHILLIPS, *J. Chem. Soc.*, 1928, 155.

⁵ PHILLIPS and DAVIES, *J. Chem. Soc.*, 1929, 535.

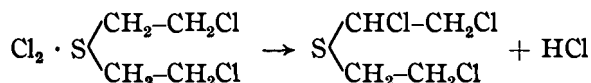
These three chloro-derivatives are obtained as colourless liquids which become faintly green on exposure to daylight. They have odours similar to that of dichloroethyl sulphide, but have no vesicant properties, while their melting points are much lower.

On examining these chloro-derivatives it was found that with the increase in the number of atoms of chlorine in their molecules, the tendency of the sulphur atom to pass from the divalent to the tetravalent condition diminished.

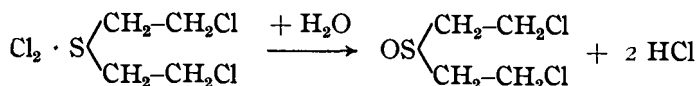
Lawson and Dawson have observed that the first product formed in the chlorination of dichloroethyl sulphide is an additive compound containing tetravalent sulphur :



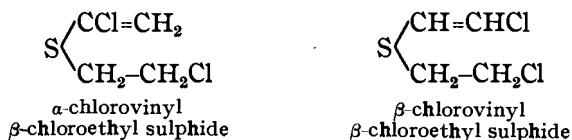
This compound is not very stable and is largely converted into $\alpha\beta\beta'$ trichloroethyl sulphide according to the equation :



A small proportion decomposes into dichloroethyl sulphoxide and hydrochloric acid :



The trichloroethyl sulphide, according to Lawson, is itself not very stable and loses another molecule of hydrochloric acid to form a vinyl compound which can exist in two isomeric forms :

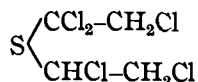


Each of these contains only two chlorine atoms, like dichloroethyl sulphide. Neither possesses vesicant properties equal to that of $\beta\beta'$ dichloroethyl sulphide however (Dawson and Lawson).

Later experiments on the action of chlorine on dichloroethyl sulphide have demonstrated that the chlorination is not limited to one chain of the molecule, but can take place in both the chloroethyl groups, and the following compounds have been prepared ¹ :

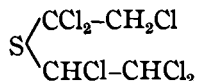
¹ PHILLIPS and DAVIES, *loc. cit.*

(a) $\alpha\alpha\beta\alpha'\beta'$ pentachloroethyl sulphide,



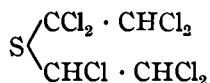
a mobile colourless liquid with density 1.57 at 20° C.

(b) $\alpha\alpha\alpha'\beta\beta'\beta'$ hexachloroethyl sulphide,



a colourless liquid boiling at 159° C. at 15 mm. mercury pressure and having a density of 1.6841 at 20° C.

(c) $\alpha\alpha\alpha'\beta\beta\beta'\beta'$ heptachloroethyl sulphide,

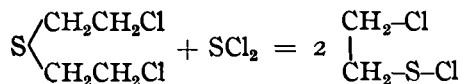


a liquid boiling at 170° to 172° C. at 15 mm. of mercury, with a density of 1.7473 at 20° C.

With Sulphur Chloride. The action of sulphur chloride on dichloroethyl sulphide has been studied by Gibson,¹ Mann and Pope.² It has been shown that the result of the reaction between these two compounds is different according to whether the sulphide reacts with sulphur monochloride or with sulphur dichloride.

Sulphur monochloride reacts very slowly with $\beta\beta'$ dichloroethyl sulphide in absence of catalysts, though in presence of iron the reaction is more lively. The products of the reaction are in each case hydrochloric acid, sulphur and a liquid consisting of trichloro- and tetrachloro-ethyl sulphides.

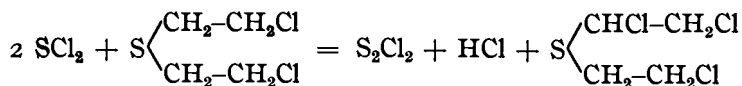
Sulphur dichloride on the contrary reacts vigorously with dichloroethyl sulphide even at 0° C. The reaction may become violent according to the ratio of dichloroethyl sulphide to sulphur dichloride and heat is always developed. The products vary according to the relative quantities of the two reactants. If the dichloroethyl sulphide is in excess, the compound $\text{Cl-S-CH}_2\text{-CH}_2\text{-Cl}$ is formed :



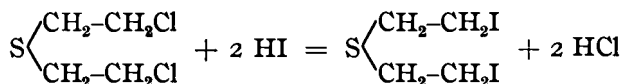
¹ GIBSON and POPE, *J. Chem. Soc.*, 1920, **117**, 271.

² MANN and POPE, *J. Chem. Soc.*, 1922, **121**, 594.

while if the sulphur dichloride is in excess, sulphur monochloride, hydrochloric acid and a trichloro-derivative are formed :

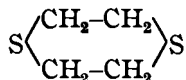


With Hydriodic Acid. By the action of hydriodic acid in aqueous or acetic acid solution on dichloroethyl sulphide, both the chlorine atoms are substituted by iodine atoms and diiodoethyl sulphide is obtained (see p. 244).

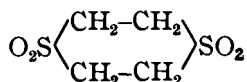


Grignard's method for the detection of dichloroethyl sulphide depends on the reaction with sodium iodide (see p. 248).

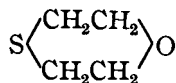
With the Alkali Sulphides. Sodium and potassium sulphides react readily with dichloroethyl sulphide to form diethylene disulphide, also termed "dithiane."



This forms white crystals with a melting point of 112° C., and has no toxic power. It boils at 115.6° C. at 60 mm. mercury pressure,¹ and is volatile in steam. It is sparingly soluble in water, but readily in alcohol and ether. This compound, which was first obtained by Meyer² in 1886, is converted into the corresponding disulphone by treatment with hydrogen peroxide in acetic acid solution³ :



Diethylene disulphide is also obtained, together with *p*-thioxane,



by distilling thiodiglycol with potassium bisulphate.⁴ It is also formed by the action of a saturated solution of hydrobromic acid in phenol on thiodiglycol.⁵

¹ J. JOHNSON, *J. Chem. Soc.*, **1933**, 1530.

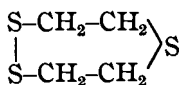
² MEYER, *Ber.*, 1886, **19**, 3259.

³ FROMM and UNGAR, *Ber.*, 1923, **56**, 2286.

⁴ FROMM, *Ber.*, 1923, **56**, 2286.

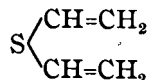
⁵ E. BELL and coll., *J. Chem. Soc.*, **1927**, 1803.

Sodium disulphide in aqueous solution reacts slowly with dichloroethyl sulphide, forming ¹ :



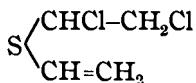
ethylene trisulphide, crystals melting at 74° C.

With Potassium Hydroxide. (a) In Alcoholic Solution. By the action of a 20% solution of potassium hydroxide in alcohol, dichloroethyl sulphide is converted into divinyl sulphide ² :

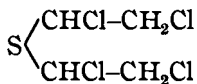


a mobile liquid with a characteristic odour which boils at 85° to 86° C. Its density at 15° C. is 0.9174. It readily polymerises, being transformed in less than a week into an opaque mass, soluble in carbon disulphide.³

Divinyl sulphide is also formed by the abstraction of two molecules of water from one of thiodiglycol.⁴ On treatment with gaseous hydrochloric acid, it forms $\alpha\alpha'$ dichloroethyl sulphide,⁵ a colourless liquid with a penetrating odour, which boils at 58.5° C. at 15 mm. mercury and has a density of 1.1972 at 15° C. On treatment of divinyl sulphide in aqueous solution with hydriodic acid,⁶ $\beta\beta'$ diiodoethyl sulphide is formed (see p. 244). With chlorine various chlorinated compounds are formed, for instance, $\alpha\beta$ dichloroethyl vinyl sulphide :



and $\alpha\beta\alpha'\beta'$ tetrachloroethyl sulphide :



Divinyl sulphide is formed quantitatively according to Helfrich⁷ when dichloroethyl sulphide is treated with sodium ethylate.

¹ FROMM, *Ber.*, 1925, **58**, 304.

² S. H. BALES and A. S. NICKELSON, *J. Chem. Soc.*, 1922, **121**, 2137; 1923, **123**, 2486.

³ L. LEWIN, *J. prakt. Chem.*, 1930, **127**, 77.

⁴ E. FROMM and UNGAR, *Ber.*, 1923, **56**, 2286.

⁵ S. H. BALES and A. S. NICKELSON, *loc. cit.*

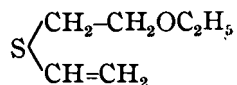
⁶ J. ALEXANDER and MCCOMBIE, *J. Chem. Soc.*, **1931**, 1913.

⁷ HELFRICH and REID, *J. Am. Chem. Soc.*, 1920, **42**, 1219, 1224.

By the action of a 50% solution of potassium hydroxide in alcohol other products besides divinyl sulphide are formed, probably its polymers.

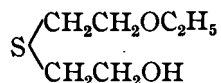
(b) In Aqueous-alcoholic Solution. By the action of a 20% solution of potassium hydroxide in aqueous alcohol on dichloroethyl sulphide, in the proportion of 1 part of the sulphide to 4 parts of potassium hydroxide, the following compounds¹ are formed, besides divinyl sulphide :

Vinyl β ethoxyethyl sulphide,



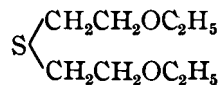
a mobile colourless liquid with a pungent odour resembling that of camphor. It boils at 65° C. at 8 mm. mercury pressure. Its density at 15° C. is 0.9532.

β ethoxy β' hydroxyethyl sulphide



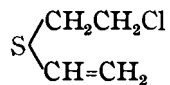
a liquid boiling at 117.5° C. at 4 mm. mercury pressure.

$\beta\beta'$ diethoxy ethyl sulphide



a liquid boiling at 225° C. at 746 mm. mercury, with a density at 20° C. of 0.9672.

By varying the proportions of potassium hydroxide and dichloroethyl sulphide, various other compounds are formed, among them vinyl β chloroethyl sulphide,²



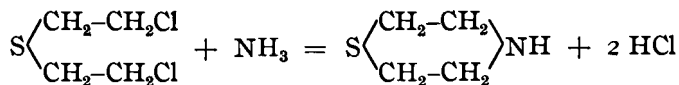
a liquid boiling at 71° to 72° C. at 50 mm. mercury, which absorbs hydrochloric acid to form $\alpha\beta'$ dichloroethyl sulphide.

With Ammonia. Dichloroethyl sulphide reacts only mildly with gaseous ammonia even on heating to 150° C. However,

¹ J. DAVIES and OXFORD, *J. Chem. Soc.*, **1931**, 234.

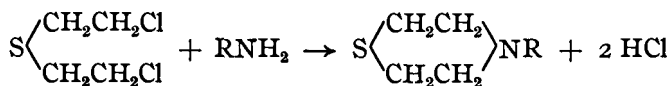
² J. DAVIES and OXFORD, *J. Chem. Soc.*, **1931**, 235.

with alcoholic ammonia on heating to 60° C. under pressure, the reaction is vigorous¹ and 1·4 thiazane is formed as follows :



This is a colourless liquid with an odour of pyridine, boiling at 169° C. at 758 mm. of mercury. It fumes in the air and is miscible with water and with the common organic solvents. On exposure to the air it absorbs carbon dioxide.

With Aliphatic Amines. In presence of sodium carbonate, dichloroethyl sulphide reacts with the aliphatic amines in alcoholic solution as follows² :



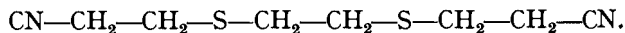
Several compounds of this type have been prepared. They are in general colourless mobile oils with densities less than unity. The following are the principal :

4 *Methyl 1·4 thiazane*, b.p. 163° to 164° C. at 757 mm. Density 0·9959 at 15° C. Completely miscible with water and with various organic solvents.

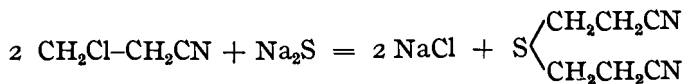
4 *Ethyl 1·4 thiazane*, b.p. 184° C. at 763 mm. Density 0·9929 at 15° C. Soluble in water.

4 *Phenyl 1·4 thiazane*, m.p. 108° to 111° C. A white powder, soluble in hot toluene.

With Potassium Cyanide. By the action of potassium cyanide on dichloroethyl sulphide dissolved in alcohol, dicyanoethyl sulphide is not formed, but a crystalline substance separates (m.p. 91° C.) of the formula $\text{C}_6\text{H}_{12}\text{S}_2(\text{CN})_2$ which, later researches³ have shown, has the structure



Dicyanoethyl sulphide has been obtained, however, by boiling sodium sulphide with the nitrile of β chloropropionic acid, dissolved in alcohol :



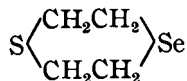
¹ W. DAVIES, *J. Chem. Soc.*, 1920, **117**, 299; CLARKE, *J. Chem. Soc.*, 1912, **101**, 1585.

² LAWSON and REID, *J. Am. Chem. Soc.*, 1925, **47**, 2821; CLARKE, *loc. cit.*

³ CLARKE, *loc. cit.*; DAVIES, *loc. cit.*

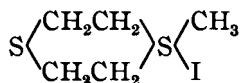
It forms crystals, melting at 24° to 25° C., which have no vesicatory properties.¹

With Sodium Selenide. By boiling dichloroethyl sulphide with an aqueous solution of sodium selenide, 1·4 selenothiane is formed²:



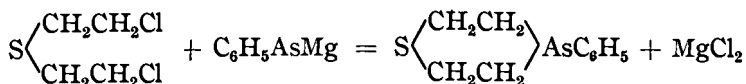
This is obtained in thin colourless leaflets, melting at 107° C. It boils at a pressure of 97 mm. of mercury at 86·5° C., and behaves chemically in a similar manner to dithiane.

With Methyl Iodide. Dichloroethyl sulphide reacts with methyl or benzyl iodide, forming the corresponding sulphonium salt. For instance, with methyl iodide, dithiane methiodide is formed:



This is a crystalline substance melting at 174° C., easily soluble in hot water, soluble with difficulty in alcohol and insoluble in ether.³

With Magnesium Phenylarsine. By treating dichloroethyl sulphide in hot benzene solution with magnesium phenylarsine in ethereal solution, phenyl thioarsane is formed⁴:



as crystals with m.p. 38° C. It boils at 134° C. at a pressure of 4 mm. of mercury. It forms additive compounds with mercuric chloride.

Like the other cyclic sulphides, it has no vesicant action and only a weak toxicity.

With Zinc and Ethyl Alcohol. When an alcoholic solution of dichloroethyl sulphide is treated on the water-bath with zinc dust, a very complex reaction takes place and various compounds are formed: ethylene, hydrogen sulphide, hydrochloric acid,

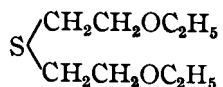
¹ NEKRASSOV, *J. Rusk. Fis. Khim. Obsc.*, 1927, **59**, 921.

² C. S. GIBSON and J. JOHNSON, *J. Chem. Soc.*, **1933**, 1529.

³ C. NENITZESCU and SCARLATESCU, *Ber.*, 1934, **67**, 1142.

⁴ JOBB and coll., *Bull. soc. chim.*, 1924, **35**, 1404.

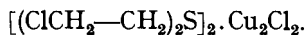
dithiane, ethyl sulphide, vinyl ethyl sulphide, ethyl mercaptan, etc. The principal product is diethyl thioglycol¹ :



This is a liquid boiling at 225° C. at a pressure of 746 mm. Density 0.9672 at 20° C. It is volatile in steam, sparingly soluble in water, but soluble in the organic solvents. It has no vesicant power.

Various other condensation products of dichloroethyl sulphide have been prepared, such as those with phenates, thiophenates, mercaptides and aromatic amines, and in every case the physical, chemical and biological properties of these have been studied.²

With Metallic Salts. Like various other organic sulphides, dichloroethyl sulphide readily reacts with the salts of the heavy metals. Thus with gold or platinum chloride, compounds are formed which, being insoluble in water, may be employed for the detection of the sulphide (see p. 248). With copper or mercury chloride stable additive chlorides are formed of the following type :



These may be employed to determine dichloroethyl sulphide quantitatively (see p. 251). Tin and titanium chlorides similarly form additive products.³

Ferric chloride decomposes dichloroethyl sulphide, forming various halogenated vinyl compounds.⁴

With Metals. At ordinary temperatures the action of pure dichloroethyl sulphide on steel, iron, lead, aluminium, zinc and tin is practically nil. At higher temperatures, about 100° C., steel is slightly corroded, but aluminium and lead are not attacked (Gibson and Pope).

On warming in contact with iron, especially in presence of water, dichloroethyl sulphide is decomposed to form thiodiglycol, hydrogen sulphide, diethylene sulphide and its polymers, hydrochloric acid, hydrogen, ethylene and ethylene dichloride.

The action of crude dichloroethyl sulphide on the steel walls of projectiles has been studied by W. Felsing and H. Odeen.⁵ They have observed that in projectiles charged with dichloroethyl

¹ KRETOV, *J. Rusk. Fis. Khim. Obsc.*, 1929, **61**, 2345.

² HELFRICH and REID, *J. Am. Chem. Soc.*, 1920, **42**, 1208, 1232; FROMM and JÖRG, *Ber.*, 1925, **58**, 305.

³ JACKSON, *Chem. Reviews*, 1934, 443.

⁴ GRIGNARD, *Ann. chim.*, 1921, [9] **15**, 5.

⁵ W. FELSING and H. ODEEN, *J. Ind. Eng. Chem.*, 1920, **12**, 1063.

sulphide (prepared by Levinstein's method, see p. 223) the internal pressure increased on maintaining at 60° C. for 8 days to about 2 atmospheres. The degree of decomposition of the sulphide was negligible, and the increase in acidity amounted to about 1%.

The outstanding physiopathological property of dichloroethyl sulphide is its vesicant action. The first symptoms of this action appear after 4-6 hours, but sometimes the latent period may extend to 24 hours.

The sensitivity of the skin to dichloroethyl sulphide varies with the individual. Fair people are more sensitive than dark and the latter more sensitive than negroes.¹

Exposure even for a short time (a few minutes) to a concentration of 0.2 mgm. of the vapours of dichloroethyl sulphide per cu. m. of air causes irritation, according to Gilchrist,² without, however, visible lesions.

On contact of liquid dichloroethyl sulphide with the skin, erythema is produced with 0.12 mgm. per sq. cm. of skin and blisters with 0.5 mgm. per sq. cm. of skin.

On inhalation, according to American experiments,³ fatal results follow exposure of 10 minutes to a concentration of 150 mgm. per cu. m. of air, or exposure of 30 minutes to a concentration of 70 mgm. per cu. m. of air.

Mortality-product: 1,500 according to both Müller and Prentiss.

For the decontamination of the skin, washing with hot soapy water is very efficacious.⁴

For the decontamination of objects, Renwanz⁵ recommends the use of bleaching powder (see p. 231).

For the decontamination of glass materials, concentrated nitric acid may be employed.⁶ This must be carried out with care because in the somewhat violent reaction liquid may be thrown out by the violent evolution of nitrous gases.

The decontamination of paper, print, documents, etc., may be carried out by exposing such objects to the action of gaseous ammonia in closed containers for several days.⁷

¹ G. FERRI, " Ricerche sulla sensibilità individuale della cute umana all'iprite e sopra alcuni fattori capaci di modificarla " (" Researches on individual sensitivity of the human skin to mustard gas and on some factors which can modify this "), *Giornale di Medicina Militare*, September, 1937.

² GILCHRIST, *The Residual Effects of Warfare Gases*, II, U.S. Government Printing Office, Washington, 1933.

³ PRENTISS, *op. cit.*

⁴ S. PRZYCHOCKI, *Heeressanitätswesen*, 1934, 23, 5, 6, Warsaw; *Gasschutz und Luftschutz*, 1936, 28.

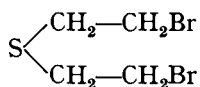
⁵ G. RENWANZ, *Die Gasmaske*, 1935, 1.

⁶ WEIDNER, *Gasschutz und Luftschutz*, 1936, 133.

⁷ ZERNIK, *Archiv. Zeitschr.*, 1936, 44, 185.

2. Dibromoethyl Sulphide

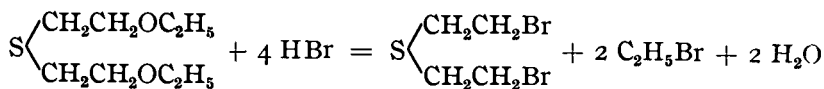
(M.Wt. 247·8)



$\beta\beta'$ dibromoethyl sulphide was examined as a possible war gas only in the post-war period (Müller). Although having similar physiopathological properties to dichloroethyl sulphide, it has some disadvantages as a war gas, especially from the manufacturing point of view (Hanslian).

Steinkopf¹ prepared dibromoethyl sulphide by the action of phosphorus tribromide on thiodiglycol. However, it may be prepared more simply by saturating an aqueous solution of thiodiglycol with hydrobromic acid.²

It may also be prepared, according to Kretov,³ by the action of hydrobromic acid or phosphorus tribromide on diethoxyethyl sulphide (see p. 238).

LABORATORY PREPARATION²

976 gm. thiodiglycol are dissolved in 400 ml. water in a flask fitted with a reflux condenser and a gas inlet-tube. It is cooled in ice and saturated with hydrobromic acid. The mixture is then heated to about 80° C. and more hydrobromic acid bubbled in until the reaction is complete. On cooling, the dibromoethyl sulphide solidifies, separating at the bottom of the flask. The aqueous layer is decanted off and the solid product washed with cold water and crystallised from ether. Yield 95%.

PHYSICAL AND CHEMICAL PROPERTIES

Dibromoethyl sulphide forms white crystals which melt at 31° to 34° C. (Steinkopf). It boils at ordinary pressure at 240° C. with decomposition and at 1 mm. pressure at 115·5° C.

The specific gravity at 15° C. is 2·05. It is insoluble in water and soluble in alcohol, ether and benzene.

The volatility at 20° C. is about 400 mgm. per cu. m. It is more rapidly decomposed by water than dichloroethyl sulphide.⁴

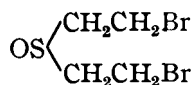
¹ STEINKOPF, *Ber.*, 1920, **53**, 1011.

² BURROWS and REID, *J. Am. Chem. Soc.*, 1934, **56**, 1720, 1722.

³ KRETOV, *J. Rusk. Fis. Khim. Obsc.*, 1929, **61**, 2345.

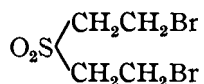
⁴ RONA, *Z. ges. expt. Med.*, 1921, **13**, 16; MÜLLER, *Die Chemische Waffe*, Berlin, 1932, 84, 111.

On treating a hot solution of dibromoethyl sulphide in chloroform with benzoyl hydrogen peroxide, dibromoethyl sulphoxide is formed :



This forms glittering crystals melting at 100° to 101° C.¹ It may also be obtained by the action of concentrated nitric acid on dibromoethyl sulphide by first maintaining the temperature at 0° C. and then allowing it to rise to room temperature to complete the reaction.²

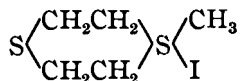
Chromic anhydride and dilute sulphuric acid react at water-bath temperature with dibromoethyl sulphide to produce dibromoethyl sulphone² :



which forms plates melting at 111° to 112° C.

Dibromoethyl sulphide, like the dichloro-compound, easily reacts with primary amines, forming the corresponding thiazane derivatives (Burrows).

It reacts with methyl iodide more readily than dichloroethyl sulphide, forming dithiane methiodide³ :

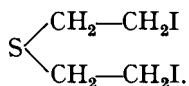


The persistence of dibromoethyl sulphide on the ground is greater than that of dichloroethyl sulphide only in dry weather.

The physiopathological properties are similar to those of dichloroethyl sulphide according to Meyer,⁴ but milder.

3. Diiodoethyl Sulphide

(M.Wt. 341.8)



$\beta\beta'$ diiodoethyl sulphide was not used as a war gas during the war of 1914-18, in spite of its great toxic power. It was obtained

¹ LEWIN, *J. prakt. Chem.*, 1930, **127**, 77.

² BURROWS and REID, *J. Am. Chem. Soc.*, 1934, **56**, 1720.

³ NENITZESCU and SCARLATESCU, *Ber.*, 1934, **67**, 1142.

⁴ A. MAYER, *Compt. rend.*, 1920, **170**, 1073.

by Helfrich¹ in 1920 by treating dichloroethyl sulphide with sodium iodide in alcoholic solution.

It is produced in the reaction between dichloroethyl sulphide and the Grignard reagent (see p. 248), and also, together with dithiane methiodide, by the action of methyl iodide on dichloroethyl or dibromoethyl sulphide.² It has also been obtained by the action of hydriodic acid on an aqueous solution of divinyl sulphide.³

PREPARATION

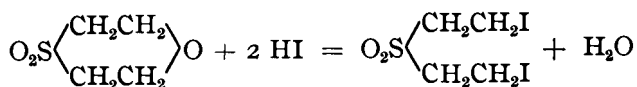
Diiodoethyl sulphide is prepared according to Grignard by treating dichloroethyl sulphide with sodium iodide in acetic acid solution and heating to 60° C. On pouring the product into water, a crystalline product is obtained and this is then purified by recrystallisation.

PHYSICAL AND CHEMICAL PROPERTIES

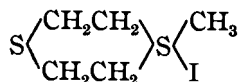
Diiodoethyl sulphide forms bright yellow prisms melting at 62° C. according to Grignard,⁴ and at 68° to 70° C. according to Kretov.⁵

It decomposes in time, especially if exposed to light, or on heating even to 100° C.

It is insoluble in water and soluble in the common organic solvents. On treatment with alkali it is readily hydrolysed. With oxidising agents it is converted into diiodoethyl sulphoxide (white crystals, melting at 104.5° C.) or into diiodoethyl sulphone (small white needles, m.p. 203° C.) This latter compound has also been prepared by the action of hydriodic acid on thioxane sulphone⁶:



Diiodoethyl sulphide reacts with methyl iodide more readily than the dichloro- compound to form dithiane methiodide⁷:



¹ HELFRICH and REID, *J. Am. Chem. Soc.*, 1920, **42**, 1208, 1232.

² NENITZESCU and SCARLATESCU, *Ber.*, 1934, **67**, 1142.

³ J. ALEXANDER and McCOMBIE, *J. Chem. Soc.*, **1931**, 1913.

⁴ GRIGNARD and RIVAT, *Ann. chim.*, 1921, **15**, 5.

⁵ KRETOV, *J. Rusk. Fis. Khim. Obsc.*, 1929, **61**, 2345.

⁶ FROMM and UNGAR, *Ber.*, 1923, **56**, 2287.

⁷ J. ALEXANDER and McCOMBIE, *loc. cit.*

Diiodoethyl sulphide has a vesicant action on the skin similar to that of dichloroethyl sulphide (Helfrich).

Analysis of the Sulphides

DETECTION OF DICHLOROETHYL SULPHIDE

The following reagents have been proposed for the detection of dichloroethyl sulphide¹:

Potassium Permanganate. A 0.003% solution of potassium permanganate, acidified with a few drops of sulphuric acid, is decolourised by air containing dichloroethyl sulphide vapour. The minimum quantity of the sulphide producing a distinct colour-change is about 0.15 mgm., according to Spica.²

β Naphthol. On passing dichloroethyl sulphide vapours through an alcoholic and strongly alkaline solution of β naphthol, a turbidity is produced which slowly settles. The β naphthol solution is prepared by adding 100 ml. N/50 sodium hydroxide solution to 1 ml. of a 10% alcoholic solution of β naphthol. As this mixture turns brown on keeping, the two solutions should not be mixed until just before using.

In order to detect very low concentrations of dichloroethyl sulphide it is necessary to pass the gas for 10–15 minutes. With this reagent as little as 0.06 mgm. dichloroethyl sulphide may be recognised.

Congo Red Paper. Detection by means of this paper depends on the formation of hydrochloric acid by the decomposition of dichloroethyl sulphide with sulphuric acid. The gas to be examined is passed through a wash-bottle containing concentrated sulphuric acid at 55° C., and then over the Congo red test-paper.

Sodium Iodoplatinate Paper. This test-paper changes from its original pink colour to violet by the action of dichloroethyl sulphide, the intensity of the violet varying with the concentration of dichloroethyl sulphide. The papers are prepared by immersing strips of filter paper in an aqueous 0.2% solution of sodium iodoplatinate just before use. To test for the presence of dichloroethyl sulphide, the treated paper is exposed in a damp condition to the gas to be examined. Sensitivity 0.02 mgm. (Spica).

Potassium Mercuri-iodide. On passing air containing dichloroethyl sulphide vapour through an aqueous solution of potassium mercuri-iodide a whitish-yellow precipitate separates. If the

¹ SCHRÖTER, *Z. angew. Chem.*, 1936, 164, gives a résumé of the methods proposed for the detection of dichloroethyl sulphide.

² SPICA, *Gazz. chim. ital.*, 1919, 49, 299.

quantity of dichloroethyl sulphide is very small the reaction may be aided by warming to 40° to 50° C. The limit of sensitivity is 0.03 mgm.

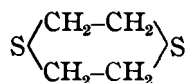
The reagent is prepared by dissolving 10 gm. potassium iodide in 70 ml. water and adding 14 gm. mercuric iodide.

This reaction is given by the alkaloids, as well as by dichloroethyl sulphide.

A method for the quantitative determination of dichloroethyl sulphide has also been based on this reaction.¹

Hydrogen Peroxide. When air containing dichloroethyl sulphide is passed through a solution containing 30% by volume of hydrogen peroxide in acetic acid, colourless acicular crystals are formed, first in the air-inlet tube and then in the liquid.

Sodium Monosulphide. On passing air containing dichloroethyl sulphide through a concentrated solution of sodium monosulphide, a white turbidity is produced, due to the formation of diethylene disulphide of the following structure (see p. 236) :



In carrying out this test in practice, Spica² recommends that the air under examination be passed through a U-tube of 4-5 mm. diameter, having a small bulb at the bend in which a few drops of the reagent are placed. In passing over the reagent, the air produces the characteristic turbidity.

Data of the sensitivity of the last two reagents are not known. None of the reagents described above is adapted for the detection of dichloroethyl sulphide in its war-gas application, either because of low sensitivity or because of similar reactions with other substances.

During the war of 1914-18 the following reagents were employed :

*Yablich's Reagent.*³ This reagent was suggested by the Chemical Warfare Service and was especially employed by the Americans. It is based on the fact that when air containing dichloroethyl sulphide is passed through a solution of selenious acid in dilute sulphuric acid and then the reagent is heated for about 10 minutes at 85° C., a yellow precipitate of metallic selenium is produced (see p. 233). If the amount of dichloroethyl sulphide present is small, a reddish-orange suspension appears. The reagent is

¹ L. BURUIANA, *Z. anal. Chem.*, 1937, **109**, 107.

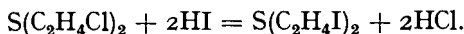
² SPICA, *Gazz. chim. ital.*, 1919, **49**, 299.

³ M. YABLICH, *J. Am. Chem. Soc.*, 1920, **42**, 266.

prepared by dissolving 1 gm. SeO_2 in 100 ml. of a solution containing equal parts by weight of sulphuric acid and water. Although many war gases give a negative reaction with this reagent, all the arsine derivatives give as positive a result as does dichloroethyl sulphide. A similar reaction is also given by carbon monoxide and hydrogen sulphide.

Sensitivity: 5 mgm. dichloroethyl sulphide per cu. m. of air.¹

*Grignard's Reagent.*² This reagent, which is fairly specific for dichloroethyl sulphide, was proposed by Grignard in 1918, but was kept secret until 1921. Detection is based on a double decomposition reaction of a type fairly frequent in organic chemistry:



The dichloroethyl sulphide is converted to diiodoethyl sulphide which separates as yellow crystals.

Grignard's contribution was to define the conditions which made the test highly sensitive and capable of being carried out rapidly without employing heat.

Preparation of the reagent:

Sodium iodide	20 gm.
7.5% copper sulphate solution.	40 drops
35% gum arabic solution	2 ml.
Water	200 ml.

The copper sulphate is added in order to catalyse the reaction, while the gum arabic causes the diiodoethyl sulphide to separate in the colloidal form instead of crystalline.

For the detection of dichloroethyl sulphide, the air under examination is passed through the reagent prepared as described above. In the presence of dichloroethyl sulphide a yellow precipitate of diiodoethyl sulphide separates. According to Grignard, 100 mgm. dichloroethyl sulphide may be detected in 1 cu. m. of air in 4 minutes.

It has been found that while the aliphatic arsines and phenyl carbylamine chloride produce a similar turbidity at high concentration (4%), other substances such as mono-, di- and trichloromethyl chloroformates, chloropicrin, benzyl bromide, acrolein, the aromatic arsines, thiodiglycol, etc., do not react.

Recently the following method has been elaborated:

Schröter's Method. This is based on the property of dichloroethyl sulphide of forming additive-compounds with gold and palladium chlorides (see p. 241).

¹ FLURY and ZERNIK, *Schädliche Gase*, Berlin, 1931, 367.

² V. GRIGNARD, RIVAT, and SCHATCHARD, *Ann. chim.*, 1921, 15, 5.

On treating an aqueous solution containing 0.1% gold chloride or 0.05% palladium chloride with dichloroethyl sulphide a turbidity of colloidal type quickly forms, and if the quantity of the sulphide is large, yellowish-red oily droplets are produced.

This reaction may also be carried out on filter paper. In this case a reddish-brown stain is formed with a 10% gold chloride solution and a yellow stain with a 0.2% palladium chloride solution.

According to Obermiller,¹ these reactions are specific for dichloroethyl sulphide and are not influenced by the presence of any other war gas, nor by the hydrolysis products of dichloroethyl sulphide.

The sensitivity with gold chloride is of the order of 10 mgm. dichloroethyl sulphide per cu. m. of air.

An apparatus has been designed for detecting the presence of dichloroethyl sulphide in a sample of air by this reaction.² The air is drawn by means of a small pump through a glass tube containing silica-gel, to which are added, after a certain number of strokes of the pump, several drops of gold chloride solution. A little more air is drawn through the tube and then a few drops of hydrogen peroxide are added.

In the presence of dichloroethyl sulphide a yellow ring forms.

Sensitivity : 12 mgm. of the sulphide per cu. m. of air.³

QUANTITATIVE DETERMINATION OF DICHLOROETHYL SULPHIDE IN AIR

*Nephelometric Method of Yablich.*⁴ This method depends on the reduction to metallic selenium, in the form of an orange-yellow suspension, of selenious acid when it reacts with dichloroethyl sulphide, and on the nephelometric measurement of the suspension formed.

The selenious acid employed in this method of analysis is prepared by dissolving 1 gm. SeO_2 in 100 ml. of an aqueous solution of sulphuric acid (1 : 1 by weight).

In practice the determination is carried out by bubbling the mixture of air and dichloroethyl sulphide through the reagent and then heating to 85° C. for 10 minutes. The solution is then allowed to cool and the quantity of gas present obtained by nephelometric comparison with a standard solution.

¹ OBERMILLER, *Z. angew. Chem.*, 1936, **49**, 162.

² SCHRÖTER, *Z. angew. Chem.*, 1936, **49**, 164.

³ STAMPE, *Dräger-Hefte*, 1935, No. **180**, 2966.

⁴ YABLICH and coll., *J. Am. Chem. Soc.*, 1920, **42**, 266, 274.

By this method quantities of dichloroethyl sulphide may be determined of the order of 0.1–0.001 mgm. with a maximum error of 0.005 mgm.

The Potentiometric Method of Hopkins. Another method of determining small quantities of dichloroethyl sulphide in air has been proposed by Hopkins.¹ It consists in hydrolysing the dichloroethyl sulphide with water at 35° C. and determining the hydrogen ion concentration of the solution obtained by a potentiometric method.

In carrying out this determination it is recommended that the gas should be bubbled through two tubes in series containing water at 35° C. In this way the dichloroethyl sulphide is hydrolysed rapidly and by measuring the hydrogen ion concentration of the solution (methyl red indicator) the quantity of dichloroethyl sulphide may be obtained.

Maxim's Method. This is based on the oxidation of the sulphur atom in dichloroethyl sulphide and its determination as barium sulphate.²

It is carried out by passing the gas containing dichloroethyl sulphide first through an ordinary combustion tube (whose length is chosen according to the quantity of gas to be examined), filled with fragments of pumice and heated to redness, and then through a wash-bottle containing a 20% solution of barium chloride and 10–20 ml. hydrogen peroxide. The dichloroethyl sulphide on passing through the combustion tube is converted into sulphur dioxide and this is oxidised to sulphuric acid and precipitated as barium sulphate.

QUANTITATIVE DETERMINATION OF DICHLOROETHYL SULPHIDE IN INDUSTRIAL PRODUCTS

The method commonly used up to the present to determine the dichloroethyl sulphide content of industrial products consists in distilling a certain quantity of the sample to be examined at reduced pressure (40 mm.) and collecting the fraction boiling between 125° and 130° C. From the volume of this fraction the purity of the product may be estimated approximately.

Two other methods which have been proposed are described below.

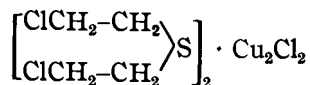
*Hollely's Method.*³ This method is based on the reaction

¹ HOPKINS, *J. Pharmacol.*, 1919, **12**, 393, 403.

² M. MAXIM, *Chem. Zeit.*, 1932, **56**, 503; REDLINGER, *Chem. Zeit.*, 1932, **56**,

³ W. HOLLELY, *J. Chem. Soc.*, 1920, **117**, 898.

between dichloroethyl sulphide and cuprous chloride, forming a double salt of definite composition :



Description of the Method : About 1 gm. of the sample is weighed accurately into a 100 ml. flask with a tight stopper. 10 ml. of a solution of cuprous chloride in absolute alcohol containing hydrochloric acid¹ are added and the mixture continually agitated, without heating, for 10 minutes so as to ensure complete solution of the dichloroethyl sulphide. At the end of this time, the mixture is cooled with water and still agitated while 50 ml. of a 5% aqueous solution of sodium chloride are added from a burette. A precipitate of the double salt separates as fine colourless needles. After allowing to stand for a short time, the solution is filtered through glass wool, the filtrate being collected in a dry receiver. The excess cuprous chloride in the filtered liquid is then estimated in the following manner :

30 ml. of the filtrate are measured into a 250 ml. flask by means of a burette and 5 ml. 20 volume hydrogen peroxide are added to oxidise the copper to the divalent condition.

The contents of the flask are then boiled, being taken almost to dryness and taken up with water several times (generally twice) so as to remove the hydrogen peroxide completely. The residue is diluted once more with 50 ml. water and a solution of sodium carbonate added until a slight precipitate is formed, this being then redissolved with a few drops of dilute acetic acid. Excess potassium iodide is added and the liberated iodine is titrated with a decinormal solution of sodium thiosulphate.

At the same time the alcoholic cuprous chloride solution is also titrated with the same thiosulphate solution, after first oxidising the cuprous chloride with 5-10 ml. hydrogen peroxide and following the procedure described.

From the results of this determination, the percentage of dichloroethyl sulphide present in the original sample may be obtained by the following calculation :

From the formula of the double salt, it follows that 127 gm. copper correspond to 318 gm. dichloroethyl sulphide, and as 1 ml. N/10 thiosulphate is equivalent to 0.00635 gm. copper,

¹ The solution of cuprous chloride must be prepared freshly immediately before use, and it is therefore advisable to have a 10% solution of hydrochloric acid in absolute alcohol available, and to dissolve 5 gm. of cuprous chloride in 50 ml. of this immediately before use.

1 ml. thiosulphate must correspond to 0.0159 gm. dichloroethyl sulphide.

Therefore the percentage will be given by the formula :

$$\% \text{ dichloroethyl sulphide} = \frac{(A - B) \times 0.0159 \times 100}{\text{weight of sample}}$$

in which

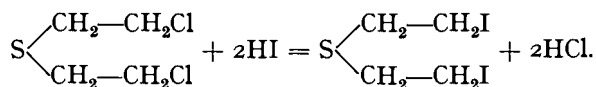
A = ml. N/10 thiosulphate equivalent to the copper in 10 ml. of the solution tested as a blank.

B = ml. N/10 thiosulphate equivalent to the excess copper in 10 ml. of the solution after reaction with dichloroethyl sulphide.

The volume resulting from the admixture of 10 ml. cuprous chloride solution with 50 ml. 5% sodium chloride solution has been experimentally found to be 59.5 ml. instead of 60 ml.

This method of determining dichloroethyl sulphide does not give exact results when thiodiglycol and chlorinated derivatives of dichloroethyl sulphide are present in the sample (Jackson).

*The Method of Grignard, Rivat and Schatchard.*¹ This method is based on the conversion of dichloroethyl sulphide to diiodoethyl sulphide by means of hydriodic acid in acetic acid solution :



and on the determination of the quantity of hydriodic acid which has not reacted.

Description of the Method : (1) The total iodine present in the hydriodic acid to be employed is first determined. 15 ml. glacial acetic acid are placed in a flask, and 5 ml. of a solution containing about 54% hydriodic acid added from a burette. A tube to serve as air condenser is fitted to the flask ; its upper end should be drawn out and bent over to prevent dust entering. The mixed acids are then warmed on the water-bath for 15 minutes to 70° C. After cooling and diluting to 50 ml., 10 ml. of 10% sodium nitrite solution are added to liberate the iodine.

The iodine is extracted with carbon tetrachloride (once with 20 ml. and four times with 10 ml.) and all the extracts are added to 100 ml. distilled water. The mixture is shaken to wash the tetrachloride, the water separated and shaken with a little carbon tetrachloride which is then added to the main bulk of the tetrachloride. The solution of iodine is finally titrated with thiosulphate and starch solution.

Let A_0 be the number of ml. of thiosulphate used.

(2) The procedure described under (1) is followed, about 1 gm.

¹ Grignard and coll., *Ann. chim.*, 1921, 15, 5, 18.

of dichloroethyl sulphide (weighed accurately = P gm.) being added to the acetic acid solution. After heating and subsequently cooling, the contents of the flask (crystals and liquid) are poured into a tared 500 ml. graduated flask containing 100 ml. carbon tetrachloride and 200 ml. water.

The flask is shaken to dissolve the diiodoethyl sulphide, the contents diluted to volume and shaken again to homogenise the solution. After allowing to stand so that the two liquids separate, 50 ml. of the aqueous layer are taken, the iodine liberated with sodium nitrite and titrated as in (I).

Let A_1 be the number of ml. of thiosulphate used.

The 100 ml. of carbon tetrachloride are decanted from the flask, the latter washed with a little carbon tetrachloride which is then added to the main bulk of tetrachloride and the free iodine in the whole titrated.

Let A_2 be the number of ml. of thiosulphate used.

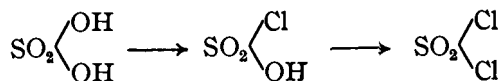
Then the percentage of dichloroethyl sulphide is given by the formula :

$$\% \text{ dichloroethyl sulphide} = \frac{0.82}{P} [10A_0 + 1.5 - (8A_1 + A_2)]$$

There are no indications in the literature of the repeatability or accuracy of the results obtained by this method.

(C) CHLOROANHYDRIDES AND ESTERS OF SULPHURIC ACID

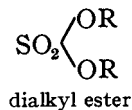
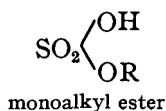
Being dibasic, sulphuric acid can form two chloroanhydrides, chlorosulphonic acid and sulphuryl chloride.



While chlorosulphonic acid may be considered as the acid chloroanhydride of sulphuric acid, sulphuryl chloride is the true chloroanhydride. The chlorine atom in these compounds, as in all the chloroanhydrides, has little stability; it is readily split off by water. However, while chlorosulphonic acid reacts with water with great readiness, sulphuryl chloride reacts very slowly.

Chlorosulphonic acid has little toxicity and has been chiefly employed in warfare as a smoke producer. Sulphuryl chloride was used particularly in admixture with other war gases (cyanogen chloride, chloropicrin, etc.).

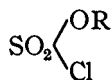
Sulphuric acid forms two types of esters like the two types of chloroanhydrides :



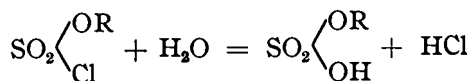
Of these esters, methyl sulphuric acid and dimethyl sulphate were employed as war gases. They have great toxic power and act on the respiratory passages and on the skin.

These esters are insoluble in water though they are decomposed on contact with water to split off the alkyl group, especially dimethyl sulphate. This same scission also takes place in presence of other substances containing the hydroxyl group. It is for this reason that dimethyl sulphate is widely employed both in the laboratory and in industry as a methylating agent.

Furthermore, beside the chloroanhydrides and the esters already mentioned, sulphuric acid can form compounds of mixed type, of the general formula :



These compounds, which may be considered as chloroanhydrides of alkylsulphuric acids, have little stability. They are readily decomposed by cold water or by the action of the alkali hydroxides with splitting off of the halogen and formation of the alkyl sulphuric acids :

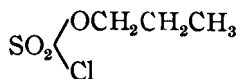


It is interesting to consider the behaviour of these substances to the hydrolysing action of water, mentioned above. While the ethers readily split off the alkyl group, the chloroanhydrides of the alkyl sulphuric acids contain an alkyl which is not easily removed. It seems that in the latter compound the chlorine atom hinders the hydrolytic process.

In the war of 1914-18 methyl chlorosulphonate and ethyl chlorosulphonate were employed as war gases. Owing to the presence of halogen in their molecules, these substances have a powerful lachrymatory action, but their toxicity is less than that of the sulphates.

Since the war several other homologues of methyl chlorosulphonate have been prepared and studied,¹ for instance :

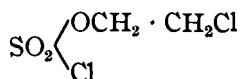
Propyl Chlorosulphonate



which is obtained by the action of sulphuryl chloride on *n*-propyl alcohol. It boils at 70° to 72° C. at a pressure of 20 mm.

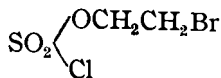
Also halogenated derivatives of ethyl chlorosulphonate :

Chloroethyl Chlorosulphonate



obtained by the action of sulphuryl chloride on glycol chlorohydrin, boils at 101° C. at 23 mm. pressure and has an odour similar to that of chloropicrin.

Bromoethyl Chlorosulphonate



obtained by the action of sulphuryl chloride on glycol bromohydrin, boils at 100° to 105° C. at 18 mm. pressure.

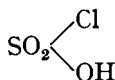
These three compounds are powerful lachrymators.

Several analogous compounds have also been prepared, such as *methyl fluorosulphonate* and *ethyl fluorosulphonate*. These are liquids with ethereal odours, having both lachrymatory and toxic properties. The ethyl derivative has greater lachrymatory power than the methyl.²

Further, a chlorinated derivative of dimethyl sulphate has been prepared, *dichloromethyl sulphate* (see p. 257). This is a colourless liquid boiling at 96° to 97° C. at 14 mm. of mercury. Unlike dimethyl sulphate, this compound is completely destitute of toxic power.³

1. Chlorosulphonic Acid

(M.Wt. 116.53)



Chlorosulphonic acid was used as a war gas in small quantities in the war of 1914-18 by the French and also by the Germans, but

¹ W. STEINKOPF and coll., *Ber.*, 1920, **53**, 1144; R. LEVAILLANT, *Compt. rend.*, 1928, **187**, 730.

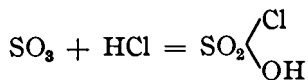
² J. MEYER and G. SCHRAMM, *Z. anorg. Chem.*, 1932, **206**, 27.

³ FUCHS and KATSCHER, *Ber.*, 1927, **60**, 2293.

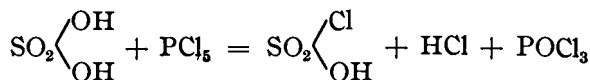
its principal use was as a smoke producer. The French employed it with dimethyl sulphate in the mixture "*Rationite*."

PREPARATION

Chlorosulphonic acid is formed by the simple addition of hydrochloric acid to sulphur trioxide :



The usual method of preparation of chloroanhydrides may also be employed :



In the laboratory, chlorosulphonic acid is usually prepared by the method of Beckurts and Otto.¹

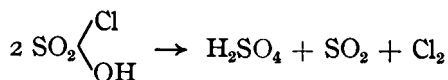
200 gm. oleum (containing 38–40% free SO₃) is placed in a tubulured retort of about 300 ml. capacity, which is connected to a condenser. By means of a glass tube passing through the stopper to the bottom of the retort, a current of dry hydrochloric acid is bubbled in. When absorption of the hydrochloric acid ceases, the chlorosulphonic acid formed is distilled. The distillate is generally slightly coloured ; it may be purified by a further distillation. The yield is almost theoretical.

Industrially, chlorosulphonic acid is prepared by a similar method, that is, by bubbling a current of dry gaseous hydrochloric acid through a solution of sulphur trioxide in sulphuric acid to saturation and separating the chlorosulphonic acid by distillation. Or more simply, it may be prepared by the direct reaction between hydrochloric acid and sulphur trioxide.

During the war large quantities were obtained as a by-product in the preparation of phosgene from carbon tetrachloride and oleum (see p. 61).

PHYSICAL AND CHEMICAL PROPERTIES

It is a colourless liquid which boils at 153° to 156° C. with partial decomposition. On heating to 158° C., however, it decomposes into sulphuric acid, chlorine and sulphur dioxide :

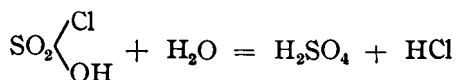


¹ BECKURTS and OTTO, *Ber.*, 1878, **11**, 2058.

It has a specific gravity of 1.776 at 18° C. On cooling strongly it solidifies to a mass melting at - 81° C.

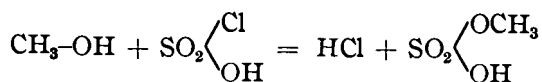
Its heat of formation from sulphur trioxide and hydrochloric acid is 14,400 calories, its heat of solution in water is 40,300 calories, and its heat of volatilisation is 12,800 calories per gm. molecule. It has a vapour density of 4.0.

It fumes in contact with air, forming sulphuric acid and hydrochloric acid :

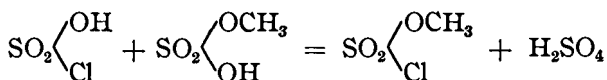


When hydrogen sulphide acts on chlorosulphonic acid, even in the cold, sulphur is formed and hydrochloric acid evolved.

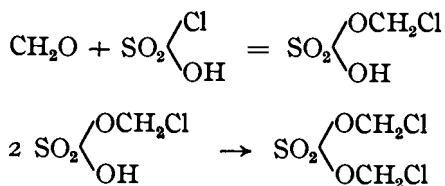
By the action of chlorosulphonic acid on methyl alcohol at - 5° C., methyl sulphuric acid is formed (see p. 261),



and this by the action of a further molecule of chlorosulphonic acid is converted into methyl chlorosulphonate ¹ (see p. 266).



On heating formaldehyde to about 70° C. with chlorosulphonic acid, dichloromethyl sulphate and also dichloromethyl ether are formed ² :

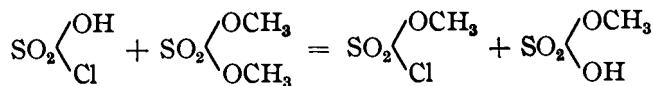


Dichloromethyl sulphate is a colourless liquid, with b.p. 96° to 97° C. at 14 mm. mercury pressure and S.G. 1.60 at room temperature. It is readily soluble in the common organic solvents, though sparingly soluble in petroleum ether. Unlike dimethyl sulphate it has no toxic power (see p. 266).

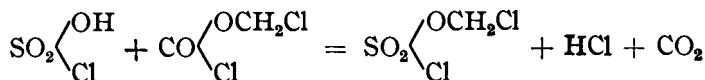
¹ R. LEVAILLANT and L. SIMON, *Compt. rend.*, 1919, **169**, 140.

² FUCHS and KATSCHER, *Ber.*, 1927, **60**, 2292.

Chlorosulphonic acid also reacts with dimethyl sulphate to form methyl chlorosulphonate ¹ :



It reacts with monochloromethyl chloroformate, forming monochloromethyl chlorosulphonate ² :

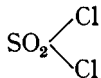


a colourless liquid, boiling at 49° to 50° C. at a pressure of 14 mm. mercury and having a density of 1.63 at room temperature. It is sparingly soluble in water with partial decomposition. It is soluble in the common organic solvents. It strongly irritates the mucous membranes (Fuchs and Katscher).

The lethal concentration for man at 30 minutes' exposure is 6,000–8,000 mgm. chlorosulphonic acid per cu. m. of air (Lindemann).

2. Sulphuryl Chloride

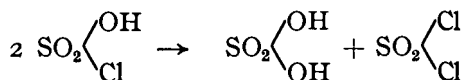
(M.Wt. 135)



Sulphuryl chloride was chiefly prepared during the war for the manufacture of methyl and ethyl chlorosulphonates, but was occasionally employed also in admixture with cyanogen chloride, phosgene or chloropicrin (Prentiss).

PREPARATION

It may be obtained by heating chlorosulphonic acid to 180° C. under pressure. The following reaction takes place :

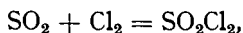


In the presence of suitable catalysts, such as salts of mercury, this reaction may be carried out at lower temperatures: at about 70° C. and ordinary pressure.

¹ R. LEVAILLANT and L. SIMON, *Compt. rend.*, 1919, **169**, 234; C. BOULIN, *Compt. rend.*, 1919, **169**, 338.

² KRAFT and ALEXEJEV, *J. Obscei Khim.*, Ser. A., 1932, **2**, 728.

However, in the laboratory it is more convenient to prepare it by synthesis from chlorine and sulphur dioxide :



in presence of camphor ¹ or activated carbon.²

10 gm. camphor are placed in a flask of about 500 ml. capacity fitted with a reflux condenser which is connected to an aspirator. A glass tube with a three-way cock leads to the bottom of the flask, which is cooled with iced water while a current of sulphur dioxide, dried by means of sulphuric acid, is passed in. The gas is rapidly absorbed by the camphor, and when this is reduced to a liquid the gas is discontinued and a current of dry chlorine bubbled through. When the chlorine is no longer absorbed and its colour no longer disappears, it is replaced by sulphur dioxide and then chlorine is again passed in.

When the flask contains 30–40 ml. liquid, both gases are passed in together, with external cooling, and when sufficient liquid has been produced, the mixed-gas current is stopped and the product distilled, collecting the fraction passing over between 68° to 70° C., which consists of sulphuryl chloride.

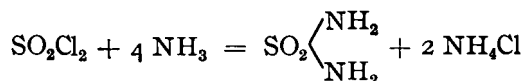
PHYSICAL AND CHEMICAL PROPERTIES

Sulphuryl chloride is a colourless liquid boiling at 69.2° C. and melting at – 54.1° C. Its specific gravity at 0° C. is 1.708 and at 20° C. 1.667.

Its vapour density is 4.6 and its heat of volatilisation 524 calories.

Sulphuryl chloride is slowly decomposed by cold water, but hot water or alkalis act rapidly and vigorously, sulphuric acid and hydrochloric acid being formed.³ When sulphuryl chloride vapour is passed through a tube heated to dull redness, decomposition takes place with formation of sulphur dioxide and chlorine.

Gaseous ammonia reacts with sulphuryl chloride to form ammonium chloride and sulphamide ⁴ :



Sulphamide forms white crystals, melting at 92° C. and soluble in water.

¹ SCHULZE, *J. prakt. Chem.*, 1881, [2] **24**, 168.

² DANNEEL, *Z. angew. Chem.*, 1926, **39**, 1553; MEYER, *Z. angew. Chem.*, 1931, **44**, 41.

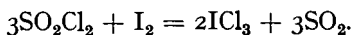
³ CARRARA and ZOPPELLARI, *Gazz. chim. ital.*, 1894, **24**, 364.

⁴ EPHRAIM, *Ber.*, 1910, **43**, 146.

Iodine in the presence of aluminium chloride reacts with sulphuryl chloride in several ways : to form iodine monochloride if the sulphuryl chloride is insufficient :



or if the sulphuryl chloride is in excess, to form iodine trichloride :

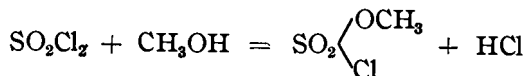


By the action of hydriodic acid on sulphuryl chloride sulphur dioxide, hydrochloric acid, sulphur and iodine are formed.¹

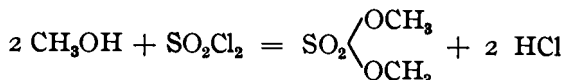
On heating to 200° C. with sulphur, sulphur monochloride and dichloride are formed. This reaction takes place at ordinary temperatures in presence of aluminium trichloride.

Sulphuryl chloride usually behaves as a chlorinating agent. For instance, with benzene chlorobenzene is formed ; with acetone mono- and di- chloroacetones ; with aniline trichloroaniline, etc.

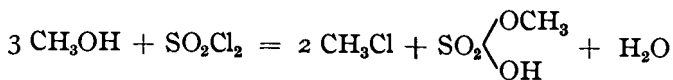
It reacts with methyl alcohol, forming various products according to conditions.² Thus in presence of excess sulphuryl chloride, methyl chlorosulphonate is produced (see p. 266) :



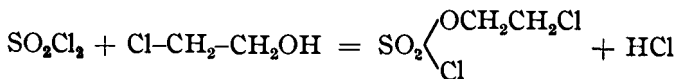
In presence of excess of the alcohol, methyl sulphate is formed :



or else methyl chloride and methyl sulphuric acid :



It also reacts with ethylene chlorohydrin, forming chloroethyl chlorosulphonate³ :



a liquid boiling at 101° C. at a pressure of 23 mm. and having a

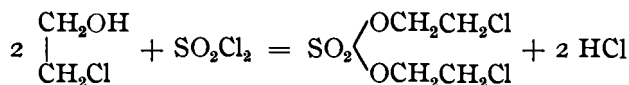
¹ BESSON, *Compt. rend.*, 1896, **122**, 467.

² R. MCKEE, *U.S. Pat.* 1641005/1927.

³ W. STEINKOFF and coll., *Ber.*, 1920, **53**, 1144 ; R. LEVAILLANT, *Compt. rend.* 1928, **187**, 730.

density of 20° C. of 1.552. It is stable during storage and has an odour like that of chloropicrin; it causes lachrymation.

On continuing the heating, the reaction proceeds further and $\beta\beta'$ dichloroethyl sulphate is formed¹:

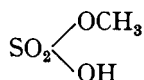


This is a colourless, inodorous liquid which distils without decomposition only under reduced pressure. The boiling point is 154° C. at 8 mm. mercury pressure. Its S.G. at 20° C. is 1.4622. On cooling it forms a crystalline mass, melting at 11° C. and insoluble in water. It is hydrolysed neither by water nor ammonia.

Liquid sulphuryl chloride has a slight corrosive action on iron, but is without action on lead.

3. Methyl Sulphuric Acid

(M.Wt. 112)



The importance of this compound as a war gas is almost nil; it had a very limited use during the war mixed with dimethyl sulphate.

PREPARATION

In the laboratory it is prepared by the action of methanol on chlorosulphonic acid. According to Claesson,² the chlorosulphonic acid is placed in a small flask, which is fitted with a tap-funnel and externally cooled with ice. Water-free methyl alcohol, previously distilled from lime, is slowly introduced in quantity stoichiometrically equivalent to the chlorosulphonic acid. As each drop of alcohol comes into contact with the chlorosulphonic acid, hydrochloric acid is evolved. At the end of addition of the alcohol the flask is heated gently while a current of dry air is passed through in order to remove the hydrochloric acid dissolved in the mixture. The product obtained contains about 90% methyl sulphuric acid.

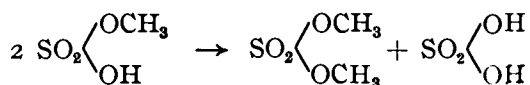
PHYSICAL AND CHEMICAL PROPERTIES

Methyl sulphuric acid is an oily liquid which may be cooled to -30° C. without solidifying. On heating to 130° to 140° C. it

¹ NEKRASSOV and KOMISSAROV, *J. prakt. Chem.*, 1929, **123**, 160; R. LEVAILLANT, *Compt. rend.*, 1928, **187**, 730.

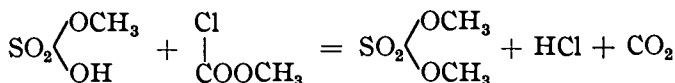
² CLAESSION, *J. prakt. Chem.*, 1879, [2] **19**, 240.

decomposes almost quantitatively into dimethyl sulphate and sulphuric acid :

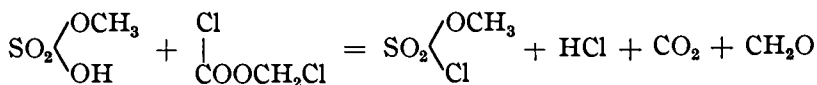


It is sparingly soluble in water and alcohol. In anhydrous ether it dissolves in all proportions.

It reacts with methyl chloroformate to form dimethyl sulphate in good yield ¹ :

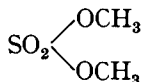


With monochloromethyl chloroformate it reacts to form methyl chlorosulphonate ² :



4. Dimethyl Sulphate

(M.Wt. 126.12)

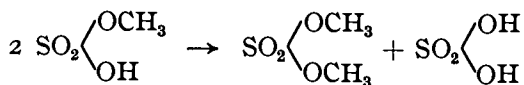


Dimethyl sulphate was used by the Germans mixed with methyl chlorosulphonate, this being the product obtained in the industrial manufacture from methanol and chlorosulphonic acid when the esterification is incomplete. Dimethyl sulphate mixed with chlorosulphonic acid was used by the French under the name of "*Rationite*."

Dimethyl sulphate, before being employed as a war gas, was used in industry as a methylating agent for amines and phenols. In recent years it has also been employed as a catalyst in the preparation of cellulose esters.³

PREPARATION

It may be obtained by the decomposition of methyl sulphuric acid at high temperatures and *in vacuo* :

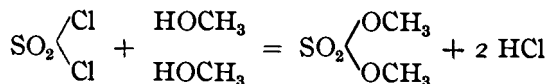


¹ M. KRAFT and F. LJUTKINA, *J. Obscei Khim.*, Ser. A., 1931, 1, 190.

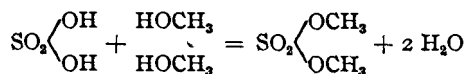
² M. KRAFT and B. ALEXEJEV, *J. Obscei Khim.*, Ser. A., 1932, 2, 726.

³ *Brit. Pat.* 306531/1929.

or by the action of methyl alcohol on sulphuryl chloride :

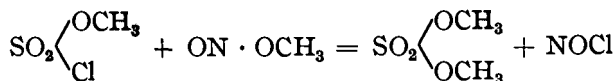


or else by the esterification of fuming sulphuric acid with methyl alcohol :



Guyot and Simon,¹ employing oleum containing 60% SO₃ in the last method have obtained a very high yield of dimethyl sulphate (about 90%).

Recently a method of preparation has been worked out based on the reaction between methyl nitrite and methyl chlorosulphonate² :



LABORATORY PREPARATION

In the laboratory it is preferable to prepare dimethyl sulphate by Ullmann's method,³ that is, by the action of methyl alcohol on chlorosulphonic acid.

100 gm. chlorosulphonic acid are placed in a 200 ml. distillation flask which is closed with a rubber stopper containing two holes. Through one of the holes passes a thermometer and through the other a tap-funnel of the "Bulk" type⁴ containing 27 gm. water-free methyl alcohol. The exit tube of the distillation flask is connected with a wash-bottle containing a little sulphuric acid, and the exit from this leads to a second bottle partly filled with water which serves to absorb the hydrochloric acid formed in the reaction.

The contents of the flask are cooled to - 10° C. by means of a freezing mixture and then the methyl alcohol allowed to enter from the tap-funnel, regulating the rate of addition so that the evolution of hydrochloric acid is not too violent. During the addition of the alcohol, the contents of the flask are repeatedly

¹ GUYOT and SIMON, *Compt. rend.*, 1919, **169**, 795.

² R. LEVAILLANT, *Compt. rend.*, 1928, **187**, 234.

³ ULLMANN, *Ann.*, 1903, **327**, 104.

⁴ This funnel has a very narrow stem (3-4 mm. diameter) which ends in a long capillary bent in a crook for 5-10 mm. at the end. The stem, which should reach almost to the bottom of the flask, should be filled with methyl alcohol before the reaction commences.

agitated and care is taken that the temperature does not rise above -5°C . The whole operation takes about $1\frac{1}{2}$ hours.

When all the alcohol has been added, the product is allowed to stand for about 12 hours and then distilled under 20 mm. mercury pressure, heating the flask on an oil bath to 140°C . The distillate consists of almost pure dimethyl sulphate, and is finally washed with a little cold water and dried with calcium chloride. Yield is 80% of theory.

INDUSTRIAL MANUFACTURE

Industrially, dimethyl sulphate is nowadays prepared almost exclusively by the action of chlorosulphonic acid on methyl alcohol at a low temperature in the presence of carbon tetrachloride and then distillation of the product at reduced pressure.

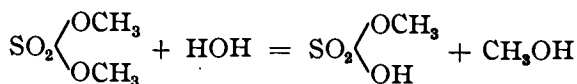
6.4 kg. 99% methanol are placed in an enamelled iron vessel fitted with a reflux apparatus, together with 20 kg. carbon tetrachloride, and then 24 kg. chlorosulphonic acid are added slowly while stirring. At the end of this operation, the carbon tetrachloride is first distilled off on a water-bath and collected for employment in another preparation, and then the dimethyl sulphate is distilled under reduced pressure.¹

PHYSICAL AND CHEMICAL PROPERTIES

Dimethyl sulphate is a colourless, inodorous liquid which boils at ordinary pressure at 188°C . with partial decomposition, while at 15 mm. of mercury pressure it boils without decomposition at 96°C . It solidifies at -31.7°C .² and has a specific gravity of 1.333 at 15°C . Its vapour density is 4.3. Its volatility at 20°C . is 3,300 mgm. per cu. m. According to this, dimethyl sulphate is unsuitable for use as an asphyxiant war gas because its volatility is too low and equally unsuitable as a vesicant because its volatility is too high.

Dimethyl sulphate is sparingly soluble in water (about 2.8%), but soluble in the common organic solvents.

It is decomposed by alkalis and partially even by cold water³:

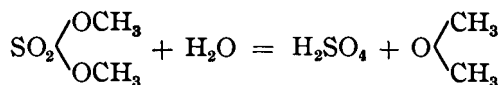


¹ Soc. prod. chim. Fontaines (Lyons), *D.R.P.*, 193830.

² TIMMERMAN, *Bull. soc. chim. belg.*, 1921, **30**, 62.

³ KREMANN, *Monatsh.*, 1907, **28**, 13.

Boulin and Simon¹ have observed that on long standing, a mixture of water and dimethyl sulphate becomes homogeneous. This is attributed to the fact that decomposition takes place as follows, in these circumstances :

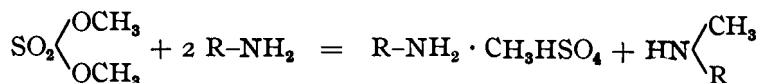


The methyl ether formed is completely soluble in the sulphuric acid also produced in the reaction.

Dimethyl sulphate reacts in a similar manner with other substances containing the hydroxyl group, such as phenols. These compounds condense readily and quantitatively in alkaline solution with dimethyl sulphate. According to Ullmann,² dimethyl sulphate may be usefully employed instead of methyl iodide for introducing methyl groups into organic molecules.

It reacts with hydrogen peroxide, forming methyl peroxide, $\text{CH}_3\text{—O—O—CH}_3$, a gas at ordinary temperatures with an odour reminiscent of nitrous gases. It boils at 13.5°C . at a pressure of 740 mm. Heated in admixture with air it explodes with violence and flame, evolving formaldehyde. The vapour of methyl peroxide irritates the respiratory passages.³

Dimethyl sulphate also reacts with amines. For instance, with the aromatic primary amines it forms the methyl sulphate of the primary amine, together with the corresponding secondary base (Ullmann) :



The tertiary amines in ethereal or benzene solution react with dimethyl sulphate, forming quaternary ammonium compounds.

Dimethyl sulphate does not attack metals. It is only to a slight extent absorbed by animal and vegetable fibres ; cotton absorbs more than wool.⁴

A normal man cannot breathe the gas for more than one minute in concentrations greater than 50 mgm. per cu. m. of air (Flury). The mortality-product, determined with cavies, is 35,000.⁵ Even at low concentrations it has a vesicant action on the skin.

¹ BOULIN and SIMON, *Compt. rend.*, 1920, **170**, 392.

² ULLMANN, *loc. cit.*

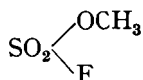
³ A. RIECHE, *Ber.*, 1928, **61**, 951.

⁴ ALEXEJEVSKY, *J. Prikl. Khim.*, 1929, **1**, 184.

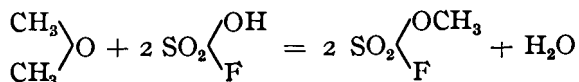
⁵ G. FERRAROLO, *Minerva medica.*, May, 1930, No. **18**.

5. Methyl Fluorosulphonate

(M.Wt. 114)



Methyl fluorosulphonate was obtained by Meyer¹ in 1932 by the action of fluorosulphonic acid on dimethyl ether :

**LABORATORY PREPARATION¹**

10 ml. fluorosulphonic acid are placed in a wash-bottle and a current of dry dimethyl ether, obtained by heating 1.3 parts methanol with 2 parts concentrated sulphuric acid to 140° C. is passed in. The methyl ether is absorbed and reacts immediately. For safety, a second wash-bottle should be inserted containing a further 10 ml. fluorosulphonic acid, and after this it is best to introduce another, containing concentrated sulphuric acid.² After 3 hours, that is, when the fluorosulphonic acid in the first bottle absorbs no more methyl ether, the product is distilled under reduced pressure. At a pressure of 160 mm. methyl fluorosulphonate distils at 45° C.

PHYSICAL AND CHEMICAL PROPERTIES

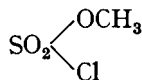
Methyl fluorosulphonate is a liquid with an ethereal odour, boiling at 92° C. at ordinary pressure. It has a specific gravity of 1.427 at 16° C., and attacks glass. In the cold it has very little attack on rubber, cork and other organic substances.

It is not miscible with water, but is rapidly saponified, especially in the presence of alkalis or acids.

It has toxic properties (Meyer).

6. Methyl Chlorosulphonate

(M.Wt. 130.55)



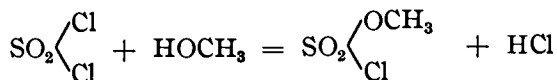
Methyl chlorosulphonate was employed by the Germans both alone, and in admixture with dimethyl sulphate (75 parts dimethyl sulphate and 25 parts methyl chlorosulphonate) under the name of "C-Stoff."

¹ J. MEYER and G. SCHRAMM, *Z. anorg. Chem.*, 1932, **206**, 27.

² E. ERLLENMEYER, *Ber.*, 1874, **7**, 699.

PREPARATION

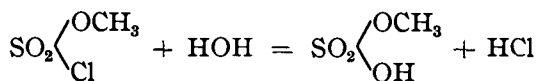
The usual method of preparing this war gas is by the action of methyl alcohol on sulphuryl chloride¹ :



65 gm. sulphuryl chloride are placed in a flask of 150–200 ml., which is fitted with a dropping funnel and a reflux condenser connected at its upper end by a tube to a flask filled with water. The function of the water in the flask is to trap the hydrochloric acid which is evolved in the reaction. 15 gm. methyl alcohol (preferably dried) are allowed to drop in slowly from the tap-funnel. During this addition the reaction mixture is agitated continuously and the flask is cooled externally with ice. When all the alcohol has been added, the flask is allowed to stand for 2–3 hours and then heated to 50° to 60° C. on the water-bath, until all the hydrochloric acid has been evolved. The liquid product is then placed in a separatory funnel, washed rapidly with iced water and the heavier layer separated and distilled *in vacuo*, the fraction boiling between 38° and 45° C. at 16 mm. pressure being collected.

PHYSICAL AND CHEMICAL PROPERTIES

It is a colourless liquid with a pungent odour and boils at ordinary pressure at 133° to 135° C. with decomposition. At 16 mm. pressure it distils unaltered at 42° C. It melts at – 70° C. and has a S.G. at 15° C. of 1.492, while its vapour density is 4.5 (air = 1). The volatility at 20° C. is 60,000 mgm. per cu. m. It is immiscible with sulphuric acid,² but miscible with carbon tetrachloride, chloroform and ethyl alcohol. It is insoluble in water, which hydrolyses it according to the equation :



That is, unlike the sulphuric esters, methyl sulphuric acid and dimethyl sulphate, it does not split off its alkyl group on hydrolysis, but only the chlorine atom.

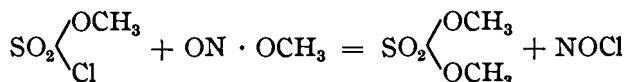
If the water is in excess, however, even the methyl sulphuric acid which is formed is decomposed into hydrochloric acid and methyl alcohol.³

¹ BEHREND, *J. prakt. Chem.*, 1877, [2] **15**, 32.

² R. LEVAILLANT and L. SIMON, *Compt. rend.*, 1919, **169**, 140.

³ L. GUYOT and L. SIMON, *Compt. rend.*, 1920, **170**, 326.

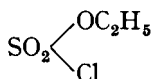
It reacts with methyl nitrite at about 140° C., forming dimethyl sulphate ¹ :



The minimum concentration capable of provoking irritation is 2 mgm. per cu. m. of air (Müller). The limit of insupportability according to Lindemann is 30–40 mgm. per cu. m. Mortality-product : 2,000 (Müller).

7. Ethyl Chlorosulphonate

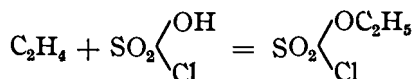
(M.Wt. 144.57)



This compound was used by the French, at the suggestion of Grignard, towards the end of 1915, because of its irritating action on the skin. It was also employed mixed with bromoacetone.

PREPARATION

It is generally prepared by the reaction of ethylene with chlorosulphonic acid in the cold ² :

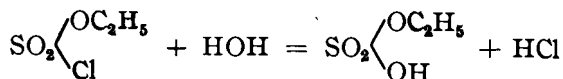


It may also be obtained by the action of fuming sulphuric acid on ethyl chloroformate.³

PHYSICAL AND CHEMICAL PROPERTIES

Ethyl chlorosulphonate is a colourless, oily liquid fuming in damp air and having a pungent odour. It boils at ordinary pressure at 152° to 153° C. and at 100 mm. pressure at 93° to 95° C. Its specific gravity at 0° C. is 1.379, and its vapour density is five times that of air. It has a low vapour pressure.

It is insoluble in water and is readily decomposed by cold water according to the equation :



That is to say, it gives up the chlorine atom and not the alkyl

¹ R. LEVAILLANT, *Compt. rend.*, 1928, **187**, 234.

² MÜLLER, *Ber.*, 1873, **6**, 228.

³ WILM, *Ber.*, 1873, **6**, 505.

group on hydrolysis, like the methyl derivative already described. However, the velocity of hydrolysis is lower.

It dissolves readily in ligroin, chloroform and ether.¹ On heating to about 160° C. it decomposes to form sulphur dioxide, sulphuric acid, hydrochloric acid and ethylene.²

When treated with aniline dissolved in ether, it forms ethyl chloride and sulphanilic acid.

Ethyl chlorosulphonate does not attack iron or steel, but attacks copper slightly and lead and tin vigorously.

The lower limit of irritation is the same as that of the methyl derivative, that is, 2 mgm. per cu. m. of air (Müller). The limit of insupportability, according to Flury, is 50 mgm. per cu. m. and the mortality-product is 3,000 (Müller) and 10,000 (Prentiss).

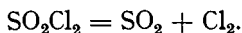
Analysis of the Sulphuric Acid Derivatives

DETECTION

The detection of these compounds is usually carried out by utilising their reaction with alkaline solutions or sometimes with water alone, in which sulphuric acid, hydrochloric acid, methyl or ethyl alcohol, etc., are formed. These may then be recognised by the usual methods of qualitative analysis.

Detection of Chlorosulphonic Acid. This substance may be detected by absorbing a sample in sodium hydroxide solution and then testing for the presence of chloride with silver nitrate and of sulphate with barium chloride.

Detection of Sulphuryl Chloride. According to Heumann and Köchling,³ when gaseous sulphuryl chloride is passed through a glass tube raised to dull red heat, decomposition takes place as follows :



By testing for chlorine and sulphur dioxide in the gas produced, it is possible to detect the presence originally of sulphuryl chloride. According to the same authorities it is advisable to confirm the presence of chlorine by means of potassium iodide and of sulphur dioxide with lead dioxide, which becomes white on being converted to sulphate.

*Detection of Dimethyl Sulphate.*⁴ In order to test for dimethyl sulphate, about 2 gm. of the sample are digested in a reflux apparatus with 50 ml. water for about 1 hour. The solution is

¹ BUSHONG, *Amer. Chem. Jour.*, 1903, **30**, 214.

² WILLCOX, *Amer. Chem. Jour.*, 1904, **32**, 471.

³ HEUMANN and KÖCHLING, *Ber.*, 1883, **16**, 602.

⁴ F. E. WESTON, *Carbon Compounds*, 1927, 95.

then distilled ; the distillate is tested for methyl alcohol and the residue for sulphuric acid.

QUANTITATIVE DETERMINATION

The quantitative determination of the sulphuric acid derivatives may be carried out as described in the paragraphs above dealing with their qualitative analysis: by decomposing the sample by warming with water or alkaline solutions and then determining the sulphuric and hydrochloric acids quantitatively.

Determination of Chlorosulphonic Acid. About 1 gm. of the sample is introduced into a small glass bulb which is then sealed in the flame and weighed accurately. This bulb is then placed in a tall glass cylinder of about 150 ml. capacity, containing about 100 ml. water. The cylinder is stoppered tightly and shaken violently so as to break the bulb, and then allowed to stand until the cloud which first forms in the cylinder completely disappears. The contents are then transferred to a 500 ml. flask and made up to volume. 200 ml. of the solution are then titrated with a decinormal sodium hydroxide solution, to the methyl-orange end-point, so as to obtain the total hydrochloric and sulphuric acid content. In another 200 ml. the hydrochloric acid is titrated with a decinormal solution of silver nitrate in presence of a few drops of potassium chromate solution, after addition of excess of pure calcium carbonate.

Calculation: If a gm. sample were taken and b ml. N/10 sodium hydroxide and c ml. N/10 silver nitrate were employed, then

$$\begin{aligned} \% \text{ HCl} &= \frac{0.9118 \times c}{a} \\ \% \text{ H}_2\text{SO}_4 &= \frac{1.00075 (b - c)}{a} \end{aligned}$$

*Determination of Sulphuryl Chloride.*¹ A simple method of determining this substance is based on its quantitative decomposition into chlorine and sulphur dioxide when it is passed through a tube heated to dull-redness (see p. 259). Then on determining the chlorine and the sulphur dioxide by one of the ordinary methods, the amount of sulphuryl chloride present in the sample may be deduced.

¹ Private communication from Dr. Rusberg (LUNGE-BERL, *Chem. Techn. Untersuchungsmethoden*, 7th edition, 1921, 877).

CHAPTER XV

ARSENIC COMPOUNDS

TOWARDS the end of the war of 1914-18, the attention of chemists searching for new war gases returned to the arsenic compounds which had already frequently been considered, on account of their great toxicity. Only a few had actually been employed, however, for their physical properties rendered them unsuitable in general. Thus all the inorganic compounds were discarded, excepting hydrogen arsenide,¹ which was tested at the commencement, but was also abandoned because of its instability² and rapid diffusion³ and arsenic trichloride, which had only a limited employment and that solely as solvent for the war gases (phosgene, hydrocyanic acid, etc.).⁴

A very large number of potential war gases was found amongst the organic derivatives however. The superiority of the organic arsenicals over the inorganic compounds is attributed to the fact that the former are, in general, soluble in the lipoids and dissolve preferentially in lecithin and cephalin, while the inorganic compounds are rapidly eliminated *viâ* the kidneys and the mucus.⁵

From the results of the researches carried out on the organic arsenic compounds, it is possible to divide these into the following groups :

- | | |
|----------------------------------|---|
| (1) <i>Aliphatic Arsines</i> : | Methyl dichloroarsine.
Ethyl dichloroarsine.
Chlorovinyl arsines. |
| (2) <i>Aromatic Arsines</i> : | Phenyl dichloroarsine.
Diphenyl chloroarsine.
Diphenyl cyanoarsine. |
| (3) <i>Heterocyclic Arsine</i> : | Phenarsazine chloride. |

Of these, the aromatic arsines were very largely used during the war, especially diphenyl chloroarsine. The aggressive action of these aromatic arsines, unlike that of all the compounds

¹ FERRAROLO, *Gazz. Intern. Medicina e Chirurgia*, 1936.

² NEKRASSOV, *Khimija Otravljajuscikh Vescestv*, Leningrad, 1929, 145.

³ MIHAI CRISTEA, *Antigaz*, 1931, Nos. 9-10.

⁴ LUSTIG, *Policlínico*, March, 1935.

⁵ HOFMANN, *Sitzb. hgl. preuss. Akad. Wiss.*, 1935, **24**, 447.

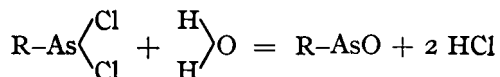
described previously, is provoked by finely divided solid particles, which on liberation in the air form true smokes and are known as the "toxic smokes." Phenyl dichloroarsine is an exception, not being a smoke.

Most of the aliphatic and aromatic arsines employed during the war of 1914-18 were substances which had been known for some time. The only new substances are the chlorovinyl arsines and phenarsazine chloride, of whose practical efficiency somewhat conflicting opinions are still held.

The fact that during the war only the compounds mentioned above were actually used does not indicate that they were superior to others which have been prepared and studied. Nevertheless, it is probable that preference will be given to those substances whose range of application is known, without using compounds of uncertain scope.

(A) ALIPHATIC ARSINES

The aliphatic arsines are substances which are generally liquid and oily, have a not unpleasant odour, are somewhat miscible with water, but are all more or less rapidly hydrolysed as follows :



These substances, though more powerfully toxic than the aromatic arsines, are of minor importance because of their rapid diffusion in the air without forming aerosols.

Even the chlorovinyl arsines, although they are easily prepared, do not seem to be sufficiently aggressive in their action to replace the aromatic arsines. According to several authorities,¹ experiments on the methods of military application of the chlorovinyl arsines have been abandoned even in America.

Of the aliphatic arsines, only ethyl dichloroarsine has been widely employed as a war gas and is considered as the typical substance for use in projectiles. Methyl dichloroarsine is classed by some German authors² as a substance which was studied in the post-war period, but according to an American authority it was actually employed by the Allies towards the end of the war, though only in small quantity.³

Since the war, various other compounds of similar properties and method of preparation have been prepared and studied.

¹ HANSLIAN, *Der Chemische Krieg*, Berlin, 1927, 62.

² U. MÜLLER, *Die Chemische Waffe*, Berlin, 1932, 111.

³ FRIES and WEST, *Chemical Warfare*, New York, 1921, 181.

For instance, dimethyl chloroarsine (b.p. 106.5° to 107° C.), dimethyl bromoarsine¹ (b.p. 128° to 129° C.), dimethyl fluoroarsine,² methyl dicyanoarsine³ (m.p. 115.5° to 116.5° C.), ethyl dibromoarsine, etc. All of these have aggressive properties inferior to those of methyl dichloroarsine.

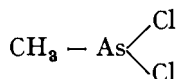
Homologues of methyl dichloroarsine have also been prepared : *n*-Butyl-dichloroarsine,⁴ $C_4H_9AsCl_2$, obtained by the action of hydrochloric acid on *n*-butyl arsenic acid in the presence of sulphur dioxide, is an oily liquid boiling at 192° to 194° C.

Iso-amyl dichloroarsine,⁵ $C_5H_{11}AsCl_2$, obtained by the action of phosphorus trichloride on iso-amyl arsenic acid, is a liquid boiling at 88.5° to 91.5° C. at 15 mm. mercury pressure.

This latter substance has great irritant power (Liebermann).

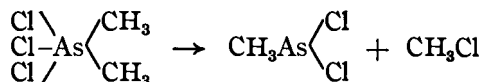
1. Methyl Dichloroarsine

(M.Wt. 161)

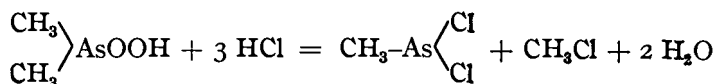


Methyl dichloroarsine was prepared by Bayer⁶ in 1858 by two different methods :

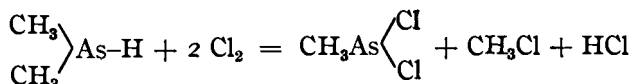
(a) By the decomposition of cacodyl trichloride at 40° to 50° C.



(b) By the action of gaseous hydrochloric acid on cacodylic acid⁷ :



Methyl dichloroarsine may also be obtained by treating dimethyl arsine with chlorine⁸ :



¹ STEINKOPF and SCHWEN, *Ber.*, 1921, **54**, 1454.

² BUNSEN, *Ann.*, 1841, **37**, 38.

³ GRYSZKIEWICZ and TROCHIMOVSKY, *Bull. soc. chim.*, 1927, **41**, 1323.

⁴ QUICK and ADAMS, *J. Am. Chem. Soc.*, 1922, **44**, 805 ; HANZLIK, *J. Pharmac.*, 1919, **14**, 221.

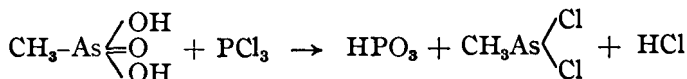
⁵ STEINKOPF and MIEG, *Ber.*, 1920, **53**, 1015.

⁶ BAYER, *Ann.*, 1858, **107**, 269.

⁷ ZAPPI and coll., *Bull. soc. chim.*, 1928, [4] **43**, 1230.

⁸ DEHN and WILCOX, *J. Am. Chem. Soc.*, 1906, **35**, 16.

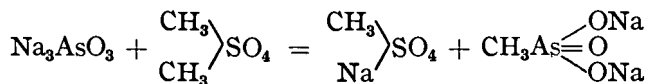
or, according to Auger,¹ by bringing about the reaction between methyl arsenic acid and phosphorus trichloride, which both reduces and chlorinates :



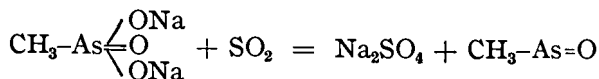
It is easily understood that this reaction, though convenient enough for the laboratory preparation of methyl dichloroarsine, is not suitable for its industrial manufacture because of the difficulty of procuring large quantities of the raw materials. The lack of an easy and simple method of manufacture may be considered as one of the principal causes which prevented methyl dichloroarsine from being employed as a war gas until the very end of the war, when only the Americans succeeded in producing it on an industrial scale by a simple method.

The method used by the Americans² commenced with sodium arsenite and dimethyl sulphate, and proceeded by the following stages :

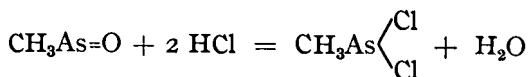
(1) Methylation of the sodium arsenite with dimethyl sulphate³ :



(2) Reduction of the sodium methyl arsenate with sulphur dioxide, after acidification :



(3) Chlorination of the methyl arsenious oxide with hydrochloric acid :



LABORATORY PREPARATION

In the laboratory, methyl dichloroarsine may be prepared by the method indicated above.⁴

100 gm. arsenious oxide are placed in a wide-mouthed glass flask of 1 litre capacity, a solution of 120 gm. sodium hydroxide in 150 gm. water is added and the whole heated on a water-bath

¹ AUGER, *Compt. rend.*, 1906, **142**, 1151.

² UEHLINGER and COOK, *J. Ind. Eng. Chem.*, 1919, **11**, 105.

³ *D.R.P.* 404589/March 15th, 1923.

⁴ NENITZRSU, *Antigaz*, 1929, No. 2.

at 80° C. until the arsenious oxide is completely dissolved. Then, without heating, but stirring vigorously with a mechanical agitator, 64 gm. dimethyl sulphate are added little by little. The reaction between sodium arsenite and dimethyl sulphate is highly exothermic and the rate of addition of the latter should be so regulated that the temperature does not rise above 85° C.

When all the dimethyl sulphate has been added, the flask is fitted with a reflux condenser and the contents boiled for 2 hours. The sodium salt of methyl arsenic acid is obtained. It is allowed to cool and a small amount of potassium iodide is added, after which a current of sulphur dioxide is passed through the liquid until it is saturated (about 6 hours). The mixture is again boiled under reflux for about an hour; during this period, an oily substance consisting of methyl arsenious oxide deposits at the bottom of the flask, where it is saturated with a current of gaseous hydrochloric acid, while the flask is cooled externally. On attaining complete saturation, the flask is connected with a Liebig's condenser and the liquid distilled. Much hydrochloric acid is evolved at first; later a mixture of hydrochloric acid and methyl dichloroarsine distils over. The distillation is continued until no more oily liquid condenses. The distillate is placed in a separatory funnel and the oily layer separated and distilled.

INDUSTRIAL MANUFACTURE

A diagram of the American plant for the manufacture of methyl dichloroarsine is shown as Fig. 15.

The reaction takes place in a Pfaudler kettle *A* of about 100 gallons capacity, which is double-walled to allow of steam-heating and fitted with a mechanical agitator *F*. At the top of the lid two three-way cocks *R* and *R'* are fitted. The cock *R* serves for the introduction of the reactants and is connected with a long leaden tube which reaches almost to the bottom. This cock also connects both with the receiver *C* containing sodium arsenite, and with the two cylinders *DD'* of sulphur dioxide, with a pipe *O* through which the dimethyl sulphate enters and also with a smaller Pfaudler vessel *B*, of about 50 gallons capacity, in which the hydrochloric acid is prepared. The sulphuric acid which is used for preparing the hydrochloric acid is contained in the vessel *G* which is fed from the storage vessel *E* by means of a pump.

The three-way cock *R'* serves to carry off the reaction products and leads one way to a water-cooled condenser *M* and the other to a reflux condenser *P*, consisting of a lead coil contained in an iron cylinder full of ice and water, and leading to two sight

bottles, *I* and *L*, by means of which any escape of gas from the apparatus may be observed.

A solution of sodium arsenite is first prepared in the container *C* by dissolving 42 kg. arsenious oxide in a solution of 64 kg. of NaOH in 188 kg. water. When it has completely dissolved the solution is introduced into the Pfaudler kettle *A* and then 64 kg. methyl sulphate are added through the pipe *O*, maintaining the temperature at about 85° C. The completion of the conversion

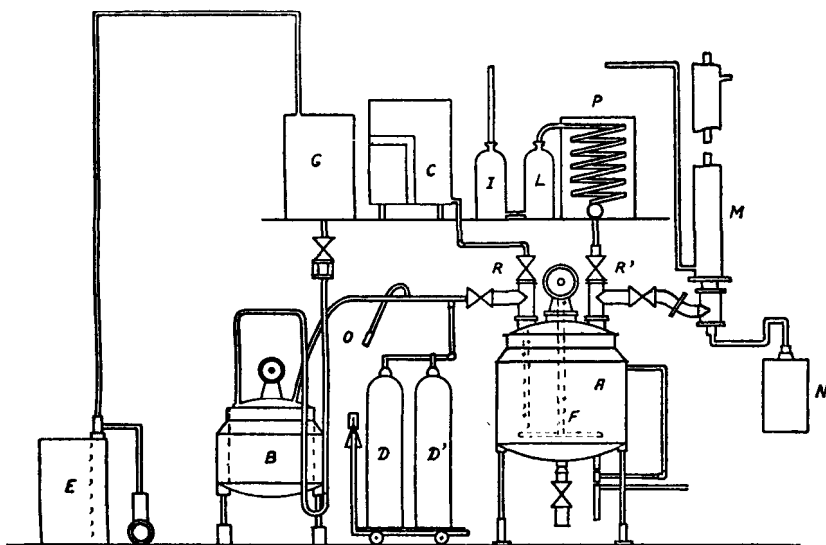


FIG. 15.

of the sodium arsenite into sodium methyl arsenate is shown by a drop in temperature. When this reaches 50° to 55° C. a current of sulphur dioxide is introduced from the cylinders *D* and *D'* and bubbles through the reaction product, which is maintained at 65° C., until complete saturation is attained and the reduction to methyl arsenious oxide complete. A current of gaseous hydrochloric acid is then passed in through the cock *R* to complete saturation, and finally the mixture is distilled.

The distillate is collected in a separatory vessel, and the oily layer dried with calcium chloride and fractionally distilled from an oil-bath. The methyl dichloroarsine passes over between 129° and 133° C.

PHYSICAL AND CHEMICAL PROPERTIES

Methyl dichloroarsine is a mobile, colourless liquid which has a characteristic odour and does not fume in the air.

METHYL DICHLOROARSINE : PROPERTIES 277

It boils at 37° C. at 25 mm.,¹ at 55.5° C. at 50 mm.,² at 72.1° C. at 100 mm.,² at 89.1° C. at 200 mm.² and at 132° to 133° C. at ordinary pressure. Its melting point is - 42.5° C. (Gibson) and its specific gravity 1.838 at 20° C. It has a vapour density of 5.5 and a coefficient of thermal expansion of 0.00102.

The vapour tension at a temperature t may be calculated from the formula (see p. 5).

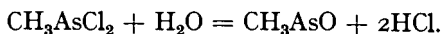
$$\log p = 8.6944 - \frac{2281.7}{273 + t}$$

The values of the vapour tension at the following temperatures are ³ :

TEMPERATURE ° C.	VAPOUR TENSION mm. mercury
- 15	0.67
0	2.17
15	5.94
25	10.83
35	19.33

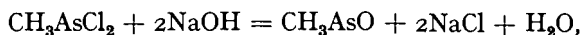
The volatility of methyl dichloroarsine at 20° C. is 74,440 mgm. per cu. m. of air.

It dissolves in water (1 gm. in 1,000 ml. water), being rapidly hydrolysed according to the equation ⁴ :



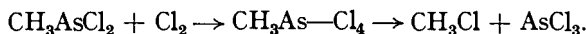
It is, however, easily soluble in the common organic solvents.

In contact with alkaline solutions, methyl dichloroarsine is quantitatively decomposed :



forming methyl arsenious oxide, as with water. This oxide is crystalline and colourless, has an odour of asafœtida and melts at 95° C. Its density is 2.48 and it is soluble in water, alcohol, ether and benzene and readily volatile in steam.⁵

Solutions of methyl dichloroarsine in carbon disulphide when cooled to - 10° C., easily absorb chlorine forming large crystals of methyl tetrachloroarsine, which decompose at 0° C. into methyl chloride and arsenic trichloride ⁶ :



¹ HERBST, *Kolloidchem. Beihefte*, 1926, **23**, 313.

² GIBSON and JOHNSON, *J. Chem. Soc.*, **1931**, 2520.

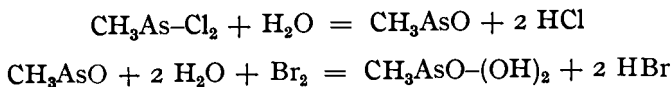
³ BAXTER and BEZZENBERGER, *J. Am. Chem. Soc.*, 1920, **42**, 1386.

⁴ ADAMS, *Private communication*; RAIZISS and GAVRON, *Organic Arsenical Compounds*, New York, 1923, 41.

⁵ RAIZISS and GAVRON, *op. cit.*

⁶ BAYER, *Ann.*, 1858, **107**, 281.

Methyl dichloroarsine reacts with bromine water, forming methyl arsenic acid :

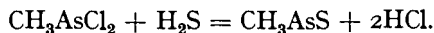


Methyl arsenic acid forms acicules with a melting point of 159° C. It is also obtained by the action of hydrogen peroxide on methyl dichloroarsine.¹

Like all the halogenated arsines, gaseous ammonia converts it quantitatively into methyl arsinimide,² CH₃As=NH. This forms crystals which have an irritating odour and vesicant power and melt at 205° C.

In dry ether solution, methyl dichloroarsine does not react with magnesium, though in presence of water the reaction is violent : methyl arsine, hydrogen, methane and a compound, (CH₃As)_x, are formed. Zinc reacts similarly.³

With hydrogen sulphide, methyl arsenious monosulphide is formed (Bayer) :

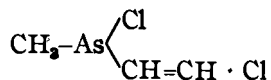


This compound forms acicular crystals or small prisms with melting point 110° C. A detection reaction for the primary arsines is based on this sulphide formation⁴ (see p. 328).

Aqueous solutions of methyl dichloroarsine reduce ammoniacal silver nitrate solutions (Nametkin).

Methyl dichloroarsine reacts with acetylene in presence of anhydrous aluminium chloride, forming a mixture of⁵ :

(i) β chlorovinyl methyl chloroarsine of the formula



This is a liquid with a boiling point of 112° to 115° C. at 10 mm. mercury pressure, which behaves chemically in a similar manner to methyl dichloroarsine. It has a lesser irritant power, but has a vesicant action on the skin, producing blisters which are difficult to heal.

¹ BACKER and coll., *Rec. trav. Chim.*, 1935, **54**, 186.

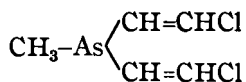
² IPATIEV and coll., *Ber.*, 1929, **62**, 598.

³ ZAPPI, *Bull. soc. chim.*, 1918, **23**, 322.

⁴ S. NAMETKIN and W. NEKRASSOV, *Z. anal. Chem.*, 1929, **77**, 285.

⁵ DAS GUPTA, *J. Ind. Chem. Soc.*, 1936, **13**, 305.

(ii) $\beta\beta'$ dichlorovinyl methylarsine



a liquid, with b.p. 140° to 145° C. at 10 mm. mercury pressure, having physiopathological properties similar to the preceding.

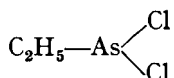
Dry methyl dichloroarsine does not attack iron or zinc (Prentiss).

The lower limit of irritation is 2 mgm. per cu. m. of air (Müller). The maximum concentration which a normal man can breathe for a period not greater than 1 minute is 25 mgm. per cu. m. of air (Lustig). The lethal index is 3,000 according to Müller and 5,600 for 10 minutes' exposure according to Prentiss.

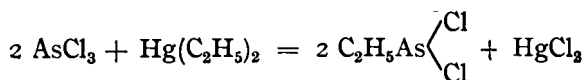
The vapours of these substances have a vesicatory action of the same type as that of dichloroethyl sulphide.¹

2. Ethyl Dichloroarsine

(M.Wt. 175)



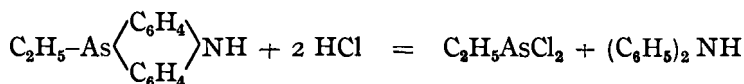
Ethyl dichloroarsine was prepared by La Coste² in 1881 by acting on mercury diethyl with arsenic trichloride :



It may also be obtained by heating ethyl arsine in a closed tube with mercuric, arsenic, antimony or stannous chloride.³



or by the decomposition of 10 ethyl 5.10 dihydrophenarsazine with gaseous hydrochloric acid⁴ :



Ethyl dichloroarsine was employed in March, 1918, by the Germans, being considered suitable for replacing dichloroethyl sulphide in offensive operations because of its immediate vesicant effect and its non-persistent character.

¹ HANZLIK, *loc. cit.*

² LA COSTE, *Ann.*, 1881, 208, 33.

³ DEHN, *Am. Chem. Jour.*, 1908, 40, 88.

⁴ GIBSON and JOHNSON, *J. Chem. Soc.*, 1931, 2518.

LABORATORY PREPARATION

In the laboratory, ethyl dichloroarsine may be obtained by the action of ethyl iodide on sodium arsenite by a method similar to that described already for the preparation of methyl dichloroarsine¹:

In a wide-mouthed vessel *A* (see Fig. 16) of about 2 litres capacity, fitted with a mercury-sealed mechanical stirrer *B*, and a

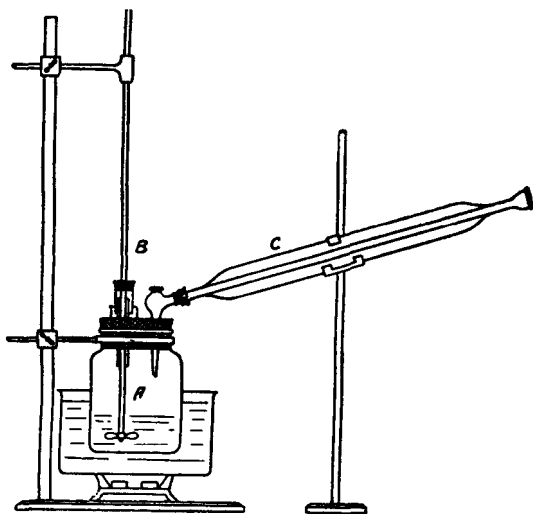


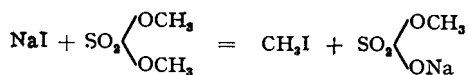
FIG. 16.

condenser *C*, 50 gm. of arsenious oxide are dissolved in a sodium hydroxide solution containing 60 gm. NaOH and 500 ml. water. 100 gm. ethyl iodide are added and the stirrer started. The vessel is then heated in a water-bath for 2 hours, the bath being gradually raised to boiling.

The solution obtained is transferred to a distillation flask and heated in a brine bath. Ether, alcohol and excess ethyl iodide pass over, and then the residue is cooled and carefully neutralised with sulphuric acid (d. 1.84), 90 gm. methyl sulphate are added and the methyl iodide is distilled off on the water-bath.² After

¹ NEKRASSOV, *loc. cit.*

² As the formation of the ethyl arsenic acid and the succeeding chlorination of the ethyl arsenious oxide takes place in acid conditions, hydriodic acid, which is present in considerable quantity, can form ethyl diiodoarsine. In order to prevent this happening, the iodine is removed as methyl iodide by addition of dimethyl sulphate, which reacts, as discovered by WIELAND (*Ber.*, 1905, **38**, 2327), in the following manner:



adding 500 ml. concentrated hydrochloric acid (d. 1.19), the remaining liquid is quickly filtered through a pleated paper and a rapid current of sulphur dioxide is passed through the filtrate. The solution, which is at first coloured, becomes almost colourless and an oily layer is deposited at the bottom of the flask. This is separated in a tap-funnel, dried over calcium chloride and distilled *in vacuo*. Yield 75–80% of theoretical.

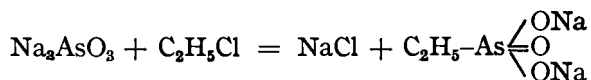
INDUSTRIAL MANUFACTURE

American Method. In America, a similar method was employed for the manufacture of ethyl dichloroarsine to that already described for methyl dichloroarsine. It consisted essentially in treating sodium arsenite with diethyl sulphate, then with diethyl sulphate, reducing the product obtained with sulphur dioxide and then chlorinating with hydrochloric acid.

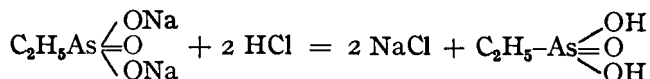
German Method. The method employed in Germany during the war of 1914–18 for the preparation of this substance differs from the American method only in the employment of ethyl chloride instead of diethyl sulphate.

The principal stages in the manufacture are as follows :

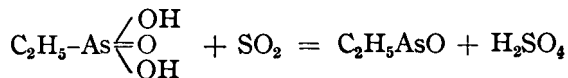
(1) Preparation of the sodium salt of ethyl arsenic acid :



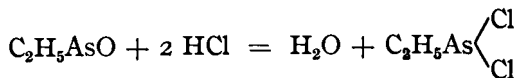
(2) Formation of ethyl arsenic acid :



(3) Reduction to ethyl arsenious oxide :



(4) Chlorination of the ethyl arsenious oxide :



Into an autoclave of 300 litres capacity a solution of sodium arsenite is first introduced. This is obtained by treating 100 parts of arsenious oxide with 300 parts of a 55% sodium hydroxide solution. The ethyl chloride is then added, in quantity 150 parts to each 100 parts of arsenious oxide, in three or four portions at

hourly intervals. The reaction between ethyl chloride and sodium arsenite, which lasts for some 10–12 hours, needs a temperature of 90° to 95° C., and a pressure of 10–15 atmospheres.

At the end of the reaction the ethyl alcohol formed from the ethyl chloride by hydrolysis is distilled off together with the excess of ethyl chloride, the residue being taken up again with water and transferred to a suitable vessel, where it is neutralised with sulphuric acid and reduced with sulphur dioxide while maintaining at 70° C. A heavy oil containing about 93% ethyl arsenious oxide is deposited. To convert this into ethyl dichloroarsine it is placed in a lead-lined iron vessel and completely saturated with gaseous hydrochloric acid, maintaining the internal temperature at 95° C. meanwhile. This operation needs about 2 days. The product is distilled *in vacuo* until oily drops begin to come over.

According to German claims, it is possible to obtain higher yields of ethyl dichloroarsine by this method than by the American method.

PHYSICAL PROPERTIES

Ethyl dichloroarsine is a mobile liquid with a characteristic odour which when highly diluted is reminiscent of fruit. It may be detected by this means at a concentration of 0.5 mgm. per cu. m. of air. It is colourless, becoming slightly yellow on exposure to air and light. It boils at ordinary pressure at 156° C. with decomposition, while at 50 mm. pressure it boils at 74° C.¹ and at 11 mm. pressure distils unchanged at 43.5° C. Its melting point is – 65° C.

The specific gravity of ethyl dichloroarsine at 14° C. is 1.742, the coefficient of thermal expansion 0.0011 and the density of the vapour six times that of air.

The volatility of ethyl dichloroarsine is lower than that of methyl dichloroarsine (Herbst) :

TEMPERATURE ° C.	VOLATILITY mgm./cu. m.
0	6,510
20	20,000
25	27,200

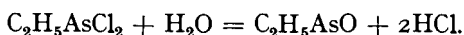
The vapour pressure at 21.5° C. is 2.29 mm. of mercury. It is readily soluble in the organic solvents : alcohol, ether, benzene, acetone, cyclohexane. It also dissolves in water (1 gm. per 1,000 ml. of water), hydrolysis taking place.

¹ GIBSON and coll., *J. Chem. Soc.*, 1931, 2518.

CHEMICAL PROPERTIES

The chemical behaviour of ethyl dichloroarsine is similar to that of methyl dichloroarsine.

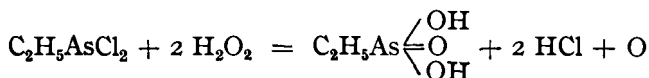
Water. Water hydrolyses dichloroarsine as follows :



The velocity of the hydrolysis is approximately equal to that of methyl dichloroarsine. The ethyl arsenious oxide which forms is a colourless oil, with a nauseating, garlic-like odour, but without vesicant action, which rapidly oxidises in the air to form colourless crystals. Its specific gravity is 1.802 at 11° C., it boils at 158° C. at 10 mm. mercury pressure ¹ and is soluble in benzene, ether and acetone.

Nitric Acid. By prolonged heating of ethyl dichloroarsine with dilute nitric acid, acicular crystals of ethyl arsenic acid, melting at 95° to 96° C. (Dehn) ² or 99° to 100° C. (Backer) ³ and soluble in water and alcohol, are formed.

Hydrogen Peroxide. Like nitric acid, hydrogen peroxide converts ethyl dichloroarsine into ethyl arsenic acid (Backer) :



Sodium Iodide. Ethyl dichloroarsine reacts with sodium iodide in acetone solution to form ethyl diiodoarsine ⁴ :



an oily, yellow liquid, boiling at 126° C. at 11 mm. pressure. On cooling with solid carbon dioxide a crystalline mass forms which melts at - 9° C.

Hydrogen Sulphide. By the action of hydrogen sulphide in aqueous or alcoholic solution on ethyl dichloroarsine, ethyl arsenious sulphide separates ⁵ :



This is a yellow oil which is soluble in chloroform and carbon disulphide and has a density of 1.8218 at 17° C. ⁶

This reaction with hydrogen sulphide may be used for the detection of small quantities (0.02-0.05 mgm.) of ethyl dichloroarsine (see p. 328).

¹ W. STEINKOFF and W. MIEG, *Ber.*, 1920, **53**, 1013.

² DEHN and MCGRATH, *J. Am. Chem. Soc.*, 1906, **28**, 347.

³ BACKER, *Rec. trav. Chim.*, 1935, **54**, 186.

⁴ BURROWS and TURNER, *J. Chem. Soc.*, 1920, **117**, 1373.

⁵ S. NAMETKIN and W. NEKRASSOV, *Z. anal. Chem.*, 1929, **77**, 285.

⁶ KRETOV and BERLIN, *J. Obscei Khim.*, Ser. A., 1931, **1**, 411.

Calcium Hypochlorite. Ethyl dichloroarsine is easily decomposed by calcium hypochlorite, either solid or in aqueous suspension.¹ Because of this property, chloride of lime is employed for the decontamination of objects contaminated with ethyl dichloroarsine.

Ethyl dichloroarsine, when dry, does not attack iron even at a temperature of 50° C. It corrodes brass strongly, however.

During the war of 1914-18, it was employed both alone and mixed with other substances. The two mixtures most commonly employed were :

(a) Dichloromethyl ether 18%, ethyl dichloroarsine 37%, ethyl dibromoarsine 45%.

(b) Dichloromethyl ether 20%, ethyl dichloroarsine 80%.

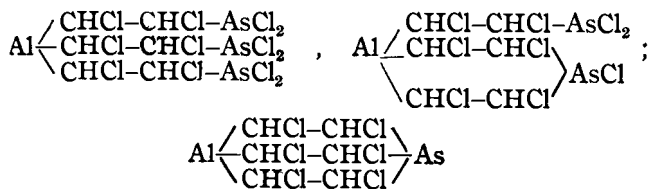
The minimum concentration capable of perceptible irritant action is 1.5 mgm. per cu. m. of air according to Lindemann. The maximum concentration supportable by a normal man for up to 1 minute is 5-10 mgm. per cu. m. (Lustig). The mortality-index is 3,000 according to Müller ; according to Prentiss it is 5,000 for 10 minutes' exposure and 3,000 for 30 minutes' exposure.

This substance, like methyl dichloroarsine, has a vesicant action on the skin,² which, according to Strughold,³ is perceptible at a concentration of 1 mgm. per sq. cm. of skin.

3. The Chlorovinyl Arsines (Lewisite)

The study of the action of acetylene on arsenic trichloride which, according to Lewis, was started in America in 1904 (Griffin), was recommenced during the last war almost simultaneously by German,⁴ American⁵ and English⁶ chemists.

These studies have shown that arsenic trichloride does not react with acetylene, even when heated to boiling, but mixed with aluminium chloride it absorbs a considerable quantity of acetylene with development of heat. In this reaction, a brown oil is formed which consists of a mixture of the following three compounds :



¹ BÜSCHER, *Giftgas! Und Wir?* Hamburg, 1932.

² HANZLIK *loc. cit.*

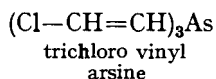
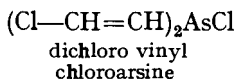
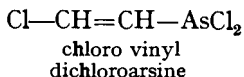
³ STRUGHOLD, *Z. Biol.*, 1923, **78**, 195.

⁴ DEFERT, *Monatsh.*, 1919, **40**, 313; WIELAND, *Ann.*, 1923, **431**, 30.

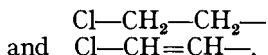
⁵ LEWIS and PERKINS, *Ind. Eng. Chem.*, 1923, **15**, 290.

⁶ GREEN, *J. Chem. Soc.*, 1921, **119**, 448; MANN and POPE, *J. Chem. Soc.*, 1922, **121**, 1754.

which are readily hydrolysed to give the following three substances :

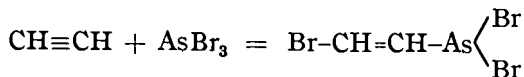


In this mixture trichlorovinyl arsine always predominates and this substance has only a minor interest as a war gas, for its toxicity is low. Chlorovinyl dichloroarsine, which, besides its irritant action on the respiratory passages, also has a vesicant action similar to that of dichloroethyl sulphide, is of much greater importance. The resemblance in the properties of these two substances has been attributed to the presence of the two similar groups :

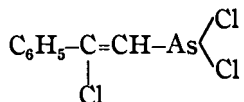


Later, various other compounds were prepared and examined for possible employment as war gases. These are similar in constitution to the chlorovinyl arsines and are prepared similarly :

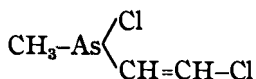
β Bromovinyl dibromoarsine (b.p. 140° to 143° C. at 16 mm. mercury pressure) was prepared by Lewis and Stiegler¹ by the action of acetylene on arsenic bromide mixed with aluminium chloride :



β Chlorostyryl dichloroarsine (b.p. 108° to 110° C. at 12 mm.) was obtained by Hunt and Turner² by acting on arsenic trichloride with phenylacetylene :



β Chlorovinyl methyl chloroarsine (b.p. 112° to 115° C. at 10 mm. mercury pressure) was obtained by Das Gupta,³ by the action of acetylene on methyl dichloroarsine (see p. 278) in the presence of anhydrous aluminium chloride :

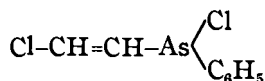


¹ LEWIS and STIEGLER, *J. Am. Chem. Soc.*, 1925, **47**, 2546.

² A. HUNT and E. TURNER, *J. Chem. Soc.*, 1925, **127**, 996.

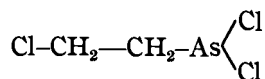
³ DAS GUPTA, *J. Ind. Chem. Soc.*, 1936, **13**, 305.

Phenyl β chlorovinyl chloroarsine (b.p. 140° to 150° C. at 10 mm. mercury pressure) was obtained by the reaction of acetylene with phenyl dichloroarsine in the presence of aluminium chloride :



All these compounds, like the chlorovinyl arsines, are oily substances, somewhat yellow in colour, with extremely unpleasant odours. Their aggressive properties are still rather indefinite with the exception of β chlorovinyl methyl chloroarsine, which does not irritate the nasal tissues like the chlorovinyl arsines, but produces blisters on the skin which heal only with difficulty.

Several compounds obtained by the action of ethylene on arsenic trichloride have also been prepared. Such, for example, is β chloroethyl dichloroarsine¹ :

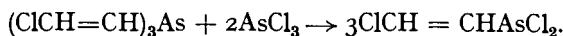


This is a liquid with a boiling point of 93° to 94° C. at a pressure of 16 mm. of mercury which is both irritant and vesicant in its action. In the liquid condition, it penetrates linen and rubber ; in the vapour state, at concentrations which can be obtained in practice, it has no action on the human skin.²

PREPARATION OF THE CHLOROVINYLS ARSINES

The mixture of the three chlorovinyl arsines is obtained, as indicated above, by the action of acetylene on arsenic trichloride.

β Chlorovinyl dichloroarsine may also be obtained by the reduction of a hot solution of β chlorovinyl arsenic acid which has been acidified with hydrochloric acid, by means of sulphur dioxide, hydriodic acid being employed as a catalyst.³ Another method of preparation is to heat a mixture of arsenic trichloride and trichlorovinyl arsine in a closed tube at 220° C. for 4 hours. The following reaction takes place⁴ :



LABORATORY PREPARATION

In the laboratory, the preparation of the chlorovinyl arsines may be carried out by condensing arsenic trichloride with

¹ RENSHAW and WARE, *J. Am. Chem. Soc.*, 1925, **47**, 2991 ; SCHERLIN and EPSTEIN, *Ber.*, 1928, **61**, 1821 ; NEKRASSOV, *Ber.*, 1928, **61**, 1816.

² FERRAROLO, *Minerva Medica*, 1935 (II), **37**, 30.

³ GIBSON and JOHNSON, *J. Chem. Soc.*, 1931, 753.

⁴ GREEN and PRICE, *J. Chem. Soc.*, 1921, **119**, 448.

acetylene in presence of aluminium chloride. The apparatus used is shown in Fig. 17. 45 gm. arsenic trichloride are placed in the vessel *A*, together with 15 gm. anhydrous aluminium chloride. While stirring and cooling with water, 6–8 litres of acetylene, which have been passed first through a sulphuric acid wash-bottle and then through a calcium chloride column *C*, are bubbled in. The reaction is accompanied by the evolution of heat, and the mixture should be cooled in order to maintain the temperature between 30° and 35° C. When the acetylene has been added, the reaction mixture is poured slowly into 200 ml. hydrochloric

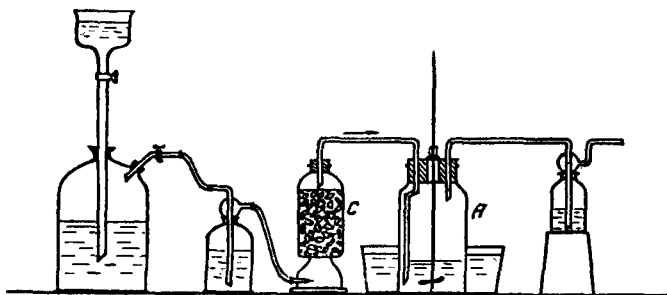


FIG. 17.

acid cooled to about 0° C. An oily layer forms and this is separated and fractionally distilled at reduced pressure (20–30 mm.). The arsenic trichloride which has not reacted distils first and then the chlorovinyl arsines as follows :

- | | | | |
|-----------------|---|-----------------|-----------------------------|
| First fraction | . | 90° to 105° C. | chlorovinyl dichloroarsine. |
| Second fraction | . | 125° to 140° C. | dichlorovinyl chloroarsine. |
| Third fraction | . | 145° to 160° C. | trichlorovinyl arsine. |

*Preparation of Chlorovinyl Dichloroarsine and Dichlorovinyl Chloroarsine from Trichlorovinyl Arsine.*¹ 80 gm. trichlorovinyl arsine and 66.2 gm. arsenic trichloride are placed in a thick-walled glass tube which is then sealed in the flame. The tube is placed in an outer tube of steel, covered with asbestos, and the whole heated for 4 hours at 220° to 250° C. After allowing to cool, the glass tube is opened at the end and the oily contents distilled under reduced pressure. The products obtained are as follows :

- | | |
|--------|-----------------------------|
| 56 gm. | chlorovinyl dichloroarsine. |
| 80 gm. | dichlorovinyl chloroarsine. |

¹ GREEN and PRICE, *J. Chem. Soc.*, 1921, 119, 448.

INDUSTRIAL MANUFACTURE

The process used in America for the manufacture of the chlorovinyl arsines may be summarised as follows¹:

6.3 kgm. arsenic trichloride and 1.16 kgm. aluminium chloride are placed in a 2-gallon enamelled autoclave, and while they are continually stirred, a current of acetylene which has been dried with sulphuric acid and calcium chloride is bubbled in. The quantity of acetylene used is measured by means of a rotary gas-meter; it is in equimolecular amount with the arsenic trichloride. During this operation the temperature slowly rises from 25° to 30° C. initially to 40° to 45° C., but it should in any case be kept below 60° C. When all the acetylene has been absorbed (about 2 hours) the product is separated by washing first with 20% hydrochloric acid, which extracts the arsenic chloride, and distilling the residue. This is carried out in a special cast-iron still of about 1 gallon capacity. The distillate is then fractionally distilled once more under reduced pressure to separate the three chlorovinyl arsines.

PHYSICAL AND CHEMICAL PROPERTIES

The three chlorovinyl arsines are colourless liquids at ordinary temperatures and, if pure, are stable. In presence of small quantities of arsenic trichloride, however, they become violet or brown in time, and the speed of this change as well as the final colour seems to depend on the quantity of arsenic chloride present.

They have high boiling points (190° to 260° C.), but on heating at ordinary pressure easily decompose. Chlorovinyl dichloroarsine is thus decomposed into dichlorovinyl chloroarsine and arsenic trichloride, dichlorovinyl chloroarsine into chlorovinyl dichloroarsine and acetylene, etc. This behaviour supports the belief that an equilibrium exists between the three chlorovinyl arsines and their components, acetylene and arsenic trichloride. The hypothesis is confirmed by the observation that from the reaction between acetylene and arsenic trichloride, it is not possible to produce any one of these compounds solely; a mixture of all three is always obtained.

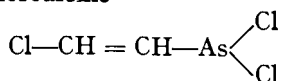
They are sparingly soluble in cold water or in dilute acids, but all—except trichlorovinyl arsine, which is insoluble in alcohol—dissolve readily in alcohol, benzene, kerosene, olive oil, petrol and other organic solvents.

¹ Detailed accounts of the best conditions for carrying out the reactions may be found in *Ind. Eng. Chem.*, 1923, 15, 290.

Chemically, they are unsaturated and unstable compounds. As Conant ¹ has pointed out, they all have a chlorine atom attached to that carbon of the vinyl group which is not adjacent to the arsenic atom. The following are therefore their correct names:

- β chlorovinyl dichloroarsine.
- $\beta\beta'$ dichlorovinyl chloroarsine.
- $\beta\beta'\beta''$ trichlorovinyl arsine.

(a) β Chlorovinyl dichloroarsine (M.Wt. 207.3)



PHYSICAL PROPERTIES

Chlorovinyl dichloroarsine when pure is a colourless liquid which boils at ordinary pressures at 190° C., with decomposition. At reduced pressure, however, it distils unchanged at the following temperatures :

MM. PRESSURE	B.P. ° C.
30	96-98 (Lewis and Perkins)
24	93-94 (Burton and Gibson) ²
15	79 (Lewis and Perkins)
12	77-78 (Wieland)
10	76 (Gibson and Johnson) ³
10	72 (Lewis and Perkins)

The melting point is +0.1° C. according to Gibson and Johnson, -13° C. according to Nekrassov, and -18.2° C. according to Libermann.

The odour of this substance recalls that of geraniums and is perceptible even at a dilution of 14 mgm. per cu. m. of air (Prentiss).

In the following table the specific gravity and corresponding specific volume are given at various temperatures :

Temperature (° C.)	S.G.	Specific Volume
0	1.9200	0.5232
10	1.9027	0.5255
15	1.8940	0.5279
20	1.8855	0.5302
25	1.8768	0.5328
30	1.8682	0.5352
40	1.8513	0.5401
50	1.8338	0.5453
60	1.8164	0.5505

¹ *Chemical Warfare Communications*, Offense Research Section of the U.S. Chemical Warfare Service (see *Ind. Eng. Chem.*, 1923, 15, 290).

² BURTON and GIBSON, *J. Chem. Soc.*, 1926, 464.

³ GIBSON and JOHNSON, *J. Chem. Soc.*, 1931, 754.

The vapour tension of β chlorovinyl dichloroarsine at temperature t may be calculated from the formula (see p. 5).

$$\log p = 9.123 - \frac{2781.69}{273 + t}$$

In the following table are given the values of the vapour tension at various temperatures :

Temperature ° C.	Vapour Tension MM. MERCURY
0	0.087
10	0.196
20	0.394
30	0.769
40	1.467
50	2.679
75	9.66
100	32.50
150	175.0
175	487.6

Following are the values of the volatility of β chlorovinyl dichloroarsine ¹ :

° C.	MGM. PER CU. M.
0	1,000
20	2,300
40	15,600

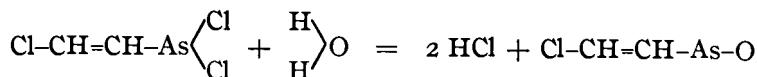
The latent heat of vaporisation is 57.9, the mean coefficient of thermal expansion between 0° C. and 50° C. is 0.00094 and the vapour density is 7.2.

It is readily soluble in benzene, absolute alcohol, olive oil, kerosene and other organic solvents. It is sparingly soluble in water (about 0.5 gm. in 1,000 ml.).²

CHEMICAL PROPERTIES

Owing to the unsaturated character of the molecule and the presence of two chlorine atoms attached to the arsenic atom, this substance is highly reactive.

Water. In contact with water, or with a damp atmosphere,³ β chlorovinyl dichloroarsine is rapidly decomposed even at ordinary temperatures, the following reaction taking place :

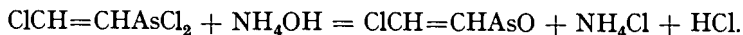


¹ SHIVER, *J. Chem. Education*, 1930, **7**, 108; VEDDER, *The Medical Aspects of Chemical Warfare*, Baltimore, 1925.

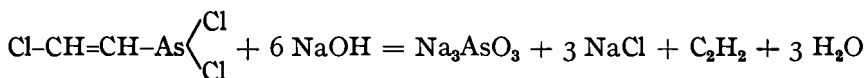
² S. NAMETKIN and W. NEKRASSOV, *Z. anal. Chem.*, 1929, **77**, 285.

³ LEWIS and PERKINS, *Ind. Eng. Chem.*, 1923, **15**, 290.

The degree of hydrolysis is notably increased by an increase in the temperature. The chlorovinyl arsenious oxide formed is a white, crystalline powder, sparingly soluble in water, alcohol and carbon disulphide and melting at 143° C. This oxide is also formed on treating β chlorovinyl dichloroarsine with aqueous ammonia solution :



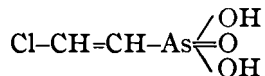
Alkalies. Alkalies completely decompose the molecule. Green and Price ¹ have shown that on adding even very dilute cold solutions of sodium hydroxide or carbonate, chlorovinyl arsenious oxide is never obtained, but acetylene and arsenious acid, as follows :



When a 15% sodium hydroxide solution is employed at temperatures below 37° C., this decomposition takes place quantitatively, and only in the case of β chlorovinyl dichloroarsine. This fact may be used for the quantitative determination of β chlorovinyl dichloroarsine in presence of dichlorovinyl chloroarsine and trichlorovinyl arsine (Lewis).

Halogens. The halogens readily react with chlorovinyl dichloroarsine. Thus on adding a dilute solution of bromine in carbon tetrachloride to a solution of β chlorovinyl dichloroarsine in the same solvent, the colour of the bromine gradually disappears while small lamellæ of a bromo-derivative separate. This melts at 122° C., and its formation has been suggested by Green and Price as a means of detecting chlorovinyl dichloroarsine.²

Nitric Acid. Chlorovinyl dichloroarsine, when treated with nitric acid, is oxidised to β chlorovinyl arsenic acid³



If concentrated nitric acid is employed, this oxidation is very violent and it is necessary to cool the reaction mixture. On the other hand, when dilute nitric acid is employed it is necessary to warm it in order to carry out the reaction. On standing, a colourless crystalline mass separates; this is β chlorovinyl arsenic acid which may be purified by recrystallisation from a

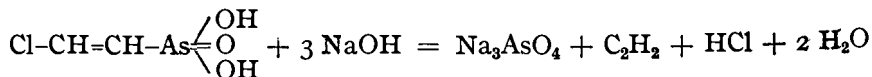
¹ GREEN and PRICE, *J. Chem. Soc.*, 1921, **119**, 448.

² GREEN and PRICE, *loc. cit.*

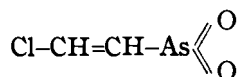
³ MANN and POPE, *J. Chem. Soc.*, 1922, **121**, 1754.

mixture of acetone and carbon tetrachloride. It forms needles, melts at 130° C. and is soluble in water and alcohol.

On warming this acid with a concentrated sodium hydroxide solution it is completely decomposed into acetylene, arsenic acid and hydrochloric acid :

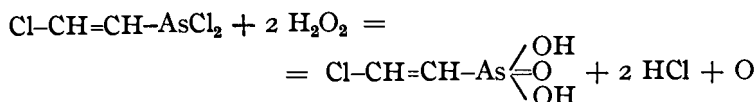


When it is heated *in vacuo* to 110° to 115° C., the acid loses a molecule of water and forms the corresponding anhydride :

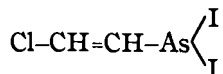


This anhydride is a white hygroscopic powder which decomposes violently at 242° C.

Hydrogen Peroxide. Chlorovinyl dichloroarsine reacts with hydrogen peroxide forming chlorovinyl arsenic acid, as with nitric acid ¹ :



Potassium Iodide. Potassium iodide reacts with β chlorovinyl dichloroarsine with evolution of heat and formation of β chlorovinyl diiodoarsine :



This iodo-derivative forms yellowish-brown crystals, m.p. 37.5° to 38.5° C. It is sparingly soluble in ligroin, but readily in alcohol and benzene.²

Hydrogen Sulphide. By the action of hydrogen sulphide on β chlorovinyl dichloroarsine in alcohol solution, the corresponding sulphide,³ ClCH = CHAsS, is formed. When pure, this forms a plastic mass insoluble in the usual organic solvents except carbon disulphide. It has a strong irritant action on the organism.⁴ A method of detecting chlorovinyl dichloroarsine is based on the formation of this sulphide ⁵ (see p. 328).

¹ WIELAND, *Ann.*, 1923, **431**, 38.

² W. LEWIS and H. STIEGLER, *J. Am. Chem. Soc.*, 1925, **47**, 2551.

³ KRETOV and coll., *J. Obscei Khim.*, Ser. A, 1931, **1**, 411.

⁴ LEWIS and STIEGLER, *loc. cit.*

⁵ S. NAMETKIN and W. NEKRASSOV, *Z. anal. Chem.*, 1929, **77**, 285

Diphenylamine. Chlorovinyl dichloroarsine reacts on heating with diphenylamine to form 10 chloro 5·10 dihydro phenarsazine¹:



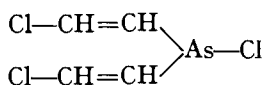
in canary-yellow crystals with melting point 191° to 193° C. (see p. 323). Pure β chlorovinyl dichloroarsine when kept in glass vessels is stable at ordinary temperatures, particularly in absence of light, while in presence of iron it is slowly converted into dichlorovinyl chloroarsine and trichlorovinyl arsine.

It does not attack steel appreciably and when stored in projectiles causes only a slight superficial rusting of the metal walls. However, it attacks lead slightly and is itself partially decomposed.

β Chlorovinyl dichloroarsine has an irritant action on the eyes and on the respiratory tract. The minimum concentration causing irritation is 0·8 mgm. per cu. m. of air; that is to say, less than can be detected by odour (Prentiss). The fatal concentration, according to Vedder, is 48 mgm. per cu. m. for 30 minutes' respiration. It also has a considerable vesicant action when allowed to remain in contact with the skin for a time.²

The lethal index is 1,500 according to Müller, and 1,200 for 10 minutes' exposure according to Prentiss.

(b) $\beta\beta'$ Dichlorovinyl Chloroarsine (M.Wt. 233·3)



PHYSICAL PROPERTIES

When pure, $\beta\beta'$ dichlorovinyl chloroarsine is a clear transparent liquid of a yellow or yellowish-brown colour. It boils at ordinary pressure at 230° C. with decomposition. The boiling points at reduced pressures are as follows³:

MM. MERCURY	° C.
11	113
15	119
30	136

The specific gravity at 20° C. is 1·702, and the vapour density 8·1.

¹ MILLER and coll., *J. Am. Chem. Soc.*, 1930, **52**, 4164; GIBSON, *J. Am. Chem. Soc.*, 1931, **53**, 376.

² H. BÜSCHER, *Grün- und Gelb-kreuz*, Hamburg, 1932, 150.

³ LEWIS and PERKINS, *loc. cit.*; WIELAND, *loc. cit.*; GRYSZKIEWICZ and coll., *Bull. soc. chim.*, 1927, **41**, 1750.

The vapour tension of $\beta\beta'$ dichlorovinyl chloroarsine may be calculated at any temperature t from the formula (see p. 5).

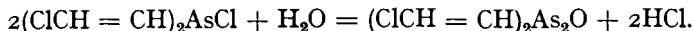
$$\log p = 9.983 - \frac{3295.3}{273 + t}$$

This substance is insoluble in dilute acids, but dissolves readily in alcohol and the common organic solvents.

CHEMICAL PROPERTIES

Like the preceding compound, this also shows great chemical reactivity owing to the unsaturated character of the molecule :

Water. Water hydrolyses it even at ordinary temperatures (Lewis and Perkins), the corresponding oxide being formed :



This forms crystals melting at 62° to 63° C., insoluble in water, sparingly soluble in cold alcohol, but soluble in hot alcohol, and in ether.

Alkalies. The alkalies decompose dichlorovinyl chloroarsine completely, forming acetylene and arsenious acid. This reaction, unlike the corresponding one with chlorovinyl dichloroarsine, takes place only above 37° C. and is never quantitative.¹

Nitric Acid. By the action of concentrated nitric acid on $\beta\beta'$ dichlorovinyl chloroarsine a crystalline product is obtained which melts at 97° to 99° C.; this is the nitrate of $\beta\beta'$ dichlorovinyl arsenic acid² : $(\text{ClCH} = \text{CH})_2\text{AsOOH} \cdot \text{HNO}_3$. This compound apparently does not ionise in solution, but when dissolved in aqueous alcohol and treated with sodium hydroxide solution until the nitric acid is neutralised, decomposition takes place. On extracting with chloroform and evaporating the extract, a crystalline mass remains which consists of dichlorovinyl arsenic acid (Mann and Pope), $(\text{CHCl} = \text{CH})_2\text{AsOOH}$. This is purified by recrystallisation from water or carbon tetrachloride, when it melts at 120° to 122° C. Like cacodylic acid, it is amphoteric, forming salts with acids as well as with bases.

According to Green and Price this reaction with nitric acid may be employed very conveniently for the identification of dichlorovinyl chloroarsine.

Hydrogen Peroxide. This arsine also is vigorously oxidised by hydrogen peroxide (Wieland). After evaporating the solution, dichlorovinyl chloroarsine remains as an oil which solidifies after

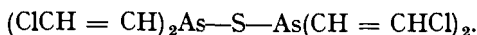
¹ LEWIS and PERKINS, *loc. cit.*

² MANN and POPE, *loc. cit.*

a time. It crystallises from hot water in brilliant prisms which melt at 120° to 122° C.

Potassium Cyanide. When an alcoholic solution of $\beta\beta'$ dichlorovinyl arsine is treated with potassium cyanide, it is converted into $\beta\beta'$ dichlorovinyl cyanoarsine,¹ $(\text{ClCH}=\text{CH})_2\text{AsCN}$, which is a colourless oil with a high toxicity (Liebermann).

Hydrogen Sulphide. When hydrogen sulphide is passed into a solution of dichlorovinyl chloroarsine in absolute alcohol an exothermic reaction takes place and dichlorovinyl arsenious sulphide is formed :

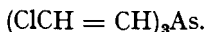


This is a viscous, yellowish-brown substance, soluble in alcohol, insoluble in water, having vigorous irritant properties on the mucous membranes and a nauseating odour (Lewis).

Chloramine-T. Treatment of dichlorovinyl chloroarsine with an equivalent amount of chloramine-T ($\text{CH}_3=\text{C}_6\text{H}_4-\text{SO}_2\text{Na}=\text{NCl}$) produces no additive-compound, unlike trichlorovinyl arsine.

The biological action of dichlorovinyl chloroarsine is similar to that of chlorovinyl dichloroarsine, but less violent.

(c) $\beta\beta'\beta''$ Trichlorovinyl arsine (M.Wt. 259.4)



PHYSICAL PROPERTIES

$\beta\beta'\beta''$ Trichlorovinyl arsine boils at atmospheric pressure at 260° C. with decomposition, but distils unaltered at 138° C. at 12 mm. pressure. On cooling, it solidifies in large crystals with m.p. 21.5° C.² It has a specific gravity at 1.572 at 20° C. and has a vapour density of 9.

The vapour tension at temperature t may be calculated from the following formula (see p. 5).

$$\log p = 9.159 - \frac{3312.4}{273 + t}$$

It is not miscible with water or with dilute acids, but dissolves readily in the common organic solvents except alcohol. It differs in this respect from the other two chlorovinyl arsines which are both soluble in all proportions in alcohol. This, and its melting point, may be used for its detection.

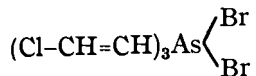
¹ LEWIS and STIEGLER, *J. Am. Chem. Soc.*, 1925, **47**, 2553.

² Various values for the melting point of this substance are quoted in the literature : 3° to 4° C. (Green and Price) ; 13° C. (Wieland) ; 23° C. (Pope).

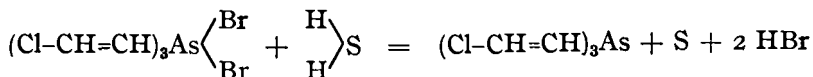
CHEMICAL PROPERTIES

Water. Trichlorovinyl arsine does not react with water and may be distilled in steam without any decomposition.

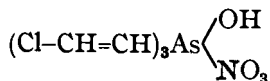
Halogens. On adding a solution of bromine in benzene to a benzene solution of trichlorovinyl arsine, cooled in a freezing mixture, small colourless needles separate, melting at 107°C . They consist of trichlorovinyl dibromo arsine (Mann and Pope) :



On treating this dibromo compound with hydrogen sulphide, it decomposes to form hydrobromic acid and trichlorovinyl arsine and deposit sulphur :

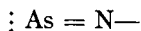


Nitric Acid. Concentrated nitric acid reacts vigorously with trichlorovinyl arsine, and in order to moderate the violence of the reaction, it is advisable to treat a small quantity of trichlorovinyl arsine (not more than 2 gm.) with an equal volume of nitric acid and warm cautiously. On allowing to cool, a colourless crystalline mass is deposited and when this is crystallised from chloroform, small needles, melting at 103°C . are obtained. This substance is trichlorovinyl hydroxyarsonium nitrate.

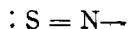


When this nitrate is treated with an aqueous solution of sodium hydroxide in equivalent quantity, the product extracted with chloroform and the solvent evaporated, a crystalline residue remains. This consists of trichlorovinyl arsenic oxide $(\text{ClCH}=\text{CH})_3\text{AsO}$. On crystallising this from benzene containing a little chloroform, long colourless needles are obtained melting at 154°C . with decomposition (Mann and Pope).

Chloramine-T. This tertiary arsine condenses with chloramine-T $(\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_2\text{Na}:\text{NCl})$ to give an additive compound of the formula $(\text{ClCH}=\text{CH})_3\text{As}=\text{N}-\text{SO}_2-\text{C}_6\text{H}_4-\text{CH}_3$. This contains the grouping



which according to Mann and Pope may be termed the "arsilimine" group, by analogy with the sulphilimine group



This compound may be obtained by treating an acetone solution of the tertiary amine (1 molecule) with chloramine-T (1 molecule) and boiling for 20 minutes. The product is filtered, the filtrate evaporated to dryness and the residue crystallised several times from ether. Colourless plates, melting at 124° C.

Unlike the previous two compounds, trichlorovinyl arsine has no irritant action on the skin or the respiratory organs.

(B) AROMATIC ARSINES

The aromatic arsines were first employed as war gases in July, 1917, by the Germans, and their use undoubtedly marked a considerable step in the progress of the chemical arm.

These arsines differ from those of the aliphatic series which have just been described, by their physical and chemical properties, and by their method of employment, as well as by their biological action. They are solids or liquids with high boiling points, have very low vapour tensions, are quite resistant to heating and are only oxidised by atmospheric oxygen with difficulty.

In order to obtain them sub-divided in the air they are employed dissolved in other war gases, or are filled into special containers so that they surround the bursting charge, or else are mixed with substances whose temperature of combustion is sufficiently high to cause the arsines to form a cloud (candles, generators, etc.). By these means disperse systems (aerosols) are formed in which the dispersed phase consists of extremely minute particles of the arsine. These remain suspended in the air for a considerable time and are not filtered out by activated carbon.

Physiologically, these compounds have a lower toxicity than the aliphatic arsines. However, they act as energetic sternutators and irritants, even at very low concentrations. This action is produced immediately after 1-2 minutes' exposure to concentrations of 0.2-0.5 mgm. substance per cu. m. of air.

During the war much diphenyl chloroarsine was employed. However, in May, 1918, it was largely substituted by diphenyl cyanoarsine by the Germans because of the superior physiological effects of the latter. Diphenyl cyanoarsine is considered as the most irritant substance employed during the war.

Since the war several other substances similar to diphenyl chloroarsine have been the subjects of experiments. For instance,

Diphenyl chlorostibine, white crystals melting at 68° C.,¹ and *diphenyl cyanostibine*, crystals melting at 115° to 116° C.² The

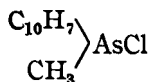
¹ MICHAELIS and GUENTER, *Ber.*, 1911, **44**, 2316.

² W. STEINKOPF and coll., *Ber.*, 1932, **65**, 409.

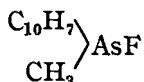
biological action of these substances is similar to that of the aromatic arsines described in this chapter.¹

Recently several arsenical derivatives of naphthalene have been prepared :

Naphthyl methyl chloroarsine :



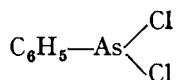
and *Naphthyl methyl fluoroarsine :*



The biological properties of these have not been reported in the literature.²

1. Phenyl Dichloroarsine

(M.Wt. 223)



Phenyl dichloroarsine was prepared in 1878 by La Coste and Michaelis³ by passing the vapours of benzene and arsenic trichloride through a heated tube. The product obtained was impure with the diphenyl compound and could be purified by distillation or crystallisation only with some difficulty. The same workers later studied another method for its preparation.⁴ This is more convenient and consists in heating mercury diphenyl to 250° C. with an excess of arsenic trichloride.

Phenyl dichloroarsine may also be obtained by heating triphenylarsine with arsenic trichloride in a closed tube to 250° C. for 30 hours⁵ :



or by heating phenyl mercuri-chloride with arsenic trichloride to 100° C. for 4-5 hours (Roeder and Blasi's method).⁶

LABORATORY PREPARATION

Roeder and Blasi's method, mentioned above, is usually employed for the preparation. 50 gm. mercuric acetate are dissolved in 50 ml. acetic acid in a thick-walled flask. 100 ml. benzene, free from thiophene, are added and the mixture heated

¹ FLURY, *Z. ges. expt. Med.*, 1921, **13**, 566.

² SPORZYNSKY, *Roczniki Chem.*, 1934, **14**, 1293.

³ LA COSTE and MICHAELIS, *Ber.*, 1878, **11**, 1883.

⁴ LA COSTE and MICHAELIS, *Ann.*, 1880, **201**, 196.

⁵ MICHAELIS and REESE, *Ber.*, 1882, **15**, 2876.

⁶ ROEDER and BLASI, *Ber.*, 1914, **47**, 2751.

for 5 hours in a boiling water-bath. After cooling, the insoluble part is filtered off and washed well with benzene, and the filtrate is evaporated to a small volume. Phenyl mercuri-chloride is thus obtained. 30 gm. of this are weighed into a flask, 100 gm. arsenic trichloride added and heated on the water-bath to 100° C. for 4-5 hours. A viscous suspension is formed first and then this is suddenly converted into a brown liquid, while crystals separate below. After filtration, the filtrate is distilled under reduced pressure. The excess of arsenic chloride passes over first and then, at a much higher temperature, the phenyl dichloroarsine.

PHYSICAL PROPERTIES

Phenyl dichloroarsine when pure is a colourless liquid which gradually turns yellow. At ordinary pressures it boils at 255° to 257° C. and at 14 mm. pressure at 124° C. At -20° C. it solidifies to a microcrystalline mass. The specific gravity is 1.654 at 20° C.

Its vapour tension at temperature t may be calculated from the formula :

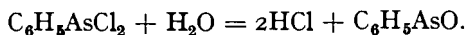
$$\log p = 9.150 - \frac{3164}{273 + t}$$

The vapour tension at 15° C. is 0.014 mm. and the volatility at 20° C. is 404 mgm. per cu. m. The coefficient of thermal expansion is 0.00073.

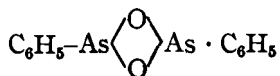
It is insoluble in water, but easily soluble in the common organic solvents.

CHEMICAL PROPERTIES

Water. Phenyl dichloroarsine on treatment with water is hydrolysed to phenyl arsenious oxide :



This forms crystals melting at 142° C.¹ and is insoluble in water and ether but soluble in alcohol, benzene and chloroform. A polymer of phenyl arsenious oxide is also formed, probably a dimer, of the formula ²

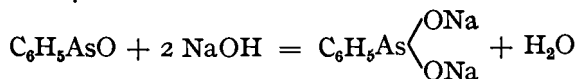


which forms crystals melting at 210° to 220° C.

¹ BLICKE, *J. Am. Chem. Soc.*, 1930, **52**, 2946.

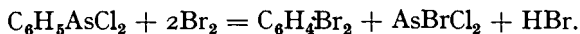
² STEINKOPF and coll., *J. prakt. Chem.*, 1934, **141**, 301.

Alkali Hydroxides. Phenyl dichloroarsine is also hydrolysed by the action of alkali hydroxide solutions. The phenyl arsenious oxide in presence of excess alkali is converted to the salt of the corresponding phenyl arsenious acid :

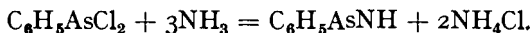


Halogens. With chlorine and phenyl dichloroarsine, an additive compound is formed, tetrachloro phenylarsine. This decomposes into phenyl arsenic acid in the presence of moisture.

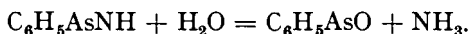
Bromine, however, forms no additive compound. By treatment of phenyl dichloroarsine with excess of bromine, the molecule is decomposed with formation of dibromobenzene, arsenic chlorobromide and hydrobromic acid,¹ as follows :



Ammonia. By the action of gaseous bromine on phenyl dichloroarsine in benzene solution, phenyl arsenimide² is obtained:

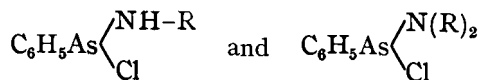


This forms crystals melting at 26.5° C. and decomposes rapidly with formation of phenyl arsenious oxide by the action of water or even on exposure to moist air :

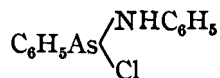


Phenyl arsenimide both dispersed in the air and in solution has a very irritant action on the skin.³

Amines. Primary and secondary amines, both of the aliphatic and aromatic series, react vigorously with phenyl dichloroarsine, giving compounds of the following types :



and liberating hydrochloric acid. With aniline, for example, a compound of the following structure is formed :



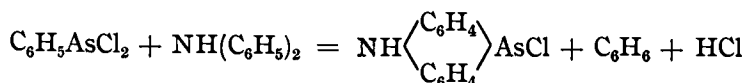
This is readily hydrolysed by the action of moisture forming phenyl arsenious oxide and aniline hydrochloride.

¹ RAIZISS and GAVRON, *Organic Arsenical Compounds*, New York, 1923, 115.

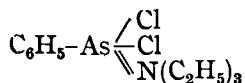
² MICHAELIS, *Ann.*, 1902, **320**, 291.

³ IPATIEV and coll., *Ber.*, 1929, **62**, 598.

With diphenylamine, 10 chloro 5·10 dihydro phenarsazine is formed ¹ :



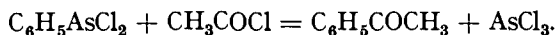
With tertiary aliphatic amines, additive products are formed ; triethylamine, for instance, forms :



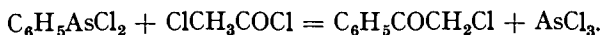
Hydrogen Sulphide. By the action of hydrogen sulphide on phenyl dichloroarsine in alcoholic solution, phenyl arsenious sulphide,² $\text{C}_6\text{H}_5\text{AsS}$, is produced in crystals melting at 152°C. ,² or 174° to 176°C. ³ This reaction is very sensitive, and as the sulphide obtained is insoluble in water, its formation may be employed to detect small quantities of the arsine (0·05 mgm. in 1 ml. water).

Silver Cyanide. By prolonged boiling (5 hours) of silver cyanide with phenyl dichloroarsine in benzene solution, phenyl dicyanoarsine,⁴ $\text{C}_6\text{H}_5\text{As}(\text{CN})_2$, is formed as crystals with an odour which is both aromatic and also resembles hydrocyanic acid. It melts at $78\cdot5^\circ$ to $79\cdot5^\circ \text{C.}$, and is readily decomposed by water or even by damp air, with formation of phenyl arsenious oxide and hydrocyanic acid.

Acid Chlorides. Phenyl dichloroarsine, when treated with the aliphatic acid chlorides, *e.g.*, acetyl chloride, in carbon disulphide solution and in presence of aluminium chloride, forms acetophenone and arsenic trichloride ⁵ :



With chloroacetyl chloride, chloroacetophenone is obtained ⁶ :



Dimethyl Arsine. With dimethyl arsine a white crystalline product, $\text{C}_6\text{H}_5\text{AsCl}_2 \cdot (\text{CH}_3)_2\text{AsH}$, is formed, which is readily decomposed by the action of moisture.⁷

¹ BURTON and GIBSON, *J. Chem. Soc.*, **1926**, 464 ; GIBSON, *J. Am. Chem. Soc.*, **1931**, **53**, 376.

² KRETOV, *J. Obscei Khim.*, Ser. A, **1931**, **1**, 411.

³ BLICKE, *J. Am. Chem. Soc.*, **1930**, **52**, 2946.

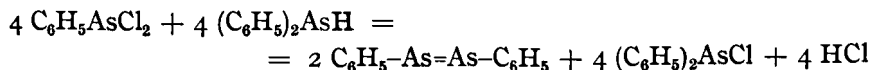
⁴ GRYSKIEWICZ and coll., *Bull. soc. chim.*, **1927**, **41**, 1323.

⁵ MALINOVSKY, *J. Obscei Khim.*, Ser. A, **1935**, **5**, 1355.

⁶ GIBSON and coll., *Rec. trav. Chim.*, **1930**, **49**, 1006.

⁷ DEHN, *J. Am. Chem. Soc.*, **1908**, **40**, 121.

Diphenyl Arsine. By the action of diphenyl arsine on phenyl dichloroarsine, arsenobenzene and diphenyl chloroarsine are formed ¹:



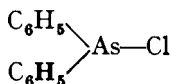
Pure phenyl dichloroarsine does not attack iron.

Phenyl dichloroarsine was employed during the war of 1914-18 first by the Germans as a solvent for diphenyl cyanoarsine and later by the French in admixture with 40% of diphenyl chloroarsine under the name of "*Sternite*."

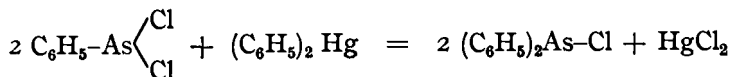
Phenyl dichloroarsine is a lung irritant, a vesicant ² and a lachrymatory. The maximum concentration which a normal man can support for not more than a minute is 16 mgm. per cu. m. of air (Flury). The mortality-product is 2,600 for 10 minutes' exposure (Prentiss).

2. Diphenyl Chloroarsine

(M.Wt. 264.5)



Diphenyl chloroarsine was prepared in 1880 by La Coste and Michaelis³ by heating mercury diphenyl with phenyl dichloroarsine:

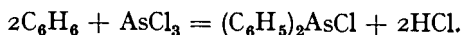


Its employment in September 1917 was a great surprise to the Allies because of its peculiar physical properties which enabled it, when properly dispersed in the atmosphere, to pass through the respirator-filters then in use.

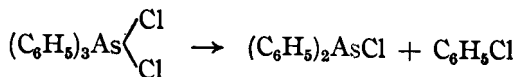
PREPARATION

Diphenyl chloroarsine may be prepared in various ways:

(1) By heating arsenic trichloride with benzene in presence of aluminium chloride:



(2) By the decomposition of dichlorotriphenyl arsine, obtained by the action of chlorine on triphenyl arsine:



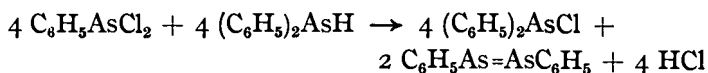
¹ BLICKE and POWER, *J. Am. Chem. Soc.*, 1932, **54**, 3353.

² HANZLICH, *loc. cit.*

³ MICHAELIS and LA COSTE, *Ann.*, 1880, **201**, 219.

(3) By the action of phenyl magnesium bromide on arsenious oxide. Triphenyl arsine is obtained at the same time.¹

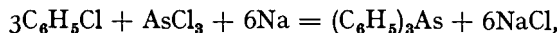
(4) By the reaction between phenyl dichloroarsine and diphenyl arsine² :



(5) By the action of arsenic trichloride on lead tetraphenyl in toluene solution³ :



During the war the Allies, in order to obtain rapid production of diphenyl chloroarsine, followed the method of Michaelis,⁴ modified by Morgan and Vining.⁵ This method consists in preparing triphenyl arsine from chlorobenzene and arsenic trichloride, in the presence of metallic sodium :



and then heating this substance with more arsenic trichloride :



The Germans, however, used an entirely different process (see p. 306), based on the reaction between the diazonium salts and sodium arsenite which Bart had studied for the first time in 1912.⁶

LABORATORY PREPARATION

The preparation of diphenyl chloroarsine in the laboratory⁷ is most conveniently carried out by Pope and Turner's⁸ modification of the method of Michaelis.

57 gm. sodium cut into slices are placed in a round-bottomed flask fitted with a reflux condenser and covered with 300 ml. benzene containing 1-2% ethyl acetate (which catalyses the reaction). After allowing this mixture to stand for $\frac{1}{2}$ hour (in order to activate the metal) 136 gm. chlorobenzene and 85% arsenic chloride are slowly added. After a few minutes the reaction is considerably accelerated, and if necessary the flask should be cooled externally with a freezing mixture. It is then

¹ Blicke and Smith, *J. Am. Chem. Soc.*, 1929, **51**, 1558.

² Blicke and Power, *J. Am. Chem. Soc.*, 1932, **54**, 3353.

³ Goddard and coll., *J. Chem. Soc.*, 1922, **121**, 978.

⁴ Michaelis and Reese, *Ber.*, 1882, **15**, 2876.

⁵ Morgan and Vining, *J. Chem. Soc.*, 1920, **117**, 780.

⁶ Bart, *D.R.P.* 250,264; Schmidt, *Ann.*, 1920, **421**, 159.

⁷ Nenitzescu, *Antigaz*, 1929, No. 2.

⁸ Pope and Turner, *J. Chem. Soc.*, 1920, **117**, 1447.

allowed to remain in the freezing mixture for 12 hours, being agitated during the first 2 hours. The contents are then filtered, the precipitate washed with hot benzene and the combined wash-liquid and filtrate distilled until the thermometer reaches 200° C. A yellow oil remains, consisting of triphenyl arsine, and, on cooling, this solidifies.

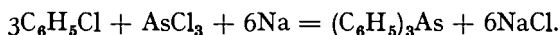
30 gm. of the triphenyl arsine obtained are weighed into a wide-mouthed vessel and heated to 350° to 360° C. while 25.5 ml. arsenic trichloride are introduced drop by drop from a tap-funnel with a capillary outlet. A dark brown product is formed and on distilling this under reduced pressure, diphenyl chloroarsine is obtained.

INDUSTRIAL MANUFACTURE

The Allied Method. The manufacture of diphenyl chloroarsine by the Allies, as indicated above, consisted of two main stages :

- (a) The preparation of triphenyl arsine.
- (b) The conversion of the triphenyl arsine into diphenyl chloroarsine.

(a) Preparation of Triphenyl Arsine. An attempt was at first made to use Michaelis's method for the industrial manufacture of triphenyl arsine, that is, the reaction of sodium with a mixture of arsenic trichloride and chlorobenzene to which a little ethyl acetate had been added to accelerate the reaction ¹ :



Various difficulties were encountered in the industrial application of this method, but these were in great part resolved by the modifications suggested first by Morgan and Vining and then by Pope and Turner.

The apparatus employed by Pope and Turner for the preparation of triphenyl arsine consists essentially of an iron reaction cylinder closed by an iron cover in which are fitted a thermometer, a mechanical agitator, a funnel, a condenser and a pipe connected with a vessel containing the sodium, which is covered with xylene.

In order to prepare triphenyl arsine, the arsenic trichloride, the chlorobenzene and the xylene are first mixed in a separate vessel, and of this mixture a half is introduced into the reaction chamber after diluting with more xylene.

The sodium container is heated to 110° C. and the reaction vessel is also warmed until it reaches about 70° C., when the fused sodium is added in small portions with constant stirring.

¹ PHILIPS, *Ber.*, 1886, 19, 1031.

After about 15 minutes the other half of the arsenic trichloride, chlorobenzene and xylene mixture is added.

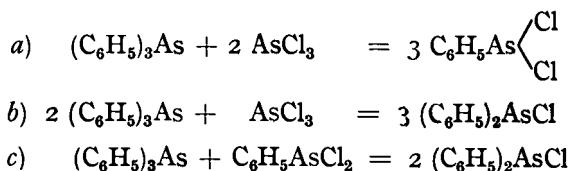
When all the sodium has been introduced, the agitation is continued until the temperature of the liquid tends to drop. At 60° C. it is filtered through a press, the filtrate being collected in a still where it is heated to 220° C. in order to remove the solvent and unreacted chlorobenzene. A liquid remains which on cooling solidifies to a bright yellow, crystalline solid consisting of triphenyl arsine.

By this method large quantities of triphenyl arsine may be prepared in a relatively pure condition and in a short time. But on the other hand it is somewhat inconvenient to have to work with molten sodium, which tends to solidify in the funnel through which it is introduced.

These inconveniences may be eliminated to a great extent by using Pope and Turner's modifications. The apparatus employed by these workers consists of a vessel fitted with a reflux condenser. The sodium, freed from grease, is placed in the same vessel to which is then added the arsenic trichloride and the chlorobenzene. Benzene is employed as the solvent instead of xylene ; as this boils at 80° C. it maintains the temperature constant at the most favourable point for the reaction.

By this method the reaction takes longer than by Morgan's method, but, on the other hand, it is easier to operate and gives a better yield of triphenyl arsine.

(b) Conversion of Triphenyl Arsine into Diphenyl Chloroarsine. This conversion was carried out first by Michaelis and Weber by heating the triphenyl arsine with the calculated quantity of arsenic trichloride in a closed tube for 10 hours at 250° C. These workers showed that the conversion takes place in three distinct stages :



which arrive at a stage of equilibrium. Morgan and Vining studied the reaction in order to find the optimum conditions for obtaining the highest yield of diphenyl chloroarsine. They proposed heating the mixture of triphenyl arsine and arsenic trichloride in a rotating autoclave at 250° to 280° C., with an internal pressure rising to 4.2-7 kgm. per sq. cm. (60-100 lb. per sq. in.). After 2 hours the heating is stopped and the product

distilled in a current of carbon dioxide at 20–30 mm. pressure. The following fractions are collected :

First fraction, 150° to 190° C., consists of a mixture of phenyl dichloroarsine and diphenyl chloroarsine.

Second fraction, 190° to 220° C., consists of diphenyl chloroarsine.

Third fraction, 220° to 250° C., consists of triphenyl arsine and diphenyl chloroarsine.

The residue consists chiefly of triphenyl arsine, which is extracted with chloroform and treated, after evaporating off the solvent, with phenyl dichloroarsine in an autoclave. About 60% of diphenyl chloroarsine is thus obtained.

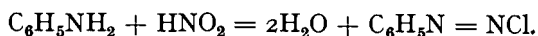
Pope and Turner have also determined the optimum conditions for carrying out this reaction. They recommend heating the triphenyl arsine in an open vessel to 350° C. and then allowing the arsenic chloride to enter from a tap-funnel terminating in a capillary tube.

The yield of diphenyl chloroarsine by this method, which has the advantage of being carried out at ordinary pressure instead of in an autoclave, as is necessary in Morgan's method, depends predominantly on the time employed in adding the arsenic trichloride.

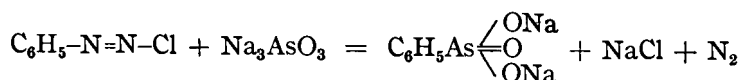
The English and French, employing the method of Michaelis, modified by Pope and Turner, succeeded in obtaining a mixture containing 60–65% diphenyl chloroarsine and 35–40% phenyl dichloroarsine, which was employed without further treatment.

German Method. The several steps in the manufacture by this method may be expressed as follows, according to Norris¹ :

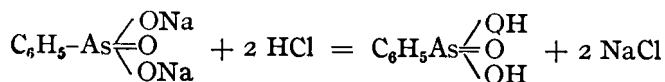
(i) Preparation of diazobenzene chloride from aniline and nitrous acid :



(ii) Reaction of diazobenzene chloride with sodium arsenite :



and formation of phenyl arsenic acid :



¹ NORRIS, *J. Ind. Eng. Chem.*, 1919, **11**, 817.

the calculated quantity of sodium nitrite. When the diazobenzene hydrochloride has been prepared, a solution of sodium arsenite is slowly run in. This latter is prepared beforehand by dissolving arsenious oxide in an aqueous sodium hydroxide solution which contains sufficient alkali to neutralise all the acid in the diazo solution and sufficient arsenious oxide to be 20% in excess of the theoretical quantity. 20 kgm. copper sulphate are also added to the diazotisation to accelerate the reaction.

The mixture is stirred continuously and maintained for 3 hours at 15° C., when sodium phenyl arsenate is formed. This is neutralised with hydrochloric acid and filtered through a press in order to separate resinous substances which are formed. The phenyl arsenic acid in the filtrate is reduced to phenyl arsenious oxide by passing a current of sulphur dioxide through. A heavy oil deposits at the bottom of the vessel and this is removed by decantation and redissolved in 40° Bè. sodium hydroxide solution. After diluting with 8 cu. m. of water, the solution is cooled to 15° C. and run slowly into another solution of diazobenzene chloride prepared as before. The sodium salt of diphenyl arsenic acid which is formed is slightly acidified with hydrochloric acid, the diphenyl arsenic acid filtered off and redissolved in 20° Bè. hydrochloric acid (1 part of the arsenic acid requires 3 parts of hydrochloric acid) and the solution obtained is then run into an iron vessel, lined internally with tiles. Sulphur dioxide is then passed through for 8 hours while the temperature is maintained at about 80° C. Diphenyl chloroarsine then separates as an oil which forms a layer at the bottom of the vessel. It is separated off and dried *in vacuo*.

PHYSICAL PROPERTIES

Crude diphenyl chloroarsine is a dark brown liquid which gradually turns into a semi-solid viscous mass.

In the pure state diphenyl chloroarsine forms colourless crystals which melt at 41° C. According to some authors it exists in two crystalline modifications, the stable one melting at 38·7° to 38·9° C. and the labile at 18·2° to 18·4° C.¹ The labile modification is easily converted into the stable form.²

¹ Somewhat differing values are reported in the literature for the melting point of diphenyl chloroarsine :

37° to 38° (LEWIS and coll., *J. Am. Chem. Soc.*, 1921, **43**, 891).

38° to 39° (STEINKOPF and coll., *Ber.*, 1928, **61**, 678).

38·5° to 39° (FROMM and coll., *Rec. trav. Chim.*, 1930, **49**, 623).

40° to 41° (GRYSZKIEWICZ and coll., *Bull. soc. chim.*, 1927, **41**, 570).

40° to 42° (BLICKE and coll., *J. Am. Chem. Soc.*, 1933, **55**, 1161).

44° (WALTON and coll., *J. Pharmacol.*, 1929, **35**, 241).

² GIBSON and VINING, *J. Chem. Soc.*, 1924, **125**, 909.

The boiling point at ordinary pressure in an atmosphere of carbon dioxide is 333° C. ; at reduced pressures the boiling points are as follows :

MM. MERCURY	° c.
5	161 (Steinkopf) ¹
10	180 (Herbst) ²
15	185 (Pope and Turner)
20	193 " "
30	205 " "
55	224 " "
102	245 " "

The vapour pressure of diphenyl chloroarsine at a temperature *t* may be calculated from the formula (see p. 5) :

$$\log p = 7.8930 - \frac{3288}{273 + t}$$

In the following table the values of the vapour pressure are given at various temperatures :

Temperature ° c.	Vapour Tension MM. MERCURY
0	0.0001
20	0.0005
25	0.0007
45	0.0036
55	0.0074
65	0.0146
75	0.0275

The volatility of diphenyl chloroarsine at ordinary temperatures is very low : at 20° C. it is 0.68 mgm. per cu. m., while at 98° C. it is 894 mgm. per cu. m. The specific heat is 0.217 calorie and the latent heat of volatilisation is 56.6 calories.

It has a coefficient of thermal expansion of 0.00075 and a specific gravity at 40° C. (solid) of 1.363 and at 45° C. (liquid) of 1.358.

It is only slightly soluble in water, 100 ml. dissolving less than 0.2 gm. However, it is readily soluble in carbon tetrachloride, phosgene, chloropicrin and phenyl dichloroarsine. In other solvents it dissolves in the following proportions :

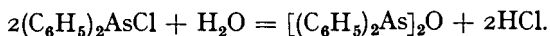
20 gm. in 100 ml. absolute alcohol
50 " " kerosene
100 " " benzene
14 " " olive oil

¹ STEINKOPF and coll., *Ber.*, 1928, **61**, 678.

² HERBST, *Kolloidchem. Beihefte*, 1926, **23**, 340.

CHEMICAL PROPERTIES

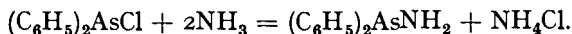
Water. Water hydrolyses diphenyl chloroarsine, forming diphenyl arsenious oxide (m.p. 92.5° to 93.5° C.) :



According to several authors¹ this reaction is slow at normal conditions of humidity, but is considerably accelerated when the arsine is brought into contact with aqueous or alcoholic solutions of the alkali hydroxides.²

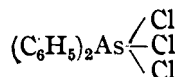
This hydrolysis is accelerated by the presence of olive oil or turpentine. In the latter case, some oxidation to diphenyl arsenic acid takes place (see p. 311).

Ammonia. With anhydrous ammonia and diphenyl chloroarsine in benzene solution, the following reaction takes place³ :

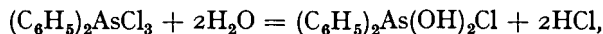


Diphenyl arsenamide forms needles melting at 53° C. It acts on the skin and on the mucous membranes both in solution and when dispersed in the air. On exposure to air, it is converted into diphenyl arsenious oxide (see above).

Chlorine. By the action of a solution of chlorine in carbon tetrachloride on a solution of diphenyl chloroarsine in chloroform, diphenyl trichloroarsine⁴ is formed, as crystals melting at 189° C. :



This trichloro- derivative on treatment with cold water forms first the chloride of diphenyl arsenic acid :



which is rapidly converted into diphenyl arsenic acid.⁵ According to Meyer, diphenyl trichloroarsine has no toxic power. Chlorine water also oxidises diphenyl chloroarsine to diphenyl arsenic acid.⁶

Bromine. Bromine, in chloroform solution, reacts with diphenyl chloroarsine also dissolved in chloroform, forming different products according to the amount of bromine: either diphenyl chloroarsine bromide, $(\text{C}_6\text{H}_5)_2\text{AsCl} \cdot \text{Br}_2$, yellow needles melting

¹ LIBERMANN, *loc. cit.*

² RONA, *Z. ges. expt. Med.*, 1921, **13**, 16.

³ IPATIEV and coll., *Ber.*, 1929, **62**, 598.

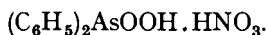
⁴ LA COSTE and MICHAELIS, *Ann.*, 1880, **201**, 222.

⁵ KAPPELMEYER, *Rec. trav. Chim.*, 1930, **49**, 79.

⁶ MICHAELIS, *Ann.*, 1902, **321**, 141.

at about 158° C., and soluble with partial decomposition in benzene¹; or diphenyl chloroarsine perbromide, $(C_6H_5)_2AsCl.Br_4$, orange-red prisms melting at 146° to 150° C. These halogenated derivatives lose the atoms of bromine which they contain on exposure to moist air.

Nitric Acid. Diphenyl chloroarsine on heating to about 40° C. with concentrated nitric acid is oxidised to diphenyl arsenic acid, $(C_6H_5)_2AsOOH$. This forms colourless crystals melting at 175° C. which are sparingly soluble in hot water, alkalis and alcohol. It is not decomposed by nitric acid, nor by boiling chromic acid. The copper and lead salts of diphenyl arsenic acid are very sparingly soluble in water, even at 100° C. Diphenyl arsenic acid dissolves in nitric acid, forming a nitrate of the formula :



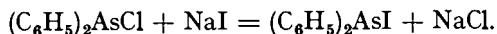
Hydrochloric Acid. On boiling diphenyl chloroarsine with hydrochloric acid, arsenic trichloride and triphenyl arsine are formed,² as follows :



Chlorosulphonic Acid. Diphenyl chloroarsine, on treatment with chlorosulphonic acid forms, besides benzene sulphonyl chloride, a chloride of diphenyl arsenic acid having the formula³ $(C_6H_5)_2AsOOH.HCl$, which forms prisms and melts at 130° C.

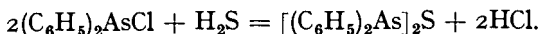
Fluorosulphonic Acid. This converts diphenyl chloroarsine into benzene sulphonyl fluoride and the sulphate of diphenyl arsenic acid, $2(C_6H_5)_2AsOOH.H_2SO_4$, melting at 117° C.

Sodium Iodide. By the action of sodium iodide on diphenyl chloroarsine dissolved in acetone, diphenyl iodoarsine⁴ is obtained :



This forms brilliant yellow crystals with m.p. 40.5° C. (or, according to Blicke,⁵ 41° to 42° C.), insoluble in water, difficultly soluble in cold alcohol, but readily soluble in hot alcohol, ether, acetone, benzene, etc.

Hydrogen Sulphide. On bubbling sulphuretted hydrogen through an alcoholic solution of diphenyl chloroarsine, diphenyl arsenious sulphide⁶ is formed :



¹ RASUVAJEV, *Ber.*, 1931, **64**, 120.

² RASUVAJEV and coll., *J. Obscei Khim.*, Ser. A, 1932, **2**, 529.

³ STEINKOPF, *Ber.*, 1928, **61**, 678.

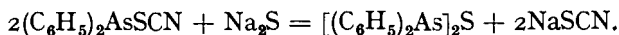
⁴ STEINKOPF and SCHWEN, *Ber.*, 1921, **54**, 1459.

⁵ BLICKE, *loc. cit.*

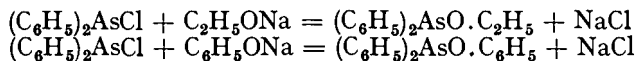
⁶ RAIZISS and GAVRON, *Organic Arsenical Compounds*, New York, 1923, 216.

This forms white acicular crystals at 67° C. It is readily soluble in benzene, carbon disulphide and chloroform, but sparingly in alcohol and ether. This sulphide may also be obtained by the action of sodium sulphide on diphenyl chloroarsine in benzene solution ¹; on treatment with mercuric cyanide or silver cyanide, diphenyl cyanoarsine is obtained (see p. 314).

Sodium Thiocyanate. By the action of sodium thiocyanate dissolved in acetone on diphenyl chloroarsine dissolved in the same solvent, diphenyl thiocyanatoarsine is formed, ² (C₆H₅)₂AsSCN, an oily, pale brown substance which is miscible in all proportions with benzene and acetone and which decomposes with water, giving up the SCN group. It boils at 230° to 233° C. at 22–23 mm. mercury pressure. It reacts quantitatively with sodium sulphide ³:

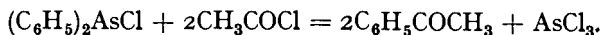


Sodium Alcoholate or Phenate. Sodium alcoholate and phenate react with diphenyl chloroarsine as follows ⁴:

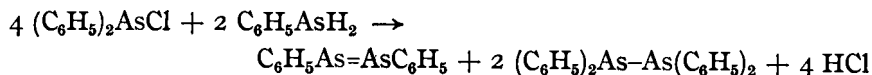


Methyl Iodide. On heating diphenyl chloroarsine with methyl iodide to 100° C. in a closed tube, a mixture of diphenyl iodoarsine (see p. 311) and dimethyl diphenyl arsonium triiodide, ⁵ (CH₃)₂(C₆H₅)₂AsI₃, is obtained.

Acyl Chlorides. When diphenyl chloroarsine is treated with one of the aliphatic acyl chlorides, like acetyl chloride, dissolved in carbon disulphide and in presence of aluminium chloride, acetophenone and arsenic trichloride are formed ⁶:



Phenyl Arsines. When diphenyl chloroarsine is treated with (mono)phenyl arsine in an atmosphere of nitrogen or carbon dioxide, ⁷ arsenobenzene and tetraphenyl diarsine are formed ⁸:



¹ MORGAN and VINING, *J. Chem. Soc.*, 1920, **117**, 777.

² STEINKOPF and W. MIEG, *Ber.*, 1920, **53**, 1013.

³ PANCENKO and coll., *J. Obscei Khim.*, Ser. A, 1932, **2**, 193.

⁴ MICHAELIS, *Ann.*, 1902, **321**, 143.

⁵ STEINKOPF and SCHWEN, *Ber.*, 1921, **54**, 1458.

⁶ MALINOVSKY, *J. Obscei Khim.*, Ser. A, 1935, **5**, 1355.

⁷ STEINKOPF and DUDEK, *Ber.*, 1929, **62**, 2494.

⁸ BLICKE and coll., *J. Am. Chem. Soc.*, 1932, **54**, 3353.

Tetraphenyl diarsine, or phenyl cacodyl, is also formed by the action of diphenyl arsine in ethereal solution on diphenyl chloroarsine. It forms crystals melting at 124° to 127° C. (Blicke).

Chloramine-T. Diphenyl chloroarsine reacts with chloramine-T in presence of water to form diphenyl arsenic acid,¹ which consists of needles melting at 175° C. (see p. 311).

When diphenyl chloroarsine is heated, it remains unchanged until a temperature of 300° to 340° C. is reached, when it becomes dark brown and on analysis it is found to have decomposed slightly.

It is not sensitive to detonation and may be employed in projectiles. It has no corrosive action on metals such as iron, lead, etc.

Owing to its low vapour tension, it is necessary, in order to utilise it as a war gas, to disperse it in the air as an aerosol which contains a high proportion of particles of diameter about 10^{-4} to 10^{-5} cm. Such a fine state of subdivision can be obtained, according to Prentiss, either by spraying solutions of diphenyl chloroarsine in certain solvents, such as phosgene, phenyl dichloroarsine, etc., this method being employed during the war, or by dispersing it by means of explosive charges. In the latter case, the time of detonation is too short for an appreciable quantity of heat to be transmitted to the diphenyl chloroarsine, and the actual dispersion is mainly due to the physical force of the explosion.

In order to attain the degree of subdivision of diphenyl chloroarsine, diphenyl cyanoarsine or phenarsazine chloride which has been mentioned above, it is first necessary to volatilise the substance by some method and then to allow the vapour to condense in the air. This is carried out by means of the so-called "*irritant candles.*"

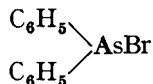
Both in the solid state and the liquid state, and even in the form of vapour, diphenyl chloroarsine causes the formation of small vesicles on the skin.² The minimum concentration causing nasal irritation is 0.1 mgm. per cu. m., according to Müller, and 0.5 mgm. per cu. m. according to Prentiss. The maximum concentration which a normal man can support for at most 1 minute is 1-2 mgm. per cu. m. (Flury and Zernick). The mortality-product is 4,000 according to Müller, but Prentiss gives 15,000 for 10 minutes' exposure.

¹ BURTON and GIBSON, *J. Chem. Soc.*, 1924, **125**, 2275.

² HANZLIK, *loc. cit.*

3. Diphenyl Bromoarsine

(M.Wt. 309)



This substance was prepared in 1880 by La Coste and Michaelis,¹ but was tested as a war gas only in the post-war period.

PREPARATION

According to Steinkopf² it may be obtained in the laboratory by heating 35 gm. diphenyl arsenious oxide with more than 1 gramme-molecule of hydrobromic acid to 115° to 120° C. for 4 hours.

Industrially, diphenyl bromoarsine is prepared by methods similar to those described above for the preparation of the chloro-compound. That is to say, by the action of arsenic tribromide on triphenyl arsine at 300° to 350° C. or else by the diazotisation method, using hydrobromic acid instead of hydrochloric acid.

PHYSICAL AND CHEMICAL PROPERTIES

Diphenyl bromoarsine forms white crystals and melts at 54° to 56° C. Its chemical properties are similar to those of diphenyl chloroarsine.

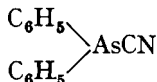
Treated with a solution of chlorine in carbon tetrachloride, yellow crystals separate on cooling and these consist of bromo dichloro diphenyl arsine, $(\text{C}_6\text{H}_5)_2\text{AsCl}_2\text{Br}$, and melt at 109° to 116° C.³

By the action of bromine on diphenyl bromoarsine in chloroform, diphenyl tribromoarsine is formed. This has the formula $(\text{C}_6\text{H}_5)_2\text{AsBr}_3$, and forms yellow crystals which melt at 126° C. Excess of bromine forms the perbromide, $(\text{C}_6\text{H}_5)_2\text{AsBr}_5$, orange-red crystals which begin to melt at 115° C.³

Diphenyl bromoarsine has similar physiopathological properties to the corresponding chloro-compound, but a milder aggressive action.

4. Diphenyl Cyanoarsine

(M.Wt. 255)



Diphenyl cyanoarsine was first prepared by Sturniolo and Bellinzoni.⁴

¹ LA COSTE and MICHAELIS, *Ann.*, 1880, **201**, 230.

² STEINKOPF and SCHWEN, *Ber.*, 1921, **54**, 1458.

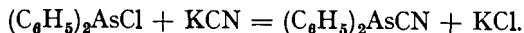
³ KAPPELMEYER, *Rec. trav. Chim.*, 1930, **49**, 77.

⁴ STURNIOLO and BELLINZONI, *Boll. Chim. Farm.*, 1919, **58**, 409.

It was employed as a war gas towards the end of the war (May, 1918) both alone and mixed with diphenyl chloroarsine.

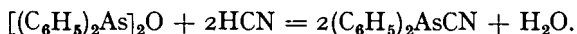
PREPARATION

This substance was made during the war ¹ by heating potassium cyanide with diphenyl chloroarsine :



However, it was later ² discovered that this method of preparing diphenyl cyanoarsine had the disadvantage that the product is sensitive to alkaline reagents such as sodium or potassium cyanide.

In the other methods worked out since the war, diphenyl cyanoarsine is prepared by treating diphenyl arsenious oxide with hydrocyanic acid, or by treating either diphenyl chloroarsine or diphenyl arsenious sulphide with the cyanide of a heavy metal. The reaction between hydrocyanic acid and diphenyl arsenious oxide may be carried out at the ordinary temperature ³ or by treatment in a closed tube at 100° C. for 2 hours ⁴ :



The reaction with the heavy metal cyanides may be brought about either by treating diphenyl chloroarsine at 150° to 160° C. for 3 hours with dry, recently prepared silver cyanide, or by the treatment of diphenyl arsenious sulphide with mercuric cyanide for 2 hours at 160° to 200° C. ⁵

LABORATORY PREPARATION

The preparation of diphenyl cyanoarsine in the laboratory may be carried out by the action of potassium cyanide on diphenyl chloroarsine.

4.5 gm. potassium cyanide are dissolved in 20–25 ml. water in a 100 ml. flask and 15 gm. diphenyl chloroarsine are added in small portions with continuous stirring. The reaction is exothermic and the flask should be cooled externally with water so as to maintain the internal temperature at 40° to 45° C. When the temperature commences to fall, the product is allowed to stand. An oil separates at the bottom of the flask and is washed with water and allowed to crystallise by cooling. The product obtained is

¹ NORRIS, *J. Ind. Eng. Chem.*, 1919, **11**, 826.

² MCKENZIE and WOOD, *J. Chem. Soc.*, 1920, **117**, 406 ; NENITZESCU, *Antigaz*, 1929, Nos. 2 and 3.

³ MCKENZIE and WOOD, *J. Chem. Soc.*, 1920, **117**, 413.

⁴ STEINKOPF and SCHWEN, *Ber.*, 1921, **54**, 1460.

⁵ MORGAN and VINING, *J. Chem. Soc.*, 1920, **117**, 777.

further purified by distillation under reduced pressure. The yield of diphenyl cyanoarsine by this method is 80–90% of the theoretical.

Steinkopf's method¹ gives higher yields :

10 gm. of diphenyl arsenious oxide and 6 gm. anhydrous hydrocyanic acid (*i.e.*, five times the theoretical amount) are placed in a glass tube, which is then sealed in the flame. The mixture is then heated for 2 hours at 100° C. The residue is then extracted with ether after cooling, the ether distilled off and the product which remains fractionally distilled at reduced pressure (13–15 mm.).

INDUSTRIAL MANUFACTURE

In Germany, according to Norris, diphenyl cyanoarsine was prepared by treating diphenyl chloroarsine with a concentrated aqueous solution of potassium cyanide and heating to 60° C. A 5% excess of the cyanide was employed and the reaction mixture stirred continuously.

PHYSICAL PROPERTIES

Diphenyl cyanoarsine forms colourless prisms with an odour of mixed garlic and bitter almonds. It melts at 35° C. (Sturniolo), at 32° to 34° C. (McKenzie), at 31.5° C. (Steinkopf). It boils at 213° C. at 21 mm. mercury pressure and at 200° to 201° C. at 13.5 mm. At 760 mm. the boiling point is calculated from the vapour pressure curve to be 377° C.² The specific gravity is 1.45.

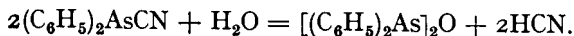
The vapour pressure is very low and at 20° C. is only 0.0002 mm. mercury. The volatility at the same temperature is 0.1–0.15 gm. per cu. m. of air.

Diphenyl cyanoarsine is sparingly soluble in water, but dissolves readily in alcohol, benzene, chloroform, ether and ligroin.

CHEMICAL PROPERTIES

Like diphenyl chloroarsine, diphenyl cyanoarsine is not very stable and its arsenic atom has a tendency to change from the trivalent to the pentavalent state.

Water. Atmospheric moisture decomposes diphenyl cyanoarsine slowly, hydrocyanic acid and diphenyl arsenious oxide being formed :



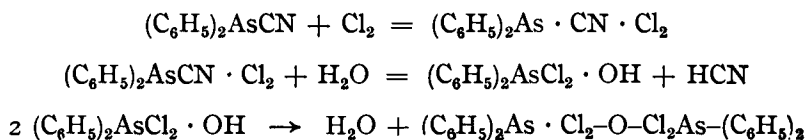
¹ STEINKOPF, *Ber.*, 1921, 54, 1460.

² HERBST, *Kolloidchem. Beihfte*, 1926, 23, 340.

This decomposition takes place more rapidly with hot water, or with aqueous or alcoholic solutions of the alkalis.

The conversion of diphenyl cyanoarsine into diphenyl arsenious oxide may be attained also by steam distillation. The oxide consists of crystals which are sparingly soluble in water, but soluble in alcohol, ether, chloroform; the melting point is 92° to 93° C.

Chlorine. Diphenyl cyanoarsine in benzene solution is converted by chlorine into a compound melting at 115° C. which, according to McKenzie, appears to be anhydride of tetraphenyl tetrachloro arsenic acid, $[(C_6H_5)_2AsCl_2]_2O$. The reaction is as follows :



This compound fumes in air and from its aqueous solution diphenyl arsenic acid separates on cooling.

Oxidising Agents. When diphenyl cyanoarsine, cooled in a water-bath, is treated with nitric acid, with 2% hydrogen peroxide or with bromine water, it is oxidised to diphenyl arsenic acid, $(C_6H_5)_2AsOOH$ which forms acicular crystals melting at 175° C. The alkali salts of this acid are readily soluble; the iron compound is a white powder which decomposes on heating.¹

Methyl Iodide. By the action of methyl iodide on diphenyl cyanoarsine, by heating in a closed tube for 6 hours at 100° C., diphenyl methyl arsonium iodide and triiodide are obtained. The latter crystallises in violet needles which melt at 69° C. and are insoluble in water and in ether.

Diphenyl cyanoarsine has such a low vapour pressure that it must be diffused as a particulate smoke in the air, in the same way as diphenyl chloroarsine. Its behaviour to active carbon is due to this state of extreme subdivision. Layers of animal or vegetable fibres, properly treated and washed, form an efficient filter.

The minimum concentration of diphenyl cyanoarsine detectable by odour is 0.01 mgm. per cu. m. according to Lindemann and 0.005 mgm. per cu. m. according to Meyer.

A normal man can support a maximum concentration of 0.25 mgm. per cu. m. of air for not more than 1-2 minutes (Flury).

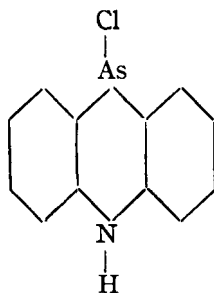
¹ G. STURNIOLO and G. BELLINZONI, *Boll. chim. farm.*, 1919, **58**, 409; *Gazz. chim. ital.*, 1919, **49**, 326.

The mortality-product is 4,000 according to Müller, or for 10 minutes' exposure according to Prentiss, 10,000.

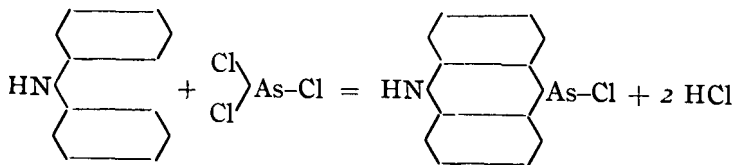
(C) HETEROCYCLIC ARSINES

The study of the heterocyclic arsines (*i.e.*, those containing the atom of arsenic in the nucleus) may be said to have commenced only during the war of 1914-18 and led to the discovery of substances whose military value is equal, or according to some authorities superior, to that of the aromatic arsines. Among these substances "*Adamsite*" has claimed most interest, particularly because of the simplicity of its method of preparation.

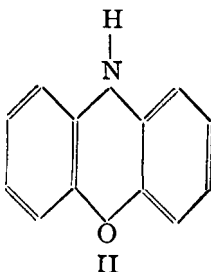
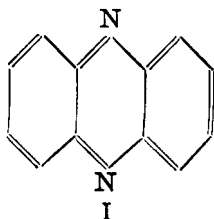
This substance, also known as "*diphenylamine chloroarsine*," has the following structure :



which has been confirmed by its mode of formation from arsenic trichloride and diphenylamine :



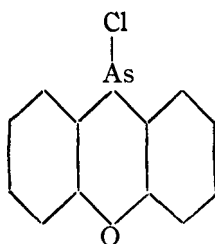
By analogy with other classes of substances of similar constitution, such as phenazine (I) and phenoxazine (II) :



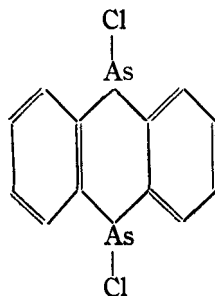
it may be accurately described as 10 chloro 5,10 dihydrophenarsazine, or, more briefly, as phenarsazine chloride.

Various analogous and homologous compounds of phenarsazine chloride have been studied.¹ Among the more important may be mentioned *phenarsazine bromide*, obtained by the action of arsenic bromide on diphenylamine,² *phenarsazine iodide*³ and *phenarsazine fluoride*,⁴ as well as *phenarsazine cyanide*.⁵ All these compounds have toxic properties similar to those of phenarsazine chloride.⁶

Substances of analogous types to that of the phenarsazine derivatives have also been prepared. Lewis⁷ first, and later Turner⁸ prepared *phenoxarsine chloride* (6 chlorophenoxarsine) :



Kalb⁹ prepared *arsanthrene chloride* :



These substances, which are very similar in properties to phenarsazine chloride, have the drawback that their preparation is in each case very laborious.

¹ BURTON and GIBSON, *J. Chem. Soc.*, **1924**, 2275 ; **1926**, 464 ; C. NENITZESCU, *Antigaz*, 1929, Nos. 2-3.

² BAYER, *D.R.P.* 281049.

³ RASUVAJEV and BENEDIKTOV, *Ber.*, 1930, **63**, 346.

⁴ GIBSON and coll., *Rec. trav. Chim.*, 1930, **49**, 1006.

⁵ GRYSKIEWICZ and coll., *Bull. soc. chim.*, 1927, **41**, 1323.

⁶ GIBSON and JOHNSON, *J. Chem. Soc.*, **1931**, 2518.

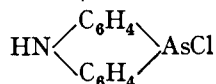
⁷ LEWIS, *J. Am. Chem. Soc.*, 1921, **43**, 892.

⁸ TURNER, *J. Chem. Soc.*, 1925, **127**, 544.

⁹ KALB, *Ann.*, 1921, **423**, 63.

Phenarsazine Chloride (*Adamsite*)

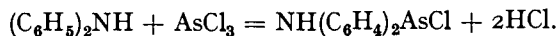
(M.Wt. 277.5)



According to Hanslian this substance was prepared in Germany by Wieland¹ in 1915, and independently in January, 1918, by Adams (whence its name of Adamsite). However, the recognition of the importance of this substance as a war gas must be attributed solely to the English and Americans who studied its chemical and biological properties.

PREPARATION

Wieland² obtained phenarsazine chloride by treating diphenylamine with arsenic chloride :

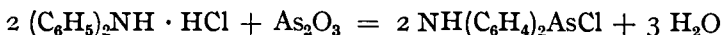
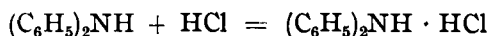


It may also be obtained by the following methods :

(a) By heating diphenyl hydrazine with arsenic trichloride.³

(b) By boiling aniline with arsenic trichloride, then adding sodium hydroxide, and treating the oxide obtained with hydrochloric acid.⁴

(c) By treatment of fused diphenylamine with concentrated hydrochloric acid and then mixing with arsenious oxide⁵ :

LABORATORY PREPARATION⁵

Contardi's method is used : this involves the treatment of diphenylamine with arsenious oxide :

42 gm. diphenylamine and 21 ml. hydrochloric acid (S.G. 1.19) are placed in a porcelain dish of about 300 ml. capacity and heated with constant stirring until all the water has been driven off. Diphenylamine hydrochloride is obtained as a white powder ; it is dried for 2-3 hours at 50° to 60° C. It is mixed with 25 gm. arsenious oxide and melted with continuous stirring. When the whole mixture is molten, the temperature is gradually raised ; at 140° C. the reaction becomes vigorous and water vapour is evolved. After 3-4 hours the temperature rises to 200° C. and

¹ Elberfelder Farbenfabrik. Bayer, *D.R.P.* 281049.

² WIELAND and RHEINHEIMER, *Ann.*, 1921, 423, 12.

³ LEWIS and HAMILTON, *J. Am. Chem. Soc.*, 1921, 43, 2218.

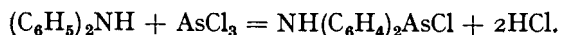
⁴ BURTON and GIBSON, *J. Chem. Soc.*, 1926, 450.

⁵ CONTARDI, *Giorn. Chim. Appl.*, 1920, 1, 11.

the evolution of water vapour ceases: the reaction may then be considered as complete. The product obtained is purified by crystallisation from xylene. Yield is almost theoretical.

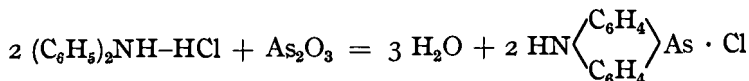
INDUSTRIAL MANUFACTURE

American Method. The process used by the Americans at Edgewood Arsenal for the manufacture of phenarsazine chloride is based on the reaction of diphenylamine with arsenic chloride :



Operating Details. 642 kgm. diphenylamine are first heated to 150° C. in a large jacketed kettle fitted with an agitator and a reflux condenser. 730 kgm. arsenic trichloride (that is, 10% excess over theoretical) are added and the heating continued for 5 hours. During the course of the reaction, the temperature rises to 250° C., and large quantities of hydrochloric acid are evolved. This passes through the condenser and is absorbed in water in a special absorption tower. At the end of the reaction, the product obtained is transferred to a vessel containing water where it is washed, then centrifuged and dried at 30° C. Yield 80%.

Italian Method. During the war, Professor Contardi proposed a method of preparation much more simple than the American process just described. In studying a new process for manufacturing diphenylamine, he observed that the hydrochloride of this base is completely dissociated into hydrochloric acid and diphenylamine when heated to slightly over 100° C. He studied the possibility of using this reaction to prepare **phenarsazine** chloride by starting from arsenious oxide and diphenylamine hydrochloride, instead of arsenic trichloride and diphenylamine. The equation of this reaction is as follows :



In order to prepare phenarsazine chloride by this method it is sufficient to mix diphenylamine hydrochloride with arsenious oxide and heat to 130° C. After the mixture is melted, the temperature is gradually raised to 200° C. When the evolution of water ceases, the reaction is complete. Yield 95% of the theoretical.

Fig. 18 shows a diagram of the plant proposed by Professor Contardi for the industrial preparation of phenarsazine chloride.

The reaction is carried out in the cast iron kettle *A*, which holds 7.5 litres and is fitted with the helical agitator *B* which imparts an ascending motion to the mass, so that a homogeneous distribution of the particles in the liquid is obtained. The kettle is closed at the top with a lid, in the centre of which is the agitator gear, and which also has a charging hole *C* for the diphenylamine hydrochloride and arsenious oxide. Above this hole a hopper is fitted. A stuffing-box also passes through the lid, supporting the thermometer *T* which indicates the temperature of the reaction mixture. At the bottom of the kettle is a tube of 10 cm. diameter closed with a plug valve *D*; through this the product is discharged. The kettle is surrounded by the walls *L* and is heated by means of the three heating coils *f*, *f'*, *f''*.

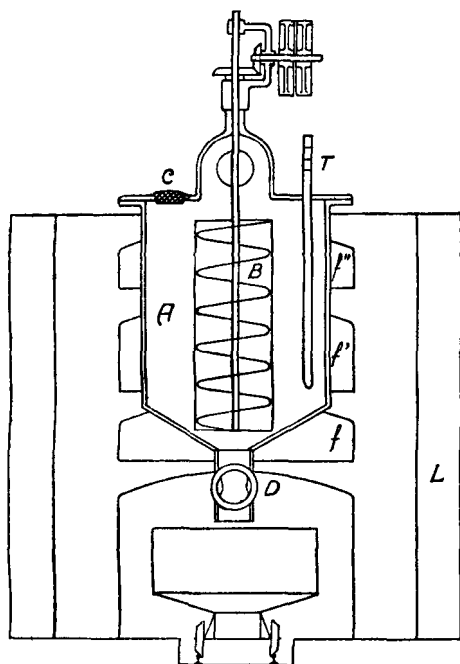


FIG. 18.

At the bottom of the kettle is a tube of 10 cm. diameter closed with a plug valve *D*; through this the product is discharged. The kettle is surrounded by the walls *L* and is heated by means of the three heating coils *f*, *f'*, *f''*.

With a battery of four kettles of this description, it is possible to make 6 tons of phenarsazine chloride by this method in 24 hours.

This process differs from the American method more particularly in saving a considerable proportion of the hydrochloric acid (more than two-thirds) and of the arsenious oxide, and also makes it unnecessary to prepare arsenic trichloride. Moreover, all the difficulties attendant on the necessity for utilising or disposing of the large quantities of arsenical products which are invariably obtained in the American process are obviated.

PHYSICAL PROPERTIES

Phenarsazine chloride in the crude state is a crystalline solid, dark green or sometimes brown in colour. It may be obtained in the pure condition by crystallisation, or, better, by vacuum sublimation. It is then of a canary-yellow colour with a melting

point of 189° to 190° C. (Burton and Gibson), 191° to 193° C. (Rasuvajev), 192.5° (Tanner),¹ or 193° to 195° C. It is practically odourless at ordinary temperatures. It has been shown recently that phenarsazine chloride, like diphenyl chlorarsine, can exist in two modifications :

A stable orthorhombic form which melts at 195° C., and a metastable form which is partly monoclinic and melts at 186° C. and partly triclinic, melting at 182° C.²

The boiling point calculated from the vapour tension curve is 410° C.

The specific heat is 0.268 calorie and the heat of volatilisation 54.8 calories.

The volatility at ordinary temperatures is low : at 20° C. it is only 0.02 mgm. per cu. m. of air.

The vapour tension at various temperatures is given in the following table :

Temperature °C	Vapour Tension MM. MERCURY
0	5×10^{-16}
20	2×10^{-13}
40	2×10^{-11}
100	2×10^{-6}
150	0.003

The specific gravity at 20° C. is 1.648. It is practically insoluble in water, and sparingly soluble in the common organic solvents such as benzene, xylene, etc., with which it forms molecular compounds of great stability. It is also insoluble in phosgene and only slightly soluble at the ordinary temperature in carbon tetrachloride. It dissolves in concentrated sulphuric acid with an intense cherry-red colour, and in arsenic trichloride to give a dark green solution.

CHEMICAL PROPERTIES

Water. Phenarsazine chloride, unlike the arsenic compounds previously described, is slowly hydrolysed by water. On adding a little water to the alcoholic solution, a turbidity appears which consists of phenarsazine oxide.³

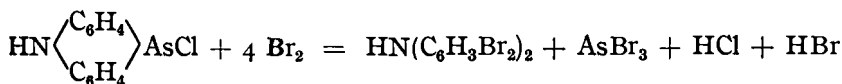
Bromine. By the action of bromine on phenarsazine chloride in acetic acid solution, a brominated derivative is not obtained,

¹ TANNER, *U.S. Pat.*, 1557384/1922.

² FISCHER, *Mikrochemie*, 1932, **12**, 257.

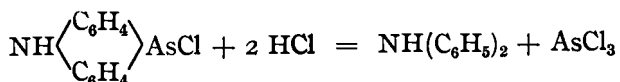
³ KAPPELMEYER, *Rec. trav. Chem.*, 1930, **49**, 82.

but the molecule is decomposed and tetrabromodiphenylamine is formed ¹ :

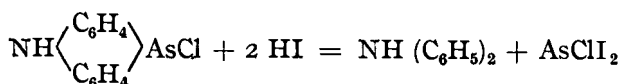


Tetrabromodiphenylamine forms lustrous crystals melting at 185° to 186° C.

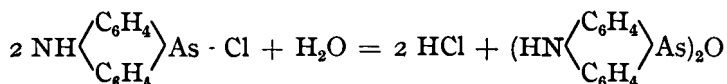
Hydrochloric Acid. When phenarsazine chloride is treated with gaseous hydrochloric acid at 160° C. it decomposes, forming arsenic trichloride and diphenylamine as follows ² :



Hydriodic Acid. On treatment with aqueous hydriodic acid on the water-bath, phenarsazine chloride forms diphenylamine as in the previous reaction ³ :

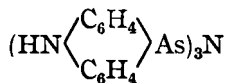


Alkalies. Phenarsazine chloride reacts with the alkalies to form phenarsazine oxide, according to the following equation :



This substance forms colourless leaflets with a melting point above 350° C. and is soluble with difficulty in most of the organic solvents. It reacts on heating with alcohols and phenols, and has a vigorous irritant action.

Ammonia. When a current of dry ammonia is passed through a solution of phenarsazine chloride in xylene, a compound of the following composition is obtained :



This is triphenarsazine amine which melts at 295° to 300° C.

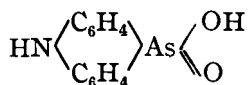
Oxidising Agents. Oxidising agents react with phenarsazine chloride, converting the arsenic atom from the trivalent to the pentavalent condition. Hydrogen peroxide in acetic acid

¹ L. ELSON and C. GIBSON, *J. Chem. Soc.*, **1929**, 1080.

² O. SEIDE and GORSKY, *Ber.*, 1929, **62**, 2187.

³ G. RASUVAJEV, *Ber.*, 1931, **64**, 2860.

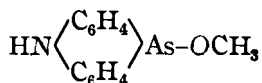
solution,¹ for instance, converts phenarsazine chloride to phenarsazinic acid :



This forms acicular crystals melting above 300° C.

However, nitric acid under certain conditions does not affect the arsenic atom, but introduces one or two nitro- groups. These groups enter at the ortho- or para- position to the NH— group.² These nitro- compounds have vigorous irritating properties according to Libermann.³

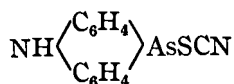
Sodium Cyanide. Phenarsazine chloride, when treated with sodium cyanide in methyl alcohol solution, does not form phenarsazine cyanide, but the corresponding methoxy- compound,



This substance melts at 194° C., and on heating with water is converted to phenarsazine oxide.

Phenarsazine cyanide has, however, been prepared by Gryskiewicz⁴ by treating phenarsazine chloride with silver cyanide. It forms bright yellow crystals which melt at 227° C. with decomposition according to Gryskiewicz or at 223° to 224° C. according to Gibson.⁵ Though it has a more efficient biological action than diphenyl cyanoarsine, it is very unstable to heating and to explosion.⁶

Potassium Thiocyanate. When phenarsazine chloride is treated in acetone solution with an aqueous solution of potassium thiocyanate, phenarsazine thiocyanate is formed⁷ :



This forms yellow crystals which melt at 229° to 230° C.

Chloramine-T. On treatment of phenarsazine chloride in cold aqueous alcoholic solution with chloramine-T,⁸ phenarsazinic acid is formed (see above).

¹ WIELAND and RHEINHEIMER, *Ann.*, 1921, **423**, 7.

² WIELAND and RHEINHEIMER, *loc. cit.*

³ G. LIBERMANN, *Khimia i Tecnologia Otravljajuscix Vescestv*, Moscow, 1931, 286.

⁴ GRYSKIEWICZ, *Bull. soc. chim.*, 1927, **41**, 1323.

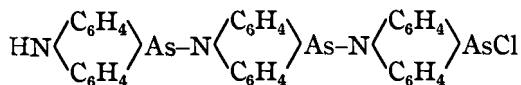
⁵ GIBSON and coll., *Rec. trav. Chim.*, 1930, **49**, 1006.

⁶ U. MÜLLER, *Militär-Wochenblatt.*, 1931, **21**, 757.

⁷ SERGEEV and coll., *J. Obscei Khim.*, Ser. A, 1931, **1**, 263.

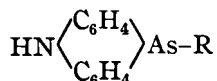
⁸ BURTON and GIBSON, *J. Chem. Soc.*, 1924, **125**, 2275.

Pyridine. When phenarsazine chloride is treated with boiling anhydrous pyridine, triphenarsazine chloride is formed ¹:



as orange-yellow crystals melting at 260° to 263° C.

Grignard Reagent. By the action of the Grignard reagent on phenarsazine chloride, the corresponding alkyl or aryl derivative is formed, *i.e.*,²



When phenarsazine chloride is heated it begins to melt at about 193° to 195° C. and remains unaltered until the temperature reaches 320° C. when it becomes dark brown. On further heating to 370° C., no more decomposition takes place. On cooling rapidly it solidifies to a crystalline mass of much darker colour than the original substance.

Unlike diphenyl chloroarsine, phenarsazine chloride attacks iron, steel, bronze and copper.

The minimum concentration causing irritant effect is, according to Müller, 0.1 mgm. per cu. m. A normal man cannot support a concentration greater than 0.4 mgm. per cu. m. for more than 1 minute. The mortality-index is 30,000 for 10 minutes' exposure and 19,500 for 30 minutes' exposure (Prentiss).

Analysis of the Arsenic Compounds

DETECTION

The presence of the arsenical war gases may be detected by applying one of the various methods proposed for detecting arsenic in substances. Among these the following, which have been much utilised for these compounds, are described:

*Gutzeit Method, Modified by Sanger and Black.*³ This method depends on the change of colour, from white to brown, of a paper impregnated with mercuric chloride solution when it is exposed to the action of hydrogen arsenide.

In order to use this paper for detecting arsenic compounds, the latter must first be converted into arsenious oxide by one of the usual decomposition methods (see p. 329 *et seq.*) and the

¹ WIELAND and RHEINHEIMER, *loc. cit.*

² AESCHLIMANN, *J. Chem. Soc.*, 1927, **129**, 413.

³ SANGER and BLACK, *J. Soc. Chem. Ind.*, 1907, **26**, 1115; *Z. anorg. Chem.*, 1908, **58**, 121.

oxide then reduced to hydrogen arsenide which can then be detected by the Gutzeit test-paper.

The reaction papers are prepared by repeatedly (four to five times) immersing strips of paper in an aqueous 5% mercuric chloride solution and allowing them to dry at the ordinary temperature. The papers after treatment must be stored away from the light in closed vessels containing phosphorus pentoxide, as they are sensitive to light and moisture.

The procedure to be followed in detecting the presence of arsenic compounds by means of these papers is as follows :

A certain quantity of the substance to be tested ¹ is decomposed by one of the methods described on p. 329 *et seq.*, for instance, by

Ewins's method. The liquid obtained, which contains arsenious oxide, is reduced with zinc and hydrochloric acid, using an apparatus like that shown in Fig. 19. This consists of a bottle of about 30 ml. capacity, fitted with a two-holed stopper, carrying a small thistle funnel which passes to within 1 mm. of the bottom of the bottle, and a bent tube connected by a rubber stopper with another small tube. The latter has a glass bulb of about

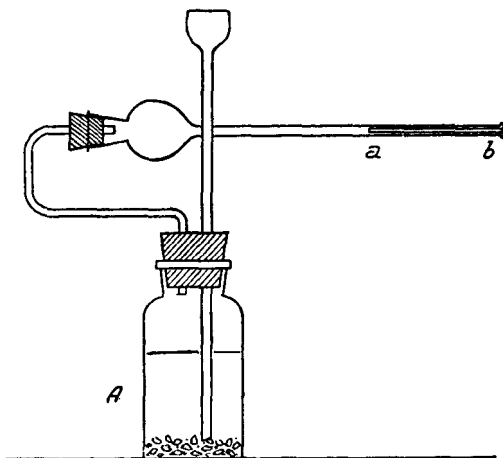


FIG. 19.

¹ The method of taking a sample depends on whether the substance to be examined is diffused in the air as vapour or as an aerosol. If the substance is in the vapour state, a part of the sample is passed through a U tube filled with dry, finely divided silica gel. Then the material absorbed on the silica is decomposed by one of the methods described on p. 329 *et seq.*, and the solution obtained is tested by the Gutzeit method.

If the substance is in the form of an aerosol, the sample must be passed through one of the following :

(a) A wash-bottle with a porous partition containing a solvent as ether, benzene, acetone, etc. (LABAT and DUFILHO, *Bull. soc. pharm. Bordeaux*, 1933, 71, 113).

(b) A glass tube filled with compressed cotton-wool.

(c) A glass tube filled with about 4 cm. anhydrous sodium sulphate held between two layers of cotton wool.

The solution obtained by method (a), or the material obtained by method (b) or (c), is treated by one of the methods described on p. 329 *et seq.* to convert the arsenic present to the oxide, and then the Gutzeit method is used. It is simpler, however, to treat the solution from (a), or an alcoholic extract of the materials from (b), or (c) directly in the Gutzeit apparatus with zinc and sulphuric acid, in presence of copper sulphate or better a few drops of platinic chloride solution.

an aqueous solution of hydrogen sulphide. In presence of a chloroarsine an opalescence or a white amorphous precipitate forms in a few minutes, according to the concentration of the chloroarsine in the sample.

In the presence of β chlorovinyl dichloroarsine an excess of hydrogen sulphide should be avoided or the sulphide will be decomposed. The sensitivity is 0.02–0.05 mgm. of chloroarsine. The sensitivity is greater if the chloroarsines are in aqueous solution than if they are in alcohol.

DETECTION OF METHYL DICHLOROARSINE

On adding a few drops of an aqueous solution of mercurous nitrate, faintly acid with nitric acid, to a solution containing methyl dichloroarsine, a grey precipitate of metallic mercury is formed.

Sensitivity : 1 mgm. of methyl dichloroarsine.

DETECTION OF ETHYL DICHLOROARSINE

When a solution of ethyl dichloroarsine is treated with an aqueous solution of mercurous nitrate, acidified with nitric acid, a white precipitate forms, and this changes to grey in a few seconds.

Sensitivity : a turbidity is easily visible in the presence of 2–5 mgm. ethyl dichloroarsine.

The limit is 1 mgm.

DETECTION OF β CHLOROVINYL DICHLOROARSINE

When a few drops of mercurous nitrate solution, slightly acidified with nitric acid, are added to a solution containing β chlorovinyl dichloroarsine, a white precipitate forms which turns grey within 12 hours.

Sensitivity : 1 mgm. β chlorovinyl dichloroarsine.

DETECTION OF PHENARSAZINE CHLORIDE

On heating a solution containing phenarsazine chloride with an aqueous solution of hydriodic acid on the water-bath, diphenylamine is formed (see p. 324), which can be distilled off in a current of steam and detected by means of the well-known reaction with nitric acid in sulphuric acid solution.

QUANTITATIVE DETERMINATION

The quantitative determination of the arsenical war gases is usually carried out by decomposing the substance by one of the usual methods and then determining the arsenic either gravimetrically or volumetrically.

Method of the German Pharmacopœia. 0.2–0.3 gm. of the substance is boiled for about 1 hour with 10 ml. concentrated

sulphuric acid and 1 ml. fuming nitric acid in a narrow-mouthed flask of Jena glass. After cooling and adding 50 ml. water, the solution is evaporated and the above treatment repeated. 10 ml. water, 2 gm. potassium iodide and sufficient water to dissolve the precipitate are then added in succession to the cooled solution. After allowing to stand for about $\frac{1}{2}$ hour, the iodine liberated is titrated without using any indicator.

*Ewins's Method.*¹ 0.1–0.2 gm. of the substance is mixed in a 300 ml. Kjeldahl flask with 10 gm. potassium sulphate, 0.2–0.3 gm. starch and 20 ml. concentrated sulphuric acid. This mixture is then heated by means of a Bunsen burner, first moderately for 10–15 minutes, then more vigorously for about 4 hours, until decomposition is complete. The liquid is cooled, transferred to a 350 ml. flask and made alkaline to litmus paper with sodium hydroxide. It is then cooled to 30° to 40° and sulphuric acid added drop by drop until the solution is faintly acid. A saturated solution of sodium bicarbonate is then added until the solution is again alkaline, 5–10 ml. being added in excess. The arsenious acid formed is then titrated with iodine solution using starch as indicator.

*Robertson's Method.*² This method consists synoptically of the following phases :

(a) Decomposition of the substance with sulphuric-nitric acid mixture.

(b) Elimination of the nitrous compounds with ammonium sulphate.

(c) Titration of the arsenite formed with iodine.

0.2 gm. of the substance is weighed into an Erlenmeyer flask and heated for about an hour with 5 ml. concentrated sulphuric acid and 1 ml. fuming nitric acid. After cooling the flask cautiously, a further 10–15 drops of fuming nitric acid are added and the flask again heated for 5 minutes to ensure complete decomposition. 1 gm. solid ammonium sulphate is then added and the contents of the flask agitated well until all the nitrogen has been evolved. They are then cooled and diluted with 60–70 ml. water. 1 gm. potassium iodide is then added and a few fragments of porous plate. A pear-shaped bulb of glass is placed in the mouth of the flask and the liquid concentrated to 40 ml. The iodine which is liberated is then decolorised with N/100 thio-sulphate and the solution diluted to 100–120 ml. with cold water. The whole is then transferred to a 500 ml. flask containing 50 ml.

¹ EWINS, *J. Chem. Soc.*, 1916, **109**, 1355.

² ROBERTSON, *J. Am. Chem. Soc.*, 1921, **43**, 182.

4 N sodium carbonate solution and the remaining acid neutralised with a slight excess of sodium bicarbonate. Starch solution is added and the arsenite present titrated with iodine.

*Rogers's Method.*¹ This method is based on the decomposition of the arsenical compound with nitric acid and ammonium persulphate and the titration of the iodine liberated on addition of potassium iodide.

About 0.5 gm. of the substance is weighed accurately into a 500 ml. flask and 10 ml. water and 5 ml. nitric acid are added. The mixture is then heated, ammonium persulphate being added until the solution becomes clear. If the liquid persistently remains yellow, showing that the substance is refractory, it is boiled for several minutes with a few ml. water and several gm. of ammonium persulphate.

The solution is then diluted with 100 ml. water, treated with about 5 ml. of a saturated solution of acid sodium ammonium phosphate and then an excess (about 40 ml.) of magnesia mixture added. A precipitate forms and is dissolved in dilute nitric acid; the solution is then heated to boiling, an excess of ammonia added, and it is then allowed to stand for about 2 hours. The precipitate is filtered off, washed with dilute ammonia and dissolved in 70 ml. dilute hydrochloric acid (3 : 2).

To the acid solution 3 gm. of potassium iodide in 6 ml. water are added and 70 ml. water. The liberated iodine is then titrated with sodium thiosulphate.

Direct methods of estimation have been proposed for certain of the war gases. Some of these are described below.

DETERMINATION OF THE ALIPHATIC ARSINES

Jurecev² suggested the following method for the determination of the aliphatic arsines present in vapour form in the air.

A known volume of the air is passed through a U tube filled with dry, fine-grained silica gel. The silica gel with the substance absorbed on it is transferred to a nickel or silver crucible and covered with a layer of magnesium oxide which is well pressed down. 6 gm. of a mixture of equal parts of sodium peroxide and sodium carbonate are added and pressed down, and this is finally covered with a layer of sodium carbonate. The crucible is heated with a small flame for about 15 minutes until the bottom is dull red. It is then allowed to cool and placed in a beaker, hot water is added and the beaker warmed on the water-bath. The solution is neutralised with dilute sulphuric acid and warmed

¹ ROGERS, *Canad. Chem. J.*, 1919, **3**, 398.

² JURECEV, *Coll. trav. chim. Czech.*, 1934, **6**, 468.

again on the water-bath to decompose the hydrogen peroxide present. The silica gel is filtered off and washed with hot water, then the liquid is allowed to cool, made up to a convenient volume and the arsenic determined in an aliquot by the colorimetric ¹ method using mercuric chloride paper (see p. 326).

DETERMINATION OF METHYL DICHLOROARSINE

For this determination, the following method has been recommended by Uehlinger and Cook ² :

5 gm. of the methyl dichloroarsine are treated with 200 ml. water and the hydrochloric acid formed by the hydrolysis neutralised to litmus. Sodium bicarbonate is then added and the solution titrated with a decinormal iodine solution.

DETERMINATION OF β CHLOROVINYL DICHLOROARSINE

This determination is usually carried out by the method of Lewis and Perkins,³ in which the β chlorovinyl dichloroarsine is decomposed by 15% sodium hydroxide solution at a temperature below 37° C. Acetylene is evolved quantitatively.

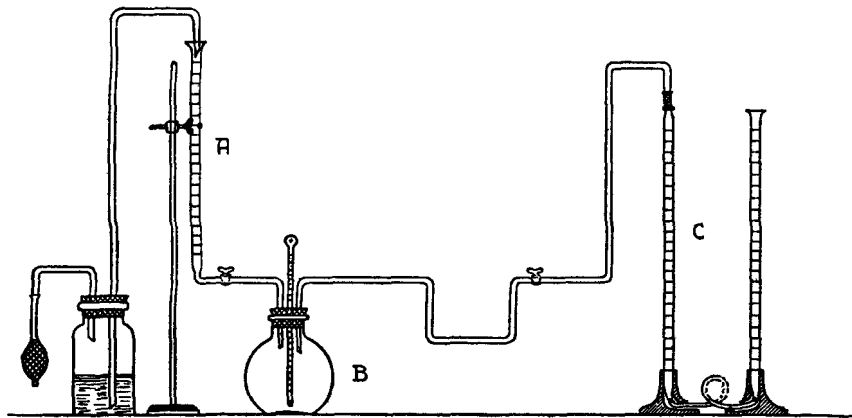


FIG. 20.

0.2-0.4 gm. of the substance is weighed into a flask B (Fig. 20) of 50 ml. capacity, and 5 ml. of 15% sodium hydroxide solution are introduced from the burette A, the liquid then being warmed to about 37° C. The decomposition of the β chlorovinyl dichloroarsine is complete after 15 minutes' agitation and then the volume of acetylene formed is read off in the burette C. From this the quantity of β chlorovinyl dichloroarsine in the sample

¹ K. UHL, *Z. angew. Chem.*, 1937, **50**, 164.

² UEHLINGER and COOK, *J. Ind. Eng. Chem.*, 1919, **11**, 105.

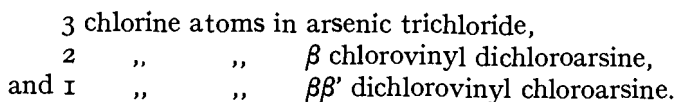
³ LEWIS and PERKINS, *Ind. Eng. Chem.*, 1923, **15**, 290.

can be calculated. The U tube contains 15% sodium hydroxide solution which ensures the complete decomposition of the sample.

DETERMINATION OF CHLOROVINYL ARSINES

In order to determine the amount of each constituent in a mixture of the chlorovinyl arsines, the method proposed by Brinton¹ may be employed. This utilises the following reactions :

(1) Cold water hydrolyses



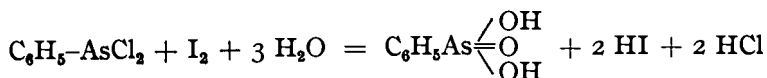
(2) By prolonged heating with alcoholic soda all four compounds are attacked with the formation of 3 molecules of sodium chloride from each.

(3) A solution of sodium bromate in dilute hydrochloric acid oxidises the arsenic trichloride and β chlorovinyl dichloroarsine to the pentavalent state.

(4) Moderate boiling with 15% sodium hydroxide causes the attack of both β chlorovinyl dichloroarsine and $\beta\beta'$ dichlorovinyl chloroarsine, but not trichlorovinyl arsine, with formation of sodium arsenite which may be titrated with sodium bromate after acidification.

DETERMINATION OF PHENYL DICHLOROARSINE

Fleury's² method may be employed for this determination ; it consists in hydrolysing the sample with water and titrating the oxide formed with iodine solution. The following reaction takes place :



A sample of phenyl dichloroarsine is weighed accurately, treated with water and alcohol and then titrated, without adding any sodium bicarbonate, with a decinormal solution of iodine, until the yellow colour is permanent. The number of ml. of iodine solution employed multiplied by 0.01115 gives the amount of phenyl dichloroarsine (in gm.) in the sample.

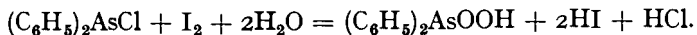
DETERMINATION OF DIPHENYL CHLOROARSINE

Fleury's method, depending on the same principle as the preceding estimation, is most frequently employed for the

¹ Chemical Welfare Communication, 1923 (see *Ind. Eng. Chem.*, 1923, **15**, 290).

² P. FLEURY, *Bull. soc. chim.*, 1920, [4] **27**, 490, 699.

determination of diphenyl chloroarsine. The titration must be carried out in benzene or chloroform solution, however, and not in aqueous alcoholic solution, and in presence of sodium bicarbonate, which accelerates the velocity of the reaction and also dissolves the diphenyl arsenic acid which is formed :



The sample (0.2–0.4 gm.) is weighed accurately and dissolved in 10–15 ml. chloroform or benzene, 20 ml. of a saturated solution of sodium bicarbonate are added and the liquid is then titrated with N/10 iodine solution, being shaken vigorously after each addition of iodine. The end of the titration is shown by the appearance of a violet colouration in the solvent. The number of ml. of N/10 iodine solution employed multiplied by 0.0132 gives the amount of diphenyl chloroarsine present in the sample, in gm.

In order to determine the amount of *diphenyl chloroarsine in air*, Sieverts¹ recommends the following method (*cp. note*, p. 327).

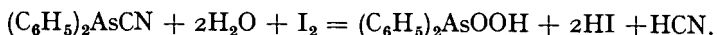
A sample of the air is taken in a glass flask of 10–15 litres capacity and washed three times with 30 ml. benzene; the benzene solutions are evaporated together on the water-bath to a volume of 10–20 ml. and then titrated with a N/1,000 solution of iodine as described above. The number of ml. of iodine employed multiplied by 0.132 gives the amount of diphenyl chloroarsine present in the sample of air.

This method is not specific, however, nor is it sufficiently sensitive; it also suffers from the inconvenience attendant on the instability of millinormal solutions of iodine.

It is better to use Jurecev's² method for this estimation; it consists in passing a known volume of the aerosol (*e.g.*, 50 litres) through a wash-bottle with a porous partition containing ether. The solvent is then evaporated off on the water-bath, the residue decomposed by one of the methods described on p. 329 *et seq.*, and the arsenic determined colorimetrically by means of mercuric chloride paper (see p. 326).

DETERMINATION OF DIPHENYL CYANOARSINE

Diphenyl cyanoarsine may be estimated in the same manner as diphenyl chloroarsine, by titration with iodine (Sieverts) :



A sample of the air to be analysed is introduced into a glass

¹ A. SIEVERTS, *Z. angew. Chem.*, 1922, **35**, 17.

² JURECEV, *Coll. trav. chim. Czech.*, 1934, **6**, 468.

flask, as in the case of diphenyl chloroarsine, and washed with alcohol (not benzene, for in the latter solvent diphenyl cyanoarsine does not react with iodine). The alcoholic solution is diluted with an equal volume of water and about 5 ml. benzene are added. The diphenyl cyanoarsine reacts quantitatively with iodine in the aqueous alcoholic solution, while the excess of iodine passes into the benzene layer.

The number of ml. of N/1,000 iodine employed multiplied by 0.127 gives the quantity of diphenyl cyanoarsine in the sample of air taken, in mgm.

It is advisable to carry out a blank determination.

DETERMINATION OF PHENARSAZINE CHLORIDE

A known volume of air containing the substance to be examined, in the form of an aerosol, is passed through a wash-bottle with a porous partition, of the type recommended by Kölliker,¹ containing ether.

The solvent is removed on the water-bath, the residue is oxidised by means of a mixture of concentrated sulphuric acid, concentrated nitric acid and hydrogen peroxide, according to Winterstein's method,² and the arsenic is determined in the solution obtained by the colorimetric method with mercuric chloride paper (see p. 326).

DETERMINATION OF ARSENIC TRICHLORIDE IN PHENYL DICHLOROARSINE

Fleury recommends the following method for the determination of the arsenic chloride present in a sample of phenyl dichloroarsine.

A known amount of the sample (equivalent to about 30 ml. N/10 iodine solution) is dissolved in 15-20 ml. 95% alcohol and titrated directly with iodine without addition of sodium bicarbonate. An excess of a saturated solution of sodium bicarbonate is then added ; if after this the solution absorbs more iodine, the presence of arsenic trichloride is indicated, and from the number of ml. of iodine solution absorbed in these conditions, the quantity of arsenic trichloride present in the sample may be calculated.

According to Delepine,³ this method may also be employed for the determination of the arsenic trichloride present in the aliphatic arsines.

¹ KÖLLIKER, *Chem. Fabrik.*, 1932, 5, 1 ; 1933, 6, 299.

² WINTERSTEIN, *Mikrochemie.*, 1926, 4, 155.

³ DELEPINE, *Rapport à l'Insp. Études et Expér. Chim.*, 26, 10, 918.

TABLE XIII. *Table of Conversion for Gas Concentrations : parts per*

M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.	M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.	M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.
2	12 230	0.0000818	51	479	0.002086	101	242.1	0.00413
3	8 150	.0001227	52	470	.002127	102	239.7	.00417
4	6 113	.0001636	53	461	.002168	103	237.4	.00421
5	4 890	.0002045	54	453	.002209	104	235.1	.00425
6	4 075	.0002454	55	445	.002250	105	232.9	.00429
7	3 493	.0002863	56	437	.002290	106	230.7	.00434
8	3 056	.000327	57	429	.002331	107	228.5	.00438
9	2 717	.000368	58	422	.002372	108	226.4	.00442
10	2 445	.000409	59	414	.002413	109	224.3	.00446
11	2 223	.000450	60	408	.002454	110	222.3	.00450
12	2 038	.000491	61	401	.002495	111	220.3	.00454
13	1 881	.000532	62	493	.00254	112	218.3	.00458
14	1 746	.000573	63	388	.00258	113	216.4	.00462
15	1 630	.000614	64	382	.00262	114	214.5	.00466
16	1 528	.000654	65	376	.00266	115	212.6	.00470
17	1 438	.000695	66	370	.00270	116	210.8	.00474
18	1 358	.000736	67	365	.00274	117	209.0	.00479
19	1 287	.000777	68	360	.00278	118	207.2	.00483
20	1 223	.000818	69	354	.00282	119	205.5	.00487
21	1 164	.000859	70	349	.00286	120	203.8	.00491
22	1 111	.000900	71	344	.00290	121	202.1	.00495
23	1 063	.000941	72	340	.00294	122	200.4	.00499
24	1 019	.000982	73	335	.00299	123	198.8	.00503
25	978	.001022	74	330	.00303	124	197.2	.00507
26	940	.001063	75	326	.00307	125	195.6	.00511
27	906	.001104	76	322	.00311	126	194.3	.00515
28	873	.001145	77	318	.00315	127	192.5	.00519
29	843	.001186	78	313	.00319	128	191.0	.00524
30	815	.001227	79	309	.00323	129	189.5	.00528
31	789	.001268	80	306	.00327	130	188.1	.00532
32	764	.001309	81	302	.00331	131	186.6	.00536
33	741	.001350	82	298	.00335	132	185.2	.00540
34	719	.001391	83	295	.00339	133	183.8	.00544
35	699	.001432	84	291	.00344	134	182.5	.00548
36	679	.001472	85	288	.00348	135	181.1	.00552
37	661	.001513	86	284	.00352	136	179.8	.00556
38	643	.001554	87	281	.00356	137	178.5	.00560
39	627	.001595	88	278	.00360	138	177.2	.00564
40	611	.001636	89	275	.00364	139	175.9	.00569
41	596	.001677	90	272	.00368	140	174.6	.00573
42	582	.001718	91	269	.00372	141	173.4	.00577
43	569	.001759	92	266	.00376	142	172.2	.00581
44	556	.001800	93	263	.00380	143	171.0	.00585
45	543	.001840	94	260	.00384	144	169.8	.00589
46	532	.001881	95	257	.00389	145	168.6	.00593
47	520	.001922	96	255	.00393	146	167.5	.00597
48	509	.001963	97	252	.00397	147	166.3	.00601
49	499	.002004	98	249.5	.00401	148	165.2	.00605
50	489	.002045	99	257.0	.00405	149	164.1	.00609
			100	244.5	.00409	150	163.0	.00613

million into mgm. per litre and vice versâ (25° C. and 760 mm. mercury)

M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.	M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.	M. Wt.	1 mgm./l. ppm.	1 ppm. mgm./l.
151	161.9	0.00618	201	121.6	0.00822	251	97.4	0.01027
152	160.9	.00622	202	121.0	.00826	252	97.0	.01031
153	159.8	.00626	203	120.4	.00830	253	96.6	.01035
154	158.8	.00630	204	119.9	.00834	254	96.3	.01039
155	157.7	.00634	205	119.3	.00838	255	95.9	.01043
156	156.7	.00638	206	118.7	.00843	256	95.5	.01047
157	155.7	.00642	207	118.1	.00847	257	95.1	.01051
158	154.7	.00646	208	117.5	.00851	258	94.8	.01055
159	153.7	.00650	209	117.0	.00855	259	94.4	.01059
160	152.8	.00654	210	116.4	.00859	260	94.0	.01063
161	151.9	.00658	211	115.9	.00863	261	93.7	.01067
162	150.9	.00663	212	115.3	.00867	262	93.3	.01072
163	150.0	.00667	213	114.8	.00871	263	93.0	.01076
164	149.1	.00671	214	114.3	.00875	264	92.6	.01080
165	148.2	.00675	215	113.7	.00879	265	92.3	.01084
166	147.3	.00679	216	113.2	.00883	266	91.9	.01088
167	146.4	.00683	217	112.7	.00888	267	91.6	.01092
168	145.5	.00687	218	112.2	.00892	268	91.2	.01096
169	144.7	.00691	219	111.6	.00896	269	90.9	.01100
170	143.8	.00695	220	111.1	.00900	270	90.6	.01104
171	143.0	.00699	221	110.6	.00904	271	90.2	.01108
172	142.2	.00703	222	110.1	.00908	272	89.9	.01112
173	141.3	.00708	223	109.6	.00912	273	89.6	.01117
174	140.5	.00712	224	109.2	.00916	274	89.2	.01121
175	139.7	.00716	225	108.7	.00920	275	88.9	.01125
176	138.9	.00720	226	108.2	.00924	276	88.6	.01129
177	136.1	.00724	227	107.7	.00928	277	88.3	.01133
178	137.4	.00728	228	107.2	.00933	278	87.9	.01137
179	136.6	.00732	229	106.8	.00937	279	87.6	.01141
180	135.8	.00736	230	106.3	.00941	280	87.3	.01145
181	135.1	.00740	231	105.8	.00946	281	87.0	.01149
182	134.3	.00744	232	105.4	.00949	282	86.7	.01153
183	133.6	.00748	233	104.9	.00953	283	86.4	.01157
184	132.9	.00753	234	104.5	.00957	284	86.1	.01162
185	132.2	.00757	235	104.0	.00961	285	85.8	.01166
186	131.5	.00761	236	103.6	.00976	286	85.5	.01170
187	130.7	.00765	237	103.2	.00969	287	85.2	.01174
188	130.1	.00769	238	102.7	.00973	288.	84.9	.01178
189	129.4	.00773	239	102.3	.00978	289	84.6	.01182
190	128.7	.00777	240	101.9	.00982	290	84.3	.01186
191	128.0	.00781	241	101.5	.00986	291	84.0	.01190
192	127.3	.00785	242	101.0	.00990	292	83.7	.01194
193	126.7	.00789	243	100.6	.00994	293	83.4	.01198
194	126.0	.00793	244	100.2	.00998	294	83.2	.01202
195	125.4	.00798	245	99.8	.01002	295	82.9	.01207
196	124.7	.00802	246	99.4	.01006	296	82.6	.01211
197	124.1	.00806	247	99.0	.01010	297	82.3	.01215
198	123.5	.00810	248	98.6	.01014	298	88.0	.01219
199	122.9	.00814	249	98.2	.01018	299	81.8	.01227
200	122.3	.00818	250	97.8	.01022	300	81.5	.01227

TABLE XIV. *List of the Most Important War Gases Employed*

1 Date first used	2 Name	3 Formula	Military Name			7 M Wt	8 M Pt °C
			4 French	5 German	6 U S A		
1914	Ethyl bromoacetate	CH ₃ Br—COOC ₂ H ₅	—	—	—	167	—
1915, Jan.	Xylyl bromide	C ₆ H ₄ (CH ₃)CH ₂ Br	—	T-Stoff	—	185	—
1915, Mar.	Chloroacetone	CH ₃ —CO—CH ₂ Cl	Tomite	A-Stoff	—	92.5	—
	Benzyl bromide	C ₆ H ₅ CH ₂ Br	Cyclite	T-Stoff	—	171	-4
	Benzyl iodide	C ₆ H ₅ CH ₂ I	Frausmitte	—	—	218	24
Apr.	Chlorine	Cl ₂	Bertholite	Chlor	—	71	-102
	Bromine	Br ₂	—	Brom	—	159.8	-7
	Ethyl chlorosulphonate	ClSO ₂ OC ₂ H ₅	Sulvinite	—	—	144.5	—
June	Methyl chlorosulphonate	ClSO ₂ OCH ₃	Villantite	C-Stoff	—	130.5	-70
	Monochloromethyl chloroformate	Cl—COO—CH ₂ Cl	—	—	—	129	—
July	Bromoacetone	CH ₃ —CO—CH ₂ Br	—	B-Stoff	BA	136.5	-54
	Bromomethylethyl ketone	C ₆ H ₅ —CO—CH ₂ Br	Homomartonite	Bn Stoff	—	151	—
Aug. Sept.	Dimethyl sulphate	SO ₂ (OCH ₃) ₂	—	D Stoff	—	126	-31.7
	Perchloromethyl mercaptan	CCl ₃ —S—Cl	Clarsite	—	—	186	—
Dec.	Phosgene	COCl ₂	Collongite	—	CG	99	-118
	Ethyl iodoacetate	CH ₃ I—COOC ₂ H ₅	—	—	SK	214	—
1916, Jan	Acrolein	CH ₂ =CH—CHO	Papite	—	—	56	-88
May	Trichloromethyl chloroformate	Cl—COOCCl ₃	Surpalite	Perstoff	—	198	-57
July	Hydrocyanic acid	HCN	Forestitute	—	—	27	-15
	Chloropicrin	CCl ₃ —NO ₂	Aquimite	Klop	PS	164.5	-69
	Cyanogen chloride	CICN	Maugunite	—	—	61.4	-6
1917	Cyanogen bromide	BrCN	—	E Stoff	—	106	52
May	Phenylcarbylamine chloride	C ₆ H ₅ NCCl ₂	—	K Stoff	—	175	—
July	Dichloroethyl sulphide	S(CH ₂ —CH ₂ Cl) ₂	Ypérite	Lost	HS	159	14.4
	Diphenyl chloroarsine	(C ₆ H ₅) ₂ AsCl	—	Clark I	DA	264.5	41
Sept	Phenyl dichloroarsine	C ₆ H ₅ AsCl ₂	—	—	—	223	-20
1918	Dichloromethyl ether	O(CH ₂ Cl) ₂	Cici	—	—	114.7	—
	Dibromomethyl ether	O(CH ₂ Br) ₂	Bibi	—	—	204	-34
Mar.	Ethyl dichloroarsine	C ₂ H ₅ AsCl ₂	—	Dick	ED	175	-65
	Thiophosgene	CSCl ₂	Lacrimite	—	—	115	—
May	Diphenylcyano arsine	(C ₆ H ₅) ₂ AsCN	—	Clark II	CDA	255	31
	Methyl dichloroarsine	CH ₃ AsCl ₂	—	Methyldick	MD	161	-42.5

Column 1. The dates are quoted from Hanslian, *Der Chemische Krieg*, Berlin, 1927.

Column 13. See p 6.

Column 16. Lower Limit of Irritation: the minimum concentration (in mgm. per cu. m.) causing irritation (Fries, Vedder; Müller).

in the War of 1914-18, in Chronological Order of their first use

9 B. Pt. °C.	10 S.G.	11 Vap. den. air = 1	12 Vap. Press. mm. Hg.	13 Volatility at 20° C. mgm./cu. m.	14 Coeff. thermal expans.	15 Princ. biolog. action.	16 LLI	17 LI	Mortality-product	
									18 German data	19 American data
168	1·53	5·8	—	—	—	Lachrym.	10	40	3,000	23,000
210-220	1·4	—	—	600	—	"	1·8	15	6,000	56,000
119	1·16	3·2	—	61,000	—	"	18	100	3,000	23,000
199	1·43	5·8	—	2,440	—	"	4	60	6,000	45,000
226	1·77	7·5	—	1,200	—	"	2	30	3,000	30,000
-33·5	1·4	2·5	—	—	0·0021	Suffoc.	10	100	7,500	56,000
59	3·1	5·5	172	—	—	Toxic	—	—	—	—
152	1·4	5	—	18,000	—	Lach. Suff.	2	50	3,000	10,000
133	1·49	4·5	—	60,000	—	"	2	40	2,000	20,000
106·5	1·46	4·5	5·6	—	—	"	2	50	—	10,000
136	1·63	4·7	9	75,000	—	"	1	10	4,000	32,000
145	1·43	5·2	—	—	—	"	1·6	11	6,000	20,000
188	1·33	4·3	—	3,300	—	Tox. Ves.	—	50	1,500	5,000
148	1·7	6·4	—	18,000	—	Lachrym.	10	70	3,000	30,000
8·2	1·4	3·5	1,173	—	0·00122	Suffoc.	5	20	450	5,000
179	1·8	7·4	0·54	3,100	—	Lachrym	1·4	15	1,500	15,000
52	0·8	1·9	—	407,000	—	"	7	50	7,000	3,500
127	1·7	6·9	10·3	26,000	0·00093	Suffoc.	5	40	500	5,000
26·5	0·7	0·9	603	873,000	0·0019	Toxic	1·1	—	1,000-4,000	2,000
112	1·6	5·7	16·9	184,000	0·0011	Lach. Suff.	2	50	2,000	20,000
12·5	1·2	2·1	1,001	3,300,000	0·0015	Tox. Lach	—	50	—	4,000
61	1·9	3·7	89	200,000	—	"	5	85	2,000	4,000
208	1·3	6·0	—	2,100	0·00089	Irritant	3	30	3,000	5,000
217·5	1·3	5·4	0·115	625	0·00088	Vesicant	—	—	1,500	15,000
333	1·3	—	0·0005	0·68	0·0007	Irritant	0·1	1	4,000	15,000
257	1·6	7·7	—	404	0·0007	"	—	16	—	2,600
105	1·3	4	—	180,000	—	Suffoc.	14	40	500	4,700
154	2·2	7	—	21,100	0·0009	"	20	50	400	4,700
156	1·7	6	—	20,000	0·0011	Suff. Ves	1	10	3,000	5,000
73·5	1·5	4	—	—	—	Suffoc.	—	—	—	—
377	1·4	—	0·0002	0·16	—	Irritant	0·1	0·25	4,000	10,000
132	1·8	5·5	8·5	74,440	0·00102	Suff. Ves.	2	25	3,000	5,600

Column 17. Limit of Insupportability: the maximum concentration (in mgm. per cu. m.) which a normal man can support without injury for 1 minute at the most (Flury; Vedder; Lustig; Lindemann; Aksenov).
 Column 18. Mortality product: the product of the concentration of the substance in air (in mgm. per cu. m.) by the duration of its action (in minutes) to cause death (Flury; Meyer). See p. 3.
 Column 19. These data are due to Prentiss, and in general refer to a time of exposure of 10 minutes. See p. 4.

TABLE XV. *List of War Gases Prepared or Studied*

Name	Formula	Military name			M. Wt.	M. Pt °C.
		French	English	American		
<i>o</i> -Nitrobenzyl bromide .	$C_6H_4(NO_2)CH_2Br$	—	—	—	216	46-47
Bromobenzyl cyanide .	$C_6H_5CHBrCN$	Camite	—	CA	196	25
Chloroacetophenone .	$C_6H_5COCH_2Cl$	—	—	CN	154.5	58
Bromoacetophenone .	$C_6H_5COCH_2Br$	—	—	—	199	50
Bromopicrin .	CBr_3NO_2	—	—	—	298	10.2
Tetrachlorodinitroethane	$(CCl_2NO_2)_2$	—	—	—	257.8	142-143
Dibromoethyl sulphide .	$S(CH_2CH_2Br)_2$	Bromlost	—	—	247.8	31-34
Diiodoethyl sulphide .	$S(CH_2CH_2I)_2$	—	—	—	341.8	62
Chlorovinyl dichloroarsine	$ClCH=CHAsCl_2$	—	Lewisite	MI	207.3	-18.2
Dichlorovinyl chloroarsine	$(ClCH=CH)_2AsCl$	—	—	—	233.3	—
Trichlorovinyl arsine .	$(ClCH=CH)_3As$	—	—	—	259.4	21
Bromovinyl dibromoarsine	$BrCH=CHAsBr_2$	—	—	—	340.6	—
Chlorostyryl dichloroarsine	$C_6H_5CCl=CHAsCl_2$	—	—	—	283.3	—
Diphenyl bromoarsine .	$(C_6H_5)_2AsBr$	—	—	—	309	54-56
Phenarsazine chloride .	$NH(C_6H_4)_2AsCl$	—	Adamsite	DM	277.4	193-194
Phenarsazine bromide .	$NH(C_6H_4)_2AsBr$	—	—	—	321.8	—
Phenarsazine cyanide .	$NH(C_6H_4)_2AsCN$	—	—	—	272.0	227

at the end of the War or immediately after the War

B. Pt. °C.	S.G.	Vap. Tens. 20°C. mm. Hg.	Volatility mg./cu. m.	Principal biological action.	Lower Limit Irritn.	Limit of Insupporty.	Mortality-product	
							German data	American data
—	—	—	—	Lachrym.	—	—	—	—
242	1·5	0·012	130	Lachrym.	0·3	30	7,500	3,500
245-47	1·3	0·013	105	Lachrym.	0·3	4·5	4,000	8,500
260	—	—	—	Lachrym.	—	—	—	—
127/118 mm.	2·8	—	—	Tox. lach.	30	—	—	—
—	—	—	—	Tox. lach.	—	—	—	—
240	2·05	—	400	Vesicant	—	—	—	—
—	—	—	—	Vesicant	—	—	—	—
190	1·9	0·394	2,300	Vesicant	0·8	48	1,500	1,200
230	1·7	—	—	Vesicant	—	—	—	—
260	1·5	—	—	—	—	—	—	—
{ 140-143/ 16 mm.	—	—	—	Irritant	—	—	—	—
{ 108-110/ 12 mm.	—	—	—	—	—	—	—	—
54-56	—	—	—	Irritant	—	—	—	—
410	1·6	2×10^{-13}	—	Sternut.	0·1	0·4	—	30,000
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—

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