PHOSGENE

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The aim of this monograph is to provide a summary of the work done with phosgene. The literature of any substance whose chief use is in the capacity of a reagent, is hard to search, since the name of the reagent does not appear in the title of the paper, nor, as a rule in the index of the journal in which the paper is published; and bearing this in mind it is not claimed that the present work embodies all the references to phosgene which have been made in the literature. However, an attempt has been made to include all the important work done on the subject up to the end of 1925.

HISTORY AND PREPARATION OF PHOSGENE

During the years 1800–1812 several investigators, including Gay-Lussac and Thenard,[1] and Murphy,[2] published statements to the effect that carbon monoxide and chlorine were mutually inactive, but in 1812 John Davy[3] (brother of Humphrey) more carefully investigated their interaction. He mixed equal volumes of the two gases, which had been dried over calcium chloride, and exposed the mixture, contained in a vessel over mercury, to sunlight. In fifteen minutes the colour of the chlorine had entirely disappeared and a new gas which was possessed of lachrymatory properties remained. This Davy christened "phosgene" (φῶς "light," and γεννάω "I give rise to") while he noted that the new gas did not fume in air, but reddened blue litmus and reacted with ammonia to give ammonium chloride. Further, he noticed that it was chemically very reactive and was decomposed by heating

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[1] Gay Lussac and Thenard. Recherches Physico-chimique, Tom. II, 150.

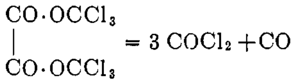
[2] Nicholson's Journal, XXX, 227.

[3] Phil. Trans. (1812), p. 144.

with zinc, antimony or arsenic, and that it combined readily on warming with the oxides of certain elements to give the metal chloride and carbon dioxide. He showed, also, that no combination of carbon monoxide and chlorine took place in the absence of sunlight, even on passing through an earthenware tube heated to redness.

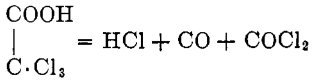
Several investigators carried on the work with phosgene which they obtained by various modifications of Davy's original method. Thus, for instance, Wilm and Wischin[4] (1868) obtained their phosgene by passing carbon monoxide, which had been purified by passage through caustic soda solution, and milk of lime, mixed with a slight excess of chlorine, which had been dried over strong sulfuric acid, into ten litre glass globes, exposed to sunlight. The phosgene was then absorbed in alcohol to give chlorocarbonic ester, of which these investigators state that they were able to prepare about 2.3 pounds a day.

Prior to 1860 only three methods (besides that of Davy), and these of little importance, had been recorded for the preparation of phosgene. They included the action of a mixture of concentrated nitric and hydrochloric acids on carbon bisulfide, discovered by Berzelius and Marcet,[5] and the decomposition of hexachloromethyl oxalate by heat (Cahours)[6] which takes place thus:



$$\begin{array}{l} CO\cdot OCCl_3 \\ | \\ CO\cdot OCCl_3 \end{array} = 3\,COCl_2 + CO$$

while Henry in 1845 pointed out that phosgene could be produced by the dry distillation of trichloracetic acid, thus:



$$\begin{array}{l} COOH \\ | \\ C\cdot Cl_3 \end{array} = HCl + CO + COCl_2$$

Later, in 1863, Schutzenberger[7] investigated the action of platinum sponge on heated chlorine and carbon monoxide. He

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[4] Z. Chem. (2), **4,** 5 (1868).

[5] Gilbert's Annalen. **48,** 161, (1814).

[6] Ann. Phys. Chem. (3), **19,** 352.

[7] C. R. **66,** 747.

stated that phosgene was produced, and also that it could be formed either by heating carbon tetrachloride with zinc oxide under pressure, or by passing a mixture of carbon monoxide, chlorine, and carbon tetrachloride vapour through a red hot tube.

$$ZnO + CCl_4 = COCl_2 + ZnCl_2$$

In 1869[8] he obtained phosgene by the interaction of chlorine monoxide and carbon bisulfide:

$$CS_2 + 3Cl_2O = = 2SOCl_2 + COCl_2$$

while Emmerling and Lengyel[9] in the same year obtained phosgene, mixed with many other products by passing a mixture of carbon oxysulfide and chlorine through a red hot porcelain tube.

THE PREPARATION OF PHOSGENE

The methods for the preparation of phosgene resolve themselves into the following chief groups:

1. The photochemical combination of carbon monoxide and chlorine.
2. The oxidation of chlorinated hydrocarbons with chromic acid.
3. The interaction of sulfur trioxide or oleum with chlorinated hydrocarbons.
4. The combination of carbon monoxide and chlorine in the presence of a solid catalyst.

The photochemical combination of carbon monoxide and chlorine has been the subject of several detailed investigations, mainly by Chapman and his co-workers, and Weigert. Chapman and Gee[10] experimented on the action of light on mixtures of equal quantities of pure carbon monoxide and chlorine, and found the reaction to be homogeneous, if the surface of the glass be not large. Glass, they found, acted as a weak catalyst, the rate of formation, in the presence of a comparatively large glass surface being 1.237 times as fast as that in an ordinary glass tube. The

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[8] Ber. **2**, 219.
[9] Ber. **2**, 546.
[10] J. C. S. **99**, 1726.

glass surface was obtained by packing the reaction tube with glass wool. Small quantities of certain substances, such as oxygen, nitric oxide, and especially ozone act as inhibitors, in some cases almost stopping the reaction, although their presence does not, apparently, affect the rate of thermal formation. Weigert[11] investigated the dissociation of phosgene with and without the presence of light, and found that although the presence and wavelength of light alters the rate at which the equilibrium is reached, it had no effect on the position of the equilibrium. This work, in so far as it relates to the wavelength of light in accelerating formation and decomposition of phosgene, was confirmed by the work of Bertholet and Gaudechov[13] whose experiments consisted in placing pure phosgene over dry mercury and exposing the tube to a strong source of ultra-violet light. As decomposition of the phosgene took place the surface of the mercury was corroded by the chlorine liberated. Tubes of different materials, allowing different amounts of short wave light to pass were used in different experiments, and the time taken for a definite film to form on the mercury was noted. Their results are shown in table 1. It is clear from these results, that ultra-violet light has a strong influence on the decomposition rate of phosgene. Coehn and Becker[12] utilised a "streaming" method for proving the same facts. They passed pure phosgene through a clear quartz tube, at room temperature, illuminating it with the light from a mercury vapour lamp. Dissociation to the extent of 4 per cent was observed in the issuing gas. In another experiment they substituted a tube of "Uviol" glass for

TABLE 1

MATERIAL OF TUBE	TIME TAKEN TO PRODUCE FILM ON MERCURY
Clear quartz	5 seconds
Uviol glass	80 seconds
Ordinary glass	More than two hours

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[11] Ann. Physik. (4), **24**, 55 and 243.

[12] Ber. **43**, 130.

[13] C. R. **156**, 1243.

the quartz tube. "Uviol" while allowing some of the ultra-violet light to pass, cuts out waves shorter than $256\mu\mu$. With this glass they observed a dissociation of 0.46 to 0.5 per cent.

The oxidation of carbon tetrachloride or chloroform by means of a mixture of potassium bichromate and concentrated sulfuric acid, although too expensive for commercial purposes, furnishes a convenient method for the laboratory preparation of the gas. It was first described by Emmerling and Lengyel[14] in 1869, who warmed chloroform with chromic acid mixture, and obtained phosgene which was passed through a tube containing metallic antimony to remove the excess of chlorine. They assumed the reaction to go:

$$2\ CHCl_3 + 3\ O = 2\ COCl_2 + H_2O + Cl_2$$

but it was shown by Erdmann[15] and others that the reaction in reality proceeds thus:

$$2\ CHCl_3 + CrO_3 + 2\ O = 2\ COCl_2 + CrO_2Cl_2 + H_2O$$

This author describes a convenient laboratory method for the preparation of phosgene from "oleum" and carbon tetrachloride. The apparatus is shown in figure 1. Carbon tetrachloride (120 grams) is placed in a round-bottomed flask, warmed by a water-bath. The flask is connected with an efficient condenser to return any volatilised tetrachloride to the reaction vessel, and "oleum" containing 80 per cent of SO_3 (120 grams) is allowed to drop in slowly from a tap-funnel inserted through the upper end of the condenser tube. The phosgene is washed with concentrated sulfuric acid and condensed in a thick glass vessel, by means of a snow and salt mixture.

This reaction,—between sulfur trioxide and carbon tetrachloride, was discovered in 1869 by Schützenberger[16] who noticed that when sulfur trioxide and carbon tetrachloride were mixed

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[14] Ann. Suppl. 7, 101.

[15] Ber. **26**, 1990.
C. R. **169**, 17.
Gazetta (1920), 5, i, 30.

[16] C. R. **69**, 352.

the smell of phosgene became immediately apparent, and a steady stream of the gas was evolved on gently warming the mixture, sulfuryl chloride remaining behind in the residue.

In the same year Dewar and Cranston[17] obtained phosgene by heating together a mixture of chlorsulfonic acid and chloroform:

$$CHCl_3 + HSO_3Cl = COCl_2 + 2\ HCl + SO_2$$

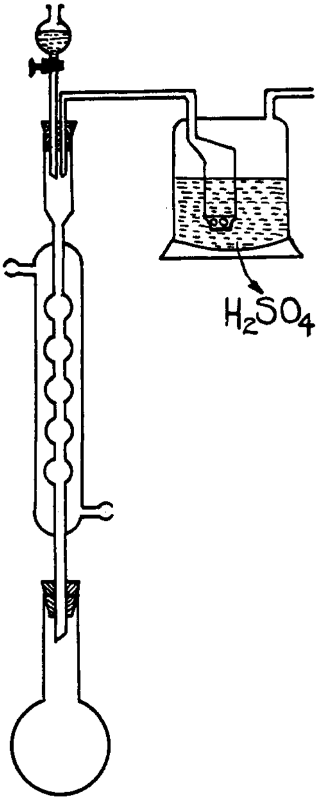

FIG. 1

and the work was repeated by Armstrong[18] who added the fact that hexachlorethane behaved in the same manner:

$$C_2Cl_6 + SO_3 = SO_2Cl_2 + 2\ COCl_2$$

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[17] Chem. News. **20**, 174.
[18] Ber. **3**, 730.

"Oleum" can take the place of pure sulfur trioxide, the most suitable concentration of SO_3 being 45 per cent (corresponding to the acid $H_2S_2O_7$) when the reaction takes the course:[19]

$$CCl_4 + H_2SO_4 \cdot SO_3 = COCl_2 + 2\ SO_3 \cdot HCl$$

while if less than 45 per cent of sulfur trioxide is present in the "oleum" the excess of sulfuric acid over that required for the above equation remains unaltered. If the sulfur trioxide is in excess of 45 per cent, this excess is said to react according to the equation:

$$CCl_4 + 2\ SO_3 = COCl_2 + S_2O_5Cl_2$$

Maugin and Simon[27] expressed the reaction between carbon tetrachloride and sulfuric acid of less than 100 per cent strength by the following equation:

$$(1 + x)\ CCl_4 + H_2SO_4 + xH_2O = SO_3HCl + (1 + x)\ COCl_2 + (1 + 2x)\ HCl$$

This process, using as it does, large quantities of "oleum" and carbon tetrachloride cannot be considered commercially, although its use attained commercial dimensions in Italy, during the late war, when large quantities of phosgene were required for offensive purposes. The reaction between phosphorus pentoxide and carbon tetrachloride was discussed by Gustavson.[20] He found that when one molecule of phosphorus pentoxide reacted with two of carbon tetrachloride phosgene and phosphorus oxychloride were produced, but that when three molecular proportions of the carbon tetrachloride were present no phosgene was observed:

$$\text{i. } P_2O_5 + 2\ CCl_4 = COCl_2 + CO_2 + 2\ POCl_3$$
$$\text{ii. } 2\ P_2O_5 + 3\ CCl_4 = 3\ CO_2 + 4\ POCl_3$$

The process which is exclusively used for the large scale manufacture of phosgene is that involving the combination of carbon monoxide and chlorine in the presence of a suitable catalyst. This process was discovered by Paterno[21] who passed the dried

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[19] J. Russ. Phys. Chem. Soc. **52**, 1.

[20] Z. Chem. (2), **7**, 615.

[21] Gazetta. 8, 233.

gases through a tube packed with animal charcoal, and found that their combination was attended by so great an evolution of heat that artificial cooling of the tube had to be resorted to. Atkinson, Heycock and Pope[22] showed that to obtain the best effect the charcoal had to be specially prepared, since many commercial samples of animal and vegetable charcoals were almost catalytically inactive. They found that the best method of preparation was as follows. Freshly crushed ox-bones were heated in sand until no further volatile matter was produced. The residual charcoal was then extracted with hot hydrochloric acid washed with water and reheated in sand. The bone charcoal was further heated in a current of chlorine for several hours. The investigators found that with a U-tube packed with this charcoal and maintained at 40° to 50° combination took place so rapidly that the gases could not be fed in fast enough. The effect of diluting one of the gases with hydrogen was examined, and it was found that if the temperature was kept below 70° no hydrogen chloride was produced; at 80° a slight amount was obtained, and at 90° and above, the formation of hydrogen chloride was considerable.

Among the other reactions, of less importance, that give rise to the formation of phosgene, the following are the most outstanding:

1. The action of carbon monoxide on platinic chloride, to give the substance $Pt\cdot CO\cdot Cl_2$, which decomposes on heating into spongy platinum and phosgene.[23, 24]
2. The decomposition of certain oxides with carbon tetrachloride[25] at temperatures about 300°. Thus:

$$CCl_4 + MO = COCl_2 + M\cdot Cl_2$$

3. Heating the lead ore "phosgenite" which decomposes to some extent according to the reaction:

$$Pb_2Cl_2CO_3 = 2\ PbO + COCl_2$$

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[22] J. C. S. **117**, 1410.
[23] Ann. Chem. Phys. (4), **21**, 358.
[24] Ann. Suppl. **8**, 242.
[25] Z. Angew. Chem. **37**, 314.

4. The use of other substances as catalysts in the carbon monoxide-chlorine combination reaction. Thus, Plotnikow[26] found that metal salts, especially anhydrous aluminium chloride would serve instead of charcoal. A mixture of carbon monoxide and chlorine passed over anhydrous aluminium chloride at 30° to 35° gave a good yield of phosgene, which the investigator attributed to the formation and decomposition of a complex $(AlCl_3)_x(COCl_2)_y$.

THE PROPERTIES OF PHOSGENE

Phosgene is a gas without colour, but with a peculiar smell; it does not usually fume in air, although it decomposes water according to the equation:

$$COCl_2 + H_2O = 2\,HCl + CO_2$$

The boiling point of phosgene has been determined by several observers and Beckmann[27] gave it as 8.2°/756 mm. a value which agrees fairly well with that obtained by Atkinson, Heycock and Pope.[22] The vapour pressure of phosgene at various temperatures was determined by Paterno and Mazzuchelli and later over a more extended range by Atkinson, Heycock and Pope (loc. cit.). These latter investigators determined the vapour pressure of phosgene at temperatures from −183° to 100° using different forms of apparatus, one for high, and one for low temperature. The apparatus shown in figure 2, was used for the temperatures from −183° to 10°. The thermojunction sealed through the junction A passes into the liquid phosgene, which is distilled into the vessel by attaching a bulb containing pure phosgene to the tube B and, whilst C is lowered distilling the phosgene into D, which is suitably cooled. The measurements of the variation of the vapour pressure with the temperature can be read off directly on the mercury manometer and the thermojunction. For higher temperatures, where the mercury manometer is of no use, the special apparatus shown in figure 3 is used. The pure phosgene was sealed up in vacuo over mercury,

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[26] J. Russ. Phys. Chem. Soc. **48**, 457.

[27] Zeit. Anorg. Chem. **55**, 370.

whilst dipping below the surface of the mercury was placed a mercury manometer of the closed pattern, the inside of which had been previously silvered. Thus by maintaining the tube in a bath of water at constant temperature the vapour pressure, although not readable directly, could be calculated from the amount of silver removed by the mercury from the inside of the manometer. The values obtained are given in tabular and graphical form. (See table 2.) The solubility, density and other physical data were very fully investigated by the last

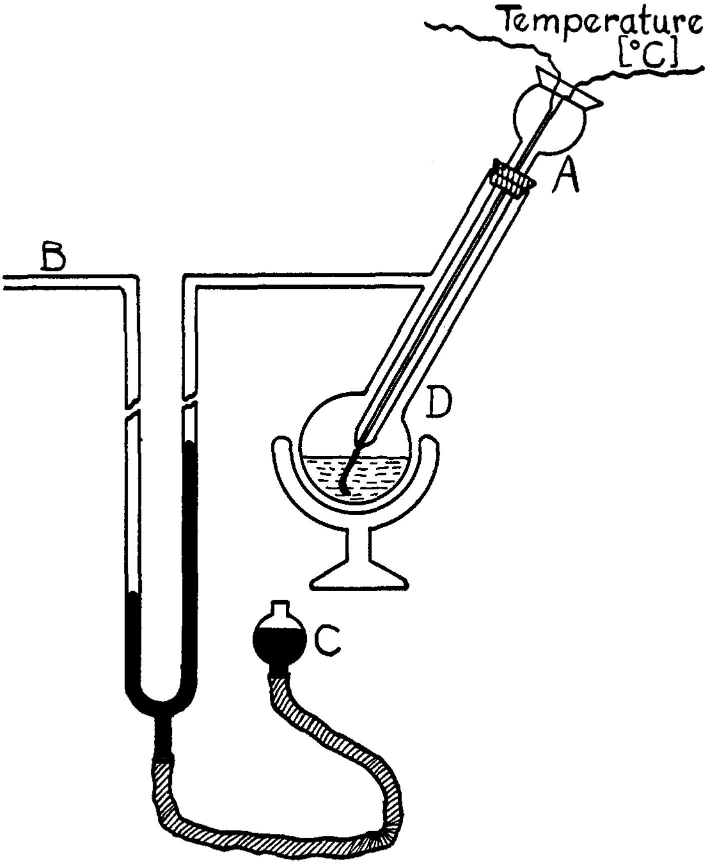

FIG. 2

named authors, and their numerical results are given, in part, in table 3. The melting and freezing points of phosgene were found to be −126 and −128° respectively, the figure for the melting point being slightly lower than that [−118°] given by Erdmann.[28] The variation of the density and temperature are given in table 4.

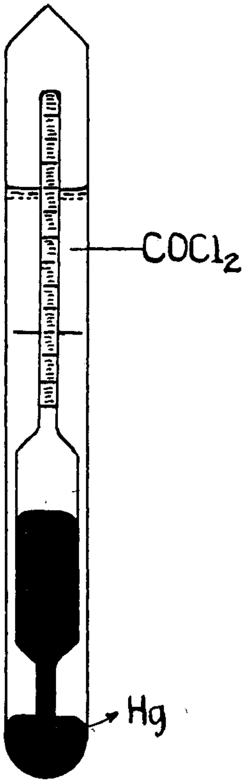

Fig. 3

As a solvent phosgene offers the advantages of dissolving a number of substances which are otherwise difficult to get into solution, and for this reason is a suitable liquid for the determination of molecular weights by the alteration of the boiling point.

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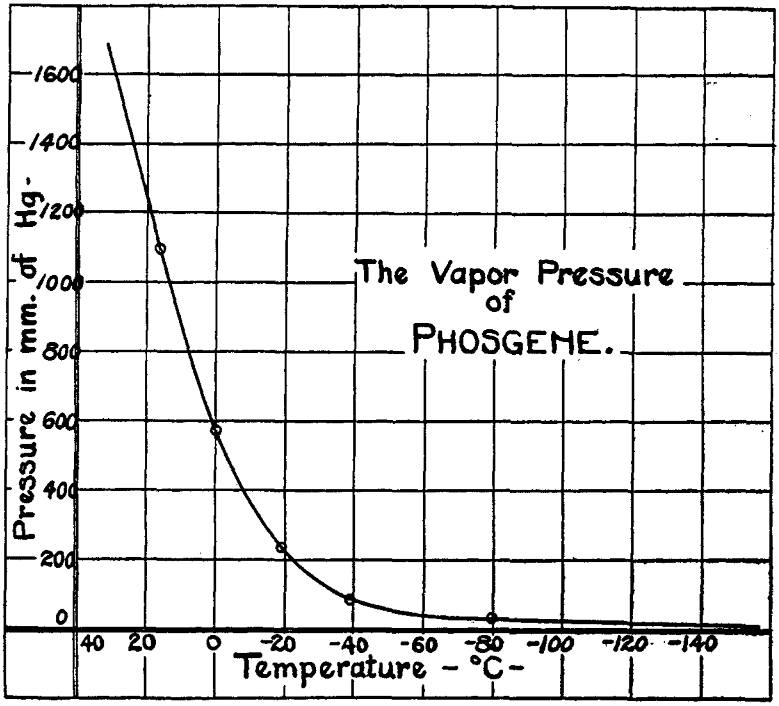
[28] Annalen. (1908), **362**, 148.

TABLE 2

METHOD USED	TEMPERATURE	PRESSURE
		mm. Hg
Water-bath	100	16.07 × 760
Water-bath	50	5.11 × 760
Water-bath	17.5	1105.5
Melting ice	0	568.3
Ice and salt mixture	−19	236.0
Freezing point of mercury	−39	89.5
Solid CO_2 and ether	−79	4.0
Boiling liquid oxygen	−183	0.0



Beckmann and Junker[29] found that the molecular elevation constant was 29, agreeing very well with the value obtained by Atkinson, Heycock and Pope (loc. cit.) by calculation (28–29).

[29] Zeit. Anorg. Chem. **55**, 371.

Beckmann obtained a value of 264 for the molecular weight of iodine by the elevation of the boiling point of phosgene solution indicating the existence of double molecules I_2 in such a solution. In acetic acid he found the value to be 124.

The heat of reaction of phosgene was given by Berthelot[30] as 18,800 from data obtained from the heat of absorption of phosgene in alkali solution. Thomsen[31] pointed out that the absorption of carbon dioxide in Berthelot's experiments was incomplete, and gave as the result of his own work the two values 26,620 and 25,650 whilst that calculated by Ingleson* is 25,500. Thomsen also gives the following values:

TABLE 3

Solubilities of phosgene

SOLVENT	TEMP.	VOLS.	TEMP.	VOLS.	TEMP.	VOLS.	TEMP.	VOLS.
Toluene	17	244.7	23.5	124.2	30.5	79.39	31.5	79.38
Xylene	12.3	457.3	16.4	225.6	16.9	217.9	23.8	103.4
	29.8	71.24						
Creosote oil	16.2	77.42						
Petroleum b.p. 180–280	12.3	263.8	15.8	163.1	16.7	143.4	22.4	79.5
Heavy lubricating oil	23.7	71.2	19.9	49.2	30	48.6		
	15.6	79.7	23.5	39.3	31	24.5		
Nitrobenzene	16.8	106.4						
a-Chloronaphthalene	17.0	104.5						
Chlorobenzene	12.3	422.1	16.6	204.1	16.7	221	24.2	99.9
Acetylene tetrachloride			16.8	149.7	25.1	89.4	29.9	24.9

$$C + O + Cl_2 = 55140 \text{ cals.}$$
$$CO + Cl_2 = 26140 \text{ cals.}$$
$$COCl_2 + Aq. = 57970 \text{ cals.}$$

THE DISSOCIATION OF PHOSGENE

The dissociation of phosgene into carbon monoxide and chlorine is extensive at temperatures above 300° and the extent of such dissociation has been determined by several investigators using various means. The earliest work was that of Bodenstein

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[30] C. R. (1878), 87, 571.

[31] Ber. **16**, 2619, (1883).

* Private communication.

and Dunant[32] who worked at the temperatures of 503°, 553°, 603°, and obtained values which can only be considered as a rough approximation to the truth. In 1909 Horak[33] published a series of results over temperatures from 384° to 500° and obtained a set of results which correspond to a higher degree of dissociation than that which has been found to exist, while in 1920 Atkinson, Heycock and Pope (loc. cit.) published a very irregular set of results which err on the other side, and express a degree of dissociation less than that observed in practice. Their results suffer from the fact that with the method used it was impossible to freeze the equilibrium before partial recombination of the gases had taken place.

TABLE 4

TEMPERATURE	DENSITY PER CUBIC CENTIMETER	TEMPERATURE	DENSITY PER CUBIC CENTIMETER
	grams		*grams*
−110	1.685	−20	1.481
−100	1.633	−10	1.459
−90	1.640	0	1.435
−80	1.617	10	1.412
−70	1.594	20	1.388
−60	1.572	30	1.363
−50	1.549	40	1.338
−40	1.526	50	1.314
−30	1.504		

Recently, the matter has been cleared up to a great extent by two series of careful and painstaking researches, by Bodenstein and Plaut[34] on the one hand, and by Ingleson on the other. The former investigators obtained results which correspond very well with those of the latter, who by working at carefully regulated temperatures, and taking great precautions that the true equilibrium was the one examined, were able to obtain very consistent results. In a long series of preliminary experiments Ingleson found that trustworthy results could not be obtained

[32] Z. Phys. Chem. **61,** 437.

[33] (See 34).

[34] Z. Phys. Chem. **110,** 399.

by the heating of phosgene in glass bulbs and that the use of a quartz bulb was necessary. They also found that more reliable results were obtained by the measurement of the actual dissociation pressure than by the freezing of the equilibrium and estimation iodometrically of the free chlorine.

TABLE 5

TEMPERATURE	K_c	AUTHOR
603	15.0	BD
553	38.0	BD
506	612.5	AHP
505	379.0	AHP
505	105.4	AHP
503	78.2	BD
500	137.5	H
486	209.5	AHP
481.4	151.6	I
475	223.9	H
460	298.7	AHP
451.3	264.8	BP
450	343.9	H
449	425.0	AHP
444.1	348.2	I
443	419.1	AHP
425	630.7	H
415	717.9	I
413.6	719.5	BP
406	1414.0	AHP
404	1123.0	H
400	954.6	AHP
399	1365.0	H
394.6	1230.0	BP
389	1409.0	I
384	2054.0	H
373.3	1884.0	BP
357	3654.0	I
341	8281.0	AHP

BD, Bodenstein and Dunant, BP, Bodenstein and Plaut; AHP, Atkinson Heycock and Pope; I, Ingleson; H, Horak.

A table containing the values of K_c, the dissociation constants at various temperatures is given (table 5).

Perkin[35] in his examination of the magnetic rotation of organic compounds, investigated the series, (*a*) phosgene, (*b*) ethyl chlorocarbonate and (*c*) diethyl carbonate and found that the difference between the magnetic rotations of the first pair was unequal to that between the values of the second pair. Delépine[36] in a series of researches dealing with the variations of physical constants obtained by substituting sulfur for the oxygen of organic compounds was not able to obtain very conclusive results. A typical series of values correlating boiling point and constitution gave the results in table 6. The critical constants of phosgene were obtained by Hakespill and Matthiesen[37] by carefully heating pure phosgene enclosed in a thick glass tube embedded in electrically heated copper and aluminium blocks. Their value for the critical temperature is 183 ± 0.5° comparing well with the value 190° calculated from the Ostwald equation:

TABLE 6

OXYGEN COMPOUND	B.P.	SULPHUR COMPOUND	B.P.	DIFF.
Carbon dioxide	−79	Carbon disulphide	47	2 × 63
Carbonyl chloride	8	Thiocarbonyl chloride	73	65
Acetic anhydride	137	Thioacetic anhydride	157	20
Furane	32	Thiophene	84	52
Phosphorus oxychloride	110	Phosphorus thiochloride	124	14

$$\alpha = l\ (2T_c - T)$$

One of the peculiar physical properties of phosgene is its ability to arrest certain isomeric changes. In 1908 Lowry and Magson[38] noted that certain nitrocamphor solutions in chloroform failed to give mutarotation phenomena. The presence of small traces of acid in the chloroform was also observed to arrest this change (N/100 acetic or hydrochloric). The active agent was shown to be the phosgene produced in an acid solution of chloroform. The presence of an extremely small trace of piperidine (N/10,000) gave chloroform, solutions in which showed, at first, rapid mutaro-

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[35] Chem. News. **69**, 224 (1894).
[36] C. R. **153**, 727.
[37] Bull. Soc. Chim.
[38] J. C. S. **93**, 119, (1908).

tation, but which on keeping, gradually lost the ability of making active solutions. On the addition of further piperidine, however the activity was restored.

REACTIONS OF PHOSGENE WITH INORGANIC COMPOUNDS

With elements

Phosgene reacts with a number of metallic elements, especially on heating, to give the chloride of the metal and carbon monoxide. Many of the light elements—sodium, potassium etc.,—react at the ordinary temperatures, but zinc, magnesium etc., only react on warming.[39] It was pointed out by Ribeau[40,41] that this reaction was probably the basis of the older method for the preparation of metallic chlorides by heating a mixture of the oxide and charcoal in a current of chlorine. It is supposed that the oxide and chlorine in the presence of carbon give phosgene, which reacts with the metal or metal oxide to give the chloride.

It has been found, also, that phosgene is capable of exciting the emission of electrons from the surface of sodium and potassium. Thus when sodium or potassium,[42] or an alloy of the two metals, is exposed to a very low pressure of phosgene, electrons are emitted and the metal acquires a positive charge, even in the complete absence of light. The metal is charged to the extent of about one volt. The phenomenon has also been observed by Richardson.[43]

The interaction of carbonyl chloride and fluorine is of interest in that it gives rise to a substance which may possibly be carbonyl difluoride. This reaction is scarcely to be expected in view of the relative strengths of the halogens, and Humiston[44] observed that fluorine had no action on liquid phosgene. When, however, fluorine and phosgene are passed through a copper tube filled with calcium fluoride heated to 200° and the issuing gases con-

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[39] Berzelius' Jahresberichte. Fort. Phys. Wiss. **16**, 162 (1837).

[40] C. R. **151**, 1432.

[41] C. R. (1892), 1160.

[42] Ann. Physik. 36, 308.

[43] Trans. Roy. Soc. **222A**, 1, 43.

[44] J. Phys. Chem. **23**, 572.

densed, a yellow liquid is obtained B.P. −42°. It is explosive and highly reactive, and is thought to be carbonyl fluoride COF_2. Attempts made during the war for the production of carbonyl fluoride on a large scale failed.

With aluminium halides

The reaction of phosgene with aluminium halides gives rise to some interesting compounds. Baud[45] investigated the interaction of phosgene with aluminium chloride (anhydrous), and obtained, in the cold, a solid compound which analysed out at $Al_2Cl_6 \cdot 5COCl_2$. On warming the compound to 30° the vapour pressure becomes equal to 760 mm. and phosgene is evolved until the formula of the remaining compound is $Al_2Cl_6 \cdot 3COCl_2$. This latter compound is a syrupy liquid solidifying at 9° but it loses a further two molecules of phosgene at 55° giving a crystalline compound $Al_2Cl_6 \cdot COCl_2$, which retains the last molecule of phosgene up to 150°. It was the existence of these complexes that led to the hypothesis that similar complexes between aluminium chloride and halogenated compounds were responsible for the Friedel-Crafts reaction. With anhydrous aluminium iodide[46] there is a strong reaction even at the ordinary temperatures, while, when phosgene is passed into aluminium iodide heated to 200° in an air-bath, a thick fluid is obtained crystallising to a brown solid on cooling. It analyses out as $Al_3(CO)_2 \cdot Cl_2 \cdot I$.

CARBONYL BROMIDE

Besson[47] made an unsuccessful attempt to prepare carbonyl bromide by the interaction of phosgene and aluminium bromide. A very small quantity of a yellow liquid B.P. 63° to 66° was obtained. Later Bartal[48] was more successful, and by reacting phosgene with a large excess of aluminium iodide obtained a yellow liquid which on fractionation gave a yellow liquid B.P.

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[45] C. R. **140**, 1688.

[46] C. Z. Anorg. Chem. **56**, 49.

[47] C. R. **120**, 190.

[48] Z. Anorg. Chem. **55**, 152.

58° to 60° consisting of a solution of bromine in carbonyl bromide. A reddish-brown solid remained behind which had the composition $AlCl_2Br$, so that, presumably, the reaction takes the course:

$$AlBr_3 + COCl_2 = COBr_2 + AlCl_2Br$$

If the phosgene be in excess of the aluminium bromide, a reaction takes place, but no carbonyl bromide can be isolated, the compound COClBr, being exclusively produced. Carbonyl bromide dissociates very easily at ordinary temperatures and cannot therefore, be obtained free from bromine. In this connection it may be noted that Berthelot[49] had previously, (and unsuccessfully) tried to prepare carbonyl bromide by the photochemical combination of bromine and carbon monoxide. It was found by Bonhoeffer[50] that carbonyl bromide was decomposed by light, even when the latter had been filtered through bromine vapour; the rapidity of the decomposition was almost too great for measurement, and violated Einstein's Law. It may be of interest to recapitulate the work done on carbonyl bromide. In 1905 Bartal[51] prepared the substance in some quantity by reacting phosgene and boron tribromide at −20°, when the reaction proceeded according to the equation:

$$BBr_3 + COCl_2 = COBr_2 + COClBr + BCl_3$$

The mixture was distilled and the following fractions collected:

1.	−20° to 12°	Excess of phosgene
2.	12° to 20°	Boron trichloride
3.	30° to 40°	Carbonyl chlorobromide
4.	60° to 70°	Carbonyl bromide

Besson[52] obtained a very small quantity of carbonyl bromide by the passage of a mixture of phosgene and hydrogen bromide through a tube heated to 200°. Other attempts, such as the interaction of phosgene and phosphonium bromide were unsuccessful. In the latter case the reaction proceeded thus:

1. $6\ PH_4Br + 5\ COCl_2 = 10\ HCl + 6\ HBr + 5\ CO + 2\ PH_3 + P_4H_2$
2. $4\ PH_4I + 8\ COCl_2 = 16\ HCl + 8\ CO + P_2I_4 + 2\ P$

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[49] C. R. **87**, 571.

[50] Z. Physik. **13**, 94.

[51] Ann. **345**, 334.

[52] C. R. **120**, 140.

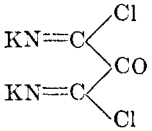
An attempt to prepare selenophosgene by the reaction:

$$SeH_2 + COCl_2 = CSeCl_2 + H_2O$$

resulted in the reaction:

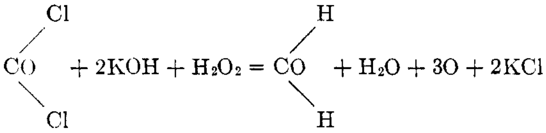
$$SeH_2 + 2\ COCl_2 = 2\ CO + SeCl_2 + HCl$$

An attempt to[53] prepare carbonyl dicyanide by the action of phosgene upon an aqueous solution of the potassium cyanide at −10° led to the formation of an addition product between potassium cyanide and phosgene to which the formula 1 has been arbitrarily assigned. It



Formula 1

breaks up into potassium chloride, potassium carbonate and azulmic acid. It was also ascertained that phosgene and silver cyanide were mutually inactive at temperatures up to 150°. The action of phosgene on hydrogen peroxide has been shown by Kleinstuck[54] to lead to the formation of formaldehyde according to the equation:



indicating that it behaves as the true acid chloride of carbonic acid.

PHOSGENE AND OXIDES

By heating metal oxides and charcoal in a current of chlorine, it was found possible to prepare the chlorides,[55] but a simpler

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[53] Nef. Ann. **287**, 309.

[54] Kleinstueck. B. **51**, 108.

[55] Œrstedt. Ober. D. vid. Serbsks. Fort. **25**, 1824.

and neater way is to heat the oxide in a current of phosgene when the pure anhydrous chloride is obtained.[56] Examples of this reaction with the optimum temperature are given in table 7. Chauvenet[57] points out that in many cases the chloride sublimes in a very pure state; thus, for example, thorium tetrachloride sublimes in fine prismatic needles, stannic chloride distils over and ferric chloride sublimes in deep garnet red crystals.

Sulfides react equally easily with phosgene[58] giving the chloride of the metal and carbon oxysulfide according to the general equation:

$$MS + COCl_2 = COS + MCl_2$$

TABLE 7

OXIDE	TEMPERATURE	CHLORIDE OBTAINED	OXIDE	TEMPERATURE	CHLORIDE OBTAINED
Vanadic acid	350	$VaCl_4$	Beryllium	450	$BeCl_2$
Tungstic acid	250	WO_2Cl_2	Aluminium	400	$AlCl_3$
Tantalic acid	400	$TaCl_5$	Iron	350	$FeCl_3$
Titanic acid	400	$TiCl_4$—TiO_2Cl_2	Chromium	600	$CrCl_3$
Silicon dioxide		No reaction	Manganese	450	$MnCl_2$
Zirconia	400	$ZrCl_4$	Nickel	550	$NiCl_2$
Thoria	650	$ThCl_4$	Uranium	450	UCl_4
Tin oxide	400	$SnCl_4$	Cerium	600	$CeCl_4$
Barium oxide	500	$BaCl_2$	Yttrium	600	YCl_3
Magnesium	450	$MgCl_2$	Lanthanum	600	$LaCl_3$
Zinc	450	$ZnCl_2$			

The temperature and products of reaction of the metallic sulfides with phosgene have been recorded (see table 8). This reaction was used by Nuricsau[59] for obtaining a fairly pure carbonyl sulfide. Cadmium sulfide was found the most suitable sulfide and was placed (alone, or mixed with asbestos) in the tube A of the apparatus shown in figure 4. The tube is heated to about 400° and a slow stream of phosgene dried over sulfuric acid is passed when a steady stream of carbonyl sulfide is obtained. This is

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[56] Chauvenet. C. R. **152**, 87.
[57] Chauvenet. C. R. **147**, 1046.
[58] Chauvenet. C. R. **152**, 1250.
[59] Nuricsau. Ber. **24**, 2967 (1891).

washed with strong caustic potash solution and dried over solid potash. The gas so obtained is about 96 per cent pure.

The natural silicates and phosphates are not so easily decomposed by phosgene as the oxides or sulfides, but on heating to 1000° decomposition takes place with many minerals according to the equation:[60]

$$3 \cdot MO \cdot P_2O_5 + 6\ COCl_2 = 3 \cdot POCl_3 + 6\ CO_2 + 3 \cdot MCl_2$$

Examples of such decomposition are:

Vivianite. $Fe_3 \cdot (PO_4)_2 \cdot 8H_2O$. Ferric chloride sublimes.

TABLE 8

SULPHIDE	FORMULA	TEMPERATURE	PRODUCT
Antimony sulphide	Sb_2S_3	300	$SbCl_3$
Bismuth sulphide	Bi_2S_3	350	$BiCl_3$
Barium sulphide	BaS	400	$BaCl_2$
Zinc sulphide	ZnS	400	$ZnCl_2$
Cadmium sulphide	CdS	400	$CdCl_2$
Copper sulphide	CuS	450	$CuCl_2$’
Mercuric sulphide	HgS	350	$HgCl_2$
Lead sulphide	PbS	350	$PbCl_2$
Iron sulphide	FeS	350	$FeCl_3$
Manganese sulphide	MnS	450	$MnCl_2$
Nickel sulphide	NiS	450	$NiCl_2$

Pyromorphite. $3 \cdot Pb_3P_2O_8 \cdot PbCl_2$ gave lead chloride, $PbCl_2$ some of which sublimed.

Uranite. Gave volatile uranium tetrachloride, calcium chloride remaining behind:

$$P_2O_5 \cdot 2 \cdot UO_2 \cdot CaO + 8 \cdot COCl_2 = 3 \cdot POCl_3 + 8 \cdot CO_2 + 2 \cdot UCl_4 + CaCl_2$$

Monazite. Thorium chloride sublimes.

Silicates react according to the following equation:

$$MSiO_3 + COCl_2 = SiO_2 + CO_2 + MCl_2$$

Examples are given in table 9.

Thus the action of phosgene on these minerals offers a method

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[60] Barlot and Chauvenet. C. R. **157,** 1153.

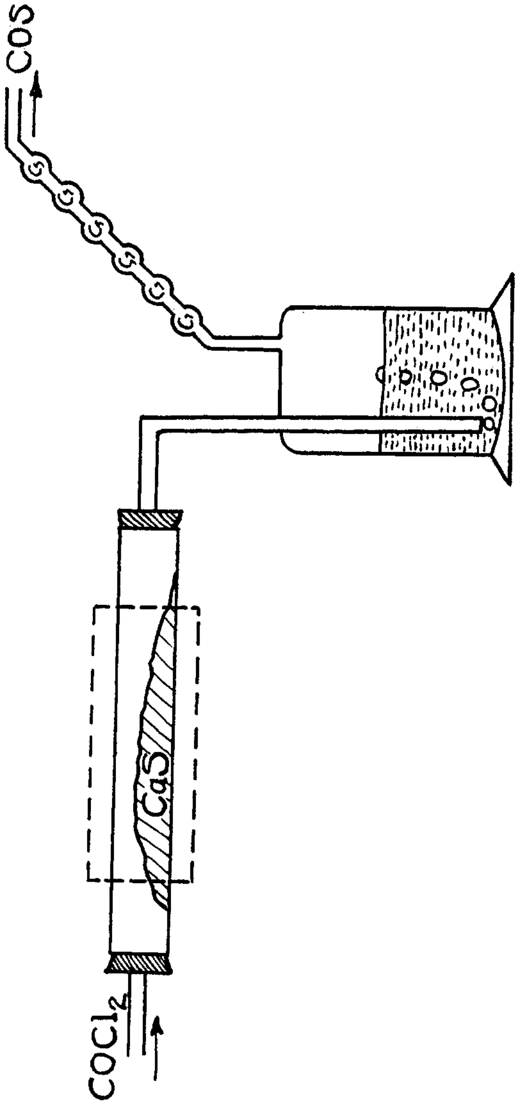

Fig. 4

for the extraction of thorium from monazite sand and for the "opening up" and analysis of refractory minerals, while it has been proposed to manufacture phosphorus oxychloride by the action of phosgene on precipitated ferric phosphate at 300° to 350°.[61]

THE DETECTION AND ESTIMATION OF PHOSGENE

Phosgene is easily detected qualitatively by aspirating the gas suspected of containing it through a saturated aqueous solution of aniline. After two hours standing the diphenylurea is filtered off and identified by its melting point 99°.[62] If the precipitate is washed with water and dried at 70° the weight gives a comparatively accurate idea of the amount of phosgene present. A variation of this method for quantitative estimation, which gives more accurate results, consists in treating the precipitate of s-diphenylurea by the Kjeldhal process, estimating the amount of ammonia formed colorimetrically by the means of Nessler's solution.[63]

TABLE 9

MINERAL	TEMPERATURE	NATURE OF REACTION
Thorite	1000–1150	Chloride sublimes
Gadolinite	1000–1150	Chloride sublimes
Cerite	1000–1150	Chloride sublimes
Zircon	1250	Chloride sublimes
Emerald	1500	No action

Chloroform which is to be used surgically for the production of anesthesia, is tested for the presence of phosgene by the aniline test above, which is stated to detect small traces. The corresponding test with p-phenetidine[64] is, however, more sensitive. The chloroform (5 cc.) is dissolved in pure dry benzene (15 cc.) and one drop of p-phenetidine added. A turbidity due to the

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[61] Jacobs. U. S. Patent. 1462753.

[62] Kling and Schnitz. C. R. **168**, 773.

[63] Kling and Schnitz. C. R. **168**, 891.

[64] Scholbein. B. Deut. Pharm. Gesell. **3**, 213.

presence of s-di-(4-ethoxy phenyl) urea indicates the presence of phosgene.

The best method of estimating phosgene in a mixture of gases[65] is by absorption. Atmospheric moisture decomposes phosgene comparatively slowly, and acid solutions retard absorption. The method which has been found best is to pass a known volume of the gas (from 2 to 3 litres) in 8 to 10 hours through 10 cc. of 10 N caustic soda solution dissolved in 50 cc. of 95 per cent alcohol. After the gas has been passed, the solution is evaporated on the water-bath and the sodium chloride formed estimated in the usual way. The accuracy of the method depends on the absence of hydrogen chloride or chlorine in the gas. If the phosgene is contaminated with these gases the analysis is correspondingly more difficult. Bertholet had to resort to the following cumbrous series of operations for the estimation of phosgene in admixture with air, carbon monoxide and chlorine. The chlorine was removed by shaking with mercury, the phosgene by warming with potassium, the oxygen by pyrogallate and the carbon monoxide with cuprous chloride. The residue was read off as nitrogen. Various iodometric methods have been used for the estimation of phosgene in the presence of chlorine, for the purposes of determining the amount of dissociation of the phosgene (q.v.). The iodometric methods are not accurate and depend for their action on the assumption that phosgene in passing through a solution of potassium iodide liberates no iodine—an assumption which is scarcely justified by facts.

The presence of chlorine is a source of secondary impurities in phosgene which is packed or transported in iron containers, since it converts the iron into ferric chloride which is soluble in phosgene to the extent of one part in a thousand. Phosgene also occurs as an impurity in commercial samples of titanium tetrachloride. It can be estimated therein by dissolving 5 or 10 cc. of the sample in 125 cc. of dilute hydrochloric acid, and aspirating the carbon dioxide formed by the decomposition of phosgene, through a mixture of 25 cc. of 2 N caustic soda and 50 cc. of N/5 baryta.

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[65] Bertholet. Bull. Soc. Chim. N.S. **13**, 9, (1870).

The carbonate produced is estimated by the usual titration with acid.

The presence of hydrochloric acid in phosgene is, however, more easily and accurately determined. The following method is used. Finely powdered mercuric cyanide (5 grams) is placed on the bottom of a 1-litre flask furnished with two exit tubes and taps. A sealed bulb containing a weighed amount of phosgene (about 1 gram) is also placed on the floor of the flask and the latter evacuated. The flask is then shaken to break the glass bulb and liberate the phosgene. Any hydrogen chloride present liberates hydrocyanic acid from the mercuric cyanide which is, however, unattacked by phosgene. After 12 to 14 hours the gases are aspirated off through N/2 caustic soda solution, and the cyanide titrated against N/10 silver nitrate solution after the addition of 5 cc. of ammonia solution (d = 0.880) and 1 cc. of 10 per cent potassium iodide solution.

THE REACTIONS OF PHOSGENE WITH AMMONIA AND PRIMARY AMINES

Davy (loc. cit.) in his original paper noted that ammonia and phosgene reacted, but Regnault[66] was the first to investigate the nature of the reaction. He prepared his phosgene by the older photochemical method and observed that four volumes of ammonia were required to neutralise one of phosgene. He isolated from the white substance produced—formerly thought to be a compound of ammonia and phosgene, or "chlorocarbonic acid" as it was then termed—ammonium chloride and a white substance which was at first thought to be urea. It failed, however, to give the precipitate with nitric acid, characteristic of urea, and gave instead a brisk effervescence. These facts led Regnault to suggest that the substance was an isomer of urea to which he gave the provisional name of "carbamide." It seems probable in view of the properties of urea, that the nitric acid used by Regnault was highly contaminated with nitrous acid. Hofmann[67] in 1849 repeated the reaction and obtained ammonium chloride

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[66] Regnault. Ann. Chim. Phys. (2). **69**, 189 (1838).

[67] Hofmann. Ann. **70**, 139 (1849).

and urea as did Natanson[68] seven years later. Both these latter investigators were able to obtain the characteristic precipitate of urea nitrate. Natanson considered this synthesis of urea to be a sequel to the work of Wöhler in 1828 and remarks: "Es entsteht hier also der Harnstoff aus drei sogenannten anorganischen Gasen, das Chlor, Kohlenoxyd und Ammoniak." Bouchardat[69] extended this work on the reaction of ammonia and phosgene and observed the formation of guanidine, cyanuric acid and a compound which he termed "melanuric acid" and which is, in all probability, cyammelide. Fenton[70] proved the presence of urea in the reaction product by the reactions with hypochlorite, by analysis and by the crystalline form. He also identified microscopically some guanidine sulfate.

Gattermann and Schmidt[71] passed phosgene over ammonium chloride heated to 400° in an air-bath. A colourless liquid distilled over which on standing gave bright needles of urea chloride (or carbamic chloride), $NH_2 \cdot CO \cdot Cl$, melting at 50°. The substance has an unpleasant smell, fumes in air and commences to distil at 60° with much decomposition into hydrogen chloride and isocyanic acid. With water the compound decomposes thus:

$$Cl \cdot CO \cdot NH_2 + H_2O = CO_2 + NH_4Cl$$

whilst on standing it decomposes into hydrogen chloride and cyammelide. Its use as a synthetic agent will be discussed later.

Werner[72] has suggested a complicated mechanism for the reaction of phosgene with ammonia. He investigated the yields of various substances when ammonia and phosgene are allowed to react at various temperatures, pure dry ammonia being passed through a 3 per cent solution of phosgene in pure benzene. His results are given in table 10. He argues from this table that since the amount of urea increases as the temperature increases,

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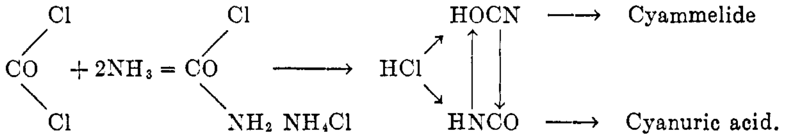
[68] Natanson. Ann. **98**, 287 (1856).
[69] Bouchardat. C. R. **69**, 962 (1869).
[70] Fenton. J. C. S. **35**, 793 (1879).
[71] Gattermann and Schmidt. Ber. **20**, 858.
[72] Werner.

it must be produced by rearrangement of ammonium cyanate produced in a somewhat roundabout way:



In view of the extreme local heating obtained in reacting these substances, it seems that the reaction may go partly in the direction indicated, but it is more likely that the urea chloride (if formed) would react immediately with ammonia thus:

$$2\ NH_3 + Cl{\cdot}CO{\cdot}NH_2 = NH_2{\cdot}CO{\cdot}NH_2$$

TABLE 10

PRODUCT	TEMPERATURE		
	20.25	40.5	65.7
Urea	31.7	37.3	41.2
Biuret	14.4	10.1	7.8
Ammelide	7.65	8.6	10.6
Cyanuric acid	3.48	6.4	5.95
Cyammelide	0.69	Trace	None

than that decomposition would take place, followed by urea synthesis from ammonium cyanate formed as fourth product in the chain of reactions. Two other points in Werner's theory of the mechanism of this reaction seem open to criticism. In the first place he accounts for the formation of biuret by the action of cyanic acid on urea, a reaction which does not take place rapidly or quantitatively under any circumstances. It seems far more likely that the biuret is obtained by the action of urea chloride on urea:

$$NH_2{\cdot}CO{\cdot}NH_2 + Cl{\cdot}CO{\cdot}NH_2 = NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + HCl$$

or by the action of phosgene, followed by ammonia on urea

$$\begin{aligned} NH_2{\cdot}CO{\cdot}NH_2 + CO_2Cl_2 &= NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}Cl + HCl \\ NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}Cl + 2\ NH_3 &= NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_4Cl \end{aligned}$$

These side reactions would probably be less extensive as the temperature rose, since the compounds containing the $-CO\cdot Cl$ group would probably be very unstable at higher temperatures. This would account for the fact that the combined amounts of urea and biuret is almost independent of the temperature (46.1, 47.4, and 49 in table).

The second point which it is difficult to see is the mechanism of the formation of allophanic ester on shaking the benzene solution with alcohol. Werner postulates the following reaction:

$$2\ NH_2\cdot CO\cdot Cl + C_2H_5\cdot OH = NH_2CO\cdot NH\cdot CO\cdot O\cdot C_2H_5 + 2\ HCl$$

It is more likely to be formed by the esterification of allophanyl chloride (produced as above) thus:

$$NH_2\cdot CO\cdot NH\cdot CO\cdot Cl + C_2H_5OH = NH_2\cdot CO\cdot NH\cdot COO\cdot C_2H_5 + HCl$$

PRIMARY AMINES

The primary amines react with phosgene violently with the liberation of much heat, which if not controlled by conducting the reaction in a diluting solvent leads to decomposition of the products. If the amine alone is used, the product depends considerably on the conditions of the experiment. By passing the vapour of phosgene through a solution of the amine in an inert solvent, e.g., benzene, the symmetrical urea is almost always formed:

$$2\cdot R\cdot NH_2 + CO\cdot Cl_2 = 4\cdot NH\cdot CO\cdot NH\cdot R$$

but by spraying an emulsion of amine and water into rapidly stirred liquid phosgene a quantity of the isocyanate can be obtained:

$$R\cdot NH_2 + CO\cdot Cl_2 = R\cdot NCO + 2\cdot HCl$$

This method of obtaining the isocyanate is not convenient, and the yield is not good. It is much better to heat the well-dried, and powdered amine hydrochloride in a stream of phosgene when the carbamyl chloride is formed which decomposes on heating into hydrogen chloride and the isocyanate:

$$\begin{aligned} R\cdot NH_2 + COCl_2 &= R\cdot NH\cdot CO\cdot Cl + HCl \\ R\cdot NH\cdot CO\cdot Cl &= R\cdot NCO + HCl \end{aligned}$$

Hofmann[73] was probably the first to observe the action of phosgene on aniline, and records that the carbanilide and aniline hydrochloride were produced. The method, obviously, gives us a way of synthesising almost any symmetrical urea of the type $R\cdot NH\cdot CO\cdot NH\cdot R$. Among many ureas that have been made in this way the following may be mentioned:

s-Di-4-methylphenyl urea	from p-toluidine[74]	m.p. 256
s-Di-4-methoxyphenyl urea	from p-phenetidine[75]	m.p. 174
s-Di-m-cymyl urea	from m-cymidine[76]	m.p. 221
s-Di-4-propylphenyl urea	from p-propylaniline[77]	m.p. 205
s-Di-4-butylphenyl urea	from p-butylaniline[78]	m.p. 283
s-Di-2-anthraquinonyl urea	from α-minoanthraquinone[79]	m.p. 300

The last of these compounds is a yellow vat dye. The first mention of the use of phosgene for converting the amine hydrochloride to the isocyanate is a note by Hentschel[80] to the effect that by heating carbanilide (the intermediate product) with phosgene, phenyl isocyanate was formed and distilled over as an oil. The method was patented by Hofmann and Schoensack.[81] The preparation of β-anthraquinonyl isocyanate, from which orange and red vat dyestuffs can be prepared, has also been protected[82] while the reaction for obtaining the intermediate carbamyl chlorides has been extensively used in synthetic organic chemistry. The value of these compounds lies in their intense reactivity, by the aid of which the following classes of compounds can be synthesised:

1. *Urethanes.* By the treatment of urea chlorides with alcohols. Thus ethyl urea chloride gives ethyl urethane on treatment with alcohol:

$$C_2H_5\cdot NH\cdot CO\cdot Cl + C_2H_5\cdot OH = C_2H_5\cdot NH\cdot CO\cdot O\cdot C_2H_5 + HCl$$

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[73] Hofmann. Ann. **70**, 139 (1849).

[74] Girard. Ber. **6**, 444 (1873).

[75] Muelhaeuser. Ber. **13**, 922 (1880).

[76] Kolbe and Warth. Ann. **221**, 172 (1883).

[77] Francksen. Ber. **17**, 1240.

[78] Pahl. Ber. **17**, 1240.

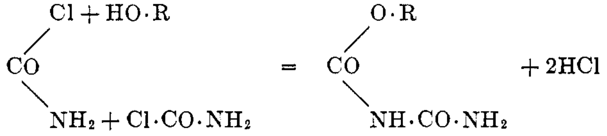
[79] Meister, Lucius and Brüning. G. P. 232739.

[80] Hentschel. Ber. **17**, 1284.

[81] Hofmann and Schoetensack. G. P. 29929.

[82] Meister, Lucius and Brüning. G. P. 232739.

Gattermann and Schmidt[83] prepared a whole series of these compounds up to and including the cetyl derivative, but found that in the case of these latter derivatives the reaction proceeded completely to the double compounds thus:

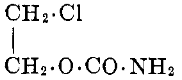


$$CO\begin{cases}Cl + HO\cdot R\\ NH_2 + Cl\cdot CO\cdot NH_2\end{cases} = CO\begin{cases}O\cdot R\\ NH\cdot CO\cdot NH_2\end{cases} + 2HCl$$

These allophanic esters are produced with the short chain alcohols to some extent. These authors also investigated the action of urea chloride on ethylene chlorhydrin, glycol and glycerol and obtained the compounds I, II and III, respectively:

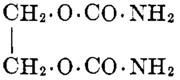
TABLE 11

SUBSTANCE	COMPOUND OBTAINED	M.P.
Thiophenol	Phenyl thioallophanate	
a-Naphthol	a-Naphthyl urethane	158
b-Naphthol	b-Naphthyl urethane	187
Thymol	Thymol allophanate	190
Guaiacol	Guaiacyl urethane	127
Pyrocatechol	Pyrocatechyl diurethane	178
Resorcin	Resorcinyl diurethane	194
Hydroquinone	Hydroquinone diurethane	236
Pyrogallol	Pyrogallol triurethane	178
Salicylaldehyde	?	128



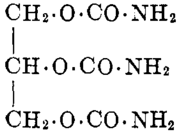
$$\begin{array}{l}CH_2\cdot Cl\\ |\\ CH_2\cdot O\cdot CO\cdot NH_2\end{array}$$

I



$$\begin{array}{l}CH_2\cdot O\cdot CO\cdot NH_2\\ |\\ CH_2\cdot O\cdot CO\cdot NH_2\end{array}$$

II



$$\begin{array}{l}CH_2\cdot O\cdot CO\cdot NH_2\\ |\\ CH\cdot O\cdot CO\cdot NH_2\\ |\\ CH_2\cdot O\cdot CO\cdot NH_2\end{array}$$

III

Phenols and heterocylic hydroxy compounds also react with urea chlorides to give urethanes. In table 11 is a list of the compounds prepared by these reactions by the last mentioned authors.

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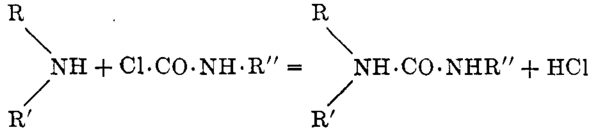
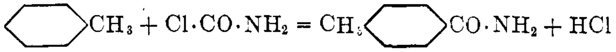
[83] Ann. **244**, 30.

2. Ureas. This second class of compounds, which may be synthesised by the use of urea chlorides does not need detailed discussion. Any unsymmetrical urea can be obtained by the interaction of a urea chloride with the appropriate amine, thus:

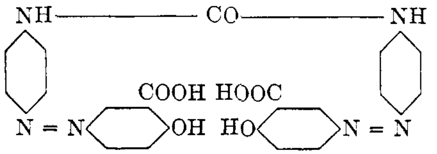


$$\begin{matrix}R\\ \\ R'\end{matrix}\!\!>\!NH + Cl\cdot CO\cdot NH\cdot R'' = \begin{matrix}R\\ \\ R'\end{matrix}\!\!>\!NH\cdot CO\cdot NHR'' + HCl$$

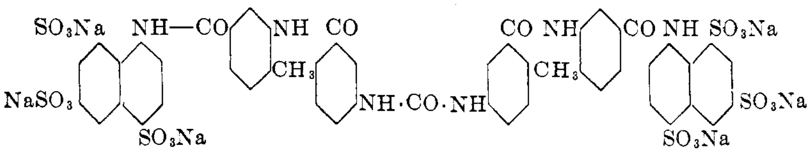
3. Aromatic acids. There are several ways in which phosgene can become responsible for the synthesis of aromatic acids and their acid chlorides. Thus the carbamyl chloride can become the acid chloride of the Friedel-Crafts reaction, and lead to the synthesis of the acid through the acid amide. Thus with toluene and carbamyl chloride in the presence of aluminium chloride we get:[84]



That substitution of the phenyl residue of the aryl amine does not often interfere with the ability of the amino group to react with phosgene is shown by the formation of compounds such as (1),[85] below, which is used as a red-brown vat dye, and (2) which is used as a therapeutic agent in trypanosomiasis, under the name "Fourneau 309":



(1)



(2)

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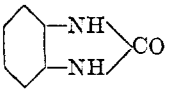
[84] See 83.

[85] B. A. and S. F. G. P. 46737. Fried. 2, 450.

DIAMINES

The reaction between ortho-diamines[86] and phosgene proceeds in exactly the manner expected, giving in the case of ortho-phenylene diamine, phenylene urea a compound occurring in white needles (4)



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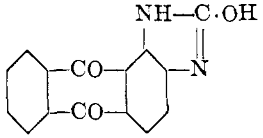
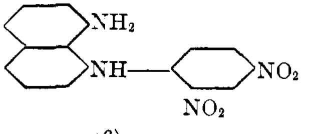


(5)

The corresponding 4-tolylene and 3-brom-4-tolylene compounds have also been prepared, while an interesting dyestuff intermediate, stated to have the formula (5) is prepared from 1:2 diaminoanthraquinone.[87] Its constitution as oxy-1:2-anthrimidazole rests on its solubility in alkalies to give orange-red salts.

With p-phenylene diamine[88] it is possible to get the double isocyanate by heating the hydrochloride of the base to 200–250° in a stream of phosgene. 1:4-di-isocyanatobenzene proves to be a white crystalline solid melting at 91°. It gives the usual derivatives on condensation with alcohols and amines, and its vapour density corresponds to the simple formula $C_6H_4\cdot(NCO)_2$. With benzidin[89] the simple compound with the two isocyanate groups is obtained in a precisely similar manner. It crystallises in splendid needles and gives the usual condensation reactions. m- and o-Tolylene diamines react normally, while compounds of the type (6) react slowly to give cyclic ureas, of which (7) is an example:[90]



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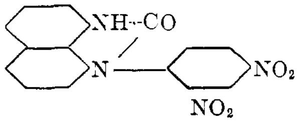

(7)

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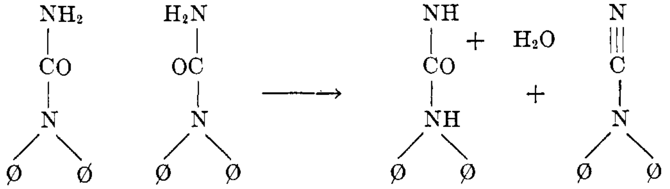
[86] Hartmann. B. **23,** 1046.
[87] Farbenfab. Heyer. G. P. 238981.
[88] Gatterman and Wramplemeyer. Ber. **18,** 2604.
[89] Snape. J. C. S. **49,** 255.
[90] Sachs. and Forster. Ber. **44,** 1744.

SECONDARY AMINES

The action of phosgene on a secondary amine generally leads to the formation of the carbamyl chloride which in the case of the normal secondary amines is a compound of considerable stability. Thus, if phosgene is treated with a well cooled solution of dimethylamine the compound dimethylcarbamyl chloride[91] is obtained as a clear colourless liquid. It is extremely reactive and gives rise to the same condensations as the primary urea chlorides. The use of an excess of the amine leads to the formation of the fully substituted urea. Thus Michler[92] obtained tetraethyl urea from diethylamine and phosgene. He also obtained diphenylcarbamic chloride from diphenylamine and phosgene and found that he could obtain di-, tri- and tetraphenyl urea by its condensation with suitable amino compounds.[93] The destructive distillation of the as-diphenyl urea prepared in this way proceeds in a peculiar manner giving cyanic acid diphenylamine, diphenylamine cyanide and water:

TABLE 12

COMPOUND	SOURCE	M.P.
Methylphenyl carbamyl chloride	Methylaniline[95]	88
Phenyl-b-naphthyl carbamyl chloride	b-Naphthylphenylamine[96]	101–102
Di-β-naphthyl carbamyl chloride	Di-β-naphthylamine[96]	171
Di-benzyl carbamyl chloride	Di-benzylamine[97]	An oil
Di-p-tolyl carbamyl chloride	Di-p-tolylamine[97]	102–103
p-Tolyl benzyl carbamyl chloride	p-Tolyl benzylamine[97]	An oil



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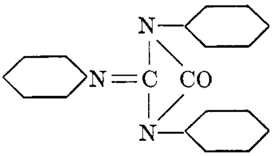
[91] Michler and Escherlich. Ber. 12, 1162 (1879).

[92] Michler. Ber. 8, 1665 (1875).

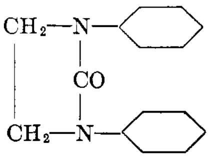
[93] Michler. Ber. 9, 396 (1876).

This, it may be added, seems to point to the formula $O=C=NH$ for cyanic acid.[94] It has been shown that mixed aryl-alkyl secondary amines yield similar compounds to the purely aryl compounds, among them being those given in table 12. Among the more interesting experiments with secondary amines are those in which the latter substance is reacted with a compound containing two secondary amino groups in the molecule.

Thus, Michler and Keller[98] found that triphenylguanidine gave the compound (8) and that ethylene diphenyl diamine behaved similarly giving the compound (9), compound (12) being to some extent produced by a side reaction. Hansen[99] obtained similar results with propylene diphenyl diamine (10), obtaining also some of the di-acid chloride (11). The extension of these



(8)



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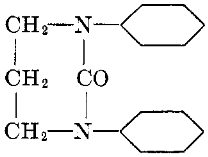
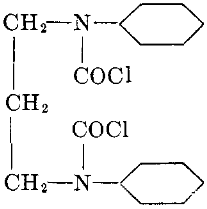
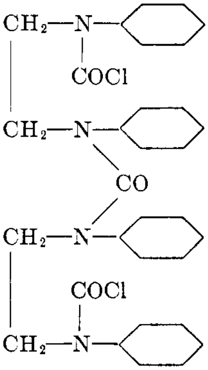


(10)



(11)



(12)

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[94] Michler. Ber. **9**, 716.

[95] Michler and Zimmermann. B. 12, 1165.

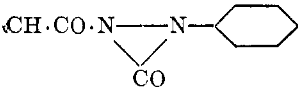
[96] Kym. Ber. **23**, 427.

[97] Hammerich. Ph.D. Thesis. Basle. Ber. **25**, 1819 (1891).

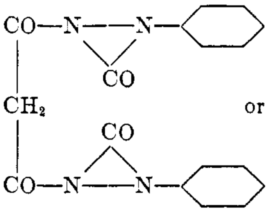
[98] Michler and Keller. Ber. **14**, 2181.

[99] Hanssen. Ber. **20**, 781.

experiments to the tetra and penta methylene diphenyl diamines would be interesting, in order to observe whether seven and eight membered rings of this type can be produced. The action of phosgene on the hydrazides is a special case of the series discussed above. Freund and Goldschmidt[100] reacted acetylphenyl hydrazine with phosgene and obtained a compound to which they attached the somewhat improbable formula (13). Other hydrazides (tabulated below) were tried and since the reaction appeared to be a general one the work was extended to the hydrazides of dibasic acids, giving the dicarbazides. Thus in the first investigation the compound from malonyl dihydrazide was accorded one of the formulas (14) or (15).

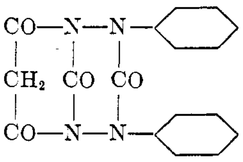


(13)



(14)

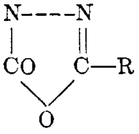
or



(15)

In addition the compounds given in table 13 were prepared.

Freund and Kuh[101] suggested that the formula of the carbazines was better represented by (16) than by the formulae previously used.



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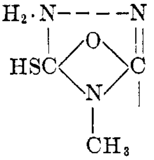

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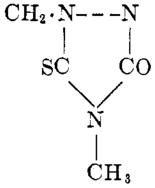

(18)

Their formula accorded well with the behaviour of the compounds, and had the merit of avoiding the improbable three-membered ring involved in the earlier formulae. The name "biazolone"

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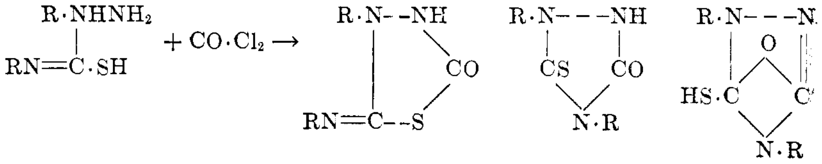
[100] Freund and Goldsmith. Ber. **21**, 1240 and 2456.

[101] Freund and Kuh. Ber. **23**, 2061.

was given to such structures. The action, however, of phosgene on the semicarbazides and thiosemicarbazides, as elucidated by Busch and Offermann[102] confirmed the fact that compounds of this type are in reality represented by the cyclic formulae. In reacting the compound 2-benzyl-4-methyl semicarbazide with phosgene they obtained the compound (21) which they finally identified as 1-benzyl-4-methyl thiazurol. This they found was unstable on heating and passed over into the compound (22) 1-benzyl-4-methyl-5-thiolendoxy triazole. The mechanism of this reaction, which is somewhat obscure was investigated by Busch and Limpach[103,104] who isolated the intermediate compound (20) a thiodiazolone anil, which on fusion or boiling in alcoholic solution changes into the triazole compound thus:

TABLE 13

COMPOUND	SOURCE	M.P.
Acetylphenylcarbazine	Acetylphenylhydrazine	
Formylphenylcarbazine	Formylphenylhydrazine	73
Propionylphenylcarbazine	Propionylphenylhydrazine	62
Benzoylphenylcarbazine	Benzoylphenylhydrazine	114
Succinylphenylcarbazine	Succinylphenylhydrazine	225
Malonylphenylcarbazine	Malonylphenylhydrazine	205
Ethylmalonylphenylcarbazine	Ethylmalonylphenylhydrazine	223
Oxalylphenylcarbazine	Oxalylphenylhydrazine	287



(19) (20) (21) (22)

Various of these series of compounds have been prepared, chief among them being those shown in table 14.

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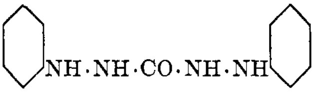
[102] Busch and Opfermann. B. **37**, 2335 (1904).

[103] Busch. Ber. **42**, 4766.

[104] Busch and Limpach. Ber. **44**, 569.

The action of phosgene on simple hydrazines does not seem to have been extensively studied. Heller[105] obtained diphenylcarbazide (23)

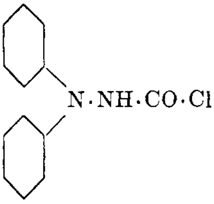


(23)

by the action of phosgene on a well cooled solution of phenyl hydrazine. It is a crystalline compound melting at 163°. Acree[106] obtained diphenyl carbazyl chloride (24) and tetraphenyl carbazide by the action of phosgene on as-diphenyl hydrazine.

TABLE 14

PARENT COMPOUND	THIAZUROL. M.P.	THIOL. M.P.
Benzylmethylthiosemicarbazide	117	157
Benzylallylthiosemicarbazide	108	161
Benzylphenylthiosemicarbazide	147	217
2-m-Tolyl-4-phenylthiosemicarbazide	125	259
2-m-Bromphenyl-4-phenyl thiosemicarbazide	118	257
2-m-Chlorphenyl-4-phenyl thiosemicarbazide	108	260
2-b-Naphthyl-4-phenyl thiosemicarbazide	133	295
2-p-Tolyl-4-phenylthiosemicarbazide	144	240
2-p-Bromophenyl-4-phenyl thiosemicarbazide	170	255



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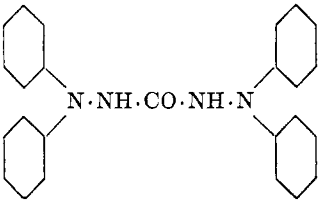

(24)

TERTIARY AMINES

Phosgene is without action on the aliphatic tertiary amines, and aromatic tertiary amines react very reluctantly save in the

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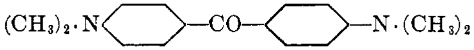
[105] Heller. Ph.D. Thesis. Ann. **263**, 269.
[106] Acree. Ber. **26**, 3154 (1903).

presence of anhydrous aluminium chloride, when the Friedel-Crafts reaction takes place with the formation of a considerable amount of acid chloride or ketone. Thus with dimethylaniline the well known Michler's ketone is obtained, tetramethyldiaminobenzophenone. At the same time a small amount of the double ketone (26) is obtained.[107]



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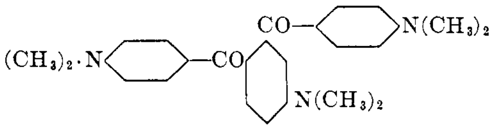
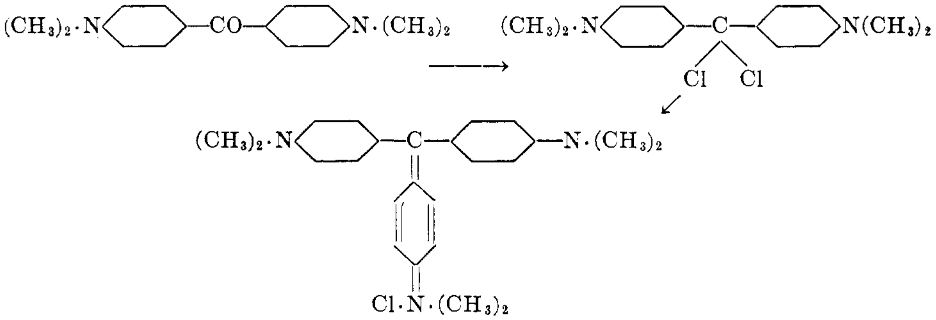


(26)

The former compound—Michler's ketone, can be reduced to the carbinol (Michler's Hydrol) in the usual way[108] and the two substances form the starting point of a large series of triphenyl methane dyes, chiefly blues and violets of the crystal violet type including Victoria Blue, Night Blue, Wool Green S, Victoria Blue 4R etc. The ketone can be condensed with the amine hydrochloride to give the dyestuff, which is said by Hofmann to be produced by the following series of reactions:[109]



The intermediate ketone need not be isolated, for the tertiary amine can be directly condensed in excess, with phosgene, in the

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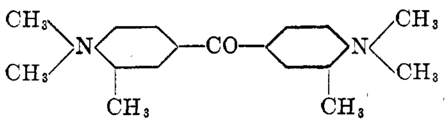
[107] Michler. Ber. **9**, 716 1899.

[108] See 107.

[109] Hofmann. Ber. **18**, 770.

presence of aluminium or zinc chloride to give the dyestuff. Thus in one typical patent[110] on this class of dyestuff, dimethyl-aniline (100 kgm.) is saturated with phosgene (18 to 20 kgm.) at 20° and allowed to stand for 24 hours. Further dimethyl-aniline (50 kgm.) and powdered zinc chloride (30 kgm.) are added. The mixture is then warmed to 40° to 50° and a further 20 kgm. of phosgene passed in, and the whole digested at 60° until a deep paste of methyl violet is formed.[111] The general applicability of such a process is limited by the fact that many substituted tertiary amines do not yield a Michler's ketone. Thus Rassov and Reuter[112] found that on condensing dimethyl-o-toluidine with phosgene a number of compounds including methyl chloride were obtained. The compounds (28) and (29) were obtained but not the compound expected (27).



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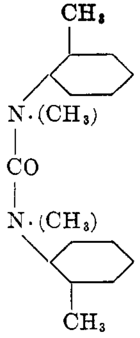

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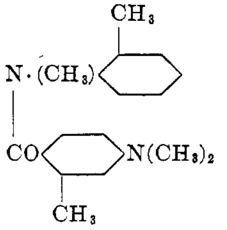

(29)

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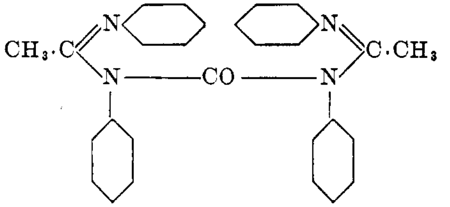
[110] Meister, Lucius and Brüning. B. P. 8694. J. C. S. I. **7,** 205 (1888).
Badische anilin und Soda-Fabrik. G. P. 26066. Ber. **17,** 60.
Badische anilin und Soda-Fabrik. G. P. 27789. Ber. **17,** 339.
Meister, Lucius and Brüning. G. P. 34463. (1884).

[111] Badische-Anilin und Soda-Fabrik. G. P. 29943. (1884) Ber. 18, 7.

[112] Rassow and Reuter. J. Pr. Ch. **85,** 489.

Loeb[113] investigated the action of phosgene on ethenyldiphenyltolamine. When one molecular proportion of phosgene and two of the base are used the compound (30) is produced, but with an excess of phosgene the compound (31) is the product of the reaction. On heating it loses a molecule of phosgene giving the cyclic compound (32).



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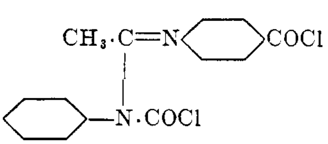

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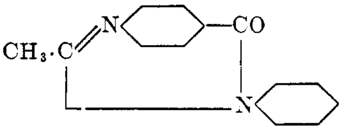

THE REACTION OF ALCOHOLS AND PHENOLS WITH PHOSGENE AND THE SYNTHESIS OF ACIDS AND ACID CHLORIDES

The reaction between alcohols and phosgene is simplicity itself and can be summarized in the equation:

$$R\cdot OH + CO\cdot Cl_2 = R\cdot CO\cdot Cl + HCl$$

The action, investigated by Dumas[114] has been a standard method for the preparation of chlorocarbonic esters since his time. Dumas extended his observations to methyl chlorocarbonate, and various other investigators have applied the method to other alcohols. Among the chief compounds mentioned are those given in table 15.

By the action of phosgene on glycerol, compounds were isolated which included glycerol carbonate (J.C.S., 1925), but the best way of obtaining glycerol carbonate is undoubtedly the action of heat on a mixture of glycerol and phenol carbonate.

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[113] Loeb. Ber. **18**, 2427.

[114] Dumas. Ann. Chim. Phys. (2), **56**, 226; (2), **58**.

The glycerol carbonate can be distilled out of the mixture in vacuo. It is a white crystalline substance m.p. 148°.[124] The action of phosgene on glycollic ester[125] gives rise to a pulverulent substance which is probably the carbonate. The action of an excess of alcohol on phosgene or of the sodium derivative of

TABLE 15

ALCOHOL	B.P. OF CHLOROCARBONATE	REFERENCE
Methyl	71.4	114, 117, 110, 123
Ethyl	90	114, 117, 121
iso-Amyl	154.4	115, 117
Propyl	115.2	116, 117
Butyl		117
iso-Butyl	128.8	118, 117
Ethylene glycol	236	122
Glycolchlorhydrin	158–160	123

TABLE 16

COMPOUND	B.P.
Dimethyl carbonate	90.6
Diethyl carbonate	126
Dipropyl carbonate	168.2
Di-iso-butyl carbonate	190.3
Di-iso-amyl carbonate	228.3
Methyl ethyl carbonate	109.2
Methylpropyl carbonate	130.8
Methylisobutyl carbonate	143.6
Ethylisobutyl carbonate	160.1
Ethylisoamyl carbonate	182.3

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[115] Medlock. Quart. J. Chem. Soc. **1**, 368 (1849).

[116] Roemer. Ber. **6**, 1101 (1873).

[117] Roese. Ann. **205**, 229.

[118] Mylius. Ber. **5**, 477, (1872).

[119] Klepl. J. Pr. Ch. (2), **26**, 448 (1882).

[120] Hentschel. Ber. **18**, 1177.

[121] Farb. Bayer. G. P. 118537.

[122] Nemirowsky. J. Pr. Ch. 2, **28**, 439.

[123] Nemirowsky. J. Pr. Ch. (2), **31**, 173.

[124] Hochstetter. G. P. 252758.

[125] Ann. **154**, 257 (1870).

alcohol on that compound leads to the formation of a symmetrically disubstituted ester of carbamic acid:

$$R\cdot O\cdot CO\cdot Cl + NaO\cdot R = R\cdot O\cdot CO\cdot O\cdot R\cdot + NaCl$$

Among the aliphatic carbonic esters obtained by Rosse (loc. cit.) who investigated the whole series very thoroughly, and others, are those given in table 16.

In the aromatic series the action of phosgene on phenols is not nearly so violent as with their aliphatic analogues. Thus phosgene and phenol require to be heated in a sealed tube[126] to obtain phenyl carbamyl chloride $C_6H_5\cdot O\cdot CO\cdot Cl$. This compound, however, will condense with ammonia in the usual way, and with amines to give urethanes, and with sodium phenate to give diphenyl carbonate. The symmetrical di-aryl substituted esters of carbonic acid can be most readily obtained by the action of phosgene on the sodium salt of the phenol concerned, preferably in a well-cooled acetone solution. The compounds given in table 17 are among those that have been prepared in this manner.

TABLE 17

PARENT SUBSTANCE	CARBAMYL CHLORIDE	DI-SUBSTITUTED ESTER OF CARBONIC ADID	REFERENCE
Phenol		m.p. 75	127, 128, 129
2:4 Dinitrophenol		m.p. 125.5	127
Cresol (?)		m.p. 125	127
Eugenol	b.p./17 mm. 174	m.p. 93	130, 131
Guaiacol	b.p./10 mm. 110		130
b-Naphthol	m.p./65–66		130
iso-Eugenol	b.p./15 mm. 155–157		130
Methyl salicylate	b.p./20 mm. 141–147		130
Ethyl-p-oxybenzoate	m.p. 55–56		130
Thiophenol		m.p. 72	131
Salicylaldehyde		m.p. 94–95	131

[126] Kempf. J. Pr. Ch. (2), **1**, 402 (1870).

[127] Hentschel. G. P. 24151. Fried. **1**, 230, 1880.

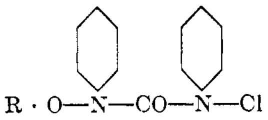
[128] Barral and Morrell C. R. **128**, 1579.
Barral and Morel. Bull. Soc. Ch. (7), **21**, 725.

[129] Einhorn. G. P. 224108.

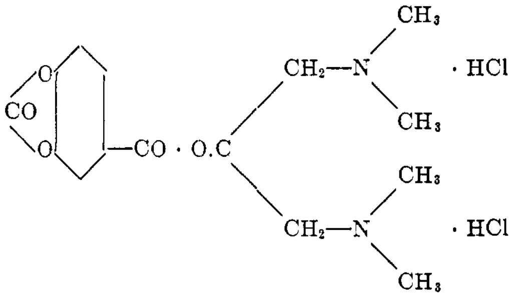
[130] Loewenberg. Chem. Zent. 1886, 390.

[131] Hofmann. Z. Ang. Ch. **21**, 1896.

With reference to certain of these esters of chlorocarbonic acid Hofmann[131] remarks that they react curiously with pyridine giving rise to compounds of the type (33)



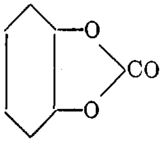
(33)



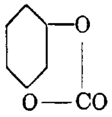
(34)

He also prepared the compound (34) in order to test its therapeutic properties.

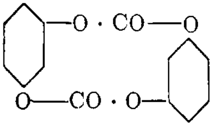
It will be noticed that the ortho-dihydric phenols condense



(35)



(36)



(37)

with phosgene to give phenylene carbonic esters as in (35). With the meta- and para- dihydric phenols, the reaction is not so simple. Bernbaum and Lune[132] reported the compound (36) as the product of the reaction, an infusible and insoluble white powder, but it more likely that the compound is in reality the double molecule (37). Many other carbonic esters, e.g., carbonyl gallic ester, etc.,[133] have been prepared, but their mere enumeration serves no useful purpose.

SYNTHESIS OF ACIDS, ACID CHLORIDES AND KETONES

Among the earlier investigators of the reactions of phosgene Harnitz and Harnitzki[134] stated that phosgene and methane

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[132] Birnbaum and Lune. Ber. **14**, 1754 (1881).

[133] Fischer and Freudenberger. Ber. **46**, 1116.

[134] Harnitz-Harnitzky. C. R. **60**, 923 (1865).

react in sunlight to give a certain amount of acetyl chloride. This was confirmed by Butlerow[135] who observed at the same time that phosgene when reacted with zinc methyl gave acetyl chloride thus:

$$(CH_3)_2\cdot Zn + 2\ CO\cdot Cl_2 = 2\ CH_3\cdot CO\cdot Cl + ZnCl_2$$

Bertholet[136] denied that any reaction took place between methane and phosgene at temperatures below a red heat, and his experiments indicated that the same inertness was to be observed in connection with ethane, ethylene, acetylene and benzene, while De Clermont and Fontaine[137] showed a similar lack of reaction between octane and phosgene. The latter investigators seem to be correct, at least for low temperatures and in the absence of catalysts. The process, however, devised by Hochstetter[138] for the preparation of methyl chloride involves the chlorination of methane by phosgene. A mixture of the gases is passed through a tube packed with wood charcoal and heated to 400° when the reaction

$$CH_4 + CO\cdot Cl_2 = CH_3\cdot Cl + CO + HCl$$

takes place. The methyl chloride is removed from the system by refrigeration.

Phosgene will act as an acid chloride in the Friedel-Crafts reaction, giving the usual products when the reaction is stimulated by the presence of anhydrous aluminium chloride. Harnitz and Harnitzki[139] stated that a small quantity of benzoyl chloride was obtained when phosgene reacted on benzene alone, but this is doubtful; Meyer[140] however, obtained a fair amount of benzoyl chloride by heating silver benzoate and phosgene in a sealed tube. The simplest way of obtaining benzoyl chloride from benzene is to allow a solution of phosgene in the latter

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[135] Lehrb. d. Org. Chemie. 297 (1868).

[136] Bertholet. Bull. Soc. Chim. N. S. **13**, 9 (1870).

[137] DeClermont and Fontaine. Bull. Soc. Chim. N. S. **13**, 494.

[138] Hochstetter. Austr. Pat. Applic. 9887.
Hochstetter. G. P. 292089. J. Soc. Chem. Ind. **35**, 867 (1916).

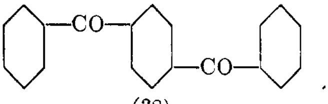
[139] Harnitz Harnitzky. C. R. **58**, 748 (1864).

[140] Meyer. Ann. **156**, 271 (1870).

hydrocarbon to stand over anhydrous aluminium chloride.[141] The reaction does not proceed quantitatively to benzoyl chloride, since if the standing is protracted or the temperature rises the second stage of the reaction sets in and benzophenone[142] is formed:

$$\begin{aligned}\text{(i) } & C_6H_6 + CO\cdot Cl_2 &&= HCl + C_6H_5\cdot COCl\\ \text{(ii) } & C_6H_5\cdot CO\cdot Cl + C_6H_6 &&= C_6H_5\cdot CO\cdot C_6H_5 + HCl\end{aligned}$$

At the same time a small quantity of the compound (38) is formed but its isolation is difficult.



(38)

TABLE 18

COMPOUND	REFERENCE	M.P. OF ACID FROM THE ACID CHLORIDE	KETONE
Benzene		120	
Toluene	141	177	m.p. 92, b.p. 240
Xylene	144		b.p. 340
Anthracene	145	206	
Anthraquinone	145	ca. 300	
Diethylaniline	146	188	
Thiophene	147		m.p. 87–88.
Methylphenylaminobenzene	148	184	

The reaction has been recently reinvestigated[143] in an attempt to synthesise anthraquinone by the reaction of an excess of phosgene on benzene or benzoyl chloride. No trace of anthraquinone could be detected.

The reaction between phosgene and aromatic hydrocarbons in

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[141] Ador and Krafts. Ber. **10**, 2173.

[142] Freidel, Krafts, and Ador. Ber. **10**, 1854.

[143] Wilson and Fuller. J. Ind. Chem. Eng. **14**, 406 (1922).

[144] Ador and Rilliet. Ber. **11**, 399.
Elbs and Olberg. Ber. **19**, 428.

[145] Graebe and Liebermann. Ber. **2**, 678 (1869).

[146] Michler and Gradmann. Ber. **9**, 1912 (1876).

[147] Gattermann. Ber. **18**, 3013.

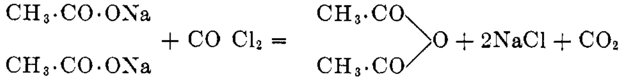
[148] Sarauw. Ber. **14**, 2180 (1881).

the presence of anhydrous aluminium chloride is fairly general and table 18 gives the results obtained with some of the commoner hydrocarbons.

Behla[149] was unable to obtain a carboxylic acid from the interaction of phosgene and dihydroanthracene, and his experiments on the interaction of phosgene and phenanthrenequinone were likewise inconclusive.[150]

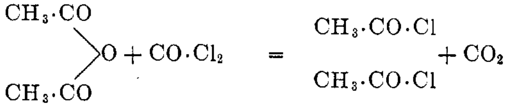
Phosgene has been found a convenient agent for the preparation of acid anhydrides and chlorides from the parent acids or their sodium salts. Thus sodium acetate successively undergoes the reactions shown below:

(i)



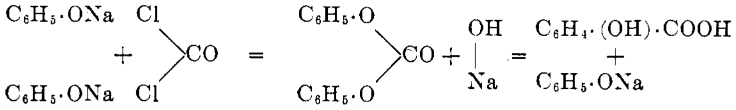
$$\begin{matrix}\mathrm{CH_3\cdot CO\cdot ONa}\\ \mathrm{CH_3\cdot CO\cdot ONa}\end{matrix} + \mathrm{CO\ Cl_2} = \begin{matrix}\mathrm{CH_3\cdot CO}\\ \mathrm{CH_3\cdot CO}\end{matrix}\!>\mathrm{O} + \mathrm{2NaCl} + \mathrm{CO_2}$$

(ii)



$$\begin{matrix}\mathrm{CH_3\cdot CO}\\ \mathrm{CH_3\cdot CO}\end{matrix}\!>\mathrm{O} + \mathrm{CO\cdot Cl_2} = \begin{matrix}\mathrm{CH_3\cdot CO\cdot Cl}\\ \mathrm{CH_3\cdot CO\cdot Cl}\end{matrix} + \mathrm{CO_2}$$

Hofmann and Schoelensack[151] patented this as a general method for the production of acid chlorides and anhydrides of acetic, propionic, butyric and benzoic acids. Later they extended the method to the production of salicylic acid from sodium phenate.[152] The sodium phenate mixed with caustic soda was heated to 140° to 200° in a stream of phosgene. The reaction may be represented:



$$\begin{matrix}\mathrm{C_6H_5\cdot ONa}\\ \mathrm{C_6H_5\cdot ONa}\end{matrix} + \begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\!>\mathrm{CO} = \begin{matrix}\mathrm{C_6H_5\cdot O}\\ \mathrm{C_6H_5\cdot O}\end{matrix}\!>\mathrm{CO} + \begin{matrix}\mathrm{OH}\\ |\\ \mathrm{Na}\end{matrix} = \begin{matrix}\mathrm{C_6H_4\cdot (OH)\cdot COOH}\\ +\\ \mathrm{C_6H_5\cdot ONa}\end{matrix}$$

The original general method for the production of the acid chlorides and anhydrides was to heat the sodium salt with phosgene in an autoclave. This method not only gave a poor yield of the desired products but was very difficult of operation

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[149] Behla. Ber. **20**, 701.

[150] Behla. Ber. **18**, 3169 (1885).

[151] Hofmann and Schoetensack. G. P. 29669.

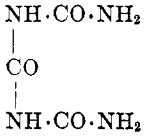
[152] Hofmann and Schoetensack. G. P. 30172.

on a technical scale. To remedy this Hochstetter[153] devised a process in which the vapour of the free acid is passed, together with phosgene through a tube heated to bright redness and filled with a catalyst material (usually wood charcoal). A better yield is obtained while the process is simple and easily controlled.

SOME MISCELLANEOUS REACTIONS OF PHOSGENE

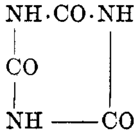
With acid-amides and compounds containing the $-CO\cdot NH_2$ *group*

Among the earlier researches on phosgene was that of Schmidt[154] who investigated its reactions on various compounds of the urea and ureide type. He found that when dry urea was heated under pressure with phosgene that the substance carbonyl di-urea was formed (39):



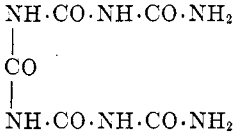
$$\begin{array}{l} NH\cdot CO\cdot NH_2 \\ | \\ CO \\ | \\ NH\cdot CO\cdot NH_2 \end{array}$$

(39)



$$\begin{array}{lr} NH\cdot CO\cdot NH & \\ | & | \\ CO & | \\ | & | \\ NH \text{——} & CO \end{array}$$

(40)

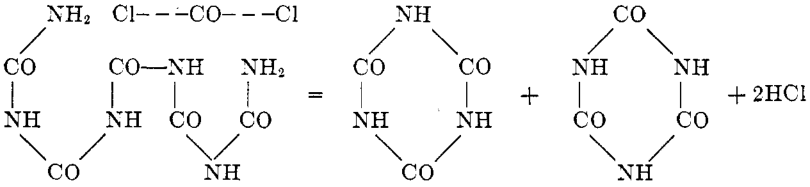


$$\begin{array}{l} NH\cdot CO\cdot NH\cdot CO\cdot NH_2 \\ | \\ CO \\ | \\ NH\cdot CO\cdot NH\cdot CO\cdot NH_2 \end{array}$$

(41)

This substance was almost exclusively formed when the mixture was heated at 100° for two days, but on heating carbonyl diurea with phosgene to 150° to 160° cyanuric acid (40) was formed by the loss of one ammonia molecule from the carbonyl-diurea (39).

Biuret behaved in the same way giving in the first instance carbonyl dibiuret (41) which on further heating with phosgene gave cyanuric acid and hydrogen chloride thus:



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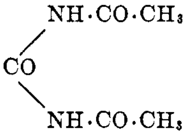
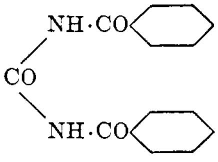
[153] Hochstetter. G. P. 283896. C. Abs. **10**, (1916), 93.
Hochstetter. G. P. 29617. C. Abs. **10**, (1916), 94.

[154] Schmidt. J. Pr. Ch. 2, **5**, 39 (1872).

Other amides behave in a similar manner, thus acetamide gives diacetylurea (41a) and benzamide gives carbonyl dibenzamide (42).

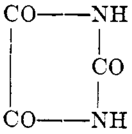


(41a)

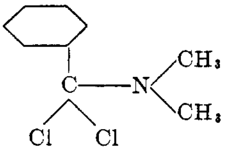


(42)

Oxamide was stated to give a mixture of carbonyl diurea, urea and carbon dioxide, but later and more careful investigations by Basarow[155] have shown that when oxamide and phosgene are heated to 170° to 180°C. parabanic acid is formed (43). The earlier work on the reaction between urea and phosgene was confirmed by Schiff.[156] An interesting case, described by Hollemann[157] is that of the interaction of phosgene and N-dimethyl benzamide, in which there is no free hydrogen on the nitrogen atom. In this case a dichloro compound of the formula (44) was formed.



(43)



(44)

Diazo and diazoamino compounds

Saranew[158] observed that with diazoaminobenzene in benzene solution the passage of phosgene gives a white crystalline compound insoluble in benzene and ligroin. It is slowly soluble in cold water but readily so in hot water which decomposes it with the evolution of nitrogen and the formation of phenol and di-

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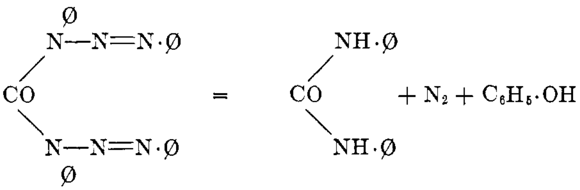
[155] Basarow. Ber. **5**, 477.

[156] Schiff. Ann. **291**, 367.

[157] Hollemann. Ber. **9**, 846 (1876).

[158] Sarauw. Ber. **14**, 2443 (1881).

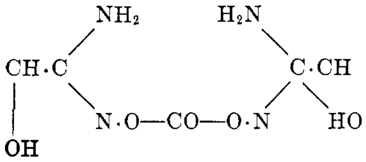
phenyl urea. This led Saranew to suggest the following for the constitution and decomposition of the compound in question:



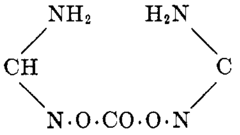
Similar phenomena were observed in the reactions of p-diazoaminotoluene but diazoaminobenzene-3-carboxylic acid,[159] in the reaction with phosgene gave benzoyl chloride m-oxybenzoic acid and nitrogen. Similar experiments with diazobenzene-p-bromaniline gave no conclusive results.

Amidoximes

By adding powdered phenyloxyethenylamidoxime to a solution of phosgene in benzene Gross[160] obtained a compound in small silvery leaflets m.p. 131°. It is soluble in alcohol and ether but not in water or dilute acids. Gross states that its formula is as in (45), but it is far more likely that condensation takes place through the amino groups, giving the symmetrically disubstituted urea.



(45)



(46)

Falk[161] obtained a similar compound from benzenylamidoxime, concerning which a similar uncertainty of constitution exists (46). Exactly the same question of constitution arises concerning the products on the interaction of phosgene and the salt of

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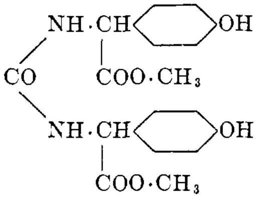
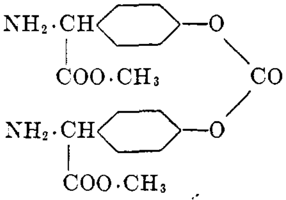
[159] Sarauw. Ber. **15**, 42.
[160] Gross. Ber. **18**, 2480.
[161] Falk. Ber. **18**, 2471.

amino-acids containing a hydroxy group. Thus Aloy and Rabout[162] observed that phosgene was without action on p-oxyphenylaminoacetic methyl ester, although on dissolving the latter in alkali phosgene gave a non-crystalline gelatinous condensation product. The authors assumed this to have the constitution (47), but it is probably the symmetrically disubstituted carbamic ester (48), seeing that its preparation requires



(47)

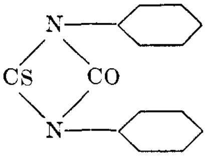


(48)

the presence of alkali. A similar compound from tyrosine[163] is also stated to have been obtained in this manner.

Thioureas and thiosemicarbazides

The reaction of phosgene on thioureas and thiosemicarbazides throws some slight light on their constitution, which from the evidence available would seem to comprise a thiol group. Thus, Will[164] found that the reaction between phosgene and diphenyl thiourea proceeded easily and that a compound was formed in small needles m.p. 87. To this compound he arbitrarily assigned the constitution



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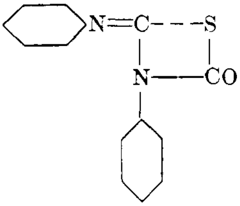

(50)

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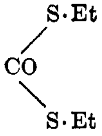
[162] Aloy and Rabaut. Bull. Soc. Chim. (4), **9**, 253.
[163] Hugouneng and Morel. C. R. **142**, 48 (1906).
[164] Will. Ber. **14**, 1486.

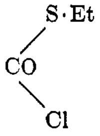
(49), but the later work of Wolf[165] has shown that the action of phosgene and thiophosgene on ureas and thioureas falls into line with that of the other chloracid chlorides, and gives rise to a cyclic compound of the type (50). The action of phosgene on thiosemicarbazides has already been discussed.

Thiols

The reaction of thiols or their alkali metal derivatives with phosgene proceeds normally. Thus Saloman[166,167] observed the formation of the compound (51) from sodium mercaptide and phosgene, and was later able to prepare the chlorocarbonyl compound (52) by using phosgene

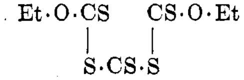


(51)



(52)

in excess. The corresponding compound from amyl mercaptan was prepared by Schoene[168] as an evil smelling liquid b.p. 190°. It undergoes the usual condensations with ammonia and amines.[169] The reaction is only capable of extension to the xanthates, when thiophosgene replaces phosgene. In this case potassium ethyl xanthate gives the



$$\begin{array}{cc} \mathrm{Et{\cdot}O{\cdot}CS} & \mathrm{CS{\cdot}O{\cdot}Et} \\ | & | \\ \multicolumn{2}{c}{\mathrm{S{\cdot}CS{\cdot}S}} \end{array}$$

(53)

compound (53). If phosgene is used none of the corresponding carbonyl derivatives are formed.

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[165] Wolf. Ber. **25**, 1456.

[166] Salomon. J. Pr. Ch. (2), **6**, 433 (1872).

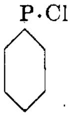
[167] Salomon. J. Pr. Ch. (2), **7**, 254 (1873).

[168] Schoene. J. Pr. Ch. (2), **30**, 416.

[169] Willcox. J. A. C. S. **28**, 1031 (1906).

Phosphines

An isolated reference[170] to the behaviour of phosphines with phosgene shows that when phenylphosphine (the phosphorus analogue of aniline) is reacted with phosgene, three compounds are formed,



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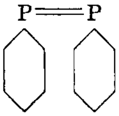

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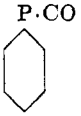

(56)

phosphenyl chloride, diphosphenyl, and the phosphorus analogue of phenyl isocyanate (56).

Aldehydes

By reacting aldehyde vapour with phosgene a colourless limpid liquid was obtained by Harnitz and Harnitzki[171] They termed it "chloracetin" and associated with it the formula C_2H_3Cl. Later it was found that the compound reacted with sodium methoxide[172,173] to give acetone—a reaction which, at the time, constituted a new synthesis of that compound,—and which was written:

$$C_2H_3Cl + Na{\cdot}O{\cdot}CH_3 = CH_3{\cdot}CO{\cdot}CH_3 + NaCl$$

Later Kekule and Zinke[174] observed that when an aldehyde and phosgene were allowed to react a large amount of paraldehyde and metaldehyde was formed, while it remained for Eckenroth[175] to point out that in addition the chloracetin of the older writers was in reality ethylidene dichloride. Thus:

$$CH_3{\cdot}CHO + CO{\cdot}Cl_2 = CH_3{\cdot}CH{\cdot}Cl_2 + CO_2$$

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[170] Michaelis and Dittler. Ber. **12**, 339.

[171] Harnitz-Harnitzky. Ann. **111**, 192 (1859).

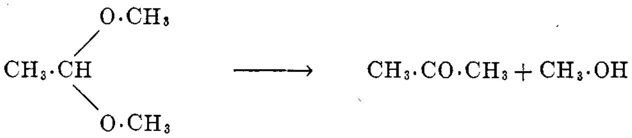
[172] Friedel. C. R. **60**, 930 (1865).

[173] Friedel. Ann. Chim. Phys. (4), **16**, 403 (1869).

[174] Kekule and Zinke. Ann. **162**, 125 (1872).

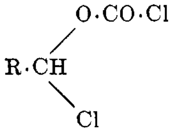
[175] Eckenroth. Ber. **18**, 518.

Its interaction with sodium methoxide is then readily explained by the formation of the intermediates:



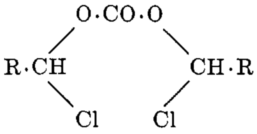
$$CH_3\cdot CH(O\cdot CH_3)_2 \longrightarrow CH_3\cdot CO\cdot CH_3 + CH_3\cdot OH$$

The action of phosgene on aldehydes in the presence of secondary bases,[176] such as quinoline or diethylamine leads to the formation of compounds such as (57) and (58):



$$R\cdot CH(O\cdot CO\cdot Cl)\cdot Cl$$

(57)



$$R\cdot CHCl\cdot O\cdot CO\cdot O\cdot CHCl\cdot R$$

(58)

Thus chloral gives a compound $C\cdot Cl_3\cdot CH(O\cdot CO\cdot Cl)\cdot Cl$ as an oil b.p. 78–80/14 mm.

Nitriles

Henle[177] passed phosgene into acetonitrile and obtained what he thought to be a compound $C_2H_5\cdot CN\cdot CO\cdot Cl_2$. In all probability the phenomenon was one of mere solution.

Heterocyclic compounds

When pyrrole potassium[178] is suspended in ether and phosgene is passed in, a vigorous reaction takes place and on evaporation of the ethereal solution an oil remains. This oil consists of two compounds di-pyrryl urea which is volatile in steam and can be recrystallised from alcohol in needles, and di-pyrryl ketone which is crystalline but non-volatile.

With pyridine the pentavalent compound (59) is formed

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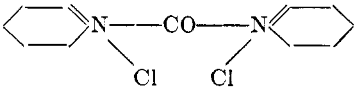
[176] Farbenfab. Bayer. G. P. 121223.

[177] Henle. Ann. **106**, 285 (1858).

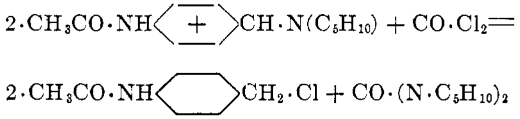
[178] Ciamician and Magnaghi. Ber. **18**, 44.

first,[179,180] although subsequent stages in the reaction have not been fully elucidated.



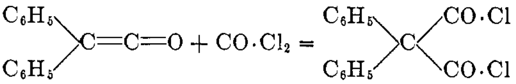
(59)

With piperidine derivatives, however, the formation of the urea is more certain. Thus in the case of p-acetylaminobenzylpiperidine observed by Kuehn[181] the action of phosgene gives rise to two compounds p-acetylaminobenzyl chloride and di-piperidyl urea:



Ketenes

The interaction of diphenylketene and phosgene has been recorded by Staudinger.[182] The reaction is one of simple addition, leading to the formation of an acid chloride of gem-diphenylmalonic acid:



$$(C_6H_5)_2C{=}C{=}O + CO{\cdot}Cl_2 = (C_6H_5)_2C(CO{\cdot}Cl)_2$$

Grignard compounds

Grignard[183] himself investigated the reaction of phosgene on the organo-magnesium halides, and observed that in no case was the ketone formed according to the equation:

$$CO{\cdot}Cl_2 + 2{\cdot}R{\cdot}MgBr = R{\cdot}CO{\cdot}R + 2{\cdot}Mg{\cdot}BrCl$$

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[179] Powell and Dehn. J. A. C. S. **39**, 1717.

[180] Heyden. G. P. 109033.

[181] Kuehn. Ber. **33**, 2900.

[182] Staudinger, Goehring and Schoeller. Ber. **47**, 40.

[183] Grignard. C. R. **136**, 815.

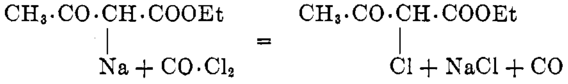
In all cases the secondary and tertiary alcohols were formed according to the equations:

1. $COCl + 3 \cdot R \cdot MgBr = R_2 \cdot CH \cdot O \cdot Mg \cdot Br + R \cdot CH_3 \cdot H + 2.MgBrCl$
2. $CO \cdot Cl_2 + 3 \cdot R \cdot MgBr = R_3 \cdot C \cdot O \cdot MgBr + 2 \cdot Mg \cdot BrCl$

Sachs and Loewy[184] observed that the main product was the tertiary alcohol and that the reaction could be extended to the aryl compounds. Thus, when phosgene is allowed to react on a benzene solution of phenyl magnesium bromide a crystalline product is obtained, which on hydrolysis yields triphenyl carbinol. Tritolyl and tribenzyl carbinols have been prepared in the same manner.

Salts of acetoacetic ester

When phosgene reacts on the sodium salt of acetoacetic ester, the reaction[185] is one of simple chlorination and leads to the formation of monochloracetoacetic ester as a limpid colourless liquid b.p. 192-200°.



$$\begin{array}{l} CH_3 \cdot CO \cdot CH \cdot COOEt \\ \qquad\qquad\quad | \\ \qquad\qquad\; Na + CO \cdot Cl_2 \end{array} = \begin{array}{l} CH_3 \cdot CO \cdot CH \cdot COOEt \\ \qquad\qquad\quad | \\ \qquad\qquad\; Cl + NaCl + CO \end{array}$$

The reaction with the copper salt[186] of acetoacetic ester, however, proceeds to the formation of a dimethyl-γ-pyrone dicarboxylic ester, which is obtained in yellow crystals m.p. 79° to 80°.

The physiological action of phosgene[187,188,189]

The extended use of phosgene in modern warfare as a poison gas lends an excuse for a short note on its physiological action. The chief effect of phosgene is said to be the change in concentration of the blood in animals submitted to its influence. Thus, during the first five to eight hours the blood is considerably di-

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[184] Sachs and Loewy. Ber. **36**, 1588.
[185] Buchka. Ber. **18**, 2090.
[186] Conrad and Gutzeit. B. **19**, 19.
[187] Hertz. J. Ind. Chem. Eng. **11**, 9.
[188] Underhill. Chem. Abs. 1910, 2929.
[189] Samartino. Arch. de. Farmacol. speri. **25**, 30.

luted, a phenomenon which is followed by a rise of temperature and at a later stage by the concentration of the blood solids.

In poisoning by phosgene the first symptoms are those of distress and dyspnoea, with coughing and the expectoration of a thin yellow mucous together with occasional vomiting. Later there is severe cyanosis which persists even after the administration of oxygen, death usually taking place from heart failure when the patient attempts some slight physical effort. Post-mortem examination shows that there is much oedema of the lungs, laryngitis, agglomeration of the oesophagus and stomach, and cellular necrosis.