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XXVIII.—Certain Aromatic Cyanates and Carbamates.

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CONTINUING some experiments on phenyl cyanate already reported (*Chem. Soc. Trans.*, 1885, 770), I examined its action on pyridine. No reaction takes place in the cold, when these liquids are mixed in about molecular proportions, but on boiling, and then allowing the mixture to remain in a vessel closed by a drying tube containing calcium chloride, beautiful crystals are formed. These are only sparingly soluble in ether, but somewhat more soluble in alcohol; on recrystallisation from the latter, small quadratic plates are obtained melting at 175° . This melting point, the form of the crystals, the relation to solvents, and the fact that a large proportion of the pyridine remains unchanged, suggested the probability that the phenyl cyanate had condensed in the presence of this base to diphenyl dicyanate. On analysis this proved to be the case.

	Calculated for		
	$C_{12}H_{10}N_2O$	Calculated for	
	$(i.e., C_5H_5N + C_6H_5NCO).$	C ₁₄ H ₁₀ N ₂ O ₂ .	Found.
Ν	14.14	11.76	12.27

Many years ago Hofmann showed (Ann., Suppl. 1, 57; Ber., 3, 765, and 4, 246) that a small quantity of triethylphosphine brought

about this change; but pyridine is more suitable as being much cheaper and more readily obtained.

The account of the preparation of a phenylene dicyanate by Gattermann and Wrampelmeyer (*Ber.*, **18**, 2604), by a method analogous to that by which Hentschel obtained phenyl cyanate (*Ber.*, **17**, 1284), suggested to me that other dicyanates might be prepared in a similar manner, and I could then examine their action upon alcohols, as I had previously done with phenyl cyanate. The action of phosgene on benzidine was first investigated.

Diphenylene Diisocyanate, $CO: N \cdot C_6H_4 \cdot C_6H_4 \cdot N: CO.$

A current of phosgene was passed over well-dried benzidine hydrochloride contained in a fractional distillation flask, heated in a paraffinbath at 230° to 250°. A small quantity of a colourless oil passed over, and solidified in the delivery tube leading from the flask. In later experiments it was found preferable, as giving a better yield, to couduct phosgene for about two hours over the salt heated in benzoic acid vapour (b. p. 250°), finally distilling over the cyanate, still in an atmosphere of phosgene, by means of a bath of diphenylamine vapour (b. p. 310°). Probably a substituted carbamide is first formed, as with aniline; and a higher temperature is required to completely decompose this and to drive off the cyanate. The two phases of reaction would, according to this hypothesis, be represented by the following equations :—

(1.)
$$\mathrm{NH}_2 \cdot \mathrm{C}_6 \mathrm{H}_4 \cdot \mathrm{C}_6 \mathrm{H}_4 \cdot \mathrm{NH}_2 + \mathrm{COCl}_2 = 2\mathrm{HCl} + \mathrm{CO} \langle \mathrm{NH}^{\mathrm{H}} \cdot \mathrm{C}_6 \mathrm{H}_4 \rangle$$
.
(2.) $\mathrm{CO} \langle \mathrm{NH}^{\mathrm{H}} \cdot \mathrm{C}_6 \mathrm{H}_4 \rangle + \mathrm{COCl}_2 = \mathrm{CO} \cdot \mathrm{N} \cdot \mathrm{C}_6 \mathrm{H}_4 \cdot \mathrm{N} \cdot \mathrm{CO} + 2\mathrm{HCl}$.

The distillate was almost pure and solidified in splendid long needles. These were quite insoluble in cold water and in hydrochloric acid, and therefore did not contain any of the original salt or free benzidine. On the other hand, traces of hydrochloric acid adhered somewhat persistently to the cyanate. On heating it, the greater part melted and then sublimed, but a portion was always decomposed. The vapour had the peculiar odour of phenyl cyanate. It softened a little under 100°, and the purest looking specimen I obtained melted at 122°. Another portion after sublimation, and in external appearance almost as pure, melted at 116° to 120°. The difficulty of obtaining it *absolutely* free from hydrochloric acid made it difficult to fix within a few degrees the melting point of the pure substance. It was soluble in ether. Analysis :— SNAPE: CERTAIN AROMATIC CYANATES

		Fo	und.
	Calculated for	~~~~~~	~
	$\mathbf{C_{14}H_8N_2O_2}.$	Ι.	II.
N	11.86	11.37	11.35

As was to be expected, this cyanate, like phenyl cyanate and phenylene dicyanate, yielded carbamates with alcohol and phenol.

$\begin{array}{c} Diphenylene-diure thane \ or \ Diethyl \ Diphenylene dicarbamate,\\ COOC_2H_5\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot COOC_2H_5. \end{array}$

A portion of the above cyanate was dissolved in just as much boiling alcohol as was necessary, the boiling continued for a few minutes, and then the solution was allowed to remain undisturbed to cool. The crystalline deposit was almost pure, and, when recrystallised from alcohol after previous boiling with animal charcoal, separated in beautiful feathers. These crystals melted about 226°, but it is somewhat difficult to determine *exactly* the melting point, as a decomposition sets in at about the same temperature.

	Calculated for	
	$C_{18}H_{20}N_2O_4.$	Found.
N	. 8·54	8.66

The constitution of this compound was further confirmed by preparing it from ethyl chlorocarbonate and benzidine. Benzidine was treated with the ethyl chlorocarbonate—an excess of the latter being present—in a vessel supplied with a reflux condenser, and heated for about 20 minutes in an oil-bath at 130°. On merely mixing, a considerable amount of heat was developed, and the reaction then mainly took place. After distilling off the excess of ethyl chlorocarbonate, the remaining brownish-white solid was washed well with water, and recrystallised from alcohol. The same peculiar feathery crystals were obtained. These melted at about 230°. The slight difference in the melting point is explained by the already-mentioned difficulty of determination. The reaction in this case is as follows :—

$2(\mathbf{NH}_{2}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{NH}_{2}) + 2(\mathbf{Cl}\cdot\mathbf{CO}\cdot\mathbf{OC}_{2}\mathbf{H}_{5}) = (\mathbf{NH}_{2}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{NH}_{2},2\mathbf{HCl}) + (\mathbf{COOC}_{2}\mathbf{H}_{5}\cdot\mathbf{NH}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{C}_{6}\mathbf{H}_{4}\cdot\mathbf{NH}\cdot\mathbf{COOC}_{2}\mathbf{H}_{5}).$

The benzidine hydrochloride which is simultaneously formed is separated by its solubility in water.

Diphenyl Diphenylenedicarbamate, $COOC_{6}H_{5}\cdot NH\cdot C_{6}H_{4}\cdot C_{6}H_{4}\cdot NH\cdot COOC_{6}H_{5}.$

Diphenyl dicyanate was heated with a slight excess of phenol in an oil-bath at 140°. These substances at first melted, and afterwards

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solidified again, showing the formation of a compound of higher melting point than either. This was found to be but sparingly soluble in most ordinary solvents, such as alcohol, ether, benzene, &c. After previously washing well with ether to remove phenol, it was recrystallised from glacial acetic acid, as this solvent seemed to be the best. A large quantity of acetic acid was required. After a second recrystallisation, the carbamate was obtained in beautiful crystalline tables. These were washed with ether many times to remove acetic acid, dried, and finally submitted to analysis.

Ca	lculated for	
C	26H ₂₀ N ₂ O ₄ .	Found.
N	6.60	6.84

The melting point was about 240°, but was difficult to determine with precision, as the substance decomposes with evolution of gas at about the same temperature.

 $CH_3 \cdot C_6 H_3 (NH_2)_2$, was next treated with Metatoluylenediamine, phosgene: metatoluylene diisocyanate, $C_8H_3(CH_3)(NCO)_2 = [1:2:4]$, was thus obtained. Toluylenediamine hydrochloride was treated with phosgene in an exactly similar manner to that described for obtaining diphenyl dicyanate, viz., successively in benzoic acid and diphenylamine vapour baths. The toluylene dicyanate passed over as a paleyellow liquid, which solidified to groups of needles almost perfectly The needles were smaller than those of diphenylene dicyanate. white. The compound as thus collected was almost pure, although contaminated to a slight extent with hydrochloric acid, which could not be readily removed. The melting point was 94°. On distilling the substance, it lost hydrochloric acid, and though it passed over mainly unchanged, was in part decomposed, the melting point being considerably lowered.

C	Calculated for $C_9H_6N_2O_2$.	Found.
N	16.09	15.56

It was soluble in ether, and possessed the strong and unpleasant odour of phenyl cyanate, especially noticeable on gently heating.

Thus, in all its properties this compound corresponds to, and is evidently identical with, that described by Lussi (*Ber.*, 7, 1263, and 8, 291). He obtained in the first place the corresponding urethane, by treating toluylenediamine with ethyl chlorocarbonate, and then distilled this urethane with phosphoric anhydride. In order to contirm the identity, a portion of the cyanate, as prepared by me, was boiled with alcohol, and on allowing it to stand, white silky needles separated. These were soluble in ether, and melted at 135° . These

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properties agree with the description of the urethane given by Lussi. For complete control, a small quantity was prepared as described by him from ethyl chlorocarbonate and metatoluylenediamine, recrystallising the product from alcohol. I thus obtained exactly similar lustrous needles, melting at 135°; they gave the following results on analysis:—

Calculate	d for
$C_{13}H_{18}N$	2O4. Found.
N	3 10.64

Lussi states the melting point to be 137° . I converted another portion of the cyanate into the phenol carbamate.

Diphenyl-toluylene Dicarbamate, $C_6H_3(CH_3)(NH \cdot COOC_6H_5)_2 = [1:2:4].$

Metatoluylene isocyanate, as prepared above, was heated with an excess of phenol in an oil-bath at from 130° to 150° for half an hour. A gelatinous mass was obtained, which when boiled with ether to remove phenol, became changed into a gray powder. This was recrystallised from hot glacial acetic acid in which it readily dissolved. Clusters of white needles separated on cooling. These were collected, well washed with ether to remove excess of acetic acid, and dried at 105° . The compound was slightly soluble in alcohol and ether and melted at 147.5° .

	Calculated for	
	C ₂₁ H ₁₈ N ₂ O ₄ .	Found.
N	7.73	7.87

The next attempt which was made was to treat orthotoluylenediamine with phosgene. I did not succeed, however, in obtaining any cyanate in this case. It was recently noticed by Gattermann and Wrampelmeyer, that whilst para- and meta-phenylenediamine are each converted respectively by phosgene into the corresponding cyanates, orthophenylenediamine is not. Their experience and my own may probably be explained by the suggestion that the orthodiamine is first converted into an ortho-substituted carbamide, and that then the NH-groups are held so firmly by the CO-group as not to permit of further decomposition by phosgene. Thus, in the above case, the reaction is probably—

$$\mathrm{C}_{6}\mathrm{H}_{3}(\mathrm{CH}_{3}) <_{\mathrm{NH}_{2}}^{\mathrm{NH}_{2}} + \mathrm{COCl}_{2} = 2\mathrm{HCl} + \mathrm{C}_{6}\mathrm{H}_{3}(\mathrm{CH}_{3}) <_{\mathrm{NH}}^{\mathrm{NH}} > \mathrm{CO}.$$

But the compound refuses to be further converted into the corresponding dicyanate, as is the case when the NH-groups are attached to carbon-atoms further apart in the benzene-ring. The corresponding urethanes which would result from the action of alcohol on these cyanates, can, however, be prepared by the action of ethyl chlorocarbonate on the amines.

Orthophenylene-diurethane, $C_6H_4(NH\cdot COOC_2H_5)_2 = [1:2]$, was prepared in this way. Orthophenylenediamine was heated with an excess of ethyl chlorocarbonate at 130°, the unaltered ethyl chlorocarbonate distilled off, and the residue washed with water and hydrochloric acid. By recrystallisation from alcohol, after previously boiling the solution with charcoal, lustrous needles melting at 88° were obtained. The dried compound was submitted to analysis.

	Calculated for	
	$C_{12}H_{16}N_2O_4.$	Found.
Ν	. 11.11	11.31

Orthotoluylenediamine also reacted with ethyl chlorocarbonate, and crystals separated from the alcoholic extract of the product. I have not as yet purified and analysed this compound.

Lastly phenylhydrazine was treated with phosgene. The latter was conducted over phenylhydrazine hydrochloride, heated at 220° to 230° in a paraffin-bath. Towards the close of the operation, the temperature was allowed to rise to 250° . A pale-brown oil distilled over, and solidified on cooling to a pasty mass. The product of the reaction possessed the powerful odour of phenyl cyanate, and the vapour strongly attacked the eyes. On heating it in a fractional distillation flask, hydrogen chloride was evolved, and a portion sublimed in splendid long needles. Pressed out on porcelain, it gradually but entirely sank into the plate. Instead of the reaction taking place as I hoped, according to the equation—

 C_6H_5 ·NH·NH₂ + $COCl_2 = C_6H_5$ ·NH·NCO + 2HCl,

a solid combination of phenyl cyanate and hydrochloric acid had been formed. That phenyl cyanate has the property of dissolving large quantities of hydrogen chloride to form a solid mass is mentioned by Hentschel (Ber., 17, 1285, and 18, 1178). That this curious combination had taken place in this case was shown by the evolution of hydrogen chloride on heating the product; by the continued characteristic and unpleasant odour of phenyl cyanate, which was so unbearable that it could not be worked with for longer than a few minutes consecutively, and lastly by its conversion into carbanilide. This was effected by simply boiling with water in a flask provided with a reflux condenser until the odour of phenyl cyanate had disappeared. The crystalline needles thus formed, after recrystallisation from alcohol, were shown to have the same melting point and percentage of nitrogen as carbanilide. Phenyl cyanate, as is well known, is readily

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converted into carbanilide by the action of water. The experiment did not allow me to determine whether phenylhydrazine was at first decomposed, yielding aniline, which, together with phosgene gave phenyl cyanate, or whether the cyanate, $C_0H_s\cdot NH\cdot NCO$, I had expected to obtain was first formed, but then decomposed, yielding phenyl cyanate.

I have much pleasure in taking this opportunity to express my best thanks to Dr. Gattermann, for valuable counsel afforded by him to me during the course of the work above described.

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