

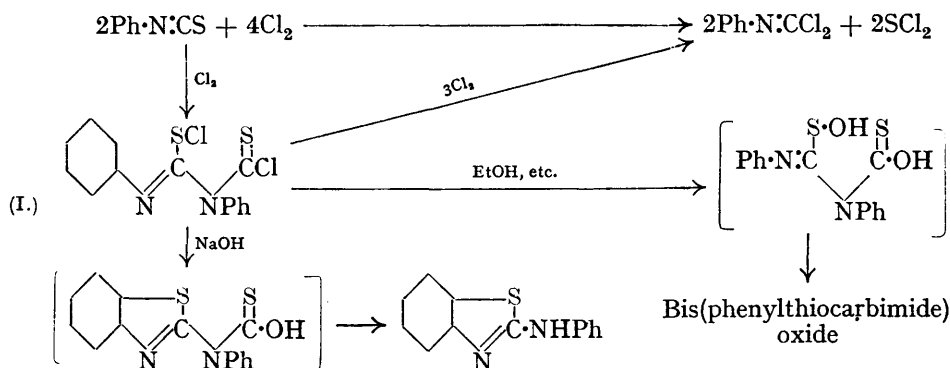
25. *The Action of Chlorine on Aryl Thiocarbimides and the Reactions of Aryl isoCyanodichlorides. Part II.*

By G. MALCOLM DYSON and THOMAS HARRINGTON.

The action of chlorine on thiocarbimides has been further investigated, and a simpler explanation of the observed reactions proposed. From the reaction product of secondary amines and *isocyanodi-*chlorides, pentasubstituted guanidines have been isolated. The action of ethyl alcohol on *iso-*cyanodichlorides has been shown to be complex, although the corresponding urethane is always a

product of the reaction. Phenols and isocyanodichlorides yield crystalline imido-carbonates. When isocyanodichlorides and a hydrocarbon react in the presence of aluminium chloride, only one chlorine atom is attacked, but when the product is poured into water, further reaction takes place, yielding compounds of the type $R \cdot NH \cdot COR'$.

DYSON and HARRINGTON (J., 1940, 191) showed that phenylthiocarbimide in an inert solvent is converted by chlorine first into an unstable chloro-addition compound, which yields, on further addition of chlorine, phenyl isocyanodichloride. This chloro-addition compound reacts with alcohol or glacial acetic to form bis(phenylthiocarbimide) oxide and with sodium hydroxide solution, yielding 1-anilinobenzthiazole. A scheme to correlate these reactions was proposed which assumed the existence of two different chloro-addition compounds. It is now considered that these are one and the same, since both react with sodium hydroxide to yield 1-anilinobenzthiazole. The modified scheme is as follows:



The structure of bis(phenylthiocarbimide) oxide can be derived from the reactions (1) oxide + hydrogen \rightarrow *s*-diphenylthiourea; (2) oxide + aniline \rightarrow *s*-diphenylurea; (3) chloro-addition compound + sodium hydroxide \rightarrow 1-anilinobenzthiazole. Reactions (1) and (2) indicate the presence in the oxide of the groups $\cdot \text{S} \cdot \text{C}(\text{NPh})_2$ and $\text{Ph} \cdot \text{N} \cdot \text{C} \cdot \text{O}$ respectively and reaction (3) indicates the presence of the group $\cdot \text{S} \cdot \text{C}(\cdot \text{NPh}) \cdot \text{NPh}$ in the chloro-addition compound. Since this is so readily converted into the oxide, we can assume that this group is also present in the oxide. Two structures for the oxide are therefore possible:

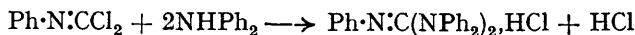


It has not been possible to discriminate between these two.

The most likely structure of the chloro-addition compound is given by (I), established by empirical analysis only, because of its extreme instability.

Evidence has been obtained to show that during the addition of chlorine to phenylthiocarbimide, chlorination also takes place in the nucleus, yielding *p*-chlorophenyl isocyanodichloride (cf. Nef, *Annalen*, 1892, 270, 282; Bly, Perkins, and Lewis, *J. Amer. Chem. Soc.*, 1922, 44, 2896).

The Action of Secondary and Tertiary Amines on isoCyanodichlorides.—Diphenylamine and phenyl isocyanodichloride reacted readily when refluxed in tetrachloroethane solution, yielding *pentaphenylguanidine hydrochloride* almost quantitatively:



From other secondary amines and isocyanodichlorides a large amount of tar was produced during the reaction and it was not possible to isolate the guanidine hydrochloride, although in several cases the guanidine itself was obtained.

Tertiary amines and isocyanodichlorides did not react under the usual conditions.

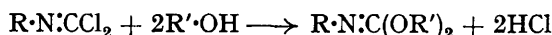
The Action of Alcohols on isoCyanodichlorides.—Sell and Zierold (*Ber.*, 1874, 7, 1228) reported that phenylurethane was the main product of the reaction between phenyl isocyanodichloride and ethyl alcohol. Lachman (*Ber.*, 1879, 12, 1349) obtained a mixture of *N*-*o*-tolylurethane and *s*-*di-o*-tolylurea by the reaction of *o*-tolyl isocyanodichloride with alcoholic potassium hydroxide, but the urethane alone by its reaction with sodium ethoxide. Lengfeld and Stieglitz (*J. Amer. Chem. Soc.*, 1894, 16, 70) and

Smith (*ibid.*, p. 372) obtained ethyl phenylimidochloroformate by treating an ethereal solution of phenyl isocyanodichloride and alcohol at 0° with an ice-cold solution of sodium ethoxide in alcohol. By allowing the reaction to take place at 50°, Smith (*loc. cit.*) obtained ethyl phenylimidocarbonate.

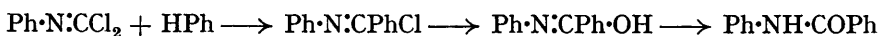
The investigations of Sell and Zierold have been further extended. Both *p*-nitrophenyl and *p*-tolyl isocyanodichloride and ethyl alcohol yielded the corresponding urethane alone, whereas phenyl and *m*-nitrophenyl isocyanodichlorides yielded the urethane and amine hydrochloride; thus phenyl isocyanodichloride produced phenylurethane and aniline hydrochloride. *m*-Tolyl isocyanodichloride and ethyl alcohol produced a mixture of *m*-tolylurethane and the hydrochloride of a base whose analysis agreed with the empirical formula $C_{20}H_{22}O_2N_2 \cdot HCl$. In the case of *o*-tolyl isocyanodichloride the greater part formed *o*-tolylurethane, but in addition a crystalline substance containing nitrogen and chlorine was isolated: its identity was not determined.

Phenols and isoCyanodichlorides.—Hantzsch and Mai (*Ber.*, 1895, **28**, 977), investigating the reaction between phenyl isocyanodichloride and sodium phenoxides, could not prepare stereoisomeric compounds of the type $Ph \cdot N:C(OR) \cdot OR$.

The reaction between isocyanodichlorides and phenols has now been studied. Reaction proceeded vigorously at 150° with evolution of hydrogen chloride and the formation of crystalline trisubstituted imido-carbonates:



The Friedel-Crafts Reaction applied to isoCyanodichlorides.—When phenyl isocyanodichloride, benzene, and aluminium chloride were refluxed together, reaction took place with evolution of hydrogen chloride, and benzanilide was isolated when the product was poured into water, the reaction being probably as follows:



Attempts to prepare the compound $Ph \cdot N:CPh \cdot OEt$ by pouring the reaction product into ethyl alcohol were not successful.

EXPERIMENTAL.

***p*-Chlorophenyl isoCyanodichloride.**—Phenylthiocarbimide (318 g.) in phenyl isocyanodichloride (289 g.) was treated with chlorine (cf. Dyson and Harrington, *loc. cit.*). On fractional distillation, phenyl isocyanodichloride was obtained, followed by a colourless oil (5 g.), b. p. 212–220°, a pale yellow oil (25 g.), b. p. 220–226°, and a pale yellow oil (5 g.), b. p. 226–230°. The product of b. p. 220–226° (10 g.) in benzene was refluxed with aniline (20 g.) for 5 hours, and the precipitated solid collected, digested with concentrated hydrochloric acid, filtered off, and dissolved in boiling water (1 l.). On cooling, triphenylguanidine hydrochloride (2 g.) crystallised; the filtrate, concentrated to 250 ml. and cooled, deposited *s*-diphenyl-*p*-chlorophenylguanidine hydrochloride (10 g.), m. p. 256° (Found: HCl, 10.4. $C_{15}H_{16}N_3Cl \cdot HCl$ requires HCl, 10.2%). The corresponding guanidine formed colourless needles, m. p. 136°, from alcohol.

The liquid, b. p. 220–226°, was therefore largely *p*-chlorophenyl isocyanodichloride.

Pentaphenylguanidine Hydrochloride.—Phenyl isocyanodichloride (10 g.) and diphenylamine (20 g.) in tetrachloroethane (25 ml.) were refluxed for 4 hours, much hydrogen chloride being evolved and the liquid becoming dark green. The solid that crystallised on cooling was collected, washed with tetrachloroethane, and recrystallised from alcohol, forming white needles (22 g.), m. p. 227° (Found: HCl, 7.5. $C_{31}H_{25}N_3 \cdot HCl$ requires HCl, 7.7%).

Pentaphenylguanidine, obtained by neutralisation of a solution of the above, separated from alcohol in white needles, m. p. 179° (cf. Steindorff, *Ber.*, 1904, **37**, 965).

***s*-Tetraphenyl-*p*-tolylguanidine.**—*p*-Tolyl isocyanodichloride (5 g.) and diphenylamine (9 g.) in tetrachloroethane (20 ml.) were refluxed for 3 hours. As a solid was not deposited on cooling, the solvent was removed on an oil-bath, and the residual tar extracted with boiling water. The hot extract was treated with 2*N*-sodium hydroxide, and the precipitated base collected and crystallised from alcohol; it formed small yellow needles (6 g.), m. p. 175° (Found: N, 9.3. $C_{32}H_{27}N_3$ requires N, 9.3%).

***s*-Tetraphenyl-*m*-tolylguanidine,** yellow needles, m. p. 174–176° (Found: N, 9.2%), and *s*-tetraphenyl-*o*-tolylguanidine, yellow needles, m. p. 172° (Found: N, 9.2%), were also prepared.

***p*-Tolylurethane.**—*p*-Tolyl isocyanodichloride (20 g.) was dissolved in alcohol (50 ml.) and gradually warmed on the water-bath. When the vigorous reaction had subsided, refluxing was continued for a further $\frac{1}{2}$ hour; on cooling, *p*-tolylurethane crystallised in white needles, m. p. 51° (Found: N, 7.7. $C_{10}H_{13}O_2N$ requires N, 7.8%). ***p*-Nitrophenylurethane,** m. p. 127°, white needles, was obtained in a similar way (Found: N, 13.2. $C_9H_{10}O_4N_2$ requires N, 13.3%). The yields in both cases were almost theoretical.

Phenyl isoCyanodichloride and Ethyl Alcohol.—Phenyl isocyanodichloride (20 g.) was treated with alcohol (50 ml.) as above, and the alcohol removed on the water-bath. On cooling, the oil which remained solidified and consisted of a mixture of phenylurethane and aniline hydrochloride. The urethane was extracted with

ligroin and after concentration, crystallised in colourless needles, m. p. and mixed m. p. 54°. The aniline hydrochloride was crystallised from aqueous alcohol; m. p. 198°. In the same way *m*-nitrophenyl isocyanodichloride yielded *m*-nitrophenylurethane, pale yellow needles from alcohol, m. p. 56°, and *m*-nitroaniline hydrochloride, m. p. 230°.

m-Tolyl isocyanodichloride and Ethyl Alcohol.—*m*-Tolyl isocyanodichloride (20 g.) and ethyl alcohol (50 ml.) were refluxed for ½ hour on the water-bath, the alcohol was distilled off, and the oily solid shaken with water. The oil which separated was extracted with ether, the extract dried with calcium chloride, and the ether distilled. The remaining oil distilled as *m*-tolylurethane (6 g.), a colourless liquid, b. p. 250—255° (decomp.).

Sodium hydroxide solution was added to the aqueous portion above; the precipitated base was collected and crystallised from alcohol, forming colourless needles (7 g.), m. p. 82°. The base was dissolved in warm alcohol, just acidified with concentrated hydrochloric acid, and cooled; the hydrochloride crystallised in colourless plates, m. p. 270° (Found: HCl, 10.4; N, 8.0. $C_{20}H_{22}O_2N_2 \cdot HCl$ requires HCl, 10.2; N, 7.8%).

o-Tolyl isocyanodichloride and Ethyl Alcohol.—*o*-Tolyl isocyanodichloride (20 g.) and ethyl alcohol (50 ml.) were treated as above. The excess of alcohol was driven off on the water-bath, and the residue steam-distilled, giving approximately equal weights of materials having m. p. 34°, 36°, 65°, 100°, and 105°. The first and second, crystallised from alcohol, gave *o*-tolylurethane (6 g.), m. p. 45°. The fourth and fifth portions crystallised from ligroin in long, feathery, white needles, m. p. 108°, containing nitrogen and chlorine (Found: *M*, 182).

Phenyl Phenylimidocarbonate.—Phenyl isocyanodichloride (10 g.) and phenol (10 g.) were heated for an hour at 150°. Vigorous evolution of hydrogen chloride occurred. The product was a clear golden-yellow liquid which on cooling set to a hard glass. This was crystallised from benzene (25 ml.), giving short white prisms (10 g.), m. p. 130°, and recrystallised from alcohol, forming needles, m. p. 136° (Found: N, 4.8. $C_{19}H_{15}O_2N$ requires N, 4.8%).

p-Tolyl phenylimidocarbonate, colourless needles, m. p. 110° (Found: N, 4.3. $C_{21}H_{19}O_2N$ requires N, 4.4%), *phenyl p*-tolylimidocarbonate, needles, m. p. 108° (Found: N, 4.4. $C_{20}H_{17}O_2N$ requires N, 4.6%), *p*-tolyl *o*-tolylimidocarbonate, long colourless needles, m. p. 115° (Found: N, 4.2. $C_{22}H_{21}O_2N$ requires N, 4.2%), *phenyl p*-bromophenylimidocarbonate, plates, m. p. 154° (Found: N, 3.7. $C_{19}H_{14}O_2NBr$ requires N, 3.8%), *phenyl p*-nitrophenylimidocarbonate, pale yellow needles, m. p. 165° (Found: N, 8.0. $C_{19}H_{14}O_4N_2$ requires N, 8.4%), and *p*-chlorophenyl *p*-nitrophenylimidocarbonate, pale yellow needles, m. p. 185° (Found: N, 6.6. $C_{19}H_{12}O_4N_2Cl_2$ requires N, 6.9%), were also prepared.

Benzanilide.—Aluminium chloride (35 g.) reacted slowly with phenyl isocyanodichloride (20 g.) in cold benzene (50 ml.), but on the water-bath hydrogen chloride was profusely evolved. After ½ hour's heating, the mixture was poured into cold water (500 ml.). The crystals (22 g.) that formed in the benzene layer were identified as benzanilide, m. p. 162° (Found: N, 7.1. Calc.: N, 7.1%).

Benzo-*p*-toluidide, m. p. 158°, and benzo-*o*-toluidide, m. p. 143°, were also prepared.

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[Received, September 30th, 1941.]