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

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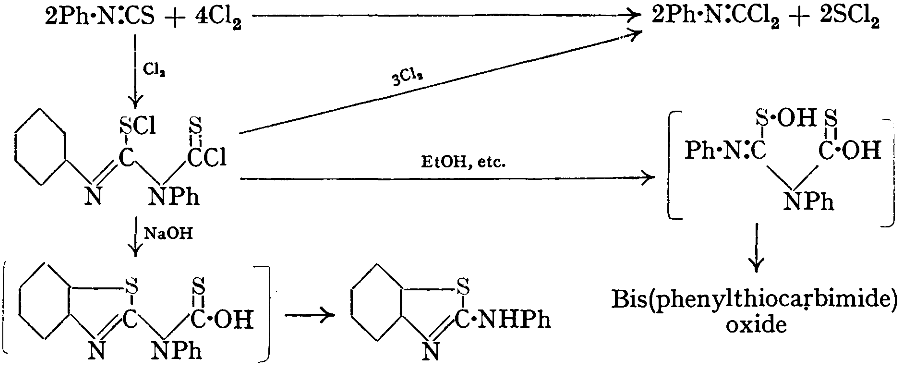
The action of chlorine on thiocarbimides has been further investigated, and a simpler explanation of the observed reactions proposed. From the reaction product of secondary amines and *iso*cyanodichlorides, pentasubstituted guanidines have been isolated. The action of ethyl alcohol on *iso*cyanodichlorides has been shown to be complex, although the corresponding urethane is always a product of the reaction. Phenols and *iso*cyanodichlorides yield crystalline imido-carbonates. When *iso*cyanodichlorides 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·NH·COR′.

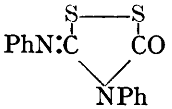
DYSON and HARRINGTON (J., 1940, 191) showed that phenylthiocarbimide in an inert solvent is converted by chlorine first into an unstable chloro-addition compound, which yields, on further addition of chlorine, phenyl *iso*cyanodichloride. This chloro-addition compound reacts with alcohol or glacial acetic 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 :

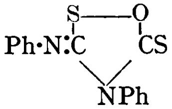


(I.)

The structure of bis(phenylthiocarbimide) oxide can be derived from the reactions (1) oxide + hydrogen ⟶ *s*-diphenylthiourea ; (2) oxide + aniline ⟶ *s*-diphenylurea ; (3) chloro-addition compound + sodium hydroxide ⟶ 1-anilinobenzthiazole. Reactions (1) and (2) indicate the presence in the oxide of the groups $\cdot S\cdot C(NPh)_2$ and Ph·N·C·O respectively and reaction (3) indicates the presence of the group ·S·C(:NPh)·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 :

(II.)





(III.)

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 *iso*cyanodichloride (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 iso*Cyanodichlorides.*—Diphenylamine and phenyl *iso*cyanodichloride reacted readily when refluxed in tetrachloroethane solution, yielding *pentaphenylguanidine hydrochloride* almost quantitatively :

$$Ph\cdot N{:}CCl_2 + 2NHPh_2 \longrightarrow Ph\cdot N{:}C(NPh_2)_2,HCl + HCl$$

From other secondary amines and *iso*cyanodichlorides 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 *iso*cyanodichlorides did not react under the usual conditions.

The Action of Alcohols on iso*Cyanodichlorides.*—Sell and Zierold (*Ber.*, 1874, **7**, 1228) reported that phenylurethane was the main product of the reaction between phenyl *iso*cyanodichloride 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 *iso*cyanodichloride 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 *iso*cyanodichloride 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 *iso*cyanodichloride and ethyl alcohol yielded the corresponding urethane alone, whereas phenyl and *m*-nitrophenyl *iso*cyanodichlorides yielded the urethane and amine hydrochloride; thus phenyl *iso*cyanodichloride produced phenylurethane and aniline hydrochloride. *m*-Tolyl *iso*cyanodichloride and ethyl alcohol produced a mixture of *m*-tolylurethane and the ***hydrochloride*** of a base whose analysis agreed with the empirical formula $C_{20}H_{22}O_2N_2,HCl$. In the case of *o*-tolyl *iso*cyanodichloride 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 iso*Cyanodichlorides.*—Hantzsch and Mai (*Ber.*, 1895, **28**, 977), investigating the reaction between phenyl *iso*cyanodichloride and sodium phenoxides, could not prepare stereoisomeric compounds of the type $Ph{\cdot}N{:}C(OR){\cdot}OR'$.

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

$$R{\cdot}N{:}CCl_2 + 2R'{\cdot}OH \longrightarrow R{\cdot}N{:}C(OR')_2 + 2HCl$$

The Friedel–Crafts Reaction applied to iso*Cyanodichlorides.*—When phenyl *iso*cyanodichloride, 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:

$$Ph{\cdot}N{:}CCl_2 + HPh \longrightarrow Ph{\cdot}N{:}CPhCl \longrightarrow Ph{\cdot}N{:}CPh{\cdot}OH \longrightarrow Ph{\cdot}NH{\cdot}COPh$$

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* iso*Cyanodichloride.*—Phenylthiocarbimide (318 g.) in phenyl *iso*cyanodichloride (289 g.) was treated with chlorine (cf. Dyson and Harrington, *loc. cit.*). On fractional distillation, phenyl *iso*cyanodichloride 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. $C_{19}H_{16}N_3Cl,HCl$ 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 *iso*cyanodichloride.

Pentaphenylguanidine Hydrochloride.—Phenyl *iso*cyanodichloride (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. $C_{31}H_{25}N_3,HCl$ 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 *iso*cyanodichloride (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 2N-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 *iso*cyanodichloride (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 ½ 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 iso*Cyanodichloride and Ethyl Alcohol.*—Phenyl *iso*cyanodichloride (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 *iso*cyanodichloride yielded *m*-nitrophenylurethane, pale yellow needles from alcohol, m. p. 56°, and *m*-nitroaniline hydrochloride, m. p. 230°.

m-*Tolyl* iso*Cyanodichloride and Ethyl Alcohol.*—*m*-Tolyl *iso*cyanodichloride (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. $C_{20}H_{22}O_2N_2$,HCl requires HCl, 10·2; N, 7·8%).

o-*Tolyl* iso*Cyanodichloride and Ethyl Alcohol.*—*o*-Tolyl *iso*cyanodichloride (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 *iso*cyanodichloride (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 *iso*cyanodichloride (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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