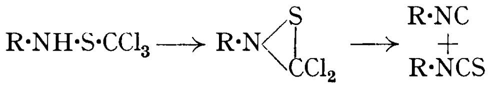
150. *The Constitution and Reactions of Thiocarbonyl Tetrachloride. Part II. Reaction with Primary Arylamines, Phenols, and Reducing Agents.*

By Joseph M. Connolly and G. Malcolm Dyson.

Hydrolysis of the compound obtained by interaction of *p*-toluidine and thiocarbonyl tetrachloride (Connolly and Dyson, J., 1934, 822) gave *p*-tolylcarbylamine and *p*-tolylthiocarbimide; if isomeric change be precluded, this is evidence for an R–N–C– link in the original compound. Experiments hereinafter described show that this link is probably due to intermediate ring formation (III) during hydrolysis, since the substance for which structure (I) had been suggested (*p*-toluidinodichloromethylchlorothiol) (I; $R = C_6H_4Me$) has been shown to be *S*-*p*-toluidinotrichloromethylthiol (II; $R = C_6H_4Me$).

$R{\cdot}NH{\cdot}CCl_2{\cdot}SCl$

(I.)



(II.) (III.)

In inert solvents (II) reacts with an arylamine (4 mols.), giving the tri-*s*-arylamino-derivative, each aryl group being derived from the amine taken :

$$\mathrm{(II)} + 4R'{\cdot}NH_2 = R'{\cdot}NH_2{,}HCl + 2HCl + R{\cdot}NH{\cdot}S{\cdot}C(NHR')_3 \longrightarrow R{\cdot}NH_2{,}HCl + S + R'{\cdot}N{:}C(NHR')_2{,}HCl$$

Had the original compound been *p*-toluidinodichloromethylchlorothiol (I), a *p*-tolyldiarylguanidine would have been obtained :

$$C_6H_4Me{\cdot}NH{\cdot}CCl_2{\cdot}SCl + 4R'{\cdot}NH_2 = C_6H_4Me{\cdot}NH{\cdot}C(NHR')_2{\cdot}SCl + 2R'{\cdot}NH_2{,}HCl$$

$$\downarrow$$

$$\mathrm{(IV)}\ C_6H_4Me{\cdot}NH{\cdot}C({:}NR'){\cdot}NHR' \text{ or } \mathrm{(V)}\ C_6H_4Me{\cdot}N{:}C(NHR')_2 + S + HCl$$

No compound of the type (IV) or (V) was detected, triarylguanidines of the type $R'{\cdot}N{:}C(NHR')_2$ only being obtained. The hydrochlorides of the latter are obtained pure and in good yield when the amine used contains the same aryl group as does the *S*-arylaminotrichloromethylthiol : this is a new and simple method of synthesising such triarylguanidines.

The action of thiocarbonyl tetrachloride on phenols is analogous to that on primary arylamines, *S-aryloxytrichloromethylthiols* being obtained. These are colourless or pale yellow oils, which decompose readily and in several cases cannot be distilled unchanged in a vacuum. They are slowly hydrolysed by boiling water, more readily by boiling 20% aqueous alkali, to the corresponding phenol. With hydrogen chloride in ether they regenerate thiocarbonyl tetrachloride and the phenol; reduction with zinc dust gives methylthiol, and excess of arylamine in an inert solvent gives triarylguanidine hydrochlorides :

$$\mathrm{R{\cdot}ONa + CSCl_4 = RO{\cdot}S{\cdot}CCl_3 + NaCl}$$
$$\mathrm{RO{\cdot}S{\cdot}CCl_3 + 5R'{\cdot}NH_2 = 2R'{\cdot}NH_2{,}HCl + HCl + RO{\cdot}S{\cdot}C(NHR')_3 \longrightarrow}$$
$$\mathrm{ROH + S + R'N{:}C(NHR')_2{,}HCl}$$

Concentrated aqueous sodium thiosulphate converts thiocarbonyl tetrachloride into carbon disulphide and a trace of thiocarbonyl chloride. Gugliamelli, Novelli, Ruiz, and Anaslasi (*Anal. Asoc. Quím. Argentina*, **1927**, **15**, 337) showed that thiocarbonyl chloride could be obtained from thiocarbonyl tetrachloride by reduction with stannous chloride in place of the more usual tin and hydrochloric acid (Dyson, " Organic Syntheses," VI, 86). A modification of this method using tetrachloroethane has resulted in a rapid and convenient method for the preparation of thiocarbonyl chloride in 65% yield. In a simple new method for preparing arylthiocarbimides in good yield without isolation of thiocarbonyl chloride, an arylamine is dissolved in hydrochloric acid containing stannous chloride and stirred with thiocarbonyl tetrachloride, the arylthiocarbimide being then removed either by filtration or by distillation in steam.

EXPERIMENTAL.

Triphenylguanidine.—*S*-Anilinotrichloromethylthiol (26 g.) was prepared by the method previously described (Connolly and Dyson, *loc. cit.*), ligroin (150 ml.) replacing ether as solvent. The ligroin solution, separated from the aqueous layer, was added to aniline (45 g.) in ligroin (100 ml.), and the whole boiled for a few minutes and kept for 48 hours with occasional shaking. Sulphur, aniline hydrochloride, and triphenylguanidine hydrochloride were filtered off together, dried, and extracted with boiling water, followed by boiling dilute hydrochloric acid. Triphenylguanidine hydrochloride, which separated from the cooled extracts, was filtered off, and converted by a slight excess of warm dilute caustic soda solution into the base, which formed colourless needles (24 g.) from alcohol, m. p. 143°; picrate, deep yellow needles m. p. 179°.

*Tri-*p*-tolylguanidine.*—This was prepared : (*a*) From *S*-*p*-toluidinotrichloromethylthiol and *p*-toluidine by the method just described for the phenyl analogue; it formed white needles from alcohol, m. p. 122°. (*b*) From the same reactants with alcohol as solvent, from which crystalline sulphur, m. p. 119°, separated on cooling. (*c*) From *S*-anilinotrichloromethylthiol (13 g.) and *p*-toluidine (24 g.) in ligroin (250 ml.); after the mixture had been boiled for a few minutes and kept for 48 hours, tri-*p*-tolylguanidine was isolated as described above; a little triphenylguanidine was formed also, from aniline liberated during the reaction, and four recrystallisations were necessary completely to purify the *p*-tolyl compound, which then had m. p. 120·5°; mixed with authentic tri-*p*-tolylguanidine (m. p. 122°), it melted at 121°.

*Phenyldi-*p*-tolylguanidine.*—Phenylthiocarbimide (30 g.) in chloroform (90 ml.) was treated with chlorine until the increase in weight was 25 g. On distillation *iso*cyanophenyl dichloride passed over as a colourless oil between 206° and 212°; on redistillation it had b. p. 209°. The dichloride (4 g.) and *p*-toluidine (9·5 g.) in benzene (150 ml.) were boiled under reflux for 16 hours. The solid obtained was washed with cold water to remove *p*-toluidine hydrochloride, and the residual phenyldi-*p*-tolylguanidine hydrochloride converted by dilute caustic alkali solution into the base, which formed white needles from alcohol, m. p. 100°.

as-*Phenyldi-*p*-tolylguanidine*, $\mathrm{C_6H_4Me{\cdot}N{:}C(NHPh){\cdot}NH{\cdot}C_6H_4Me}$.—Di-*p*-tolylthiourea (20 g.) in benzene (350 ml.) at 40° was stirred with mercuric oxide (18 g.) for ½ hour, the filtered liquid allowed to evaporate after 2 hours, and monomeric di-*p*-tolylcarbodi-imide extracted from the residue by ether as a thick oil (11 g.). Di-*p*-tolylcarbodi-imide (7 g.) and aniline (4 g.) in benzene (40 ml.) were boiled for 12 hours, the benzene removed by evaporation, and the oily residue boiled with concentrated hydrochloric acid (25 ml.) and extracted with boiling water. The cooled extract deposited crystals of *as*-phenyldi-*p*-tolylguanidine hydrochloride; the base formed small colourless needles from alcohol, m. p. 89°.

When aniline reacted with *S*-*p*-toluidinotrichloromethylthiol and with *S*-*p*-chloroanilinotrichloromethylthiol, triphenylguanidine was obtained in yields of 60 and 62%, respectively, the course of the reaction between amines and arylaminotrichloromethylthiols being thus further confirmed.

S-*Phenoxytrichloromethylthiol*, $\mathrm{PhO{\cdot}S{\cdot}CCl_3}$.—Phenol (25 g.) in 2*N*-sodium hydroxide (200 ml.) was treated at intervals with 5 g. portions of thiocarbonyl tetrachloride (40 g. in all), the solution being cooled and shaken between each addition. After 15 minutes an oil was extracted in ether (180 ml.) and washed twice with water. Having been dried over anhydrous potassium carbonate, the ether was removed at 15° in a vacuum, leaving S-*phenoxytrichloromethylthiol* as a pale yellow oil of characteristic odour, b. p. 196°/760 mm. (decomp.), which was distilled in a high vacuum (Found : S, 13·3. $C_7H_5OCl_3S$ requires S, 13·1%).

The following analogues were prepared : p-*tolyloxy*-, pale yellow oil, b. p. 183°/755 mm. (decomp.) (Found : S, 12·6. $C_8H_7OCl_3S$ requires S, 12·4%); 2-*chlorophenoxy*-, pale yellow oil, with pungent characteristic odour, b. p. 180°/756 mm. (decomp.) (Found : S, 11·6. $C_7H_4OCl_4S$ requires S, 11·5%); *s*-xylyloxy-, deep yellow oil with pungent odour, unstable and could not be purified; *diphenylyl-2-oxy-*, colourless prisms from ligroin, m. p. 58° (Found : S, 10·3. $C_{13}H_9OCl_3S$ requires S, 10·0%).

Reduction of S-*Phenoxytrichloromethylthiol*.—The thiol was dropped slowly on zinc dust suspended in glacial acetic acid, and the mixture heated until reaction commenced. The gases evolved were swept by a stream of air through (*a*) dilute caustic soda solution, (*b*) alcohol, and (*c*) a freshly prepared solution of isatin (1 mg.) in sulphuric acid (100 ml.). The alkali solution gave an intense violet colour with sodium nitroprusside; the alcoholic solution gave a white precipitate of crystalline mercury methyl mercaptide with alcoholic mercuric chloride solution, and the isatin solution turned green, these reactions indicating the presence of methylthiol, the characteristic odour of which was also apparent.

Triphenylguanidine.—*S*-Phenoxytrichloromethylthiol, prepared as already described, in ligroin (200 ml.) was boiled with aniline (25 g.) for 5 hours. The solid which separated was extracted with boiling water and with boiling dilute hydrochloric acid. The cooled extracts deposited *s*-triphenylguanidine hydrochloride, which gave 9 g. of the base, pale yellow needles from alcohol, m. p. and mixed m. p. 143°.

The following analogues gave triphenylguanidine and tri-*p*-tolylguanidine by reaction with aniline and *p*-toluidine, respectively :

Trichloromethylthiol.	% Yield of triphenylguanidine.	% Yield of tri-*p*-tolylguanidine.
S-*p*-Tolyloxy-	46	40
S-*o*-Chlorophenoxy-	46	24
S-Xylyloxy-	50	—
S-Phenoxy-	60	43
S-Diphenylyl-2-oxy-	50	—

Phenylthiocarbimide.—Aniline (14 g.), dissolved in hydrochloric acid (1·5 l.; 2 pts. conc. acid and 5·5 pts. water), was stirred with stannous chloride (105 g.). When the latter had completely dissolved, thiocarbonyl tetrachloride (60 g.) was slowly dropped in. Stirring was continued for 7 hours, and the mixture distilled in steam after 24 hours. Phenylthiocarbimide was obtained as a pale yellow oil, b. p. 222° (yield, 70%). The following analogues were also prepared : *p*-chlorophenyl-, yield 99%; *p*-phenetyl-, yield 66%; *m*-2-xylyl-, yield 53%; *m*-tolyl-, yield 72%; 2 : 4-dibromophenyl-, yield 75%; *p*-tolyl-, yield 62%; *p*-anisyl-, yield 47%; 3-carboxyphenyl-, yield 70%. The method is unsuitable for obtaining thiocarbimides from semialiphatic amines (*e.g.*, benzylamine), nitroamines, and naphthylamines.

Thiocarbonyl Chloride.—Hydrochloric acid (12%; 16 l.), stannous chloride (1120 g.), thiocarbonyl tetrachloride (640 g.), and tetrachloroethane (1·5 l.) were vigorously stirred for 3 hours. The tetrachloroethane layer was syphoned off, dried over calcium chloride, and fractionated. Thiocarbonyl chloride passed over at 72—74°. Yield, 255 g. (64% of the theoretical).

The authors express their thanks to the Chemical Society for grants.

LOUGHBOROUGH COLLEGE, LEICESTERSHIRE.

[*Received, February 26th,* 1935.]