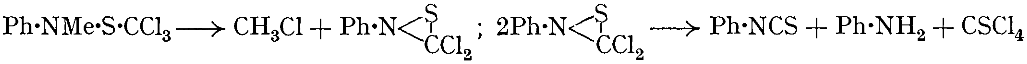
341. *The Constitution and Reactions of Thiocarbonyl Tetrachloride. Part IV. Reaction with Secondary and Tertiary Amines.*

By Christopher S. Argyle and G. Malcolm Dyson.

Secondary arylalkylamines have been shown to react with thiocarbonyl tetrachloride to give very unstable compounds of the type $NR_1R_2\cdot S\cdot CCl_3$, but with diarylamines the reaction is more complex and triphenylmethane dyes are formed together with a new, deep red substance, which is similar to the triphenylmethane dyes in structure but retains at least one diarylamino-group attached to the methane carbon atom through the nitrogen atom.

Tertiary amines and thiocarbonyl tetrachloride yield dyes of the crystal-violet type when heated alone or in the presence of condensing agents such as zinc or aluminium chloride. The mechanism of this reaction has been elucidated by the isolation of substances of the type $NR_2\cdot C_6H_4\cdot S\cdot CCl_3$, the $\cdot S\cdot CCl_3$ group of which is capable of furnishing the methane carbon of the triphenylmethane structure.

Investigation of the reaction between thiocarbonyl tetrachloride and primary arylamines (J., 1935, 679) has been extended to secondary and tertiary amines. Dialkyl- and arylalkylamines give S-*dialkyl-* and S-*arylalkyl-aminotrichloromethylthiols*, $NR_1R_2\cdot S\cdot CCl_3$ (I), colourless or pale yellow oils. The former distil readily in a vacuum, but most of the latter compounds are unstable at the ordinary temperature and in no case distil unchanged. Thermal decomposition of *S*-arylalkylaminotrichloromethylthiols gives thiocarbonyl tetrachloride, the hydrochloride of the original amine, the arylthiocarbimide, and the alkyl chloride. For instance, from *S*-methylanilinotrichloromethylthiol, thiocarbonyl tetrachloride, methylaniline hydrochloride, phenylthiocarbimide, and methyl chloride are obtained by decomposition at 140° :



$$\mathrm{Ph\cdot NMe\cdot S\cdot CCl_3 \longrightarrow CH_3Cl + Ph\cdot N{<}\overset{S}{\underset{CCl_2}{|}}\ ;\ 2Ph\cdot N{<}\overset{S}{\underset{CCl_2}{|}} \longrightarrow Ph\cdot NCS + Ph\cdot NH_2 + CSCl_4}$$

With dry hydrogen chloride in ligroin, these thiols (I) quantitatively regenerate the hydrochloride of the original amine and thiocarbonyl tetrachloride; reduction with zinc dust and glacial acetic acid gives methylthiol; excess of arylamine in ligroin gives a triarylguanidine hydrochloride. The thiols are hydrolysed slowly by boiling water, more readily by boiling 20% aqueous alkali, to give carbylamines and thiocarbimides, methyl-*p*-toluidinotrichloromethylthiol yielding under these conditions both *p*-tolylcarbylamine and *p*-tolylthiocarbimide.

With diarylamines, the reaction takes an entirely different course. Diphenylamine and thiocarbonyl tetrachloride give *NN'N''-triphenylpararosaniline hydrochloride* (II) and a *compound*, (III) or (IV). An identical mixture of coloured products is obtained also

(III.) $C(NPh_2)_2{:}C_6H_4{:}NHPhCl$ $\qquad$ $C(NPh_2)(C_6H_4\cdot NHPh){:}C_6H_4{:}NHPhCl$ (IV.)

from diphenylamine and thiocarbonyl chloride; in dilute ethereal solution they give tetraphenylthiocarbamide (Bergreen, *Ber.*, 1888, **21**, 340), followed by a considerable quantity of dark red products, better obtained by heating diphenylamine and thiocarbonyl chloride or tetrachloride in absence of solvent.

Chloropicrin, trichloromethanesulphonyl chloride, and *S*-*p*-tolyltrichloromethylthiol react similarly with diphenylamine at 150° :

$$CCl_3\cdot NO_2 + 3NHPh_2 = C_{37}H_{30}N_3Cl + HNO_2 + 2HCl$$
$$CCl_3\cdot SO_2Cl + 3NHPh_2 = C_{37}H_{30}N_3Cl + SO_2 + 3HCl$$
$$CCl_3\cdot S\cdot C_6H_4Me + 3NHPh_2 = C_{37}H_{30}N_3Cl + C_6H_4Me\cdot SH + 2HCl$$

NN'N''-Triphenylpararosaniline hydrochloride (II) is identical in solubilities with that obtained from carbonyl chloride and diphenylamine; it dyes wool mordanted with alumina a deep blue, and is completely reduced by nascent hydrogen to a colourless leuco-base, the colour reappearing on addition of a mild oxidising agent, *e.g.*, calcium hypochlorite. Concentrated sulphuric acid dissolves it with a brownish-yellow colour, a blue precipitate being produced on dilution; further action of the acid gives first an insoluble monosulphonic acid and then a trisulphonic acid, easily soluble in water. Solutions of the compound in alcohol give a red colour with alkali, gradually fading; immediate extraction with ether gives a red basic compound (picrate, bronze needles, blue solution in benzene).

The red compound, oxidised with alkaline potassium permanganate, gives phenylcarbylamine, indicating the presence of a Ph·N·C· group; from the oxidation with acid potassium permanganate, diphenylamine was isolated, indicating a $NPh_2\cdot$ link. With sodium hydroxide, it forms a red ether-soluble base, the colour gradually fading on standing; reduction with zinc and hydrochloric acid gives a colourless compound. When warmed with concentrated sulphuric acid, it gives an insoluble monosulphonic acid, and with fuming nitric acid in glacial acetic acid it affords *pp'*-dinitro-*N*-nitrosodiphenylamine, from which *pp'*-dinitrodiphenylamine was prepared. A vigorous reaction takes place with acetyl chloride in acetic anhydride, but the acetyl compound could not be isolated in the crystalline state. Dry distillation of the red compound gives diphenylamine (cf. *NN'N''*-triphenylpararosaniline hydrochloride).

These properties indicate that the compound is of the triphenylmethane-dye type, containing one or two diphenylamino-groups intact, the bulk of evidence confirming the former (see IV).

The initial formation of tetraphenylthiocarbamide and the final formation of (II), in the reaction between thiocarbonyl chloride and diphenylamine, probably occurs by a series of para-migrations, comparable with those of the semidine and the benzidine transformation:

$$C(NPh_2)_2{:}S \longrightarrow NPh_2\cdot CS\cdot C_6H_4\cdot NHPh \longrightarrow NHPh\cdot C_6H_4\cdot CS\cdot C_6H_4\cdot NHPh$$

At the same time, diphenylthiocarbamyl chloride is formed, and reacts with the migration products. This supposition is based on the behaviour of other secondary amines with thiocarbonyl chloride: dimethyl- and diethyl-amine both react with it on warming, but dipropylamine must be subjected to prolonged boiling with it in toluene before reaction proceeds to the tetrapropylthiocarbamide stage (Delépine, *Bull. Soc. chim.*, 1910, **7**, 989). As the molecular weight of the groups increases, there is an increasing tendency for the reaction to stop at the dialkyl- or diaryl-thiocarbamyl chloride: in the case of arylalkylamines, *e.g.*, ethylaniline, this is the main product of the reaction. Hence, in this case, diphenylthiocarbamyl chloride is probably formed and immediately reacts with diphenylamine, giving some tetraphenylthiocarbamide, and also with both migration products of the latter, giving, in the first case, the red compound (III or IV) and, in the case of the doubly migrated compound, the hydrochloride (II). In accordance with this view, di-*p*-tolylamine gives no coloured products.

The balance of the evidence points to formula (IV) as the structure of the red component.

Tertiary Amines.—Rathke (*Ber.*, 1886, **19**, 397) noted that a violet dye was formed when thiocarbonyl tetrachloride and dimethylaniline react. He suggested that it was produced by partial decomposition of the tetrachloride into sulphur and carbon tetrachloride, which then reacted separately, thus:

$$S + 2C_6H_5\cdot NMe_2 = S(C_6H_4\cdot NMe_2)_2 + 2H \quad . \quad . \quad . \quad . \quad . \quad (i)$$
$$CCl_4 + 3C_6H_5\cdot NMe_2 = C(C_6H_4\cdot NMe_2)_3Cl + 3HCl \quad . \quad . \quad . \quad . \quad (ii)$$

Further decomposition of thiocarbonyl tetrachloride he assumed to give chlorine and thiocarbonyl chloride, the former rendering ineffective much of the hydrogen of the reaction (i), and the latter converting a portion of the dimethylaniline into 4 : 4'-bis(dimethylamino)-diphenyl thioketone (Michler's thioketone). Since he did not isolate the thioketone, and suggested the probable formation of another sulphur compound to account for the low yield of dye, it was considered desirable to reinvestigate the reaction.

Thiocarbonyl tetrachloride and dimethylaniline gave S-p-*dimethylaminophenyltrichloromethylthiol*, $NMe_2\cdot C_6H_4\cdot S\cdot CCl_3$ (V), and tris-*p*-dimethylaminophenylmethane, in addition to crystal-violet. The thiol is analogous to the various *p*-substituted aryltrichloromethylthiols described by Zincke, Jörgensen, and Frohneberg (*Ber.*, 1909, **42**, 2721; 1910, **43**, 837).

The thiol (V) is hydrolysed by water to carbon dioxide, hydrogen chloride (traces of hydrogen sulphide), and *p*-dimethylaminophenylthiol; reduction gives some dimethylaniline and methylthiol; concentrated nitric acid in glacial acetic acid gives a *dinitro*-derivative, and dry hydrogen chloride in ligroin quantitatively precipitates the hydrochloride. The compound reacts readily with primary arylamines giving S-(p-*dimethylaminophenyl*)-NN′-*diaryl*iso*thiocarbamides* (VI), the constitution of which has been established by hydrolysis in alcoholic ammonia solution at 120° to *p*-dimethylaminophenylthiol and diarylguanidines (VII; R′ = H):

$$\text{(VI.)}\quad \mathrm{NMe_2{\cdot}C_6H_4{\cdot}S{\cdot}C(\colon NR){\cdot}NHR + NH_3 = NMe_2{\cdot}C_6H_4{\cdot}SH + NR'\colon C(NHR)_2}\quad \text{(VII.)}$$

With alcoholic aniline at 170°, the compounds (VI) give *p*-dimethylaminophenylthiol and triarylguanidines (VII; R′ = Ph). With chloroform and alcoholic potash they give carbylamines; reduction with tin and hydrochloric acid regenerates the primary amine from which they were prepared; and they are unaffected by aqueous alkalis weaker than 80% potassium hydroxide, which gives some *p*-dimethylaminophenylthiol.

Compounds of the type (VI) have been prepared alternatively from carbodiaryldi-imide monohydrochloride and potassium *p*-dimethylaminophenylthiol:

$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}SK + CCl(\colon NR){\cdot}NHR = NMe_2{\cdot}C_6H_4{\cdot}S{\cdot}C(\colon NR){\cdot}NHR}$$

[cf. formation of tetraphenyl*iso*thiocarbamide: $\mathrm{Ph{\cdot}SNa + CCl(\colon NPh){\cdot}NPh_2 = Ph{\cdot}S{\cdot}C(\colon NPh){\cdot}NPh_2}$, and of diphenylethyl*iso*carbamide: $\mathrm{EtONa + CCl(\colon NPh){\cdot}NHPh = C(OEt)(\colon NPh){\cdot}NHPh}$ (*Ber.*, 1903, **36**, 965; 1895, **28**, Ref. 778)].

S-Arylaminotrichloromethylthiols react with diarylamines, and, in presence of condensing agents, *e.g.*, aluminium chloride or zinc chloride, with aromatic tertiary amines, to give dyes identical with those obtained from thiocarbonyl tetrachloride and the corresponding amine, the same dyes being produced from diphenylmethylamine directly with thiocarbonyl tetrachloride and indirectly with the thiol (V):

$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}S{\cdot}CCl_3 + 3NPh_2Me \longrightarrow [NMe_2{\cdot}C_6H_4{\cdot}S{\cdot}C(C_6H_4{\cdot}NMePh)_3] \longrightarrow}$$
$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}SH + C(\colon C_6H_4\colon NMePhCl)(C_6H_4{\cdot}NMePh)_2}$$

Diphenylamine reacts similarly, and dimethylaniline condenses with the thiol in presence of aluminium chloride to give crystal-violet. The rate of reaction of dialkylanilines with thiocarbonyl tetrachloride diminishes with increase in the size of the alkyl groups.

Triphenylamine reacts with thiocarbonyl chloride or tetrachloride at 180° to give hexaphenylrosaniline hydrochloride.

p-Bromo-dimethyl- and -diethyl-aniline, dimethyl-*p*-toluidine, and tetramethyldiaminodiphenylmethane react rapidly with thiocarbonyl tetrachloride on heating, with partial demethylation, thiocarbonyl chloride distilling. Tribenzylamine, similarly, gives benzyl chloride and thiocarbonyl chloride.

EXPERIMENTAL.

S-*Dimethylaminotrichloromethylthiol*, $\mathrm{NMe_2{\cdot}S{\cdot}CCl_3}$.—Dimethylamine (33% aqueous solution) was added slowly to a well-stirred mixture of thiocarbonyl tetrachloride (20 g.) in ether (150 ml.) and sodium hydroxide (8 g.) in water (250 ml.) kept below 30°, until a slight excess of amine was present. After 15 minutes, the ethereal layer was removed, the residue extracted with ether (25 ml.), and the combined extracts washed with water, dried over potassium carbonate, and freed from ether in a vacuum at 15°. The residual *S-dimethylaminotrichloromethylthiol* distilled as a colourless oil, b. p. 74°/15 mm., with a characteristic odour (Found: S, 16·9. $\mathrm{C_3H_6NCl_3S}$ requires S, 16·5%).

The following analogues were prepared: *Diethyl* compound, colourless oil, b. p. 96°/15 mm. (Found: S, 14·6. $\mathrm{C_5H_{10}NCl_3S}$ requires S, 14·4%); di*iso*butyl compound, pale yellow oil, b. p. 127°/15 mm. (decomp.).

Arylalkylaminotrichloromethylthiols were prepared as pale yellow, unstable oils by the above method, sodium hydroxide being replaced by sodium carbonate: *Methylanilino*-compound, with characteristic odour (Found: S, 12·8. $\mathrm{C_8H_8NCl_3S}$ requires S, 12·5%); *methyl*-p-*toluidino*-compound (Found: S, 12·2. $\mathrm{C_9H_{10}NCl_3S}$ requires S, 11·8%). The corresponding ethylanilino-, ethyl-*o*-toluidino-, and ethyl-α-naphthylamino-compounds (pale yellow oils) were prepared but were excessively unstable.

S-Dibenzylaminotrichloromethylthiol (colourless oil) decomposed on attempted distillation in a vacuum, giving a distillate containing a large proportion of benzyl chloride, b. p. 179—180° (*p*-nitro-derivative, m. p. 71°). The benzylanilino-compound was not isolated owing to instability.

Reduction of S-*dimethylaminotrichloromethylthiol.* The thiol (5 g.) was dropped slowly on zinc dust (50 g.) and glacial acetic acid (50 ml.), and the mixture heated until reaction commenced. The gases evolved were passed through two tubes (20 × 9 cm.), the first containing anhydrous calcium chloride, and the second finely-crystallised lead acetate (20 g.); with the latter was connected a small wash-bottle containing 1 ml. of a fresh solution of isatin (10 mg.) in concentrated sulphuric acid (100 ml.). When air was passed through the system, any hydrogen sulphide was held by the lead acetate, and methylthiol produced a grass-green colour with the isatin reagent.

Reaction with aniline. S-Dimethylaminotrichloromethylthiol (20 g.) in ligroin (150 ml.) was boiled under reflux for 10 hours with aniline (45 g.). The ligroin was decanted, the residue distilled in steam, and the hot solution filtered from sulphur. Triphenylguanidine hydrochloride, which separated from the cooled filtrate, was filtered off and converted by sodium hydroxide solution into the base; colourless needles (17 g.) from alcohol, m. p. 143°; picrate, yellow needles, m. p. 179°.

The yields of triphenylguanidine obtained from other trichloromethylthiols are shown in the table below:

Trichloromethylthiol.	% Yield of triphenylguanidine.	Trichloromethylthiol.	% Yield of triphenylguanidine.
S-Diethylamino-	60	*S*-Ethylanilino-	32
S-Di*iso*butylamino-	46	*S*-Methyl-*p*-toluidino-	37
S-Methylanilino-	35	*S*-Piperidyl-	28

NN'N''-*Triphenylpararosaniline Hydrochloride* (II) *and an Isomeric Red Compound* (?IV).—(*a*) Diphenylamine (20 g.) and thiocarbonyl chloride or tetrachloride (10 g.) were warmed until violent effervescence started; reaction then proceeded without the aid of external heat. The cooled melt was warmed first with acetone (20 ml.), the solution being rejected, then with ether (150 ml.) to remove tetraphenylthiocarbamide and the excess of diphenylamine, and finally extracted with acetone (200 ml.), the cooled (0°) extract being poured into pure dry ether (1 l.). The whole was kept for an hour, and the precipitated *compound* (IV) was collected, washed with ether, and dried in a vacuum over concentrated sulphuric acid; it formed deep red, microcrystals from amyl alcohol, m. p. 280° (decomp.) (Found: H, 5·8; Cl, 6·3. $C_{37}H_{30}N_3Cl$ requires H, 5·4; Cl, 6·5%).

(*b*) Three portions of diphenylamine (20 g.) and thiocarbonyl chloride were heated as described above, and the residues extracted with just sufficient boiling absolute alcohol to effect solution. The united extracts were cooled, and the deposited crystals filtered off, washed with alcohol, and recrystallised from glacial acetic acid, NN'N''-*triphenylpararosaniline hydrochloride* being obtained as a brown crystalline powder (10—12 g.) (Found: C, 80·8; H, 5·5; Cl, 5·9. $C_{37}H_{30}N_3Cl$ requires C, 80·4; H, 5·4; Cl, 6·4%), soluble in hot acetone, alcohol, glacial acetic acid, and boiling aniline or nitrobenzene, but insoluble in water, ether, chloroform, or benzene.

Nitration of (IV).—Fuming nitric acid (12 ml.) was added slowly to the red compound (5 g.) in glacial acetic acid (25 ml.). The mixture was warmed on the water-bath for 10 minutes; reaction then proceeded without the aid of external heat. The resultant orange solution was poured into water (250 ml.), *pp'*-dinitro-*N*-nitrosodiphenylamine (7·5 g.) being obtained. When this substance (3·5 g.) and aniline (15 ml.) were heated at 120° for ½ hour, and the resultant solution poured into cold 5% hydrochloric acid (200 ml.), *pp'*-dinitrodiphenylamine (1·5 g.) was formed; recrystallised from alcohol, it had m. p. 215°.

Sulphonation of (IV).—The dye (15 g.) was heated to 70° with concentrated sulphuric acid (100 ml.) until solution was complete, and the still warm solution poured on ice. The product, washed with water and recrystallised from alcohol, formed deep red, small crystals with a green reflex (12 g.). Analysis showed that they probably consist of a mixture of the monosulphonic acid and the sulphate of the dye base.

Formation of S-p-*Dimethylaminophenyltrichloromethylthiol and Crystal-violet.*—Dimethylaniline (40 g.) was stirred mechanically, and thiocarbonyl tetrachloride (20 g.) gradually added, the temperature being kept below 20°. After 24 hours, the dark mass was heated at 60° for 3 hours with stirring, and the product extracted with water (250 ml.) at 60° and immediately cooled to 0°. Concentrated hydrochloric acid (10 ml.), added slowly with vigorous stirring, precipitated a substance which, after being collected and washed with water, formed a black crystalline mass. Recrystallisation from ligroin (charcoal) gave S-p-*dimethylaminophenyl-*

trichloromethylthiol (12 g.) in large colourless prisms, m. p. 71°, with a characteristic odour (Found: S, 11·8; Cl, 39·2; *M*, 280. $C_9H_{10}NCl_3S$ requires S, 11·8; Cl, 39·4%; *M*, 270·5). It formed a *dinitro*-derivative, yellow needles, m. p. 123°, from alcohol (Found: Cl, 28·8. $C_9H_8O_4N_3Cl_3S$ requires Cl, 29·2%), and a *monobromo*-derivative, orange-yellow plates, m. p. 146° (decomp.), from glacial acetic acid (Found: S, 9·1. $C_9H_9NCl_3BrS$ requires S, 8·8%). The hydrochloride, from the base in ligroin with dry hydrogen chloride, formed white needles, m. p. 129—130° (decomp.), completely hydrolysed by water to the original base.

The dye in the filtrate from the previous preparation was precipitated by gradual addition of saturated brine; yield, 12 g. Recrystallisation from water gave crystal-violet ($8H_2O$) in long prisms with a bronze reflex; leuco-base, needles from alcohol, m. p. 172°.

The analogous p-*diethylamino-thiol* formed colourless needles, m. p. 44° (Found: S, 11·0; Cl, 35·6. $C_{11}H_{14}NCl_3S$ requires S, 10·7; Cl, 35·7%), but the methylethyl, di-*n*-propyl, and di-*n*-butyl analogues separated as black viscous oils which could not be crystallised.

p-*Dimethylaminophenylthiol*.—*p*-Dimethylaminophenyltrichloromethylthiol (5 g.) and water (200 ml.) were heated under reflux for 3 hours, the mixture made alkaline with sodium hydroxide solution, and the thiol distilled in steam. *p*-Dimethylaminophenylthiol collected as a pale yellow solid, m. p. 32°, which gave a blood-red salt with lead acetate and rapidly oxidised in air to *bis*-(p-*dimethylaminophenyl*) *disulphide*, yellow needles, m. p. 118° (Found: S, 21·3. $C_{16}H_{20}N_2S_2$ requires S, 21·05%), from alcohol; mixed m. p. with an authentic specimen (m. p. 117·5°) prepared from sulphur monochloride and dimethylaniline, 117°.

S-(p-*Dimethylaminophenyl*)-NN′-*diphenyl*iso*thiocarbamide* (VI; R = Ph).—*S*-*p*-Dimethylaminophenyltrichloromethylthiol (10 g.) was added in small portions to aniline (18 g.) in alcohol (200 ml.), and the whole heated on the water-bath for 15 minutes. The iso*thiocarbamide* crystallised on cooling; it formed long glistening needles (11·5 g.), m. p. 175°, from ethyl acetate (Found: S, 9·5. $C_{21}H_{21}N_3S$ requires S, 9·2%). The *di*-p-*tolyl* analogue formed white needles, m. p. 142° (Found: S, 8·7. $C_{23}H_{25}N_3S$ requires S, 8·5%), the *di*-p-*chlorophenyl* analogue glistening plates, m. p. 157° (Found: S, 7·7; Cl, 17·4. $C_{21}H_{19}N_3Cl_2S$ requires S, 7·7; Cl, 17·1%), and the p-*bromophenyl* analogue glistening plates, m. p. 167° (Found: S, 6·5; Br, 31·6. $C_{21}H_{19}N_3Br_2S$ requires S, 6·2; Br, 31·7%).

The p-*diethylamino*-compound formed colourless prisms, m. p. 128° (Found: S, 8·9. $C_{23}H_{25}N_3S$ requires S, 8·5%), and the p-*di*-n-*propylamino*-compound glistening needles, m. p. 125° (Found: S, 8·1. $C_{25}H_{29}N_3S$ requires S, 7·9%), both from ligroin.

Reactions of the iso*Thiocarbamide* (VI; R = Ph).—(i) *With ammonia*. *S*-(*p*-Dimethylaminophenyl)-*NN*′-diphenyl*iso*thiocarbamide (4 g.) and alcoholic ammonia (10 ml.) were heated for 2 hours at 120°. After being freed from ammonia in a vacuum at 15°, the resultant alcoholic solution gave the following tests: (*a*) lead acetate gave a blood-red salt; (*b*) alcoholic mercuric chloride produced an orange precipitate; (*c*) the solution in dilute sodium hydroxide gave a purple colour with sodium nitroprusside; (*d*) hydrogen peroxide gave bis-(*p*-dimethylaminophenyl) disulphide, yellow needles, m. p. 118°, from alcohol; mixed m. p. with an authentic specimen 118° (Found: S, 21·3%). The filtrate from the disulphide was evaporated to dryness, and the residue crystallised from water. Diphenylguanidine separated in colourless leaflets, m. p. 147° (perchlorate, white needles, m. p. 162°).

(ii) *With aniline*. The same *iso*thiocarbamide (2 g.), aniline (0·5 g.), and alcohol (10 ml.) were heated at 170° for 2 hours. The *p*-dimethylaminophenylthiol which was formed rapidly oxidised to the disulphide, which formed yellow needles, from alcohol, m. p. and mixed m. p. 118°. The filtrate from the disulphide, on evaporation, gave triphenylguanidine (colourless needles from alcohol, m. p. 143°; picrate, yellow needles, m. p. 179°).

Preparation of (VI; R = Ph) *from Carbodiphenyldi-imide Monohydrochloride*.—Thiocarbanilide (20 g.) in benzene (250 ml.) at 40° was vigorously stirred, and freshly precipitated mercuric oxide (30 g.) added slowly. After ½ hour, the solution was filtered and the solvent evaporated, leaving carbodiphenyldi-imide as a viscous oil. Dry hydrogen chloride, passed into the solution of this product in ligroin (50 ml.) at 0°, precipitated the monohydrochloride, m. p. 90—92°, free from the dihydrochloride.

Bis-(*p*-dimethylaminophenyl) disulphide (10 g.) was boiled with alcohol (100 ml.) and potassium hydroxide (20 g.) for ½ hour. Glacial acetic acid (17 g.) was added to the cold solution, and the above monohydrochloride was then added slowly, the whole being finally warmed on the water-bath for 15 minutes. The *iso*thiocarbamide (VI; R = Ph) and unchanged disulphide separated on cooling; the former was obtained by fractional recrystallisation from alcohol as glistening needles (1 g.), m. p. 175°, undepressed on admixture with the product obtained from *S*-*p*-dimethylaminophenyltrichloromethylthiol.

Formation of NN′N″-*Triphenylpararosaniline Hydrochloride and the Compound* (IV).—*S*-*p*-Tolyltrichloromethylthiol (5 g.) and diphenylamine (8 g.) were heated at 150° for 4 hours. The cooled melt was washed with ether (50 ml.) and extracted with acetone (100 ml.), and the cooled extract filtered. The residue was washed with benzene (100 ml.), affording *NN′N″*-triphenylpararosaniline hydrochloride (1·5 g.) in small crystals with a copper reflex. The filtrate was poured into pure dry ether (500 ml.), and after standing for 1 hour, the precipitate was collected, washed with ether, and dried in a vacuum. The product, a crystalline solid (1 g.) with a green reflex, had the properties previously described for compound (IV). The absorption spectra of the two compounds in alcoholic solution, measured with a Hilger industrial spectrophotometer, were identical.

Formation of Crystal-violet.—Aluminium chloride (5 g.) was added during 15 minutes to a stirred mixture of *S*-*p*-tolyltrichloromethylthiol (5 g.) and dimethylaniline (7·5 g.), and the product warmed on the water-bath for ½ hour. Thio-*p*-cresol, m. p. 43°, and the excess of dimethylaniline were distilled in steam, and the dye (1·5 g.) precipitated from the cooled solution by addition of saturated brine solution (leuco-base, m. p. 172°).

NN′N″-*Triphenyl*-NN′N″-*trimethylpararosaniline Hydrochloride.*—Diphenylmethylamine (15 g.) and thiocarbonyl tetrachloride (5 g.) were heated at 100° for ½ hour and for a further hour at 120—130°; hydrogen chloride was evolved. The product, after cooling, was washed with ether (50 ml.) and dissolved in acetone (150 ml.), and the cold solution poured into pure dry ether (500 ml.). The precipitate was washed with ether and dried in a vacuum, giving the dye *hydrochloride* (9 g.) as a brown, crystalline solid with a yellowish-green reflex (Found : Cl, 6·2. $C_{40}H_{36}N_3Cl$ requires Cl, 6·0%).

Hexaphenylpararosaniline Hydrochloride and Hexaphenyltriaminotriphenylcarbinol.—Triphenylamine (6·4 g.) and thiocarbonyl chloride (2 g.) were heated at 180° for 2 hours. The product, washed with boiling ether (25 ml.), was extracted with boiling acetone (200 ml.), and the extract filtered. Evaporation of the solvent gave hexaphenylpararosaniline hydrochloride as a deep blue mass with a red metallic lustre, easily soluble in acetone or alcohol. Ammonia precipitated from the alcoholic solution *hexaphenyltriaminotriphenylcarbinol,* which was soluble in benzene and reprecipitated on addition of alcohol (Found : C, 86·4; H, 6·0. $C_{55}H_{43}ON_3$ requires C, 86·7; H, 5·6%). The carbinol was soluble in concentrated sulphuric acid with a blue-violet colour, changing to pure blue on addition of alcohol; water produced a blue precipitate.

Reaction between Tribenzylamine and Thiocarbonyl Tetrachloride.—The amine (15 g.) and the tetrachloride (10 g.) were heated at 100°. Thiocarbonyl chloride (3 g.) distilled as a red liquid, b. p. 72°, and by warming with an excess of aniline gave thiocarbanilide (white plates, m. p. 152°, from alcohol). Extraction of the residue with ether gave benzyl chloride (3·5 g.), b. p. 179° (*p*-nitro-derivative, m. p. 71°). *p*-Bromo-dimethyl- and -diethyl-aniline, dimethyl-*p*-toluidine, and bis-(*p*-dimethylaminophenyl)methane react analogously.

The authors thank the Chemical Society and Imperial Chemical Industries, Ltd., for grants.

LOUGHBOROUGH COLLEGE, LEICESTERSHIRE. [*Received, July 27th,* 1937.]