176. *The Constitution and Reactions of Thiocarbonyl Tetrachloride. Part I. Reaction with Arylamines.*

By Joseph M. Connolly and G. Malcolm Dyson.

Rathke (*Annalen*, 1873, **167**, 195) prepared thiocarbonyl tetrachloride from chlorine and carbon disulphide, using 0·1% of iodine as catalyst, and formulated it $CCl_3{\cdot}SCl$ (I). Certain of its reactions, notably its reduction by sulphites and nascent hydrogen to thiocarbonyl chloride, suggest the structure $CCl_2 \leftarrow SCl_2$ (II). To investigate the reactions of thiocarbonyl tetrachloride and to decide between these structures is the purpose of the present investigation.

The parachor of thiocarbonyl tetrachloride is 266·1, from which Briscoe, Peel, and Robinson (J., 1929, 1048) concluded that (I) is correct; a conclusion invalidated by the better agreement of the experimental figure with that calculated for (II) (C, 4·8; 4Cl, 217·2; S, 46·5; one semi-polar bond, —1·6; total, 266·9) than with that calculated for (I) (268·5). The formation of potassium mercaptomethanetrisulphonate (Backer, *Rec. trav. chim.*, 1930, **49**, 1048) from potassium sulphite and thiocarbonyl tetrachloride was considered evidence for (I), but involves an assumption that the three sulphonic groups attached to the methane carbon have replaced three chlorine atoms. It appears that the potassium salt cited is not formed directly from thiocarbonyl tetrachloride, since we have isolated thiocarbonyl chloride as an intermediate. The reaction follows the course :

$$\begin{aligned} CSCl_4 + K_2SO_3 + H_2O &= CSCl_2 + K_2SO_4 + 2HCl \\ 2HCl + K_2SO_3 &= 2KHSO_3 + 2KCl \\ 2KHSO_3 + CSCl_2 &= CS(SO_3K)_2 + 2HCl \\ CS(SO_3K)_2 + KHSO_3 &= C(SH)(SO_3K)_3 \end{aligned}$$

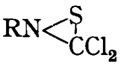
Alternatively, if, as Backer suggests (*ibid.*, 1931, **50**, 268; 1932, **51**, 988), the final product is to be written $CH(SO_3K)_2{\cdot}S(SO_3K)$, the last equation must be modified so that the addition is inverted. This avoids the cumbrous and improbable explanation suggested by Backer for the attachment of hydrogen to the methane carbon.

Compounds obtained from the interaction of thiocarbonyl tetrachloride and arylamines were formulated $R{\cdot}NH{\cdot}S{\cdot}CCl_3$ (Johnson and Hemmingway, *J. Amer. Chem. Soc.*, 1916, **38**, 1860), but no structural evidence was advanced, it being assumed that the reactive chlorine atom was attached to sulphur (I). This is in direct opposition to the observation (Rathke, *loc. cit.*) that this chlorine atom is not removed during oxidation of thiocarbonyl tetrachloride to trichloromethanesulphonyl chloride, $CCl_3{\cdot}SO_2Cl$. In the absence of direct evidence on this point, four formulæ are possible for the product of interaction of thiocarbonyl tetrachloride and arylamines :

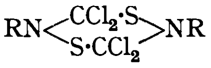
$R{\cdot}NH{\cdot}S{\cdot}CCl_3$	$R{\cdot}NH{\cdot}SCl \rightarrow CCl_2$	$R{\cdot}NH{\cdot}CCl_2{\cdot}SCl$	$R{\cdot}NH{\cdot}CCl \leftarrow SCl_2$
(III.)	(IV.)	(V.)	(VI.)

Boiling water hydrolyses the p-*tolyl* derivative to *p*-tolylthiocarbimide, hydrogen chloride, thiocarbonyl tetrachloride, and *p*-toluidine hydrochloride. Hydrogen chloride in chloroform solution quantitatively regenerates the hydrochloride of the original amine and thiocarbonyl tetrachloride; dilute alkali solution produces both *p*-tolylthiocarbimide and *p*-tolylcarbylamine, even in the cold. These reactions point to the presence in the compound of an $R^-N^-C^-$ group and, if isomerisation during hydrolysis be precluded, excludes formulæ (III) and (IV).

The compounds of this series react with potassium hydroxide in alcohol, the elements of hydrogen chloride being eliminated (Rathke; Johnson and Hemmingway; *locc. cit.*) with formation of cyclic compounds, to which Johnson and Hemmingway ascribed structure

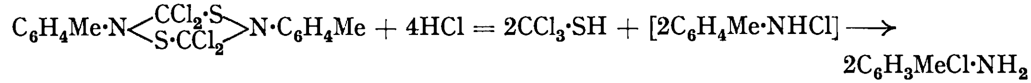
(VII.) 

$$RN{<}\begin{matrix} S \\ CCl_2 \end{matrix}$$

 (VIII.)

$$RN{<}\begin{matrix} CCl_2{\cdot}S \\ S{\cdot}CCl_2 \end{matrix}{>}NR$$

(VII), no evidence being adduced. We have shown that they are represented by the structure (VIII). For instance, the *compound* for which R is *p*-tolyl decomposes at 145°, has the molecular weight 410—420 (benzene depression), and is unaffected by water, hydrochloric acid, tin and hydrochloric acid, potassium permanganate, and hydrogen peroxide, and by alkalis weaker than 80% potassium hydroxide, which decomposes it to form some *p*-tolylcarbylamine. In ether it reacts with hydrogen chloride, giving 3-chloro-*p*-toluidine hydrochloride and *trichloromethylthiol* :



$$C_6H_4Me{\cdot}N{<}\begin{matrix}CCl_2{\cdot}S\\ S{\cdot}CCl_2\end{matrix}{>}N{\cdot}C_6H_4Me + 4HCl = 2CCl_3{\cdot}SH + [2C_6H_4Me{\cdot}NHCl] \longrightarrow 2C_6H_3MeCl{\cdot}NH_2$$

With hydrogen bromide in ether it regenerates the original amine and forms an orange oil, presumably $CCl_2Br{\cdot}SBr$. The *p*-tolyl compound cannot be acetylated or benzoylated. These facts support formula (VIII). Similar compounds were prepared from aniline, *p*-chloroaniline, and *p*-anisidine, but both *s*-tribromoaniline and 3 : 5-dibromo-*p*-toluidine failed to react; with *m*-2-xylidine and 2 : 4-dichloroaniline, only the corresponding thiocarbimide could be obtained when the product of interaction with thiocarbonyl tetrachloride was stirred with alcoholic potash ($R{\cdot}NH{\cdot}CCl_2{\cdot}SCl \longrightarrow R{\cdot}NCS$).

EXPERIMENTAL.

p-*Toluidinodichloromethylchlorothiol* (V ; $R = C_7H_7$).—*p*-Toluidine (11·6 g.) was slowly added to a stirred mixture of thiocarbonyl tetrachloride (20 g.) in ether (120 ml.) and sodium carbonate (8 g.) in water (230 ml.), kept below 30°. After 15 minutes the ethereal layer was removed, the residue extracted with ether (20 ml.), and the combined extracts washed with water and freed from ether by spontaneous evaporation. The *chlorothiol* formed long white needles, m. p. 73°, from ligroin (Found : S, 12·6. $C_8H_8NCl_3S$ requires S, 12·5%).

The corresponding phenyl, *p*-anisyl, *p*-chlorophenyl, and 2 : 6-xylyl compounds, obtained by the same method, were oils which readily decomposed but were characterised by conversion into cyclic compounds.

2 : 2 : 5 : 5-*Tetrachloro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrahydro*-3 : 6-*dithiapyrazine* (VIII; $R = C_7H_7$).—Potassium hydroxide (8 g.) in alcohol (75 ml.) was added slowly with stirring to an ethereal solution of the previous preparation. After 4 hours the *compound* was filtered off and freed from potassium chloride by extraction in ligroin. It formed white needles, m. p. 142·5° (violent decomp.) (Found : S, 14·8. $C_{16}H_{14}N_2Cl_4S_2$ requires S, 14·5%).

The following analogues were prepared : *phenyl*, white needles, m. p. 145·5° (decomp.) (Found : S, 15·5. $C_{14}H_{10}N_2Cl_4S_2$ requires S, 15·5%); p-*anisyl*, colourless rhombs, m. p. 113° (decomp.) (Found : S, 13·4. $C_{16}H_{14}O_2N_2Cl_4S_2$ requires S, 13·55%); p-*chlorophenyl*, white needles, m. p. 160° (decomp.) (Found : S, 13·3. $C_{14}H_8N_2Cl_6S_2$ requires S, 13·3%).

Trichloromethylthiol.—The preceding tetrachlorodi-*p*-tolyltetrahydrodithiapyrazine (20 g.) in ether (1 l.) was saturated with dry hydrogen chloride (9 hrs.). After 24 hours, the 3-chloro-*p*-toluidine hydrochloride was removed, and the filtrate evaporated to 500 ml. and again saturated with hydrogen chloride. Further evaporations and saturations were carried out until the filtrate gave no further precipitate of hydrochloride (70 ml.). Ether was removed at 55°, and the oil washed with saturated sodium bicarbonate solution, dried over calcium chloride, and distilled in a vacuum, yielding an orange oil with a repulsive odour, b. p. 125°/15 mm. (Found : S, 21·3; Cl, 70·0. $CHCl_3S$ requires S, 21·1; Cl, 70·3). In air *trichloromethylthiol* was slowly oxidised to a yellow crystalline substance, m. p. 96°, probably the disulphide. It decomposed into sulphur dichloride and a crystalline solid when heated under ordinary pressure. In an evacuated apparatus it was decomposed by sodium, evolving hydrogen. With alcoholic mercuric chloride it yielded a white precipitate (acid filtrate), a reaction characteristic of mercaptans. Oxidation with fuming nitric acid gave chloropicrin.

m-*Xylyl-2-thiocarbimide.*—*m*-2-Xylidine (13 g.) in ether (50 ml.) was stirred with sodium carbonate (10 g.) in water (200 ml.) and thiocarbonyl tetrachloride (20 g.) in ether (50 ml.). After 2 hours, the ethereal layer was separated and mixed slowly with potassium hydroxide (10 g.) in alcohol (100 ml.). The mixture was freed from precipitated potassium chloride and evaporated spontaneously. The residue was distilled in steam, yielding 5 g. of a pale yellow oil (compare Dyson, George, and Hunter, J., 1927, 436).

Potassium Mercaptomethanetrisulphonate.—Backer's method was first repeated (*loc. cit.*); by using potassium carbonate and potassium sulphite, thiocarbonyl chloride was isolated. It was then found that the latter compound reacted with potassium sulphite to give potassium mercaptomethanetrisulphonate. Thiocarbonyl chloride (10 g.) was slowly added to a stirred solution of potassium sulphite (85 g.) in water (105 ml.) until the orange oil disappeared. The product separated in crystals which were obtained in large transparent pyramids from water (Found: S, 28·8. Calc. for $CHO_9S_4K_3,2H_2O$: S, 29·2%). The water of crystallisation is lost at 105°.

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