169. *The Constitution and Reactions of Thiocarbonyl Tetrachloride. Part III. Reaction with Primary Alkylamines and Phenols.*

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S-Aryloxytrichloromethylthiols, obtained by the action of thiocarbonyl tetrachloride on sodium phenoxides (Connolly and Dyson, J., 1935, 679), have been further investigated. *S*-Phenoxytrichloromethylthiol in ethereal solution with sodium ethoxide (1 mol.) in dry ethyl alcohol gives sodium phenoxide and a yellow oil. Since no sodium chloride separates, the trichloromethyl group is unaffected, an interchange of groups taking place :

$$C_6H_5\cdot O\cdot S\cdot CCl_3 + EtONa = EtO\cdot S\cdot CCl_3(I) + C_6H_5\cdot ONa$$

S-Ethoxytrichloromethylthiol (I) yields thiocarbonyl tetrachloride and alcohol with dry hydrogen chloride in dry ether, and *s*-triphenylguanidine hydrochloride with aniline in ligroin. It was synthesised from thiocarbonyl tetrachloride and one molecular proportion of sodium ethoxide : $EtONa + CCl_3\cdot SCl = (I) + NaCl$. *S*-Alkoxytrichloromethylthiols, with excess of the corresponding sodium alkyloxide in dry alcohol, form tetra-alkyl esters of orthocarbonic acid :

$$(I) + 3NaOEt \longrightarrow EtO\cdot S\cdot C(OEt)_3 + 3NaCl \longrightarrow 3NaCl + C(OEt)_4 + Na_2S$$

The yields are higher than those obtainable by other methods (*e.g.*, chloropicrin).

Thiocarbonyl tetrachloride reacts on primary alkylamines as on primary arylamines, giving *S*-alkylaminotrichloromethylthiols. These are pale yellow oils decomposing spontaneously on standing, though not as rapidly as the corresponding aryl derivatives. They are similar in properties to the latter (Connolly and Dyson, J., 1934, 822; 1935, 679), except that hydrolysis with hydrochloric acid chiefly yields the amine hydrochloride and little thiocarbimide. Compounds analogous to the tetrachlorodiaryltetrahydrodithiapyrazines cannot be obtained by treating the thiols with alcoholic potash. Treatment with the corresponding alkylamine in ligroin solution yields the trialkylguanidine hydrochloride. This is a new method for the synthesis of trialkylguanidine hydrochlorides, specimens of which for comparison were prepared by another method, *s*-dialkylthiourea being converted into the sulphate of its methyl derivative by methyl sulphate and into the trialkylguanidine sulphate by a further molecular proportion of the amine, followed by conversion into the guanidine base, then into its hydrochloride :

$$2CS(NHR)_2 \xrightarrow{Me_2SO_4} [NHR\cdot C(SMe){:}NR]_2SO_4 \xrightarrow{2NH_2R} [NR{:}C(NHR)_2]_2SO_4 + 2MeSH$$

Experimental.

n-*Heptylamine.*—*n*-Heptaldoxime (258 g.) in dry alcohol (4 l.) was placed in a 12 l. three-necked flask fitted with twin 180 cm. reflux condensers. Sodium (500 g.) was added in large pieces through the centre neck as rapidly as possible, consistent with safety. After the reduction, water (6 l.) was added slowly, and the mixture distilled, 9 l. of the distillate being collected in 50% hydrochloric acid (600 ml.). The acid distillate was concentrated to 700 ml. under reduced pressure and treated with 40% potash solution (1 l.) and the amine layer was separated, dried over caustic potash, and distilled; the *n*-heptylamine (127 g.) obtained had b. p. 154°.

*iso*Amylamine, b. p. 94—97°, was prepared similarly from *iso*valeraldoxime.

Allylamine, b. p. 53°, was prepared by the hydrolysis of allylthiocarbimide with boiling 30% hydrochloric acid.

S-n-*Heptylaminotrichloromethylthiol*.—*n*-Heptylamine (3·5 g.) in ether (10 ml.) was added to a stirred mixture of anhydrous potassium carbonate (2 g.) in water (50 ml.) and thiocarbonyl tetrachloride (5 g.) in ether (20 ml.). After 15 minutes, the ethereal layer was removed, washed twice with *N*-hydrochloric acid and once with water, and dehydrated over anhydrous potassium carbonate, and the ether removed in a vacuum at room temperature. The chlorothiol, an almost colourless oil with a geranium-like odour, decomposed spontaneously on standing and violently on heating to 170°.

The corresponding allyl compound, prepared by the same method, was also an unstable oil, decomp. 170°.

Triallylguanidine Hydrochloride.—*S*-Allylaminotrichloromethylthiol was prepared in ligroin solution by adding allylamine (3 g.) to thiocarbonyl tetrachloride (5 g.) in ligroin (100 ml.). Allylamine (6 g.) was then added, and the mixture boiled under reflux for 9 hours. After cooling, the ligroin layer was decanted, and the residue extracted with dilute hydrochloric acid. The extract, on concentration, yielded colourless rhombs of *triallylguanidine hydrochloride*, m. p. and mixed m. p. (with a specimen prepared by another method) 176° (Found: Cl, 16·8. $C_{10}H_{15}N_3$,HCl requires Cl, 16·5%).

The *tribenzyl* and the *tri*iso*amyl* analogue, prepared by the same method, were colourless microcrystalline powders, m. p. 201° and 206° respectively (Found for the former: Cl, 9·4. $C_{22}H_{23}N_3$,HCl requires Cl, 9·7%. Found for the latter: Cl, 12·0. $C_{16}H_{35}N_3$,HCl requires Cl, 11·6%).

Tribenzylguanidine Hydrochloride (*Method* II).—Benzylamine (4 g.) in chloroform (40 ml.) was converted into benzylthiocarbimide by shaking with thiocarbonyl chloride (3·7 g.) and water (150 ml.) for 15 minutes. The chloroform layer was removed, washed with water, and boiled with benzylamine (4 g.) for 30 minutes. On evaporation, *s*-dibenzylthiourea, a white microcrystalline powder, was obtained. This was methylated by gentle boiling for 1½ hours with methyl sulphate (0·9 g.) and water (1 ml.). Benzylamine (1·4 g.) was then added, and the mixture heated on a water-bath for 9 hours. Methylthiol was evolved and the mixture solidified. The solid was extracted with hot water; the extract on cooling yielded crystals of tribenzylguanidine sulphate. These were removed, dissolved in hot water, and made alkaline with caustic soda, and the liberated base (an oil) extracted with ether. The ethereal extract was washed with water, shaken with concentrated hydrochloric acid, and diluted, and the ether evaporated. Tribenzylguanidine hydrochloride separated, on cooling, as a microcrystalline powder, m. p. 203°.

The triallyl and the tri*iso*amyl analogue were prepared by the same method as white crystalline powders, m. p. 176° and 205° respectively.

S-*Ethoxytrichloromethylthiol*.—*S*-Phenoxytrichloromethylthiol, prepared from thiocarbonyl tetrachloride (40 g.) in dry ether (200 ml.) (*loc. cit.*), was shaken with a solution of sodium (6 g.) in dry ethyl alcohol (100 ml.). After 7 minutes, the mixture was shaken with water (700 ml.) to remove alcohol and sodium phenoxide, and ether (30 ml.) was added. The extract was dried (anhydrous potassium carbonate) and evaporated in a vacuum at room temperature. The residual *S*-ethoxytrichloromethylthiol was washed with water, dried, and obtained as a yellow oil with a pungent fruity odour, b. p. 155° (decomp.). It was also prepared by adding thiocarbonyl tetrachloride (18·6 g.) in dry ether (100 ml.) to sodium (3 g.) in dry ethyl alcohol (50 ml.); after 7 minutes, the mixture was poured into water, and the product isolated as before as a pale yellow oil, b. p. 160° (decomp.).

Tetraethyl Orthocarbonate.—To a solution of sodium (15 g.) in dry ethyl alcohol (240 ml.) in a flask fitted with a reflux condenser was added thiocarbonyl tetrachloride (20 g.) in dry ether (100 ml.). *S*-Ethoxytrichloromethylthiol was first formed and this then reacted violently with the excess of sodium ethoxide, sodium chloride being precipitated. After 4 hours, the mixture was poured into water (1 l.) and extracted twice with ether (160 ml.). Removal of the ether from the dried extract (calcium chloride) left a residue (10 g.), from which, on fractionation, tetraethyl orthocarbonate (8 g.) was obtained as a colourless liquid, b. p. 158°, $d_4^{17°}$ 0·916. Hydrolysis with 80% potash solution yielded potassium carbonate and ethyl alcohol.

*S-iso*Butoxytrichloromethylthiol, a colourless oil, b. p. 181° (decomp.)/760 mm., in reaction with sodium *iso*butoxide, yielded tetra*iso*butyl orthocarbonate as a pale yellow oil, b. p. 238°.

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