154. *Some Unsaturated Sulphides derived from the Chloroethylenes.*

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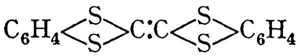
The reactivity of a halogen atom attached to a carbon atom adjacent to a double bond is very limited. Displacement has been brought about only by means of vigorous treatment with alkali hydroxide or alkoxide, by alcoholic alkali-metal mercaptides, and by aromatic bases in the presence of alkali.

Thus dichloroethylene, when heated with alcoholic potash, affords chloroacetylene (Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4233), and when heated with alkali mercaptides in alcoholic solution it readily gives rise to dialkyl- or diaryl-substituted dithioethylenes

(Fromm and others, *Annalen*, 1912, **394**, 325; *Ber.*, 1922, **55**, 1014). Di-(*o*-carboxyphenylthio)ethylene has been obtained by the action of dichloroethylene on sodium thiosalicylate (Münsch, *Z. angew. Chem.*, 1908, **21**, 2059; Bohn, *Ber.*, 1910, **43**, 994).

Trichloroethylene, when heated with alcoholic potash, affords αβ-dichlorovinyl ethyl ether (Paternò and Oglialoro, *Ber.*, 1874, **7**, 81; D.R.-P. 216,940) and it is readily converted by mineral acids into chloroacetic acid (Simon and Chavanne, *Compt. rend.*, 1923, **176**, 309; D.R.-PP. 359,910, 377,524, 383,029, etc.). It reacts with aniline in the presence of alkali to give phenylglycinediphenylamidine (Ruggli and Marszak, *Helv. Chim. Acta*, 1928, **11**, 180). Tribromoethylene, when treated with alcoholic potassium phenoxide (Ssabanejew and Dworkowitsch, *Annalen*, 1883, **216**, 280), gives first phenyl ββ-dibromovinyl ether and finally phenoxyacetic acid. D.R.-P. 210,644 reports a product obtained by the interaction of trichloroethylene and thiosalicylic acid, and ascribes to it the constitution $CCl_2{:}CH{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$.

Tetrachloroethylene, heated with sodium ethoxide at 100—120°, yields, together with other products, ethyl dichloroacetate (Geuther and others, J., 1864, **17**, 316; 1873, **26**, 314). When treated with *o*-dithiolbenzene in a sealed tube at 110—120° for 7 hours, it gives rise to the indigoid compound  $C_6H_4{<}\substack{S\\S}{>}C{:}C{<}\substack{S\\S}{>}C_6H_4$ (Hartley and Smiles, J., 1926, 2263).

Experiments have now been carried out on the reaction of ethyl mercaptan, monothioethylene glycol, and of thiophenol with these substances under various conditions. It has been found that dichloroethylene very readily gives rise to a disubstituted compound with thiophenol and with ethyl mercaptan, but does not react readily with monothioethylene glycol. Even in the presence of a large excess of dichloroethylene no chlorovinylthio-compound could be isolated.

Dichloroethylene reacts with an alcoholic solution of sodium sulphide, but the product is not ββ′-dichlorodivinyl sulphide, but a resinous polymer.

Attempts have been made to bring about the interaction of acetylene and sulphur monochloride and dichloride without success. A mixture of αα′- and ββ′-dichlorodivinyl sulphides has been obtained by thermal decomposition of αβα′β′-tetrachlorodiethyl sulphide. This decomposition was reported by Kliger (*J. Gen. Chem.*, Vol. III, LXV, No. 8), but we find that, contrary to Kliger's statements, the tetrachloro-compound is sufficiently stable to distil at 15 mm. (cf. Alexander and McCombie, J., 1931, **1913**), although when heated at ordinary pressures it loses hydrogen chloride and gives rise to a liquid, b. p. 75—80°/15 mm., which appears to be a mixture of dichlorodivinyl sulphides. This product does not give a crystalline sulphilimine when treated with chloramine-T, but it reacts readily with alcoholic solutions of sodium thiophenoxide and sodium β-naphthoxide, giving oily products from which crystalline fractions were obtained. Attempts have been made to determine the constitution of the thiophenol derivative by reduction to known compounds, but this was not achieved. Catalytic reduction in neutral solution could not be effected, and acid or alkaline reagents either had no effect or brought about a fission of the molecule with formation of thiophenol. The action of sodium in alcohol brought about its conversion into what seemed to be a geometrical isomeride.

Di-iodoethylene reacts with alcoholic solutions of alkali-metal mercaptides, giving rise to acetylene and the disulphide.

Trichloroethylene reacts smoothly in alcoholic solution with one molecule of sodium thiophenoxide, giving rise to a dichloro-compound, C_2HCl_2SPh, in good yield. The constitution of this compound is of interest in view of the conflicting constitutions assigned to the ethyl derivative (Paternò and Oglialoro, *loc. cit.*), the phenoxy-derivative of tribromoethylene (Ssabanejew and Dworkowitsch, *loc. cit.*), and the carboxyphenylthio-derivative (D.R.-P. 210,644). Evidence has been obtained which will admit only of the *phenyl αβ-dichlorovinyl sulphide* structure. Thus, although no further chlorine atom can be displaced by further treatment with thiophenol, one, and one only, can be brought into reaction with sodium methoxide, suggesting their unsymmetrical disposition. A *tetrachloro*-derivative is formed smoothly when the substance is treated with chlorine in carbon tetrachloride; there is no evidence that this contains the CCl_3 group. Finally, it is slowly decomposed by boiling aqueous caustic alkali, giving thiophenol and glycollic acid.

In contrast to these results, evidence has been obtained that all three chlorine atoms of trichloroethylene can be displaced by the ethylthio-group by means of ethyl mercaptan.

Tetrachloroethylene reacts with two molecular proportions of sodium thiophenoxide in alcoholic solution to give what is, in all probability, the symmetrical *compound*, $SPh\cdot CCl{:}CCl\cdot SPh$, which should be capable of existing in *cis*- and *trans*-isomeric forms. No evidence of isomerism was observed in this case, but, by the interaction of tetrachloroethylene and monothioethylene glycol and treatment of the hydroxy-compounds so formed with thionyl chloride, two compounds were obtained, each a tetrachloro-compound, which may have been geometrically isomeric substances of the symmetrical structure $CH_2Cl\cdot CH_2\cdot S\cdot CCl{:}CCl\cdot S\cdot CH_2\cdot CH_2Cl$.

EXPERIMENTAL.

Diphenylthioethylene.—Sodium (1 atom) was dissolved in absolute alcohol and thiophenol (1 mol.) was added immediately, followed by dichloroethylene (0·5 mol.). The mixture was heated under reflux during 24 hours and sodium chloride, which separated slowly, was removed. The filtrate was evaporated, and the residue poured into water. The oily layer was dried and distilled, b. p. 235—242°/760 mm.; it solidified when cold and on crystallisation from light petroleum afforded colourless plates, m. p. 62° (Found: C, 68·5; H, 5·05. $C_{14}H_{12}S_2$ requires C, 68·8; H, 4·92%). There was a little oily by-product.

Dichlorodivinyl Sulphide.—αβα′β′-Tetrachlorodiethyl sulphide (Alexander and McCombie, *loc. cit.*), when distilled at atmospheric pressure, decomposed with evolution of hydrogen chloride. The distillate, b. p. 75—80°/15 mm. after redistillation, was a colourless, unpleasantly smelling liquid which darkened when kept (Found: Cl, 46·6. $C_4H_4Cl_2S$ requires Cl, 45·8%). The chlorine could not be completely replaced by iodine by means of methyl-alcoholic sodium iodide.

Di(phenylthio)divinyl Sulphide.—Sodium (1 atom) was dissolved in absolute alcohol, thiophenol (1 mol.) added, and the solution warmed under reflux with dichlorodivinyl sulphide (0·5 mol.). After 1 hour sodium chloride and an oil had separated. The oil solidified to a crystalline solid on cooling and shaking. This was separated by filtration and freed from sodium chloride by extraction with cold water. Recrystallised from hot alcohol, it formed colourless plates, m. p. 78°. This substance was halogen-free and unsaturated towards bromine (Found: C, 63·3; H, 4·9. $C_{16}H_{14}S_3$ requires C, 63·6; H, 4·6%).

Addition of water to the alcoholic filtrate precipitated quantities of halogen-free oil, from which no further crystalline substance could be isolated.

Isomeric Di(phenylthio)divinyl Sulphide.—In the course of experiments designed to convert the di(phenylthio)divinyl sulphide into known derivatives of diethyl sulphide, the substance (1 g.) was dissolved in absolute alcohol (50 c.c.), and an excess (1 g.) of sodium added. The solution, which became turbid, was filtered; the filtrate, on standing, deposited small shining plates, m. p. 128—140°, which, when recrystallised from aqueous acetone, had m. p. 138°. Analysis, together with the fact that the substance was still unsaturated towards bromine, showed that reduction had not taken place. It is suggested that the product was a geometrical isomeride of the original sulphide (Found: C, 63·1; H, 4·75. $C_{16}H_{14}S_3$ requires C, 63·6; H, 4·6%. $C_{16}H_{18}S_3$ requires C, 62·7; H, 5·6%).

Di-(β-naphthyloxy)divinyl Sulphide.—This substance was prepared in poor yield by adding β-naphthol (2 mols.) to sodium (2 atoms), dissolved in absolute alcohol, and heating the mixture with dichlorodivinyl sulphide (1 mol.) during 3 hours. Sodium chloride separated. The alcoholic filtrate, on standing overnight, gave a further small deposit, which, recrystallised from hot acetone, afforded colourless plates, m. p. 151—152° (Found: C, 77·1; H, 4·7. $C_{24}H_{18}O_2S$ requires C, 77·8; H, 4·75%).

Phenyl αβ-Dichlorovinyl Sulphide.—Trichloroethylene (1 mol.) was added to a solution of sodium (1·2 atoms) and thiophenol (1·2 mols.) in absolute alcohol. The mixture was heated under reflux during 24 hours; sodium chloride (1 mol.) had then separated. The *product*, isolated and distilled, was a colourless liquid, b. p. 145—150°/22 mm. (Found: Cl, 34·7. $C_8H_6Cl_2S$ requires Cl, 34·6%). The use of an excess of thiophenoxide afforded the same product.

Phenyl α-Chloro-β(?)-methoxyvinyl Sulphide.—The preceding sulphide was heated at 100° during 6 hours with solid sodium methoxide in excess (3 mols.). The *product* was filtered, poured into water, separated, dried, and distilled. It was a pale yellow oil, b. p. 160—165°/20 mm. (Found: Cl, 14·8. C_9H_9OClS requires Cl, 15·4%).

Phenyl ααββ-Tetrachloroethyl Sulphide.—Phenyl αβ-dichlorovinyl sulphide was dissolved in carbon tetrachloride, and a trace of iodine added. Chlorine was passed through the solution, kept at 0°, until absorption ceased. The *product*, when distilled, afforded a pale yellow oil, b. p. 175—182°/20 mm. (Found: Cl, 46·8. $C_8H_6Cl_4S$ requires Cl, 44·3%). The high chlorine figure, together with the evolution of a little hydrogen chloride during chlorination, points to the occurrence of some substitution. When the substance was boiled with acid or alkali, no trace of chloroform could be detected among the products : it therefore probably does not contain the trichloromethyl group. On standing, it rapidly loses hydrogen chloride, giving, possibly, phenyl αββ-trichlorovinyl sulphide.

Action of Alkali on Phenyl αβ-Dichlorovinyl Sulphide.—The substance (5 g.) was treated with 10% aqueous caustic soda (100 c.c.) and sufficient ethyl alcohol to produce a homogeneous solution. The mixture was heated under reflux during 3 hours, the alcohol distilled, and the residue acidified, distilled in steam to remove thiophenol, and evaporated to dryness. The product, containing sodium chloride, was completely soluble in water, reduced alkaline potassium permanganate only slowly, when warmed, and gave no precipitate with ammonium oxalate. It was therefore free from oxalic acid and from glyoxal. The presence of glycollic acid was shown by preparation of the phenylurethane. The mixture (2·3 g.) was heated with an excess (4 g.) of phenyl *iso*cyanate at 130° for 3 hours. Water was then added and the insoluble portion was fractionally crystallised from alcohol, giving carbanilide (m. p. 236°) and a substance, sparingly soluble in water, soluble in aqueous alkali, m. p. (after three crystallisations) 143° (cf. Lambling, *Compt. rend.*, 1868, **66**, 1276 ; Fischer, *Ber.*, 1914, **47**, 775).

Trichloroethylene and Ethyl Mercaptan.—Sodium (1 atom) was dissolved in absolute alcohol and ethyl mercaptan (1 mol.) was added, followed by trichloroethylene (1 mol.). The mixture was heated under reflux for 2 hours; sodium chloride (1 mol.) had then separated. The filtrate was poured into an excess of water and the oil which separated was dried and distilled. It boiled over a very wide range (70—150°/20 mm.) and was further fractionated through a column : Fraction (1), b. p. 77—80°/30 mm. (Found : Cl, 42·7%); fraction (2), b. p. 135—140°/20 mm. [Found : Cl, 12·8. $C_2HCl_2{\cdot}SEt$ requires Cl, 45·2%. $C_2HCl(SEt)_2$ requires Cl, 19·5%]. It is evident, therefore, that whilst fraction (1) is a fairly pure monosubstituted derivative, fraction (2) contains a considerable proportion of the trisubstituted product $C_2H(SEt)_3$. This affords an interesting contrast to the action of thiophenol.

s-*Dichlorodiphenylthioethylene.*—Sodium thiophenoxide (2 mols.) in alcohol was treated with tetrachloroethylene (1 mol.). Sodium chloride (2 mols.) separated after 48 hours' heating under reflux. This was removed; the alcoholic filtrate, on standing, deposited colourless needles, which, recrystallised twice from alcohol, had m. p. 71—72° (Found : C, 53·7; H, 3·4. $C_{14}H_{10}Cl_2S_2$ requires C, 53·6; H, 3·2%).

No other product was isolated. This *compound* was recovered unchanged after heating during 5 hours under reflux in alcohol in presence of an excess of sodium thiophenoxide.

Tetrachloroethylene and Monothioethylene Glycol.—Sodium (1 atom) was dissolved in absolute alcohol and monothioethylene glycol (1 mol.) was added, followed by tetrachloroethylene (0·5 mol.). Reaction was complete and sodium chloride (1 mol.) was filtered off after 2 hours' boiling. The alcohol was distilled from the filtrate and the semi-solid residue was dried and boiled with thionyl chloride (2 mols.) during 30 minutes. The product was distilled, a colourless oil being collected at 150—160°/35 mm. (a) and a dark brown liquid passing over between 160° and 230° which solidified when cooled in ice (b). Product (a) was redistilled and collected at 145—147°/30 mm. (Found: Cl, 48·7. $C_6H_8Cl_4S_2$ requires Cl, 48·5%). Product (b), pressed on porous earthenware and crystallised from light petroleum, afforded colourless prisms, m. p. 72—73°, containing sulphur and chlorine (Found : C, 25·7; H, 3·0. $C_6H_8Cl_4S_2$ requires C, 25·2; H, 2·8%). Neither of these compounds absorbed bromine readily.

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