III.—1 : 3-*Dithiolan.*

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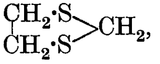
THE isolation of 1 : 3-*dithiolan*,  $\left.\begin{array}{l}CH_2\cdot S\\ CH_2\cdot S\end{array}\right>CH_2$, and of 1 : 3-*dithian*, although inferred (Baumann and Walter, *Ber.*, 1893, **26**, 1129; Autenrieth and Wolff, *Ber.*, 1899, **32**, 1375), has not been described. The preparation of ethylene dimercaptan (Meyer, *Ber.*, 1886, **19**, 3263; Fasbender, *Ber.*, 1887, **20**, 461; Frasetti, *Ber.*, 1905, **38**, 491) may be more conveniently effected by an extension of Purgotti's method (*Gazzetta*, 1892, **22**, 416). The condensation of formaldehyde and ethylene dimercaptan actually yields two products, dithiolan and a voluminous solid *polymeride*. Dithiolan could not be obtained by the reduction of ethylene trithiocarbonate (compare Hurtley and Smiles, J., 1926, 1821), but it is directly obtained by distilling a mixture of formaldehyde, sodium ethylene thiosulphate, and hydrochloric acid.

Dithiolan is converted by hydrogen peroxide into a liquid *monoxide*, the green solution of which in sulphuric acid immediately becomes deep red on addition of a drop of anisole. With platinic chloride the monoxide gives an orange-red *compound*, $(C_3H_5S_2)_2PtCl_3,H_2O$ (compare Tschugaev and Benewolenski, *Z. anorg. Chem.*, 1913, **82**, 420). In presence of hydrochloric acid, one molecule of the monoxide undergoes oxidation at the expense of another, one-half of the material being recovered as dithiolan, and the remainder precipitated as an insoluble amorphous *dioxide* (compare the first oxidation product of tetramethoxythianthren; Fries, Koch, and Stunkenbrock, *Annalen*, 1929, **468**, 166).

1 : 3-Dithian was obtained by treating trimethylene dibromide with sodium thiosulphate, formaldehyde, and hydrochloric acid.

EXPERIMENTAL.

Ethylene Dimercaptan.—Ethylene dibromide (200 c.c.), water (20 c.c.), sodium thiosulphate (100 g.), and alcohol (100 c.c.) were mechanically shaken for 6 hours at 50—60°. The stiff pasty product was collected, boiled with excess of hydrochloric acid, and distilled in steam, yielding 9 g. of the mercaptan, b. p. 144°. If the hydrolysis is conducted with alkali, no mercaptan is formed.

Condensation of Ethylene Dimercaptan with Formaldehyde.—The mercaptan was slowly added to formalin solution, containing a trace of hydrochloric acid, below 25°. The clear solution, when gently warmed, suddenly became turbid with separation of 1 : 3-dithiolan and its *polymeride*. The former was distilled in steam and purified as described below. The polymeride, m. p. 105—110°, after being washed with ether, was practically insoluble in any organic solvent; it dissolved with effervescence in nitric acid, giving a red solution [Found : C, 34·1; H, 6·1. $(C_3H_6S_2)_n$ requires C, 34·0; H, 5·7%].

1 : 3-*Dithiolan* was more conveniently obtained by treating sodium ethylene thiosulphate, prepared as described above, with a mixture of hydrochloric acid and twice the calculated amount of formalin. Steam distillation furnished a 50—60% yield of the dithiolan, which was purified by refluxing it for several hours with aqueous alkali; it then boiled at 175°/760 mm. and 61°/11 mm. and had $d^{17°}$ 1·259, $n_D^{15°}$ 1·5975, whence $[R_L]_D = 29{\cdot}7$ (calc., 29·8) (compare Le Bas, *Trans. Faraday Soc.*, 1920, **15**, 231) (Found : C, 34·2; H, 5·8; *M*, 111. $C_3H_6S_2$ requires C, 34·0; H, 5·7%; *M*, 106). It yielded a mercurichloride, m. p. 119°, on treatment with mercuric chloride, and gave Baumann and Walter's disulphone (*loc. cit.*), m. p. 224°, in 80% yield on oxidation with perhydrol in glacial acetic acid at 50°.

1 : 3-*Dithiolan Monoxide*.—Perhydrol (9 c.c.) in 20 c.c. of glacial acetic acid was added very slowly to specially purified 1 : 3-dithiolan (10 c.c.) in 20 c.c. of glacial acetic acid. After several days, the solvent was removed below 40°, first at 11 mm. and finally at 1 mm. (neglect to remove every trace of solvent at as low a temperature as possible causes complete decomposition in the subsequent distillation) and the residue was distilled over a trace of magnesium carbonate, giving 8 g. of an oil, b. p. 115—120°/1 mm. (Found : C, 30·1; H, 5·3; *M*, 118. $C_3H_6OS_2$ requires C, 29·5; H, 5·0%; *M*, 122).

The *monoxide* is miscible with water, and is decomposed by warm hydrochloric acid into dithiolan (identified by its mercurichloride, m. p. 119°) and a *dioxide*, m. p. 134° (Found : C, 26·3, 26·4; H, 4·7, 4·3. $C_3H_6O_2S_2$ requires C, 26·0; H, 4·4%). It is insoluble in all the usual solvents, including aqueous alkali.

With platinic chloride, an aqueous solution of dithiolan monoxide yields a flocculent precipitate, which may be recrystallised from hot water; m. p. 146—150° (decomp.) [Found : C, 14·0; H, 2·7; Cl, 20·3; Pt, 36·7. $(C_3H_5S_2)_2PtCl_3,H_2O$ requires C, 13·6; H, 2·3; Cl, 20·1; Pt, 36·8%].

With methyl iodide, dithiolan monoxide yields a *methiodide*, m. p. 96° (Found : I, 47·7. $C_4H_9OIS_2$ requires I, 48·1%).

1 : 3-*Dithian*.—Trimethylene dibromide (30 c.c.), sodium thiosulphate (120 g.), and alcohol (100 c.c.) were shaken at 60° for 2 days. The solid which separated was distilled in steam with formalin and hydrochloric acid, and the distillate extracted with ether. The *dithian* crystallised readily and melted at 54° (Found : C, 40·1, 40·0; H, 7·1, 6·6. $C_4H_8S_2$ requires C, 40·0; H, 6·7%). On oxid-

ation with perhydrol in glacial acetic acid, it gave Autenrieth and Wolff's disulphone (*loc. cit.*), m. p. 330°, in almost quantitative yield.

The author is indebted to the Carnegie Trustees for a Teaching Fellowship and to Imperial Chemical Industries for a grant towards the cost of materials.

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