379. *Monothioethylene Glycol and Thiodiglycol.*

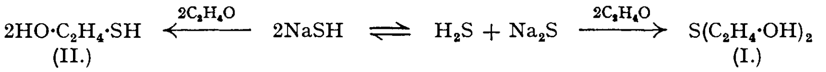
By F. N. Woodward.

Gaseous ethylene oxide (2 mols.) and hydrogen sulphide (1 mol.) react in stirred preformed thiodiglycol (I) at 45—60° to give (I) in quantitative yield. Excess of hydrogen sulphide results in formation of (I) and monothioethylene glycol (II) in the ratio 2 : 3.

Before 1932, 2 : 2′-dihydroxydiethyl sulphide (thiodiglycol) (I) was only obtainable by the interaction of ethylene chlorohydrin and sodium sulphide (Gomberg, *J. Amer. Chem. Soc.*, 1919, **41**, 1414), and 2-hydroxyethanethiol (monothioethylene glycol) (II) only from ethylene chlorohydrin and sodium hydrogen sulphide (Carius, *Annalen*, 1862, **124**, 257). Bennett (*J.*, 1921, **119**, 422; 1922, **121**, 2146) improved the latter method and obtained the pure thiol in 50—55% yield and studied its properties in detail. In the course of many preparations of (II) by Bennett's method we have only obtained 25—30% yields and we have been unable to obtain it by the reduction of 2 : 2′-dihydroxydiethyl disulphide as described by Fromm and Jorg (*Ber.*, 1925, **58**, 304).

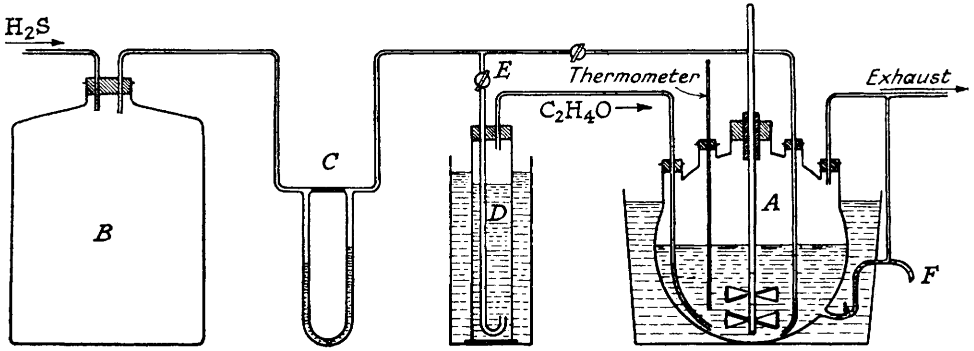
The possibility of preparing (I) and (II) by the interaction of ethylene oxide and hydrogen sulphide was first suggested and investigated in these laboratories in 1932, but at the request of the War Office, under whose ægis the investigation was carried out, the results were not then published. The lifting of this restriction now permits us to record these early findings.

The first method developed allowed equimolecular amounts of ethylene oxide and alcoholic sodium hydrogen sulphide to react in the presence of excess of hydrogen sulphide, whereby on acidification of the reaction product a mixture of (I) and (II) in 24% and 30% yields respectively was obtained according to the scheme



$$\underset{\text{(II.)}}{2HO{\cdot}C_2H_4{\cdot}SH} \xleftarrow{2C_2H_4O} 2NaSH \rightleftharpoons H_2S + Na_2S \xrightarrow{2C_2H_4O} \underset{\text{(I.)}}{S(C_2H_4{\cdot}OH)_2}$$

Subsequently it was found preferable to allow the gaseous reactants to mix in briskly stirred preformed (I) at 45—60°; 2 mols. of the oxide and 1 mol. of the sulphide then yielded pure (I) almost quantitatively, whilst with excess hydrogen sulphide 60% yields of (II) and 40% of (I) were obtained under the best conditions.



Interaction of (II) and ethylene chlorohydrin in the presence of anhydrous sodium carbonate afforded (I) in 50% yield.

Since 1932, several variations of the method have been described independently. Tschitschibabin (F.P. 704,216, August 1934) proposed the use of water, certain lower alcohols, alumina, and activated charcoal as catalysts, and Nenitzescu and Scarlatescu (*Ber.*, 1935, **68**, 587; *Antigaz*, Bucharest, 1935, Oct. 9th, p. 12; Dec. 11th, p. 3) claimed a high yield of (I) by passing a mixture of ethylene oxide and hydrogen sulphide up a column packed with rings moistened with (I); Tseou and Pan (*J. Chinese Chem. Soc.*, 1939, **7**, 29) used a similar method, whilst Othmer and Kein (*Ind. Eng. Chem.*, 1940, **32**, 160) studied the kinetics of the reaction.

EXPERIMENTAL.

Ethylene Oxide and Sodium Hydrogen Sulphide.—A solution of sodium (23 g.) in rectified spirits (400 c.c.) was saturated with hydrogen sulphide (6 hours). Ethylene oxide (44 g.) and hydrogen sulphide were then bubbled through the mixture during one hour, the temperature being kept below 30° throughout. After standing overnight, the reaction mixture was poured into water, the solution neutralised by the addition of glacial acetic acid (60 c.c.), and finally extracted with ether. The ethereal extract was dried (Na_2SO_4), the solvent removed, and the residue distilled. A lower fraction (24 g.) was obtained, b. p. 58°/12 mm., identified as 2-hydroxyethanethiol through its bis-α-naphthylurethane, m. p. 173°, and a higher fraction (29 g.) b. p. 147°/6 mm., which afforded a *bis-α-naphthylurethane*, m. p. 143°, identical with that obtained from an authentic sample of (I) (Found: S, 7·09. $C_{26}H_{12}O_4N_2S$ required S, 7·15%).

Ethylene Oxide and Hydrogen Sulphide.—Hydrogen sulphide and vapourised ethylene oxide were introduced separately into the five-necked litre flask *A* (see Fig.) through tubes dipping beneath the surface of 100 c.c. of (I). The mixture was agitated by a stirrer at 1900 r.p.m. and a reaction temperature of 50—60° was maintained. The hydrogen sulphide, after being scrubbed through aqueous sodium hydrogen sulphide to remove hydrochloric acid, was allowed to pass through the compensating vessel *B* at 40—45 l./hr., as measured on the flow-meter *C*, whilst the ethylene oxide was evaporated in a measuring cylinder *D* immersed in a water-bath at 15—20°, uniform evaporation being ensured by means of a small hydrogen sulphide leak through the side tube *E*. The ethylene oxide input rate, measured by noting the rate of diminution in volume of the liquid in *D*, was maintained at 0·5 c.c./min., corresponding to 200% excess of hydrogen sulphide. The reaction product contained (I) and (II) (44%) only, the overall efficiency of conversion of ethylene oxide being about 90%. The thiol (II) obtained by distillation (b. p. 96—97°/100 mm.) from the reaction product had the following characteristics: b. p. 53·5°/10 mm., 68°/20 mm., 77°/37mm., 78·5°/40 mm., 92°/78 mm., 98/100 mm., 157°/748 mm.; $d_{4°}^{25°}$ 1·1196; $\eta_{25°}$ 2·488 centipoise (Found: SH, 39·6. Calc. for C_2H_6OS: SH, 39·8%).

Thiodiglycol from 2-Hydroxyethanethiol.—Ethylene chlorohydrin (20 g., 0·25 mol.) and 2-hydroxyethanethiol (19·5 g., 0·25 mol.) were heated over the steam-bath for 5 hours with sodium carbonate

(26 g.). After filtration, the reaction product was distilled, and after removal of some of the unreacted starting material, 2 : 2′-dihydroxydiethyl sulphide was obtained, b. p. 146°/7 mm., in 50% yield.

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