11. *New Organic Sulphur Vesicants. Part V. 2-Chloroethyl 2-Chloro*iso*propyl Sulphide.*

By A. HAMILTON, (the late) R. C. G. MOGGRIDGE, and F. N. WOODWARD.

The synthesis of the three diol isomers (I; X = OH), (II), and 2-hydroxyethyl 2-hydroxy-*n*-propyl sulphide from 2-hydroxyethanethiol and allyl alcohol, trimethylene chlorohydrin, and 1-chloro-2-hydroxypropane, respectively, is described. Conversion of (I; X = OH) into (I; X = Cl) is effected by concentrated hydrochloric acid.

2-CHLOROETHYL 2-chloro*iso*propyl sulphide (I; X = Cl) was prepared by Williams and Woodward (see Part II), who obtained the related diol (I; X = OH) by reduction of 1-(2-hydroxyethylthio)propaldehyde. This synthesis of (I; X = Cl) involved five stages and

$$\underset{\text{(I.)}}{X{\cdot}C_2H_4{\cdot}S{\cdot}CHMe{\cdot}CH_2X} \qquad \underset{\text{(II.)}}{HO{\cdot}C_2H_4{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$$

gave an overall yield of only 8%. A more direct synthesis has now been found in that (I; X = OH) is prepared by addition of 2-hydroxyethanethiol to allyl alcohol. In the absence of a catalyst these compounds interact to give the " abnormal " *product* (II); this behaviour is apparently general for thiol–olefin additions (cf., *inter alia*, Kharasch, Read, and Mayo, *Chem. and Ind.*, 1938, **16**, 752; Ipatieff, Pines, and Friedman, *J. Amer. Chem. Soc.*, 1938, **60**, 2371; Jones and Reid, *ibid.*, p. 2452; Ipatieff and Friedman, *ibid.*, 1939, **61**, 71). The constitution of (II) was confirmed by synthesis from 2-hydroxyethanethiol and 1 : 3-propylenechlorohydrin.

If, however, 2-hydroxyethanethiol and allyl alcohol were heated together in presence of sulphur (Jones and Reid, *loc. cit.*), the " normal " product (I; X = OH) was obtained in 55—60% yield. It could be converted into (I; X = Cl) by the action of concentrated hydrochloric acid at 80—90°, the overall yield then being *ca.* 40%.

A third diol isomer, *viz.*, 2-hydroxyethyl 2-hydroxy-*n*-propyl sulphide has now been prepared from 2-hydroxyethanethiol and 1-chloro-2-hydroxypropane (cf. E.P. 185,402; *Chem. Zentr.*, 1923, II, 684, in which is described the preparation, but not the characterisation, of this compound).

EXPERIMENTAL.

*2-Hydroxyethyl 3-Hydroxy-*n*-propyl Sulphide* (II).—(*a*) Allyl alcohol and 2-hydroxyethanethiol (Bennett, *J.*, 1921, **119**, 423) were mixed in equimolecular proportion and heated under reflux for 3 hours. Distillation of the mixture gave the *diol* (II) in 50% yield, as a colourless oil, b. p. 144°/2·5 mm. (Found: S, 23·3; OH, 24·55. $C_5H_{12}O_2S$ requires S, 23·45; OH, 25·0%); *bis*-p-*nitrobenzoate*, colourless prisms, m. p. 110°, from alcohol (Found: C, 52·1; H, 3·4; N, 6·5. $C_{19}H_{18}O_8N_2S$ requires C, 52·5; H, 4·2; N, 6·45%).

(*b*) Trimethylene chlorohydrin (*Org. Synth.*, **8**, 112) (0·5 g.-mol.) was added to 2-hydroxyethanethiol (0·5 g.-mol.) in sodium ethoxide solution (250 c.c.; 2N), reaction occurring with evolution of heat. The product, isolated by removal of sodium chloride, concentration, and distillation, boiled at 141—146°/2 mm. (Found: S, 23·3%); bis-*p*-nitrobenzoate, m. p. 110°, identical (mixed m. p.) with that obtained as above.

*2-Hydroxyethyl 2-Hydroxy*iso*propyl Sulphide* (I; X = OH).—Allyl alcohol (29 g.), 2-hydroxyethanethiol (39 g.), and sulphur (0·5 g.) were mixed and heated under reflux for 6 hours; on distillation of the mixture the required diol (II) was obtained in 55—60% yield as a colourless oil, b. p. 136—137°/5 mm.; the *bis*-p-*nitrobenzoate*, needles from alcohol, m. p. 113° (Found: C, 52·65; H, 4·5; N, 6·60. $C_{19}H_{18}O_8N_2S$ requires C, 52·5; H, 4·2; N, 6·45%), was identical (mixed m. p.) with that of the diol (I; X = OH), prepared by the method of Williams and Woodward, and showed marked depression of m. p. when mixed with the bis-*p*-nitrobenzoate of (II).

*2-Chloroethyl 2-Chloro*iso*propyl Sulphide* (I; X = Cl).—Either the distilled diol (I; X = OH) or the crude reaction product was treated with concentrated hydrochloric acid (10 vols.) at 80—90° for one hour with occasional shaking. The product separated as a heavy oil, b. p. 69—71°/2 mm., 79—81°/5 mm., overall yield (from 2-hydroxyethanethiol) *ca.* 40%, whether crude or pure (I; X = OH) was used (Found: S, 18·6; Cl, 40·55. Calc. for $C_5H_{10}Cl_2S$: S, 18·5; Cl, 41·0%); tribromophenoxide, m. p. 128° (Found: S, 4·15; Br, 62·85. Calc. for $C_{17}H_{14}O_2SBr_6$: S, 4·2; Br, 63·0%).

*2-Hydroxyethyl 2-Hydroxy-*n*-propyl Sulphide.*—1-Chloro-2-hydroxypropane (10·2 g.) was added to 2-hydroxyethanethiol (8·6 g.) in a solution of sodium ethoxide (1 equiv.) in alcohol, reaction occurring with evolution of heat. The *product*, isolated by removal of sodium chloride and solvent, had b. p. 120—125°/2·5 mm. (Found: S, 23·6; OH, 24·65. $C_5H_{12}O_2S$ requires S, 23·5; OH, 25·0%); *bis*-p-*nitrobenzoate*, m. p. 85° (Found: S, 7·5. $C_{19}H_{18}O_8N_2S$ requires S, 7·4%).

The authors wish to thank Dr. R. J. Rosser for helful suggestions; they are also indebted to the Chief Scientist, Ministry of Supply, for permission to publish this work.

H.M. RESEARCH ESTABLISHMENT, SUTTON OAK.

[*Received, January 9th,* 1947.]