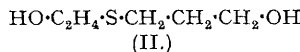
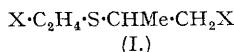


11. New Organic Sulphur Vesicants. Part V. 2-Chloroethyl 2-Chloroisopropyl Sulphide.

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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-chloroisopropyl 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



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. $\text{C}_5\text{H}_{12}\text{O}_2\text{S}$ 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. $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2\text{S}$ 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-Hydroxyisopropyl 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. $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2\text{S}$ 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-Chloroisopropyl 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 $\text{C}_5\text{H}_{10}\text{Cl}_2\text{S}$: S, 18.5; Cl, 41.0%); tribromophenoxide, m. p. 128° (Found: S, 4.15; Br, 62.85. Calc. for $\text{C}_5\text{H}_9\text{Br}_3\text{OS}$: 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. $\text{C}_5\text{H}_{12}\text{O}_2\text{S}$ requires S, 23.5; OH, 25.0%); *bis-p*-nitrobenzoate, m. p. 85° (Found: S, 7.5. $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2\text{S}$ requires S, 7.4%).

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