

44. Reactions of 1 : 2-Dichloro-3 : 4-epoxybutane and Related Compounds.

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1 : 2-Dichloro-3 : 4-epoxybutane has been prepared as a mixture of isomers by oxidation of 3 : 4-dichlorobut-1-ene with performic acid. Hydration of the epoxide isomers leads to corresponding isomeric glycols and 4-chlorotetrahydrofuran-3-ols; the reactions of these compounds with alkali have been studied. The epoxides have been dehydrochlorinated to 2-chloro-3 : 4-epoxybut-1-ene and converted into isomeric 1 : 3 : 4-trichlorobutan-2-ols by hydrogen chloride.

OXIDATION of 3 : 4-dichlorobut-1-ene to 1 : 2-dichloro-3 : 4-epoxybutane by peracetic acid has been recently described in a patent,¹ but the use of performic acid has been reported to give the corresponding glycol² in rather poor yield. It has now been found, however, that by limiting the reaction time and using $\frac{1}{4}$ — $\frac{1}{2}$ molar quantities of formic acid the epoxide can be produced in reasonable yield.

However, although the glycol can be isolated (as a mixture of the two isomers) under Owen's conditions the yield depends on the time of heating of the crude product with water. Short heating leads to moderate yields of glycol, but longer heating gives almost completely a mixture of *cis*- and *trans*-4-chlorotetrahydrofuran-3-ols: 1 : 3 : 4-trichlorobutan-2-ol was also found in the product and evidently arose from reaction of the epoxide with hydrogen chloride produced by slow decomposition of the dichlorobutene. Further, the two isomeric glycols could be converted into the two chlorohydrins thermally (without solvent), by alcoholysis (with an acid catalyst), or by prolonged boiling with water. Only the *trans*-chlorohydrin (XV) has been previously reported³ and its synthesis from 2 : 5-dihydrofuran has been repeated with hypochlorous acid replaced by *tert.*-butyl hypochlorite.

The epoxide prepared from 3 : 4-dichlorobut-1-ene and performic acid was found by vapour-phase chromatography to consist of two isomers (IX, XI), and concentrates of these isomers were obtained by fractional distillation. These two epoxides yielded the corresponding glycols (XII, XVI) and chlorotetrahydrofuranols (XIII, XV) on hydration.

As reported by Reppe *et al.*³, the *trans*-4-chlorotetrahydrofuran-3-ol (XV) gave 3 : 4-epoxytetrahydrofuran (XX) on alkali treatment; heating it with silver or cuprous oxide in a high-boiling inert solvent led to the same result. On the other hand, the *cis*-chlorohydrin (XIII) yielded red polymers on reaction with alkali, but heating it with cuprous or silver oxide in diisopropylbenzene gave, not an isomeric epoxide, but tetrahydrofuran-3-one (XVIII). Similar differences of behaviour between *cis*- and *trans*-halogenohydrins with alkali have been reported previously.⁴ Both the epoxide (XX) and the ketone (XVIII), on catalytic reduction, gave tetrahydrofuran-3-ol (XIX).

The epoxytetrahydrofuran (XX), a water-soluble liquid, was synthesised, in poor yield, by reaction of peroxytrifluoroacetic acid with 2 : 5-dihydrofuran (XIV). Ring-opening of this epoxide with acid methanol provided *trans*-4-methoxytetrahydrofuran-3-ol (XXI; R = Me), and hydration yielded a *trans*-tetrahydrofuran-3 : 4-diol (XXVI) identical with that obtained by acid dehydration of DL-erythritol.

Reaction of either isomer of 1 : 2-dichloro-3 : 4-epoxybutane with alkali led to dehydrochlorination, with the formation of mainly 2-chloro-3 : 4-epoxybut-1-ene (II), identified by synthesis from chloroprene;⁵ a by-product from this reaction, when sodium methoxide was used, was 1-chloro-2 : 3-epoxy-4-methoxybutane, formed through initial 1 : 2-epoxide

¹ Union Carbide Co., B.P. 784,620.

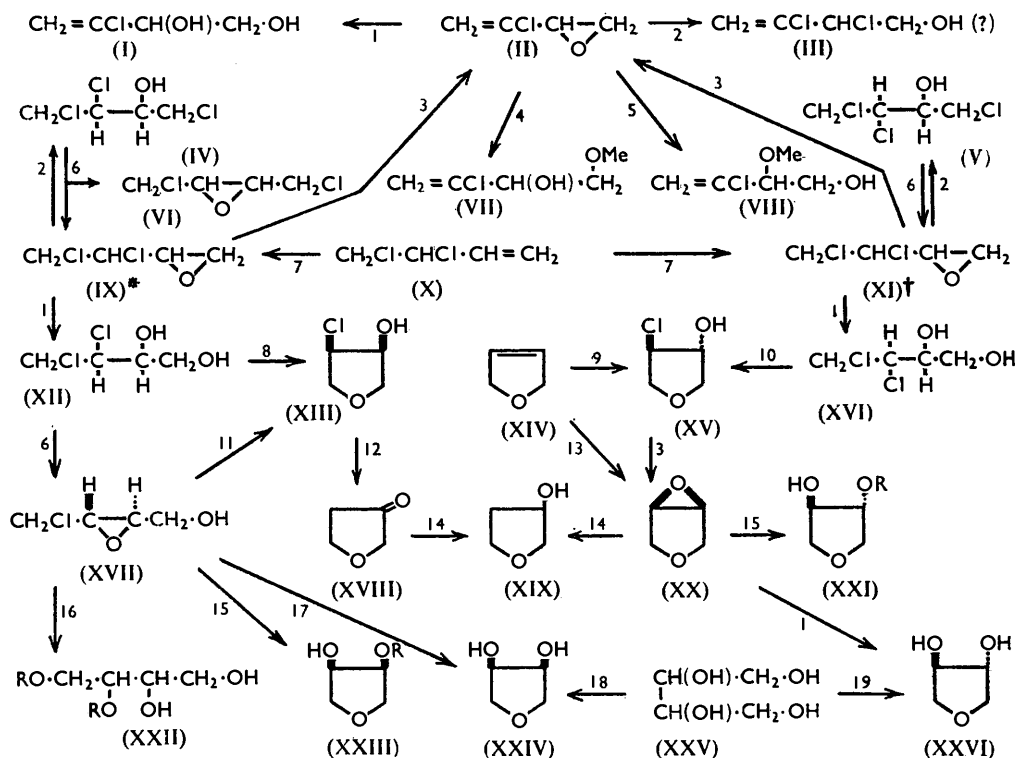
² Owen, *J.*, 1949, 241.

³ Reppe, *et al.*, *Annalen*, 1955, 596, 1.

⁴ Bartlett, *J. Amer. Chem. Soc.*, 1935, 57, 224.

⁵ Cf. Petrov, *J. Gen. Chem., U.S.S.R.*, 1939, 9, 2232; 1952, 22, 1516.

ring opening to give 3 : 4-dichloro-1-methoxybutan-2-ol followed by ring closure by loss of hydrogen chloride from positions 2 and 3. The 2-chloro-3 : 4-epoxybut-1-ene (II) on hydration with aqueous acid gave the corresponding glycol (I). Opening of the epoxide ring with sodium methoxide yielded 3-chloro-1-methoxybut-3-en-2-ol (VII), but use of acid methanol led to reverse opening, to give 3-chloro-2-methoxybut-3-en-1-ol (VIII); these structures were confirmed by catalytic hydrogenation to the corresponding known methoxybutanols. Ring opening of the epoxy-butene (II) by ethereal hydrogen chloride or aqueous hydrochloric acid gave the same dichlorobutenol (III); Petrov⁵ claimed that the primary alcohol is formed in such an addition, although the properties given for both the primary and the corresponding secondary alcohol appear to be very similar, and it seems possible that a mixture of the two is formed.



Reagents: 1, Hydration. 2, HCl. 3, Alkali. 4, NaOMe. 5, Acid-MeOH. 6, NaOH. 7, H₂CO₃H. 8, Heat or alcoholysis. 9, Bu⁺OCl. 10, Heat, alkali, or alcoholysis. 11, Heat. 12, Ag₂O. 13, CF₃CO₂H. 14, H₂-Ni. 15, Acid-ROH. 16, NaOR. 17, Aq. H₂CO₂H. 18, Dehydration(meso). 19, Dehydration(racemic).

* Low-boiling isomer.

† High-boiling isomer.

Treatment of the isomeric 1 : 2-dichloro-3 : 4-epoxybutanes with hydrogen chloride produced two isomers (IV, V) of 1 : 3 : 4-trichlorobutan-2-ol, both of which were present in the reaction product of hydrogen chloride and 1 : 4-dichloro-2 : 3-epoxybutane. The *erythro*-trichlorobutanol (IV) with alkali gave, not only the lower-boiling epoxide isomer (IX) from which it came, but also 1 : 4-dichloro-2 : 3-epoxybutane (VI); the *threo*-trichlorobutanol (V) gave only its precursor (XI) under these conditions.

The two isomeric 3 : 4-dichlorobutane-1 : 2-diols behaved differently on reaction with alkali. The *threo*-isomer (XVI), m. p. 63—65°, derived from the higher-boiling epoxide (XI), when treated with 1 mol. of alkali lost hydrogen chloride from the 1 : 4-positions to give *trans*-4-chlorotetrahydrofuran-3-ol (XV), together with some epoxytetrahydrofuran (XX), whereas the *erythro*-isomer (XII), m. p. 69—70°, under similar conditions lost

hydrogen chloride from the 2:3-positions to yield mainly 4-chloro-2:3-epoxybutan-1-ol (XVII).

This chloroepoxybutanol was converted into the *cis*-chlorotetrahydrofuranol (XIII) by heat, and into *cis*-tetrahydrofuran-3:4-diol (XXIV) (identical with that from dehydration of *meso*-erythritol) by hydration. Reaction with alkanols, under acid-catalysed conditions, yielded *cis*-4-alkoxytetrahydrofuran-3-ols (XXIII), different from the corresponding *trans*-compounds (XXI) produced from epoxytetrahydrofuran under similar conditions. However, on further treatment with aqueous or alcoholic alkali or metal alkoxide, the chloroepoxybutanol was not converted into a tetrahydrofuran derivative by 1:4-ring closure but yielded an open-chain erythritol, or erythritol ether (XXII); aqueous sodium hydroxide gave *meso*-erythritol, methanolic sodium hydroxide yielded what was probably a methoxybutanetriol, and sodium methoxide provided a dimethoxybutanediol (probably mainly 3:4-dimethoxybutane-1:2-diol since analysis showed it to contain *ca.* 70% of vicinal hydroxy-groups). Although solid derivatives of these erythritol ethers were obtained, the original products may have been mixtures of positional isomers.

The probable nature of the stereoisomers involved in the present work is indicated in the reaction scheme; inversions would presumably occur at opening or closing of epoxide rings, but not at formation of tetrahydrofuran systems.

EXPERIMENTAL

Preparation of 1:2-Dichloro-3:4-epoxybutane.—(a) *By performic acid oxidation of 3:4-dichlorobut-1-ene.* The following was typical of experiments giving the best yields of epoxide. The dichlorobutene (500 g.) and 98% formic acid (140 g.) were stirred together at 60° and 85% hydrogen peroxide (185 c.c.) was added gradually so as to maintain the temperature at *ca.* 60° during 1 hr. Stirring was continued at this temperature for a further 4 hr. The organic layer was separated, washed with water, dried, and distilled to give fractions: (1) (8.1 g.) b. p. <39°/40 mm.; (2) (141.4 g.) b. p. 39—42°/40 mm.; (3) (8.1 g.) b. p. <65°/11 mm.; (4) (200.9 g.) b. p. 65—72°/11 mm.; and residue (138.8 g.). Fraction (2) was unchanged dichlorobutene, fraction (4) the crude epoxide, and the residue a mixture of glycol, glycol esters, and trichlorobutanol. The aqueous layer on distillation gave crude glycol (67 g.).

Crude *epoxide*, distilled at 100 mm. from magnesium oxide and under nitrogen, gave fractions as tabulated [Found: (low-boiling isomer) C, 34.05; H, 4.3; Cl, 50.3; (high-boiling isomer) C, 34.3; H, 4.4; Cl, 50.6. $C_4H_6OCl_2$ requires C, 34.0; H, 4.25; Cl, 50.35%]. Infrared spectroscopy showed that the fractions were free from unsaturation, hydroxyl, carbonyl, ether, or ester groups (except as noted in the Table). An epoxide equivalent (by the Nicolet-Poulter method) on a mixed isomer fraction gave a value of 143.3 (calc. 141).

B. p.	Wt. (g.)	n_D^{20}	Epoxide isomers (%) *		B. p.	Wt. (g.)	n_D^{20}	Epoxide isomers (%) *	
			low-boiling	high-boiling				low-boiling	high-boiling
100—110°	25.3	1.4758		†	114°	493.3	1.4740	85	15
110—112.5	21.5	1.4747	94	†	114—116	451.5	1.4746	70	30
112.5—113	7.9	1.4740	96	†	116—117	153.7	1.4768	10	90
113	30.8	1.4738	94	6	117—118.5	60.0	1.4767	5	95
113—114	30.8	1.4740	88	12	118.5—119	45.3	1.4758	<5	98

* By infrared spectroscopy or vapour-phase chromatography. † Contained dichlorobutene.

(b) *Via the bromohydrin.* *N*-Bromosuccinimide (76 g.) in water (320 c.c.) was stirred with 3:4-dichlorobut-1-ene (50 g.) in ether (320 c.c.) at room temperature until the solid had dissolved (2 days). The ethereal layer and extracts were combined, washed with sodium hydrogen carbonate solution, dried, and distilled, to give impure bromohydrin (43.8 g.), b. p. 60—67°/0.3 mm.; from the distillate a small quantity of 1:2-dibromo-3:4-dichlorobutane, m. p. 80—81°, separated.

The crude bromohydrin (38 g.) was suspended in water (20 c.c.) and vigorously stirred during the addition (10 min.) of sodium hydroxide (7.3 g.) in water (30 c.c.). Stirring was continued for a further 1½ hr., and the product worked up normally. There were obtained

impure epoxide (12.3 g.) and fractions (14.2 g.) containing tetrahalogenobutanes. Fractionation of the impure epoxide gave a distillate (11.0 g.), b. p. 175—177°, n_D^{20} 1.4810, shown by spectroscopy to be similar to, but slightly less pure than, that obtained by performic acid oxidation, and to consist almost completely of the low-boiling isomer.

Preparation of 3 : 4-Dichlorobutane-1 : 2-diol.—(a) *By performic acid oxidation of 3 : 4-dichlorobut-1-ene.* This was an unsatisfactory method, based on that described by Owen² who obtained only 2.0 g. of crude glycol from 12 g. of 3 : 4-dichlorobut-1-ene. From dichlorobutene (360 g.), 98—100% formic acid (740 c.c.), and 30% hydrogen peroxide (380 c.c.) at 45° during 21½ hr. were obtained unchanged olefin (160 g.) and fractions (i) (27.5 g.), b. p. <128°/15 mm., n_D^{20} 1.4865, (ii) (80.0 g.), b. p. 128—138°/15 mm., n_D^{20} 1.4900, (iii) (108.7 g.), b. p. 138—148°/15 mm., n_D^{20} 1.4911, and (iv) (12.8 g.), b. p. >148°/15 mm., n_D^{20} 1.4928. Some glycol was obtained by crystallisation of fractions (iii) and (iv) but the infrared spectra of the last three fractions showed that formates were still present. Further hydrolysis of the high-boiling fractions (186.8 g.) by boiling water (600 c.c.) for a further 1½ hr. gave fractions: (1) (16.7 g.), b. p. 88—95°/13 mm., n_D^{20} 1.4781, (2) (24.0 g.), b. p. 95—100°/13 mm., n_D^{20} 1.4845, (3) (65.1 g.), b. p. 100—106°/13 mm., n_D^{20} 1.4900, (4) (6.8 g.), b. p. 106—130°/13 mm., n_D^{20} 1.4943, and a residue (14.2 g.). These fractions were shown spectroscopically, and by the m. p.s and mixed m. p.s of their phenylurethanes, to consist of *cis*- and *trans*-4-chlorotetrahydrofuran-3-ols and 1 : 3 : 4-trichlorobutan-2-ol as obtained from alcoholysis of similar oxidation products (see p. 252). The extent of conversion of the glycol formate into the chlorotetrahydrofuranols was variable.

(b) *By hydration of the epoxides.* (i) The lower-boiling epoxide (20 g.) was heated, with shaking, with 1% aqueous sulphuric acid (50 c.c.) until the mixture became homogeneous, and then further epoxide (53.3 g.) added portionwise with heating and shaking until clear after each addition. The cooled solution was neutralised with solid sodium hydrogen carbonate, saturated with sodium chloride, and extracted with ethyl acetate. Evaporation of the solvent left crystalline *erythro*-3 : 4-dichlorobutane-1 : 2-diol (48.5 g.), which, after recrystallisation from carbon tetrachloride-ethyl acetate or carbon tetrachloride-chloroform, had m. p. 69.5—71° (Found: C, 29.9; H, 4.6; Cl, 44.8. Calc. for C₄H₈O₂Cl₂: C, 30.2; H, 5.0; Cl, 44.7%) [*bisphenylurethane*, m. p. 146—148° (Found: C, 54.35; H, 4.5; Cl, 17.8; N, 7.2. C₁₈H₁₈O₄N₂Cl₂ requires C, 54.4; H, 4.5; Cl, 17.9; N, 7.05%)].

(ii) The higher-boiling epoxide (5.7 g.) was treated as in (i) and yielded solid *threo*-glycol (4.5 g.), m. p. 63—65° (from carbon tetrachloride-chloroform) (Found: C, 30.35; H, 5.1; Cl, 44.8%) [*bisphenylurethane*, m. p. 170—172° (Found: C, 54.3; H, 4.4; Cl, 18.1; N, 7.2%)].

Preparation of Isomers of 4-Chlorotetrahydrofuran-3-ol.—(a) *cis-Chlorohydrin.* (i) *erythro*-3 : 4-Dichlorobutane-1 : 2-diol (10 g.) was heated under reflux for 2 hr. with water (50 c.c.), the water removed under reduced pressure, and the residue distilled to give fractions (1) (4.4 g.), b. p. 83—85°/11 mm., n_D^{20} 1.4880, and (2) (2.4 g.), b. p. 138—140°/11 mm., and a residue (0.8 g.). Fraction (2) and the residue were unchanged glycol which crystallised. Fraction (1) was *cis*-4-chlorotetrahydrofuran-3-ol [*phenylurethane*, m. p. 132—133° (Found: C, 54.7; H, 4.6; Cl, 14.9; N, 5.5. C₁₁H₁₂O₃NCl requires C, 54.7; H, 5.0; Cl, 14.7; N, 5.8%)].

(ii) The *erythro*-glycol (3.0 g.) was heated at 180—200° for ½ hr. Hydrogen chloride was given off and the liquid darkened. Distillation gave the chlorohydrin (1.5 g.), b. p. 87—90°/15 mm., n_D^{20} 1.4891, identical spectroscopically with the product from (i).

(b) *trans-Chlorohydrin.* (i) *threo*-3 : 4-Dichlorobutane-1 : 2-diol (2.6 g.) was heated at 180—200° for ¾ hr., giving hydrogen chloride and darkening. Distillation gave *trans*-4-chlorotetrahydrofuran-3-ol (0.7 g.), b. p. 101—101.5°/14 mm., n_D^{20} 1.4796 [*phenylurethane*, m. p. 132—134° (Found: C, 54.9; H, 4.8; Cl, 14.65; N, 5.4%), depressed in m. p. on admixture with the phenylurethane of the *cis*-isomer]. The column drainings (0.8 g.) were found spectroscopically to consist of a mixture of the chlorohydrin and unchanged glycol.

(ii) Sodium hydroxide (5.0 g.) in water (6 c.c.) and methanol (18 c.c.) was added dropwise, during 10 min. at room temperature, to a stirred solution of the *threo*-glycol (20 g.) in methanol (20 c.c.). The mixture was heated for ¼ hr. on the water-bath, cooled, filtered, and distilled. The distillate (5.8 g.), b. p. 102—104°/12—13 mm., n_D^{20} 1.4810 (Found: C, 39.8; H, 6.0; Cl, 28.75. Calc. for C₄H₇O₂Cl: C, 39.2; H, 5.7; Cl, 29.0%), gave the infrared spectrum and phenylurethane, m. p. and mixed m. p. 130—132°, of the *trans*-chlorohydrin. The residue (3.2 g.) was *erythro*-3 : 4-dichlorobutane-1 : 2-diol. The low recovery in this reaction was due to the formation of 3 : 4-epoxytetrahydrofuran, lost in the solvent removal, by further reaction of the chlorohydrin.

(iii) 2 : 5-Dihydrofuran (15.5 g.) was dissolved in acetic acid (70 g.) and water (5 g.), and *tert.*-butyl hypochlorite (30 g.) added with stirring and cooling during 2 hr. Then the mixture was heated at 40–45° for $\frac{1}{4}$ hr., cooled, and extracted with ether. Distillation provided 3-acetoxy-4-chlorotetrahydrofuran (7.4 g.), b. p. 86–89°/11 mm., n_D^{20} 1.4577 (Found: C, 43.9; H, 5.7. Calc. for $C_6H_9O_3Cl$: C, 43.8; H, 5.5%). Alcoholysis with ethanol and toluene-*p*-sulphonic acid yielded the *trans*-chlorohydrin (3.2 g.), b. p. 100–102°/11–12 mm., n_D^{20} 1.4799 (Found: C, 39.4; H, 5.7; Cl, 29.1. Calc. for $C_4H_7O_2Cl$: C, 39.2; H, 5.7; Cl, 29.0%), identical with that above (infrared spectrum).

(c) *Mixed isomers.* 3 : 4-Dichlorobut-1-ene (360 g.) and 98% formic acid (1 l.) were stirred at 40° and 30% hydrogen peroxide (760 c.c.) was added gradually; stirring at this temperature was continued for ca. 20 hr. Water, formic acid, and unchanged dichlorobutene were then removed under reduced pressure and the residue was combined with that from a similar experiment. The combined products (248 g.) were heated under reflux with ethanol (400 c.c.) and toluene-*p*-sulphonic acid (2 g.) until production of ethyl formate (continuously taken off) was complete; the excess of ethanol was removed and the residue distilled to yield fractions (1) (161 g.), b. p. 40–120°/15 mm., and (2) (101.5 g.), b. p. 120–137°/13 mm. Fraction (2) provided crystalline glycol. Fraction (1) was acetylated with acetic anhydride, and the acetates were distilled to give fractions (i) (1.4 g.) b. p. 70–90°/12 mm., (ii) (142.0 g.) b. p. 90–96°/12 mm., n_D^{20} 1.4573, (iii) (6.6 g.) b. p. 96–115°/12 mm., and (iv) (24.8 g.) b. p. 115–138°/12 mm., n_D^{20} 1.4653, and residue (23.2 g.).

Fraction (ii) consisted of a mixture of the acetates of *cis*- and *trans*-4-chlorotetrahydrofuran-3-ol and hydrolysis, followed by fractionation of the product, gave the *cis*-isomer, b. p. 98–92°/12 mm., n_D^{20} 1.4883 (phenylurethane m. p. 132–133°), the *trans*-isomer, b. p. 99–103°/12 mm., n_D^{20} 1.4864 (phenylurethane m. p. 132–134°), and mixtures. These products were identical with those obtained from the corresponding isomeric glycols, above.

Fraction (iv), on redistillation, had b. p. 115–117°/12 mm., n_D^{20} 1.4752, and on alcoholysis yielded 1 : 3 : 4-trichlorobutan-2-ol, b. p. 105°/12 mm., n_D^{20} 1.5047 (Found: C, 27.25; H, 4.2; Cl, 59.3; OH, 9.6. Calc. for $C_4H_7OCl_3$: C, 27.0; H, 3.9; Cl, 60.0; OH, 9.6%) [*phenylurethane* m. p. 134–136° (Found: C, 44.6; H, 4.3; N, 4.8. $C_{11}H_{12}O_2NCl_3$ requires C, 44.5; H, 4.05; N, 4.7%)].

Reaction of Isomeric 4-Chlorotetrahydrofuran-3-ols with Bases.—(a) *cis*-Isomer. (i) The chlorohydrin (35.5 g.) was gradually added to fused potassium hydroxide at ca. 200° and the temperature raised to 250°. Liquid and gaseous products came off rapidly and the former were condensed, dried, and redistilled to give fractions: (1) (1.2 g.) b. p. 64–120°/760 mm., (2) (6.0 g.) b. p. 120–155° (mainly 135–138°)/760 mm., n_D^{20} 1.4432. Fraction (1) gave the 2 : 4-dinitrophenylhydrazone of tetrahydrofuran-3-one (see below); (2) consisted mainly of this ketone (infrared).

The residue in the reaction flask, when treated with water to remove inorganic compounds, left a red, chloroform-soluble polymer (10.5 g.). The aqueous extract also liberated acidic material (5.0 g.) on acidification, but this was not examined. The red polymer was found, from its infrared spectrum, to contain tetrahydrofuran rings, hydroxyl groups, and two carbonyl functions (alkyl ketone and tetrahydrofuranone type): these suggest self-condensation of tetrahydrofuranone with some ring-opening.

(ii) Treatment of the chlorohydrin with concentrated aqueous sodium hydroxide at room temperature gave a similar red polymer.

(iii) Diisopropylbenzene (30 g.) and a mixture (60 g.) of silver oxide and cuprous oxide were heated to 150° under a short, unpacked column, and the chlorohydrin (40 g.) added gradually as the product distilled off: the bath-temperature was raised to 220°. The wet distillate was dried and redistilled, to yield tetrahydrofuran-3-one (16.8 g.), b. p. 137–138°, n_D^{20} 1.4366 [2 : 4-dinitrophenylhydrazone, m. p. 159–161° (from ethanol) (Found: C, 45.2; H, 3.85; N, 20.85. Calc. for $C_{10}H_{10}O_5N_4$: C, 45.1; H, 3.8; N, 21.0%) (lit.,⁶ m. p. 155°)].

The ketone (4 g.) in ethanol (5 c.c.) was hydrogenated at atmospheric pressure in the presence of Raney nickel (1 g.). Distillation of the products gave tetrahydrofuran-3-ol (3.0 g.), b. p. 177–179°, n_D^{20} 1.4481 [phenylurethane, m. p. and mixed m. p. 118.5–120.5° (Found: C, 64.0; H, 6.2; N, 6.75. Calc. for $C_{11}H_{13}O_3N$: C, 63.8; H, 6.3; N, 6.8%)].

(b) *trans*-Isomer. (i) The chlorohydrin (24 g.) was suspended in water (15 c.c.), and sodium hydroxide (8 g.) in water (15 c.c.) was added, with stirring, at room temperature. The exo-

⁶ Yur'ev, Korobitsyna, and Savina, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 91.

thermic reaction caused the temperature to rise to 37°. The solution was saturated with sodium chloride and extracted three times with ether; the extracts yielded, on distillation, 3 : 4-epoxytetrahydrofuran (5.1 g.), b. p. 135—143°. Continuous extraction overnight of the aqueous phase with ether gave further epoxide (8.6 g.). The redistilled epoxide had b. p. 143—144°, n_D^{20} 1.4466 (Found: C, 56.5; H, 7.1. Calc. for $C_4H_6O_2$: C, 55.8; H, 7.0%), and its infrared spectrum showed it to contain a tetrahydrofuran ring but no carbonyl group. It gave an epoxide equivalent of *ca.* 85% of the calculated value by the Nicolet-Poulter method.

(ii) Cuprous oxide (10 g.) and diisopropylbenzene (10 g.) were heated together to *ca.* 150° and the chlorohydrin (10 g.) was added gradually. The product was taken off overhead from a heated, packed column, and the bath-temperature gradually raised to 220°. The wet product (7.6 g.) was dried and redistilled, to provide 3 : 4-epoxytetrahydrofuran (4.7 g.), b. p. 143—145°, n_D^{20} 1.4442.

The epoxide (6 g.) in ethanol (20 c.c.) was hydrogenated (Raney nickel) at 110°/150 atm. for 4 hr. Distillation of the product gave unchanged epoxide (2.0 g.) and tetrahydrofuran-3-ol (1.6 g.); the latter gave a phenylurethane, m. p. and mixed m. p. 119—120°.

(iii) 85% Hydrogen peroxide (12 g.) and methylene chloride (50 c.c.) were stirred and cooled in ice; trifluoroacetic anhydride (50.8 g.) was added in 15 min. The resulting solution was stirred for 10 min. in the cold, and then dropped, during $\frac{1}{2}$ hr., into a stirred suspension of oven-dried sodium carbonate (95 g.) in methylene chloride (200 c.c.) containing 2 : 5-dihydrofuran (14 g.). The solvent gently boiled during the addition, and the mixture was heated for a further $\frac{1}{2}$ hr. under reflux before filtration and washing of the separated solid with a little methylene chloride. Distillation of the dried methylene chloride solution gave a little unchanged dihydrofuran and 3 : 4-epoxytetrahydrofuran (1.0 g.), b. p. 130—140°, identical spectroscopically with the epoxide from (i) and (ii) above.

Reactions of 3 : 4-Epoxytetrahydrofuran.—(a) *Hydration.* The epoxide (5 g.) and water (5 g.) were heated together under reflux for 3 hr., the water and unchanged epoxide were removed and the residue was distilled, to give *trans*-tetrahydrofuran-3 : 4-diol (0.4 g.), b. p. 160—165°/15 mm., which although crystallising in the receiver was too hygroscopic for further purification. It provided a *bisphenylurethane*, m. p. 206—208° (Found: C, 63.0; H, 5.2; N, 8.3. $C_{18}H_{18}O_5N_2$ requires C, 63.2; H, 5.2; N, 8.2%).

Heating DL-erythritol³ (16 g.) with phosphoric acid (0.4 g.) in a vacuum gave *trans*-tetrahydrofuran-3 : 4-diol (*ca.* 8 g.), b. p. 159—160°/13 mm., which yielded a bisphenylurethane, m. p. 207—208°, identical with that above.

(b) *Reaction with methanol.* The epoxide (6.5 g.) was added to boiling methanol (15 c.c.) containing a drop of sulphuric acid: heating was continued for 3 $\frac{1}{2}$ hr. Addition of solid hydrogen carbonate, followed by filtration and distillation, gave a main fraction (3.7 g.), b. p. 103—104°/13 mm., n_D^{20} 1.4545, which showed in its infrared spectrum the presence of a tetrahydrofuran ring, an associated hydroxy- and a methoxy-group; it was *trans*-4-methoxytetrahydrofuran-3-ol [*phenylurethane*, m. p. 97—99° (from benzene-light petroleum) (Found: C, 61.2; H, 6.5; N, 6.0. $C_{12}H_{15}O_4N$ requires C, 60.8; H, 6.3; N, 5.9%)].

Reaction of 1 : 2-Dichloro-3 : 4-epoxybutane with Alkali.—(i) 1 : 2-Dichloro-3 : 4-epoxybutane (low-boiling isomer; 22 g.) in methanol (11 c.c.) was treated with sodium hydroxide (6.4 g.) in water (8 c.c.) and methanol (22 c.c.) during $\frac{3}{4}$ hr. at room temperature with stirring. Stirring was continued until all the alkali had been consumed, and the product then diluted with water and extracted with ether. Distillation of the product gave fractions: (1) (2.6 g.) b. p. 102—109°/1 atm., n_D^{20} 1.4539; (2) (8.1 g.) b. p. 71—74°/15 mm., n_D^{20} 1.4553, and (3) (0.9 g.) b. p. 74—128°/15 mm., n_D^{20} 1.4592, and a residue (2.7 g.). Fraction 1 was unsaturated (infrared spectrum), but contained no OH, OMe or $>CO$ group; it gave a low epoxide equivalent (85%) by the Nicolet-Poulter method. Redistillation gave 2-chloro-3 : 4-epoxybut-1-ene, b. p. 109—110.5°/1 atm., n_D^{20} 1.4570 (Found: C, 45.8; H, 5.6; Cl, 33.5. C_4H_5OCl requires C, 45.9; H, 4.8; Cl, 34.0%): it formed azeotropes with methanol or ethanol. Fraction 2 contained unsaturation, hydroxyl, and methoxyl functions; it reacted very slowly with α -naphthyl isocyanate to give the α -*naphthylurethane*, m. p. 94—95°, of 3-chloro-1-methoxybut-3-en-2-ol (Found: C, 63.1; H, 5.1; Cl, 11.7; N, 4.7. $C_{16}H_{16}O_3NCl$ requires C, 62.8; H, 5.2; Cl, 11.6; N, 4.6%).

(ii) 1 : 2-Dichloro-3 : 4-epoxybutane (high-boiling isomer; 22 g.) in methanol (11 c.c.) was treated during 25 min., at *ca.* 60° with stirring, with sodium hydroxide (6.9 g.) in water (8 c.c.) and methanol (22 c.c.). Distillation of the product gave fractions: (1) (8.5 g.) b. p. 93—110°/1

atm., and (2) (5.0 g.) b. p. 65—73°/15 mm., n_D^{20} 1.4561, and a residue (1.7 g.). Fraction (1), after drying, was found to be identical with the unsaturated epoxide above, from the low-boiling dichloroepoxybutane, and fraction (2) was again 3-chloro-1-methoxybut-3-en-2-ol, yielding the above α -naphthylurethane.

(iii) 1 : 2-Dichloro-3 : 4-epoxybutane (mixed isomers; 100 g.) was dropped on molten potassium hydroxide (70 g.) at 150—160°, finally raised to 200°; the product flashed off into the receiver, and heating was continued until no more product distilled. Fractionation of the dried distillate gave the unsaturated epoxide and starting material; the latter was recycled, and there were finally obtained 2-chloro-3 : 4-epoxybut-1-ene (60.3 g.) and 1 : 2-dichloro-3 : 4-epoxybutane (3.3 g.).

(iv) Chloroprene (25 g.) in ether (250 c.c.) was stirred with *N*-bromosuccinimide (50 g.) in water (250 c.c.) at room temperature until all the solid had dissolved (3½ hr.); the reaction was slightly exothermic. The ether extracts on distillation yielded the bromohydrin (9.4 g.) of chloroprene; this had b. p. 78—85°/13 mm., n_D^{20} 1.5234 (Petrov⁶ gives b. p. 77—77.25°/10 mm., n_D^{20} 1.5228); also formed were higher-boiling products, presumably tetrahalogenobutanols. The bromohydrin was converted into 2-chloro-3 : 4-epoxybut-1-ene (2.1 g.), b. p. 105—109°, n_D^{20} 1.4460, by Petrov's method; its infrared spectrum was identical with that of material prepared from 1 : 2-dichloro-3 : 4-epoxybutane.

Reactions of 2-Chloro-3 : 4-epoxybut-1-ene.—(a) *Reaction with sodium methoxide.* (i) The chloroepoxybutene (3.0 g.), derived from the low-boiling dichloroepoxybutane, was heated under reflux for 2 hr. with methanol containing a little sodium methoxide. Distillation provided 3-chloro-1-methoxybut-3-en-2-ol, b. p. 71—72°/15 mm., n_D^{20} 1.4602, identical spectroscopically with that above.

(ii) The chloroepoxybutene from the high-boiling dichloroepoxybutane when treated as in (i) gave the same 3-chloro-1-methoxybut-3-en-2-ol (1.9 g.), b. p. 70—73°/13 mm., n_D^{20} 1.4601, as above (α -naphthylurethane, m. p. and mixed m. p. 94—95°).

Catalytic hydrogenation of the chloromethoxybutenol at atmospheric pressure was carried out with a Raney nickel catalyst and in the presence of aqueous-ethanolic sodium hydroxide (a slight excess over stoichiometric based on the chlorine content); in 29½ hr. reaction was complete and yielded 1-methoxybutan-2-ol, b. p. 133—137°/1 atm., n_D^{20} 1.4114 [3 : 5-dinitrobenzoate, m. p. and mixed m. p. 92—94° (from methanol) (Found: C, 48.65; H, 4.9; N, 9.5. Calc. for C₁₂H₁₄O₇N₂: C, 48.3; H, 4.7; N, 9.4%)].

Similar hydrogenation of the crude chloromethoxybutenol fraction obtained by direct reaction of 1 : 2-dichloro-3 : 4-epoxybutane with sodium methoxide gave, in addition to 1-methoxybutan-2-ol, a fraction, b. p. 72—73°/14 mm., n_D^{20} 1.4436, identified as 1-chloro-2 : 3-epoxy-4-methoxybutane by comparison of its infrared spectrum with that of the synthetic compound.⁷

(b) *Reaction with acid methanol.* The chloroepoxybutene (15 g.) was heated under reflux for 2 hr. with methanol containing sulphuric acid (2 drops). The product was neutralised, filtered, and distilled, to give 3-chloro-2-methoxybut-3-en-1-ol (16.2 g.), b. p. 68—69.5°/13 mm., n_D^{20} 1.4602; it provided an α -naphthylurethane, m. p. 82—84° (from ethanol-light petroleum) (Found: C, 63.15; H, 5.3; Cl, 11.6; N, 4.7. C₁₆H₁₆O₈NCl requires C, 62.8; H, 5.2; Cl, 11.6; N, 4.6%). On catalytic hydrogenation [as for the isomer; cf. (a)], there was obtained 2-methoxybutan-1-ol, b. p. 141—144°, n_D^{20} 1.4154 [3 : 5-dinitrobenzoate, m. p. 60—62°, undepressed on admixture with an authentic specimen, m. p. 62—64° (Found: C, 48.8; H, 4.7; N, 9.55. Calc. for C₁₂H₁₄O₇N₂: C, 48.3; H, 4.7; N, 9.4%)].

(c) *Hydration.* The chloroepoxybutene (3.0 g.) was added to 98% formic acid (2 c.c.); the exothermic reaction was completed by further heating and then the formate was hydrolysed by boiling water. Distillation gave fractions: (1) (1.1 g.) b. p. 111—112°/15 mm., n_D^{20} 1.4790, and (2) (0.7 g.) b. p. 112—160°/15 mm., and a residue (1.0 g.). Fraction (1) provided the *phenylurethane*, m. p. 126—128° (from benzene) (Found: C, 60.3; H, 4.9; Cl, 9.55; N, 7.7. C₁₈H₁₇O₄N₂Cl requires C, 59.9; H, 4.7; Cl, 9.85; N, 7.8%), of 3-chlorobut-3-ene-1 : 2-diol.

(d) *Reaction with hydrogen chloride.* (i) Chloroepoxybutene (5 g.) was added to an excess of ethereal hydrogen chloride; the reaction was exothermic. After 1 hr. the solution was diluted further with ether, washed with sodium hydrogen carbonate solution, dried, and distilled. The product (4.1 g.), b. p. 73—76°/14 mm., n_D^{20} 1.4932 (claimed by Petrov⁶ to be 2 : 3-dichlorobut-3-en-1-ol), reacted very slowly with α -naphthyl isocyanate, to give an

⁷ Adams, Hawkins, Oldham, and Thompson, unpublished work.

α -naphthylurethane, m. p. 91—93° (Found: C, 58.4; H, 4.1; Cl, 22.3; N, 4.7. $C_{15}H_{13}O_2NCl_2$ requires C, 58.1; H, 4.2; Cl, 22.9; N, 4.5%).

(ii) The chloroepoxybutene (5 g.), stirred with concentrated hydrochloric acid (6 c.c.) for 1 hr. at 0°, gave the same dichlorobutenol (4.9 g.) as in (i), b. p. 73—77°/14 mm., n_D^{20} 1.4940 (α -naphthylurethane, m. p. and mixed m. p. 91—93°).

Reaction of 1 : 2-Dichloro-3 : 4-epoxybutane with Hydrogen Chloride.—(i) 1 : 2-Dichloro-3 : 4-epoxybutane (low-boiling isomer; 22 g.) was treated, with shaking and cooling, with an excess of ethereal hydrogen chloride. Distillation provided *erythro*-1 : 3 : 4-trichlorobutan-2-ol (25.8 g.), b. p. 108—109°/14 mm., n_D^{20} 1.5051; this alcohol had a hindered hydroxyl group (infrared spectrum) and gave a phenylurethane, m. p. 134—136° (Found: C, 44.7; H, 4.1; Cl, 35.5; N, 4.75. Calc. for $C_{11}H_{13}O_2NCl_3$: C, 44.5; H, 4.05; Cl, 35.9; N, 4.7%), identical with that isolated from one of the crude products of oxidation of 3 : 4-dichlorobut-1-ene by performic acid.

The *erythro*-trichlorobutanol (17.6 g.), suspended in water (10 c.c.), was treated with sodium hydroxide (4.0 g.) in water (8 c.c.), with stirring for 1 hr. at room temperature and at 40° for $\frac{1}{4}$ hr. The solution was saturated with sodium chloride and extracted with ether; distillation provided a liquid (9.2 g.), b. p. 72.5—81°/13 mm., n_D^{20} 1.4742, and residue (4.5 g.). The distillate was a mixture of low-boiling 1 : 2-dichloro-3 : 4-epoxybutane (ca. 45%) and 1 : 4-dichloro-2 : 3-epoxybutane (ca. 55%) (infrared spectrum).

(ii) 1 : 2-Dichloro-3 : 4-epoxybutane (high-boiling isomer; 23.8 g.) was treated with ethereal hydrogen chloride as in (i), and gave *threo*-1 : 3 : 4-trichlorobutan-2-ol (27.0 g.), b. p. 106—107°/14 mm., n_D^{20} 1.5039 (Found: C, 26.8; H, 4.05; Cl, 59.7. $C_4H_7OCl_3$ requires C, 27.0; H, 3.94; Cl, 60.0%), having an associated hydroxyl group (infrared spectrum): it yielded a *phenylurethane*, m. p. 90—92.5° (from light petroleum) (Found: C, 44.7; H, 4.2; Cl, 36.3; N, 4.85%).

Treatment of the *threo*-trichlorobutanol with alkali gave a product, b. p. 71—73°/13 mm., n_D^{20} 1.4761, shown spectroscopically to be entirely high-boiling 1 : 2-dichloro-3 : 4-epoxybutane.

Reaction of 1 : 4-Dichloro-2 : 3-epoxybutane with Hydrogen Chloride.—This was carried out for comparison with the above. 1 : 4-Dichloro-2 : 3-epoxybutane^{1,7} (20 g.) in ether (60 c.c.) was heated under reflux, and hydrogen chloride passed through the solution for 8 hr. The ethereal solution was further diluted with ether, washed with sodium hydrogen carbonate solution, dried, and distilled, to give 1 : 3 : 4-trichlorobutan-2-ol (20.5 g.), b. p. 104—105°/14 mm., n_D^{20} 1.5039; this was a mixture of isomers (spectrum) but it gave the phenylurethane, m. p. and mixed m. p. 136.5—139° (Found: C, 44.3; H, 4.0; Cl, 35.8; N, 4.8%), of the *erythro*-isomer.

This trichlorobutanol, when treated with alkali, gave a product, b. p. 69.5—74.5°/14 mm., n_D^{20} 1.4743, which contained (from the infrared spectrum) low-boiling 1 : 2-dichloro-3 : 4-epoxybutane (44%), the high-boiling isomer (34%), and 1 : 4-dichloro-2 : 3-epoxybutane (ca. 20%).

Preparation of 4-Chloro-2 : 3-epoxybutan-1-ol.—Sodium hydroxide (5 g.) in water (6 c.c.) and methanol (15 c.c.) was added, during 5 min., to a stirred solution of *erythro*-1 : 2-dichlorobutane-3 : 4-diol, and the mixture finally heated on the water-bath for 5 min. The cooled and filtered product was distilled, to give 4-chloro-2 : 3-epoxybutan-1-ol (13.3 g.), b. p. 106—110°/15 mm., n_D^{20} 1.4735 (Found: OH, 14.1%; epoxide equiv., 135.9. $C_4H_7O_2Cl$ requires OH, 13.9%; epoxide equiv., 122.5); the infrared spectrum confirmed the absence of unsaturation, carbonyl group, or tetrahydrofuran ring. It yielded a *phenylurethane*, m. p. 79—81° (Found: C, 55.0; H, 4.85; Cl, 14.5; N, 5.7. $C_{11}H_{12}O_3NCl$ requires C, 54.7; H, 5.0; Cl, 14.7; N, 5.8%).

The above preparation was also carried out in the absence of methanol.

Reactions of 4-Chloro-2 : 3-epoxybutan-1-ol.—(a) *Thermal decomposition.* The epoxide (5 g.) was heated at 220° for 1½ hr.; it became dark purple. Distillation gave *cis*-4-chlorotetrahydrofuran-3-ol (2 g.), b. p. 88—90°/15 mm., n_D^{20} 1.4871, and residue (1.8 g.). The product was identified spectroscopically.

(b) *Hydration.* The epoxide (5 g.) and formic acid (4 drops) were heated for $\frac{1}{2}$ hr., and, after the addition of water (25 c.c.), boiled for a further 1½ hr. Distillation gave fractions (1) (1.2 g.) b. p. <140°/12 mm., and (2) (2.0 g.) b. p. 140—145°/12 mm., and a residue (1.0 g.).

Fraction (2) gave the *phenylurethane*, m. p. 186—188° (from ethanol), of *cis*-tetrahydrofuran-3 : 4-diol (Found: C, 63.55; H, 5.3; N, 8.3. $C_{18}H_{18}O_5N_2$ requires C, 63.2; H, 5.2; N, 8.2%), undepressed on admixture with the derivative of the tetrahydrofuran diol obtained by dehydration of *meso*-erythritol with sulphuric acid (cf. Reppe *et al.*³).

(c) *Alcoholysis.* (i) A mixture of the epoxide (5 g.), ethanol (25 c.c.), and toluene-*p*-sulphonic acid (trace) was heated under reflux for 57 hr. Distillation, after normal working up, gave

fractions (1) (1.3 g.) b. p. 85—88°/12 mm., n_D^{20} 1.4553, (2) (0.7 g.) b. p. 88—102°/12 mm., n_D^{20} 1.4579, and (3) (0.6 g.) b. p. 102—112°/12 mm., n_D^{20} 1.4620, and a residue (0.3 g.). The infrared spectra of these fractions showed them to contain a hindered hydroxyl group, a tetrahydrofuran ring, and an aliphatic ether, in agreement with *cis*-4-ethoxytetrahydrofuran-3-ol. Fraction (1) gave a *phenylurethane*, m. p. 73—75° (Found: C, 62.1; H, 7.0; N, 5.8. $C_{13}H_{17}O_4N$ requires C, 62.15; H, 6.8; N, 5.6%).

(ii) The epoxide (10 g.) was heated under reflux for 20 hr. with methanol (50 c.c.) containing sulphuric acid (3 drops). Distillation of the product gave fractions (1) (4.5 g.), b. p. 77—78°/13 mm., n_D^{20} 1.4544, and (2) (2.1 g.), b. p. 78—93°/13 mm., n_D^{20} 1.4620, and a residue (1.2 g.). The infrared spectrum of fraction (1) was in agreement with that of *cis*-4-methoxytetrahydrofuran-3-ol; fraction (2) contained mainly the same compound, but there was also present some of the *trans*-isomer (as from 3 : 4-epoxytetrahydrofuran). Fraction (1) gave a *phenylurethane*, m. p. 92—94° (from benzene—light petroleum, then ethanol) (Found: C, 61.1; H, 6.4; N, 5.9. $C_{12}H_{15}O_4N$ requires C, 60.8; H, 6.3; N, 5.9%).

(d) *Reaction with alkali.* (i) The epoxide (12.2 g.) was heated with sodium hydroxide (4 g.) in water (4 c.c.) and methanol (10 c.c.); the product was extracted with ether, and the extract gave a distillate (5.0 g.), b. p. *ca.* 220° (bath)/15 mm., and a residue (7.8 g.). The distillate, which contained an alkoxy group (Zeisel), provided a *phenylurethane*, m. p. 204—205° (Found: C, 63.1; H, 5.5; N, 8.2. $C_{28}H_{27}O_7N_3$ requires C, 63.3; H, 5.5; N, 8.5%), depressed on admixture with the phenylurethane of *trans*-tetrahydrofuran-3 : 4-diol; the phenylurethane is probably a tris-derivative of a methoxybutanetriol.

(ii) The epoxide (12.2 g.) was added to a stirred solution of sodium methoxide (from 2.5 g. of sodium) in methanol (50 c.c.). The temperature was raised to 68° during $\frac{1}{2}$ hr., and kept thereat for 2 $\frac{1}{2}$ hr. The solution was cooled, treated with ethereal hydrogen chloride and then sodium hydrogen carbonate, filtered, and distilled, giving fractions (1) (1.0 g.) b. p. 94—109.5°/13 mm., n_D^{20} 1.4551, (2) (1.3 g.) b. p. 109.5—112.5°/13 mm., n_D^{20} 1.4488, (3) (3.3 g.) b. p. 112.5—116°/13 mm., n_D^{20} 1.4474, and (4) (1.4 g.) b. p. 116—135°/13 mm., n_D^{20} 1.4492, and a residue (2.0 g.). Infrared spectroscopy showed that these fractions were rather similar and contained hydroxyl and methoxyl functions. Fraction 3 was probably largely 3 : 4-*dimethoxybutane*-1 : 2-*diol* (Found: OH, 20.9; OMe, 39.6; vicinal OH, 70. $C_6H_{14}O_4$ requires OH, 22.7; OMe, 41.3%); it provided a *bisphenylurethane*, m. p. 158—160° (from ethanol—light petroleum) (Found: C, 61.8; H, 6.3; N, 7.35. $C_{20}H_{24}O_6N_2$ requires C, 61.85; H, 6.2; N, 7.2%).

(iii) The epoxide (1.7 g.) was heated under reflux for 7 $\frac{1}{2}$ hr. with sodium hydroxide (0.7 g.) in water (20 c.c.). After neutralisation, the product was evaporated to dryness, and the residue extracted with ethanol. Distillation of the extract gave an oil (0.5 g.), b. p. 200—320° (bath)/0.5 mm.; crystallisation from ethanol, then methanol, gave *meso*-erythritol, m. p. and mixed m. p. 120—122°.

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