547. *Some Reactions of* 1 : 2-3 : 4-*Diepoxybutane.*

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The addition of amines, alcohols, phenols, and certain other reactive substances to 1 : 2-3 : 4-diepoxybutane has been studied and the structures of the principal addition products have been established. In general, the mode of addition is such as to produce 1 : 4-derivatives of butane-2 : 3-diol.

1 : 2-3 : 4-Diepoxybutane was first prepared by Przybytek (*Ber.*, 1884, **17**, 1093) who obtained a substance of molecular formula $C_4H_6O_2$, m. p. −15°, by treating an ethereal solution of 1 : 4-dichlorobutane-2 : 3-diol with solid potassium hydroxide. Griner (*Compt. rend.*, 1893, **117**, 555) later obtained the same substance by using the higher-melting form of 1 : 4-dibromobutane-2 : 3-diol in place of the dichloro-compound. On hydrolysis, the new compound gave *meso*erythritol, and with hydrogen chloride 1 : 4-dichlorobutane-2 : 3-diol was regenerated. Certain other addition reactions were investigated by Przybytek (*loc. cit.*; *Ber.*, 1887, **20**, 3237) but only in the case of aniline was the structure of the product demonstrated experimentally.

By treating the lower-melting form of 1 : 4-dibromobutane-2 : 3-diol with potassium hydroxide in ether, Griner obtained a second stereoisomeric form of 1 : 2-3 : 4-diepoxybutane, m. p. 4°. This substance yielded dl-erythritol on hydrolysis and gave the lower-melting form of 1 : 4-dibromobutane-2 : 3-diol on treatment with hydrobromic acid.

A convenient starting material for the preparation of both forms of 1 : 2-3 : 4-diepoxybutane is the higher-melting (53—54°) form of 1 : 4-dibromobut-2-ene. On hydrolysis, this compound gives but-2-ene-1 : 4-diol which, by bromination and subsequent treatment of the dibromo-compound with potassium hydroxide in ether, affords 1 : 2-3 : 4-diepoxybutane identical with that obtained by Przybytek (Prévost, *Compt. rend.*, 1926, **183**, 1292). Oxidation of 1 : 4-dibromobut-2-ene (m. p. 53—54°) with dilute potassium permanganate, however, yields the lower-melting form of 1 : 4-dibromobutane-2 : 3-diol from which Griner (*loc. cit.*) prepared the other stereoisomeric form of the diepoxide.

A further possible source of 1 : 2-3 : 4-diepoxybutane is the mixture of butadiene dichlorohydrins obtained by Evans and Owen (*J.*, 1949, 239) by the action of hypochlorous acid upon 2-chlorobut-3-en-1-ol. As the latter compound is readily prepared from the commercially available 3 : 4-epoxybut-1-ene (Kadesch, *J. Amer. Chem. Soc.*, 1946, **68**, 44), it seemed possible that reasonably large amounts of the diepoxide might be obtained from this source with no great difficulty. It was found, however, that the overall yield on 3 : 4-epoxybut-1-ene was low (15%) and that the product, which consisted predominantly of the *meso*-form, was less free from stereoisomeric impurity than that prepared by Prévost's method. Recently, the direct oxidation of 3 : 4-epoxybut-1-ene to 1 : 2-3 : 4-diepoxybutane by perbenzoic acid was reported by Everett and Kon (*J.*, 1950, 3131) but they did not state whether their product consisted of the dl- or the *meso*-form.

Except for the work of Przybytek, Griner, and Prévost and the recent investigation by Ross (*J.*, 1950, 2257), the properties of 1 : 2-3 : 4-diepoxybutane have been little investigated.

Przybytek (*Ber.*, 1884, **17**, 1093) demonstrated that addition of aniline gives 1 : 4-dianilinobutane-2 : 3-diol but did not investigate the structures of the other adducts which he obtained. In the present investigation, the structures of the products obtained from 1 : 2-3 : 4-diepoxybutane and piperidine, methanol, phenols, naphthalene-β-thiol, and various other reactive substances have been examined, and most of them are shown by oxidation with periodic acid to be 1 : 4-disubstituted derivatives of butane-2 : 3-diol, only those diols bearing hydroxyl groups on adjacent carbon atoms being susceptible to cleavage by this reagent.

The supposed DL- and *meso*-forms of 1 : 2-3 : 4-diepoxybutane reacted with piperidine in ether giving two 1 : 4-dipiperidinobutane-2 : 3-diols, m. p.s 62° and 106°, both of which were oxidised by periodic acid to piperidinoacetaldehyde. The compound of m. p. 62° was, however, oxidised much more rapidly than that of m. p. 106° (see table).

It is known (Criegee, *Sitzungsber. Ges. Beförder. ges. Naturwiss., Marburg*, 1934, **69**, 25; Price and Knell, *J. Amer. Chem. Soc.*, 1942, **64**, 552) that periodic acid oxidises *cis*-glycols more rapidly than the *trans*-isomers. In the case of 1 : 4-dipiperidinobutane-2 : 3-diol in sulphuric acid, mutual repulsion of the piperidinium ions will bring the two hydroxyl groups close together in the mean position in the D- or the L-form, but will set them apart in the *meso*-form. The DL-form would therefore be expected to behave in a similar manner to a *cis*-glycol and to be oxidised more rapidly by periodic acid than the *meso*-form. The greater rate of oxidation of the 1 : 4-dipiperidinobutane-2 : 3-diol of m. p. 62° therefore affords evidence (see table) that

Oxidation of stereoisomeric 1 : 4-*dipiperidinobutane*-2 : 3-*diols at a concentration of* 12 *g./l. in* 0·05M-*potassium periodate*–0·25N-*sulphuric acid solution.*

Time, mins.		25	90	100	125	1080	1530	2590
% Oxidation of 2 : 3-diol	m. p. 106°	6·5	16	—	—	67	82	100
	m. p. 62°	—	—	100	—	—	—	—

this substance is the DL-form and that the isomeric compound of m. p. 106° is the *meso*-form. As the addition of piperidine to 1 : 2-3 : 4-diepoxybutane does not involve an addition or replacement at an asymmetric carbon atom, it may be concluded that the stereoisomeric compounds from which the 1 : 4-dipiperidinobutane-2 : 3-diols of m. p. 62° and 106° are derived are the DL- and the *meso*-form of 1 : 2-3 : 4-diepoxybutane respectively.

meso-1 : 2-3 : 4-Diepoxybutane reacted with methanol in the presence of a trace of perchloric acid to give 1 : 4-dimethoxybutane-2 : 3-diol, which was oxidised by periodic acid to methoxyacetaldehyde (identified as the 2 : 4-dinitrophenylhydrazone), thus demonstrating its structure.

On treatment with aqueous sodium phenoxide, 1 : 2-3 : 4-diepoxybutane yielded 4-phenoxybutane-1 : 2 : 3-triol (I) and 1 : 4-diphenoxybutane-2 : 3-diol (II). The former compound readily

(I.) $PhO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ $PhO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OPh$ (II.)

consumed 2 molecular proportions of periodic acid in dilute sulphuric acid but (II) was not attacked under these conditions, probably on account of its very low solubility in aqueous solutions. In acetic acid containing a small proportion of water, however, oxidation of (II) occurred readily with formation of phenoxyacetaldehyde.

With aqueous sodium *p*-chlorophenoxide, 1 : 2-3 : 4-diepoxybutane gave 4-*p*-chlorophenoxybutane-1 : 2 : 3-triol and 1 : 4-di-*p*-chlorophenoxybutane-2 : 3-diol, but with sodium β-naphthyloxide and sodium β-thionaphthyloxide, only 1 : 4-di-β-naphthyloxy- and 1 : 4-di-β-naphthylthio-butane-2 : 3-diol respectively were identified. The very low solubilities of the latter substances in practically all solvents in the cold precluded demonstration of their structures by periodate oxidation and the above formulations are given only by analogy with the phenoxy-derivatives.

Condensation of *meso*-1 : 2-3 : 4-diepoxybutane with ethyl sodiomalonate and treatment of the product with acid and then with ammonia yielded a substance which has been formulated as 1 : 1′ : 6 : 6′-tetracarbamylhexane-3 : 4-diol (III). This substance was oxidised by periodic acid in dilute sulphuric acid but the product was not identified.

$$(H_2N{\cdot}CO)_2CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CH(CO{\cdot}NH_2)_2 \qquad \text{(III.)}$$

Treatment of 1 : 2-3 : 4-diepoxybutane with ethylmagnesium bromide and subsequent decomposition of the magnesium complex with hydrobromic acid yielded 1 : 4-dibromobutane-2 : 3-diol. Reactions of a similar type have been reported between epichlorohydrin and ethylmagnesium bromide (Koelsch and McElvain, *J. Amer. Chem. Soc.*, 1929, **51**, 3390).

Isomerisation of 1 : 2-3 : 4-diepoxybutane occurred readily on heating it with zinc chloride. The only carbonyl compound identified among the products was diacetyl.

Experimental.

But-2-ene-1 : 4-*diol*.—This was prepared from 1 : 4-dibromobut-2-ene (m. p. 53—54°) either by Prévost's method (*Compt. rend.*, 1926, **183**, 1292) or by direct hydrolysis as follows: 1 : 4-dibromobut-2-ene (138 g.), lead monoxide (286 g.), and water (500 c.c.) were boiled under reflux for 20 hours, the reaction mixture was filtered, and the filtrate concentrated to 100 c.c. The residue was fractionated under reduced pressure, giving but-2-ene-1 : 4-diol (27·2 g., 49%), b. p. 130—140°/16 mm.

meso-1 : 2-3 : 4-*Diepoxybutane*.—But-2-ene-1 : 4-diol was brominated in ether (Prévost, *loc. cit.*), giving 2 : 3-dibromobutane-1 : 4-diol (m. p. 134°), which yielded *meso*-1 : 2-3 : 4-diepoxybutane (m. p. −19°) when treated with potassium hydroxide in ether (Prévost, *loc. cit.*).

DL-1 : 2-3 : 4-*Diepoxybutane*.—1 : 4-Dibromobut-2-ene (m. p. 53—54°) was oxidised to 1 : 4-dibromobutane-2 : 3-diol with dilute potassium permanganate (Griner, *Compt. rend.*, 1893, **117**, 554), and the diol converted into DL-1 : 2-3 : 4-diepoxybutane by potassium hydroxide in ether (*idem, ibid.*).

meso-1 : 2-3 : 4-*Diepoxybutane from* 3 : 4-*Epoxybut*-1-*ene*.—3 : 4-Epoxybut-1-ene (308 g.) gave on treatment with hydrochloric acid (Kadesch, *loc. cit.*) 2-chlorobut-3-en-1-ol (300 g., 64%); this was converted into a mixture of butadiene dichlorohydrins (310 g., 44% on epoxybutene), which were separated by Evans and Owen's method (*loc. cit.*). The three fractions obtained, *viz.*, (i) solid 2 : 3-dichlorobutane-1 : 4-diol, (ii) the dichlorobutanediol, b. p. 117—130°/1 mm., and (iii) 2 : 4-dichlorobutane-1 : 3-diol, were separately converted into 1 : 2-3 : 4-diepoxybutane by solid potassium hydroxide in ether. The three products thus obtained were characterised by treatment with piperidine in ether and subsequent examination of the 1 : 4-dipiperidinobutane-2 : 3-diols thus formed.

The product obtained from fraction (i) and potassium hydroxide was homogeneous and consisted of almost pure *meso*-1 : 2-3 : 4-diepoxybutane, the piperidino-compound melting sharply at 106°. Fraction (ii), however, gave with potassium hydroxide a mixture of 1 : 2-3 : 4-diepoxybutane (b. p. 140—142°/761 mm.) and a chlorine-containing substance (b. p. 176—180°/16 mm.) in almost equal quantities. The diepoxybutane was somewhat impure *meso*-form, and gave a piperidino-compound, m. p. 92—100°, raised to 106° by several recrystallisations. Fraction (iii) gave predominantly *meso*-1 : 2-3 : 4-diepoxybutane (piperidino-compound, m. p. 95—102°; 106° after several recrystallisations) in poor yield. Treatment of the mixed dichlorohydrins (310 g.) with potassium hydroxide in ether without previous separation gave *meso*-1 : 2-3 : 4-diepoxybutane (54 g., 14—15% on epoxybutene) satisfactory for use where complete absence of stereoisomeric impurity was not essential.

meso-1 : 4-*Dipiperidinobutane*-2 : 3-*diol*.—*meso*-1 : 2-3 : 4-Diepoxybutane (3 g.) in anhydrous ether (15 c.c.) was mixed with piperidine (6 g.) in ether (20 c.c.). After 48 hours at room temperature, easily volatile matter was removed by gentle warming under reduced pressure. The residue was redissolved in ether, and the solution treated with carbon and filtered. When most of the ether was allowed to evaporate at ordinary temperature, crystals of meso-1 : 4-*dipiperidinobutane*-2 : 3-*diol* (3·6 g.) separated; after recrystallisation from ether, these had m. p. 106° (Found: C, 65·95; H, 10·85; N, 10·95. $C_{14}H_{28}O_2N_2$ requires C, 65·6; H, 10·9; N, 10·9%). The dihydrochloride, prepared by mixing a solution of the base with ethereal hydrogen chloride, had m. p. 298°.

DL-1 : 4-*Dipiperidinobutane*-2 : 3-*diol*.—(*a*) A solution of 1 : 4-dibromobutane-2 : 3-diol (30 g.) (m. p. 85°) in benzene (50 c.c.) was mixed with one of piperidine (42 g.) in benzene (50 c.c.) and refluxed for 1 hour, a gentle reaction taking place with separation of a crystalline product. The slightly sticky product was removed by filtration, the filtrate extracted with 5N-hydrochloric acid (2 × 75 c.c.), and the sticky product dissolved in the hydrochloric acid extract. The clarified (carbon) solution was basified with sodium hydroxide, cooled, and extracted with ether (4 × 100 c.c.). The ethereal solution was dried ($MgSO_4$) and the ether removed, leaving a residue which set solid. By pouring the dry ethereal solution into an excess of saturated ethereal hydrogen chloride and recrystallising the product from absolute ethanol containing some hydrogen chloride, DL-1 : 4-*dipiperidinobutane*-2 : 3-*diol dihydrochloride*, m. p. 258—259°, was obtained (Found: N, 8·0; Cl, 21·1. $C_{14}H_{30}O_2N_2Cl_2$ requires N, 8·5; Cl, 21·6%). Treatment of a solution of the hydrochloride in methanol with 2 equivalents of sodium methoxide, filtration from sodium chloride, evaporation to dryness, and extraction of the residue with boiling benzene gave DL-1 : 4-*dipiperidinobutane*-2 : 3-*diol*, m. p. 62° after crystallisation from ether (Found: C, 66·05; H, 10·9; N, 10·4. $C_{14}H_{28}O_2N_2$ requires C, 65·6; H, 10·9; N, 10·9%).

(*b*) DL-1 : 2-3 : 4-Diepoxybutane (2·7 g.) in anhydrous ether (13·5 c.c.) was mixed with piperidine (5·4 g.) in ether (20 c.c.). After 2 days at room temperature, the ether was removed, and the oily residue converted into the hydrochloride by treatment with ethereal hydrogen chloride. The hydrochloride was purified and the base regenerated as in (*a*), giving a crystalline product, m. p. and mixed m. p. with (*a*), 62°.

Periodic Acid Oxidation of the Stereoisomeric 1 : 4-*Dipiperidinobutane*-2 : 3-*diols*.—The compounds were shaken with a 5—10% excess of 0·05M-potassium periodate in 0·25N-sulphuric acid at 20° until completely dissolved. At intervals, aliquot portions (10 ml.) of the solution were withdrawn and run into 0·1N-sodium arsenite (25 ml.) containing excess of sodium hydrogen carbonate. After addition of potassium iodide solution (1 c.c.; 20% w/v) and 15 minutes' storage the excess of arsenite was determined by titration with 0·1N-iodine solution. When oxidation by periodic acid was complete, the solution containing the oxidation products was treated with sulphur dioxide until the colour of the iodine at first liberated by this reagent had just been discharged. After removal of excess of sulphur dioxide under reduced pressure, the solution was treated with a slight excess of semicarbazide hydrochloride and sufficient sodium acetate to remove the acidity towards Congo-red. The solution was then concentrated to about one-tenth of its original volume. On cooling and basification by cautious addition of 2N-sodium hydroxide, *piperidinoacetaldehyde semicarbazone* separated; it crystallised from water in elongated prisms, m. p. 163° (Found: C, 52·1; H, 8·75; N, 30·3. $C_8H_{16}ON_4$ requires C, 52·2; H, 8·7; N, 30·45%). No depression of m. p. was observed on mixing the semicarbazones obtained from DL- and *meso*-dipiperidinobutanediols together or with a sample prepared from bromoacetal (p. 2486).

Piperidinoacetaldehyde Semicarbazone from Bromoacetal.—Piperidinoacetal was prepared by Stoermer and Burkert's method (*Ber.*, 1894, **27**, 2016), bromoacetal being used in place of chloroacetal. Piperidinoacetal (0·8 g.) was boiled under reflux for 10 minutes with 2N-hydrochloric acid (5 c.c.), the solution cooled, sodium acetate (2 g.) and semicarbazide hydrochloride (0·5 g.) were added, and the mixture was heated on the steam-bath for 1 hour. On filtration and basification of the filtrate with sodium hydroxide, piperidinoacetaldehyde semicarbazone, m. p. 163°, separated. The m. p. of this substance is reported erroneously by Stoermer (*Ber.*, 1898, **31**, 2543) as 76°.

1 : 4-*Dimethoxybutane*-2 : 3-*diol.*—*meso*-1 : 2-3 : 4-Diepoxybutane (5 g.) in methanol (50 c.c.) was treated with 1 drop of 65% perchloric acid and boiled under reflux for 2 hours. After removal of excess of methanol under reduced pressure, the product was distilled, giving a colourless liquid, b. p. 115°/10 mm. On treatment with 3 : 5-dinitrobenzoyl chloride in pyridine–benzene, 1 : 4-*bis*-3 : 5-*dinitrobenzoyloxydimethoxybutane* was obtained; it crystallised from 2-ethoxyethanol in pale yellow needles, m. p. 225° (Found : C, 44·7; H, 3·55; N, 10·65. $C_{20}H_{18}O_{14}N_4$ requires C, 44·6; H, 3·35; N, 10·4%).

Oxidation of 1 : 4-*Dimethoxybutane*-2 : 3-*diol with Periodic Acid.*—This oxidation was carried out in the manner described for the dipiperidino-compounds. After reduction of the excess of periodate and iodate with sulphur dioxide and removal of excess of the latter, the solution was shaken with a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, and the yellow precipitate collected, washed with water, and crystallised from methanol, giving orange needles, m. p. and mixed m. p. (with authentic sample of methoxyacetaldehyde 2 : 4-dinitrophenylhydrazone) 119° (Found : C, 42·4; H, 4·15; N, 22·55; OCH_3, 11·7. Calc. for $C_9H_{10}O_5N_4$: C, 42·5; H, 3·95; N, 22·05; OCH_3, 12·2%).

1 : 4-*Diphenoxybutane*-2 : 3-*diol.*—(*a*) Phenol (3·8 g.) in water (20 c.c.) and 11N-sodium hydroxide (3·6 c.c.) was treated with *meso*-1 : 2-3 : 4-diepoxybutane (1·8 g.) at 15—20°. The temperature was raised gradually to 100° and kept thereat for 1 hour. After cooling, the crystalline product was filtered off, and washed with 2N-sodium hydroxide and then with water. Crystallisation from ethanol yielded 1 : 4-*diphenoxybutane*-2 : 3-*diol*, m. p. 185° (Found : C, 70·25; H, 6·4. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·55%). The alkaline liquors were clarified (carbon) and acidified. The crystalline product which separated on storage was filtered off and extracted twice with ether to remove phenol. The residue crystallised from ethanol in the form of white platelets, m. p. 132—133°, of 4-*phenoxybutane*-1 : 2 : 3-*triol* (Found : C, 60·5; H, 6·95. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·05%). This compound was oxidised by potassium periodate–sulphuric acid solution in the manner previously described, titration showing that 98 g. of compound were oxidised by 1 g.-mol. of periodic acid (HIO_4), *i.e.*, approx. 2 mols. of periodic acid per mol. of triol.

1 : 4-Diphenoxybutane-2 : 3-diol was not oxidised by periodic acid under the usual conditions, as it was very sparingly soluble in water. Its oxidation was effected by rapidly cooling a solution of 0·17 g. in acetic acid (30 c.c.) to 25° and adding sodium periodate (0·17 g.) in dilute sulphuric acid (1 c.c.; 1 : 3). After 20 hours at 25°, water (25 c.c.) was added, the solution treated with sulphur dioxide, excess of the latter removed, and the solution added to a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The product, collected and purified by crystallisation from ethanol, had m. p. 134° (Hatch and Nesbitt, *J. Amer. Chem. Soc.*, 1945, **67**, 39, give m. p. 138° for phenoxyacetaldehyde 2 : 4-dinitrophenylhydrazone).

(*b*) 1 : 4-Diphenoxybutane-2 : 3-diol was obtained in poor yield by heating *meso*-1 : 2-3 : 4-diepoxybutane (0·9 g.) with phenol (1·9 g.) for 10 hours at 135—140° in a sealed tube.

1 : 4-*Di*-p-*chlorophenoxybutane*-2 : 3-*diol.*—*meso*-1 : 2-3 : 4-Diepoxybutane (1·8 g.) was added to *p*-chlorophenol (5·2 g.) in water (20 c.c.) and 11N-sodium hydroxide (3·6 c.c.), and the temperature raised to 100° during 15 minutes and kept at 100° for 1 hour. 1 : 4-*Di*-p-*chlorophenoxybutane*-2 : 3-*diol* separated from the liquors and was purified by crystallisation from ethanol; it formed silvery leaflets, m. p. 186—187° (Found : Cl, 20·9. $C_{16}H_{16}O_4Cl_2$ requires Cl, 20·7%). The liquors gave on acidification 4-p-*chlorophenoxybutane*-1 : 2 : 3-*triol*, silvery plates (from ethanol), m. p. 136° (Found : C, 51·6; H, 5·7; Cl, 15·2. $C_{10}H_{13}O_4Cl$ requires C, 51·6; H, 5·6; Cl, 15·25%).

1 : 4-*Di*-β-*naphthyloxybutane*-2 : 3-*diol* was obtained in a similar manner to the corresponding phenoxy-derivative, β-naphthol (5·8 g.) being used in place of phenol. It formed silvery white leaflets (from 2-ethoxyethanol), m. p. 253—254° (Found : C, 77·0; H, 5·4. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

1 : 4-*Di*-β-*naphthylthiobutane*-2 : 3-*diol.*—Naphthalene-β-thiol (3·2 g.) in water (20 c.c.) and 10N-sodium hydroxide (2·5 c.c.) was treated with *meso*-1 : 2-3 : 4-diepoxybutane (0·9 g.) at 50°. After being heated on the steam-bath for 1 hour, the reaction mixture was cooled, and the product filtered off, and washed with 2N-sodium hydroxide, water, and then methanol. Crystallised from ethanol and then from 2-ethoxyethanol the *diol* formed rosettes of needles, m. p. 167° (Found : C, 70·6; H, 5·6; S, 16·0. $C_{24}H_{22}O_2S_2$ requires C, 70·95; H, 5·4; S, 15·75%).

Condensation of 1 : 2-3 : 4-*Diepoxybutane with Ethyl Sodiomalonate.*—Sodium (2·3 g.) in ethanol (40 c.c.) was treated with ethyl malonate (16 g.), and *meso*-1 : 2-3 : 4-diepoxybutane (4·3 g.) added. The mixture became warm and began to deposit a yellow precipitate. After 30 minutes at room temperature, it was boiled under reflux for 20 minutes and cooled, the precipitate filtered off, and the ethanol removed from the filtrate. The residue and precipitate were united and treated with an excess of dilute sulphuric acid (1 : 6), giving an oil which was extracted with ether (3 × 40 c.c.). The extract was dried ($MgSO_4$), and the ether and excess of ethyl malonate were removed from the product by distillation. The residue was dissolved in ethanol and warmed with excess of aqueous ammonia (*d* 0·88). A crystalline precipitate of 1 : 1 : 6 : 6-*tetracarbamylhexane*-3 : 4-*diol* separated; purified by crystallisation from ethanol (carbon), it had m. p. 225—227° (decomp.) (Found : C, 41·3; H, 6·65; N, 19·1. $C_{10}H_{18}O_6N_4$ requires C, 41·4; H, 6·2; N, 19·3%).

On treatment with potassium periodate in water and subsequent removal of excess of periodate with sulphur dioxide, the tetra-amide was oxidised to a substance giving a yellow precipitate with 2 : 4-dinitrophenylhydrazine, but owing to the very small amount of material this was not identified.

Condensation of 1 : 2-3 : 4-*Diepoxybutane with Ethylmagnesium Bromide.*—*meso*-1 : 2-3 : 4-Diepoxybutane (4·3 g.) in ether (25 c.c.) was added dropwise to ethylmagnesium bromide prepared from magnesium (2·5 g.) and ethyl bromide (11·5 g.) in ether (60 c.c.), the mixture being cooled in an ice-bath. After 2 hours at room temperature, the reaction mixture was refluxed for 1½ hours and set aside for 65 hours. Dilute hydrobromic acid was then added until the initial precipitate had just dissolved, after which the ethereal layer was separated, and the aqueous layer extracted with more ether (3 × 100 c.c.). The ethereal extract was dried ($MgSO_4$ + $NaHCO_3$), the ether removed, and the residue distilled under reduced pressure (b. p. 134°/14 mm.), giving silvery plates, m. p. 107—111°, raised to 134—135° by crystallisation from benzene (Found : C, 19·65; H, 3·15. Calc. for $C_4H_8O_2Br_2$: C, 19·35; H, 3·25%).

Isomerisation of 1 : 2-3 : 4-*Diepoxybutane.*—1 : 2-3 : 4-Diepoxybutane (2·2 g.) was mixed with fused zinc chloride (0·5 g.), the mixture becoming hot spontaneously. After 2 hours, it was distilled cautiously, giving a distillate (1·6 g.) which was redistilled. The product (0·4 g.), b. p. 85—95°, gave a phenylhydrazone, m. p. 250° not depressed on admixture with an authentic sample of diacetyl bisphenylhydrazone (Found : C, 72·25; H, 6·7; N, 21·6. Calc. for $C_{16}H_{18}N_4$: C, 72·2; H, 6·75; N, 21·1%).

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