80. *Alicyclic Glycols. Part IX.** 1 : 3-*Bishydroxymethyl*cyclo*hexane.*

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The *cis*- and the *trans*-form of this diol (I) have been synthesised by reduction of the corresponding stereoisomers of hexahydro*iso*phthalic ester with lithium aluminium hydride, and the *trans*-diol has been resolved. Melting points of all derivatives of the *cis*-diol are higher than those of the corresponding *trans*-compounds. The intramolecular anhydro-compound, 3-oxa*bicyclo*[3 : 3 : 1]nonane (III) has been obtained from the *cis*-diol by hydrolysis of the dimethanesulphonate with aqueous alkali, and by reaction of the monotoluene-*p*-sulphonate with 2 : 6-lutidine, but ring-closure does not occur so readily as with the 1 : 2-isomer (Part VIII *). Fission of the tetrahydropyran ring in (III) has been effected with hydrogen bromide, acetyl chloride, acetyl bromide, and *p*-nitrobenzoyl bromide.

In the preceding paper it was shown that reduction of a *cis*- or a *trans*-hexahydrophthalic ester with lithium aluminium hydride occurred without epimerisation and gave the corresponding stereoisomer of 1 : 2-bishydroxymethyl*cyclo*hexane. Since the configurations of the hexahydro*iso*phthalic acids have been rigorously established, by anhydride-formation from the *cis*-acid (Baeyer and Villiger, *Annalen*, 1893, **276**, 261; Goodwin and Perkin, *J.*, 1905, **87**, 841) and by resolution of the *trans*-isomer (Böeseken and Peek, *Rec. Trav. chim.*, 1925, **44**, 845), both stereoisomers of the hitherto unknown 1 : 3-bishydroxymethyl*cyclo*hexane (I) should be readily obtainable by the same prodecure.

Over a freshly-prepared W-6 Raney nickel catalyst (Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695) hydrogenation of diethyl *iso*phthalate proceeded smoothly at 100°/100 atm. with only slight hydrogenolysis, and gave a good yield of the hexahydro-ester (with a catalyst prepared only two days before use a temperature of 150—200° was required, and considerable hydrogenolysis occurred). The hexahydro-ester was hydrolysed, and the *cis*-acid, which was the main product, was isolated as the insoluble calcium salt (Baeyer and Villiger, *loc. cit.*; Goodwin and Perkin, *loc. cit.*). The *trans*-isomer was obtained by partial isomerisation of the *cis*-acid with hydrochloric acid at 180° (Goodwin and Perkin, *loc. cit.*); unchanged *cis*-acid was removed as calcium salt and the *trans*-acid isolated from the residue. The acids were esterified and then individually reduced with lithium aluminium hydride to give *cis*-1 : 3-bishydroxymethyl*cyclo*hexane, m. p. 55°, and the liquid *trans*-isomer. The latter was resolved through the bis-(—)-menthylurethane, but owing to the unfavourable physical properties of this derivative the separation was more difficult than with the 1 : 2-isomer, and the (—)-*trans*-diol so obtained, $[\alpha]_D^{20}$ —9·6°, may not have been optically pure; its isolation, however, provides independent proof of the configuration.

The diols were characterised by the preparation of several derivatives, and it is noteworthy that in every case the *cis*-compound has the higher melting point. This inversion of the usual order occurs also with the derivatives of *cyclo*hexane-1 : 3-diol (Clarke and Owen, *J.*, 1950, 2103), and may be attributed to the different spatial arrangement of the bonds joining 1 : 3-substituents (compared with 1 : 2- and 1 : 4-) to the ring. Thus, with the more stable chair conformation it is the *trans*-1 : 3-compound in which the groups are attached in a way (one " equatorial " bond, one " polar ") similar to that in the *cis*-1 : 2- and *cis*-1 : 4-compounds, and *vice versa*. These considerations, which apply also to the dimethyl*cyclo*hexanes and methyl*cyclo*hexylmethanols, are discussed more fully in Part XI (*J.*, 1953, 408). Another interesting difference in behaviour was observed in the relative reactivities of the ditoluene-*p*-sulphonates towards sodium iodide in acetone; unlike the 1 : 2-compounds, the *cis*-1 : 3-derivative reacted more rapidly than the *trans*-isomer, and the solid *cis*-di-iodide (II) so formed was more stable than the liquid *trans*-di-iodide.

Steric considerations show that the *cis*-diol should be capable of forming an intramole-

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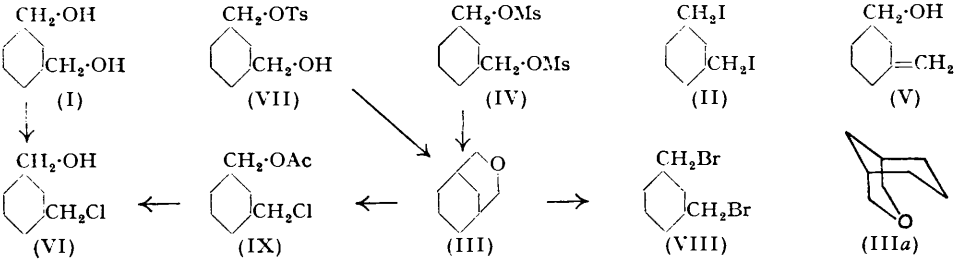
* Part VIII, preceding paper.

cular ether, 3-oxa*bicyclo*[3 : 3 : 1]nonane (III), which, amongst other possibilities, could have the strainless " double-chair " structure (III*a*) (a similar conformation may apply to the anhydride of *cis*-hexahydro*iso*phthalic acid); no such product would be expected from the *trans*-diol. The methods which had been successful in the preparation of octahydro*iso*benzofuran from 1 : 2-bishydroxymethyl*cyclo*hexane (Part VIII) were therefore applied to *cis*-(I) and its derivatives. Hydrolysis of the dimethanesulphonate (IV) with aqueous alkali gave the oxide (III) in 30% yield, accompanied by a small amount of unsaturated material, the main product being the *cis*-diol; this contrasts with the behaviour of the 1 : 2-isomer, which gave no diol on hydrolysis. In a comparative experiment the *trans*-form of (IV) gave no cyclic oxide; the main product was the *trans*-diol, but an unsaturated product was also obtained, which probably contained 3-methylene*cyclo*hexylmethanol (V), characterised as the 3 : 5-dinitrobenzoate. Dehydration of the *cis*-diol with sulphuric acid in acetone gave the oxide in very small yield, and under more vigorous conditions, such as alumina at 200—250°, or hot 50% sulphuric acid, only unsaturated material was obtained. With fuming hydrochloric acid the diol gave a mixture of mono- and di-chlorides, with much polymer; the monochloride (VI) was characterised as the *p*-nitrobenzoate.



(Ms = $CH_3 \cdot SO_2 \cdot$; Ts = *p*-$C_6H_4Me \cdot SO_2 \cdot$.)

Reynolds and Kenyon (*J. Amer. Chem. Soc.*, 1950, **72**, 1593; U.S.P. 2,544,899) described a method for the preparation of tetrahydro-furan and -pyran systems which involves treatment of the appropriate diol, in boiling pyridine or 2 : 6-lutidine, with 1 mol. of a sulphonyl chloride. Treatment of *cis*-(I) under these conditions with benzenesulphonyl chloride and 2 : 6-lutidine resulted only in the formation of a mixture of mono- and di-chlorides, the presence of (VI) being confirmed by conversion into the *p*-nitrobenzoate mentioned above. Production of a chloride, rather than a sulphonyl ester, from an alcohol and a sulphonyl chloride in pyridine is known to take place at high temperatures (Tipson, *J. Org. Chem.*, 1944, **9**, 235), or even at low temperatures with highly reactive compounds (Miles and Owen, *J.*, 1950, 2938), and this side reaction was encountered by Reynolds and Kenyon in some of their experiments.

Reynolds and Kenyon (*loc. cit.*) described a variation of their method, in which cyclisation was effected by reaction of a monosulphonate of a diol with the organic base. Reaction of *cis*-(I) with 1 mol. of toluene-*p*-sulphonyl chloride in pyridine gave a crude monotoluene-*p*-sulphonate (VII), which with boiling 2 : 6-lutidine gave the oxide (III) in 36% yield; this route, however, gave variable results, probably owing to the critical conditions of monotoluene-*p*-sulphonation. The best method, therefore, is the hydrolysis of the *cis*-dimethanesulphonate, but from the relative yields of cyclic ether in the 1 : 2- and the 1 : 3-series it is clear that the six- is formed much less readily than the five-membered oxide ring; although a cyclic oxide was prepared from 3-hydroxymethyl*cyclo*hexanol (Clarke and Owen, *J.*, 1950, 2108) no analogous product was obtained from 4-hydroxymethyl*cyclo*hexanol (Owen and Robins, *J.*, 1949, 326).

3-Oxa*bicyclo*[3 : 3 : 1]nonane was a volatile, waxy solid, m. p. 113—115°, very soluble in organic solvents, and could be satisfactorily purified only by sublimation. With hydroferricyanic acid it formed a complex which was less stable than that from octahydro*iso*benzofuran.

Although a tetrahydropyran ring can usually be cleaved by most of the reagents which attack tetrahydrofuran systems (cf. Jones and Taylor, *Quart. Reviews*, 1950, **4**, 195), more drastic conditions are sometimes required and the yields are often poorer. This distinction is well illustrated in the reactions of (III). Unlike octahydro*iso*benzofuran (cf. Part VIII) it did not readily react with hydrogen bromide at 70—80°, but with hydrogen bromide in acetic acid at 100° it gave *cis*-1 : 3-bisbromomethyl*cyclo*hexane (VIII), the configuration of which was proved by reaction with potassium acetate and deacetylation of the resulting diacetate to the *cis*-diol. Also in contrast to octahydro*iso*benzofuran, it failed to react with acetyl chloride or acetyl bromide in the absence of a catalyst, though in the presence of zinc chloride it readily gave *cis*-3-chloromethyl- (IX) and *cis*-3-bromomethyl-*cyclo*hexylmethyl acetate. Deacetylation of (IX) gave the chlorohydrin (VI), characterised as the *p*-nitrobenzoate, identical with that prepared from the mixtures of mono- and di-chlorides. Similarly, deacetylation and *p*-nitrobenzoylation of the bromo-compound gave *cis*-3-bromomethyl*cyclo*hexylmethyl *p*-nitrobenzoate, which was also obtained by direct reaction of the oxide with *p*-nitrobenzoyl bromide in the presence of zinc chloride.

EXPERIMENTAL

Dimethyl cis-*Hexahydro*iso*phthalate.*—Diethyl *iso*phthalate (195 g.) in ethanol (300 c.c.) was hydrogenated over freshly-prepared W-6 Raney nickel (Adkins and Billica, *loc. cit.*) (40 g.) at 100°/100 atm. When uptake was complete the catalyst was filtered off and the filtrate distilled to give the crude hexahydro-ester (170 g.), b. p. 85—125° (mainly 120—125°)/1 mm., n_D^{20} 1·4568. This was hydrolysed with boiling ethanolic alkali, water added, and the ethanol distilled off. The residual aqueous solution was acidified, and then made alkaline with ammonia and treated with excess of calcium chloride solution. The precipitated calcium salt was filtered off, and the acid regenerated from it by concentrated hydrochloric acid. Crystallisation from hot water gave the *cis*-acid (100 g.), m. p. 161—162° (Goodwin and Perkin, *loc. cit.*, gave m. p. 161—163°), which was converted into the dimethyl ester (100 g.), b. p. 94—96°/0·2 mm., n_D^{20} 1·4580, by methanol and sulphuric acid.

Dimethyl trans-*Hexahydro*iso*phthalate.*—The *cis*-acid (40 g.) and concentrated hydrochloric acid (60 c.c.) were heated together for 16 hours at 180° (sealed tube). Excess of aqueous ammonia was then added, and the *cis*-acid precipitated as the calcium salt as described above. This was filtered off, and the filtrate acidified and continuously extracted with ether. The acid thus obtained was dissolved in the minimum amount of aqueous ammonia (*d* 0·88) and treated with calcium chloride to precipitate a further small quantity of *cis*-acid. The filtered solution was acidified, and the precipitated acid crystallised from hot water to give the pure *trans*-acid (8·6 g.), m. p. 147—148° (Goodwin and Perkin, *loc cit.*, gave m. p. 148°). The acid was esterified in the usual way to give the *trans*-dimethyl ester (7·8 g.), b. p. 83—85°/0·1 mm., n_D^{18} 1·4592.

1 : 3-*Bishydroxymethyl*cyclo*hexane.*—(i) The *cis*-dimethyl ester (50 g.) in dry ether (50 c.c.) was added dropwise to a stirred, cooled solution of lithium aluminium hydride (11·5 g.) in dry ether (500 c.c.). After 1 hour water and dilute sulphuric acid were added and the diol was isolated by continuous extraction with ether. Removal of ether from the dried (K_2CO_3) extracts gave cis-1 : 3-*bishydroxymethyl*cyclo*hexane* (35 g., 97%) as a viscous oil, which slowly crystallised and had m. p. 50—53°, raised to 54—55° by recrystallisation from dry ether (Found : C, 66·2; H, 11·3. $C_8H_{16}O_2$ requires C, 66·6; H, 11·2%).

(ii) Similarly, reduction of the *trans*-dimethyl ester (14·1 g.) with lithium aluminium hydride (3·5 g.) gave trans-1 : 3-*bishydroxymethyl*cyclo*hexane* (9·2 g., 91%), b. p. 112—114°/0·1 mm., n_D^{24} 1·4941 (Found : C, 66·5; H, 11·0%).

Derivatives of the cis-*Diol.*—Treatment of the *cis*-diol (0·5 g.) with toluene-*p*-sulphonyl chloride (1·45 g.) in pyridine (5 c.c.) for 20 hours at 0°, followed by precipitation with ice, gave the *ditoluene*-p-*sulphonate* (1 g., 64%), which crystallised from methanol in plates, m. p. 99—100° (Found: C, 58·3; H, 6·5; S, 14·1. $C_{22}H_{28}O_6S_2$ requires C, 58·4; H, 6·2; S, 14·2%). A similar procedure gave the *dimethanesulphonate* (75%), needles, m. p. 74—75° (Found : C, 40·1; H, 6·9; S, 21·3. $C_{10}H_{20}O_6S_2$ requires C, 40·0; H, 6·7; S, 21·35%), from methanol, and the *di*-p-*nitrobenzoate*, a microcrystalline powder (95%), m. p. 151—152° (Found : C, 59·3; H, 5·1; N, 6·1. $C_{22}H_{22}O_8N_2$ requires C, 59·7; H, 5·0; N, 6·3%), from methanol–acetone.

The *cis*-diol (0·3 g.) with phenyl *iso*cyanate (0·6 g.) at 100° (1 hr.) gave the *bisphenylurethane* (0·6 g., 76%), m. p. 128—129° [from benzene–light petroleum (b. p. 60—80°)] (Found : C, 68·9; H, 6·75; N, 7·3. $C_{22}H_{26}O_4N_2$ requires C, 69·1; H, 6·85; N, 7·3%).

Derivatives of the trans-*Diol.*—Under conditions identical with those described above, including crystallisation solvents, there were obtained : the *ditoluene*-p-*sulphonate* (51%), plates, m. p. 86—87° (Found : C, 58·4; H, 6·5; S, 13·7%); the *dimethanesulphonate* (48%), needles, m. p. 64—65° (Found : C, 39·9; H, 6·9; S. 20·6%); the *di*-p-*nitrobenzoate* (67%), m. p. 122—123° (Found : C, 59·7; H, 5·2; N, 6·2%); and the *bisphenylurethane* (70%), m. p. 107—108° (Found : C, 69·3; H, 6·9; N, 7·4%).

Resolution of (±)-trans-1 : 3-*Bishydroxymethyl*cyclo*hexane*.—The *trans*-diol (5 g.) and (−)-menthyl *iso*cyanate (13·5 g.) in dry benzene (15 c.c.) were heated on the steam-bath overnight. Benzene was distilled off, and the syrupy residue dissolved in light petroleum (b. p. 40—60°). On cooling to 0° the urethane separated as a gelatinous mass, which was filtered off, pressed to remove solvent, and washed with light petroleum (b. p. 40—60°). The material so obtained was dried *in vacuo* to an amorphous powder (11 g.), m. p. 68—72°, $[\alpha]_D^{22}$ −59·1° (*c*, 2 in C_6H_6). Six further similar purifications gave a (−)-*menthylurethane* (2·05 g.), m. p. 92—95°, $[\alpha]_D^{22}$ −57·9° (Found : C, 71·5; H, 10·9; N, 5·3. $C_{30}H_{54}O_4N_2$ requires C, 71·1; H, 10·7; N, 5·5%). No solvent was found from which the urethane could be satisfactorily crystallised (cf. *inter al.*, Morgan and Pettet, *J.*, 1931, 1124; Fieser and Creech, *J. Amer. Chem. Soc.*, 1939, **61**, 3502).

The urethane (1·7 g.) was boiled under reflux for 48 hours in ethanol (30 c.c.) containing potassium hydroxide (2 g.). The solution was then steam-distilled to remove ethanol and (−)-menthylamine, and the diol was isolated by continuous extraction of the residual aqueous solution with ether. Distillation gave the (−)-trans-*diol* (0·36 g.) as a viscous oil, b. p. 113—115°/0·1 mm., n_D^{20} 1·4911, $[\alpha]_D^{20}$ −9·6° (*c*, 5 in EtOH) (Found : C, 67·0; H, 11·3%). The *ditoluene*-p-*sulphonate* had m. p. 73—74°, $[\alpha]_D^{20}$ −13° (*c*, 0·7 in C_6H_6) (Found : C, 58·05; H, 6·3%).

1 : 3-*Bisiodomethyl*cyclo*hexane*.—(i) The *cis*-ditoluene-*p*-sulphonate (1·5 g.) was boiled under reflux for 1½ hours with sodium iodide (4 g.) in acetone (50 c.c.). Sodium toluene-*p*-sulphonate (1·15 g., 89%) was filtered off, and acetone distilled from the filtrate. Water and chloroform were added, and the product, isolated from the chloroform solution, on distillation gave the cis-*di-iodide* (0·8 g.), m. p. 28°, b. p. 98—100°/3×10^{-4} mm., n_D^{19} 1·6055 (Found : C, 26·8; H, 3·8; I, 68·5. $C_8H_{14}I_2$ requires C, 26·4; H, 3·9; I, 69·7%).

(ii) The *trans*-ditoluene-*p*-sulphonate (1·9 g.) reacted much more slowly under similar conditions and gave an impure *trans*-di-iodide (1·2 g.) (Found : I, 63·5%).

Reaction of the cis-*Diol with Hydrochloric Acid*.—The *cis*-diol (10 g.) and fuming hydrochloric acid (10 c.c.) were heated at 80—90° for 4 hours (sealed tube). The product was extracted with ether, washed with aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). Distillation gave a main fraction (1·1 g.), b. p. 70—78°/0·03 mm., n_D^{18} 1·4916 (Found : Cl, 33·1. Calc. for $C_8H_{15}OCl$: Cl, 21·8. Calc. for $C_8H_{14}Cl_2$: Cl, 39·2%), and a large involatile residue. Treatment of the mixture of mono- and di-chlorides with *p*-nitrobenzoyl chloride in pyridine gave a small yield of cis-3-*chloromethyl*cyclo*hexylmethyl* p-*nitrobenzoate*, which crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 69° (Found : C, 57·7; H, 6·0; N, 4·4. $C_{15}H_{18}O_4NCl$ requires C, 57·8; H, 5·8; N, 4·5%).

3-*Oxa*bicyclo[3 : 3 : 1]*nonane*.—(i) A suspension of the *cis*-dimethanesulphonate (30 g.) in 15% aqueous potassium hydroxide (100 c.c.) was boiled under reflux for 3 hours. A solid sublimed into the condenser during the hydrolysis; this was washed out with ether, and the ethereal solution dried (K_2CO_3) and evaporated. Sublimation of the residue at 110° (bath)/140 mm. gave 3-*oxa*bicyclo[3 : 3 : 1]*nonane* (3·1 g.), as a waxy solid with a camphoraceous odour, m. p. 105—110°, raised to 113—115° by resublimation (Found : C, 75·9; H, 11·3. $C_8H_{14}O$ requires C, 76·1; H, 11·2%). The small oily residue from the sublimation was unsaturated. The aqueous solution from the hydrolysis was steam-distilled to remove traces of volatile material and then continuously extracted with ether to give the *cis*-diol (10·5 g.), identified as the ditoluene-*p*-sulphonate, m. p. and mixed m. p. 99—100°.

In a comparative experiment, similar treatment of the *trans*-dimethanesulphonate (2·8 g.) gave no sublimate, but steam-distillation afforded a volatile oil, isolated by extraction with ether, which on distillation gave an unsaturated liquid (0·25 g.), b. p. 110—112°/20 mm., n_D^{25} 1·4798 (Found : C, 72·2; H, 10·8%); this probably contained 3-methylene*cyclo*hexylmethanol, since it gave a 3 : 5-*dinitrobenzoate*, crystallising from methanol in needles, m. p. 57° (Found : C, 55·9; H, 5·3. $C_{15}H_{16}O_6N_2$ requires C, 56·25; H, 5·0%). Ether-extraction of the non-volatile residue from the steam-distillation gave the *trans*-diol (0·5 g.), identified as the ditoluene-*p*-sulphonate, m. p. and mixed m. p. 86—87°.

(ii) To a solution of the *cis*-diol (4·5 g.) in chloroform–pyridine (1 : 1; 100 c.c.) kept at 0°, a solution of toluene-*p*-sulphonyl chloride (6·1 g.) in the same solvent (100 c.c.) was added drop-wise during 4 hours, with vigorous stirring. The mixture was kept at 0° overnight and then concentrated under reduced pressure below 35°. The product was worked up into chloroform, washed and dried in the usual way, and isolated as an oil. This was dissolved in methanol (*ca.* 10 c.c.), cooled to 0°, and filtered from a small quantity of ditoluene-*p*-sulphonate. Evaporation then gave the crude *cis*-monotoluene-*p*-sulphonate, probably contaminated with some unchanged diol (Found : S, 7·7. Calc. for $C_{15}H_{22}O_4S$: S, 10·7%). A solution of this product (3·9 g.) in 2 : 6-lutidine (7 c.c.) was boiled under reflux for an hour. The mixture, which had separated into two layers, was cooled and added to an excess of dilute sulphuric acid. Ether-extraction, followed by sublimation, gave 3-oxa*bicyclo*[3 : 3 : 1]nonane (0·6 g.), m. p. 113—114°. Repetition of this process on a larger scale gave a much smaller yield of the oxide.

(iii) The *cis*-diol (5 g.) in boiling 2 : 6-lutidine (15 g.) was treated with benzenesulphonyl chloride (6·2 g.), added dropwise during 15 minutes. After being heated for a further 15 minutes the solution was poured into excess of concentrated hydrochloric acid and extracted with ether. The dried (K_2CO_3) extracts were evaporated to a yellow oil, which on sublimation gave only a trace of oxide. Distillation of the residue yielded a mixture of mono- and di-chloride (2·6 g.), b. p. 148—151°/35 mm., n_D^{22} 1·4834 (Found : Cl, 28·1. Calc. for $C_8H_{15}OCl$: Cl, 21·8. Calc. for $C_8H_{14}Cl_2$: Cl, 39·2%), which gave *cis*-3-chloromethyl*cyclo*hexylmethyl *p*-nitrobenzoate, m. p. and mixed m. p. 69°.

This mixture (2 g.) was boiled for 16 hours with 10% aqueous potassium hydroxide (20 c.c.). The product, isolated by steam-distillation and ether-extraction, on sublimation gave the crystalline oxide (50 mg.) and left a residue which was unsaturated and contained chlorine.

Ring-fission of 3-*Oxa*bicyclo[3 : 3 : 1]*nonane*.—(i) *With hydrogen bromide.* The oxide (0·75 g.) and hydrogen bromide in acetic acid (20 c.c. of 50% solution) were heated at 100° for 4 hours (sealed tube). Hydrogen bromide and acetic acid were removed under reduced pressure and the residue was dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). Distillation gave cis-1 : 3-*bisbromomethyl*cyclo*hexane* (1·33 g.), b. p. 93—96°/0·4 mm., n_D^{16} 1·5384 (Found : C, 35·8; H, 5·4; Br, 58·8. $C_8H_{14}Br_2$ requires C, 35·6; H, 5·2; Br, 59·2%).

This dibromide (1·2 g.) was boiled under reflux for 24 hours with potassium acetate (10 g.) in acetic acid (50 c.c.) containing acetic anhydride (1 c.c.). The bulk of the acetic acid was removed under reduced pressure, and water added to the residue. Extraction with ether gave cis-1 : 3-*bisacetoxymethyl*cyclo*hexane* (0·63 g.), b. p. 105—107°/0·5 mm., n_D^{15} 1·4598 (Found : C, 63·3; H, 8·9. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%), which on deacetylation by treatment of a portion (0·45 g.) with sodium (0·1 g.) dissolved in dry methanol (30 c.c.) for 24 hours at room temperature gave the *cis*-diol (0·3 g.), characterised as the ditoluene-*p*-sulphonate, m. p. and mixed m. p. 99—100°.

(ii) *With acetyl chloride.* The oxide (0·3 g.), acetyl chloride (0·25 g.), and zinc chloride (20 mg.) were heated under reflux on the steam-bath for 30 minutes, by which time boiling had ceased. The product was dissolved in chloroform, washed with sodium hydrogen carbonate solution and with water, and dried (Na_2SO_4). Distillation gave cis-3-*chloromethyl*cyclo*hexylmethyl acetate* (0·4 g.), b. p. 68—70°/0·3 mm., n_D^{22} 1·4711 (Found : C, 59·1; H, 8·4; Cl, 16·8. $C_{10}H_{17}O_2Cl$ requires C, 58·7; H, 8·35; Cl, 17·3%). Catalytic deacetylation with 1% hydrogen chloride in methanol, followed by *p*-nitrobenzoylation, gave the *p*-nitrobenzoate, m. p. and mixed m. p. 69°.

(iii) *With acetyl bromide.* The oxide (2 g.), acetyl bromide (2·5 g.), and zinc chloride (0·1 g.) reacted as above to give cis-3-*bromomethyl*cyclo*hexylmethyl acetate* (3·2 g.), b. p. 92—95°/0·4 mm., n_D^{22} 1·4890 (Found : C, 48·3; H, 7·0; Br, 32·7. $C_{10}H_{17}O_2Br$ requires C, 48·2; H, 6·9; Br, 32·1%). Catalytic deacetylation with 1% hydrogen chloride in methanol, followed by *p*-nitrobenzoylation, gave the cis-p-*nitrobenzoate*, needles [from light petroleum (b. p. 60—80°)], m. p. 79° (Found : C, 50·6; H, 5·1; N, 3·9. $C_{15}H_{18}O_4NBr$ requires C, 50·6; H, 5·1; N, 3·9%).

(iv) *With* p-*nitrobenzoyl bromide.* The oxide (0·15 g.), *p*-nitrobenzoyl bromide (0·4 g.), and zinc chloride (trace) were heated at 100° for 15 minutes. The product, isolated by chloroform extraction as in (ii), was a solid, which on crystallisation from light petroleum (b. p. 60—80°) gave *cis*-3-bromomethyl*cyclo*hexylmethyl *p*-nitrobenzoate (0·4 g.), m. p. and mixed m. p. 79°.

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