Alicyclic Glycols. Part XIII.* 1 : 2-Bishydroxymethylcyclopentane.

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The *cis-* and the *trans-*form of the above glycol have been obtained by reduction of the corresponding stereoisomers of dimethyl *cyclo*pentane-1 : 2-dicarboxylate with lithium aluminium hydride. Syntheses of the intra-molecular ethers, *cis-* and *trans-*3-oxa*bicyclo*[3 : 3 : 0]octane, and of the related cyclic sulphides, *cis-* and *trans-*3-thia*bicyclo*[3 : 3 : 0]octane, are described. The *trans-*sulphide is also obtained by a cyclisation which occurs during the partial desulphurisation of *trans-*1 : 2-bismercaptomethyl-*cyclo*pentane. The *trans-*oxide (IX) and the *trans-*sulphide (XIII) are of special interest because of the presence of two mutually *trans-*fused five-membered rings.

The tetrahydrofuran ring in each cyclic oxide is readily broken by reaction with acetyl bromide; the products have been used to synthesise *cis-* and *trans-*2-methyl*cyclo*pentylmethanol.

SYNTHESES of the various bishydroxymethyl*cyclo*hexanes, and their uses in elucidating the configurations of the dimethyl*cyclo*hexanes and the methyl*cyclo*hexylmethanols, were described by Haggis and Owen (*J.*, 1953, 389, 399, 404, 408); later, Birch and Dean (*J.*, 1953, 2477) prepared the 1 : 3-bishydroxymethyl*cyclo*pentanes and converted them into the 1 : 3-dimethyl*cyclo*pentanes, thus establishing the configurations of the latter. When the present work was begun, neither of the 1 : 2-bishydroxymethyl*cyclo*pentanes (I) and (VI) had been described, but each was easily prepared by reduction with lithium aluminium hydride of the appropriate stereoisomer of dimethyl *cyclo*pentane-1 : 2-dicarboxylate (some improvements in the preparation of the 1 : 2-dicarboxylic acid from *cyclo*pentanone are outlined in the experimental section). Subsequently, the *trans-*diol has been described by Halford and Weissmann (*J. Org. Chem.*, 1952, **17**, 1276) and by Bailey and Sorenson (*J. Amer. Chem. Soc.*, 1954, **76**, 5421), though no derivatives were recorded; the physical constants of our product differed considerably from those of the former authors, but agreed with those of the latter. The *cis-* and the *trans-*diol each gave a crystalline toluene-*p*-sulphonate, methanesulphonate, and α-naphthylurethane.

Haggis and Owen (*J.*, 1953, 389) described three methods by which the cyclic oxide, octahydro*iso*benzofuran (V), could be obtained from 1 : 2-bishydroxymethyl*cyclo*hexane : (i) by direct dehydration over alumina, or by heating in acid solution; (ii) by alkaline hydrolysis of the dimethanesulphonate; (iii) as a by-product in the preparation of the dimethanesulphonate or ditoluene-*p*-sulphonate. Although the oxide (V) was isolated in the *cis*- and the *trans*-form by use of the corresponding stereoisomer of the diol, it was expected in the present investigation that 3-oxa*bicyclo*[3 : 3 : 0]octane would be obtainable by similar methods only as the *cis*-form (II), since the strain involved in the *trans*-fusion of two five-membered rings rendered the formation of the *trans*-oxide much more doubtful. This view was supported by small-scale comparative experiments with *cis*- and with *trans*-1 : 2-bishydroxymethyl*cyclo*pentane, which showed that only the former was dehydrated to the oxide when heated with alumina or aqueous sulphuric acid. On a preparative scale, reaction of the *cis*-diol with boiling 18% sulphuric acid gave the pure oxide (II) in 76% yield. It was also obtained by hydrolysis of the *cis*-dimethanesulphonate with boiling aqueous potassium hydroxide, although it was then contaminated with a small proportion of an unsaturated compound, probably the isomeric 2-methylene*cyclo*pentylmethanol (IV) since it gave a small amount of formaldehyde on ozonolysis. The cyclic oxide was also formed, together with the *cis*-dimethanesulphonate, when the latter was prepared by slow addition of methanesulphonyl chloride to a solution of the *cis*-diol in pyridine; reversed order in addition gave only traces of the oxide.

Although no cyclic oxide could be prepared by dehydration of the *trans*-diol, alkaline hydrolysis of the *trans*-dimethanesulphonate (VII) unexpectedly gave a 67% yield of pure *trans*-3-oxa*bicyclo*[3 : 3 : 0]octane (IX), the physical constants of which were slightly different from those of the *cis*-isomer. Both compounds had the strong odour character-istic of cyclic oxides; their stereochemical individuality follows from the ring-fission re-actions described later. The freedom of the *trans*-oxide from unsaturated material (cf. the *cis*-oxide prepared from the dimethanesulphonate) indicates that the competing elimin-ation reaction is suppressed. This is probably due to the shielding effect of the 1-methane-sulphonyloxymethyl group in the ester (VII), which hinders the attack by OH⁻ on the neighbouring hydrogen atom attached to $C_{(2)}$; in the *cis*-compound (III) the hydrogen atom is not so protected.

The *trans*-ditoluene-*p*-sulphonate (VIII) reacted smoothly with potassium thiolacetate to give *trans*-1 : 2-bisacetylthio*cyclo*pentane (XV). In the *cyclo*hexane series, conversion of a bisthiolacetate into the corresponding dimethyl*cyclo*hexane was carried out by de-sulphurisation in methanol with Raney nickel, and with the relatively small amounts of materials available there had been considerable difficulty in isolating the pure hydrocarbon. Even greater difficulty would arise with the more volatile dimethyl*cyclo*pentanes, and some exploratory experiments were therefore carried out involving desulphurisation in the absence of an organic solvent. The bisthiolacetate (XV) was hydrolysed to the dithiol with aqueous sodium hydroxide, and the resulting solution was treated directly with Raney nickel. The result was unexpected; in addition to some hydrocarbon there was formed a volatile crystalline solid, which contained sulphur and was identified as *trans*-3-thia*bicyclo*[3 : 3 : 0]octane (XIII) by synthesis from the *trans*-ditoluene-*p*-sulphonate (VIII) and sodium sulphide. The *cis*-isomer, a liquid, was similarly synthesised from the *cis*-ditoluene-*p*-sulphonate. The infrared spectra of the two sulphides (determined by Mr. R. L. Erskine, Spectrographic Laboratory), although similar in general form, exhibited marked differences in detail, and showèd each isomer to be free from the other. Each sulphide on oxidation with hydrogen peroxide gave a different crystalline sulphone.

Desulphurisation with Raney nickel is probably a free-radical reaction (Hauptmann and Wladislaw, *J. Amer. Chem. Soc.*, 1950, 72, 707, 711; Bonner, *ibid.*, 1952, 74, 1034; Birch and Dean, *Annalen*, 1954, 585, 234) and the formation of the sulphide (XIII) can clearly occur through the intermediate diradical (XIV); the isolation of the sulphide (XIII) under the above conditions is undoubtedly due to its insolubility in the aqueous reaction medium, which retards its further desulphurisation to the hydrocarbon.

Compounds containing two *trans*-fused five-membered rings are very rare. The only well-authenticated homocyclic examples are *trans-bicyclo*[3 : 3 : 0]octane (XVI) and the

β-ketone (XVII) from which it was derived by reduction (Barrett and Linstead, *J.*, 1935, 436, 1069); the structure of a steroid derivative considered to contain the system (XVI) (Wendler, Hirshmann, Slates, and Walker, *Chem. and Ind.*, 1954, 901) is based only on the probable stereochemical course of a pinacolic change. In the heterocyclic field, *allo*biotin and *epiallo*biotin contain the *trans*-2 : 4-diaza-7-thia*bicyclo*[3 : 3 : 0]octane system (Harris, Mozingo, Wolf, Wilson, and Folkers, *J. Amer. Chem. Soc.*, 1945, 67, 2102); the anhydride of *trans-cyclo*pentane-1 : 2-dicarboxylic acid, which would provide a further example, may not be monomeric (cf. Bredt, *Annalen*, 1924, 437, 9). In view of the fact that the ketone (XVII) could not be prepared by Dieckmann cyclisation of diethyl *trans-cyclo*pentane-1 : 2-diacetate but only by the more vigorous method of heating the *trans*-acid with barium hydroxide at 320—350°, it is all the more surprising that the ring-closures leading to the *trans*-oxide (IX) and the *trans*-sulphide (XIII) should occur under such comparatively mild conditions. Also significant in this connection is the extreme ease with which *trans*-2-acetylthio*cyclo*pentanol is isomerised to 2-mercapto*cyclo*pentyl acetate by cold dilute alkali (Harding and Owen, *J.*, 1954, 1528), because if this acetyl migration follows the usual mechanism it must involve the formation of the intermediate *trans*-fused orthoacetate (XVIII). These results clearly indicate that the *trans*-fused compounds are formed much more readily than would be expected on conventional stereochemical grounds.

Fission of the tetrahydrofuran ring in the *trans*-oxide (IX) with acetyl bromide gave *trans*-2-bromomethyl*cyclo*pentylmethyl acetate (X), the configuration of which was confirmed by its conversion into *trans*-1 : 2-bisacetoxymethyl*cyclo*pentane, followed by hydrolysis to the *trans*-diol (VI), identified as the ditoluene-*p*-sulphonate. Reaction of the acetate bromide (X) with potassium thiolacetate gave *trans*-2-acetylthio*cyclo*pentyl-methyl acetate (XI), which after desulphurisation and hydrolysis furnished *trans*-2-methyl*cyclo*pentylmethanol (XII). A similar series of reactions, starting from the *cis*-oxide, gave the *cis*-isomer of (XII). Both alcohols were liquids, the physical properties of which were in accordance with the Auwers–Skita rules; the *cis*- and the *trans*-3 : 5-dinitro-benzoate, the *cis*- and the *trans*-α-naphthylurethane, and the *cis*-phenylurethane were obtained crystalline. Anziani and Cornubert (*Bull. Soc. chim.*, 1948, 857) obtained a
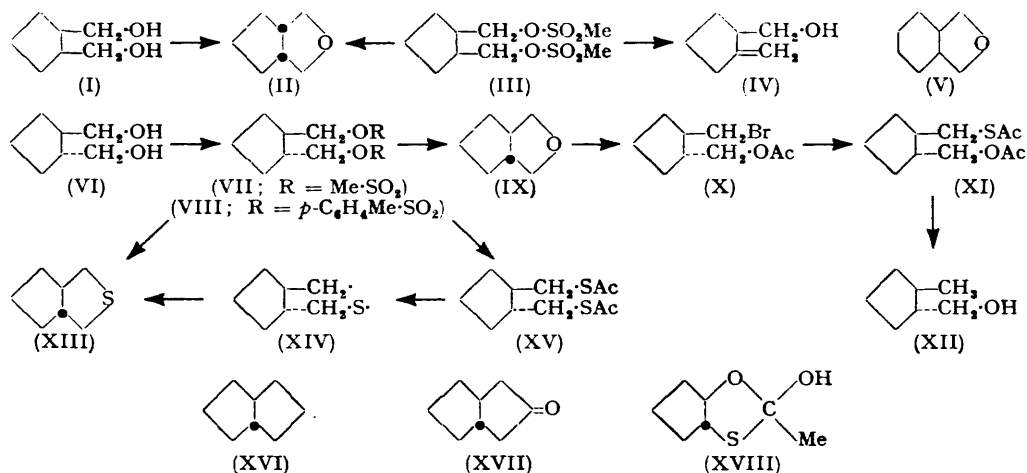
by-product from the interaction of *cis*-2-methyl*cyclo*hexylamine and nitrous acid, which they suggested might be one of the 2-methyl*cyclo*pentylmethanols, but the structure was not established. Nenitzescu and Vantu (*Bull. Soc. chim. France*, 1935, 2, 2209), by reduction of ethyl 2-methyl*cyclo*pentanecarboxylate with sodium and alcohol, prepared a 2-methyl*cyclo*pentylmethanol of undetermined configuration (no crystalline derivatives were described). The physical constants indicate that their product was probably mainly the *trans*-form, as would be expected on stereochemical grounds, this being less hindered than the *cis*-isomer. This conclusion is supported by a comparison of the properties of their

1 : 2-dimethyl*cyclo*pentane (obtained by reduction of the bromide derived from the alcohol) with those of the pure stereoisomers described by Forziati and Rossini (*J. Res. Nat. Bur. Stand.*, 1949, **43**, 473).

Very recently, Pines and Hoffman (*J. Amer. Chem. Soc.*, 1954, **76**, 4417) have obtained *trans*-2-methyl*cyclo*pentylmethanol from *trans*-2-methyl*cyclo*pentanecarboxylic acid, the assignment of configuration being based on the conversion of the alcohol, through its toluene-*p*-sulphonate, into *trans*-1 : 2-dimethyl*cyclo*pentane. Our stereospecific synthesis of the alcohol, taken in conjunction with the latter correlation, provides an independent chemical proof of the configurations of the 1 : 2-dimethyl*cyclo*pentanes, hitherto founded only on physical data.

EXPERIMENTAL

*cyclo*Pentanone cyanohydrin was prepared from the ketone and liquid hydrogen cyanide, catalysed by the addition of a few drops of 60% aqueous potassium hydroxide, by Cook and Linstead's method (*J.*, 1934, 959), except that the mixture was kept at 0° for 14 hr. Distillation of the acidified product gave the hydroxy-nitrile, b. p. 122°/21 mm., n_D^{20} 1·4562, in 91% yield. The hydroxy-acid, obtained by hydrolysis (Meerwein and Unkel, *Annalen*, 1910, **376**, 152), gave ethyl 1-hydroxy*cyclo*pentanecarboxylate, b. p. 88°/15 mm., n_D^{16} 1·4510, in 80% yield by esterification with ethanol and sulphuric acid in benzene, with azeotropic removal of the water formed (cf. Cook and Linstead, *loc. cit.*).

Dehydration of *cyclo*pentanone cyanohydrin with thionyl chloride by Bauer and Cymerman's method (*J.*, 1950, 1826) gave 1-cyano*cyclo*pentene, b. p. 76—78°/39 mm., n_D^{17} 1·4730, in 84% yield, though the product always contained traces of halogen and sulphur (Found : S, 0·8%). With ethanol–sulphuric acid (Cook and Linstead, *loc. cit.*) it gave ethyl *cyclo*pent-1-enecarboxylate, b. p. 81—83°/20 mm., n_D^{20} 1·4598; this was also obtained by dehydration of ethyl 1-hydroxy*cyclo*pentanecarboxylate with phosphorus pentachloride (Cook and Linstead, *loc. cit.*), but the product, b. p. 87—89°/21 mm., n_D^{17} 1·4582, contained traces of halogen, and although the latter could be removed by heating with diethylaniline the yield of pure unsaturated ester was then low.

*cyclo*Pentane-1 : 2-*dicarboxylic Esters.*—To a boiling, stirred solution of potassium cyanide (15 g.) in water (30 c.c.), under reflux, ethyl *cyclo*pent-1-enecarboxylate (54·5 g.) in ethanol (200 c.c.) and potassium cyanide (25 g.) in water (50 c.c.) were simultaneously added during 1 hr. (cf. Aspinall and Baker, *J.*, 1950, 743). Heating was continued for 7 hr., then potassium hydroxide (36 g.) was added and the mixture was boiled for a further 6 hr. The solution was cooled, acidified with concentrated hydrochloric acid (120 c.c.), and steam-distilled to remove unsaturated acid, which was recovered from the distillate by ether-extraction and re-esterified for further use. The *trans*-dicarboxylic acid slowly separated from the undistilled portion, and on recrystallisation from water gave 37·5 g. (61%), m. p. 161° (Aspinall and Baker, *loc. cit.*, obtained 44%). With methanol–sulphuric acid it gave the methyl ester (77%), b. p. 115°/12 mm., n_D^{20} 1·4491, and with ethanol–toluene-*p*-sulphonic acid–carbon tetrachloride (azeotropic removal of water) the ethyl ester (86%), b. p. 248°/770 mm., 133°/17 mm., n_D^{15} 1·4451.

A solution of the *trans*-acid (22 g.) in acetic anhydride (250 c.c.) was boiled under reflux for 3 hr. and then concentrated under reduced pressure. Distillation of the residue through a short Fenske column gave the *cis*-anhydride (11·8 g.), b. p. 100—102°/1·5 mm., which solidified and on recrystallisation from light petroleum (b. p. 40—80°) gave large plates, m. p. 72°. Brief alkaline hydrolysis gave the *cis*-acid, m. p. 134—135°, which with diazomethane in dry ether gave the *methyl ester* (96%), b. p. 129°/20 mm., n_D^{20} 1·4528 (Found : C, 58·4; H, 7·75. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%).

1 : 2-*Bishydroxymethyl*cyclo*pentane.*—(i) A solution of dimethyl *cis-cyclo*pentane-1 : 2-dicarboxylate (7·7 g.) in dry ether (75 c.c.) was slowly added (20 min.) to a stirred solution of lithium aluminium hydride (2·6 g.) in dry ether (150 c.c.) at 0°. Stirring was maintained for a further hour at 0°, water and 10% sulphuric acid were then cautiously added until no solid remained, and the ether layer was removed; the aqueous portion was continuously extracted with ether for 24 hr. Evaporation of the dried (K_2CO_3) extracts and distillation of the residue gave cis-1 : 2-*bishydroxymethyl*cyclo*pentane* (5·1 g., 95%), b. p. 103°/0·15 mm., n_D^{21} 1·4840 (Found : C, 64·7; H, 10·9. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8%).

(ii) Similar reductions of the *trans*-dimethyl and the *trans*-diethyl esters gave the *trans*-diol, b. p. 147°/11 mm., 100°/0·02 mm., n_D^{22} 1·4760 (Found : C, 64·5; H, 10·8%). Halford and Weissmann (*loc. cit.*) give b. p. 117—118°/0·6 mm., n_D^{25} 1·4480. Bailey and Sorenson (*loc. cit.*) give b. p. 127—129°/2·4 mm., n_D^{25} 1·4771.

Derivatives of the cis-*Diol.*—The cis-diol (1 g.) and toluene-*p*-sulphonyl chloride (4·5 g.) in pyridine (10 c.c.) at 0° gave the cis-*ditoluene*-p-*sulphonate* (2·5 g.), which crystallised from methanol in fluffy needles, m. p. 82° (Found : C, 57·75; H, 6·4; S, 14·4. $C_{21}H_{26}O_6S_2$ requires C, 57·5; H, 6·0; S, 14·6%).

Addition of a solution of the cis-diol (9·7 g.) in pyridine (40 c.c.) to methanesulphonyl chloride (21 g.) in pyridine (60 c.c.) gave in the same way the cis-*dimethanesulphonate* (18·7 g.), m. p. 59° (from aqueous methanol) (Found : C, 37·9; H, 6·4; S, 22·0. $C_9H_{18}O_6S_2$ requires C, 37·8; H, 6·4; S, 22·4%). Reversed addition of the reagents gave a much lower yield of the derivative, accompanied by the cyclic oxide (see below).

Reaction of the cis-diol·(0·15 g.) with α-naphthyl *iso*cyanate (0·46 g.) for 1 hr. at 100° gave the cis-*bis*-α-*naphthylurethane*, m. p. 149° (from aqueous ethanol) (Found : C, 73·8; H, 6·3; N, 6·1. $C_{29}H_{28}O_4N_2$ requires C, 74·3; H, 6·0; N, 6·0%).

Derivatives of the trans-*Diol.*—By the methods used for the cis-derivatives there were obtained the trans-*ditoluene*-p-*sulphonate* (87%), thick needles (from methanol), m. p. 64° (Found : C, 57·6; H, 6·2; S, 14·3%); the trans-*dimethanesulphonate* (85%), needles (from methanol), m. p. 60° (Found : C, 38·05; H, 6·5; S, 22·5%), depressed to 52—54° on admixture with the cis-isomer; and the trans-*bis*-α-*naphthylurethane* (40%), m. p. 155° [from benzene–petroleum (b. p. 60—80°)] (Found : C, 74·5; H, 6·2; N, 5·9%).

trans-1 : 2-*Di*(*acetylthiomethyl*)cyclo*pentane*.—The *trans*-ditoluene-*p*-sulphonate (6 g.), potassium thiolacetate (4·7 g.), thiolacetic acid (0·1 c.c.), and ethanol (60 c.c.) were boiled together under reflux for 4 hr. The solvent was then removed under reduced pressure and the residue was shaken with water and chloroform. The chloroform solution was washed, dried, and concentrated; distillation of the residue gave the trans-*bisthiolacetate* (2·9 g., 86%), b. p. 116—118°/0·05 mm., n_D^{21} 1·5297 (Found : C, 53·7; H, 7·3; S, 26·1. $C_{11}H_{18}O_2S_2$ requires C, 53·65; H, 7·4; S, 26·0%).

Comparative Dehydrations of the Stereoisomeric 1 : 2-*Bishydroxymethylcyclopentanes.*—(i) A solution of the cis-diol (55 mg.) in 18% aqueous sulphuric acid (0·3 c.c.) was kept at 100°. After 5 min. a strong odour of cyclic oxide was present; no unsaturation could be detected even after 4 hours' heating. In an identical experiment with the *trans*-diol, no odour of oxide could be detected; after 4 hr. the solution was unsaturated towards neutral permanganate.

(ii) A mixture of cis-diol (40 mg.) and dried alumina (150 mg.) was slowly heated to 210° (oil-bath); a strong odour of the cyclic oxide was evident. No oxide could be detected in a similar experiment with the *trans*-diol.

cis-3-*Oxabicyclo*[3 : 3 : 0]*octane*.—(i) The cis-diol (9·4 g.) and 18% aqueous sulphuric acid (50 c.c.) were boiled together under reflux for 20 min., and the mixture was then distilled until no more oil was present, water being gradually added to the distillation flask to maintain the volume. The distillate was extracted with ether to give an oil, which on distillation furnished cis-3-oxabicyclo[3 : 3 : 0]octane (6·15 g., 76%), b. p. 149°, n_D^{20} 1·4590 (Found : C, 74·8; H, 10·8. $C_7H_{12}O$ requires C, 75·0; H, 10·8%); the compound has a characteristic camphoraceous odour.

(ii) Methanesulphonyl chloride (34 g.) was slowly added (1 hr.) to a solution of the cis-diol (15·6 g.) in pyridine (85 c.c.) at 0°. The mixture was set aside at 0° overnight and then diluted with ice and water; the precipitated oil partly crystallised. The solid (4·9 g.) was collected, and on recrystallisation gave the cis-dimethanesulphonate (4·3 g.), m. p. 59°. The oil was taken up in ether, and the aqueous portion was extracted with ether. The combined extracts were washed successively with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water, and were dried (Na_2SO_4) and evaporated. Distillation of the residue gave a fraction (1·5 g.), b. p. 60—80°/20 mm., which on redistillation over sodium gave the cis-oxide, n_D^{25} 1·4600 (Found : C, 74·7; H, 10·6%).

(iii) A suspension of the cis-dimethanesulphonate (17 g.) in 15% aqueous potassium hydroxide (180 c.c.) was vigorously boiled under reflux for 2 hr. The condenser was then rearranged for distillation, and boiling was continued until no more oil was collected in the distillate. The latter was extracted with ether, and distillation of the product gave fractions (4·9 g., 74%), b. p. 152—167°, n_D^{18} 1·4623—1·4772, which, although containing much cis-oxide (odour), were unsaturated to bromine water. A portion (0·1 g.) of the highest-boiling fraction was ozonised in ethyl acetate (3 c.c.), the exit gases being passed through water; this solution, together with the distillate obtained by steam-distillation of the ozonolysis product, on treatment with dimedone gave the formaldehyde derivative (9 mg.), m. p. and mixed m. p. 188°. The usual 30—35% recovery of formaldehyde from a ⋮CH_2 group being assumed, the yield corresponds to the presence of *ca.* 10% of 2-methylenecyclopentylmethanol.

trans-3-*Oxabicyclo*[3 : 3 : 0]*octane*.—Reaction of the *trans*-dimethanesulphonate (10·5 g.)

with boiling 18% aqueous potassium hydroxide (70 c.c.) for $1\frac{1}{2}$ hr., followed by working-up as described for the similar reaction with the *cis*-isomer, gave trans-3-*oxa*bicyclo[3 : 3 : 0]*octane* (2·75 g., 67%), b. p. 158°, n_D^{23} 1·4631 (Found : C, 74·7; H, 10·9%). The product was free from unsaturated material; it had a strong odour, similar to that of the *cis*-compound.

cis-3-*Thia*bicyclo[3 : 3 : 0]*octane*.—A solution of sodium sulphide nonahydrate (3 g.) in water (4 c.c.) was added to a solution of the *cis*-ditoluene-*p*-sulphonate (1·95 g.) in hot ethanol (5 c.c.). The mixture was boiled under reflux for 30 min., then diluted with water (20 c.c.) and distilled, more water being added as required. The first portion of the distillate, mainly alcoholic, was clear, and was reserved. The distillate then became cloudy, and it was collected until it became clear again ; extraction of this aqueous fraction with ether, followed by evaporation of the washed and dried (K₂CO₃) extracts, and distillation of the residue, gave cis-3-*thia*bicyclo[3 : 3 : 0]*octane* as a colourless oil (0·25 g.), b. p. 180—184°, n_D^{21} 1·5218 (Found: C, 65·6; H, 9·7; S, 25·0. C₇H₁₂S requires C, 65·6; H, 9·4; S, 25·0%), with a powerful and characteristically sulphurous odour.

To the alcoholic portion of the original distillate, a warm saturated solution of mercuric chloride in ethanol was added until no more solid was precipitated. The *adduct* was collected, washed with ethanol, and recrystallised from ethanol to give white felted needles (0·81 g.), m. p. 163—164° (Found : C, 21·3; H, 3·3; S, 7·3; Cl, 17·4. C₇H₁₂S,HgCl₂ requires C, 21·0; H, 3·0; S, 8·0; Cl, 17·7%).

Oxidation of the cyclic sulphide (0·15 g.) in acetic acid (0·5 c.c.) by the addition of 30% hydrogen peroxide (0·5 c.c.) was exothermic. The hot solution was evaporated on the steam-bath to a solid residue, which on recrystallisation from water gave the cis-*sulphone* as long needles, m. p. 70° (Found : C, 52·2; H, 7·7; S, 19·6. C₇H₁₂O₂S requires C, 52·5; H, 7·55; S, 20·0%).

trans-3-*Thia*bicyclo[3 : 3 : 0]*octane*.—(i) Reaction of the *trans*-ditoluene-*p*-sulphonate (1·8 g.) in ethanol (10 c.c.) with sodium sulphide nonahydrate (3 g.) in water (4 c.c.) was carried out as for the *cis*-compound. The cloudy aqueous portion of the distillate on extraction gave trans-3-*thia*bicyclo[3 : 3 : 0]*octane* (0·3 g.), b. p. 190—195°, which solidified in colourless needles, m. p. 29°, n_D^{21} 1·5233 (Found : C, 66·0; H, 9·5; S, 24·5%), somewhat volatile at room temperature, and possessing an odour similar to that of the *cis*-isomer.

The alcoholic portion of the original distillate gave the mercuric chloride adduct, long white needles, m. p. 181—182° (from ethanol) (Found : C, 21·4; H, 3·2; S, 8·0%).

Oxidation of the cyclic sulphide with hydrogen peroxide gave the trans-*sulphone*, fine needles, m. p. 120° (from water) (Found : C, 52·1; H, 7·5; S, 19·6%).

(ii) *trans*-1 : 2-Bisacetylthio*cyclo*pentane (5·9 g.), sodium hydroxide (5 g.), and water (25 c.c.) were stirred at 75° for 4 hr. under nitrogen. More alkali (5 g.) in water (10 c.c.) was added, and the mixture was boiled under reflux for 4 hr.; it was then homogeneous. Moist Raney nickel (*ca.* 30 g.) was added in small portions during 5 hr. at 75°; no free thiol could then be detected. The solution was then slowly distilled; considerable difficulty was experienced owing to frothing, and it was necessary to redistil the distillate. The first fraction (*ca.* 5 c.c.), containing oily drops in suspension, was saturated with potassium carbonate, and the upper layer was removed, dried (Na), and distilled to give (i) (probably) crude *trans*-1 : 2-dimethyl*cyclo*pentane (50 mg.), b. p. up to 98°, n_D^{20} 1·4185 (last drop, n_D^{20} 1·4240), which had a slight odour of the cyclic sulphide, and (ii) a less volatile oil, having a powerful odour of cyclic sulphide, which crystallised in the side-arm and had m. p. 28°, not depressed on admixture with the synthetic *trans*-sulphide.

Further distillation of the aqueous solution gave fractions which were cloudy and odorous; when stored at 0° they deposited needles which were collected and converted into the mercuric chloride adduct, m. p. 178° (Found : C, 21·3; H, 3·3; S, 7·95%). Repeated recrystallisation failed to raise the m. p. to that of the synthetic *trans*-compound, though the crystalline form was similar to that of the latter, and quite distinct from that of the *cis*-adduct.

Infrared Spectra.—Copies of the spectra of the *cis*- and the *trans*-sulphide have been deposited with the Chemical Society. Photocopies (prince 3*s*. 0*d*. each) may be obtained from the General Secretary on application, quoting C.S. nos. 213 (*cis*) or 214 (*trans*).

2-Bromomethyl*cyclo*pentylmethyl *Acetate*.—(i) Freshly distilled acetyl bromide (8·4 g.) was added to cis-3-*oxa*bicyclo[3 : 3 : 0]octane (6·3 g.; prepared by the method of direct dehydration); there was only a slow rise in temperature, and the mixture was therefore heated at 100° for 25 min. The liquid, which had become pale brown, was cooled, poured into ice-water, and extracted with chloroform. Evaporation of the washed (aqueous sodium hydrogen carbonate) and dried (Na₂SO₄) extracts, and distillation of the residue gave cis-2-*bromomethylcyclopentyl-methyl acetate* as a colourless oil (11·6 g., 88%), b. p. 96°/1 mm., n_D^{20} 1·4899 (Found : C, 45·95; H, 6·6; Br, 33·3. C₉H₁₅O₂Br requires C, 46·0; H, 6·4; Br, 34·0%). Use of a slightly impure

cyclic oxide (prepared from the *cis*-dimethanesulphonate) resulted in a vigorous reaction on addition to the acetyl bromide, and the product obtained, b. p. 96—98°/2 mm., n_D^{22} 1·4900, was not quite pure (Found : C, 45·6; H, 6·7; Br, 36·1%).

(ii) A similar reaction between the *trans*-oxide (3·5 g.) and acetyl bromide (4·3 g.) gave trans-2-*bromomethylcyclopentylmethyl acetate* (4·8 g., 65%), b. p. 98°/1·5 mm., n_D^{18} 1·4861 (Found : C, 45·9; H, 6·6; Br, 34·15%).

1 : 2-*Bisacetoxymethylcyclopentane.*—(i) *trans*-2-Bromomethyl*cyclo*pentylmethyl acetate (1·1 g.), fused potassium acetate (2 g.), and dry ethanol (21 c.c.) were boiled together under reflux for 18 hr. The solvent was removed under reduced pressure, and the residue was treated with water and ether. The ethereal extract gave a product which still contained halogen, and the oil was therefore mixed with silver acetate (3 g.) and acetic acid (10 c.c.) and boiled under reflux for 3 hr. Working up as before gave the *trans*-diacetate (0·35 g.), b. p. 104°/1 mm., n_D^{24} 1·4522 (Found : C, 61·3; H, 8·5. Calc. for $C_{11}H_{18}O_4$: C, 61·7; H, 8·45%). Bailey and Sorenson (*loc. cit.*) give b. p. 116°/2 mm., n_D^{25} 1·4471. The product was added to methanolic sodium methoxide (20 c.c., containing 0·1 g. of sodium), and the solution was boiled for 90 min., then neutralised with carbon dioxide and evaporated to dryness. Treatment of the residue with toluene-*p*-sulphonyl chloride and pyridine gave the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 64°.

(ii) *cis*-2-Bromomethyl*cyclo*pentylmethyl acetate (1·4 g.) and potassium acetate (3·1 g.), in boiling acetic acid (25 c.c.) for 12 hr., gave a halogen-containing product which was treated further with silver acetate, as described above. The crude *cis*-diacetate (0·4 g.), b. p. 107—111°/2 mm., n_D^{20} 1·4525 (Found : C, 62·5; H, 8·6%), was deacetylated with methanolic sodium methoxide and the diol characterised as the *cis*-ditoluene-*p*-sulphonate, which after purification by chromatography on magnesium trisilicate had m. p. 78—79°, mixed m. p. 80°; the yield was very poor.

2-*Acetylthiomethylcyclopentylmethyl Acetate.*—(i) A solution of *cis*-2-bromomethyl*cyclo*pentylmethyl acetate (9·0 g.), potassium thiolacetate (9·0 g.), and thiolacetic acid (0·1 g.) in ethanol (90 c.c.) was boiled under reflux for 30 min. under nitrogen. The product still contained halogen, and was combined with that from a similar reaction (on 3·5 g. of bromide acetate) and treated for 2 hr. with potassium thiolacetate (5 g.) in boiling ethanol (75 c.c.). The solvent was removed under reduced pressure, and the residue was shaken with water and extracted with chloroform to give cis-2-*acetylthiomethylcyclopentylmethyl acetate* (10·2 g.), b. p. 92—94°/0·0003 mm., n_D^{13} 1·5012 (Found : C, 57·2; H, 8·0; S, 13·6. $C_{11}H_{18}O_3S$ requires C, 57·4; H, 7·9; S, 13·9%).

(ii) Reaction of *trans*-2-bromomethyl*cyclo*pentylmethyl acetate (4·6 g.) with potassium thiolacetate (3·0 g.) and thiolacetic acid (0·1 c.c.) in boiling ethanol for 1¼ hr. gave, when worked up as above, trans-2-*acetylthiomethylcyclopentylmethyl acetate* (3·85 g., 85%), b. p. 129°/1 mm., n_D^{22} 1·4902 (Found : C, 57·4; H, 8·2; S, 13·65%).

2-*Methylcyclopentylmethanol.*—(i) Freshly prepared Raney nickel (*ca.* 30 g.) was added in portions to a boiling solution of *cis*-2-acetylthiomethyl*cyclo*pentylmethyl acetate (7·4 g.) in boiling ethanol (100 c.c.). After 5 hr. no thiol or thiolacetate could be detected, and the solution was filtered. Sodium hydroxide (2·5 g.) was added, and the solution was boiled for 2 hr. and then concentrated to small bulk. The residue was diluted with water and extracted with ether to give cis-2-*methylcyclopentylmethanol* (2·2 g.), b. p. 114°/78 mm., n_D^{17} 1·4632 (Found : C, 73·6; H, 12·0. $C_7H_{14}O$ requires C, 73·6; H, 12·35%). The 3 : 5-*dinitrobenzoate* crystallised from methanol in flakes, m. p. 66—67° (Found : C, 54·7; H, 5·2; N, 9·3. $C_{14}H_{16}O_6N_2$ requires C, 54·55; H, 5·2; N, 9·1%); the *phenylurethane* formed felted needles, m. p. 64°, from light petroleum (b. p. 40—60°) (Found : C, 72·2; H, 8·0; N, 6·3. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2; N, 6·0%); and the *α-naphthylurethane*, needles, m. p. 92° [from light petroleum (b. p. 60—80°)] (Found : C, 76·6; H, 7·6; N, 5·1. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·5; N, 4·9%).

(ii) Similar treatment of *trans*-2-acetylthiomethyl*cyclo*pentylmethyl acetate (3·6 g.) gave *trans*-2-methyl*cyclo*pentylmethanol (0·85 g.), b. p. 110—111°/81 mm., n_D^{18} 1·4531 (Found : C, 73·1; H, 12·45%). The 3 : 5-*dinitrobenzoate* formed small plates [from light petroleum (b. p. 60—80°)], m. p. 56° (Found : C, 54·8; H, 5·4; N, 9·1%); and the *α-naphthylurethane*, felted needles, m. p. 98° [from light petroleum (b. p. 60—80°)] (Found : C, 76·2; H, 7·6; N, 5·1%).

Nenitzescu and Vantu (*loc. cit.*) give b. p. 171—172°/758 mm., n_D^{20} 1·4512, for their alcohol of unknown configuration. Pines and Hoffman (*loc. cit.*) give b. p. 103°/53 mm., n_D^{20} 1·4533 (α-naphthylurethane, m. p. 98·5—99·5°).

Added in Proof.—Professor Pines has very kindly provided us with a sample of his carbinol;

the α-naphthylurethane prepared from it is identical (m. p. and mixed m. p.) with our *trans*-derivative of m. p. 98°. The trans-*phenylurethane*, which earler had failed to crystallise, subsequently solidified and from a concentrated solution in light petroleum (b. p. 40—60°) formed nodules, m. p. 47—48° (Found : C, 71·9 ; H, 8·1 ; N, 6·2%) ; it follows that the alcohol obtained by Anziani and Cornubert (*loc. cit.*) (phenylurethane, m. p. 92—94°), was not a 2-methyl-*cyclo*pentylmethanol.

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