770. *Alicyclic Glycols. Part VI.* Derivatives of* cyclo*Pentane-1 : 2-diol.*

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The following derivatives of the *trans*-diol are prepared by reaction of *cyclo*pentene oxide with the appropriate acid: *trans*-2-chloro-, -2-bromo-, -2-iodo-, -2-acetoxy-, -2-methanesulphonyloxy-, and -2-toluene-*p*-sulphonyloxy-*cyclo*pentanol. The monoacetate of the *cis*-diol is obtained by reaction of *trans*-2-toluene-*p*-sulphonyloxy*cyclo*pentyl acetate with alcoholic potassium acetate, according to the method used by Winstein in the *cyclo*hexane series. Reaction of the *trans*-monotoluene-*p*-sulphonate with sodium iodide, lithium bromide, or lithium chloride gives the *trans*-2-halogeno*cyclo*pentanol; *trans*-2-chloro*cyclo*pentanol is also obtained from the *cis*-monotoluene-*p*-sulphonate and lithium chloride. The steric results of these substitutions are the same as in the *cyclo*hexane field, and indicate that Winstein's neighbouring-group effect applies also to *cyclo*pentane compounds. Alkaline hydrolysis of the *trans*-monotoluene-*p*-sulphonate gives *cyclo*pentene oxide, and proceeds several hundred times faster than with the *cis*-isomer, which gives *cyclo*pentanone; both derivatives are considerably more reactive than their *cyclo*hexane analogues.

The participation of toluene-*p*-sulphonyl and methanesulphonyl derivatives of *cyclo*hexane-1 : 2-, -1 : 3-, and -1 : 4-diols in substitution and elimination reactions has been described in earlier publications in this series (Clarke and Owen, *J.*, 1949, 315; 1950, 2103; Owen and Robins, *J.*, 1949, 320). In this and the following paper the preparation and reactions of derivatives of *cyclo*pentane-1 : 2- and -1 : 3-diols will be considered, and their behaviour compared with that of their *cyclo*hexane analogues.

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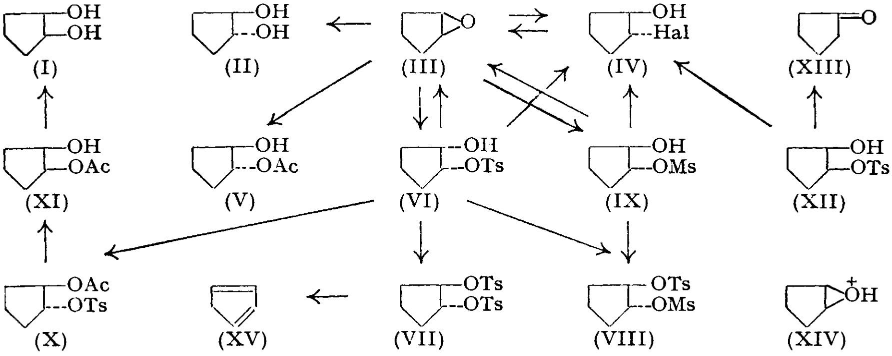
* Part V, Clarke and Owen, *J.*, 1950, 2108.

The liquid *cis*- (I) and the solid *trans*-forms (II) of *cyclo*pentane-1 : 2-diol have been known for many years, and their configurations are established (see, *inter al.*, Böesken, *Rec. Trav. chim.*, 1928, **47**, 683; Helferich and Hiltmann, *Ber.*, 1937, **70**, 308). In the present investigation, the use of performic acid (cf. Swern, Billen, Findley, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 1786) for the hydroxylation of *cyclo*pentene gave the *trans*-diol in 64% yield; with peracetic acid only 37% was attained. The *cis*-diol was prepared by low-temperature hydroxylation of *cyclo*pentene with neutral aqueous potassium permanganate; the mild conditions resulted in a higher yield (34%) than has previously been recorded (cf. Böeseken, *loc. cit.*). Other methods of *cis*-hydroxylation also studied were the interaction of *cyclo*pentene with (i) anhydrous hydrogen peroxide in *tert.*-butanol in the presence of osmic acid (cf. Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302), and (ii) aqueous sodium chlorate with osmic acid as catalyst (cf. Milas and Terry, *ibid.*, 1925, **47**, 1412; Milas, *ibid.*, 1927, **49**, 2005), but the yields under the usual conditions were 2·5% and nil, respectively, in marked contrast to the results obtained with *cyclo*hexene, 58% and 44% respectively (*idem, ibid.*, 1937, **59**, 2345; Clarke and Owen, *J.*, 1949, 315).

Treatment of *cis*- and *trans*-*cyclo*pentane-1 : 2-diol with excess of toluene-*p*-sulphonyl chloride or methanesulphonyl chloride in pyridine gave the *cis*- and the *trans*-ditoluene-*p*-sulphonate and dimethanesulphonate, all four derivatives being solid. The *cis*- and the *trans*-dimethanesulphonate had identical melting points (82°), but showed marked depression on admixture.

For the preparation of mono-derivatives of a *trans*-diol, the most convenient method is often the fission of the corresponding epoxide with an appropriate reagent. The necessary *cyclo*pentene oxide (III) was prepared by dehydrohalogenation of the *trans*-chlorohydrin (IV) obtained by addition of hypochlorous acid to *cyclo*pentene; only a small amount of the *cis*-chlorohydrin is formed in the latter reaction (Godchot, Mousseron, and Granger, *Compt. rend.*, 1935, **200**, 748). Attempts to prepare the *cis*-chlorohydrin by reduction of 2-chloro*cyclo*pentanone with *tert.*-butylmagnesium chloride, following the method used by Bartlett and Rosen (*J. Amer. Chem. Soc.*, 1935, **57**, 224) for the *cyclo*hexane analogue, were unsuccessful. Reduction of 2-chloro*cyclo*pentanone with aluminium *iso*propoxide in *iso*propyl alcohol gave a mixture of *cyclo*pentanol and *cis*-2-chloro*cyclo*pentanol. In the corresponding reduction of 2-chloro*cyclo*hexanone, Mousseron and Combes (*Bull. Soc. chim.*, 1947, 604) obtained *cyclo*hexanol together with *cis*- and *trans*-2-chloro*cyclo*hexanol.



(Ts = p-$C_6H_4Me{\cdot}SO_2^-$; Ms = $Me{\cdot}SO_2^-$)

Stereochemically pure *trans*-2-halogeno*cyclo*pentanols were prepared by reaction of *cyclo*pentene oxide with anhydrous hydrogen chloride, bromide, and iodide, in ether. Each halogenohydrin gave a crystalline *p*-nitrobenzoate, and also reacted readily with aqueous alkali (or aqueous silver nitrate in the case of the iodohydrin) to give *cyclo*pentene oxide. Whilst the *trans*-chlorohydrin had previously been characterised, the bromo- and iodo-compounds were hitherto ill-defined and no solid derivatives had been reported.

Reaction of *cyclo*pentene oxide with acetic acid at 100° gave a 40% yield of the *trans*-

monoacetate (V), which was also obtained (yield 17%) by reaction of peracetic acid with *cyclo*pentene.

Criegee and Stanger (*Ber.*, 1936, **69**, 2753) obtained a 10% yield of a liquid toluene-*p*-sulphonate, which was not identified, by treatment of *cyclo*pentene oxide with toluene-*p*-sulphonic acid in ether. Under apparently similar conditions we have obtained a 69% yield of *trans*-*cyclo*pentane-1 : 2-diol monotoluene-*p*-sulphonate (VI), characterised by conversion into the crystalline *trans*-ditoluene-*p*-sulphonate (VII), *trans*-methanesulphonate toluene-*p*-sulphonate (VIII), and *trans*-benzoate toluene-*p*-sulphonate. The *trans*-monomethanesulphonate (IX) was prepared in 59% yield by reaction of the oxide with ethereal methanesulphonic acid; it was characterised by conversion into the *trans*-dimethanesulphonate and into (VIII).

Mono-derivatives of the *cis*-diol were more difficult to obtain. Attempted monoacetylation, by the gradual addition of 1 mol. of acetic anhydride to a dilute solution of the diol in pyridine at 0°, gave a mixture, containing some diacetate, which could not easily be separated. Winstein, Hess, and Buckles, however, have shown (*J. Amer. Chem. Soc.*, 1942, **64**, 2796) that the acetate toluene-*p*-sulphonate of *trans*-*cyclo*hexane-1 : 2-diol, on treatment with potassium acetate in ethanol, gives the *cis*-monoacetate, this steric result being due to the intermediate formation of a cyclic ethyl orthoacetate. The *trans*-monotoluene-*p*-sulphonate (VI) was therefore acetylated to give (X), which when treated with boiling alcoholic potassium acetate gave the pure *cis*-monoacetate (XI) in 44% yield; the configuration was proved by deacetylation to the *cis*-diol (I) and characterisation of the latter.

The monosulphonates of *cis*-*cyclo*hexane-1 : 2-diol had been obtained (Clarke and Owen, *J.*, 1949, 315) by toluene-*p*-sulphonation or methanesulphonation of the *cis*-monoacetate, followed by deacetylation with methanolic hydrogen chloride. This procedure was therefore applied to the *cis*-monoacetate (XI), but as neither the *cis*-acetate toluene-*p*-sulphonate nor the deacetylated material could be crystallised or distilled the *cis*-monotoluene-*p*-sulphonate was not obtained pure. A more satisfactory method was the treatment of a pyridine solution of the *cis*-diol with 1 mol. of toluene-*p*-sulphonyl chloride in chloroform, added over a period of 3 days; this gave the pure mono-derivative (XII) in 40% yield. Under these conditions, also, the *trans*-monotoluene-*p*-sulphonate (VI) was prepared from the *trans*-diol in 56% yield; for this derivative, however, the route *via* the oxide is more convenient. The *cis*-compound (XII) was characterised by conversion into the crystalline *cis*-ditoluene-*p*-sulphonate and *cis*-benzoate toluene-*p*-sulphonate.

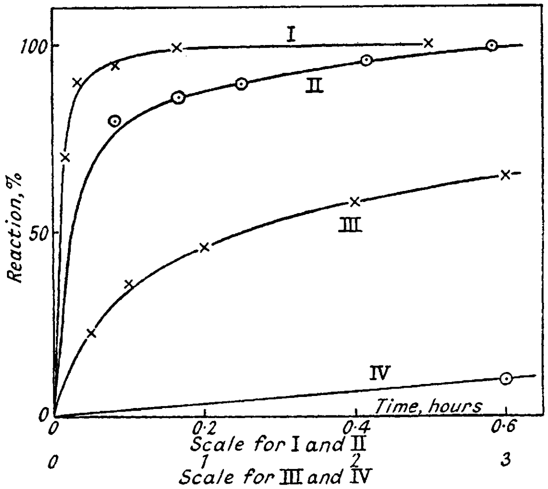
trans-*cyclo*Pentane-1 : 2-diol monotoluene-*p*-sulphonate (VI) reacted readily with sodium iodide in boiling acetone, and a 46% yield of *trans*-2-iodo*cyclo*pentanol (IV) was obtained; the monomethanesulphonate behaved similarly. These results are in striking contrast to those obtained with the monosulphonates of *cyclo*hexane-1 : 2-diol (Clarke and Owen, *loc. cit.*), which required more vigorous treatment and gave only a very poor yield of 2-iodo*cyclo*hexanol. Although unsaturated products were also formed in both series, the proportion of substitution to elimination is much greater with the *cyclo*pentane derivatives, though it is possible that this is due only to a difference in stability between the two iodohydrins.

Substitution by bromine was carried out by the use of lithium bromide in boiling ethanol. The *trans*-mono-methanesulphonate and -toluene-*p*-sulphonate gave *trans*-2-bromo*cyclo*pentanol in 38% and 45% yield respectively. With boiling alcoholic lithium chloride the yields of *trans*-2-chloro*cyclo*pentanol were 50% and 56% respectively, slightly lower than those of *trans*-2-chloro*cyclo*hexanol from the corresponding *cyclo*hexane derivatives; the proportion of substitution product is therefore approximately the same in both series for this particular reagent. The *cis*-monotoluene-*p*-sulphonate (XII) also reacted with lithium chloride to give the *trans*-chlorohydrin (IV) and *cyclo*pentanone (XIII).

The steric results of these substitution reactions are the same as in the *cyclo*hexane series, and although Winstein and his collaborators have not studied any *cyclo*pentane compounds in their investigations of the neighbouring-group effect, it is very probable that their conclusions are equally applicable in this field. The retention of configuration in the reactions of the *trans*-monosulphonates of *cyclo*pentane-1 : 2-diol with halides can thus be interpreted as resulting from two successive inversions, one at the formation of a cyclic intermediate (XIV) and the second on fission of this by reaction with halide ion. With the *cis*-compound (XII), bimolecular substitution occurs directly, with consequent inversion to give the *trans*-chlorohydrin. Further evidence for the applicability of Winstein's reasoning to *cyclo*pentane derivatives is afforded by the successful preparation of the *cis*-monoacetate (XI) referred to above.

The *trans*-ditoluene-*p*-sulphonate (VII) was largely unaffected by treatment for 48 hours with sodium iodide in boiling acetone or lithium chloride in boiling ethanol, though a little *cyclo*pentadiene (XV) was detected in the latter reaction. This low reactivity compared with that of the mono-derivative can be attributed to the strong deactivation produced on one group by the electron-attracting effect of the other (cf. Winstein, Grunwald, and Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821).

Reactions of the sulphonates with alkali were studied qualitatively and quantitatively. The *trans*-monotoluene-*p*-sulphonate (VI) with aqueous sodium hydroxide gave *cyclo*pentene oxide (III) which was further hydrolysed to the *trans*-diol (II). The *cis*-derivative (XII) gave *cyclo*pentanone. These results are similar to those observed with the monotoluene-*p*-sulphonates of *cyclo*hexane-1 : 2-diol, except that in the latter the *trans*-derivative also gave some *cyclo*pentylformaldehyde, formed by ring-contraction; no such by-product (*cyclo*butylformaldehyde) was encountered in the present case. The *trans*-ditoluene-*p*-sulphonate with methanolic potassium hydroxide gave *cyclo*pentadiene (XV) as the only recognisable product. Quantitative experiments clearly indicated the differences in rate of reaction between the *cis*- and the *trans*-monotoluene-*p*-sulphonates (see Fig.). At a concentration of only 0·005M in 0·01N-alcoholic potassium hydroxide at 20°, the *trans*-compound had reacted to the extent of over 90% in 3 minutes, whereas the *cis*-isomer in a solution ten times as concentrated underwent 36% reaction in 30 minutes. In such circumstances, accurate kinetic measurements for the *trans*-compound were not possible, but a rough estimate showed that the second-order velocity constant was about 800 times that of the *cis*-isomer. In 50% aqueous dioxan the reaction, as would be expected, was even faster, being complete with the *trans*-monotoluene-*p*-sulphonate within one minute; the *trans*-monomethanesulphonate behaved similarly. This difference in reactivity between *cis*- and *trans*-monotoluene-*p*-sulphonates has been previously encountered with the *cyclo*hexane-1 : 2-diol derivatives, and the reaction curves for these (taken from Part I) are included in the Figure. Consideration of these relative rates of reaction also shows that the *cyclo*pentane compounds are considerably more reactive than their *cyclo*hexane analogues. This provides a further illustration of the parallelism between toluene-*p*-sulphonates and halides, since Mousseron (*Bull. Soc. chim.*, 1946, 610) has found that the unimolecular



I, *Monotoluene*-p-*sulphonate of* trans-cyclo*pentane*-1 : 2-*diol* (0·005 *mol./l.*) *in* 0·01N-KOH–MeOH (20°).

II, *Monotoluene*-p-*sulphonate of* trans-cyclo*hexane*-1 : 2-*diol* (0·05 *mol./l.*) *in* 0·1N-KOH–MeOH (17°).

III, *Monotoluene*-p-*sulphonate of* cis-cyclo*pentane*-1 : 2-*diol* (0·05 *mol./l.*) *in* 0·1N-KOH–MeOH (20°).

IV, *Monotoluene*-p-*sulphonate of* cis-cyclo*hexane*-1 : 2-*diol* (0·05 *mol./l.*) *in* 0·1N-KOH–MeOH (17°).

velocity constant for the solvolysis of *trans*-2-chloro*cyclo*pentanol is about 20 times greater than for *trans*-2-chloro*cyclo*hexanol. The same relative reactivity of the ring systems is also observed in the bimolecular reactions of *cyclo*pentyl and *cyclo*hexyl halides, and in the solvolysis of various alkyl*cyclo*pentyl and alkyl*cyclo*hexyl chlorides (Brown, Fletcher, and Johannesen, *J. Amer. Chem. Soc.*, 1951, **73**, 212; Brown and Borkowski, *ibid.*, 1952, **74**, 1894).

EXPERIMENTAL

*cyclo*Pentanone (*Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 192) was hydrogenated in alcoholic solution over Raney nickel at 70°/100 atm., to give *cyclo*pentanol (average yield, 75%). This was converted in 70% yield into *cyclo*pentene, b. p. 44—45°, by dehydration over phosphoric acid (*op. cit.*, Coll. Vol. II, p. 153).

trans-cyclo*Pentane*-1 : 2-*diol*.—A mixture of 30% aqueous hydrogen peroxide (13 g.) and formic acid (105 g.) was added to *cyclo*pentene (6·6 g.), much heat being generated. The temperature was allowed to fall to 40° and was so maintained for 4 hours. The formic acid was removed under reduced pressure, and the residue was dissolved in 10% aqueous sodium hydroxide (50 c.c.) and boiled under reflux for 45 minutes; water was then distilled off, and the residue twice distilled under reduced pressure, to give pure *trans-cyclo*pentane-1 : 2-diol (6 g., 60%), m. p. 50°, b. p. 93°/2 mm.

The di-*p*-nitrobenzoate, prepared in pyridine, had m. p. 140—141° (crude), raised on crystallisation from ethanol to 143° (lit., 145°).

Ditoluene-p-*sulphonate and Dimethanesulphonate of* trans-cyclo*Pentane*-1 : 2-*diol*.—Toluene-*p*-sulphonyl chloride (7·6 g.) in pyridine (20 c.c.) was added dropwise, during 1 hour, to a solution of the *trans*-diol (2 g.) in pyridine (20 c.c.), the temperature being kept at about 0° throughout the addition and for a further 20 hours. Most of the pyridine was then removed below 30° under reduced pressure, and the residue was treated with crushed ice, which precipitated the crude derivative, m. p. 103—104°. Recrystallisation from methanol gave colourless plates of pure *ditoluene*-p-*sulphonate* (5·3 g., 66%), m. p. 109° (Found: C, 55·4; H, 5·0; S, 15·6. $C_{19}H_{22}O_6S_2$ requires C, 55·6; H, 5·4; S, 15·6%).

Similar treatment of the *trans*-diol (1·85 g.) in pyridine (10 c.c.) with methanesulphonyl chloride (4·33 g.) in pyridine (10 c.c.) gave the *dimethanesulphonate* (3·90 g., 84%), small needles, m. p. 82° (from methanol) (Found: C, 32·7; H, 5·5; S, 24·8. $C_7H_{14}O_6S_2$ requires C, 32·6; H, 5·5; S, 24·8%).

cis-cyclo*Pentane*-1 : 2-*diol*.—A solution of *cyclo*pentene (21·8 g.) in ethanol (600 c.c.) was cooled to −40°, and a solution of potassium permanganate (40 g.) and anhydrous magnesium sulphate (30 g.) in water (800 c.c.) was added with vigorous stirring during 2 hours. The manganese dioxide was filtered off and thoroughly washed with hot water, and the combined filtrates were evaporated to *ca.* 100 c.c. and continuously extracted with ether for 48 hours. The dried ($MgSO_4$) extract was evaporated and distilled, to give *cis-cyclo*pentane-1 : 2-diol (11·1 g., 34%), b. p. 88—92°/2 mm., n_D^{21} 1·4770. The di-*p*-nitrobenzoate had m. p. 111—113° (crude), raised on crystallisation from ethanol to 117° (lit., 117—118°).

Ditoluene-p-*sulphonate and Dimethanesulphonate of* cis-cyclo*Pentane*-1 : 2-*diol*.—Toluene-*p*-sulphonyl chloride (5·3 g.) in pyridine (10 c.c.) was added to the *cis*-diol (1·4 g.) in pyridine (5 c.c.) at −10°, and the mixture was set aside at 0° overnight. The product was isolated as for the *trans*-compound described above; recrystallisation from methanol gave the cis-*ditoluene*-p-*sulphonate* as prisms (3·9 g., 69%), m. p. 92° (Found: C, 55·6; H, 5·1; S, 15·4%).

The cis-*dimethanesulphonate*, similarly prepared from *cis*-diol (1·15 g.) and methanesulphonyl chloride (2·7 g.) in pyridine (20 c.c.), crystallised from methanol in small plates (2·6 g., 89%), m. p. 82° (Found: C, 32·9; H, 5·7; S, 24·6%). A mixture with the *trans*-isomer, also of m. p. 82°, had m. p. *ca.* 64°.

2-*Chloro*cyclo*pentanol*.—Aqueous hypochlorous acid (*Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 158) was added dropwise with vigorous stirring to *cyclo*pentene (51 g.) in a 5-l. flask, maintained at 0°, until excess of hypochlorous acid was present. The product was steam-distilled from the aqueous suspension and extracted from the distillate with ether, to give 2-chloro*cyclo*pentanol (55·8 g., 61%), b. p. 88—90°/20 mm., n_D^{20} 1·4818. The procedure subsequently described in *Org. Synth.* (1950, **30**, 24) gives a yield of 52—56%.

Reduction of 2-*Chloro*cyclo*pentanone*.—Aluminium *iso*propoxide (20 g.) was dissolved in dry *iso*propyl alcohol (600 c.c.) and 2-chloro*cyclo*pentanone (16·5 g.) (Kötz, *Annalen*, 1913, **400**, 50) was added; the solution was heated on a steam-bath, and the acetone formed was removed by fractionation through a 6″ Fenske column. The reaction mixture became dark red and some solid separated. After being heated for 3½ hours it was cooled, and dilute hydrochloric acid (35 c.c. of concentrated acid and 175 c.c. of water) was added. Extraction with ether gave a colourless liquid (6 g.), b. p. 57—65°/15 mm., n_D^{19} 1·4683, which reduced aqueous potassium permanganate, contained chlorine, and gave no ketonic reactions. The product (2 g.) was treated with 2N-sodium hydroxide (10 c.c.); heat was evolved, but after the suspension had been shaken for 12 hours no *cyclo*pentene oxide could be detected. The product (1 g.) from this hydrolysis was identified as a mixture of *cyclo*pentanol (phenylurethane, m. p. and mixed m. p. 132°) and *cyclo*pentanone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 144—145°).

cyclo*Pentene Oxide*.—Rothstein's method (*Compt. rend.*, 1936, **209**, 761), involving the treatment of 2-chloro*cyclo*pentanol with aqueous sodium hydroxide, gave an emulsion which was difficult to break; furthermore, the method involves extraction of the oxide with ether, in which it is very volatile, thus making separation on a small scale difficult. For the preparation of amounts up to 10 g. the following procedure was satisfactory.

A vigorously stirred mixture of 2-chloro*cyclo*pentanol (15 g.) and potassium hydroxide (45 g.) in water (16 c.c.) was gradually heated to 140° in an oil-bath, the product, together with some water, being condensed and collected. The lower, aqueous layer of the distillate was saturated with potassium carbonate, and the *cyclo*pentene oxide was separated, dried (K_2CO_3), and distilled, to give 5·4 g. (52%), b. p. 102°, n_D^{16} 1·4370.

Reaction of cyclo*Pentene Oxide with Hydrogen Halides*.—(i) *Hydrogen chloride*. *cyclo*Pentene oxide (3·8 g.) in dry ether (20 c.c.) was cooled to 0° and 1·5N-ethereal hydrogen chloride (35 c.c.) was added dropwise with cooling, the reaction being very vigorous. After 5 hours at 0°, the excess of hydrogen chloride was removed with water and then saturated aqueous sodium hydrogen carbonate; evaporation of the dried (Na_2SO_4) solution gave *trans*-2-chloro*cyclo*pentanol (3·8 g., 70%), b. p. 78°/15 mm., n_D^{16} 1·4808. It gave *cyclo*pentene oxide when treated with aqueous alkali as described above.

The product (0·5 g.) was treated in dry pyridine (5 c.c.) with *p*-nitrobenzoyl chloride (0·80 g.), to give trans-2-*chloro*cyclo*pentyl* p-*nitrobenzoate* (0·9 g., 80%), m. p. (crude) 76°, unchanged on recrystallisation from ethanol from which it formed colourless needles (Found: C, 53·7; H, 4·7; N, 5·2. $C_{12}H_{12}O_4NCl$ requires C, 53·4; H, 4·5; N, 5·2%). The chlorohydrin was also characterised as the α-*naphthylurethane* which after recrystallisation from light petroleum (b. p. 100—120°) had m. p. 105° (Found: N, 4·9. $C_{16}H_{16}O_2NCl$ requires N, 4·8%).

trans-2-*Chloro*cyclo*pentyl Acetate*.—*trans*-2-Chloro*cyclo*pentanol (2·8 g.) was kept with acetic anhydride (2·4 g.) in pyridine (20 c.c.) for 60 hours at room temperature. The solution was then diluted with water and extracted with chloroform. The extracts were washed with 2N-sulphuric acid (five times), water (once), and saturated aqueous sodium hydrogen carbonate (once), and after being dried (Na_2SO_4) and evaporated they gave trans-2-*chloro*cyclo*pentyl* acetate (2·7 g., 70%), b. p. 83°/15 mm., n_D^{18} 1·4563 (Found: C, 51·3; H, 6·5. $C_7H_{11}O_2Cl$ requires C, 51·7; H, 6·8%).

(ii) *Hydrogen bromide*. Dry hydrogen bromide was passed through a solution of *cyclo*pentene oxide (4·0 g.) in dry ether (30 c.c.), cooled to 0°, until no more was absorbed. The product was worked up as described above, to give *trans*-2-bromo*cyclo*pentanol (5·8 g., 73%), b. p. 92°/15 mm., n_D^{20} 1·5162.

The bromohydrin (0·7 g.) in pyridine (5 c.c.) with *p*-nitrobenzoyl chloride (0·8 g.) gave trans-2-*bromo*cyclo*pentyl* p-*nitrobenzoate*, which after two recrystallisations from ethanol formed fine needles, 1·1 g. (81%), m. p. 98° (Found: C, 46·1; H, 3·9; N, 4·4. $C_{12}H_{12}O_4NBr$ requires C, 45·9; H, 3·9; N, 4·5%).

(iii) *Hydrogen iodide*. Dry hydrogen iodide was passed into a cooled solution of *cyclo*pentene oxide (2·6 g.) in dry ether (20 c.c.); much heat was evolved and iodine was liberated. The solution was washed with aqueous sodium thiosulphate and with aqueous sodium hydrogen carbonate, and evaporated, to give *trans*-2-iodo*cyclo*pentanol (1·5 g., 23%), b. p. 55—58°/0·2 mm., n_D^{20} 1·5670, as a yellow liquid, which gave the strong characteristic odour of *cyclo*pentene oxide when treated with aqueous silver nitrate.

Treatment of the iodohydrin (0·9 g.) in pyridine (5 c.c.) with *p*-nitrobenzoyl chloride (0·87 g.) gave trans-2-*iodo*cyclo*pentyl* p-*nitrobenzoate*, which crystallised from ethanol in plates (1·2 g., 80%), m. p. 108° (Found: C, 40·0; H, 3·4; N, 3·7. $C_{12}H_{12}O_4NI$ requires C, 39·9; H, 3·4; N, 3·9%).

Monoacetate of trans-cyclo*Pentane*-1 : 2-*diol*.—(i) Acetic acid did not react at room temperature with *cyclo*pentene oxide either in the absence of any other solvent or in ether, with or without a trace of concentrated sulphuric acid. Reaction occurred, however, when the oxide

(2·9 g.) was heated with glacial acetic acid (5 c.c.) at 100° for 15 hours. The excess of acid and unchanged oxide were distilled off, and the residue was distilled, to give the *monoacetate* (2·03 g., 40%), b. p. 93—97°/20 mm., n_D^{20} 1·4553 (Found: C, 58·3; H, 8·5. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%).

Treatment of a portion of this product with *p*-nitrobenzoyl chloride in pyridine gave the *acetate* p-*nitrobenzoate* of *trans-cyclo*pentane-1 : 2-diol, which crystallised from ethanol in microscopic needles, m. p. 80—81° (Found: C, 57·7; H, 5·2; N, 4·8. $C_{14}H_{15}O_6N$ requires C, 57·3; H, 5·2; N, 4·8%).

(ii) *cyclo*Pentene (5 g.) was slowly added, with cooling, to a solution containing peracetic acid, prepared from glacial acetic acid (35 g.) and 30% aqueous hydrogen peroxide (8 g.). After 16 hours at room temperature, the solution (which still had an odour of *cyclo*pentene) was carefully neutralised with aqueous sodium hydroxide, with cooling, and extracted with ether, to give the *trans*-monoacetate (1·8 g., 17%), b. p. 60—64°/0·2 mm., n_D^{23} 1·4575 (Found: sap. equiv., 147. Calc. for $C_7H_{12}O_3$: equiv., 144).

Monotoluene-p-*sulphonate of* trans-cyclo*Pentane*-1 : 2-*diol*.—A solution of *cyclo*pentene oxide (10 g.) in anhydrous ether (50 c.c.) was slowly added to a suspension of dry toluene-*p*-sulphonic acid (21 g.) in anhydrous ether (50 c.c.) at 0°; the acid dissolved during the addition. The solution was left for 16 hours at room temperature, and was then washed with water, dried (Na_2SO_4), and evaporated, finally at 0·2 mm., to give the *monotoluene*-p-*sulphonate* of *trans-cyclo*pentane-1 : 2-diol (21 g., 69%), n_D^{22} 1·5280 (Found: S, 11·9. $C_{12}H_{16}O_4S$ requires S, 12·5%), as a pale yellow viscous liquid. On treatment with toluene-*p*-sulphonyl chloride in pyridine it gave the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 109°.

The trans-*benzoate toluene*-p-*sulphonate*, prepared in 67% yield by reaction of the monotoluene-*p*-sulphonate (1 g.) with benzoyl chloride (0·55 g.) in pyridine (10 c.c.), crystallised from methanol in long needles, m. p. 113—114° (Found: C, 63·2; H, 5·7; S, 8·8. $C_{19}H_{20}O_5S$ requires C, 63·3; H, 5·6; S, 8·9%).

Treatment of the monotoluene-*p*-sulphonate (0·63 g.) in pyridine (3 c.c.) with methanesulphonyl chloride (0·28 g.) for 2 hours at 0°, followed by dilution with water, precipitated the trans-*methanesulphonate toluene*-p-*sulphonate* (0·60 g., 73%), m. p. 72—74°, which crystallised from methanol, with almost quantitative recovery, in small prisms, m. p. 75° (Found: C, 46·7; H, 5·3; S, 18·9. $C_{13}H_{18}O_6S_2$ requires C, 46·7; H, 5·3; S, 19·2%).

Monomethanesulphonate of trans-cyclo*Pentane*-1 : 2-*diol*.—*cyclo*Pentene oxide (12 g.) in anhydrous ether (25 c.c.) was added slowly to a stirred solution of methanesulphonic acid (13·5 g.) in dry ether (50 c.c.) at 0°. The solution was kept for 16 hours at 0° and then worked up as for the similar reaction with toluene-*p*-sulphonic acid, to give the crude *trans*-monomethanesulphonate as a pale yellow liquid (15·2 g., 59%), n_D^{22} 1·4730 (Found: S, 13·7. Calc. for $C_6H_{12}O_4S$: S, 17·8%). Owing to its high reactivity, some decomposition had probably occurred during the work up. It was characterised by reaction with methanesulphonyl chloride in pyridine, to give the *trans*-dimethanesulphonate, m. p. and mixed m. p. 82°, and by conversion with toluene-*p*-sulphonyl chloride in pyridine into the *trans*-methanesulphonate toluene-*p*-sulphonate, identical (m. p. and mixed m. p. 75°) with that prepared from the monotoluene-*p*-sulphonate.

Monoacetate of cis-cyclo*Pentane*-1 : 2-*diol*.—To a solution of the *trans*-monotoluene-*p*-sulphonate (6 g.) in pyridine (50 c.c.), acetic anhydride (2·5 g.) was added, with cooling. After 24 hours at room temperature, water (100 c.c.) was added, and the solution was extracted with chloroform. The extract was washed successively with dilute sulphuric acid, water, and saturated sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated, to give the crude *trans*-acetate toluene-*p*-sulphonate (5·8 g.). This product (5·0 g.), fused potassium acetate (8 g.), and dry ethanol (75 c.c.) were boiled under reflux for 24 hours. The solution was then cooled, filtered from potassium salts, and evaporated to dryness under reduced pressure. Extraction of the residue with ether gave the *monoacetate* of *cis-cyclo*pentane-1 : 2-diol (1·25 g., 44%), b. p. 104—106°/20 mm., n_D^{17} 1·4576 (Found: C, 58·3; H, 8·6. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). With *p*-nitrobenzoyl chloride in pyridine it gave the cis-*acetate* p-*nitrobenzoate*, which crystallised from ethanol in white nodules, m. p. 93—94° (Found: N, 4·8. $C_{14}H_{15}O_6N$ requires N, 4·8%). The m. p. was depressed on admixture with the *trans*-acetate *p*-nitrobenzoate.

The monoacetate (0·71 g.) was dissolved in dry methanol (50 c.c.) containing a trace of sodium and set aside for 16 hours. After the addition of a few drops of water, the solution was neutralised with carbon dioxide and evaporated to an oil, which was taken up in dry ether and filtered to remove sodium carbonate. Evaporation then gave *cis-cyclo*pentane-1 : 2-diol (0·3 g.), which was characterised by conversion into the ditoluene-*p*-sulphonate; one recrystallisation from methanol gave 0·93 g. (75%), m. p. 90—92°, raised on further recrystallisation to 92°, undepressed on admixture with the *cis*-derivative previously described.

Monotoluene-p-*sulphonate of* cis-cyclo*Pentane*-1 : 2-*diol*.—To a solution of *cis*-*cyclo*pentane-1 : 2-diol (3·8 g.) in dry pyridine (75 c.c.), maintained at −10°, a solution of toluene-*p*-sulphonyl chloride (7·0 g.) in chloroform (75 c.c.) was gradually added with stirring over a period of three days (during the nights the mixture was stored at *ca.* 0°). After a further day at 0°, most of the solvent was removed under reduced pressure below 30° and the residue was diluted with water (100 c.c.). The precipitated oil was taken up in chloroform (80 c.c.), and washed with dilute sulphuric acid, water, and sodium hydrogen carbonate. Evaporation of the dried ($MgSO_4$) solution, finally at 0·2 mm., gave the cis-*monotoluene*-p-*sulphonate* as a pale yellow oil (3·8 g., 40%), n_D^{22} 1·5290 (Found: S, 12·7. $C_{12}H_{16}O_4S$ requires S, 12·5%). The product was completely soluble in cold methanol, and therefore contained no appreciable amount of ditoluene-*p*-sulphonate. Treatment of a portion with toluene-*p*-sulphonyl chloride in pyridine gave the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 92°.

The cis-*benzoate toluene*-p-*sulphonate* was prepared by reaction of the *cis*-monotoluene-*p*-sulphonate (0·5 g.) with benzoyl chloride (0·27 g.) in pyridine (5 c.c.). Three recrystallisations of the product from methanol gave small needles (0·23 g.), m. p. 92—93° (Found: C, 63·3; H, 5·7; S, 9·0. $C_{19}H_{20}O_5S$ requires C, 63·3; H, 5·6; S, 8·9%).

Reactions of the Monotoluene-p-*sulphonate and Monomethanesulphonate of* trans-cyclo*Pentane*-1 : 2-*diol with Metal Salts*.—(a) *Sodium iodide.* (i) A solution of the monotoluene-*p*-sulphonate (6·0 g.) and sodium iodide (9·5 g.) in pure acetone (70 c.c.) was boiled under reflux for 4 hours; some iodine was formed, and sodium toluene-*p*-sulphonate (3·5 g., 77%) was deposited. The solid was removed and the bulk of the acetone was distilled off, the distillate being unsaturated to bromine in carbon tetrachloride. Water (20 c.c.) was added to the residue, which was then extracted with ether. The ethereal extracts were washed with aqueous sodium thiosulphate, dried (Na_2SO_4), and evaporated to an oil, which on distillation gave *trans*-2-iodo*cyclo*pentanol (2·35 g., 46%), b. p. 95—97°/1·5 mm., n_D^{20} 1·5647. This was characterised by conversion of a portion into *trans*-2-iodo*cyclo*pentyl *p*-nitrobenzoate which when recrystallised from ethanol had m. p. and mixed m. p. 108°.

(ii) When the reaction period was increased to 24 hours, the theoretical amount of sodium toluene-*p*-sulphonate was deposited but considerably more iodine was liberated. The yield of *trans*-2-iodo*cyclo*pentanol fell to 26% and a lower-boiling fraction of *cyclo*pentanone was isolated and characterised as the 2 : 4-dinitrophenylhydrazone, m. p. 143°.

(iii) Treatment of the monomethanesulphonate (3·95 g.) with sodium iodide (8·5 g.) in boiling acetone (60 c.c.) for 5 hours gave sodium methanesulphonate (2·4 g.) and *trans*-2-iodo*cyclo*pentanol (2·2 g., 47%), b. p. 54°/0·1 mm., n_D^{16} 1·5638. The latter was not quite pure, as indicated by the slightly low refractive index and by the semi-solid nature of the crude *p*-nitrobenzoate; recrystallisation of the latter, however, gave the pure derivative, m. p. and mixed m. p. 108°.

(b) *Lithium bromide.* (i) The monotoluene-*p*-sulphonate (5 g.) and lithium bromide (5·6 g.) in dry ethanol (40 c.c.) were boiled under reflux for 24 hours. The solvent was removed under reduced pressure and water (30 c.c.) was added to the yellow residue, which was then extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave *trans*-2-bromo*cyclo*pentanol (1·45 g., 45%), b. p. 92—93°/15 mm., n_D^{18} 1·4990, characterised as *trans*-2-bromo*cyclo*pentyl *p*-nitrobenzoate, m. p. and mixed m. p. 98°, after recrystallisation from ethanol.

(ii) Treatment of the monomethanesulphonate (3·0 g.) with lithium bromide (4·5 g.) in dry ethanol (30 c.c.) in a similar way gave *trans*-2-bromo*cyclo*pentanol (1·05 g., 38%), b. p. 92—94°/15 mm., n_D^{18} 1·5015, which was again characterised as the *p*-nitrobenzoate, m. p. and mixed m. p. 98°.

(c) *Lithium chloride.* (i) A solution of the monotoluene-*p*-sulphonate (6·2 g.) and dry lithium chloride (3·5 g.) in dry ethanol (25 c.c.) was boiled under reflux for 24 hours, the solution remaining colourless throughout. The ethanol was distilled off and the residue diluted with water (30 c.c.). The product was extracted with chloroform, and the extract was dried (Na_2SO_4) and evaporated to a residue which when distilled gave *trans*-2-chloro*cyclo*pentanol (1·93 g., 66%), b. p. 80—82°/16 mm., n_D^{23} 1·4767; reaction of a portion with *p*-nitrobenzoyl chloride in pyridine gave *trans*-2-chloro*cyclo*pentyl *p*-nitrobenzoate, m. p. and mixed m. p. 76°.

(ii) Similarly, treatment of the monomethanesulphonate (3·0 g.) with lithium chloride (2·5 g.) in boiling ethanol (20 c.c.) for 24 hours gave *trans*-2-chloro*cyclo*pentanol (1 g., 50%), b. p. 75—77°/10 mm., n_D^{16} 1·4786; the *p*-nitrobenzoate had m. p. and mixed m. p. 76°.

*Reaction of the Monotoluene-*p*-sulphonate of* cis-cyclo*Pentane-*1 : 2*-diol with Lithium Chloride.*—The *cis*-monotoluene-*p*-sulphonate (2·6 g.) in dry ethanol (35 c.c.) was boiled under reflux with lithium chloride (1·5 g.) for 24 hours. The solution was then concentrated, diluted with water, and extracted with ether, to give an oil which on distillation was separated into fractions (i) (0·17 g.), b. p. 50°/100 mm., n_D^{27} 1·3742, and (ii) (0·17 g.), b. p. 90—95°/25 mm., n_D^{27} 1·4663. The former contained no chlorine and when treated with aqueous 2 : 4-dinitrophenylhydrazine sulphate gave *cyclo*pentanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 144°. Fraction (ii) was treated with *p*-nitrobenzoyl chloride (0·2 g.) in pyridine (2 c.c.) to give, after 3 recrystallisations from ethanol, *trans*-2-chloro*cyclo*pentyl *p*-nitrobenzoate, m. p. and mixed m. p. 76°.

*Reactions of the Ditoluene-*p*-sulphonate of* trans-cyclo*Pentane-*1 : 2*-diol with Metal Salts.*—(a) *Sodium iodide.* The *trans*-ditoluene-*p*-sulphonate (1·4 g.) and sodium iodide (4 g.) in acetone (50 c.c.) were heated under reflux for 48 hours. The iodine which had been formed was removed by the addition of aqueous sodium thiosulphate (the amount required indicated the presence of 0·3 atomic proportion of iodine), and the acetone was distilled off. Dilution of the residue with water precipitated unchanged ditoluene-*p*-sulphonate (1·1 g., 79%).

(b) *Lithium chloride.* A solution of the *trans*-ditoluene-*p*-sulphonate (2·5 g.) and lithium chloride (2·5 g.) in dry ethanol (25 c.c.) was boiled under reflux for 40 hours. The colourless solution was concentrated to remove acetone and then diluted with water; unchanged ditoluene-*p*-sulphonate (1·4 g., 56%) was precipitated. Extraction of the filtrate with ether gave only a trace of a chlorine-containing oil.

*Alkaline Hydrolysis of the Toluene-*p*-sulphonates.*—(a) *Qualitative.* (i) A suspension of the *trans*-monotoluene-*p*-sulphonate (7 g.) in 0·5N-aqueous sodium hydroxide (60 c.c.) was rapidly stirred at 85—90°; the characteristic odour of *cyclo*pentene oxide was soon apparent. After 2 hours the solution became homogeneous, and it was cooled, extracted once with chloroform to remove any unchanged toluene-*p*-sulphonate, and then continuously extracted with ether for 2 days. Evaporation of the dried (Na_2SO_4) ethereal extracts gave an oil, from which *trans-cyclo*pentane-1 : 2-diol (0·73 g., 26%), b. p. 82°/0·2 mm., was obtained by distillation. It was characterised by conversion into the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 109°. The poor yield of diol was probably due to loss of the volatile *cyclo*pentene oxide.

(ii) The *cis*-monotoluene-*p*-sulphonate (0·6 g.) was dissolved on 0·6N-methanolic sodium methoxide (4 c.c.); the solution became hot and sodium toluene-*p*-sulphonate was precipitated. A few drops of water were added, and the excess of alkali was neutralised with carbon dioxide. The solution was filtered, acidified with sulphuric acid, and treated with aqueous 2 : 4-dinitrophenylhydrazine sulphate, to give a yellow precipitate which was purified by chromatography from benzene solution on alumina; recrystallisation from ethanol then gave *cyclo*pentanone 2 : 4-dinitrophenylhydrazone (0·11 g.), m. p. and mixed m. p. 144°.

(iii) A solution of the *trans*-ditoluene-*p*-sulphonate (0·2 g.) in N-methanolic potassium hydroxide (12 c.c.) was boiled under reflux for 20 hours, *cyclo*pentadiene being formed [the diene is conveniently detected by passage of a slow stream of nitrogen through the apparatus and thence through a solution of sodium nitroprusside in 1% methanolic potassium hydroxide, a red precipitate being formed (Scagliarini and Lucchi, *Chem. Abs.*, 1940, **34**, 2287)]. The precipitated potassium toluene-*p*-sulphonate (0·17 g., 85%) was removed, and the solution was concentrated to remove methanol, and then diluted with water and continuously extracted with ether for 24 hours; evaporation of the extracts gave no residue.

(b) *Quantitative.* (i) The *trans*-monotoluene-*p*-sulphonate (0·2786 g.) was diluted with methanol to 100 c.c., to give a 0·0109M-solution. A portion (10 c.c.) was quickly mixed with 0·0232N-methanolic potassium hydroxide (10 c.c.) and kept at 20° for a known time before the rapid addition of 0·02N-aqueous hydrochloric acid (10 c.c.). The excess of acid was estimated by back-titration, and the percentage reaction of the toluene-*p*-sulphonate was then calculated. The results are shown in the Figure. The second-order velocity coefficient decreased markedly as the reaction proceeded; extrapolation to zero time gave the value $k_2 = 140$ mole l.$^{-1}$ min.$^{-1}$. Owing to the high rate, the possible experimental error is considerable, and this result can be regarded only as being of the correct order of magnitude.

(ii) The *cis*-monotoluene-*p*-sulphonate (2·25 g.) was diluted with methanol to 100 c.c., to give a 0·0879M-solution. Reactions were carried out, as described above, with equal volumes of 0·2384N-methanolic potassium hydroxide. The results are shown in the Figure. Second-order velocity coefficients again showed a decrease with time. Extrapolation to zero gave $k_2 = 0·17$ mole l.$^{-1}$ min.$^{-1}$.

(iii) When an approximately 0·0100M-solution of either the *trans*-monotoluene-*p*-sulphonate or *trans*-monomethanesulphonate in dioxan was treated with an equal volume of 0·0246N-aqueous sodium hydroxide at 20°, complete reaction had occurred when the first measurement was made (1 minute).

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