526. *Alicyclic Glycols. Part XII.* Derivatives of* cyclo*Heptane*-1 : 2-*diol.*

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Some monoesters, simple diesters, and mixed diesters of *cis*- and of *trans*-*cyclo*heptane-1 : 2-diol have been prepared. *trans*-2-Chloro-, -2-bromo-, and -2-iodo-*cyclo*heptanol are obtained by fission of *cyclo*heptene oxide with the corresponding hydrogen halide and also by reaction of the monotoluene-*p*-sulphonate of the *trans*-diol with lithium chloride, lithium bromide, and sodium iodide, respectively; a *trans*-halogenohydrin is also obtained by reaction of the monotoluene-*p*-sulphonate of the *cis*-diol with the appropriate metal salt. With calcium carbonate and aqueous acetone, *trans*-2-acetoxy-*cyclo*heptyl toluene-*p*-sulphonate gives *cis*-2-acetoxy*cyclo*heptanol; an ethyl ether, also, is formed when ethanol is the solvent. The *trans*-monotoluene-*p*-sulphonate reacts with alkali much more rapidly than does the *cis*-isomer; the products are *cyclo*heptene oxide and *cyclo*heptanone, respectively. Comparison with the corresponding *cyclo*pentane and *cyclo*hexane derivatives shows that for the *cis*- and for the *trans*-monotoluene-*p*-sulphonates of the 1 : 2-diols the order of reactivity towards alkali is *cyclo*pentane > *cyclo*heptane > *cyclo*hexane.

The *cis*- and the *trans*-form of *cyclo*heptane-1 : 2-diol were first prepared by Böeseken and Derx (*Rec. Trav. chim.*, 1921, **40**, 529; Derx, *ibid.*, 1922, **41**, 312), the *cis* being obtained in poor yield by hydroxylation of *cyclo*heptene with buffered aqueous permanganate, and the *trans* by acid hydrolysis of *cyclo*heptene oxide; support for the configuration of the *trans*-diol was provided by Godchot and Mousseron (*Compt. rend.*, 1934, **198**, 837; **199**, 1233; *Bull. Soc. chim.*, 1946, 643) who obtained from it a pair of diastereoisomeric strychnine sulphates. In marked contrast to the *cyclo*pentane- and *cyclo*hexane-1 : 2-diols, both stereoisomers of *cyclo*heptane-1 : 2-diol yield *iso*propylidene derivatives and augment the conductivity of boric acid (Böeseken and Derx, *loc. cit.*; Derx, *loc. cit.*; Böeseken, *Rec. Trav. chim.*, 1939, **58**, 856). Both stereoisomers are formed by reduction of tropolone (Cook, Gibb, Raphael, and Somerville, *Chem. and Ind.*, 1950, 427; Doering and Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 836).

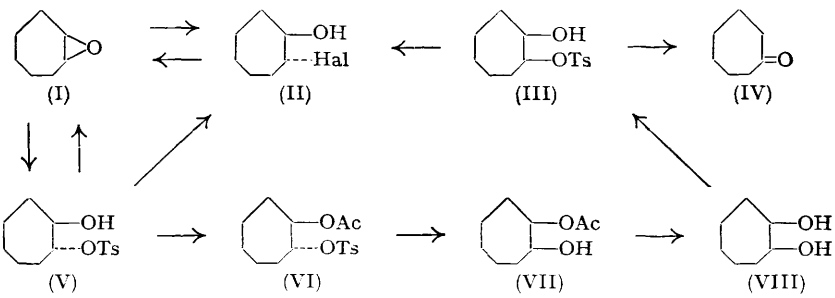
For the present investigation, the *cis*-diol was prepared by Derx's method (*loc. cit.*), and the yield was improved to 35% by carrying out the hydroxylation at −40°. Very

* Part XI, Haggis and Owen, *J.*, 1953, 408.

poor yields of *cis*-diol were obtained by hydroxylation of *cyclo*heptene, in the presence of osmic acid, with either hydrogen peroxide in *tert.*-butanol (cf. Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302) or aqueous sodium chlorate (cf. Milas and Terry, *ibid.*, 1925, **47**, 1412; Milas, *ibid.*, 1927, **49**, 2005); towards these reagents *cyclo*heptene thus behaves like *cyclo*pentene and unlike *cyclo*hexene (cf. Owen and Smith, *J.*, 1952, 4026). The *trans*-diol was obtained in 53% yield by hydroxylation of *cyclo*heptene with performic acid. Each stereoisomer was characterised as the crystalline bis-3 : 5-dinitrobenzoate, dimethanesulphonate, and ditoluene-*p*-sulphonate.

Monohalides (II) were synthesised by ring-fission of *cyclo*heptene oxide (I) with the appropriate hydrogen halide in ether, and the resulting *trans*-2-chloro-, -2-bromo-, and -2-iodo-*cyclo*heptanol were each characterised as crystalline 3 : 5-dinitrobenzoate; each halogenohydrin gave the oxide (I) when warmed with aqueous alkali. Reaction of the oxide with acetic acid, with toluene-*p*-sulphonic acid, and with methanesulphonic acid gave respectively the *trans*-monoacetate, the *trans*-monotoluene-*p*-sulphonate (V), and the *trans*-monomethanesulphonate, which were characterised as the following mixed esters: *trans*-acetate 3 : 5-dinitrobenzoate, *trans*-methanesulphonate 3 : 5-dinitrobenzoate, *trans*-methanesulphonate toluene-*p*-sulphonate (obtained from the monomethanesulphonate and from the monotoluene-*p*-sulphonate), and the *trans*-benzoate toluene-*p*-sulphonate.

In studies on the *cyclo*hexane-1 : 2-diols (Clarke and Owen, *J.*, 1949, 315) and *cyclo*pentane-1 : 2-diols (Owen and Smith, *loc. cit.*) the *cis*-monoacetates were obtained by reaction of the appropriate *trans*-acetate toluene-*p*-sulphonate with ethanol and calcium carbonate or potassium acetate, according to the general method of Winstein and Buckles (*J. Amer. Chem. Soc.*, 1942, **64**, 2780; Winstein, Hess, and Buckles, *ibid.*, p. 2796). When this method was applied to the acetate toluene-*p*-sulphonate (VI) of *trans-cyclo*heptane-1 : 2-diol, a pure monoacetate could not be isolated, the product being contaminated with an ethoxy-containing material presumably formed by alcoholysis of the toluene-*p*-sulphonyloxy-group; this type of side reaction has apparently not previously been observed under these conditions. However, by carrying out the reaction with calcium carbonate in aqueous acetone, instead of ethanol, the pure *cis*-monoacetate (VII) was obtained; its



configuration was confirmed by hydrolysis to the *cis*-diol (VIII). Toluene-*p*-sulphonylation of the *cis*-monoacetate gave the *cis*-acetate toluene-*p*-sulphonate, but attempts to convert this into the *cis*-monotoluene-*p*-sulphonate, by preferential alcoholysis of the acetate residue with methanolic hydrogen chloride, were unsuccessful. The *cis*-monotoluene-*p*-sulphonate (III) was therefore prepared by partial toluene-*p*-sulphonylation of the *cis*-diol under mild conditions; it was characterised as the crystalline *cis*-benzoate toluene-*p*-sulphonate.

Reactions of the monotoluene-*p*-sulphonates with metallic salts, and with alkali, were carried out so that comparison could be made with the corresponding reactions in the *cyclo*hexane and *cyclo*pentane series (Clarke and Owen, *loc. cit.*; Owen and Smith, *loc. cit.*). With lithium chloride, lithium bromide, and sodium iodide, the *trans*-ester (V) gave the respective *trans*-halogenohydrin (II), identified in each case as the 3 : 5-dinitrobenzoate, identical with that already obtained from the halogenohydrin prepared from the oxide. The *trans*-chlorohydrin was also obtained by reaction of the *cis*-monotoluene-*p*-sulphonate (III) with lithium chloride, and the *trans*-bromohydrin by reaction of the

cis-acetate toluene-*p*-sulphonate with lithium bromide, followed by acid hydrolysis of the resulting *trans*-bromide acetate. The overall retention of configuration in replacement of the *trans*-toluene-*p*-sulphonyloxy-group, and inversion in replacement of the *cis*-group, is thus similar to that observed with the five- and six-membered rings, and can be explained by similar mechanisms.

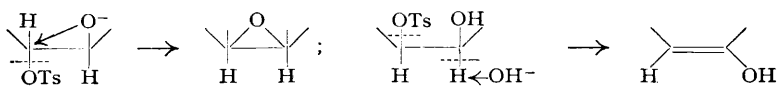
With alkali, the *trans*-monotoluene-*p*-sulphonate readily gave *cyclo*heptene oxide, whereas the *cis*-isomer reacted more slowly and gave *cyclo*heptanone (IV). This behaviour, also, corresponds to that in the smaller ring-systems, and indicates that the *cyclo*heptane ring is not sufficiently flexible to allow of the easy formation of a *trans*-1 : 2-oxide; with larger rings, *e.g.*, *cyclo*decane, both a *cis*- and a *trans*-1 : 2-oxide can be obtained by reaction of the *cis*- and the *trans-cyclo*olefin, respectively, with perbenzoic acid (Prelog, Schenker, and Günthard, *Helv. Chim. Acta*, 1952, **35**, 1598), and each oxide would probably be formed also from the monotoluene-*p*-sulphonate of the 1 : 2-diol of opposite configuration.*

Quantitative experiments were carried out to determine the rates of reaction of the monotoluene-*p*-sulphonates (III) and (V) with methanolic potassium hydroxide at 20°, and the reaction of the monotoluene-*p*-sulphonate of *trans-cyclo*hexane-1 : 2-diol, previously recorded by Clarke and Owen (*loc. cit.*) at 17°, was repeated at 20° by the modified technique. Approximate second-order velocity constants at 20°, calculated from the data given in the present and the earlier papers, are recorded below.

Reactions of the monotoluene-p-*sulphonates of* cyclo*alkane*-1 : 2-*diols with methanolic potassium hydroxide at* 20°.

Ring size	5		6		7	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
k_2 (mole l.$^{-1}$ min.$^{-1}$)	0·17	140	0·005 (17°)	15	0·018	25

The absolute values of the rate constants are dependent upon the composition of the solvent (see, *e.g.*, Owen and Smith, *loc. cit.*), and may therefore be slightly affected by variation in the water-content of the methanolic alkali used on different occasions. Furthermore, in several cases they diminished as the reaction proceeded, and the values quoted are then those obtained by extrapolation to zero time. Nevertheless, although great accuracy cannot be claimed (particularly for the high rates encountered with the more reactive compounds) it is clear that for each ring-size the *trans*-compound is several hundred times more reactive than the *cis*-isomer; for the former the rate-determining step is the attack by the neighbouring anionic oxygen on the carbon atom carrying the toluene-*p*-sulphonyloxy-group, accompanied by fission of the C–OTs bond, and this evidently occurs more readily than the elimination reaction undergone by the *cis*-isomer, in which fission of a C–H bond is involved :



(Ts = *p*-$C_6H_4Me{\cdot}SO_2$)

It is significant that the *cis*-monotoluene-*p*-sulphonates give the ketones, and not the 2-en-1-ols; elimination thus occurs towards the CH(OH) rather than the CH_2 group, probably because the hydroxyl group ($-I$ effect) weakens the C–H bond of the carbon atom to which it is attached, thus favouring attack by OH^- (or OMe^-) at that position.

Brown and Borkowski (*J. Amer. Chem. Soc.*, 1952, **74**, 1894; cf. Brown, Fletcher, and Johannesen, *ibid.*, 1951, **73**, 212) have measured the rates of solvolysis of various 1-methyl-*cyclo*alkyl chlorides and report the values k_1 = 1·32, 0·0106, and 1·15 hr.$^{-1}$ at 25° for the five-, six-, and seven-membered rings, respectively. The greater reactivity of certain other *cyclo*pentane and *cyclo*heptane compounds, compared with the corresponding *cyclo*-

* Mousseron's claim (*Bull. Soc. chim.*, 1946, 629) to have obtained *trans-cyclo*pentene oxide is not supported by adequate experimental evidence, and his views on the stereochemistry of oxide formation and oxide fission cannot be accepted.

hexane derivatives, was previously emphasised by Prelog (*J.*, 1950, 420). The present results are thus in general agreement with expectation, although the very high reactivities of the monotoluene-*p*-sulphonates of *cyclo*pentane-1 : 2-diol are not encountered with the *cyclo*heptane compounds. Strict comparison with the halides is, however, not justifiable, because the reactions undergone by the monotoluene-*p*-sulphonates are of the S_N2 and *E*2 types, and would clearly be subject to different steric factors from those operating in the S_N1 and *E*1 reactions of the halides.

Experimental

Hydrogenation of *cyclo*heptanone in alcohol, over Raney nickel at 150°/120 atm., gave *cyclo*heptanol, b. p. 95°/35 mm., n_D^{19} 1·4760, in almost quantitative yield. The 3 : 5-*dinitrobenzoate* crystallised from aqueous ethanol in needles, m. p. 79° (Found : C, 54·5; H, 5·3; N, 9·3. $C_{14}H_{16}O_6N_2$ requires C, 54·5; H, 5·2; N, 9·1%).

Dehydration of *cyclo*heptanol by distillation over naphthalene-β-sulphonic acid (Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057) or phosphoric acid (Dehn and Jackson, *ibid.*, 1933, **55**, 4284) gave *cyclo*heptene (in *ca.* 70% yield), b. p. 112—113°, n_D^{20} 1·4580.

trans-cyclo*Heptane*-1 : 2-*diol*.—A mixture of formic acid (560 g.) and 30% aqueous hydrogen peroxide (73 g.) was slowly added to *cyclo*heptene (24 g.), the temperature being kept below 45° during the addition, and at 45—50° for a further 4 hr. The homogeneous solution was then concentrated under reduced pressure to remove formic acid, and the residue was boiled under reflux for 1·5 hr. with 10% aqueous sodium hydroxide (390 c.c.). The solution was neutralised with hydrochloric acid and evaporated to dryness; extraction of the residue with boiling chloroform gave the *trans*-diol, which was purified by distillation (b. p. 155—156°/22 mm.) and subsequent crystallisation from toluene. The yield was 20 g. (53%), and the m. p. 64—65°.

Treatment of the *trans*-diol in pyridine with the appropriate acid chloride (2·2 mols.) for 2 days at 0°, followed by removal of most of the pyridine under reduced pressure below 40° and dilution of the residue with crushed ice, gave : the *bis*-3 : 5-*dinitrobenzoate*, plates (from benzene), m. p. 164—165° (after being dried in high vacuum at 100°) (Found : C, 48·5; H, 3·7; N, 10·7. $C_{21}H_{18}O_{12}N_4$ requires C, 48·65; H, 3·5; N, 10·8%); the *ditoluene*-p-*sulphonate*, needles (from methanol), m. p. 112° (Found : C, 57·8; H, 6·2; S, 14·3. $C_{21}H_{26}O_6S_2$ requires C, 57·5; H, 6·0; S, 14·6%); and the *dimethanesulphonate*, plates (from methanol), m. p. 104° (Found : C, 37·9; H, 6·1; S, 22·3. $C_{19}H_{18}O_6S_2$ requires C, 37·8; H, 6·3; S, 22·4%).

cis-cyclo*Heptane*-1 : 2-*diol*.—A solution of potassium permanganate (12·8 g.) and magnesium sulphate heptahydrate (20 g.) in water (600 c.c.) was added during 5 hr. to a vigorously stirred solution of *cyclo*heptene (9·6 g.) in ethanol (250 c.c.) kept at *ca.* −40°. The cooling bath was then removed, and the mixture kept overnight at room temperature. The solid was filtered off and washed with water, and the filtrate and washings were concentrated to small bulk and continuously extracted with ether, to give the *cis*-diol (4·5 g., 35%), m. p. 46—47° after recrystallisation from dry ether.

The following derivatives were prepared as described for the *trans*-isomers : the cis-*bis*-3 : 5-*dinitrobenzoate*, yellow needles (from chloroform–ethanol–dioxan), m. p. 96° (Found : C, 49·3; H, 4·1%); the cis-*ditoluene*-p-*sulphonate*, plates (from benzene–light petroleum), m. p. 104—105° (Found : C, 57·8; H, 6·2; S, 14·8%); and the cis-*dimethanesulphonate*, plates (from ether), m. p. 50° (Found : C, 37·75; H, 6·4; S, 22·4%).

cyclo*Heptene Oxide*.—Reaction of *cyclo*heptene (9·6 g.) with perbenzoic acid (21·9 g.) in dry chloroform (300 c.c.) (*Org. Synth.*, Coll. Vol. I, 2nd ed., p. 431; cf. Traube, *Chem. Eng. News*, 1949, **27**, 46) was complete in 48 hr. at 0°, as judged from occasional estimations of per-acid content in the mixture. The solution was then freed from acid by washing it with aqueous sodium carbonate, and was dried (Na_2SO_4) and evaporated to an oil, distillation of which furnished *cyclo*heptene oxide (8·9 g.), b. p. 65—67°/25 mm., n_D^{22} 1·4620. Derx (*loc. cit.*) gave b. p. 161°, $n_D^{18·5}$ 1·46499, but recorded no yield.

Reactions of cyclo*Heptene Oxide with Hydrogen Halides*.—(i) *With hydrogen chloride*. 0·9N-Ethereal hydrogen chloride (15 c.c.) was slowly added to a solution of *cyclo*heptene oxide (1·1 g.) in dry ether (10 c.c.) at 0°. After 6 hr. at room temperature, the solution was washed with water and with aqueous sodium hydrogen carbonate, then dried (Na_2SO_4) and evaporated, to give *trans*-2-chloro*cyclo*heptanol (0·7 g.), b. p. 45°/0·5 mm., n_D^{21} 1·4960. When a portion was heated with 10% aqueous sodium hydroxide it gave *cyclo*heptene oxide (characteristic

odour). Another portion, with 3 : 5-dinitrobenzoyl chloride in pyridine, gave trans-2-*chloro*cyclo*heptyl* 3 : 5-*dinitrobenzoate*, which crystallised from chloroform–methanol in needles, m. p. 113° (Found : C, 48·9; H, 4·4; N, 8·0. $C_{14}H_{15}O_6N_2Cl$ requires C, 49·05; H, 4·4; N, 8·2%).

(ii) *With hydrogen bromide.* Dry hydrogen bromide was passed into a solution of *cyclo*heptene oxide (1·1 g.) in dry ether (15 c.c.) at 0° until no more was absorbed. The solution was then worked up as above to yield a liquid (1·3 g.), b. p. 53°/0·01 mm., n_D^{18} 1·5310, consisting of *trans*-bromohydrin, probably containing some 1 : 2-dibromo*cyclo*heptane (Found : C, 40·5; H, 6·1. Calc. for $C_7H_{13}OBr$: C, 43·5; H, 6·7%). It readily furnished trans-2-*bromo*cyclo*heptyl* 3 : 5-*dinitrobenzoate*, flattened needles (from chloroform–ethanol), m. p. 121° (Found : C, 43·4; H, 4·1; N, 6·9. $C_{14}H_{15}O_6N_2Br$ requires C, 43·4; H, 3·9; N, 7·2%).

(iii) *With hydrogen iodide.* Similar reaction of the oxide (1·1 g.) in dry ether (15 c.c.) with dry hydrogen iodide gave trans-2-iodo*cyclo*heptanol, n_D^{19} 1·5630, which decomposed on attempted distillation. The crude product gave the 3 : 5-*dinitrobenzoate*, needles (from methanol), m. p. 134° (Found : N, 6·4. $C_{14}H_{15}O_6N_2I$ requires N, 6·45%).

Monoacetate of trans-cyclo*Heptane*-1 : 2-*diol.*—A solution of *cyclo*heptene oxide (1·1 g.) in acetic acid (5 c.c.) was kept at 100° for 15 hr. and then distilled, to give the trans-*monoacetate* (1·0 g.), b. p. 81—82°/0·5 mm., n_D^{17} 1·4670 (Found : C, 62·8; H, 9·3. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%).

With 3 : 5-dinitrobenzoyl chloride in pyridine it gave the trans-*acetate* 3 : 5-*dinitrobenzoate*, which crystallised from benzene in plates, m. p. 96—97° (Found : C, 52·7; H, 5·1; N, 7·9. $C_{16}H_{18}O_8N_2$ requires C, 52·45; H, 4·95; N, 7·65%).

Monotoluene-p-*sulphonate of* trans-cyclo*Heptane*-1 : 2-*diol.*—A solution of *cyclo*heptene oxide (15 g.) in dry ether (50 c.c.) was added during 40 min. to a cooled and stirred suspension of toluene-*p*-sulphonic acid (27·5 g.) in dry ether (70 c.c.), the temperature being kept at *ca.* 0°. The resulting clear solution was kept at room temperature overnight, then washed with ice-water (2 × 30 c.c.), dried (Na_2SO_4), and evaporated below 30°, the last traces of solvent being removed at 10^{-4} mm.; the trans-*monotoluene*-p-*sulphonate* was a viscous oil (23·6 g.), n_D^{18} 1·5300, which could not be distilled without decomposition (Found : S, 10·8. $C_{14}H_{20}O_4S$ requires S, 11·3%). When warmed with aqueous sodium hydroxide it gave *cyclo*heptene oxide (characteristic odour; no precipitate with 2 : 4-dinitrophenylhydrazine sulphate).

Treatment of the monotoluene-*p*-sulphonate with the appropriate acid chloride in pyridine for 24 hr. at 0° gave the following derivatives : the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 112°; the trans-*methanesulphonate toluene*-p-*sulphonate*, needles (from methanol), m. p. 120° (Found : C, 49·8; H, 6·2; S, 18·0. $C_{15}H_{22}O_6S_2$ requires C, 49·7; H, 6·1; S, 17·7%); and the trans-*benzoate toluene*-p-*sulphonate*, needles (from methanol), m. p. 101° (Found : C, 64·9; H, 6·3; S, 8·2. $C_{21}H_{24}O_5S$ requires C, 64·9; H, 6·2; S, 8·25%).

Monomethanesulphonate of trans-cyclo*Heptane*-1 : 2-*diol.*—Interaction of *cyclo*heptene oxide (2·2 g.) in dry ether (10 c.c.) with methanesulphonic acid (2·3 g.) in dry ether (15 c.c.) was carried out as for the reaction with toluene-*p*-sulphonic acid (see above), and gave the crude *trans*-monomethanesulphonate as an oil (2·4 g.), n_D^{18} 1·4870 (Found : S, 13·8. Calc. for $C_8H_{16}O_4S$: S, 15·4%). With the appropriate acid chloride in pyridine it gave : the *trans*-dimethanesulphonate, m. p. and mixed m. p. 104°; the *trans*-methanesulphonate toluene-*p*-sulphonate, m. p. and mixed m. p. 120°; and the trans-*methanesulphonate* 3 : 5-*dinitrobenzoate*, needles, m. p. 106° (from methanol) (Found : C, 45·1; H, 4·7; N, 6·7. $C_{15}H_{18}O_9N_2S$ requires C, 44·8; H, 4·5; N, 7·0%).

Acetate Toluene-p-*sulphonate of* trans-cyclo*Heptane*-1 : 2-*diol.*—Acetic anhydride (10·5 g.) in pyridine (20 c.c.) was added to a stirred solution of the *trans*-monotoluene-*p*-sulphonate (21 g.) in pyridine (50 c.c.) at 0°. The mixture was kept for 24 hr. at room temperature and then diluted with water and worked up by chloroform-extraction in the usual way. Evaporation of the washed and dried extracts gave the trans-*acetate toluene*-p-*sulphonate* as an oil (20 g.), n_D^{18} 1·5130 (Found : S, 9·8. $C_{16}H_{22}O_5S$ requires S, 9·8%).

Monoacetate of cis-cyclo*Heptane*-1 : 2-*diol.*—(i) The *trans*-acetate toluene-*p*-sulphonate (2·6 g.), ethanol (40 c.c.), and calcium carbonate (3·4 g.) were boiled together under reflux for 46 hr. The mixture was then cooled, filtered, concentrated to small bulk, and diluted with water; the precipitated oil was isolated by extraction with ether, and on distillation furnished a main fraction (0·7 g.), b. p. 87—89°/0·5 mm., n_D^{19} 1·4720, which was probably a mixture of the acetate and the ethyl ether (Found: C, 64·6; H, 9·6; OEt, 3·0. Calc. for $C_9H_{16}O_3$: C, 62·8; H, 9·3. Calc. for $C_{11}H_{20}O_3$: C, 66·0; H, 10·1; OEt, 22·5%).

(ii) A mixture of *trans*-acetate toluene-*p*-sulphonate (7·6 g.), calcium carbonate (7·5 g.), acetone (55 c.c.), and water (55 c.c.) was boiled under reflux for 2 days, and was then filtered

and worked up as above, to give the cis-*monoacetate* (1·8 g.), b. p. 89—90°/0·5 mm., n_D^{21} 1·4718 (Found: C, 63·0; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%). With 3 : 5-dinitrobenzoyl chloride in pyridine it gave the cis-*acetate* 3 : 5-*dinitrobenzoate*, leaflets (from methanol), m. p. 53° (Found: C, 52·5; H, 4·9. $C_{16}H_{18}O_8N_2$ requires C, 52·45; H, 4·95%).

Treatment of the *cis*-monoacetate (0·44 g.) with sodium (0·05 g.) in dry methanol (20 c.c.) for 24 hr. at room temperature, followed by neutralisation with carbon dioxide, evaporation to dryness, and extraction of the residue with dry ether, furnished, on evaporation of the extracts, the *cis*-diol (0·26 g.), m. p. 44—46°, characterised as the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 103°.

Acetate Toluene-p-*sulphonate of* cis-cyclo*Heptane*-1 : 2-*diol*.—Reaction of the *cis*-monoacetate (5·7 g.) with toluene-*p*-sulphonyl chloride (9·5 g.) in pyridine (25 c.c.) at 0° gave the cis-*acetate toluene*-p-*sulphonate* as an oil (9·0 g.), n_D^{22} 1·5110 (Found: S, 9·8. $C_{16}H_{22}O_5S$ requires S, 9·8%).

Monotoluene-p-*sulphonate of* cis-cyclo*Heptane*-1 : 2-*diol*.—A solution of toluene-*p*-sulphonyl chloride (3·4 g.) in pure chloroform (30 c.c.) was added in small portions during 3 days to a solution of the *cis*-diol (2·35 g.) in pyridine (20 c.c.) at 0°. The mixture was kept at 0° for two more days and was then diluted with chloroform (75 c.c.) and washed successively with 2N-sulphuric acid, aqueous sodium hydrogen carbonate, and water. Evaporation of the dried (Na_2SO_4) chloroform solution at 30° under reduced pressure, finally at 10^{-3} mm., gave the cis-*monotoluene*-p-*sulphonate* as a viscous oil (3·1 g.), n_D^{23} 1·5312 (Found: S, 10·7. $C_{14}H_{20}O_4S$ requires S, 11·3%).

Treatment of a small portion of the product with toluene-*p*-sulphonyl chloride in pyridine gave the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 103°. Reaction of another portion with benzoyl chloride in pyridine gave the cis-*benzoate toluene*-p-*sulphonate*, which crystallised from methanol in needles, m. p. 86° (Found: C, 64·6; H, 6·4; S, 8·6. $C_{21}H_{24}O_5S$ requires C, 64·9; H, 6·2; S, 8·25%).

Reactions of the Monotoluene-p-*sulphonates with Metallic Salts*.—(a) *Lithium chloride*. (i) A solution of the *trans*-monotoluene-*p*-sulphonate (2 g.) and lithium chloride (1·4 g.) in ethanol (25 c.c.) was boiled under reflux for 24 hr. and then concentrated to small volume and diluted with water (25 c.c.). The precipitated oil, isolated by extraction with ether, on distillation gave *trans*-2-chloro*cyclo*heptanol (0·4 g.), b. p. 48—50°/0·6 mm., n_D^{14} 1·4938, characterised as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 113°.

(ii) Similar treatment of the *cis*-monotoluene-*p*-sulphonate (0·8 g.) with lithium chloride (1·0 g.) in ethanol (10 c.c.) also gave the *trans*-chlorohydrin (0·2 g.), b. p. 100°/15 mm., n_D^{20} 1·4865 (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 112°). The crude chlorohydrin gave a slight precipitate with 2 : 4-dinitrophenylhydrazine sulphate, and probably contained a small amount of *cyclo*heptanone.

(b) *Lithium bromide*. The *trans*-monotoluene-*p*-sulphonate (2·5 g.) and lithium bromide (2·9 g.) in acetone (20 c.c.) were boiled under reflux for 4 hr.; lithium toluene-*p*-sulphonate (0·73 g.), which had been gradually deposited, was then filtered off. The filtrate did not give any more solid on further heating, and it was concentrated and worked up with water and ether as described above, to yield *trans*-2-bromo*cyclo*heptanol (1·2 g.), b. p. 55—56°/0·4 mm., n_D^{20} 1·5175, identified as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 121°.

(ii) The *cis*-acetate toluene-*p*-sulphonate (3·0 g.), on similar treatment for 5 hr. with lithium bromide (2·0 g.) in acetone (15 c.c.), gave, on evaporation of the ethereal extracts, a crude acetate bromide, which was dissolved in 0·2N-methanolic hydrogen chloride (25 c.c.) and kept for 16 hr. at room temperature. Evaporation of this solution and distillation of the residual oil gave a main fraction (0·6 g.), b. p. 70—72°/1 mm., n_D^{22} 1·5008, which furnished the same *trans*-3 : 5-dinitrobenzoate, m. p. and mixed m. p. 121°.

(c) *Sodium iodide*. When a solution of the *trans*-monotoluene-*p*-sulphonate (2·1 g.) and sodium iodide (3·6 g.) in acetone (20 c.c.) was boiled under reflux for 20 min., it became brown and deposited sodium toluene-*p*-sulphonate (1·2 g.). The filtrate was worked up as described above (except that the ethereal extract was washed with aqueous sodium thiosulphate) and furnished crude *trans*-2-iodo*cyclo*heptanol (1·2 g.), n_D^{20} 1·5685, identified as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 134°.

Formation of cyclo*Heptanone from the* cis-*Monotoluene*-p-*sulphonate*.—(i) The monotoluene-*p*-sulphonate (0·57 g.) in 0·1N-methanolic potassium hydroxide (40 c.c.) was set aside for 5 days at room temperature. Back-titration with standard acid showed that the reaction was then complete, and the solution was acidified and treated with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate. The precipitated derivative was collected, washed with water, and dried

(yield, 0·46 g., 80%); one recrystallisation from ethanol gave *cyclo*heptanone 2 : 4-dinitrophenylhydrazone, m. p. 145°.

(ii) A solution of the *cis*-acetate toluene-*p*-sulphonate (2·5 g.) in ethanol (10 c.c.) and 2N-aqueous sodium hydroxide (20 c.c.) was boiled under reflux for 1 hr. and then steam-distilled. The distillate gave *cyclo*heptanone 2 : 4-dinitrophenylhydrazone (1·5 g., 67%), m. p. 144°.

Rates of Reaction of the Monotoluene-p-*sulphonates with Alkali.*—(i) *trans-cyclo*Heptane-1 : 2-diol monotoluene-*p*-sulphonate (0·568 g.) was diluted with methanol to 40 c.c., and the temperature adjusted to 20°. A 5-c.c. portion was diluted with methanol (40 c.c.) at 20°, then rapidly mixed with 5 c.c. of 0·0875N-methanolic potassium hydroxide, also at 20°, thus giving a 0·005M-solution of the ester in 0·00875N-alkali, and kept at this temperature for a known time before being titrated directly with 0·107N-sulphuric acid (phenolphthalein indicator). Preliminary experiments indicated the approximate titres for various times of reaction, and in the final experiments about 90% of the required amount of acid was added in one lot, and the titration completed within about 10 sec. In spite of the rapidity of the reaction, results obtained in this way were indistinguishable from those found by stopping of the reaction by addition of excess of acid, followed by back-titration with standard alkali.

The % reaction was: 33 (2 min.); 57 (5 min.); 78 (10 min.); 95 (30 min.). The corresponding values of k_2 were 25, 24, 25, and 20 mole l.$^{-1}$ min.$^{-1}$.

(ii) *cis-cyclo*Heptane-1 : 2-diol monotoluene-*p*-sulphonate (0·421 g.) was dissolved in 0·086N-methanolic potassium hydroxide (40 c.c.) at 20° (to give a 0·037M-solution of ester) and kept at that temperature. The % reaction, determined as described above, was: 9 (1 hr.); 23 (3½ hr.); 58 (21 hr.); 81 (45 hr.); the corresponding values of k_2 were 0·017, 0·014, 0·009, and 0·009 mole l.$^{-1}$ min.$^{-1}$.

(iii) *trans-cyclo*Hexane-1 : 2-diol monotoluene-*p*-sulphonate (Criegee and Stanger, *Ber.*, 1936, **69**, 2753) (0·540 g.) was diluted with methanol to 40 c.c.; experiments were carried out as described above, on 5-c.c. portions mixed at 20° with 5 c.c. of 0·090N-methanolic potassium hydroxide. The % reaction was: 70 (2½ min.); 89 (5 min.); 95 (10 min.); and the corresponding values of k_2 were 14·2, 15·1, and 11·0 mole l.$^{-1}$ min.$^{-1}$.

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