212. *Alicyclic Glycols. Part XIV.* The Tetralin-2 : 3-diols and the* cyclo*Hex-4-ene-1 : 2-diols.*

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New syntheses of three of these diols are described. The infrared spectra show the presence of intramolecular hydrogen bonding in all four. The rates of reaction of the monotoluene-*p*-sulphonates with alkali, and the rates of oxidation of the tetralin-2 : 3-diols with lead tetra-acetate, are higher than for the corresponding stereoisomers of *cyclo*hexane-1 : 2-diol, probably because of less hindrance by axially disposed hydrogen atoms. The results indicate that the *cyclo*hexene ring in both sets of compounds is in the half-chair conformation.

In contrast to the extensive information which is now available on the relation between stereochemistry and reactivity in *cyclo*hexane systems, comparatively little is known about the *cyclo*hexene analogues. The preferred conformation [1,2] of *cyclo*hexene itself is the " half-chair " form (I) [or the alternative half-chair with which (I) is interconvertible] in which only the valencies at $C_{(4)}$ and $C_{(5)}$ are in the normal axial and equatorial positions, those at $C_{(3)}$ and $C_{(6)}$ being termed " quasi-axial " and " quasi-equatorial." Similar considerations have been applied [2,3] to the tetralin system in the classical fixed-bonded structure (II), although the bond common to both rings is not of course identical with the ordinary double bond in *cyclo*hexene. The present paper is concerned with the stereoisomers of tetralin-2 : 3-diol and of *cyclo*hex-4-ene-1 : 2-diol; in the half-chair conformations, the hydroxyl groups in these compounds would all be in true axial or equatorial positions.

Tetralin-*trans*-2 : 3-diol can be readily obtained [4,5] by hydrolysis of 2 : 3-dibromotetralin, or by hydration of 2 : 3-epoxytetralin,but no convenient preparation of the *cis*-isomer has been reported. Leroux [5] obtained a mixture of stereoisomers by reaction of the same dibromide with silver acetate in acetic acid (which was probably [6] not anhydrous) followed by hydrolysis of the resulting diacetates, and by fractional crystallisation he separated the *cis*-diol from a molecular compound of the *cis*- and *trans*-forms; later workers [7] effected a separation by formation of the *iso*propylidene derivative of the *cis*-diol. The configurations assigned in the early work were erroneous, being based on

* Part XIII, Owen and Peto, *J.*, 1955, 2383.

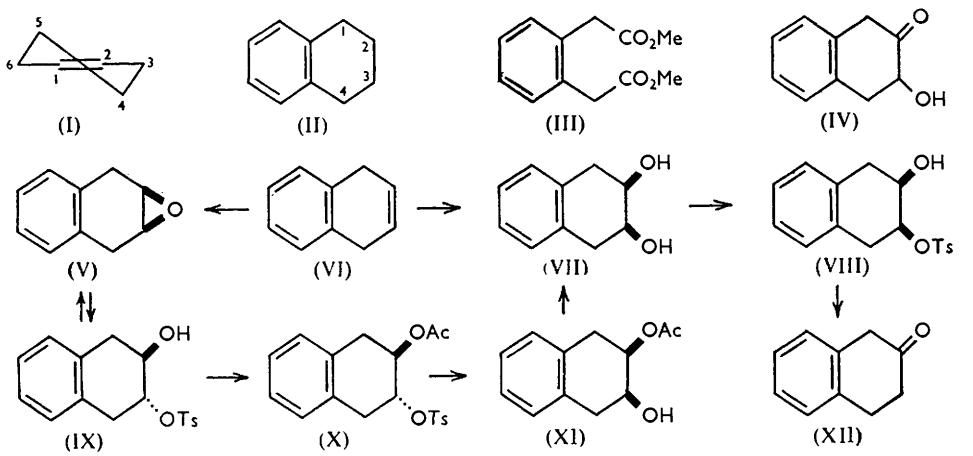
[1] Beckett, Freeman, and Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 4227; Raphael and Stenlake, *Chem. and Ind.*, 1953, 1286.
[2] Barton, Cookson, Klyne, and Shoppee, *ibid.*, 1954, 21.
[3] Lasheen, *Acta Cryst.*, 1952, **5**, 593; cf. Mosettig and Scheer, *J. Org. Chem.*, 1952, **17**, 764.
[4] Bamberger and Lodter, *Ber.*, 1893, **26**, 1833; *Annalen*, 1895, **288**, 74.
[5] Leroux, *Ann. Chim.* (*France*), 1910, **21**, 458.
[6] Cf. Winstein and Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2787.
[7] Böeseken and Derx, *Rec. Trav. chim.*, 1921, **40**, 519.

the assumption of *cis*-opening of an epoxide ring, but they were corrected by Böeseken and Derx; [7] rigid confirmation has recently been provided [8] by resolution of the *trans*-diol.

Hydroxylation of a *cyclo*alkene with buffered aqueous permanganate has been successfully used for the preparation of *cis*-diols in the *cyclo*pentene,[9] *cyclo*hexene,[10] and *cyclo*heptene [11] series, and we therefore applied the method to 1 : 4-dihydronaphthalene (VI) but the yield of tetralin-*cis*-2 : 3-diol (VII) was very low, and only slightly better results were obtained by the use of sodium chlorate–osmium tetroxide. Woodward's method [12] (silver acetate and iodine in wet acetic acid) gave, however, the *cis*-diol in 60% yield. The poor results from the first two methods were probably due to the low solubility of the hydrocarbon in the reaction media. An alternative route to the *cis*-diol, *via* the *trans*-monotoluene-*p*-sulphonate, is described below.

As a possible new approach to the tetralin-2 : 3-diols, the acyloin cyclisation of dimethyl *o*-phenylenediacetate (III) by sodium and liquid ammonia [13] was investigated, but instead of the expected ketol (IV) the only identifiable product was naphthalene-2 : 3-diol, possibly formed by disproportionation of the ketol.

Monoesters of tetralin-*trans*-2 : 3-diol were prepared by reaction of 2 : 3-epoxytetralin (V) with acetic, toluene-*p*-sulphonic, and methanesulphonic acid, which gave the *trans*-monoesters, *e.g.*, (IX). These were characterised as the following simple and mixed diesters: *trans*-acetate toluene-*p*-sulphonate (X) (obtained from the monoacetate and from the monotoluene-*p*-sulphonate), *trans*-ditoluene-*p*-sulphonate, *trans*-methanesulphonate toluene-*p*-sulphonate, *trans*-benzoate toluene-*p*-sulphonate, *trans*-dimethanesulphonate, *trans*-acetate methanesulphonate. The *cis*-monoacetate (XI) was prepared in good yield by reaction of either the *trans*-acetate toluene-*p*-sulphonate (X) or the *trans*-acetate methanesulphonate with aqueous acetone in the presence of calcium carbonate

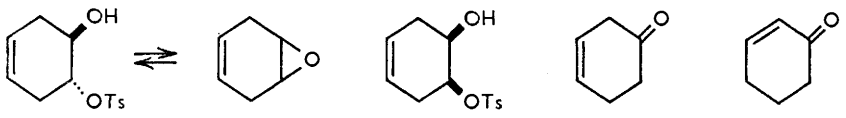


(Ts = *p*-$C_6H_4Me\cdot SO_2$)

(cf. ref. 11), and the configuration of the product was confirmed by deacetylation to the *cis*-diol (VII). Reaction of the *cis*-monoacetate with toluene-*p*-sulphonyl chloride in pyridine gave the *cis*-acetate toluene-*p*-sulphonate; attempts to prepare the *cis*-monotoluene-*p*-sulphonate (VIII) by preferential alcoholysis of the acetyl group in this derivative were not successful, but it was obtained by direct esterification of the *cis*-diol under controlled conditions, and was characterised as the *cis*-ditoluene-*p*-sulphonate and the *cis*-acetate toluene-*p*-sulphonate.

[8] Lettré and Lerch, *Chem. Ber.*, 1952, **85**, 394.
[9] Owen and Smith, *J.*, 1952, 4026.
[10] Clarke and Owen, *J.*, 1949, 315.
[11] Owen and Saharia, *J.*, 1953, 2582.
[12] Cf. Ginsburg, *J. Amer. Chem. Soc.*, 1953, **75**, 5746.
[13] Cf. Sheehan and Coderre, *ibid.*, p. 3997.

The monosulphonates of tetralin-2 : 3-diol behaved qualitatively towards alkali as did the corresponding derivatives of *cyclo*pentane-,[9] *cyclo*hexane-,[10] and *cyclo*heptane-1 : 2-diol.[11] Thus, the *trans*-monotoluene-*p*-sulphonate (IX) and the *trans*-monomethanesulphonate gave the epoxide (V) whilst the *cis*-monotoluene-*p*-sulphonate (VIII) and the *cis*-acetate toluene-*p*-sulphonate gave β-tetralone (XII). The rates of these reactions are discussed later.



(XIII) (XIV) (XV) (XVI) (XVII)

Reaction of *trans*-monotoluene-*p*-sulphonate (IX) with lithium chloride resulted in the expected [11] overall retention of configuration (two successive inversions) and gave *trans*-3-chlorotetralin-2-ol. In a similar reaction the *cis*-monotoluene-*p*-sulphonate gave a ketonic product, probably mainly β-tetralone.

Syntheses of both forms of *cyclo*hex-4-ene-1 : 2-diol have recently been described, the *cis*-isomer being obtained [14] by Diels–Alder reaction of vinylene carbonate with butadiene, and the *trans*-form by controlled hydroxylation of *cyclo*hexa-1 : 4-diene with silver benzoate and iodine.[15] Different methods were used in the present work. The *trans*-diol was prepared by hydration of 4 : 5-epoxy*cyclo*hexene (XIV), and the *cis*-isomer from the same source *via* the *trans*-monotoluene-*p*-sulphonate (XIII), *trans*-acetate toluene-*p*-sulphonate, and *cis*-monoacetate, as described above in the tetralin series; yields were excellent at all stages. Direct monotoluene-*p*-sulphonation of the *cis*-diol under mild conditions gave the *cis*-monotoluene-*p*-sulphonate (XV), which was characterised as the *cis*-acetate toluene-*p*-sulphonate, identical with that prepared by toluene-*p*-sulphonation of the *cis*-monoacetate. The monotoluene-*p*-sulphonates (XIII) and (XV) behaved qualitatively towards alkali in the expected way, the former giving the epoxide (XIV), and the latter *cyclo*hex-2-enone (XVII) by isomerisation of the initially formed 3-enone (XVI).

The results of reaction-rate measurements on the monotoluene-*p*-sulphonates of the tetralin-2 : 3-diols and of the *cyclo*hex-4-ene-1 : 2-diols are shown in the Table, which also includes, for comparison, data [11] on the corresponding derivatives of *cyclo*hexane-1 : 2-diol. The *trans*-compounds reacted very rapidly, and their rate constants can only be regarded as approximate, but the *trans* : *cis* rate-ratio, *ca.* 4000 : 1 for both the tetralin and the *cyclo*hexene derivatives, is roughly the same as that, 3000 : 1, observed for the *cyclo*hexane analogues. That the absolute values are 5—10 times as great as for the *cyclo*hexane

	Bimolecular rate constant (mole^{-1} l. min.$^{-1}$)		Infrared absorption max. (cm.$^{-1}$)		
	Alkaline hydrol. of monotoluene-*p*-sulphonate	$Pb(OAc)_4$ oxidn.	Free OH	Bonded OH	$\Delta\nu$
Tetralin-*cis*-2 : 3-diol	0·037	14·8	3622	3590	32
Tetralin-*trans*-2 : 3-diol	*ca.* 150	1·52	3630	3598	32
*cyclo*Hex-4-ene-*cis*-1 : 2-diol	0·023	—	3622	3590	32
*cyclo*Hex-4-ene-*trans*-1 : 2-diol	*ca.* 100	—	3630	3595	35
*cyclo*Hexane-*cis*-1 : 2-diol ...	0·005 *	8·1 †	3626	3587	39 ‡
*cyclo*Hexane-*trans*-1 : 2-diol	15 *	0·33	3634	3602	32 ‡

* Ref. 11. † Ref. 17. ‡ Ref. 19.

compound of corresponding configuration can probably be attributed to the absence of axial hydrogen atoms at the ends of the alicyclic double bond; consequently there will be less steric hindrance to the attainment by the toluene-*p*-sulphonyloxy-group (and also

[14] Newman and Addor, *J. Amer. Chem. Soc.*, 1955, **77**, 3789.
[15] McCasland and Horswill, *ibid.*, 1954, **76**, 1654.

by the hydroxyl group in the *trans*-compounds) of the axial position which is required, both with the *cis*- and the *trans*-compounds, for the energetically favoured planar four-centre displacement mechanism [16] (*i.e.*, toluene-*p*-sulphonyloxy-group and neighbouring hydrogen both axial for ketone formation, toluene-*p*-sulphonyloxy-group and neighbouring hydroxyl both axial for epoxide formation).

Oxidations of the *cyclo*hex-4-ene-1 : 2-diols with lead tetra-acetate were not attempted, because of the complications arising from the presence of the double bond, but rate measurements were made at 25° on the two tetralin-2 : 3-diols (see Table). The *cis* : *trans* rate-ratio is of the same order as for the *cyclo*hexane-1 : 2-diols, and very much smaller than would be expected for a boat conformation of the *cyclo*hexene ring; in the latter form, the *cis*-diol should exhibit reactivity of a much higher order of magnitude.[17] The somewhat higher values for the tetralin-2 : 3-diols than for the corresponding *cyclo*hexane compounds may again be due to decreased steric hindrance, particularly with the *trans*-isomer where crowding of the axial hydrogen atoms in the *cyclo*hexane system tends to resist the attainment by the two C–OH bonds of the closer approach to co-planarity which would facilitate formation of the supposed [18] cyclic transition state.

Confirmatory evidence for the half-chair conformation of the tetralin- and the *cyclo*hexene-diols was provided by their infrared spectra (see Table). Dilute solutions in carbon tetrachloride showed in all four cases absorption maxima of the type which Kuhn [19] has shown to be characteristic of the presence of both free and intramolecularly bonded hydroxyl groups, the relative intensities of the two peaks being independent of concentration. The separations of the bands, $\Delta\nu$, show good agreement with those reported for the *cyclo*hexane-1 : 2-diols, there being no significant difference between the *cis*- and the *trans*-forms. This indicates [19] that the distance between the hydroxyl groups in each stereoisomer is the same, a condition which can be satisfied only in the half-chair conformation. This conformation is of course itself stabilised by the intramolecular hydrogen bonding, and it does not follow from the above observations that tetralin and *cyclo*hexene necessarily exist in the same form.

Experimental

Analyses were by Miss J. Cuckney and her staff, and absorption spectra by Mr. R. L. Erskine, B.Sc., A.R.C.S., and Mrs. A. I. Boston. A calcium fluoride prism was used for the infrared absorption measurements.

Dimethyl o-*Phenylenediacetate*.—Treatment of ωω′-dicyano-*o*-xylene (19 g.) with 50% sulphuric acid (340 g.) under reflux for 2 hr., followed by cooling in ice, gave *o*-phenylenediacetic acid (22 g., 93%), m. p. 151—152° (lit.,[20] m. p. 150°). Esterification by the azeotropic method, using methanol, benzene, and sulphuric acid, gave the *dimethyl* ester (86%), b. p. 110°/0·2 mm., n_D^{21} 1·5120 (Found: C, 64·8; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%).

Acyloin Cyclisation of Dimethyl o-*Phenylenediacetate*.—The ester (2 g.) in dry ether (180 c.c.) was added to a solution of sodium (1·6 g.) in liquid ammonia (300 c.c.) and dry ether (200 c.c.) during 2 hr. Evaporation to dryness, followed by decomposition of the excess of sodium with dry methanol (4 c.c.) in dry ether (30 c.c.), afforded a yellow residue which was acidified with acetic acid (5 g.) in dry ether (70 c.c.), and then diluted with water. The ether layer was washed successively with water, aqueous sodium hydrogen carbonate, again with water, and then dried (Na_2SO_4). Removal of the solvent gave a semi-solid residue which on recrystallisation from benzene gave naphthalene-2 : 3-diol (0·3 g., 21%), m. p. and mixed m. p. 163—164°.

Tetralin-trans-2 : 3-*diol*.—2 : 3-Epoxytetralin,[21] on hydration with aqueous acetic acid,[4,5] gave the *trans*-diol, m. p. 135—136°. Infrared absorption: see Table. Treatment of the diol with a slight excess of the appropriate acid chloride in pyridine for 12 hr. at room temperature

[16] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.
[17] Eliel and Pillar, *J. Amer. Chem. Soc.*, 1955, **77**, 3600; and references there cited.
[18] Cf. Waters, *J.*, 1956, 840.
[19] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; 1954, **76**, 4323.
[20] Moore and Thorpe, *J.*, 1908, **93**, 175.
[21] Cook and Hill, *J. Amer. Chem. Soc.*, 1940. **62**, 1995.

gave the *trans*-ditoluene-*p*-sulphonate, plates (from methanol), m. p. 143—144° (Found: C, 60·9; H, 5·2; S, 13·45. Calc. for $C_{24}H_{24}O_6S_2$: C, 61·0; H, 5·1; S, 13·6%) (lit.,[22] m. p. 140—141°); and the trans-*dimethanesulphonate*, needles (from methanol), m. p. 141° (Found: C, 45·2; H, 5·1; S, 19·6. $C_{12}H_{16}O_6S_2$ requires C, 45·0; H, 5·0; S, 20·0%).

Tetralin-cis-2 : 3-*diol*.—(i) A solution of potassium permanganate (7·8 g.) and magnesium sulphate (12·2 g.; hydrated) in water (365 c.c.) was added to a vigorously stirred suspension of 1 : 4-dihydronaphthalene [21] (8 g.; purified through the mercuric acetate addition compound[23]) in ethanol (150 c.c.) at *ca.* −15° during 2 hr. The mixture was left overnight at room temperature, then filtered, and the solution was saturated with sodium chloride and continuously extracted with ether to give a solid, which on repeated crystallisation, first from benzene and then from water, gave the *cis*-diol (0·21 g., 2%), m. p. 124° (lit.,[24] m. p. 124—125°).

(ii) 1 : 4-Dihydronaphthalene (8 g.) and a solution of sodium chlorate (17 g.) in water (200 c.c.) containing osmium tetroxide (0·1 g.) were vigorously stirred together for 24 hr. at 50°; there was still a strong characteristic odour of 1 : 4-dihydronaphthalene. The mixture was then cooled, made alkaline with 10% aqueous sodium hydroxide, washed with a little ether to remove the unchanged hydrocarbon, and then continuously extracted with ether to give tetralin-*cis*-2 : 3-diol (1·1 g., 11%), m. p. 123—124° (from water).

(iii) To a stirred mixture of 1 : 4-dihydronaphthalene (6 g.), acetic acid (380 c.c.), water (1 c.c.), and silver acetate (16 g.), iodine (11 g.) was added in small portions during 30 min. The mixture was stirred for a further 3 hr. at room temperature, and for 3 hr. at 100°; it was then filtered and evaporated to dryness. The residue was dissolved in methanol (300 c.c.), treated with excess of potassium hydroxide (5 g. after neutralisation), and set aside overnight. The solution was then neutralised with acetic acid, and evaporated, with addition of water, to remove methanol. Continuous ether-extraction of the residual aqueous solution gave the *cis*-diol (4·5 g., 59%), m. p. 124° (from water). Infrared absorption: see Table.

Treatment of the *cis*-diol with toluene-*p*-sulphonyl chloride (2·1 mol.) in pyridine gave the cis-*ditoluene*-p-*sulphonate*, plates (from methanol), m. p. 124° (Found: C, 60·75; H, 5·3; S, 13·4. $C_{24}H_{24}O_6S_2$ requires C, 61·0; H, 5·1; S, 13·6%).

Monoacetate of Tetralin-trans-2 : 3-*diol*.—2 : 3-Epoxytetralin (1 g.) in acetic acid (5 c.c.) was heated on the steam-bath for 20 hr. Removal of most of the excess of acid under reduced pressure, followed by dissolution of the residue in ether, washing with aqueous sodium hydrogen carbonate, and evaporation of the dried (Na_2SO_4) solution, gave a solid residue (1 g.). Recrystallisation from ether–light petroleum (b. p. 60—80°) gave needles of the trans-*monoacetate*, m. p. 92° (Found: C, 69·9; H, 7·1. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

Treatment of the *trans*-monoacetate with toluene-*p*-sulphonyl chloride (1·1 mol.) in pyridine at room temperature overnight, followed by dilution with cold water, gave an oil which slowly solidified. Recrystallisation from methanol gave the trans-*acetate toluene*-p-*sulphonate*, needles, m. p. 85° (Found: C, 62·9; H, 5·7; S, 8·9. $C_{19}H_{20}O_5S$ requires C, 63·3; H, 5·6; S, 8·9%).

Monotoluene-p-*sulphonate of Tetralin*-trans-2 : 3-*diol*.—A solution of 2 : 3-epoxytetralin (7·0 g.) in dry ether (20 c.c.) was added dropwise to a stirred suspension of toluene-*p*-sulphonic acid (13 g.) in dry ether (30 c.c.) at room temperature; the reaction mixture became warm. It was set aside for 24 hr., then washed with water until neutral, dried (Na_2SO_4), and evaporated to a solid (12·3 g., 80%) which, on recrystallisation from ether–light petroleum (b. p. 60—80°), gave the trans-*monotoluene*-p-*sulphonate*, plates, m. p. 88—89° (Found: C, 63·8; H, 5·8; S, 9·9. $C_{17}H_{18}O_4S$ requires C, 64·1; H, 5·7; S, 10·1%).

Treatment of the *trans*-monotoluene-*p*-sulphonate with slight excess of the appropriate acid chloride in pyridine at room temperature overnight, followed by dilution with water, gave the *trans*-ditoluene-*p*-sulphonate, plates (from methanol), m. p. and mixed m. p. 143—144°; the trans-*methanesulphonate toluene*-p-*sulphonate*, needles (from methanol), m. p. 133—134° (Found: C, 54·5; H, 5·2; S, 16·05. $C_{18}H_{20}O_6S_2$ requires C, 54·5; H, 5·1; S, 16·2%); and the trans-*benzoate toluene*-p-*sulphonate*, felted needles (from methanol), m. p. 160° (Found: S, 7·5. $C_{24}H_{22}O_5S$ requires S, 7·6%).

The monotoluene-*p*-sulphonate with acetic anhydride in pyridine gave the *trans*-acetate toluene-*p*-sulphonate, m. p. and mixed m. p. 85°.

Monomethanesulphonate of Tetralin-trans-2 : 3-*diol*.—2 : 3-Epoxytetralin (2·8 g.) in dry

[22] Prajer, *Roczniki Chem.*, 1954, **28**, 55.
[23] Sand and Genssler, *Ber.*, 1903, **36**, 3705.
[24] Verkade, Coops, Maan, and Verkade-Sandbergen, *Annalen*, 1928, **467**, 217.

ether (10 c.c.) was treated with methanesulphonic acid (2·3 g.) in dry ether (20 c.c.) as for the reaction with toluene-*p*-sulphonic acid. A crystalline solid soon began to separate and next day it was collected and washed twice with a little ether (yield, 4 g., 86%; m. p. 100°). Recrystallisation from 1 : 1 aqueous methanol gave the trans-*monomethanesulphonate*, needles, m. p. 103° (Found: C, 54·6; H, 6·0; S, 13·0. $C_{11}H_{14}O_4S$ requires C, 54·5; H, 5·8; S, 13·2%).

Reaction of the product with methanesulphonyl chloride (1·3 mol.) in pyridine at room temperature gave the *trans*-dimethanesulphonate, m. p. and mixed m. p. 141°.

The monomethanesulphonate (2·1 g.) with acetic anhydride (2 g.) in pyridine (4 c.c.) gave the trans-*acetate methanesulphonate* (2·25 g.), prisms (from methanol), m. p. 95° (Found: S, 11·2. $C_{13}H_{16}O_5S$ requires S, 11·3%).

Monoacetate of Tetralin-cis-2 : 3-*diol*.—(i) A mixture of the *trans*-acetate toluene-*p*-sulphonate (7·5 g.), calcium carbonate (8 g.), acetone (50 c.c.), and water (50 c.c.) was heated on the steam-bath for 48 hr. The mixture was then cooled and filtered, and the acetone removed under reduced pressure, whereupon an oil separated from the aqueous residue. When cooled, the oil solidified (3·1 g., 72%; m. p. 95—97°), and on recrystallisation from aqueous methanol gave the cis-*monoacetate*, needles, m. p. 98° (Found: C, 69·9; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

(ii) The *trans*-acetate methanesulphonate (2·45 g.) on similar treatment with calcium carbonate (2·9 g.) in 50% aqueous acetone (50 c.c.) gave the *cis*-monoacetate (1·1 g., 62%), m. p. and mixed m. p. 98°.

A solution of the *cis*-monoacetate (0·6 g.) in methanol (10 c.c.) containing sodium methoxide (from 0·05 g. of sodium) was boiled under reflux for 30 min. Neutralisation with carbon dioxide, followed by evaporation to dryness and treatment with a little water, afforded a crystalline residue which was recrystallised from water, to give the *cis*-diol (0·4 g.), m. p. and mixed m. p. 124°.

Treatment of the *cis*-monoacetate with toluene-*p*-sulphonyl chloride in pyridine gave the cis-*acetate toluene*-p-*sulphonate*, prisms (from methanol), m. p. 128° (Found: C, 63·4; H, 5·6; S, 8·8. $C_{19}H_{20}O_5S$ requires C, 63·3; H, 5·6; S, 8·9%).

Monotoluene-p-*sulphonate of Tetralin*-cis-2 : 3-*diol*.—A solution of toluene-*p*-sulphonyl chloride (5·23 g., 1 mol.) in dry pyridine (50 c.c.), cooled to 0°, was added in small portions to a solution of tetralin-*cis*-2 : 3-diol (4·5 g.) in pyridine (40 c.c.) also at 0° during 3 days. The solution was kept at 0° for another 2 days, then diluted with ice and water; the insoluble brown oil solidified on prolonged trituration. Recrystallisation from ether–light petroleum (b. p. 60—80°) gave the cis-*monotoluene*-p-*sulphonate* (3·2 g., 37%), m. p. 107° (Found: C, 64·1; H, 5·9; S, 9·95. $C_{17}H_{18}O_4S$ requires C, 64·1; H, 5·7; S, 10·1%).

Treatment of the *cis*-monotoluene-*p*-sulphonate with acetic anhydride in pyridine gave the *cis*-acetate toluene-*p*-sulphonate, m. p. and mixed m. p. 128°.

2 : 3-*Epoxytetralin from the Monotoluene*-p-*sulphonate and the Monomethanesulphonate of Tetralin*-trans-2 : 3-*diol*.—(i) The *trans*-monotoluene-*p*-sulphonate (0·5 g.) was dissolved in a mixture of 5% aqueous sodium hydroxide (20 c.c.) and methanol (25 c.c.), and kept at room temperature for 30 min. Dilution with water and extraction with ether gave the epoxide, which after recrystallisation from light petroleum (b. p. 60—80°) had m. p. and mixed m. p. 42°.

(ii) The *trans*-monomethanesulphonate, on similar treatment gave the epoxide, m. p. and mixed m. p. 42°.

β-*Tetralone from the Monotoluene*-p-*sulphonate of Tetralin*-cis-2 : 3-*diol*.—The *cis*-monotoluene-*p*-sulphonate (0·4 g.) was suspended in 0·5N-sodium hydroxide (10 c.c.) and steam-distilled until the distillate became clear. A portion of the distillate, treated with a drop of alkali and shaken for a few seconds, gave the deep blue colour characteristic of β-tetralone; another portion gave the semicarbazone, m. p. and mixed m. p. 190° (from ethanol).

Reactions of the Monotoluene-p-*sulphonates of Tetralin*-2 : 3-*diol with Lithium Chloride*.—(i) A mixture of the *trans*-monotoluene-*p*-sulphonate (1·2 g.), lithium chloride (1 g.), and ethanol (10 c.c.) was refluxed on the steam-bath for 24 hr. Removal of the solvent followed by dilution with water precipitated *trans*-3-chlorotetralin-2-ol, which after recrystallisation from aqueous methanol formed needles (0·48 g., 70%), m. p. 117° (lit.,[4] m. p. 117·5°).

(ii) Similar treatment of the *cis*-monotoluene-*p*-sulphonate (0·4 g.) with lithium chloride (0·4 g.) in ethanol (10 c.c.) gave a liquid product which formed a precipitate on treatment with 2 : 4-dinitrophenylhydrazine sulphate, but no pure derivative could be isolated.

4 : 5-*Epoxy*cyclo*hexene*.—*cyclo*Hexa-1 : 4-diene, prepared by dehydration of quinitol with

sulphuric acid,[25] and carefully fractionated through a 50 × 2 cm. Fenske column, had b. p. 88·5—89·5°/764 mm., n_D^{24} 1·4700 (lit.,[26] b. p. 88·7—88·9°/764 mm., n_D^{20} 1·4725). The light absorption in EtOH, $\lambda_{max.}$ 2560 Å (ε 52), indicated the presence of less than 1% of the 1 : 3-diene.

Solutions of the 1 : 4-diene (24·7 g.) in chloroform (100 c.c.), and of perbenzoic acid (48·1 g). in chloroform (590 c.c.) were separately cooled to −10°, and the latter was then added to the former at the same temperature in portions of 10 c.c. during 7 days. The mixture was kept for two more days in the refrigerator and was then washed with ice-cold 10% aqueous sodium hydroxide and with water, and dried (Na_2SO_4). Most of the solvent was then removed on the steam-bath through a column, and the residue was distilled through a short Vigreux column, to give 4 : 5-epoxy*cyclo*hexene (17·5 g., 59%), b. p. 39—40°/11 mm., n_D^{20} 1·4810 (Found: C, 75·0; H, 8·6. Calc. for C_6H_8O: C, 75·0; H, 8·4%) (lit.,[27] b. p. 41—43°/14 mm.).

cyclo*Hex*-4-*ene*-trans-1 : 2-*diol*.—A mixture of 4 : 5-epoxy*cyclo*hexene (9·6 g.), acetic acid (6 g.), and water (90 c.c.) was heated on the steam-bath for 4 hr.; it was then cooled, neutralised with solid sodium hydrogen carbonate, saturated with sodium chloride, and extracted with ether (3 × 50 c.c.). The dried (Na_2SO_4) extracts were evaporated to a solid (5·8 g.), m. p. 94—96°. The aqueous solution on continuous extraction with ether gave more solid (4·6 g.), m. p. 96—97°. The combined product was recrystallised from light petroleum (b. p. 80—100°), to give *cyclo*hex-4-ene-*trans*-1 : 2-diol (9·3 g., 82%), prisms, m. p. 97° (lit.,[15] m. p. 96°) (Found: C, 63·2; H, 9·1. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·8%). Infrared absorption: see Table.

Treatment of the diol with toluene-*p*-sulphonyl chloride (2·1 mol.) in pyridine at room temperature for 12 hr. gave the trans-*ditoluene*-p-*sulphonate*, prisms (from methanol), m. p. 116° (Found: C, 56·7; H, 5·5; S, 15·4. $C_{20}H_{22}O_6S_2$ requires C, 56·85; H, 5·25; S, 15·2%).

Monotoluene-p-*sulphonate of* cyclo*Hex*-4-*ene*-trans-1 : 2-*diol*.—A solution of 4 : 5-epoxy-*cyclo*hexene (15·7 g.) in dry ether (100 c.c.) was slowly added to a stirred suspension of toluene-*p*-sulphonic acid (42 g.) in dry ether (80 c.c.) at 0°. The stirring was continued for 1 hr. at room temperature and the solution was then washed with water until neutral, dried (Na_2SO_4), and evaporated to a solid residue (39 g.), m. p. 65—66°. Recrystallisation from ether–light petroleum (b. p. 40—60°) gave the *trans*-monotoluene-*p*-sulphonate, needles, m. p. 67° (Found: C, 58·2; H, 6·25; S, 11·7. $C_{13}H_{16}O_4S$ requires C, 58·2; H, 6·0; S, 11·95%). On reaction with toluene-*p*-sulphonyl chloride in pyridine this gave the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 116°.

Treatment of the *trans*-monotoluene-*p*-sulphonate (39 g.) in pyridine (80 c.c.) with acetic anhydride (20 g.) for 36 hr. at 0°, followed by dilution with water, and recrystallisation of the precipitated solid from aqueous methanol gave the trans-*acetate toluene*-p-*sulphonate* (43 g.), needles, m. p. 87—88° (Found: C, 58·3; H, 6·1. $C_{15}H_{18}O_5S$ requires C, 58·0; H, 5·8%).

Monoacetate of cyclo*Hex*-4-*ene*-cis-1 : 2-*diol*.—A mixture of the *trans*-acetate toluene-*p*-sulphonate (20 g.), calcium carbonate (20 g.), acetone (165 c.c.), and water (165 c.c.) was boiled on the steam-bath for 48 hr. After filtration, the solution was concentrated under reduced pressure, then saturated with sodium chloride and extracted continuously with ether, to give an oil, which on distillation furnished the cis-*monoacetate* (9·35 g., 93%), b. p. 94°/2 mm., n_D^{22} 1·4792 (Found: C, 62·1; H, 8·2. $C_8H_{12}O_3$ requires C, 61·5; H, 7·8%).

Treatment of the product with toluene-*p*-sulphonyl chloride in pyridine gave the cis-*acetate toluene*-p-*sulphonate*, prisms (from methanol), m. p. 85° (Found: C, 57·7; H, 5·6; S, 10·4. $C_{15}H_{18}O_5S$ requires C, 58·0; H, 5·8; S, 10·3%). A mixed m. p. with the *trans*-isomer was 60—63°.

cyclo*Hex*-4-*ene*-cis-1 : 2-*diol*.—A solution of the *cis*-monoacetate (9 g.) and sodium (0·08 g.) in methanol (80 c.c.) was refluxed for 30 min., then cooled, neutralised with carbon dioxide, and concentrated under reduced pressure. The residue was dissolved in water (5 c.c.), saturated with sodium chloride, and extracted with ether to give the *cis*-diol (6·3 g., 96%), which crystallised from ether–light petroleum (b. p. 60—80°) in flakes, m. p. 80—81° (lit.,[14] m. p. 80·3—81·1°) (Found: C, 63·2; H, 9·0. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·8%). Infrared absorption: see Table.

Treatment of the *cis*-diol with toluene-*p*-sulphonyl chloride (2 mol.) in pyridine for 12 hr. at room temperature gave the cis-*ditoluene*-p-*sulphonate*, prisms (from methanol), m. p. 110° (Found: C, 56·9; H, 5·6; S, 15·2. $C_{20}H_{22}O_6S_2$ requires C, 56·85; H, 5·25; S, 15·2%).

[25] Senderens, *Compt. rend.*, 1923, **177**, 1183.
[26] Wibaut and Haak, *Rec. Trav. chim.*, 1948, **67**, 85.
[27] Tiffeneau and Tchoubar, *Compt. rend.*, 1941, **212**, 581.

Monotoluene-p-*sulphonate of* cyclo*Hex*-4-*ene*-cis-1 : 2-*diol*.—A solution of toluene-*p*-sulphonyl chloride (5 g.) in pure dry chloroform (35 c.c.) was added to a solution of the *cis*-diol (3 g.) in pyridine (8 c.c.) in small portions during 3 days at 0°. The mixture was kept at 0° for a further 24 hr. and it was then diluted with chloroform, washed with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water and dried (Na_2SO_4). Removal of the solvent gave an oil which was dissolved in boiling ether (20 c.c.); light petroleum (b. p. 40—60°) was added to faint turbidity and the mixture was left in the refrigerator. A solid (4·3 g.), m. p. 70—72°, separated and on fractional crystallisation from methanol gave the *cis*-ditoluene-*p*-sulphonate (0·8 g., 7%), m. p. and mixed m. p. 110°, and the cis-*monotoluene*-p-*sulphonate* (2·3 g., 33%), needles, m. p. 78° (Found: C, 58·3; H, 6·3; S, 11·5. $C_{13}H_{16}O_4S$ requires C, 58·2; H, 6·0; S, 11·95%).

Treatment of the *cis*-monotoluene-*p*-sulphonate in pyridine with a slight excess of toluene-*p*-sulphonyl chloride gave the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 110°.

Reactions of the Monotoluene-p-*sulphonates of* cyclo*Hex*-4-*ene*-1 : 2-*diol with Alkali*.—(i) The *trans*-monotoluene-*p*-sulphonate when shaken with 10% aqueous sodium hydroxide at room temperature gave 4 : 5-epoxy*cyclo*hexene (characteristic odour). The acidified mixture gave no precipitate with 2 : 4-dinitrophenylhydrazine sulphate. Similar treatment of the *cis*-isomer gave a solution which gave a positive reaction with the latter reagent.

(ii) The *cis*-monotoluene-*p*-sulphonate (0·5 g.), suspended in 10% aqueous sodium hydroxide (10 c.c.), was steam-distilled. Treatment of the distillate with aqueous 2 : 4-dinitrophenylhydrazine sulphate gave *cyclo*hex-2-enone 2 : 4-dinitrophenylhydrazone, orange needles (from methanol), m. p. 162—163° (Found: C, 51·95; H, 4·55; N, 19·9. Calc. for $C_{12}H_{12}O_4N_4$: C, 52·2; H, 4·4; N, 20·3%), $\lambda_{max.}$ (in $CHCl_3$) 3770 Å (ε 27,000). Birch [28] gives m. p. 165—166°. The derivative of *cyclo*hex-3-enone [28] has m. p. 131—132°.

Quantitative Alkaline Hydrolysis of the Monotoluene-p-*sulphonates*.—(i) Tetralin-*trans*-2 : 3-diol monotoluene-*p*-sulphonate (1·1555 g.) was dissolved in methanol (80 c.c.) and kept at 19°. A 5-c.c. portion was diluted with 40 c.c. of methanol at 19° and then rapidly mixed with 5 c.c. of 0·0837N-methanolic potassium hydroxide at 19°, thus giving a 0·00454M-solution of the ester in 0·00837N-alkali, and kept at this temperature for a known time. 0·1N-Hydrochloric acid (10 c.c.) was then rapidly added, and the excess of acid was titrated with standard alkali, bromophenol-blue being used as indicator.

The % reaction was: 64 (1 min.); 83 (2 min.); 89 (3 min.). The corresponding values of k_2 were 157, 155, and 133 mole^{-1} l. min.$^{-1}$.

(ii) Tetralin-*cis*-2 : 3-diol monotoluene-*p*-sulphonate (0·8508 g.) was dissolved in 0·0837N-methanolic potassium hydroxide (80 c.c.) at 19° (to give a 0·0334M-solution of the ester) and kept at that temperature under nitrogen. A 5 c.c.-portion was removed at intervals, added to 0·1N-hydrochloric acid (10 c.c.), and back-titrated with alkali. The % reaction was: 24 (1·5 hr.), 43 (3·5 hr.), 54 (5 hr.), 67 (7 hr.), 76 (9 hr.); and the corresponding values of k_2 were 0·038, 0·035, 0·035, 0·038, 0·039 mole^{-1} l. min.$^{-1}$.

(iii) For *cyclo*hex-4-ene-*trans*-1 : 2-diol monotoluene-*p*-sulphonate the method described in (i) was used, the rate measurements being made on a 0·00354M-solution of the ester in 0·00819N-methanolic potassium hydroxide. The % reaction was: 59 (1 min.), 74 (2 min.), 85 (3 min.), 90 (4 min.); and the corresponding values of k_2 were 130, 103, 104, and 98 mole^{-1} l. min.$^{-1}$.

(iv) *cyclo*Hex-4-ene-*cis*-1 : 2-diol monotoluene-*p*-sulphonate, as a 0·0351M-solution in 0·0819N-methanolic potassium hydroxide, gave the following values for % reaction: 19 (2 hr.), 32 (3·5 hr.), 39 (5 hr.), 54 (8 hr.); and respective k_2 values of 0·023, 0·024, 0·023, 0·023 mole^{-1} l. min.$^{-1}$.

Rates of Oxidation of the Tetralin-2 : 3-*diols with Lead Tetra-acetate*.—Rates for the *cis*- and for the *trans*-diol, in acetic acid at 25°, were determined by Cordner and Pausacker's method,[29] bimolecular rate constants being calculated from the slopes of the plots of $\log_{10} b(a - x)/a(b - x)$ against t. Results are given in the Table. As a control, a run was carried out on *cyclo*hexane-*trans*-1 : 2-diol, which gave $k_2 = 0{\cdot}33$ mole^{-1} l. min.$^{-1}$. Eliel and Pillar [17] give 0·316.

This work, and that described in the following paper, was carried out during the tenure (by M. E. A.) of a Foreign Scholarship awarded by the Government of Pakistan.

Department of Organic Chemistry, Imperial College of Science and Technology, South Kensington, London, S.W.7. [*Received, November 7th*, 1957.]

[28] Birch, *J.*, 1946, 593.
[29] Cordner and Pausacker, *J.*, 1953, 102.