435. *Alicyclic Glycols. Part XVII.*[1] *The Decalin-2 : 3-diols.*

By Md. Erfan Ali and L. N. Owen.

Confusion over the identity, individuality, and configuration of certain *trans*-decalin-2 : 3-diols has been resolved by a re-investigation of earlier claims and by the synthesis of the three possible stereoisomers; the three *cis*-decalin-2 : 3-diols have also been synthesised. The configurations of the six diols are established by relation to the ketols described in the preceding paper. The degrees of hydrogen-bonding, as shown by the infrared spectra of the diols, and the rates of oxidation by lead tetra-acetate, are in accord with the conformations compatible with the assigned configurations.

There are six possible racemic or *meso*-forms of decalin-2 : 3-diol. In the *cis*-fused system, one *trans*- ($2\alpha : 3\beta \equiv 2\beta : 3\alpha$) * and two *cis*-diols ($2\alpha : 3\alpha$ and $2\beta : 3\beta$) are capable of existence, but none has been described. In the *trans*-decalin configuration, there are two *trans*-diols ($2\alpha : 3\beta$ and $2\beta : 3\alpha$) and one *cis* ($2\alpha : 3\alpha = 2\beta : 3\beta$); the preparation of these has been studied by several investigators, but the results are conflicting in many respects.

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* *cis*-Decalin-$2\alpha : 3\beta$- and -$2\beta : 3\alpha$-diols are enantiomorphs, but as the present paper is concerned only with *meso* or racemic forms they are in effect identical.

[1] Part XVI, preceding paper.

Leroux[2] obtained a diol, m. p. 160°, (i) by alkaline hydrolysis of a 2 : 3-dibromo-*trans*-decalin, (ii) by acidic or alkaline hydrolysis of 2 : 3-epoxy-*trans*-decalin (IV), and (iii) from the corresponding iodohydrin. On the incorrect assumption that epoxides undergo *cis*-fission, the diol was assigned a *cis*-configuration. By reaction of the same dibromide with silver acetate, and hydrolysis of the product, he obtained a diol, m. p. 141° (erroneously assigned a *trans*-configuration), and a molecular compound, m. p. 125°, which he showed to be composed of equimolecular amounts of the two diols, m. p.s 160° and 141°, not separable by fractional crystallisation. The positions of the hydroxyl groups in all these products were established by oxidation to *cyclo*hexane-*trans*-1 : 2-diacetic acid. Hückel and Naab[3] confirmed these observations but found that the diol, m. p. 141°, gave an *iso*propylidene derivative from which it could be regenerated, and they therefore corrected the earlier configurational assignments, at the same time pointing out that the higher-melting isomer (for which they gave m. p. 163°) must be one of the two possible *trans*-diols. Lehmann and Krätschell,[4] by treatment of 3-chloro-2-oxo-*trans*-decalin with boiling 40% sodium hydroxide obtained a diol, m. p. 168°, which they suggested was formed by disproportionation of the initially-formed ketol; its structure was confirmed by oxidation to *cyclo*hexane-*trans*-1 : 2-diacetic acid, but it was not compared with the diol, m. p. 163°, described by the earlier workers.

The later work of Ganapathi,[5, 6] which, as will be shown, included a number of erroneous observations and incorrect interpretations, confused the situation. He reported the formation of three diols, m. p.s 166°, 128—129°, and 141°, by reduction of *trans*-decalin-2 : 3-dione (V) under various conditions. The first of these he considered to be identical with Leroux's diol, m. p. 160°, *and* with Lehmann and Krätschell's diol, m. p. 168°, and in a repetition of Leroux's experiments claimed that the diol obtained either from the dibromide or from the epoxide had m. p. 166°; he did not quote a mixed m. p. with his own product from the diketone. He also considered his diol, m. p. 128—129°, to be identical with Leroux's product of m. p. 125°, and yet to be a single stereoisomer, to which he assigned a *cis*-configuration. Other claims were that none of the diols reacted with acetone, and that his compound, m. p. 128—129°, was quantitatively isomerised by acetone–sulphuric acid into that of m. p. 166°. His fallacious arguments[6] for allocations of configuration need not be considered, as they are based on the assumption that there are one *trans*- and two *cis*-diols.

Other incidental references have been made to the *cis*-diol, m. p. 141°,[4, 7, 8] and the *trans*-diol, m. p. 163°,[8] but no suggestion has been made as to the precise configuration of the latter.

We began our investigation with a re-examination of some of Ganapathi's experiments. Reduction of the diketone (V) with aluminium amalgam in moist ether, aqueous ethanol, or dry ethanol gave in good yield a product, m. p. 128—129°, unaltered by fractional crystallisation; it was thus either an individual stereoisomer, as claimed by Ganapathi, or a molecular compound. On treatment with acetone–sulphuric acid it gave, in almost equal yields, a diol, m. p. 168°, and the *iso*propylidene derivative (VII) of *trans*-decalin-2α : 3α-diol; hydrolysis of the derivative furnished the *cis*-diol (VI), m. p. 141°. By mixing equal amounts of the two diols the original material, m. p. 128—129°, was regenerated; the latter is therefore unquestionably a molecular compound. Ganapathi's reported[6] quantitative isomerisation of his diol, m. p. 128—129°, into one of m. p. 166° can thus be attributed to inaccurate quantitative experimentation coupled with a failure

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[2] Leroux, *Ann. Chim. (France)*, 1910, **21**, 458.

[3] Hückel and Naab, *Annalen*, 1933, **502**, 136.

[4] Lehmann and Krätschell, *Ber.*, 1935, **68**, 360.

[5] Ganapathi, *J. Indian Chem. Soc.*, 1938, **15**, 407.

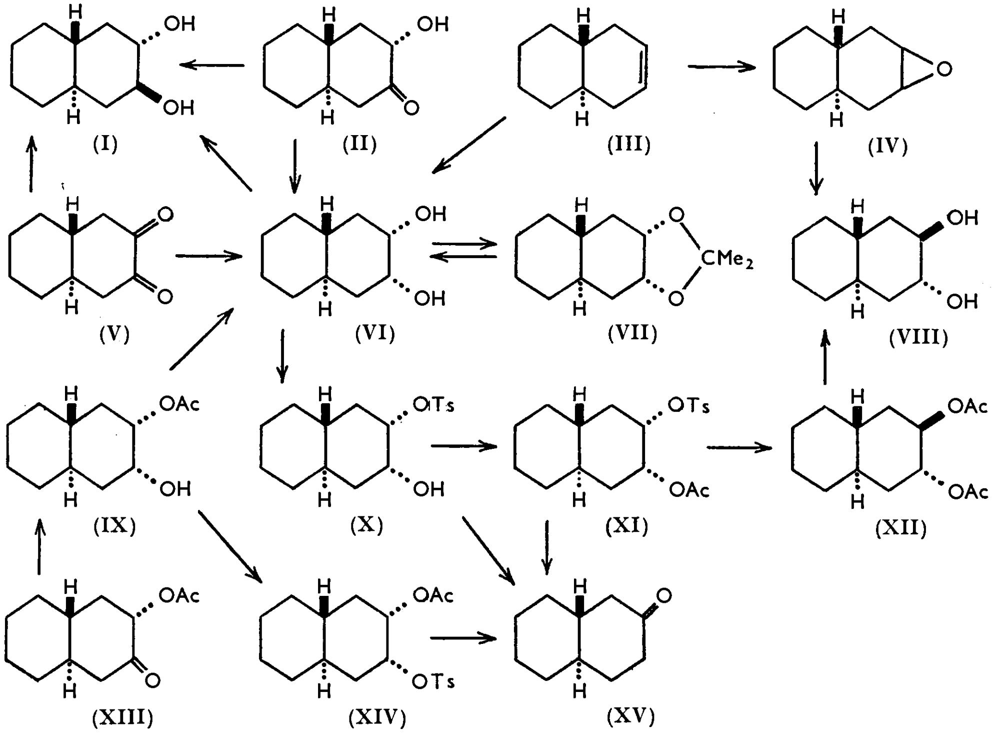
[6] *Idem, Ber.*, 1939, **72**, 1381.

[7] Lehmann and Krätschell, *Ber.*, 1934, **67**, 1857; Burnop, Elliott, and Linstead, *J.*, 1940, 720; Cosciug, *Ann. Sci. Univ. Jassy*, 1941, I, **27**, 303, 320; Mousseron and Granger, *Bull. Soc. chim. France*, 1943, **10**, 42.

[8] Criegee, Büchner, and Walther, *Ber.*, 1940, **73**, 571.

to detect any *iso*propylidene derivative. It is also untrue that the diol, m. p. 168° (166°), from the diketone is identical with that obtained from 2 : 3-epoxy-*trans*-decalin (IV); we find that the epoxide gives a diol, m. p. 163°, as stated by Hückel and Naab,[3] and that there is a large depression of melting point on admixture with the diol, m. p. 168°. These must therefore be the two possible *trans*-diols. Contrary to Ganapathi,[6] it follows that the molecular compound, m. p. 128—129° (141° + 168°), is *not* identical with that of m. p. 125° (141° + 163°); this again is immediately evident from a determination of mixed melting point.

It is now recognised [9,10] that hydration of an epoxy*cyclo*hexane normally leads to a diaxial diol. Consequently the compound, m. p. 163°, should be the 2β : 3α-diol (VIII), and the isomer, m. p. 168°, the 2α : 3β-diol (I); it is understandable that the latter, with the more stable diequatorial conformation, should be the product formed under the drastic alkaline conditions used by Lehmann and Krätschell.[4]



The availability of 3-oxo-*trans*-decalin-2α-ol (II), of established [1] configuration, enabled us to confirm these deductions. Reduction of the ketol with aluminium amalgam, sodium amalgam, or lithium aluminium hydride and also reduction of the dimeric ketol with lithium aluminium hydride gave in each case the molecular compound, m. p. 128—129°, from which the two constituent diols (I) and (VI) were again isolated by the process already described; the α-configuration at $C_{(2)}$ in the ketol (II) clearly demands the allocation of the 2α : 3β-configuration (I) to the *trans*-diol so produced. Catalytic hydrogenation of the ketol, and of its dimer,[1] over platinum in acetic acid, gave the 2α : 3α-diol (VI) as the main product, in agreement with the expectation [9] that under these conditions the reduction would proceed with preferential formation of an axial hydroxyl group. This stereospecific

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[9] Barton, *J.*, 1953, 1027.

[10] Fürst and Scotoni, *Helv. Chim. Acta*, 1953, **36**, 1332, 1410; Schmidlin and Wettstein, *ibid.*, p. 1241.

reduction was even more clearly illustrated by hydrogenation of the ketol acetate (XIII), which gave an almost quantitative yield of the monoacetate (IX) of the 2α : 3α-diol. A more convenient preparative route to the latter diol, however, was the *cis*-hydroxylation of *trans*-Δ^2-octalin (III), by Woodward's method,[11] with iodine and silver acetate in aqueous acetic acid. Toluene-*p*-sulphonation of the axial hydroxyl group in the 2α-monoacetate (IX) was slow, but afforded the 2α-acetate 3α-toluene-*p*-sulphonate (XIV), which with alkali showed behaviour typical[12] of a monotoluene-*p*-sulphonate of a *cis*-diol and gave *trans*-decalin-2-one (XV).

Epimerisation of the 2α : 3α-diol with sodium ethoxide gave the diequatorial 2α : 3β-isomer, whilst conversion into the diaxial 2β : 3α-diol was effected as follows. Reaction of the 2α : 3α-diol with one mol. of toluene-*p*-sulphonyl chloride in pyridine gave an excellent yield of a monotoluene-*p*-sulphonate, which was only slowly converted by an excess of the reagent into the ditoluene-*p*-sulphonate. Since an equatorial hydroxyl group is usually esterified more readily than one in an axial position, the monoester is the 2α-toluene-*p*-sulphonate (X). On acetylation it gave the 3α-acetate 2α-toluene-*p*-sulphonate (XI), which, like its precursor (X), on treatment with alkali gave *trans*-decalin-2-one (XV). When the mixed ester (XI) was treated with sodium acetate in boiling acetic anhydride it was slowly converted, by inversion at $C_{(2)}$, into the *trans*-diacetate (XII), which on hydrolysis furnished the 2β : 3α-diol (VIII).

The three possible *cis*-decalin-2 : 3-diols, hitherto unknown, have also been synthesised by methods which prove their structures. Reduction of 3-oxo-*cis*-decalin-2α-ol (XX)[1] with lithium aluminium hydride afforded a mixture of two diols which were separated by reaction with acetone; that, m. p. 125°, unaffected by this treatment must be the 2α : 3β-diol (XVII), whilst the isomer, m. p. 100°, obtained by hydrolysis of the *iso*propylidene derivative, has the 2α : 3α-configuration (XVI). Similar reduction of the acetate (XXII) of 3-oxo-*cis*-decalin-2β-ol[1] also gave a mixture, separable in the same way into the 2β : 3α-diol [identical with the 2α : 3β-diol (XVII)] and the 2β : 3β-diol (XVIII), m. p. 118°. The diol (XVII) was also obtained by hydrogenation of *trans*-2 : 3-diacetoxytetralin (XXI) over platinum in acetic acid, followed by hydrolysis of the resulting 2α : 3β-diacetoxy-*cis*-decalin; this reduction occurred stereospecifically by *cis*-addition, no other product being detected. Similar reduction of *cis*-2 : 3-diacetoxytetralin (XIX) gave a mixed diacetate, from which, after hydrolysis, some 2α : 3α-diol (XVI) was obtained; this would be the expected product from the most favourable orientation of the diacetoxytetralin on the catalyst, *i.e.* with the bulky axial acetoxy-group on the side remote from the catalyst surface, leading, after addition of hydrogen to the side adsorbed on the catalyst, to a *trans*-configuration between the acetoxy-groups and the bridgehead hydrogen atoms. The nonhomogeneity of the product, however, indicates that other orientations occur on the catalyst; probably some 2β : 3β-diacetoxy-*cis*-decalin was also formed, and the possibility of some *trans*-addition cannot be excluded. Some experiments were also carried out on the hydrogenation, over platinum, of naphthalene-2 : 3-diol, but as the main product formed under mild conditions was the molecular compound of tetralin-*cis*- and -*trans*-2 : 3-diol it was evident that complete hydrogenation would lead to a mixture, and this approach was therefore not pursued.

The infrared absorption maxima of the diols in the 3000 cm.$^{-1}$ region (in dilute carbon tetrachloride solution), and the rates of oxidation by lead tetra-acetate are given in the Table, which also includes, for comparison, the corresponding data for the two *cyclo*-hexane-1 : 2-diols. The frequency difference, $\Delta\nu$, between the maxima for the bonded and the unbonded hydroxyl groups is a measure of the strength of the intramolecular hydrogen bonding,[13, 14] and the figures for the *trans*-decalin-2α : 3α- and the -2α : 3β-diol are in good

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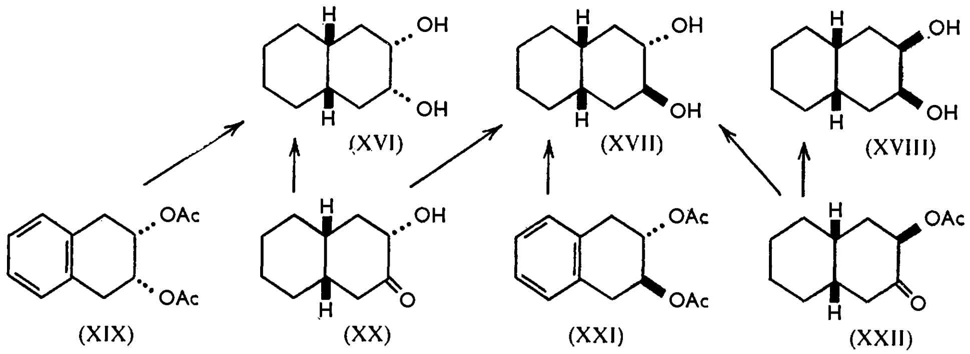
[11] Cf. Ginsburg, *J. Amer. Chem. Soc.*, 1953, **75**, 5746.

[12] Clarke and Owen, *J.*, 1949, 315; Owen and Saharia, *J.*, 1953, 2582.

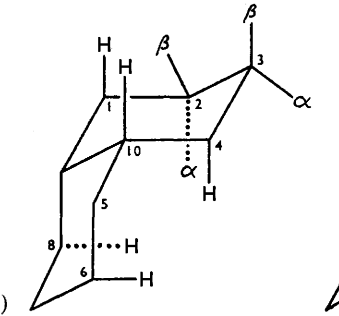
[13] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

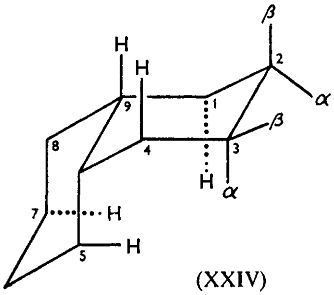
[14] *Idem, ibid.*, 1954, **76**, 4323.

agreement with those for the *cyclo*hexanediols of corresponding configuration; the diaxial *trans*-decalin-2β : 3α-diol, as expected, showed no hydrogen bonding. In the *cis*-decalin series the greater degree of bonding in the 2α : 3α-diol is explicable if inter-ring repulsions [15] are considered, because in each possible double-chair form (XXIII) and (XXIV) there is a strong non-bonded interaction between one hydroxyl group and an axial hydrogen atom in the other ring, *viz.* $O_{(2)}$–$H_{(8)}$ and $O_{(3)}$–$H_{(5)}$, respectively; steric strain is thus the same in both conformations * and can only be relieved by displacement of the axial hydroxyl group, at $C_{(2)}$ or $C_{(3)}$, respectively, towards its equatorial position, thus bringing it nearer to the other hydroxyl group. By applying Kuhn's findings,[13] a frequency difference of 45 cm.$^{-1}$ can be accounted for by a reduction in projection angle (between the two C–OH bonds, viewed along the $C_{(2)}$–$C_{(3)}$ axis) from the normal value of 60° to one of 40°. A scale model shows that such a distortion can be brought about without undue strain, and that it increases the $O_{(2)}$–$H_{(8)}$ or $O_{(3)}$–$H_{(5)}$ distance from 1·7 Å to 2·2 Å. *cis*-Decalin-2α : 3β-diol will clearly exist preferentially in the particular double-chain form (XXIV) in which the hydroxyl groups are in diequatorial rather than diaxial positions; consequently, non-bonded interaction between $O_{(2)}$ and $H_{(8)}$ does not arise, and Δν is not enlarged. In the 2β : 3β-diol there is neither $O_{(2)}$–$H_{(8)}$ nor $O_{(3)}$–$H_{(5)}$ interaction in either of the forms (XXIII) or (XXIV).


(XVI) (XVII) (XVIII)

(XIX) (XX) (XXI) (XXII)


(XXIII)


(XXIV)

The rates of oxidation of *trans*-decalin-2α : 3α- and -2α : 3β-diol were practically identical with those of the corresponding *cyclo*hexane-1 : 2-diol. For the *trans*-diols this is not surprising, but the similarity between the *cis*-diols is interesting because the two C–OH bonds in *trans*-decalin-2α : 3α-diol, unlike those in *cyclo*hexane-*cis*-1 : 2-diol, cannot become coplanar even if the ring is in a boat form. This is because coplanarity of the C–OH bonds in the 2α : 3α-diol requires coplanarity of $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$, *i.e.* a boat form with sides

* These are mirror images for the 2α : 3α- and also for the 2β : 3β-, but not for the 2α : 3β-diol.

[15] Cf. Mills, *J.*, 1953, 260; Dauben, Tweit, and Mannerskantz, *J. Amer. Chem. Soc.*, 1954, **76**, 4420.

2, 3, 9, and 10, but owing to the *trans*-junction of the rings only boat forms with sides 1, 9, 3, and 4, or 1, 2, 4, and 10, are possible; the coplanar arrangement is momentarily attained in passing from the chair to either of the boats, but the conformation is highly unfavourable. It seems unlikely, therefore, from the similarity in rates, that the oxidation of *cyclo*hexane-*cis*-1 : 2-diol with lead tetra-acetate can involve a *planar* cyclic intermediate, though both with this diol and with *trans*-decalin-2α : 3α-diol there may be some small displacement towards such a state. The comparatively slow rate of oxidation of the diaxial *trans*-decalin-2β : 3α-diol is in accordance with expectation, there being no anomaly such as that reported by Djerassi *et al.*,[16] who found with certain *allo*steroid-2 : 3-diols that the diaxial compound was oxidised more rapidly than its diequatorial isomer. The behaviour of *cis*-decalin-2α : 3β-diol was almost identical with that of *cyclo*hexane-*trans*-1 : 2-diol, but *cis*-decalin-2α : 3α-diol was oxidised three times as fast as *cyclo*hexane-*cis*-1 : 2-diol, thus providing further evidence that the two hydroxyl groups in the 2α : 3α-diol are closer together than in any of the other isomers.

		Infrared absorption max. (cm.$^{-1}$)			
Diol	M. p.	Free OH	Bonded OH	Δν	Oxidn. rate constant (mole^{-1} l. min.$^{-1}$; 25°)
*cyclo*Hexane-*cis*-1 : 2-	—	3626	3587	39 *	8·1 †
,, *trans*-1 : 2- ...	—	3634	3602	32 *	0·33 ‡
trans-Decalin-2α : 3α-	141°	3625	3588	37	8·1 §
,, 2α : 3β-	168	3630	3600	30	0·37
,, 2β: 3α-	163	3630	—	0	0·028 §
cis-Decalin-2α : 3α-	100	3632	3587	45	24·0
,, 2β : 3β-	118	3625	3592	33	—
,, 2α : 3β-	125	3627	3597	30	0·29

* Ref. 13. † Ref. 17. ‡ Ref. 18. § Criegee *et al.*[8] give 4·6 and 0·021 at 20° for two *trans*-decalin-2 : 3-diols, m. p.s 141° and 163°, respectively.

Rates of oxidation by sodium metaperiodate, also, were measured for *trans*-decalin-2α : 3β- and -2β : 3α-diol. The bimolecular rate constant for the diequatorial diol was about ten times that for the diaxial isomer, a ratio similar to that observed for the oxidations with lead tetra-acetate.

EXPERIMENTAL

trans-*Decalin-2-one* 2 : 4-*dinitrophenylhydrazone*, prepared from the ketone in the usual way, formed yellow needles (from ethyl acetate), m. p. 174° (Found: C, 57·6; H, 6·1; N, 16·9. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·1; N, 16·9%).

Reduction of trans-*Decalin*-2 : 3-*dione*.—(i) *In moist ether*. Following Ganapathi's method,[5] treatment of the diketone (0·35 g.) with aluminium amalgam (1·5 g.) in ether (150 c.c.) saturated with water gave a product which was recrystallised from light petroleum (b. p. 80—100°) to give the *molecular compound*, m. p. 128—129°, of *trans*-decalin-2α : 3α-diol and *trans*-decalin-2α : 3β-diol (0·28 g., 78%) (Found: C, 70·7; H, 10·8. $2C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%). Ganapathi [5] gave m. p. 126° for his product, considered to be a single stereoisomer.

(ii) *In aqueous ethanol*. A solution of the diketone (0·31 g.) in ethanol (50 c.c.) was added to aluminium amalgam (1 g.). Water was occasionally added to maintain a steady reaction, which was complete in 8 hr. The aluminium hydroxide was filtered off and washed with ethanol, and the combined filtrate and washings were evaporated to a crystalline residue, which on recrystallisation from light petroleum (b. p. 80—100°) gave the same molecular compound (0·20 g., 62%), m. p. and mixed m. p. 126—128°. Fractional crystallisation from benzene did not separate the components.

(iii) *In dry ethanol*. A mixture of the diketone (0·15 g.), aluminium amalgam (0·5 g.), and dry ethanol (25 c.c.) was stirred and heated at 70° until (6 hr.) all the amalgam had reacted.

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[16] Djerassi and Ehrlich, *J. Org. Chem.*, 1954, **19**, 1351; cf. Djerassi, Grossnickle, and High, *J. Amer. Chem. Soc.*, 1956, **78**, 3166, footnote 58.

[17] Eliel and Pillar, *J. Amer. Chem. Soc.*, 1955, **77**, 3600.

[18] Ali and Owen, *J.*, 1958, 1066.

The mixture was then diluted with water, filtered, and worked up; it gave the same molecular compound, m. p. and mixed m. p. 128—129°.

Separation of the Molecular Compound of trans-*Decalin*-2α : 3α- *and* -2α : 3β-*diol by Reaction with Acetone.*—The molecular compound (0·40 g.) in dry acetone (30 c.c.) containing sulphuric acid (0·1 g.) was kept for 24 hr. at room temperature. The solution was then made faintly alkaline with concentrated ammonia and the precipitated ammonium sulphate was filtered off. Evaporation of the filtrate gave an oil, which was dissolved in hot light petroleum (b. p. 80—100°) (2 c.c.). When this was cooled in ice a solid crystallised, which was recrystallised from benzene, giving trans-*decalin*-2α : 3β-*diol* (0·18 g., 45%), needles, m. p. 168° (Found: C, 70·4; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%); infrared absorption: see Table. The mother liquor was evaporated and the residue was again treated with light petroleum (b. p. 40—60°) (1 c.c.) and cooled in ice to give a small amount of the same diol, m. p. 166°. The oil obtained by evaporation of the solution was distilled to give 2α : 3α-iso*propylidenedioxy*-trans-*decalin* (0·22 g., 44%), b. p. 90°/16 mm., n_D^{20} 1·4728 (Found: C, 74·1; H, 10·7. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%); Hückel and Naab[3] reported its formation, but recorded no analysis or physical constants.

Hydrolysis of the *iso*propylidene compound (0·22 g.) with 2N-sulphuric acid (2 c.c.) for 2 hr. on the steam-bath, followed by extraction with ether and evaporation of the dried (Na_2SO_4) extract, gave a solid which after two recrystallisations from benzene furnished *trans*-decalin-2α : 3α-diol (0·14 g.), m. p. 141°; infrared absorption: see Table.

A 1 : 1 mixture of the 2α : 3β- and 2α : 3α-diol, dissolved in benzene and evaporated, gave the original molecular compound, m. p. 128—129°.

trans-*Decalin*-2β : 3α-*diol*.—Prepared by Hückel and Naab's method[3] from 2 : 3-epoxy-*trans*-decalin, this had m. p. 163°; infrared absorption: see Table. A mixture with the 2α : 3β-diol (m. p. 168°) had m. p. *ca.* 130°. Equal amounts of the 2β : 3α- and the 2α : 3α-diol were dissolved in hot benzene; on cooling, the molecular compound, m. p. 125°, was deposited. A mixture of this with the 2α : 3β- and 2α : 3α-molecular compound (m. p. 128—129°) had m. p. 110—115°.

Reduction of 3-*Oxo*-trans-*decalin*-2α-*ol*.—(i) *With aluminium amalgam in aqueous ethanol.* The ketol (0·15 g.) in ethanol (50 c.c.) was reduced with aluminium amalgam (1 g.) as described above for *trans*-decalin-2 : 3-dione. The product crystallised from light petroleum (b. p. 80—90°) to give the molecular compound, m. p. and mixed m. p. 128—129°, of *trans*-decalin-2α : 3α- and -2α : 3β-diol (0·08 g., 53%). The product was separated into its constituents by reaction with acetone, as described above.

(ii) *With sodium amalgam.* The ketol (0·14 g.), 3% sodium amalgam (2·5 g.), methanol (15 c.c.), and water (2 c.c.) were stirred until the evolution of hydrogen had ceased. The alcohol layer was then neutralised with 2N-hydrochloric acid and evaporated to dryness. The residue was extracted with ether to yield a product which on recrystallisation from benzene gave the above molecular compound (0·11 g., 78%), m. p. and mixed m. p. 129—130°.

(iii) *With lithium aluminium hydride.* The ketol (0·15 g.) in dry ether (10 c.c.) was added to a stirred solution of lithium aluminium hydride (0·30 g.) in dry ether (15 c.c.). After an hour, an excess of dilute sulphuric acid was added, and the ether layer was removed; the aqueous portion was extracted with ether, and the combined ethereal solutions were evaporated to a crystalline residue, m. p. 122—126°. Two recrystallisations from light petroleum (b. p. 80—90°) gave the same molecular compound (0·146 g., 96%), m. p. and mixed m. p. 128—130°.

(iv) *By catalytic hydrogenation.* The ketol (0·15 g.) in acetic acid (10 c.c.) was hydrogenated over platinum oxide (0·03 g.) at 19° and 760 mm.; 22 c.c. of hydrogen were absorbed (calc. 21·4 c.c.) during 3 hr. Removal of the catalyst followed by evaporation of the solvent under reduced pressure gave an oil which was diluted with water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated to a solid (0·145 g.), m. p. 133—135°. This was fractionally crystallised five times from benzene to give *trans*-decalin-2α : 3α-diol (0·048 g., 31·5%), m. p. and mixed m. p. 140—141°, as the less soluble portion, and the molecular compound of *trans*-decalin-2α : 3α- and -2α : 3β-diol (*ca.* 6 mg., 4%), m. p. and mixed m. p. 128—129°, from the more soluble fractions.

Reduction of trans-A/B : trans-D/E-5a : 12a-*Dihydroxy*-6 : 13-*dioxaperhydropentacene*.—(i) *With lithium aluminium hydride.* Because of the very low solubility of the dimer[1] in ether, this reduction was effected in a Soxhlet extraction apparatus, with the dimer (0·2 g.) in the thimble and a solution of lithium aluminium hydride (0·2 g.) in dry ether (100 c.c.) in the flask. Refluxing was maintained for 2 days, during which most of the dimer disappeared. The mixture was then diluted with sulphuric acid, and the product isolated as usual to give the molecular compound, m. p. and mixed m. p. 128—129°.

(ii) *By catalytic hydrogenation.* Hydrogenation of a suspension of the dimer (0·078 g.) in acetic acid (10 c.c.) over platinum oxide (0·03 g.) during 14 hr., followed by working up as before and one crystallisation from benzene, furnished *trans*-decalin-2α : 3α-diol, m. p. and mixed m. p. 139—140°.

*Hydrogenation of 2α-Acetoxy-3-oxo-*trans-*decalin.*—The acetate [1] (3·8 g.) in acetic acid (100 c.c.) was hydrogenated at 19° and 760 mm. over platinum oxide (0·2 g.); 453 c.c. of hydrogen were taken up during 7 hr. (calc., 433 c.c.). The filtered solution was concentrated under reduced pressure, diluted with water, and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and with water, and evaporated to a solid (3·8 g.), m. p. 79—82°, which on recrystallisation from light petroleum (b. p. 40—60°) gave trans-*decalin-2α : 3α-diol 2-monoacetate,* needles, m. p. 83° (Found: C, 67·5; H, 9·5. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%).

Treatment of this monoacetate (0·10 g.) with a trace of sodium methoxide in dry methanol (8 c.c.) for 30 min. under reflux, followed by isolation of the product as usual, gave *trans*-decalin-2α : 3α-diol (0·08 g.), m. p. and mixed m. p. 141°.

trans-*Decalin-2α : 3α-diol 2-Acetate 3-Toluene-*p-*sulphonate.*—The above 2-monoacetate (0·13 g.) was treated with toluene-*p*-sulphonyl chloride (0·13 g.) in pyridine (1·5 c.c.) at room temperature overnight. Dilution with water gave unchanged monoacetate, m. p. and mixed m. p. 81—82°. This was again treated with toluene-*p*-sulphonyl chloride (0·13 g.) in pyridine (0·5 c.c.) at room temperature for 96 hr. Dilution with crushed ice gave a solid which was recrystallised from methanol, giving trans-*decalin-2α : 3α-diol 2-acetate 3-toluene-*p-*sulphonate* (0·09 g., 41%), needles, m. p. 106—107° (Found: C, 62·2; H, 7·2; S, 8·7. $C_{19}H_{26}O_5S$ requires C, 62·3; H, 7·15; S, 8·75%).

Treatment of this mixed ester (0·014 g.) with 2N-methanolic sodium methoxide (0·5 c.c.) for 3 days at room temperature, followed by acidification with 2N-sulphuric acid and treatment with aqueous 2 : 4-dinitrophenylhydrazine sulphate, gave *trans*-2-decalone 2 : 4-dinitrophenylhydrazone (0·012 g., 95%), which after recrystallisation from ethyl acetate had m. p. and mixed m. p. 173—174°.

cis-*Hydroxylation of* trans-Δ^2-*Octalin.*—Prepared by Leroux's method,[2] *trans*-Δ^2-octalin had b. p. 188—190°, n_D^{23} 1·4832; it probably [3] contained *ca.* 10% of Δ^1-octalin.

The olefin (6 g.), acetic acid (380 c.c.), water (1 c.c.), and silver acetate (16 g.) were stirred at room temperature during the gradual (30 min.) addition of iodine (11 g.) and for a further 3 hr. The mixture was heated on the steam-bath for another 3 hr., then cooled, filtered, and concentrated under reduced pressure. The residue was treated with methanol (300 c.c.) and filtered again. The solution was brought to pH 10 with methanolic potassium hydroxide and then treated with a solution of potassium hydroxide (5 g.) in methanol (100 c.c.) for 18 hr. at room temperature under nitrogen. Neutralisation with 50% aqueous acetic acid followed by removal of the alcohol under reduced pressure gave an oily suspension which solidified. This was washed with a little water and dissolved in methanol. The solution was decolorised with charcoal, concentrated to small volume, and diluted with a little water, to give *trans*-decalin-2α : 3α-diol (3·2 g., 42·7%), flakes, m. p. and mixed m. p. 141°.

The mother liquor was diluted with more water, and set aside. After several days the solid which had separated was collected, dissolved in hot water and treated with charcoal. From the colourless solution, trans-*decalin-*cis-*1 : 2-diol* (0·15 g., 2%), crystallised in long needles, m. p. 109° (Found: C, 70·3; H, 10·5. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%). A few minutes' oxidation of this diol (0·03 g.) with potassium permanganate (0·035 g.) in water (3 c.c.) on the steam-bath followed by filtration gave a solution which was washed several times with ether and then acidified with dilute sulphuric acid. Extraction with ether followed by removal of the solvent and crystallisation of the solid from water gave β-*trans*-2-carboxy*cyclo*hexylpropionic acid, m. p. 138—139°. A mixed m. p. was the same as that of an authentic specimen, 142°. The 1 : 2-diol was derived from the small proportion of *trans*-Δ^1-octalin present in the original olefin. By analogy with the stereochemical mode of *cis*-addition to steroid olefins by this method,[19] the product was probably the 1β : 2β-diol.

Epimerisation of trans-*Decalin-2α : 3α-diol.*—To the solution obtained by reaction of sodium

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[19] Klass, Fieser, and Fieser, *J. Amer. Chem. Soc.*, 1955, **77**, 3829; Henbest, *J.*, 1957, 926; Shoppee, Jones, and Summers, *ibid.*, p. 3100.

(0·5 g.) with ethanol (20 c.c.) the diol (0·4 g.) was added. The mixture was heated at 170° for 5 hr., then cooled, neutralised with hydrochloric acid, and evaporated to dryness. The residue was extracted four times with boiling light petroleum (b. p. 80—100°), and the extracts were evaporated to a solid which was freed from a small amount of oily impurity by drainage on porous tile. Recrystallisation from benzene then afforded *trans*-decalin-2α : 3β-diol, m. p. and mixed m. p. 168°; a further crop was obtained by concentration of the mother liquor (total yield, 0·26 g.).

trans-*Decalin*-2α : 3α-*diol* 2-*Monotoluene*-p-*sulphonate*.—Toluene-*p*-sulphonyl chloride (2·23 g.) in pure chloroform (30 c.c.) was added in small portions to the 2α : 3α-diol (2 g.) in pyridine (10 c.c.) during 4 days at 0°. The mixture was kept at 0° for a further 24 hr. and was then diluted with chloroform and washed with water, dilute sulphuric acid, aqueous sodium hydrogen carbonate, and again with water. Removal of the solvent from the dried (Na_2SO_4) solution and two recrystallisations from aqueous methanol gave trans-*decalin*-2α : 3α-*diol* 2-*monotoluene*-p-*sulphonate* (3 g., 78%), m. p. 113° (Found: C, 62·8; H, 7·55; S, 9·7. $C_{17}H_{24}O_4S$ requires C, 62·95; H, 7·5; S, 9·9%).

Treatment of this derivative (0·03 g.) with 2N-methanolic sodium methoxide (1 c.c.) for 18 hr. at room temperature, followed by acidification with sulphuric acid and addition of 2 : 4-dinitrophenylhydrazine sulphate solution, gave *trans*-2-decalone 2 : 4-dinitrophenylhydrazone (0·02 g., 80%), which after recrystallisation from ethyl acetate had m. p. and mixed m. p. 174°.

trans-*Decalin*-2α : 3α-*diol Ditoluene*-p-*sulphonate*.—(i) A solution of the 2α : 3α-diol (0·1 g.) and toluene-*p*-sulphonyl chloride (0·3 g.) in dry pyridine (1 c.c.) was kept for 48 hr. at room temperature and then treated with crushed ice; the precipitate was crystallised from methanol, giving the 2α : 3α-*ditoluene*-p-*sulphonate* (0·04 g., 14%), prisms, m. p. 151° (Found: C, 60·3; H, 6·4; S, 13·2. $C_{24}H_{30}O_6S_2$ requires C, 60·2; H, 6·3; S, 13·4%). The mother liquor, on dilution with water, gave a solid which after several recrystallisation from aqueous methanol gave the 2-monotoluene-*p*-sulphonate (0·15 g., 78%), m. p. and mixed m. p. 112°.

(ii) Treatment of the 2-monotoluene-*p*-sulphonate (0·20 g.) with toluene-*p*-sulphonyl chloride (0·14 g.) in pyridine for 96 hr. at room temperature, followed by dilution with water, gave a solid, m. p. 118—125°, which after recrystallisations from methanol gave the 2α : 3α-ditoluene-*p*-sulphonate (0·15 g., 50%), m. p. and mixed m. p. 151°.

trans-*Decalin*-2α : 3α-*diol* 3-*Acetate* 2-*Toluene*-p-*sulphonate*.—A mixture of acetic anhydride (1·4 g.), pyridine (9 c.c.), and *trans*-decalin-2α : 3α-diol 2-monotoluene-*p*-sulphonate (1·4 g.) was kept for 5 days at room temperature. Dilution with water gave a solid which on recrystallisation from aqueous methanol formed the 2α : 3α-*diol* 3-*acetate* 2-*toluene*-p-*sulphonate* (1·53 g., 97%), needles, m. p. 122° (Found: C, 62·6; H, 7·4; S, 8·4. $C_{19}H_{26}O_5S$ requires C, 62·3; H, 7·15; S, 8·75%). Treatment of this derivative with 2N-methanolic sodium methoxide, as described above for the monotoluene-*p*-sulphonate, gave *trans*-decalin-2-one, isolated as the 2 : 4-dinitrophenylhydrazone (90%), m. p. and mixed m. p. 173—174°.

trans-*Decalin*-2β : 3α-*diol Diacetate*.—A solution of *trans*-decalin-2α : 3α-diol 3-acetate 2-toluene-*p*-sulphonate (0·81 g.) and potassium acetate (0·62 g.) in acetic acid (10 c.c.) and acetic anhydride (5 c.c.) was heated for 12 hr. on the steam-bath and then boiled under reflux for 18 hr. Dilution of the cooled mixture with water, followed by neutralisation with solid sodium hydrogen carbonate and extraction with ether, gave a crude product, m. p. 107—112°; the m. p. of a mixture with the original compound was 115—117°.

The recovered material was then boiled under reflux with sodium acetate (2 g.) in acetic anhydride (15 c.c.) for 48 hr. The mixture was then cooled and worked up as above to give a liquid, which on distillation gave an oil (0·1 g.), b. p. 78—120°/3 mm., n_D^{20} 1·4769. Recrystallisation of the solidified oil from aqueous methanol gave *trans*-decalin-2β : 3α-diol diacetate, flakes, m. p. 85° (the reported [2,3] m. p. for the diacetate of a *trans*-decalin-*trans*-2 : 3-diol is 85°).

Treatment of this diacetate under reflux with a trace of sodium methoxide in methanol (5 c.c.) for 30 min. followed by evaporation to dryness, trituration with a few drops of water, and crystallisation from aqueous methanol gave *trans*-decalin-2β : 3α-diol, m. p. and mixed m. p. 163°.

Reduction of 3-*Oxo*-cis-*decalin*-2α-*ol*.—A solution of the ketol [1] (0·25 g.) in dry ether (15 c.c.) was added to a stirred solution of lithium aluminium hydride (0·6 g.) in dry ether (20 c.c.). The mixture was then refluxed for an hour and worked up as described for the reduction of the *trans*-ketol giving a solid (0·23 g., 90%), m. p. 75—85°, which was dissolved in acetone (40 c.c.) containing sulphuric acid (0·1 c.c.). After 24 hr. at room temperature, the solution was neutralised with concentrated ammonia, filtered, and evaporated to an oil, which was diluted with light petroleum (b. p. 80—100°) (2 c.c.). The precipitate was crystallised from ether to give cis-*decalin*-2α : 3β-*diol* (0·02 g., 10%), long needles, m. p. 125° (Found: C, 70·4; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%). Infrared absorption: see Table. Reaction of the diol with a slight excess of toluene-*p*-sulphonyl chloride in pyridine for 3 days at room temperature gave the *ditoluene*-p-*sulphonate*, prisms (from methanol), m. p. 126—127° (Found: C, 60·5; H, 6·5; S, 13·3. $C_{24}H_{30}O_6S_2$ requires C, 60·2; H, 6·3; S, 13·4%).

The petroleum solution remaining after isolation of the above diol was evaporated and the residue distilled to give 2α : 3α-iso*propylidenedioxy*-cis-*decalin* (0·07 g., 27%), b. p. 118°/10 mm. (Found: C, 74·1; H, 10·6. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%). This derivative (0·06 g.) was heated on the steam bath for 1 hr. with 2N-sulphuric acid (4 c.c.), and the cooled solution then extracted with ether to give a solid, recrystallisation of which from light petroleum (b. p. 60—80°) gave cis-*decalin*-2α : 3α-*diol* (0·03 g.), m. p. 100° (Found: C, 70·4; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%); infrared absorption: see Table.

Reduction of 3-*Oxo*-cis-*decalin*-2β-*yl Acetate.*—The 2β-acetate [1] (0·42 g.) was reduced with lithium aluminium hydride (0·6 g.) in boiling ether (35 c.c.) as described above. The product (0·28 g., 82%), m. p. 114—116°, was treated with acetone containing a trace of sulphuric acid and worked up in the same way to give *cis*-decalin-2α : 3β-diol (0·15 g., 53%), m. p. and mixed m. p. 125°, and 2β : 3β-iso*propylidenedioxy*-cis-*decalin* (0·08 g., 23%), b. p. 119°/11 mm. (Found: C, 74·1; H, 10·8. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%). Hydrolysis of the *iso*propylidene compound (0·07 g.) with 2N-sulphuric acid gave cis-*decalin*-2β : 3β-*diol* (0·03 g.), needles (from light petroleum, b. p. 80—100°), m. p. 118° (Found: C, 70·8; H, 10·95. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·65%); infrared absorption: see Table.

Hydrogenation of trans-2 : 3-*Diacetoxytetralin.*—*trans*-2 : 3-Diacetoxytetralin (0·9 g.) [obtained from the hydrogenation products of naphthalene-2 : 3-diol (see below)], dissolved in acetic acid (20 c.c.) containing a few drops of ethanolic hydrogen chloride,[20] was hydrogenated over platinum oxide (0·05 g.) at 17° and 764 mm.; 253 c.c. of hydrogen were absorbed during 24 hr. (calc.: 257 c.c.). The filtered solution was evaporated and the residue was dissolved in ether, washed with aqueous sodium hydrogen carbonate, and with water, and dried ($MgSO_4$). Removal of the solvent followed by distillation of the residue afforded cis-*decalin*-2α : 3β-*diol diacetate* (0·6 g., 65%), b. p. 110°/2 × 10^{-3} mm., n_D^{23} 1·4756 (Found: C, 66·2; H, 8·8; O, 25·1. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7; O, 25·2%).

Treatment of the diacetate with a trace of sodium methoxide in dry methanol under reflux for 30 min., and recrystallisation of the product from ether, gave *cis*-decalin-2α : 3β-diol, m. p. and mixed m. p. 125°.

cis-2 : 3-*Diacetoxytetralin.*—Treatment of *cis*-tetralin-2 : 3-diol monoacetate [18] (2·1 g.) with acetic anhydride (1·4 g.) in pyridine (8 c.c.) for 48 hr. at room temperature, followed by dilution with water and crystallisation from aqueous methanol, gave *cis*-2 : 3-diacetoxytetralin (2·2 g., 87%), prisms, m. p. 58° (lit.,[2] m. p. 59°).

Hydrogenation of cis-2 : 3-*Diacetoxytetralin.*—The diacetate (2·16 g.) in acetic acid (25 c.c.) was hydrogenated over platinum oxide (0·1 g.) at 19° and 768 mm. for 96 hr.; 595 c.c. of hydrogen were absorbed. Working up of the product as described for the *trans*-isomer gave a diacetate (1·93 g., 87%), b. p. 102°/3 × 10^{-2} mm., n_D^{23} 1·4722—1·4805 (Found: C, 66·3; H, 8·7. Calc. for $C_{14}H_{22}O_4$: C, 66·1; H, 8·7%). Catalytic deacetylation of this product with methanolic sodium methoxide gave a solid, m. p. 78—84°, which was fractionally crystallised from light petroleum (b. p. 80—100°), giving *cis*-decalin-2α : 3α-diol (0·3 g.), m. p. and mixed m. p. 100°, as the less soluble fraction. The more soluble component could not be isolated pure.

Hydrogenation of Naphthalene-2 : 3-*diol.*—The technical grade material was treated in boiling benzene first with charcoal and then with Raney nickel. Recrystallisation from benzene then gave a colourless product, m. p. 162° [lit.,[21] m. p. 163·5—164° (corr.)]. This (50 g.) was hydrogenated in ethanol (200 c.c.), containing platinum oxide (0·4 g.), at 125° and 100 atm. until absorption ceased (78 hr.). The mixture was filtered and evaporated; the semi-solid residue was mixed with 10% aqueous sodium hydroxide (250 c.c.) and extracted with ether. Solvent was removed from the dried (Na_2SO_4) extract, and the residue (11·6 g.) fractionally crystallised from benzene, giving, as the less soluble fraction (7·6 g.), the molecular compound, m. p. 141°, of tetralin-2 : 3-*cis*- and -*trans*-diol (Found: C, 72·9; H, 7·5. Calc. for $C_{10}H_{12}O_2$:

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[20] Brown, Durand, and Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 1594.

[21] Machek and Sitzber, *Monatsh.*, 1933, **62**, 195.

C, 73·1; H, 7·4%) [lit.,[22] m. p. 141·8—142·8° (corr.)]. The more soluble fraction gave tetralin-*cis*-2 : 3-diol, m. p. 120—121° (Found: C, 73·4; H, 7·5%) (lit.,[22] m. p. 124—125°).

The aqueous layer was acidified with dilute sulphuric acid and extracted with ether. Removal of the solvent from the dried (Na_2SO_4) extract and crystallisation of the residue from benzene gave unchanged naphthalene-2 : 3-diol (13·8 g.), m. p. and mixed m. p. 160°.

The molecular compound, m. p. 141° (7 g.), was treated with acetic anhydride (9·5 g.) in pyridine (10 g.) and benzene (200 c.c.) according to Leroux's method.[2] The oily product (9·9 g.) was dissolved in ethanol and cooled in ice, whereupon *trans*-2 : 3-diacetoxytetralin (2·6 g.), m. p. 110°, separated (Found: C, 67·9; H, 6·6. Calc. for $C_{14}H_{16}O_4$: C, 67·7; H, 6·5%) (lit.,[3] m. p. 111°). Deacetylation of a portion of this diacetate gave tetralin-*trans*-2 : 3-diol, m. p. and mixed m. p. 135—136°.

Rates of Oxidation with Lead Tetra-acetate.—Cordner and Pausacker's method [23] was used, solutions (*ca.* 0·02M) of the diols in acetic acid being mixed with equal volumes of a 0·0365M-solution of lead tetra-acetate in acetic acid at 25°. Plots of log $b(a - x)/a(b - x)$ against t were linear, and the bimolecular rate constants were calculated from the expression $k = (2{\cdot}303 \times \text{slope})/(a - b)$. Results are shown in the Table.

Rates of Oxidation with Sodium Metaperiodate.—(i) *trans*-Decalin-2β : 3α-diol (55·0 mg.) was dissolved in ethanol (2 c.c.) and diluted with water to 25 c.c. A 5-c.c. portion was mixed at 20° with 5 c.c. of 0·0224M-aqueous sodium metaperiodate, and after a known time the reaction was stopped by the addition of 5 c.c. of 10% potassium iodide in N-sulphuric acid and the liberated iodine titrated with thiosulphate. A blank experiment was carried out under the same conditions with no diol. The % reaction was: 24 (2·5 min.), 50 (7 min.), 62 (10·5 min.), 98 (120 min.), and the bimolecular rate constant for the first three determinations 10·4, 10·6, and 10·7 mole^{-1} l. min.$^{-1}$.

(ii) A solution of *trans*-decalin-2α : 3β-diol (60·1 mg.) was prepared and used in exactly the same way. The % reaction was: 66 (1 min.), 73 (1·5 min.), 85 (2·5 min.), 100 (15 min.), and k_2 for the first three determinations 131, 113, and 114 mole^{-1} l. min.$^{-1}$. Owing to the very rapid reaction, these figures can only be regarded as approximate.

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[22] Verkade, Coops, Maan, and Verkade-Sandbergen, *Annalen*, 1928, **467**, 217.
[23] Cordner and Pausacker, *J.*, 1953, 102.