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ORGANIC REACTIONS IN A SOLID MATRIX—II*

ALUMINA-INDUCED OXIRANE REARRANGEMENTS†

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Abstract—Rearrangement of oxiranes, on contact with active Al_2O_3, earlier studied with methyldialkyl-substituted 1,2-epoxides, has now been extended to 1,2-dialkyl epoxides (cyclohexene oxide, cycloheptene oxide) and β-himachalene monoepoxide (tetrasubstituted). Isomerisation of citronellol epoxide has been investigated to detect any participation of the OH function in oxirane opening. To gauge the importance of topology of the substrate rearrangement of 3β,4β-epoxycarane has been studied and the results compared with those obtained earlier with 3α,4α-epoxycarane.

IN AN earlier paper[1] we reported that methyldialkyl-substituted 1,2-epoxides, on exposure to active Al_2O_3, chiefly pass into the corresponding allylic alcohols. In order to extend the scope of this reaction, two 1,2-dialkyl epoxides (cyclohexene epoxide and cycloheptene epoxide), one tetrasubstituted 1,2-epoxide (β-himachalene monoepoxide) and an epoxy alcohol (citronellol epoxide) have now been isomerised over Al_2O_3; rearrangement of 3β,4β-epoxycarane has also been studied and the results compared with those obtained earlier with 3α,4α-epoxycarane in order to evaluate the importance of steric factors. Present paper describes the results of these investigations.

RESULTS

Cyclohexene and cycloheptene epoxides. 1,2-Epoxycyclohexane, on exposure to Al_2O_3,[1] furnished a product (80% on weight basis), which was shown by programmed GLC (and TLC) to contain five components in the approx ratios of 1:7:1·2:1·7:1·6 (having RRT of 0·4, 1·0, 4·96, 7·24 and 7·84 respectively). Al_2O_3 chromatography effected only partial separation. The major product (RRT: 1·0), which was obtained pure, was identified as *trans*-cyclohexane-1,2-diol by comparison (IR, mixed m.p.) with authentic samples of *cis*-[2] and *trans*-cyclohexane-1,2-diol.[3] The two components with highest retention times, were obtained as a mixture, which analysed for $C_{12}H_{22}O_3$ (M^+, $m/e = 214$) and from its IR and PMR data (Experimental) was recognised as a mixture of isomeric 2,2′-dihydroxydicyclohexyl ethers (I); it was later possible to separate these two isomers by dry column chromatography[4] using silica gel containing boric acid[5] and identify the two compounds (m.p. 129–130° and 128–129°) as the two isomeric 2,2′-dihydroxy-dicyclohexyl ethers‡ described earlier by Cope *et al.*[6] The compound having RRT of 4·96 could be obtained in only 90%

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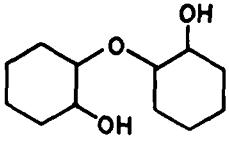
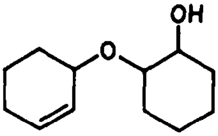
* Part I: *Tetrahedron* **24**, 5817 (1968)

† Communication No. 1492, National Chemical Laboratory, Poona, India.

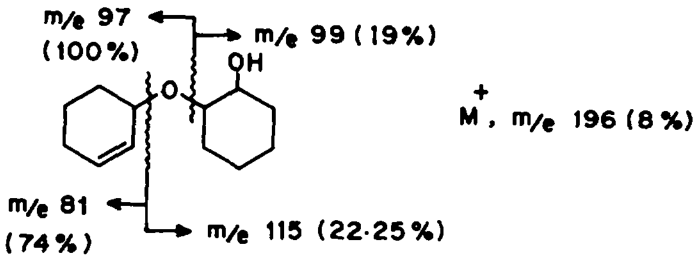
‡ Eight diastereoisomers are possible; the stereochemistry of these two is discussed later.


OH
O
OH

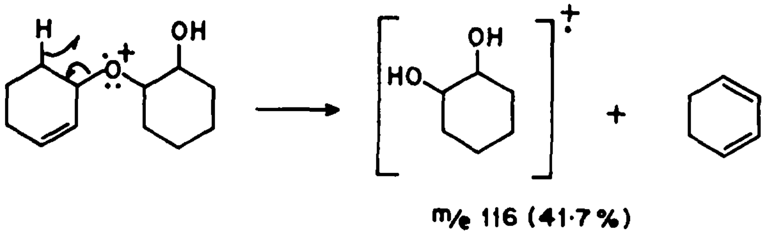
I


OH
O

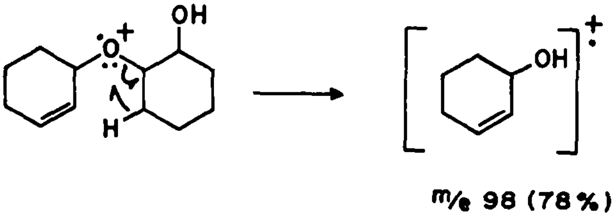
II


m/e 97
(100%)
m/e 99 (19%)
OH
O
M+, m/e 196 (8%)
m/e 81
(74%)
m/e 115 (22·25%)

III


H
OH
O+
HO
OH
+
m/e 116 (41·7%)

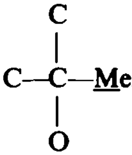
IV


OH
O+
H
OH
m/e 98 (78%)

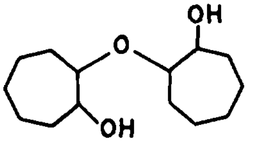
V

purity (GLC). From its spectral characteristics (M^+, $m/e = 196$. IR: OH 3490, 1090 cm^{-1}; PMR: two $-\underset{|}{C}\underline{H}-O-$, 2H unresolved multiplet located between 170–210 c/s; one $-C{=}C-\underset{|}{C}\underline{H}-O-$, 1H unresolved multiplet located between 220–240 c/s; two olefinic protons, 1H unresolved multiplet centred at 334 c/s and, 1H broad singlet at 345 c/s) the compound is assigned the structure II. This is in full accord with the results of electron-impact fragmentation summarised in III–V (the values in paranthesis represent relative intensity).

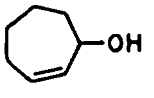
1,2-Epoxycycloheptane,[7] on a similar treatment with Al_2O_3, gave essentially similar results. Thus, of the total product (yield ~70%) *trans*-cycloheptane-1,2-diol[7, 8] accounts for ~25%, while 2,2′-dihydroxy-dicycloheptyl ethers (two isomers, VI)[9] were formed to the extent of 20%. However, no 2-hydroxycycloheptyl-2′-cycloheptenyl ether (analogue of II) was apparently, formed, but, instead, cycloheptenol (VII)[10] was produced to the extent of 45%. Structure VI, arrived at by earlier authors[9] on the basis of elemental analysis, is fully supported by spectroscopic data obtained now. Thus, for example, the solid isomer (m.p. 88·5–89·5°. $C_{14}H_{26}O_3$; M^+, $m/e = 242$; IR: OH 3400, 3300, 1070, 1048, 1035, 1010 cm^{-1}) shows in its PMR spectrum ($CHCl_3$) a 4H, unresolved multiplet at 170–215 c/s assignable to four $-\underset{|}{C}\underline{H}O-$ units; its acetate displays absorption for two $-\underset{|}{C}\underline{H}O-$ proton (2H, unresolved m between 195–215 c/s), two $-\underset{|}{C}\underline{H}OAc$ (2H, unresolved m between 270–294 c/s) and two O$\underline{A}$c (6H, s at 117 c/s). The important ions in the mass spectrum of the diol, are readily rationalised in terms of the fragmentations depicted in VIII and IX.

β-*Himachalene epoxide* (XI). β-Himachalene (X)[11] on controlled epoxidation with mono-perphthalic acid yielded a mono-epoxide, which from its PMR spectrum (quaternary Me signals at 51 and 57 c/s;  $C-\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-\underline{Me}$, 3H, s at 76·5 c/s; vinylic Me, 3H, d centred at 105 c/s, $J = 1$ c/s; $-C{=}\underset{|}{C}H$, 1H, broad hump centred at 321 c/s, $W_H = 9$ c/s) is clearly XI; the stereochemistry of the oxirane ring has been assigned, assuming attack by the per-acid from the less hindered (concave) α-face. Treatment of this oxide with Al_2O_3 (25 times) gave a product (80%) showing essentially five components by GLC and having relative ratios of 13:7:3:41:36 (RRT: 1, 1·23, 1·45, 2·89 and 3·82 respectively); with a higher Al_2O_3/oxide ratio (50/1) increased amounts of components with RRT 1, 1·23 and 1·45 were formed at the expense of other two components. Of these, the four major components have been obtained pure and structures assigned.

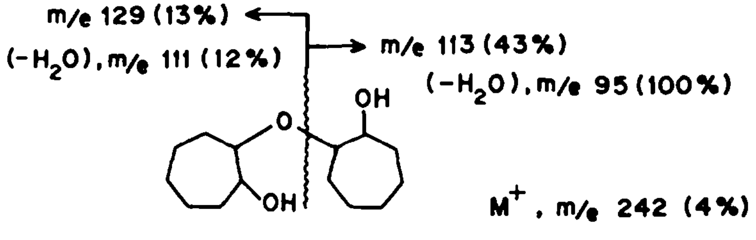
Compound with RRT = 1 ($C_{15}H_{22}$; M^+, $m/e = 202$, 97%) shows the following spectral characteristics; UV: λ_{max} 242·5 mμ (ε, 6313); IR: C=C 1640, 1615, 825 cm^{-1}; PMR: quaternary Me's at 42, 59 c/s; two vinylic Me's, 6H, partly overlapping singlets



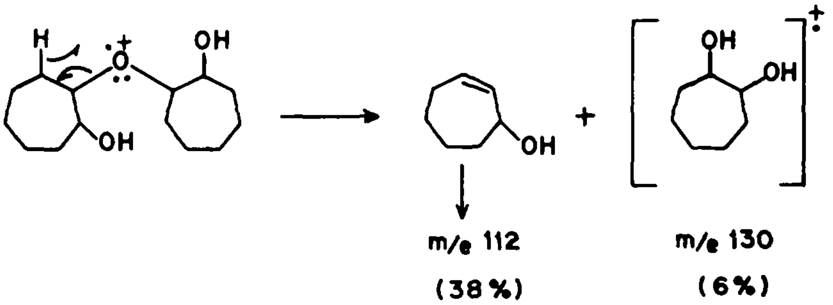
VI



VII



VIII

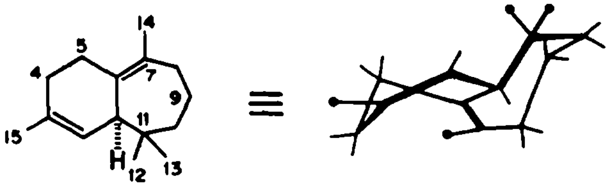


IX

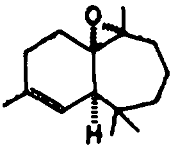
at 106 and 108 c/s; $-\underset{|}{C}{=}\underset{|}{C}-C\underline{H}_2-\underset{|}{C}{=}C$, essentially a 2H doublet centred at 157 c/s, J = 4 c/s; three vinylic protons, 3H, overlapping multiplets located between 326–356 c/s. These data and mechanistic considerations (*Discussion*) suffice to unequivocally assign structure XII to this hydrocarbon. Its mass spectrum shows important ions at m/e 159 (36%), 146 (39%), 145 (33%), 131 (100%), 105 (39%) and 91 (48%). These fragments can be interpreted in terms of structure XII, as summarised in XIII and XIV.

The component with RRT = 1·23 was readily recognised from its spectral characteristics as the known[12] ar-himachalene (XV).

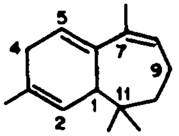
The compound having RRT = 2·89 analyses for $C_{15}H_{24}O$ (M^+, m/e = 220, 9%) and is clearly alcohol XVI from its structural features: two quaternary Me's (PMR: 3H, s at 59 and 67 c/s), one vinylic Me (PMR: 3H, d centred at 103 c/s, J = 1 c/s),



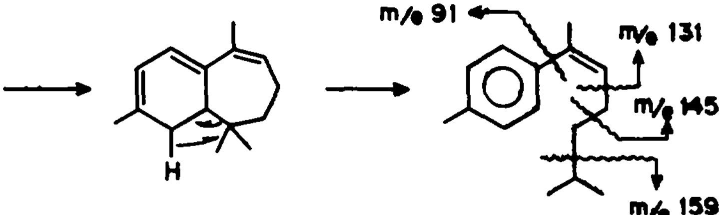
X



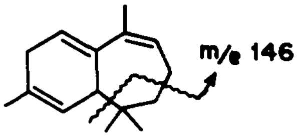
XI



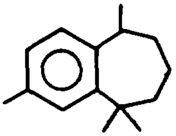
XII



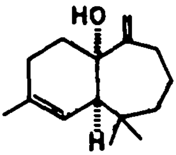
XIII



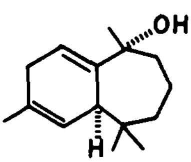
XIV



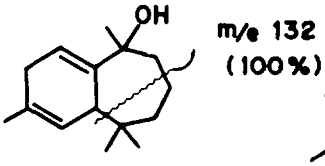
XV



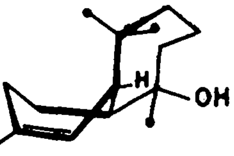
XVI



XVII



XVIII



XIX

$-\underset{|}{C}{=}CH_2$ (IR: 1630, 910 cm^{-1}. PMR: 1H, partly split s at 289 c/s and, 1H, d centred at 309 c/s with $J = 1{\cdot}5$ c/s), $-\underset{|}{C}{=}CH-$ (IR: 820 cm^{-1}. PMR: 1H, broad s at 324 c/s, $W_H = 6$ c/s), $-\overset{|}{\underset{|}{C}}-OH$ (IR: 3400, 1040 cm^{-1}; PMR: no $-\underset{|}{C}\underline{H}-O-$); the configuration of the OH group is based on the fact[1] that these alumina-induced oxirane ring openings, proceed with retention of configuration of the original C—O bond.

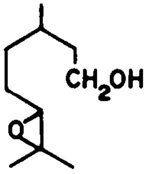
The compound with the highest RRT (= 3·82) is also an allylic tertiary alcohol and has been shown to be XVII from its structural features: two quaternary Me's (PMR: 3H singlets at 37 and 58·5 c/s), $-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}-\underline{\mathrm{Me}}$ (PMR: 3H, s at 84 c/s), one vinylic Me (PMR: 3H, d at 105 c/s, J = 1·5 c/s), $-\mathrm{C}{=}\mathrm{CH}-\mathrm{CH_2}-\underset{|}{\mathrm{C}}{=}\mathrm{C}-$ (PMR: 2H, ill-defined m centred at 152 c/s), $-\underset{|}{\mathrm{C}}{=}\mathrm{CH}-\overset{|}{\underset{|}{\mathrm{CH}}}-\underset{|}{\mathrm{C}}{=}\underset{|}{\mathrm{C}}-$ (PMR: 1H, m centred at 180 c/s), two olefinic protons (PMR: 1H, d of tr, centred at 333 c/s, J = 3 c/s; 1H, q centred at 358 c/s, J_1 = 4 c/s and J_2 = 3 c/s), $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{OH}$ (IR: 3300, 1100 cm^{-1}; PMR: no $-\underset{|}{\mathrm{C}}\underline{\mathrm{H}}\mathrm{O}-$). Its mass spectrum ($M^+$, m/e = 220, 23%; $M^+ - H_2O$, m/e = 202, 37%) shows the base peak at m/e 132, and this is fully consistent with the assigned structure XVII, as indicated in XVIII.

It may be noted that one of the quaternary Me's in XII (42 c/s) as well as in XVI (37 c/s) is considerably shielded. An examination of models (Dreiding) shows that though several well-defined conformations are possible for each of these compounds, the most probable (least non-bonded interactions) conformations have the $C_{11}\beta$–Me fully exposed to the π-electron cloud of both the ethylenic linkages; one such conformation for XVII is shown in XIX.

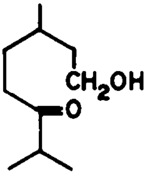
(+)-*Citronellol epoxide* (XX). Citronellol epoxide (XX)[13] isomerisation over Al_2O_3 was investigated to detect any participation of the OH function in oxirane cleavage. This oxide proved to be fairly resistant to Al_2O_3, as under the standard conditions[1] (25 times Al_2O_3) almost 66% of the oxide remained unchanged. However, by using a very large excess (75 times) of Al_2O_3, isomerisation could be pushed to near completion. The product (yield, 71·8%) from such a reaction shows essentially four GLC components (RRT: 1, 3·64, 4·76 and 8·93; relative % 44, 7, 10 and 38 respectively); another component (~5%) which did not elute under the GLC conditions (Experimental) employed, was detected during column chromatography.

Of the above five components four were readily recognised as the unchanged epoxide (RRT: 3·64), keto alcohol XXI (RRT: 4·76), glycol XXII (RRT: 8·93) and the triol XXIII (obtained during column chromatography) by their spectral characteristics and comparison of their properties with those recorded in literature.[13]

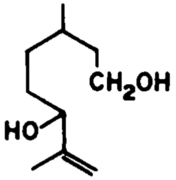
The component with the least retention time (RRT = 1) analyses for $C_{10}H_{20}O_2$ (M^+, m/e = 172, 4%) and shows following structural features: $\mathrm{C}\underline{\mathrm{H}}_3-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$ (PMR: 3H, d centred at 58 c/s, J = 6 c/s), $(\mathrm{C}\underline{\mathrm{H}}_3)_2\underset{|}{\mathrm{C}}-\mathrm{O}-$ (PMR: 6H, s at 63 c/s), three protons of type $-\underset{|}{\mathrm{C}}\underline{\mathrm{H}}-\mathrm{O}-$ (PMR: a complex 3H m located between 180–250 c/s), OH (IR: 3350, 1120 cm^{-1}). The above data, taken in conjunction with mechanistic considerations (Discussion) suggest two possible alternatives, XXIV and XXV. The



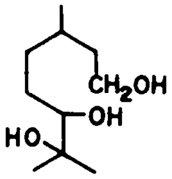
XX



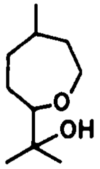
XXI



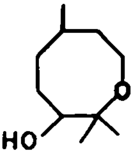
XXII



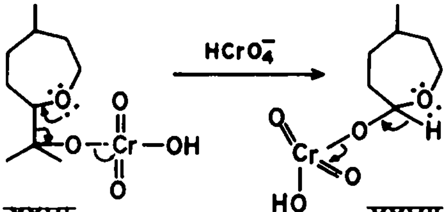
XXIII



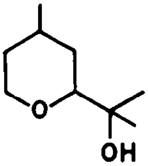
XXIV



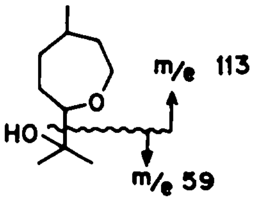
XXV



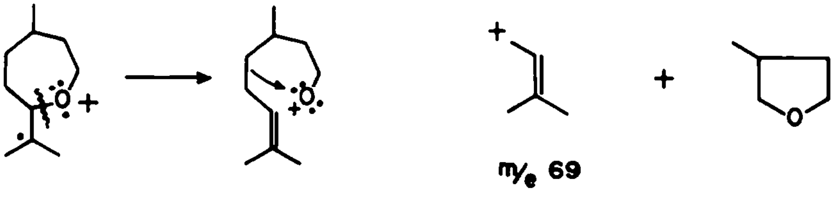
XXVI XXVII



XXVIII



XXIX



XXX

compound is resistant to acetylation (Ac_2O–pyridine 48 hr at ~25°) and was also recovered unchanged from attempted pyridine-chromic acid[14] oxidation. Oxidation with Jones reagent[15] gives β-methyladipic acid. All these results are consistent only with structure XXIV, chromic acid oxidation to give β-methyladipic acid proceeding through XXVI, XXVII.[16] Surprisingly, the epoxy alcohol XXIV was found to be resistant to dehydration with I_2 or $KHSO_4$, under the usual conditions. However, a close analogy is on record:[13] compound XXVIII is also resistant to dehydration. Structure XXIV is fully consistent with its mass spectrum which displays, besides other, ions at *m/e* 113 (55%), 69 (100%) and 59 (93%); this fragmentation is readily rationalized in terms of XXIX and XXX.

This compound (XXIV), as expected* is not stereochemically homogeneous. Though it could not be resolved by GLC, the two diastereoisomers could be resolved by TLC (R_f 0·40, 0·44) and later, one of these (R_f 0·4) obtained pure by IDCC.[17] This showed a mass spectrum virtually identical with that obtained for the original mixture. PMR spectrum was also essentially the same, except for cleaner signals in the 180–250 c/s region. These data have been recorded in the Experimental.

(−)3β,4β-*Epoxycarane* (XXXI). 3β,4β-Epoxycarane[19,20] (XXXI) when exposed to active Al_2O_3 gives a product (yield 65·2%), shown by GLC to consist of at least nine components (Table 1). By systematic chromatography GLC components 1, 7, 8 and 9, accounting for over 80% of the product, could be obtained pure. From their spectral characteristics (Experimental) the four components were recognised as the known 3-isocaranone[21] (XXXII), *cis*-car-4(7)-en-3-ol[22] (XXXIII), carandiol XXXIV[23] and XXXV[24] respectively.

TABLE 1. REARRANGEMENT OF 3β,4β-EPOXYCARANE OVER ALUMINA

GLC peak No.	RRT*	% of total product (by GLC)	Structure
1	1	22	XXXII
2	1·12	7	—
3	1·23	4	—
4	1·33	2	—
5	1·41	2	—
6	1·52	4	—
7	1·74	44	XXXIII
8	3·37	14	XXXIV
9	4·55	1	XXXV

* Column: 300 cm × 0·5 cm, packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh); temp: programmed 100°→200°, 8°/min; gas: 70 ml/min.

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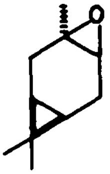
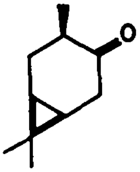
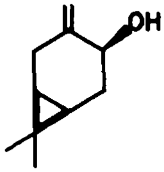
* The asymmetric centre in citronellol is quite away from the olefinic linkage, hence in its reaction with peracid, any significant asymmetric induction is ruled out. The epoxide thus is expected to be a mixture of two diastereoisomers (its PMR spectrum gives no clue to its composition). This, in turn, will lead to stereochemical mixture of other products.



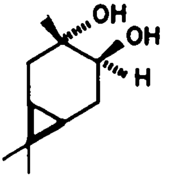
XXXI



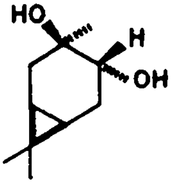
XXXII



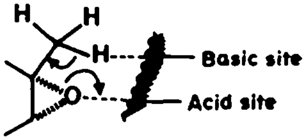
XXXIII



XXXIV



XXXV



XXXVI

DISCUSSION

From the results described in a previous[1] and the present communication, it is clear that oxiranes, irrespective of their degree of substitution and other structural features are quite sensitive to active Al_2O_3 and, in general, four different types of reactions have been observed:

(i) transformation into an allylic alcohol, (ii) hydration to *trans*-glycol, (iii) isomerisation to a ketone (in case of trisubstituted oxiranes), (iv) typical carbonium ion rearrangements.

By far the most general reaction observed, is the transformation of epoxides into the corresponding allylic alcohol(s) and has been observed in every oxirane, so far investigated; in the case of cyclohexene epoxide, though no cyclohexenol was isolated as such, its anion was certainly involved in a further reaction with unchanged epoxide to give II. At least in one case it has been demonstrated[1] that the allylic alcohol does not arise by dehydration of the corresponding glycol. It is also clear from the work of pinene oxide,[1] 3α,4α-epoxycarane[1] and 3β,4β-epoxycarane that the isomerisation of the epoxide to the corresponding allylic alcohol proceeds with retention of configuration of the original C—O bond. In the case of a single tetrasubstituted oxirane (β-himachalene epoxide) studied, significant quantities of dienes resulted, apparently from the allylic tertiary alcohol. Hydration to a *trans*-glycol has been observed most with 1,2-disubstituted epoxides, to a lesser degree with trisubstituted epoxides and was not observed with the tetrasubstituted β-himachalene epoxide (XI). Isomerisation of the trisubstituted epoxides to the corresponding ketones has been known[25] for sometime, but is only a minor reaction; a similar isomerisation of a 1,2-disubstituted epoxide has not been observed. Depending on favourable stereoelectronic factors, typical carbonium ion rearrangements (1-methyl-1,2-epoxycycloheptane[1], α-pinene epoxide[1], 3α,4α-epoxycarane[1] but *not* 3β,4β-epoxycarane, caryophyllene epoxide[26]) have been detected, but again to a minor extent.

In a single case investigated (citronellol epoxide) participation of the suitably placed OH function in epoxide opening has been observed. Natural products, genesis of which assumes such a participation, have been recently isolated.[27]

It is generally agreed now that Al_2O_3 has dipolar character[28] and there are both electron-donor[29] and electron acceptor[30] sites on Al_2O_3 surface. The reaction described above can be rationalised in terms of this character of Al_2O_3. Thus, for example, epoxide opening to an allylic alcohol, the most general reaction observed, can be visualised in terms of XXXVI. The *trans*-opening to a glycol would apparently require Al_2O_3 surface, both on the front and back side of epoxide; such a requirement will be met, if the reaction occurs in submicro holes, crevices or between channels in Al_2O_3 particles and this has been postulated[31] earlier to explain certain reactions on Al_2O_3 at higher temperatures. It may be noted that the formation of glycol XXXV from 3β,4β-epoxycarane (XXXI) requires epoxide opening to a secondary carbonium ion, a reaction not observed with this epoxide in a homogeneous phase; however, this is only a very minor pathway as compared to the alternative opening to a tertiary carbonium ion. Internal participation of OH, in case of citronellol epoxide (XX) results in the hydroxy ether XXIV. The formation of dicyclohexyl ethers (I, II) and dicycloheptyl ether (VI) is readily understood by attack of the glycol (or allylic alcohol) anion on the unchanged epoxide; the stereochemistry of the product should follow from the expected trans-diaxial openings. The absence of any ring-contraction product in the case of 3β,4β-epoxycarane (XXXI) reaction, highlights the importance of stereoelectronic factors and suggests further that such reactions are concerted.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine, before drying (Na_2SO_4). All yields are on a w/w basis. Optical rotations were measured in $CHCl_3$ at $\sim 25°$.

IR spectra were recorded as smears (liquids) or Nujol mulls (solids) on a Perkin-Elmer Infracord, model 137-E. PMR spectra were taken with 10–20% soln in CCl_4 with TMS as the internal standard, on a Varian A-60 spectrometer; signals are recorded in c/s relative to TMS as zero. Mass spectra were recorded on a a CEC mass spectrometer, model 21-110B, using an ionizing potential of 70 eV and a direct inlet system.

GLC were carried out on 'Aerograph', model A-350-B using a 300 cm × 0·8 cm column (packed with 30% diethyleneglycol polysuccinate on 30–60 mesh Chromosorb-W) for preparative runs and, a 300 cm × 0·5 cm column (packed with 20% diethyleneglycol polysuccinate on 60–80 mesh Chromosorb-W) for analytical chromatography, unless otherwise stated; H_2 was used as the carrier gas.

IDCC[17] were carried out on TLC grade silica gel (−250 mesh) and were based on preliminary TLC's to find out the conditions most suitable for optimum separations. TLC was carried out on silica gel layers

(0·3 mm) containing 15% gypsum; the plates were activated at 100–110° (45 min).

Al_2O_3 used for chromatography was made neutral by the HNO_3 method[32] and graded according to Brockmann.[33] The silica gel for column chromatography was washed with water till sulphate-free, dried and activated at 125–130°/6–8 hr and standardised according to Hernandez.[34] $AgNO_3$-silica gel was prepared according to Gupta and Dev.[35]

Standard procedure for reaction with Al_2O_3. The epoxide was added to a thick slurry of 25 times (unless stated otherwise) its wt of Al_2O_3 (water-washed, Brockmann activity I; pH 9·4) suspended in hexane (30 ml for every 25 g Al_2O_3) in a suitable stoppered flask, flushed with N_2, and mechanically shaken for 6 hr and then kept aside for 18 hr. The hexane was filtered and the Al_2O_3 washed with 5% MeOH in Et_2O (800 ml for 1 g epoxide, added in several portions); in case of cyclohexene and cycloheptene epoxides, Al_2O_3 was finally soxhleted with MeOH to recover the diols completely. The solvent extracts were combined, freed of solvent and the residue suitably treated.

Action of Al_2O_3 *on 1,2-epoxycyclohexane.* Cyclohexene epoxide[36] (5·0 g) when treated with Al_2O_3 (125 g; 150 ml hexane) according to the standard procedure, yielded a syrup, which after distillation (b.p. 60–160°/7–2 mm) became semisolid (yield, 3·93 g). Programmed GLC (column: 150 cm × 0·5 cm, packed with 20% Silicone SE-30 on Chromosorb W of 60–80 mesh; temp: 80–250°, 10°/min; gas: 90 ml/min) indicated five components, as already stated under "Results".

The product (3·8 g) was chromatographed on Al_2O_3/II (26 cm × 3·7 cm) with GLC monitoring:

Fraction 1	ether	100 ml × 3	50 mg; rejected
Fraction 2	ether	100 ml × 1	350 mg; mostly component with RRT = 4·96
Fraction 3	ether	100 ml × 3	474 mg; mixture of component with RRT = 7·24, 7·84
Fraction 4	ether	100 ml × 2	
	2% MeOH in ether	100 ml × 15	780 mg; as above
Fraction 5	10% MeOH in ether	100 ml × 2	50 mg; rejected
Fraction 6	25% MeOH in ether	100 ml × 10	1·9 g; solid, component with RRT = 1

trans-*Cyclohexane-1,2-diol.* Fraction 6 was crystallised from acetone to furnish colourless prisms (1·7 g), m.p. 103–104°; mixed m.p. with an authentic sample of *trans*-cyclohexane-1,2-diol[3] (m.p. 103–104°) remained undepressed, whereas admixture with *cis*-diol[2] (m.p. 91–93°) lowered the m.p. to 70–71°. The *cis*- and *trans*-diols readily separate on TLC (solvent: C_6H_6-EtOAc-acetone, 65:25:10): R_f (*cis*-), 0·283; R_f (*trans*-), 0·191; R_f (azobenzene), 0·783; PMR ($CHCl_3$): —C$\underline{\text{H}}$(OH)·C$\underline{\text{H}}$(OH)— (*cis*-diol: 2H, partly split broad singlet centred at 225 c/s; *trans*- diol: 2H, broad s centred at 200 c/s). No *cis*-isomer could be detected (TLC, PMR) in the total crude material (fraction 6).

2,2′-Dihydroxy-dicyclohexyl ether 5 (I). Fractions 3 and 4 each a mixture, were combined, m.p. 98–99°; IR: OH 3333, 1075 cm^{-1}; PMR: four —$\underset{|}{\text{C}}\underline{\text{H}}$O (4H, unresolved m at 170–220 c/s, with a peak at 195 c/s); in the derived acetate (Ac_2O–NaOAc method), b.p. 180° (bath)/1 mm, a 2H, broad signal at 190–220 c/s (two —$\underset{|}{\text{C}}\underline{\text{H}}$O) and a 2H, broad signal at 267–297 c/s (two —$\underset{|}{\text{C}}\underline{\text{H}}$OAc), besides a 6H, s at 123 c/s (two —OAc), are observed. Mass: important ions at *m/e* 214 (M^+; 5%), 196 (M^+—H_2O; 19%), 116 (42%), 99 (72%), 98 (83%), 81 (100%). (Found: C, 67·17; H, 10·49. $C_{12}H_{22}O_3$ requires: C, 67·30; H, 10·28%).

The above mixture of isomers (800 mg) was chromatographed[4] on silica gel/IIB containing 10% boric acid (92 g; 60 cm × 1·7 cm) using 1% MeOH in ether as eluent and with TLC monitoring (air-dried plates of silica gel-10% boric acid; solvent: 1% MeOH in ether) the various dug out sections were combined. In this way pure compounds, besides unresolved mixture (~250 mg), were obtained: compound with RRT = 7·24 (~400 mg), m.p. 129–130° (CCl_4–light petroleum), R_f 0·54; compound with RRT = 7·84 (35 mg), m.p. 128–129° (CCl_4-light petroleum), R_f 0·66. (Lit.[6]: records two isomers of m.p. 125·2–126·0° and 124·2–124·8°).

2-Hydroxy-cyclohexyl-2′-cyclohexenyl ether (II). Fraction 2 was purified by preparative GLC (temp: 200°; gas 100 ml/min), b.p. 200° (bath)/20 mm.

Action of Al_2O_3 *on 1,2-epoxycycloheptane*

Cycloheptene epoxide (15·5 g) was shaken with Al_2O_3 (388 g; 465 ml hexane) as usual to finally give after distillation, a semisolid product (11·1 g), b.p. 80–120°/6–4 mm. This material (10·68 g) was chromatographed over Al_2O_3/II (39 cm × 5·5 cm) with TLC monitoring (solvent: A, 25% EtOAc in C_6H_6; B, C_6H_6-EtOAc-acetone, 65:25:10):

Fraction 1	ether	400 ml × 1	a few mg, rejected
Fraction 2	ether	200 ml × 2	4·8 g, VII
Fraction 3	ether	200 ml × 1	0·4 g, mixture of VII and VI (solid)
Fraction 4	ether	200 ml × 2	0·83 g, VI (solid)
Fraction 5	ether	200 ml × 1	0·4 g, VI (both isomers)
Fraction 6	ether	200 ml × 1	0·3 g, VI (essentially liquid isomer)
Fraction 7	1% MeOH in ether	200 ml × 5	0·7 g, viscous liquid VI (liquid isomer)
Fraction 8	10% MeOH in ether	200 ml × 7	2·5 g, cycloheptan-1,2-diol

trans-*Cycloheptane-1,2-diol.* Fraction 8 was crystallised from light petroleum to furnish colourless plates, m.p. 62·5–63·5°; IR: OH 3300, 1065, 1040 cm^{-1}; PMR ($CHCl_3$): 2H, unresolved m at 199–218 c/s (two $\underset{|}{\mathrm{C}}\underline{\mathrm{H}}\mathrm{O}$—). (Found: C, 64·66; H, 10·78. $C_7H_{14}O_2$ requires: C, 64·58; H, 10·84%). (Lit.[7]: *trans*-diol, m.p. 64–65°; *cis*-diol, m.p. 46–47°).

2,2′-Dihydroxy-dicycloheptyl ether (VI). Fraction 4 on crystallisation from light petroleum furnished white prisms, m.p. 88·5–89·5°, mixed m.p. with an authentic sample of VI (solid isomer) prepared according to a known procedure (action of diol on epoxide in presence of $BF_3.Et_2O$)[9] remained undepressed. (Found: C, 69·88; H, 10·99. $C_{14}H_{26}O_3$ requires: C, 69·38; H, 10·81%) (Lit.[9]: m.p. 85·5–86·1°). The *acetate* (Ac_2O–NaOAc method) was obtained only as a liquid b.p. 220° (bath)/5 mm.

Fraction 7 was distilled to give liquid isomer of VI, b.p. 200° (bath)/6 mm; IR: OH 3330, 1080, 1040 cm^{-1}; PMR ($CHCl_3$): 4H, unresolved m at 184–231 c/s (four —$\underset{|}{\mathrm{C}}\mathrm{HO}$—); in the derived acetate (Ac_2O–NaOAc method), b.p. 220° (bath)/5 mm, a 2H broad signal at 196–224 c/s (two —$\underset{|}{\mathrm{C}}\underline{\mathrm{H}}\mathrm{O}$—) and a 2H broad signal at 270–295 c/s (two —$\underset{|}{\mathrm{C}}\underline{\mathrm{H}}\mathrm{OAc}$), besides a 6H, s at 118 c/s (two —O$\underline{\mathrm{Ac}}$), are observed. Mass: important ions at *m/e* 242 (M^+; 4%), 113 (63%), 112 (53%), 95 (100%). (Found: C, 68·64; H, 10·75. $C_{14}H_{26}O_3$ requires: C, 69·38; H, 10·81%).

Cycloheptenol (VII). Fraction 2 (2·0 g) was subjected to IDCC using $AgNO_3$–silica gel (15%, IIB, 40 cm × 3·5 cm; solvent: 25% EtOAc in C_6H_6) to get pure VII, b.p. 120° (bath)/25 mm, n_D^{25} 1·4815; IR: OH 3300, 1040 cm^{-1}; PMR: —$\underset{|}{\mathrm{C}}\underline{\mathrm{H}}\mathrm{OH}$ (1H, unresolved m at 248–268 c/s), —C$\underline{\mathrm{H}}$=C$\underline{\mathrm{H}}$— (2H, broad s at 340 c/s). (Lit.[10a]: b.p. 72°/7 mm, n_D^{25} 1·4890).

The RRT of VII, *trans*-diol, VI (solid isomer) and VI (liquid isomer) are 1·0, 2·8, 14·4 and 15·2 respectively. (Programmed GLC. Column: 150 × 0·5 cm, packed with 20% Silicone SE-30 on Chromosorb W of 60–80 mesh; temp: 100–250°, 10°/min; gas: 100 ml/min).

β-Himachalene mono-epoxide (XI). β-Himachalene (18·5 g; 0·091 mole) in ether (100 ml) was cooled (~0°) and with stirring treated with an ethereal soln of mono-peiphthalic acid[37] (197 ml, containing 11·8 g per acid; 0·0648 mole) during 0·5 hr. After another 3 hr at 0–2°, the precipitated phthalic acid was filtered off, the filtrate washed with 10% Na_2CO_3aq., brine and dried. The solvent was flashed off and the residue (17·0 g, b.p. 110–115°/2 mm) containing ~35% unchanged hydrocarbon was purified by chromatography (Al_2O_3/II, 38·5 cm × 3·8 cm; material chromatographed: 11·8 g). Light petroleum (150 ml × 3) eluted essentially β-himachalene (6·3 g); further elution with light petroleum (150 ml × 7) and then with C_6H_6 (150 ml × 3) gave mono-oxide (5·0 g): b.p. 150°/9 mm, n_D^{25} 1·5030, $[\alpha]_D$ +187·3 (*c*, 3·3%). (Found: C, 81·23; H, 10·67. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

Action of Al_2O_3 *on β-himachalene mono-epoxide.* β-Himachalene mono-epoxide (4·78 g) was treated with Al_2O_3 (239 g; 240 ml hexane) in the usual fashion. The product (3·91 g, b.p. 111–130°/6 mm) on GLC (temp: 190°; gas: 100 ml/min) showed five components in the approximate ratio 22:12:4:34:28 and having RRT of 1, 1·23, 1·45, 2·89 and 3·82 respectively. This material (3·58 g) was chromatographed on Al_2O_3/II (35 cm × 2·3 cm) with GLC monitoring:

Fraction 1	light petroleum	100 ml × 2	0·717 g, mixture of XII, XV
Fraction 2	light petroleum	100 ml × 3	negligible
Fraction 3	50% C_6H_6 in light petroleum	100 ml × 1	0·119 g, mixture, rejected
Fraction 4	50% C_6H_6 in light petroleum	100 ml × 5	0·816 g, mostly XVI
	C_6H_6	100 ml × 5	
Fraction 5	1% MeOH in C_6H_6	100 ml × 4	0·494 g, mixture of XVI, XVII
Fraction 6	1% MeOH in C_6H_6	100 ml × 3	1·257 g, essentially XVII

Himachala-2,5,7-triene (XII) *and ar-himachalene* (XV). Fraction 1 (0·65 g) was subjected to IDCC (15% $AgNO_3$–silical gel/IIA, 3·5 cm × 40 cm; solvent: 5% $CHCl_3$ in light petroleum). The component with higher R_f (~100 mg) was distilled, b.p. 130° (bath)/3 mm, n_D^{20} 1·5312 and, identified as XV by comparison (IR, PMR, GLC) with an authentic specimen.[12]

The component with lower R_f (~100 mg) was distilled to give pure XII: b.p. 130° (bath)/3 mm, n_D^{20} 1·5313. (Found: C, 88·49; H, 11·49. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%).

6α-Hydroxy-1α-himachala-2,7(14)-diene (XVI). Fraction 4 (0·76 g) was rechromatographed (Al_2O_3/II, 11·5 cm × 2·5 cm) to finally get pure XVI (0·529 g): b.p. 180° (bath)/4 mm, $[\alpha]_D$ −64·43 (*c*, 3%). Mass: important ions at *m/e* 202 (45%), 159 (85%), 132 (47%), 105 (100%), 91 (63%). (Found: C, 81·32; H, 10·90. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

7α-Hydroxy-1α-himachala-2,5-diene (XVII). Fraction 6 (0·42 g) was, likewise, purified by rechromatography (Al_2O_3/II, 11·2 cm × 1·9 cm) to finally give after distillation pure XVII (0·234 g): b.p. 150° (bath)/3 mm, $[\alpha]_D$ −57·14 (*c*, 2·6%). Due to rapid deterioration, a satisfactory elemental analysis could not be obtained.

(+)-Citronellol epoxide (XX). (+)-Citronellol (α_D +3·36; 15·6 g) was treated at 0° with an ether soln of monoperphthalic acid (355 ml, 21·8 g of acid). Usual work-up after 18 hr at 0° and 4 hr at room temp (~25°) gave, after distillation XX (13·25 g): b.p. 130°/6 mm, n_D^{25} 1·4451, α_D +2·2. This compound has been prepared earlier[13] by saponification of its acetate; PMR: $\underline{\mathrm{H}}_3\text{C--}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$ (3H, d at 56 c/s, *J* = 6 c/s); $(\underline{\mathrm{Me}})_2\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C{-}CH}}$ (3H, s at 73·5 and 75 c/s); $>\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C{-}C\underline{H}}}$-- (1H, tr centred at 153 c/s, *J* = 5 c/s); $\text{—C}\underline{\mathrm{H}}_2\mathrm{OH}$ (2H, tr centred at 215 c/s, *J* = 6·5 c/s). (Lit.[13]: b.p. 112–113°/5 mm; n_D^{15} 1·4370).

Action of Al_2O_3 *on citronellol epoxide.* The epoxide (6·0 g) was treated with a large excess of Al_2O_3 (450 g; 450 ml hexane) and then worked up in the usual manner to give a product (4·31 g; b.p. 107–130°/30–2 mm) which on GLC (temp: 195°; gas: 70 ml/min) showed four components, as already stated (Results). This material (4·0 g) was chromatographed on Al_2O_3/II (26 cm ± 2·6 cm):

Fraction 1	light petroleum	100 ml × 5	46 mg, rejected

Fraction 2	25% C_6H_6 in light petroleum	100 ml × 2	80 mg, essentially XXIV
Fraction 3	25% C_6H_6 in light petroleum	50 ml × 7	0·499 g, pure XXIV
Fraction 4	25% C_6H_6 in light petroleum	50 ml × 1	0·166 g, essentially XXIV
	50% C_6H_6 in light petroleum	50 ml × 1	
Fraction 5	50% C_6H_6 in light petroleum	50 ml × 6	0·439 g, mixture of XXIV, XX and XXI
Fraction 6	25% light petroleum in C_6H_6	50 ml × 5	0·177 g, mixture of XXIV, XX, XXI and XXII
Fraction 7	25% light petroleum in C_6H_6	100 ml × 3	0·308 g, essentially XXII
	C_6H_6	100 ml × 5	
Fraction 8	1% MeOH in C_6H_6	100 ml × 3	1·243 g, pure XXII
	3% MeOH in C_6H_6	100 ml × 2	
Fraction 9	3% MeOH in C_6H_6	100 ml × 1	0·090, mixture of XXII and XXIII
Fraction 10	3% MeOH in C_6H_6	100 ml × 3	0·253 g' pure XXIII
	10% MeOH in C_6H_6	100 ml × 2	

5-Methyl-2-(2'-hydroxyisopropyl)-oxepane (XXIV). Fraction 3 was distilled to give XXIV: b.p. 124°/52 mm, n_D^{25} 1·4558, $[\alpha]_D$ −4·39 (*c*, 3·2%) TLC (solvent: C_6H_6–EtOAc–EtOH, 74·5 : 25 : 0·5) shows two spots (R_f 0·40, 0·44). (Found: C, 68·92; H, 11·61. $C_{10}H_{20}O_2$ requires: C, 69·72; H, 11·70%).

This compound (0·2174 g) in acetone (10 ml) was treated with Jones reagent till a brownish tinge persisted (2 ml). After 2 hr the reaction mixture was worked up in the usual manner to give a solid, which was crystallised from $CHCl_3$–light petroleum to furnish needles (99 mg), m.p. 79·5–81°, identified as *β-methyladipic acid.* (Found: C, 52·74; H, 8·31. $C_7H_{12}O_4$ requires: C, 52·49; H, 7·55%) (Lit.[18]: m.p. 84°); methyl ester: n_D^{25} 1·4283; PMR: $CH_3-\overset{|}{\underset{|}{C}}H$ (3H, d centred at 57 c/s, J = 6 c/s); two $C\underline{H}_2COOMe$ (4H, m located between 125–148 c/s); two $COO\underline{Me}$ (6H singlet at 217 c/s).

IDCC of fraction 5 (see below) furnished as one of the components, one of the diastereoisomers of XXIV, as indicated by TLC (R_f 0·40), GLC, IR, PMR and mass spectrum; $[\alpha]_D$ −11·5 (*c*, 3·13%); PMR $C\underline{H}_3\overset{|}{\underset{|}{C}}H$ (3H, d centred at 58 c/s, J = 6 c/s), $(C\underline{H}_3)_2C-O-$ (6H, s at 63 c/s); $C\underline{H}-O-$ (1H, broad d centred at 186 c/s, J = 10 c/s) $\underset{|}{C}\underline{H}_2-O-$ (2H, m located between 210–240 c/s).

6-Oxo-3,7-dimethyl-octan-1-ol (XXI). Fraction 5 (0·8 g) was subjected to IDCC (silica gel/IIA, 40 cm × 3·5 cm; solvent: C_6H_6–EtOAc–EtOH, 74·5 : 25 : 0·5) and after pooling fractions in the usual manner, all three components (XXIV, XX and XXI) could be separated.

Least polar fraction (107 mg) was identified as XXIV (isomer with R_f 0·40).

The middle cut provided 6-oxo-3,7-dimethyl-octan-1-ol[13] (92 mg): b.p. 100° (bath)/7 mm, n_D^{25} 1·4472; IR: OH 3300, 1060 cm^{-1}; C=O 1705 cm^{-1}; PMR: $C\underline{H}_3-\overset{|}{\underset{|}{C}}H$ (3H, d centred at 53·5 c/s, J = 5 c/s), $(C\underline{H}_3)_2CH$ (6H, d centred at 63 c/s, J = 7 c/s), $-C\underline{H}_2.CO.C\underline{H}-$ (a tr centred at 145 c/s with J = 6 c/s, overlapping $C\underline{H}$ absorption), $-C\underline{H}_2OH$ (2H, tr centred at 214 c/s, J = 6 c/s) (Lit.[13]: b.p. 105–106°/12 mm, n_D^{15} 1·4526).

Most polar fraction (55 mg) was identified as XX.

6-Hydroxy-3,7-dimethyl-oct-7-en-1-ol (XXII). Fraction 8 was distilled to give pure XXII: b.p. 137°/4 mm, n_D^{25} 1·4675; IR: OH 3250, 1060 cm^{-1}; $--\underset{|}{C}{=}CH_2$ 1650, 900 cm^{-1}; PMR: $C\underline{H}_3\overset{|}{\underset{|}{C}}H$ (3H, d centred at 53·5 c/s, J = 6·5 c/s), one vinylic Me (3H, s at 102 c/s), $—C\underline{H}_2OH$ (2H, tr centred at 215 c/s, J = 6 c/s), $--\underset{|}{C}{=}C\underline{H}_2$ (broad 1H s at 284 c/s and 291 c/s) (Lit.[13]: b.p. 118–119°/3 mm, n_D^{15} 1·4526).

3,7-Dimethyl-octan-1,6,7-triol (XXIII). Fraction 10 on distillation gave XXIII: b.p. 220° (bath)/3 mm, n_D^{25} 1·4670. PMR: $C\underline{H}_3—\overset{|}{\underset{|}{C}}H$ (3H, d centred at 54 c/s, J = 5 c/s), $(C\underline{H}_3)_2\underset{|}{C}—O--$ (3H, s at 69 and 71 c/s), $C\underline{H}OH$ (1H, broad hump centred at 195 c/s), $C\underline{H}_2OH$ (2H, tr centred at 219 c/s, J = 6 c/s) (Lit.[13]: b.p. 161–162°/2 mm, n_D^{15} 1·4732).

Action of Al_2O_3 *on 3β,4β-epoxycarane.* 3β,4β-*Epoxycarane.*[19] (10·23 g) when treated with active Al_2O_3 (255 g: 260 ml hexane) under standard conditions, gave a product (6·67 g, b.p. 120–180°/45–6 mm) which was chromatographed on Al_2O_3/II (25 cm ± 3·5 cm):

Fraction 1	light petroleum	200 ml × 1	20 mg, rejected
Fraction 2	light petroleum	200 ml × 1	1·4 g, pure XXXII
Fraction 3	light petroleum	200 ml × 4	0·53 g, mixture of XXXII and XXXIII
Fraction 4	25% C_6H_6 in light petroleum	200 ml × 2	1·74 g, XXXIII, slightly contaminated with XXXII
Fraction 5	25% C_6H_6 in light petroleum	200 ml × 1	2·48 g, essentially XXXIII
	50% C_6H_6 in light petroleum	200 ml × 3	
	C_6H_6	200 ml × 2	
Fraction 6	C_6H_6	200 ml × 2	0·235 g, mixture of XXXIII and XXXIV
	1% MeOH in C_6H_6	200 ml × 2	
Fraction 7	1% MeOH in C_6H_6	100 ml × 4	1·1 g, XXXIV
Fraction 8	3% MeOH in C_6H_6	200 ml × 2	0·1 g, XXXIV, XXXV
Fraction 9	3% MeOH in C_6H_6	200 ml × 1	0·1 g, XXXV

3-Isocaranone (XXXII). Fraction 2 was distilled to get 3-isocaranone, b.p. 114–115°/40 mm, n_D^{25} 1·4685; IR, PMR compared with authentic sample.[1]

cis-*Car-4(7)-en-3-ol* (XXXIII). Fraction 5 (1·56 g) was purified by IDCC (silica gel/IIA, 40 cm × 3·5 cm; solvent: 10% EtOAc in C_6H_6): b.p. 140° (bath)/40 mm, n_D^{25} 1·4975, $[\alpha]_D$ + 15·4 (*c*, 2·8%); IR: OH 3300, 1080 cm^{-1}; $—\underset{|}{C}{=}CH_2$ 1650, 900 cm^{-1}; PMR: $(CH_3)_2\underset{|}{C}—$ (3H, s at 58, 60·5 c/s), $--C{=}\underset{|}{C}--C\underline{H}_2$ ≮ (2H, broad s at 154 c/s), $--\underset{|}{C}{=}CH_2$, (a pair of broad 1H s at 281, 290 c/s), $C\underline{H}OH$ (1H, m centred at 237 c/s) (Lit.[22]: b.p. 101–103°/10 mm, n_D^{20} 1·5008, α_D +12·9).

3β,4α-*Carandiol* (XXXIV). Fraction 7 (0·41 g) was rechromatographed (Al_2O_3/II, 12·8 cm × 1·6 cm) to get pure XXXIV (0·344 g); b.p. 130° (bath)/8 mm, $[\alpha]_D$ +89·7; IR: OH 3350, 1080, 1050 cm^{-1}; PMR: $(C\underline{H}_3)_2\underset{|}{C}—$, $C\underline{H}_3—\overset{|}{\underset{|}{C}}—OH$ (6H, s at 64 c/s, 3H, s at 69 c/s), $C\underline{H}OH$ (1H, tr centred at 209 c/s, J = 6 c/s) (Lit.[23]: b.p. 103–104°/0·2 mm, $[\alpha]_D$ +87°, PMR).

3α,4β-*Carandiol* (XXXV). Fraction 9 was crystallised from light petroleum to give crystals (42 mg), m.p. 88–90°, mixed m.p. with an authentic sample prepared according to a known[24] procedure was not depressed; PMR: $(C\underline{H}_3)_2\underset{|}{C}$— (6H, s at 60 c/s), $C\underline{H}_3$—$\overset{|}{\underset{|}{C}}$—OH (3H, s at 73 c/s), $C\underline{H}OH$ (1H, qu centred at 200 c/s, $J_1 = 10$ c/s, $J_2 = 8$ c/s) (Lit.[24]: m.p. 88°, PMR).

REFERENCES

[1] V. S. Joshi, N. P. Damodaran and Sukh Dev, *Tetrahedron* **24**, 5817 (1968); Also see: I. C. Nigam and L. Levi, *Canad. J. Chem.* **46**, 1944 (1968)

[2] M. F. Clarke and L. N. Owen, *J. Chem. Soc.* 315 (1949)

[3] J. B. Brown, H. B. Henbest and E. R. H. Jones, *Ibid.* 3639 (1950)

[4] B. Loev and M. M. Goodman, *Chem. & Ind.* 2026 (1967)

[5] See e.g.: M. Lato, B. Brunelli, G. Ciuffini and T. Mezzetti, *J. Chromatog.* **34**, 26 (1968)

[6] A. C. Cope, H. E. Johnson and J. S. Stephenson, *J. Am. Chem. Soc.* **78**, 5599 (1956)

[7] L. N. Owen and G. S. Saharia, *J. Chem. Soc.* 2852 (1953)

[8] J. S. Brimacombe, A. B. Foster, M. Stacey and D. H. Whiffen, *Tetrahedron* **4**, 351 (1956)

[9] A. C. Cope and W. N. Baxter, *J. Am. Chem. Soc.* **76**, 279 (1954)

[10] [a] A. C. Cope, T. A. Liss and G. W. Wood, *Ibid.* **79**, 6287 (1957);
[b] W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.* **85**, 468 (1963)

[11] T. C. Joseph and Sukh Dev, *Tetrahedron* **24**, 3809 3841 (1968)

[12] R. C. Pandey and Sukh Dev, *Ibid.* **24**, 3829 (1968)

[13] P. Teisseire and B. Corbier, *Recherches* **13**, 78 (1963)

[14] R. H. Cornforth, J. W. Cornforth and G. Popjak, *Tetrahedron* **18**, 1351 (1962)

[15] R. G. Curtis, I. Heilbron, E. R. H. Jones and G. F. Woods, *J. Chem. Soc.* 457 (1953); A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *Ibid.* 2548 (1953)

[16] See e.g.: A. Chawla and Sukh Dev, *Tetrahedron Letters* 4837 (1967)

[17] V. K. Bhalla and Sukh Dev, *J. Chromatog.* **26**, 54 (1967)

[18] W. Kuhn and H. Schinz, *Helv. Chim. Acta* **36**, 161 (1953)

[19] H. Kuczynski and Z. Chabudzinski, *Roczniki Chim.* **34**, 177 (1960); K. Gollnick, S. Schroeter, G. Ohloff, G. Schade and G. O. Schenck, *Liebigs Ann.* **687**, 14 (1965)

[20] W. Cocker and D. H. Grayson, *Tetrahedron Letters* 4451 (1969); B. A. Arbuzov and Z. G. Isaeva, *Izv. Akad. Nauk U.S.S.R.* 1401 (1969)

[21] See e.g. H. C. Brown and A. Suzuki, *J. Am. Chem. Soc.* **89**, 1933 (1967)

[22] B. A. Arbuzov and Z. G. Isaeva, *Bull. Acad. Sci. USSR* 1841 (1968)

[23] P. J. Kropp, *J. Am. Chem. Soc.* **88**, 4926 (1966)

[24] P. Teisseire, A. Galfre, M. Plattier, P. Rouiller and B. Corbier, *Recherches* **16**, 119 (1967)

[25] G. Buchi, R. E. Erickson and N. Wakabayashi, *J. Am. Chem. Soc.* **83**, 927 (1961); G. Berti, F. Bottari and A. Marsili, *Tetrahedron Letters* 1 (1964)

[26] A. S. Gupta, Ph.D thesis, Punjab University (1965)

[27] J. W. Breen, E. Ritchie, W. T. L. Sidwell and W. C. Taylor, *Aust. J. Chem.* **19**, 455 (1966); W. R. Chan, D. R. Taylor and T. Yee, *J. Chem. Soc.* 311 (1970)

[28] S. E. Tung and E. Mcininch, *J. Catalysis* **3**, 229 (1964)

[29] G. M. Schwab and H. Kral, *Proceedings of the 3rd International Congress on Catalysis* Vol. I, p. 433 (1965). B. D. Flockhart, C. Naccache, J. A. N. Scott and R. C. Pink, *Chem. Comm.* 238 (1965)

[30] H. Pines and W. O. Hagg, *J. Am. Chem. Soc.* **82**, 2471 (1960); M. van Tongelen, *J. Catalysis* **5**, 535 (1966)

[31] J. Manassen and H. Pines, *Third Cong. on Catalysis* Vol. II, p. 845; *Advances in Catalysis* **16**, 49–90 (1966)

[32] D. D. Evans and C. W. Shoppee, *J. Chem. Soc.* 543 (1953)

[33] H. Brockmann and H. Schodder, *Ber. Dtsch. Chem. Ges.* **74**, 73 (1941)

[34] R. Hernandez, R. Hernandez, Jr., and L. R. Axelrod, *Analyt. Chem.* **33**, 370 (1961)

[35] A. S. Gupta and Sukh Dev, *J. Chromatog.* **12**, 189 (1963)

[36] C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.* **77**, 2549 (1955)

[37] G. B. Payne, *J. Org. Chem.* **24**, 1354 (1959)