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ORGANIC REACTIONS IN A SOLID MATRIX*—I
ALUMINA-INDUCED OXIRANE REARRANGEMENTS†‡

V. S. JOSHI, N. P. DAMODARAN and SUKH DEV
National Chemical Laboratory, Poona, India

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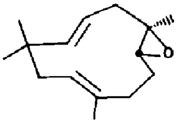
Abstract—A fairly general transformation of methyldialkyl-substituted 1,2-epoxides to the corresponding vinylidene, allylic secondary alcohols, on contact with active Al_2O_3, is described. A systematic study of some of the reaction variables of this transformation has also been carried out. The epoxides thus studied include those derived from the following olefins: 1-methylcyclopentene, 1-methylcyclohexene, 1-methylcycloheptene, α-pinene and Δ^3-carene.

DURING work[1] on the isolation and purification of humulene epoxides, it was noticed that unless the activity of the Al_2O_3 was carefully controlled to grade II (or weaker) considerable loss of material occurred, by conversion of the epoxides to alcohols (IR), during contact with active Al_2O_3. It was finally established[1] that humulene epoxide-II (I) on being shaken with Al_2O_3 (grade I) in an hexane solution gives in ~60% yield humulenol-II (II). A survey of the literature showed that Prelog *et al.*[2] had earlier noted that *trans*-cyclodecene epoxide on chromatography over strongly activated Al_2O_3 was converted, in part, into an allylic alcohol, which was not studied further. Besides this lone example, there does not appear to be any other record of a similar transformation of an epoxide on an Al_2O_3 column, though their isomerization to carbonyl compounds[3] under chromatographic conditions§ had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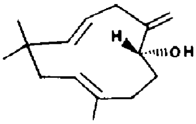

II

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[*] This general title has been chosen to report on organic reactions occurring on a solid surface (in a solid matrix), the latter besides holding the substrate (e.g. by adsorption, or by clathrate/molecular complex formation, or by a readily reversible chemical reaction) also provides nearby, a suitable reaction centre. A solvent, when employed, acts essentially as a dispersing vehicle.

Though we got interested in this type of reactions only by a chance observation of an oxirane ring rearrangement during a column chromatography, we feel there is considerable scope for interesting work in this area.

[†] Communication No. 1193, National Chemical Laboratory, Poona.

[‡] Delivered as a lecture at Laboratorium für organische Chemie, E.T.H., Zurich, in June 1966.

[§] Secondary reactions caused by active Al_2O_3 during chromatography have been summarized.[4] Various other reactions on Al_2O_3, essentially under the conditions of chromatography, reported since the appearance of this Review[4] include: epimerisation,[5] 1,5-hydride shift,[6] Cannizzaro reaction,[7] Favorskii rearrangement,[8] acyloin rearrangement,[9] skeletal rearrangement of quadricyclanone,[10] shifting of ethylenic linkages,[11] elimination reactions (t-alcohols,[12] halides,[13] tosylates,[14] sulphones[15]) and hydrolysis.[16]

been noticed and, a number of investigators had studied the reaction of epoxides on Al_2O_3 at elevated temperatures (200–300°).[17] In order to check the generality of this transformation, humulene epoxide-I, dihydrohumulene epoxides, humulene dioxide and caryophyllene oxide were all exposed to active Al_2O_3 in hexane solution and in each case, the major product formed was the corresponding vinylidene, allylic alcohol.[1,*] These results prompted us to undertake a systematic study of this reaction in order to explore its scope and, we describe below the results of such an investigation.

Reaction conditions. In order to determine the behaviour of a simple epoxide towards Al_2O_3 under the conditions employed (HNO_3-washed Al_2O_3, Brockmann grade I, room temp ~25°, N_2) for the above oxides, 1-methyl-1,2-epoxycyclohexane[19] was reacted with Al_2O_3 (24 hr). By this treatment the epoxide was totally transformed, but the product contained mostly (90%) 1-methyl-*trans*-cyclohexane-1,2-diol,[20] besides a mixture (~1:1) of 2-methylene-cyclohexanol[21] and 2-methyl-Δ^2-cyclohexenol.[22] It was next decided to study the various reaction parameters in order to optimise the conversion of this epoxide to the olefinic alcohols. Tables 1–3 summarize the results of the effect of mode of preparation of Al_2O_3, its activity and the reaction temperature and the substrate–Al_2O_3 ratio, respectively. As a result of this work, the following conditions were considered most suitable for this transformation and were employed throughout the subsequent work with other substrates:

TABLE 1. REARRANGEMENT OF 1-METHYL-1,2-EPOXYCYCLOHEXANE: EFFECT OF MODE OF PREPARATION OF ALUMINA

No.	Alumina*	Unchanged epoxide (%)†	Product distribution (% by GLC)‡		
	Mode of prep (activation temp.)		Unsatd. alcs.	Glycol	2-methyl cyclohexanone
1	HNO_3-washed (450°)	—	10	90	—
2	Water-washed (450°)	—	23	77	—
3	EtOAc-treated (250°)	8	19	81	—
4	EtOAc-treated (450°)	18	31	63	6
5	From $Al(OPr^i)_3$ (250°)	—	—	95	5
6	No. 4, doped with pyridine (450°)	—	4	96	—

* Brockmann grade I; 100–250 mesh size; epoxide/Al_2O_3, 1/25 (w/w);
† After reaction for 24 hr at ~25–30° in hexane (30 ml for 25 g of Al_2O_3).
‡ Total recovery: ~80%.

Mode of preparation: water-washed; Temp of activation: 450°/6 hr; Brockmann grade: I; Mesh size: 100–250 mesh; Substrate–Al_2O_3 ratio: 1:25 (w/w); Solvent: Hexane, 30 ml for 25 g of Al_2O_3; Reaction temp: Room temp (~25–30°); Reaction time: 24 hr.

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[*] Since the publication of our advance communication,[1] the application of this reaction to caryophyllene epoxide has been reported[18] from another Laboratory also.

TABLE 2. REARRANGEMENT OF 1-METHYL-1,2-EPOXYCYCLOHEXANE: EFFECT OF ACTIVITY OF ALUMINA

Brockmann grade*	Unchanged epoxide (%)†	Product distribution (% by GLC)	
		Unsatd. alcs.	glycol
I	0	23	77
II	0	7	93
III	87	15	85

* Water-washed Al_2O_3 (450°).

† All other conditions as above (Table 1).

TABLE 3. REARRANGEMENT OF 1-METHYL-1,2-EPOXYCYCLOHEXANE: EFFECT OF REACTION TEMPERATURE AND SUBSTRATE-ALUMINA RATIO*

No.	Reaction temp	Al_2O_3–epoxide–ratio (w/w)	Unchanged epoxide (%)	Product distribution (% by GLC)	
				Unsatd. alcs.	glycol
1	0°	25	0	22	78
2	25°	25	0	23	77
3	40°	25	0	33	67
4	25°	5	66	3	26
5	25°	15	2	10	82
6	25°	20	0	22	78

* Water-washed Al_2O_3 (450°) grade I; reaction time: 24 hr in hexane.

RESULTS

Under the standard reaction conditions described above, the behaviour of the oxides, derived from the following olefins, was next investigated: 1-methylcyclopentene, 1-methylcycloheptene, (+)-α-pinene and (+)-Δ^3-carene.

1-*Methyl*-1,2-*epoxycyclopentane*[23] on treatment with Al_2O_3 gave a mixture of products, which was separated by inverted-dry-column-chromatography (IDCC)[24] on silica gel to give a diol (m.p. 62–63°) identified as 1-methyl-*trans*-cyclopentane-1,2-diol[25] (~15%) and a mixture of unsaturated alcohols (80%), in which 2-methylene-cyclopentanol[21] predominated (90% by GLC). The latter was separated by IDCC on SiO_2 gel–$AgNO_3$ and identified by its spectroscopic (IR, PMR) and other properties.

1-*Methyl*-1,2-*epoxycycloheptane*, when shaken with Al_2O_3 gave a product, which was separated by IDCC into a monohydric alcohol fraction (~90%) and a glycol fraction (~10%); the latter was not investigated further. The major product was resolved by IDCC ($AgNO_3$–SiO_2 gel) into the expected 2-methylene-cycloheptanol

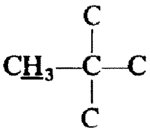
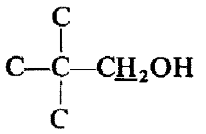
(80%) which was readily identified by its spectroscopic properties (Table 4, 5) and a saturated alcohol (~20%). This alcohol ($C_8H_{16}O$) shows the following structural characteristics (PMR):  $C\underline{H}_3{-}C(C)(C){-}C$ (3H, singlet, 54 c/s),  $C{-}C(C)(C){-}C\underline{H}_2OH$ (2H, sharp singlet, 197 c/s); and hence, is assigned the structure III. The formation of this alcohol is rationalized in terms of the aldehyde IV, as originating from the epoxide by a carbonium ion rearrangement (vide Discussion), and then undergoing a Cannizzaro reaction on Al_2O_3. Though the Cannizzaro acid (V) was not isolated

TABLE 4. PMR DATA OF SOME α-METHYLENE CARBINOLS

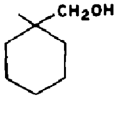
No.	Compound	$>C{=}C\underline{H}_2$		$-C\underline{H}OH$	
		signal (c/s)*	multiplicity† (*J* in c/s)	signal (c/s)*	multiplicity (*J* in c/s)
1	2-Methylene-cyclopentanol	295 (1H) 305 (1H)	d (2) d (2)	260	b
2	2-Methylene-cyclohexanol	279 (1H) 295 (1H)	s s	239	b
3	2-Methylene-cycloheptanol	289 (1H 299 (1H)	t (1) t (1)	250	t (6)
4	*trans*-Pinocarveol	286 (1H) 297 (1H)	t (1) t (1)	261	d (6·5)
5	$\Delta^{4(10)}$-Caren-3α-ol	285 (2H)	t (2·5)	241	t (3·5)

* If not a singlet, position given is the centre of the multiplet.
† s = singlet, d = doublet, t = triplet and b = broad singlet.

TABLE 5. IR DATA OF SOME α-METHYLENE CARBINOLS

No.	Compound	$>C{=}CH_2$		CHOH	
		ν_{max} (cm^{-1})	δ_{max} (cm^{-1})	ν^{OH}_{max} (cm^{-1})	δ^{C-O}_{max} (cm^{-1})
1	2-Methylene-cyclopentanol	1667	890, 905	3300	1062, 1095
2	2-Methylene-cyclohexanol	1665	905	3350	1090
3	2-Methylene-cycloheptanol	1660	910	3400	1030
4	*trans*-Pinocarveol	1650	900	3380	1005, 1025
5	$\Delta^{4(10)}$-Caren-3α-ol	1655	890	3340	1045

in this case, this has been done in other cases described below and a Cannizzaro reaction taking place on Al_2O_3 surface has previous analogy.[7]



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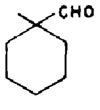

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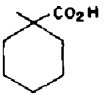
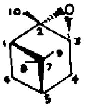


V

(+)-2α,3α-*Epoxypinane* (VI),[26,*] resulting from the perphthalic acid epoxidation of (+)-α-pinene, on exposure to active Al_2O_3 in hexane gave a product, shown by programmed GLC (and by TLC) to contain three main components (~1:4:2, having RRT of 1, 1·41 and 2·59 respectively), besides traces (≯2% by GLC) of glycol.

The component with RRT of 1, was identified from its IR spectrum to be pinocamphone (VII); the spectrum was compared with the spectra of pinocamphone and isopinocamphone recorded by Teisseire *et al.*[28] as well as with that of an authentic sample of isopinocamphone (VIII) obtained according to the procedure of Zweifel and Brown.[29] Mixed GLC of isopinocamphone with the total product showed that ~5% of isopinocamphone (RRT 1·1) is also possibly present.



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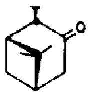
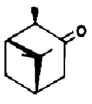


VII



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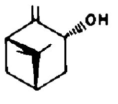
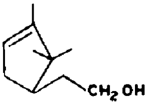
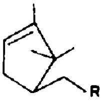


IX



X



XI: R = CHO
XII: R = COOMe

The major component (RRT, 1·41) was identified from its physical properties and spectral data (Table 4, 5) to be the expected vinylidene, allylic alcohol, *trans*-pinocarveol (IX).[30–32]

The third component (RRT, 2·59) was recognised as the primary, mono-olefinic alcohol X from its spectral characteristics: CH_2OH (IR: 1060, 3300 cm^{-1}; PMR: 2H, overlapping triplets centred at 216 c/s, $J = 6$ c/s), $-\underset{|}{C}{=}CH-$ (IR: 806 cm^{-1}; PMR: 1H, broad singlet, 312 c/s), two quaternary methyls (PMR: two 3H singlets at 47 and 59 respectively), one vinylic methyl (PMR: 3H, broad singlet, 97 c/s). This compound has been recently described[33] but, since the reported PMR data are at some variance with ours, we have prepared X by the $LiAlH_4$ reduction of the known aldehyde (XI), obtainable from α-pinene oxide (VI) according to Arbusow;[34] the product thus obtained was indistinguishable (IR, PMR) from the one obtained

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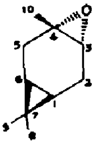
[*] The reasonable assumption that the peracid should attack α-pinene from the side opposite to the quaternary dimethyl bridge, has been recently confirmed[27] by a stereo-specific synthesis of VI; also see: Suzuki *et al.*[36]

by the Al_2O_3 reaction. As already stated in the case of III, this compound also results from a Cannizzaro-type reaction of the aldehyde XI on Al_2O_3 surface, the aldehyde itself being first formed from the oxide by a rearrangement similar to that observed by Arbusow[34] with $ZnBr_2$. The occurrence of a Cannizzaro reaction was confirmed by isolation of the Cannizzaro acid (as the methyl ester XII) from the spent Al_2O_3 by extraction with aq alc. Na_2CO_3 (~10%) and, by a demonstration of the formation of both the alcohol X and the corresponding acid on shaking the aldehyde XI with Al_2O_3, under the reaction conditions employed for the oxide.

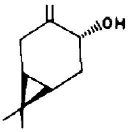
(+)-3α,4α-*Epoxycarane* (XIII),[35, 36] obtained by the perphthalic acid epoxidation of (+)-Δ^3-carene, on Al_2O_3 treatment furnished a product consisting essentially of three components (GLC, ~2:11:15, with RRT of 1, 1·19 and 1·37 respectively). IDCC of the total alcohols on $AgNO_3$–SiO_2–gel gave only two components (RRT 1, 1·37) in a pure state.

The major component (RRT, 1·37) was identified as (−)-$\Delta^{4(10)}$-caren-3α-ol (XIV)[37] from its physical constants and spectroscopic characteristics (Tables 4 and 5). The next less abundant constituent (RRT, 1·19) could not be obtained free from XIV but from the PMR spectrum of this impure sample, as well as its $[\alpha]_D$ and GLC composition data it was clear (Experimental) that this must be the isomeric Δ^4-caren-3α-ol (XV).[37]

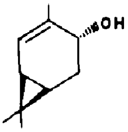
The minor alcohol (RRT, 1) shows in its PMR spectrum signals for —C—$C\underline{H}_2OH$ (2H, singlet, 195 c/s) and three quaternary methyls (3H, singlet at 55 c/s and, 6H singlet at 59 c/s) and hence has been formulated as XVI, the product of ring-contraction and a subsequent Cannizzaro reaction. Its configuration at C_4 is discussed below.



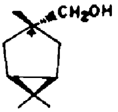
XIII



XIV



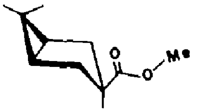
XV



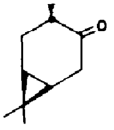
XVI

XVII

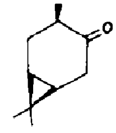
XVIII



XIX



XX



XXI

As expected, the acid corresponding to XVI was present in the spent Al_2O_3 and could be isolated and identified as its methyl ester (XVII). In analogy with the reaction[34] of α-pinene oxide with $ZnBr_2$, the action of this reagent on carene oxide (XIII) was next investigated* to see if the aldenyde XVII could be prepared by this method for correlation with XVI. Action of catalytic quantity of $ZnBr_2$ on carene oxide in refluxing benzene gave a product (~80%), shown to contain at least four components (GLC, ~2:3:3:3 with RRT of 1, 2·26, 5·73 and 6·43 respectively), which were separated by column chromatography. The component with the least retention time was identified (IR, PMR) as *p*-cymene, containing ~3–5% of *m*-cymene. The two components with the highest retention times were recognised from their IR and PMR spectra as 3-caranone[39] (XX; RRT 5·73) and 3-iso-caranone[39] (XXI; RRT 6·43). The compound with RRT of 2·26 was found to be the required aldehyde XVIII (IR: CHO 2700, 1730 cm^{-1}; PMR: three quaternary methyls as a 9H singlet at 60 c/s, $\underline{H}C{=}O$ as a 1H singlet at 575 c/s). Oxidation of the total product with Ag_2O furnished an acid, the methyl ester of which was identical (IR) with that of the acid isolated from the Al_2O_3 reaction. $LiAlH_4$ reduction of this ester gave an alcohol, identical (IR) with the earlier sample from the Al_2O_3 reaction.

The PMR spectrum of the methyl ester (XVII), shows the three quaternary Me signals at 59, 59 and 69 c/s. Of these, the 69 c/s signal can be assigned[40] to the Me attached to the carbon carrying the carbomethoxy group. Thus, the two geminal quaternary methyls have the same chemical shift, which is possible only if the carbomethoxy group is *trans* to the three-membered ring (as in XVII), as in the alternative configuration (XIX), one (*endo*) of the geminal methyls should be considerably influenced by the anisotropy of the carbonyl group.[41] The PMR spectrum of the corresponding aldehyde (vide supra) is also consistent with this conclusion. Hence, the directly related alcohol (XVI) must have the configuration shown.

Some relevant PMR and IR data of the vinylidene, allylic secondary alcohols, obtained during this work have been collected in Tables 4 and 5 for ready reference.

DISCUSSION

It has been clearly demonstrated that 1,2-epoxides are quite sensitive to active Al_2O_3 and it is conceivable that many naturally occurring epoxides might have been missed by virtue of their being transformed into other products during separation of natural products by chromatography on Al_2O_3 of high activity. In general, three different reactions have been met with so far:

(i) epoxide ring-cleavage to a *trans*-glycol.
(ii) typical carbonium-ion rearrangements.
(iii) transformation into an allylic alcohol.

By far, the last reaction is most general and has been observed with every epoxide studied so far and, thus has a preparative utility.† At least in one case (2-methylenecyclohexanol) it was demonstrated that the allylic alcohol does not arise by dehydration of the corresponding glycol, because when 1-methyl-*trans*-1,2-cyclohexanediol was shaken with Al_2O_3 under the same conditions, it was recovered unchanged. Furthermore, both in the case of pinene oxide (VI) and carene oxide (XIII), it has

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* This reaction has been earlier studied by Arbuzov,[38] who reports the formation of an aldehyde of undetermined structure, besides p-cymene and 3-caranones.

† Conversion of certain 1,2-epoxides into allylic alcohols has been accomplished with finely divided sodium,[42] as well as with di-isobutyl-aluminium hydride.[43]

been demonstrated that the reaction (epoxide to allylic secondary alcohol) proceeds with retention of configuration at the tertiary carbon (i.e. at the resulting secondary alcohol carbon).

Sufficient evidence has accumulated to show that Al_2O_3 has dipolar character and there are both electron-donor and electron acceptor sites on Al_2O_3 surface.[44] The reactions observed above can be grossly interpreted in terms of this character of Al_2O_3, but undoubtedly further refinement is necessary in order to explain the *differences* observed with the various epoxides. However, such a discussion will be deferred to a future date, when the results of further research on this reaction, in progress in this Laboratory, will have become available.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether 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 $CHCl_3$.

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.

Analytical GLC were run on "Aerograph", model A-350-B, using a 150 cm × 5 mm column packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh) with H_2 as carrier gas. Temp-programmed GLC were run on the same machine between 50° and 160° at a rate of heating ~10°/min. Relative retention times (RRT) are reported under non-programming conditions.

IDCC[24] were carried out on TLC grade silica gel (−250 mesh) unless stated to the contrary, and were based on preliminary TLC's to find out the conditions most suitable for optimum separations.

Alumina used for chromatograpny was made neutral by the HNO_3 method[45] and graded according to Brockmann.[46] The silica gel used for column chromatography was washed with water till sulphate-free, dried and activated at 125–130°/6–8 hr and standardized according to Hernandez.[47] $AgNO_3$–silica gel was prepared according to Gupta and Dev.[48]

Preparation of alumina

(i) HNO_3-*washed alumina.* An aqueous slurry of commercial alumina (−100, +250 mesh) was stirred mechanically with gradual, dropwise addition of conc. HNO_3, so that after 2 hrs stirring, the aqueous layer was still acidic (congo red). The alumina was washed repeatedly by decantation with hot water, till neutral, filtered, washed with distilled water, and then alcohol. It was dried in air and activated at 450°/6 hr: activity, I; pH, 9·4.

(ii) *Water-washed alumina.* Commercial alumina was repeatedly washed with boiling water till washings were neutral (phenolphthalein). The product was filtered, washed with distilled water and then with alcohol. Drying and activation as in (i), gave a product, activity I; pH, 9·4.

(iii) EtOAc-*treated alumina.* (a) Commerical alumina was kept covered with EtOAc, with occasional shaking (30 hr). It was filtered, washed with MeOH, water and again with MeOH, dried and activated at 250°/54 hr, activity ~I; pH, 7·0. (b) Inactive Al_2O_3 prepared as above was activated at 450°/6 hr, activity I; pH, 8·0.

(iv) *From* $Al(OPr^i)_3$. $Al(OPr^i)_3$ (412 g), prepared according to a standard method, was digested with water (4 l.) on a water-bath (4 hr.) The precipitated $Al(OH)_3$ was filtered, washed with hot water, dried in air, and activated at 250°/24 hr: activity I; pH 7·0.

(v) *Pyridine-doped* Al_2O_3. This material was prepared from sample (iii b) according to the procedure of von Rudloff.[49]

Standard procedure for reaction with Al_2O_3

For all the epoxides reported in this paper, the following general procedure was adopted for reaction with Al_2O_3. The epoxide was added to a thick slurry of 25 times its wt of Al_2O_3 suspended in hexane (30 ml for every 25 g Al_2O_3), in a suitable, stoppered flask, flushed with N_2, and shaken (mechanically) for 6 hr and then kept aside for 18 hr. The hexane was filtered and the Al_2O_3 washed with Et_2O–MeOH

(5%; 800 ml for 1 g epoxide; added in several portions). The combined solvent was removed by careful fractionation and a part of the residue was distilled *in vacuo* for temp-programmed GLC.

Action of Al_2O_3 *on 1-methyl-1,2-epoxycyclohexane*

1-Methyl-1,2-epoxycyclohexane was prepared according to the method of Guss and Rosenthal,[19] as a colorless, mobile liquid, b.p. 60–61°/40 mm, n_D^{20} 1·4412 (Lit.[19] b.p. 40–42°/12 mm, n_D^{20} 1·4455. IR spectrum: 1,2-epoxide 843, 765 cm^{-1}. PMR spectrum: $C\underline{H}_3—\overset{|}{\underset{|}{C}}—O—$ (76 c/s, 3H, s); $—CH_2—\overset{O}{\overbrace{CH—C}}$ (167 c/s, 1H, t with $J = 2$ c/s).

In a typical run, 1-methyl-1,2-epoxycyclohexane (3·4 g) was shaken with Al_2O_3 (water-washed, activated at 450°/6 hr, activity I; 85 g), suspended in hexane (102 ml), for 6 hr and then left at room temp (30°; 16 hr). Usual work up and distillation gave a semisolid material (2·78 g; b.p. 70–105°/13-5 mm). For RRT, GLC was carried out at 70° at a H_2 flow of 30 ml/min.

*1-Methyl-*trans*-cyclohexane-1,2-diol.* The above reaction product (2·78 g) was chromatographed on Al_2O_3/III (100 g; 2·8 × 29 cm):

Frac. 1	Pet. ether	25 ml × 20	Nil	
Frac. 2	Pet. ether + 25% benzene	25 ml × 4	0·174 g	Unidentified.
Frac. 3	Pet. ether + 25% benzene	25 ml × 12	0·618 g	Mixture of 2-methylene-cyclohexanol and 2-methyl-Δ^2-cyclohexenol.
Frac. 4	Pet. ether + 50% benzene up to Benzene–MeOH 4%	25 ml × 16 400 ml × 2	1·792	Solid; m.p. 83–84°

Frac. 4 was recrystallized from $CHCl_3$–pet. ether to give colorless prisms of 1-methyl-*trans*-cyclohexane-1,2-diol, m.p. 83–84° (lit.[20] m.p. 84°). (Found: C, 65·12; H, 10·97. $C_7H_{14}O_2$ requires: C, 64·63; H, 10·76%).

2-Methylene cyclohexanol and 2-methyl-Δ^2*-cyclohexenol.* Frac. 3 (0·298 g) from the above column chromatography was subjected to IDCC on $AgNO_3$ (10%)-silica gel (act. I–IIa; 85 g; 2·5 cm × 25 cm) using pet. ether–EtOAc–acetone (8:1:1) as solvent system. Two main pooled fractions were obtained by scoopula probing, supplemented by TLC screening:

Frac. 1	0·104 g	lower R_f band
Frac. 2	0·150 g	higher R_f band

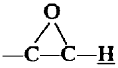
Frac. 1 on distillation gave pure 2-methylene-cyclohexanol as a colorless liquid (103·5 mg), b.p. (bath) 140–150°/36 mm; n_D^{25} 1·4780 (Lit.[21] b.p. 83–85°/26 mm).

Repetition of the IDCC (conditions same as above) with Frac. 2 gave pure 2-methyl-Δ^2-cyclohexenol as a colorless liquid (130 mg), b.p. 140–150° (bath)/36 mm; n_D^{25} 1·4793 (Lit.[22] 125°/25 mm n_D^{25} 1·4838). IR spectrum: C=C 811 cm^{-1}; OH 3400, 990 cm^{-1}. PMR spectrum: $C\underline{H}_3—C{=}C—$ (104 c/s, 3H, s); $\underline{H}C{=}C—$ (317 c/s, 1H, s); $C\underline{H}—OH$ (233 c/s, 1H, t with $J = 4$ c/s).

Preparation of the remaining epoxides of this series

All the other epoxides used in the present investigation were prepared by epoxidation of the corresponding olefin with slightly more than one mole of monoperoxyphthalic acid[50] in ethereal soln at temperatures varying from 0°–30°, for as much time as is sufficient for one mol. of peracid to be consumed (iodometric titration and TLC screening). The usual work-up, followed by distillation *in vacuo* gave the epoxide, whose purity was checked by GLC and TLC (and wherever necessary, further purified by fractionation).

Action of Al_2O_3 *on 1-methyl-1,2-epoxycyclopentane*

1-Methyl-1,2-epoxycyclopentane was prepared from 1-methylcyclopentene by the general method (53·5% yield). The fraction b.p. 107–108°/710 mm; n_D^{20} 1·4279 (Lit.[23] b.p. 110·8–111°/760 mm; n_D^{15} 1·4311) was used. IR spectrum: 1,2-epoxide 1260, 830, 880 cm^{-1}. PMR spectrum: $C\underline{H}_3-C-O$ (86 c/s, 3H, s);  $-\overset{O}{C-C}-\underline{H}$ (182 c/s, 1H, s). This epoxide (5 g) was treated with Al_2O_3 (125 g, hexane 150 ml) and the product worked up according to the standard procedure to give a pale yellow liquid (5·1 g), b.p. 90–100°/95–3 mm. For RRT, GLC was carried out at 60° at a H_2 flow of 30 ml/min.

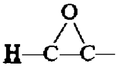
1-*Methyl*-trans-*cyclopentane*-1,2-*diol and* 2-*methylene-cyclopentanol*. These were separated from the crude reaction mixture (2·8 g) by IDCC on silica gel (125 g, IIA; 3·3 cm × 25 cm) using pet. ether–EtOAc–acetone (8:1:1) as solvent system. Pooling by TLC screening afforded two fractions:

Frac. 1	0·327 g	lower R_f band
Frac. 2	0·35 g	upper R_f band

Frac. 1 was distilled and then recrystallized from $CHCl_3$–pet. ether b.p. 100°/3 mm, m.p. 62–63° (Lit.[25] m.p. 65°). (Found: C, 62·24; H, 10·64. $C_6H_{12}O_2$ requires: C, 62·05; H, 10·35%).

Frac. 2 (1 g) was further purified by IDCC on $AgNO_3$ (15%)–SiO_2 gel (250 g, IIB; 4·7 cm × 25 cm; solvent system: C_6H_6–EtOAc–EtOH, 7:2:1) to get pure 2-methylene-cyclopentanol: b.p. 120° (bath)/115 mm, n_D^{20} 1·4777. (Lit.[25] b.p. 85–86°/68 mm, n_D^{25} 1·4750).

Action of Al_2O_3 *on 1-methyl-1,2-epoxycycloheptane*

Pure 1-methyl-1,2-epoxycycloheptane does not appear to have been reported in the literature. A homogeneous (GLC, TLC) sample was obtained in 75% yield from 1-methylcycloheptene by the general method described above, as a colorless, mobile liquid, b.p. 75°/45 mm; n_D^{20} 1·4538. IR spectrum: 1,2-epoxide 1250, 875, 825 cm^{-1}. PMR spectrum: $C\underline{H}_3-C-O-$ (75 c/s, 3H, s);  $\underline{H}-\overset{O}{C-C}-$ (162 c/s, 1H, t with $J = 5$ c/s). (Found: C, 76·14; H, 11·4. $C_8H_{14}O$ requires: C, 76·17; H, 11·18%).

The above epoxide (5·8 g) was treated with Al_2O_3 (175 g; hexane 175 ml) according to the standard procedure to afford 4·0 g of a liquid product (b.p. 80–115°/9–2 mm). For RRT, GLC was carried out at 90° at a H_2 flow of 30 ml/min.

2-*Methylene-cycloheptanol and the alcohol* III. The crude reaction product (2·03 g) was subjected to IDCC on silica gel (125 g, IIA; 3·3 cm × 25 cm) employing pet. ether–EtOAc–acetone (8:1:1).

Frac. 1	0·171 g	lower-most band
Frac. 2	0·050 g	middle band, discarded
Frac. 3	1·715 g	upper band

Frac. 1 was distilled (103 mg; b.p. 115 (bath)/2 mm) and showed ~90% GLC purity. PMR spectrum: $C\underline{H}_3-C-OH$ (68 c/s, 3H, s); $-C\underline{H}-OH$ (198 c/s, 1H), indicates that the major component is 1-methyl-cycloheptane-1,2-diol.

Repetition of IDCC of Frac. 3 (1·008 g) on $AgNO_3$ (15%)–SiO_2 gel (250 g; IIB; 4·7 cm × 25 cm; solvent system: C_6H_6–EtOAc, 3:1) furnished four fractions:

Frac. 1	0·367 g	lowermost band (4 cm–6·6 cm from origin)
Frac. 2	0·100 g	next band (6·6–8·6 cm)
Frac. 3	0·134 g	middle band (8·6–10·6 cm)
Frac. 4	0·189 g	upper band (> 10·6 cm), discarded

Frac. 1, b.p. (bath) 110°/7 mm, n_D^{25} 1·4859, was pure 2-methylene-cycloheptanol. (Found: C, 76·14; H, 11·18. $C_8H_{14}O$ requires: C, 75·7; H, 11·37%).

Frac. 2 consisted of a mixture of 2-methylene-cycloheptanol and alcohol III (GLC).

Frac. 3, b.p. (bath) 110°/7 mm, n_D^{25} 1·4652, was pure IV. IR spectrum: OH 3350, 1060, 1042 cm^{-1}. (Found: C, 75·58; H, 12·0. $C_8H_{16}O$ requires: C, 74·94; H, 12·58%).

Action of Al_2O_3 *on* (+)-2,3-*epoxy*-α-*pinene* (VI)

Compound VI (b.p. 91–93°/27 mm; n_D^{20} 1·4690; $[\alpha]_D^{34}$ +53·8, neat) was prepared in 45·7% yield from

(+)-α-pinene ($[\alpha]_D$ +21°, neat), by the general method. (Lit.[32] b.p. 81°/21 mm; n_D^{20} 1·4685; $[\alpha]_D$ +64·3).

Compound VI (4·85 g), on treatment with Al_2O_3 (121·5 g, hexane 147 ml) according to the standard procedure, yielded a liquid material (2·25 g; b.p. 80–100°/7–2 mm), containing 3 main components VII, IX and X (~1:4:2) besides traces of glycol ($\not> 2\%$). For RRT, GLC was carried out at 85° and a flow rate of 30 ml/min.

(+) trans-*Pinocarveol* (IX), *pinocamphone* (VII) *and the alcohol* X. The crude reaction product (0·938 g) was resolved into VII, IX, and X by IDCC on silica gel (125 g; IIA; 3·3 × 25 cm) employing pet. ether–EtOAc–acetone (8:1:1) for development. The usual manipulations afforded the following pooled fractions, in the increasing order of R_f.

Frac. 1	0·269 g	Pure X
Frac. 2	0·112 g	Mixture of X and IX
Frac. 3	0·299 g	Pure IX
Frac. 4	0·129 g	Mixture of IX and VII
Frac. 5	0·140 g	Pure VII
Frac. 6	0·009 g	Rejected

Frac. 1 on distillation afforded pure X as a colorless liquid (110 mg; b.p. bath 90°/0·75 mm, n_D^{20} 1·4680 (Lit.[33] b.p. 105°/8 mm; n_D^{20} 1·4710). IR spectrum: C=C 806 cm^{-1}; OH 3300, 1060 cm^{-1}. PMR spectrum: C$\underline{H}_3$—C=C— (97 c/s, 3H, s, b); —C$\underline{H}_2$ OH (216 c/s, 2H, t with J = 6 c/s) —C=C$\underline{H}$ (312 c/s, 1H, s, b).

Distillation of Frac. 3 furnished pure (−)-*trans*-pinocarveol IX as a colorless oil (260 mg), b.p. (bath) 100°/2·5 mm; n_D^{25} 1·4965; $[\alpha]_D^{31}$ −45·3 (c, 2·2) (Lit.[32] b.p. 86–87°/9 mm; n_D^{20} 1·4987; $[\alpha]_D$ −58·8).

Frac. 5 was distilled to afford pure pinocamphone VII as a colorless liquid (112 mg), b.p. (bath) 100°/2 mm. (Lit.[28] b.p. 67°/5 mm; n_D^{15} 1·4733; $[\alpha]_D$ +22·5). IR spectrum: C=O 1709 cm^{-1}. PMR spectrum: quaternary methyls (54 c/s, 3H, s; 79 c/s, 3H, s); C$\underline{H}_3$—CH (62 c/s, 3H, d with J = 7·5 c/s).

Isolation of Cannizzaro acid (as its Me *ester* XII) *from spent* Al_2O_3

The Al_2O_3 left after exhaustive extraction with methanolic Et_2O was air-dried and refluxed with aq ethanolic Na_2CO_3 (~10%, 150 ml) for 1 hr. The soln was filtered hot and the Al_2O_3 once again extracted with aq EtOH–Na_2CO_3 (50 ml). The combined alkaline soln was extracted with Et_2O to remove neutral materials (negligible) and the aqueous layer was acidified (1:1 H_3PO_4aq), saturated with $(NH_4)_2SO_4$ and extracted with Et_2O (100 ml × 3). Solvent removal furnished the crude acid (410 mg), which was converted into methyl ester (CH_2N_2) and distilled to give XII as a pale yellow liquid (325 mg), b.p. (bath) 110°/2 mm, n_D^{20} 1·4590. IR spectrum: C=C 800 cm^{-1}; C=O (ester) 1750 cm^{-1}; PMR spectrum: quaternary methyls (49, 61 c/s); C$\underline{H}_3$—C= (97 c/s, 3H, s); —C=C—$\underline{H}$ (312 c/s, 1H, b).

α-Campholenic aldehyde XI *and the alcohol* X

α-Campholenic aldehyde XI prepared by the known method,[34] was not completely homogeneous (TLC). The distilled aldehyde XI (0·9 g), b.p. 105–107°/3 mm, in dry Et_2O (5 ml) was stirred with a slurry of LAH (0·0763 g) in dry Et_2O (5 ml) at 0°/1 hr and then at room temp (30°) for 5 hr. The usual work-up (saturated Rochelle salt solution, 20 ml, for decomposing the Al-complex) gave impure X (665 mg; b.p. 79–85°/4·5 mm). Pure X was isolated by IDCC on $AgNO_3$ (5%)-SiO_2 gel (125 g, IIB, 3·3 cm × 25 cm) using pet. ether–EtOAc–acetone (7:2:1) as solvent system. The lowest major band on distillation, gave a colorless liquid (168 mg), b.p. (bath) 90°/1·75 mm; n_D^{20} 1·4680.

Cannizzaro reaction of aldehyde XI *with* Al_2O_3 *and isolation of* X *and* XII

α-Campholenic aldehyde XI (0·5 g) was treated with Al_2O_3 (12·5 g, hexane 15 ml) according to the standard procedure and the neutral reaction products were extracted in the usual way (Et_2O–MeOH). This material was distilled (228 mg), b.p. (bath) 90°/1·5 mm and contained the desired alcohol X besides some unchanged XI. Alcohol X was isolated by IDCC on silica gel (25 g; IIB; 1·5 cm × 25 cm, C_6H_6–EtOAc, 4:1). The lower band afforded pure X (13·3 mg).

The acid (strongly adsorbed on the Al_2O_3) from the Cannizzaro reaction was isolated as described earlier with 10% aq EtOH–Na_2CO_3 and converted into its methyl ester (CH_2N_2): b.p. (bath) 110°/1·5 mm.

Action of Al_2O_3 *on* (+)-*3α,4α-epoxycarane* XIII

Compound XIII was prepared from (+)-Δ^3-carene in 63% yield, b.p. 102–103°/48 mm; n_D^{20} 1·4650; $[\alpha]_D^{30}$ +12·5 (neat). (Lit.[36]: b.p. 92–93°/23 mm; n_D^{20} 1·4664; $[\alpha]_D^{26\cdot5}$ +13·35).

Compound XIII (10 g) treated with Al_2O_3 (250 g, hexane 300 ml) in the standard manner afforded a neutral product (6·2 g), b.p. 75–100°/30–2 mm, containing XVI, XV and XIV in the ratio 2:11:15 (GLC). For RRT, GLC was carried out at 110° with H_2 flow rate of 30 ml/min.

(−)-Δ$^{4(10)}$-Caren-3-α-ol XIV *and alcohol* XVI

The above Al_2O_3 reaction product (4·6 g) was subjected to IDCC on $AgNO_3$ (15%)-SiO_2 gel (500 g; IIB; 6·6 cm × 25 cm; C_6H_6-EtOAc-EtOH, 14:5:1). The following pooled fractions were obtained (bands cut in the increasing order of R_f).

Frac. 1	0·200 g	liquid, rejected
Frac. 2	2·19 g	solid, ~pure XIV, m.p. 45–48
Frac. 3	0·638 g	liquid, mixture of XIV and XV
Frac. 4	0·718 g	pure XVI
Frac. 5	0·235 g	reddish liquid, rejected

A sample from Frac. 2 was sublimed (bath 45°/0·7 mm) to give pure XIV m.p. 49–50°, $[\alpha]_D^{29}$ −110·9 (*c*, 3·2) [Lit.[37] m.p. 56–57°, $[\alpha]_D^{25}$ −118·7 (*c*, 3·4)].

Frac. 4 was distilled to yield XVI as a colorless liquid (247 mg), b.p. (bath) 110°/2·5 mm); n_D^{20} 1·4742. IR spectrum: OH 3400, 1020 cm^{-1}. (Found: C, 77·91; H, 11·66. $C_{10}H_{18}O$ requires: C, 77·86; H, 11·76%).

Frac. 3 (mixture of XV and XIV in the ratio 67:33 according to GLC) was distilled b.p. (bath) 110°/1·5 mm and had an $[\alpha]_D^{21}$ +103 (*c*, 0·95) · $[\alpha]_D$, calculated for a mixture of authentic XV and XIV ($[\alpha]_D$ +204 and −118)[37] in the ratio 68:32 comes to +103. The PMR spectrum of this fraction showed, in addition to all the signals for XIV (see Table 4), the following signals for XV, clearly separated from those of XIV with the intensities integrating approximately for a 65:35 ratio of XV and XIV. Quaternary methyls (49 c/s, 3H, s; 64·5 c/s, 3H, s); $C\underline{H}_3$—C= (105 c/s, 3H, s partly split); —C$\underline{H}$—OH (217, 1H, t, with $J = 5$); —C=C$\underline{H}$ (332 c/s; 1H, b).

Isolation of the Cannizzaro acid (as its methyl ester XVII*) from spent* Al_2O_3

The spent Al_2O_3, from reaction with the carene epoxide, was worked up in the same manner as for α-pinene epoxide to yield the crude acid (233 mg) which was directly esterified with CH_2N_2 to give the methyl ester XVII (128 mg), b.p. (bath) 160°/25 mm; n_D^{20} 1·4549. (Found: C, 71·94; H, 9·99. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%). IR spectrum: ester C=O 1724 cm^{-1}. PMR spectrum: —C—C$\underline{H}_3$ (69 c/s, 3H, s); HC—C—(C$\underline{H}_3$)$_2$ (59 c/s, 6H, s); —OC$\underline{H}_3$ (220 c/s, 3H, s).

Action of $ZnBr_2$ *on* XIII

Freshly distilled carene epoxide XIII (5·1 g) was refluxed with dry C_6H_6 (25 ml) for 1 hr and half the C_6H_6 distilled off to remove traces of moisutre, azeotropically. The residual soln was refluxed with freshly fused $ZnBr_2$ (0·1 g) for 2·5 hr. The cooled soln was washed with water (5 ml × 3). Removal of C_6H_6 and distillation gave a colorless liquid (2·85 g), (b.p. 95–110°/30 mm → 84–86°/2 mm). GLC at 80° (H_2 flow, 50 ml/min) showed the presence of 4 components (~2:3:3:3) with RRT 1, 2·26, 5·73 and 6·43).

p-*Cymene and* XX. The reaction product (2·85 g) of XIII with $ZnBr_2$, was chromatographed on SiO_2–gel (85 g; IIB; 2·9 cm × 24 cm) and gave the following fractions:

Frac 1	Pet. ether (50 ml × 5)	0·289 g
Frac. 2	Pet. ether–C_6H_6 (1:1)	0·603 g

The remaining material was apparently polymerized as it could not be eulted from the column.

Frac. 1 was identified to be essentially *p*-cymene, though traces of *m*-isomer were discernible from its IR spectrum: 1120, 1090, 830 cm^{-1} (*p*-); 1170, 1140, 810–750 cm^{-1} (*m*-).

Frac. 2, b.p. (bath) 90°/2 mm, n_D^{30} 1·4742 was identified as 3-isocaranone RRT 6·43. IR spectrum: C=O 1720 cm^{-1}. PMR spectrum: quaternary methyls (57 c/s, 3H, s; 65 c/s, 3H, s); C$\underline{H}_3$—CH (72 c/s, 3H, d with J = 6 c/s).

Isolation of aldehyde (XVIII). In the above experiment, practically no aldehyde fraction was obtained, apparently because of adverse reaction conditions. In subsequent experiments, the polymerization of the aldehydic component could be minimized by shortening the reaction time and the overall yield could also be raised, e.g. carene epoxide (2 g), $ZnBr_2$ (0·05 g) in C_6H_6 (10 ml) were refluxed for 1 hr to give a product (1·54 g) from which the aldehyde (XVIII) was isolated by IDCC (250 g; IIA; 4·7 cm × 25 cm; solvent C_6H_6). The central band corresponding to the aldehyde only (TLC screening) was worked up to give, after distillation, a colorless liquid (176 mg), b.p. (bath 100–120°/9 mm). Satisfactory analysis could not be obtained owing to rapid deterioration.

Preparation of the methyl ester XVII. The total product (2 g) of reaction of XIII with $ZnBr_2$, was oxidized with Ag_2O (from 2 g of $AgNO_3$ in 8 ml H_2O and 0·825 g NaOH in 8 ml H_2O) in EtOH (15 ml). After 24 hrs at room temp (30°) and the usual work up, the crude acid (723 mg) was isolated and directly converted into methyl ester (CH_2N_2), a colourless liquid (416 mg), b.p (bath) 160°/25 mm; n_D^{20} 1·4549.

Preparation of the alcohol XVI. A soln of the above methyl ester (0·35 g in 5 ml Et_2O) was reduced with LAH (0·093 g in 10 ml Et_2O) by stirring for 1 hr at 0° and 4 hrs at 30°. The usual work-up (Rochelle salt) gave the crude XVI which was distilled to give a colorless liquid (122 mg), b.p. (bath) 110°/2·5 mm, n_D^{20} 1·4742.

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