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# ORGANIC REACTIONS IN A SOLID MATRIX—III*

## SILICA GEL-INDUCED OXIRANE REARRANGEMENTS†

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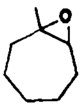
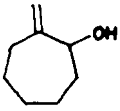
**Abstract**—1-Methyl-1,2-epoxycycloheptane, 2α,3α-epoxypinane and 3α,4α-epoxycarane are shown to undergo typical carbonium ion rearrangements in contact with active silica gel. Humulene epoxide-II and caryophyllene oxide did not undergo any transformation under these conditions. All these results are in complete contrast to their behaviour on exposure to alumina.

IT HAS been demonstrated[1] that methyldialkyl-substituted 1,2-epoxides essentially rearrange to vinylidene, allylic secondary alcohols on contact with active $Al_2O_3$. A minor, but fairly general, side reaction observed was transformation of these oxides to typical carbonium ion rearrangement products. Thus, for example, 1-methyl-1,2-epoxycycloheptane (I), on exposure to active $Al_2O_3$ at room temp furnished a product containing 2-methylene-cycloheptanol (II), 80%) and 1-methyl-cyclohexylmethanol (III, 20%; derived from the corresponding aldehyde). We now find that the carbonium ion rearrangement constitutes the chief pathway open to oxirane ring isomerisation in a silica gel matrix.


I



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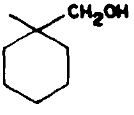
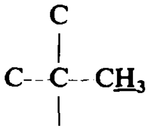
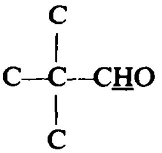


III

1-*Methyl*-1,2-*epoxycycloheptane* (I)[1] on being shaken with active (IIA) silica gel (50 times) in hexane furnished a product (75%), shown by GLC to consist of essentially two components, with relative retention times (RRT) of 1 (75%) and 2·43 (25%), which were separated by preparative GLC. With lesser amounts (25 times) of silica gel, considerable amounts of the starting epoxide remained unchanged.

The major product was readily recognised as the known[2] 1-formyl-1-methylcyclohexane from its spectral characteristics:  $\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C\underline{H}_3}$ (PMR: 3H, s at 58 c/s),  $\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C\underline{H}O}$ (IR: 1710, 2680 $cm^{-1}$; PMR: 1H, s at 560 c/s). Its characterisation

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* Part II: preceding paper.

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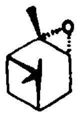
was completed by preparation of its 2,4-DNP, oxidation ($Ag_2O$) to 1-carboxy-1-methylcyclohexane[2a, 3] and, reduction (LAH) to 1-methylcyclohexylmethanol (III).[1, 4]

The other component (RRT, 2·43) was identified (IR, PMR) as 2-methylcycloheptanone.[5]

(+)-2α,3α-*Epoxypinane* (IV)[1], when shaken in hexane solution with silica gel furnished a product, which was shown by GLC to consist of at least six components having RRT's of 1·00, 1·02, 1·47, 1·80, 2·64 and 6·03; the compound of RRT 1 being the starting epoxide. The product distribution was dependent on the activity of silica gel and the silica gel-substrate ratio (Table 1). It may be noted from Table 1 that even with silica gel of activity IVA, very little unchanged epoxide remained, though the yield of GLC component 6 rose sharply at the expense of component 2.



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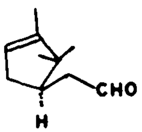

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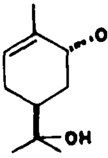
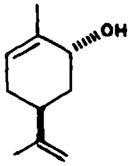


VI



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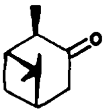


VIII

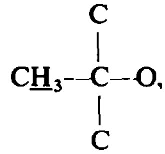
The major product (experiment 1, Table 1), was readily identified (mixed GLC, IR, PMR) as 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde (α-campholene aldehyde: V) by comparison with an authentic specimen obtained[1] by the action of anhydrous $ZnBr_2$ on pinene epoxide according to Arbusow.[7]

TABLE 1. REARRANGEMENT OF 2,3-EPOXYPINANE OVER SILICA GEL

| No. | Activity[a] | Silica gel/substrate ratio | Total recovery (%) | Product composition (% by GLC | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | GLC component No: → increasing RRT[b] | | | | | |
| | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| | | | | IV | V | ? | VIII | VII | VI |
| 1 | IIA | 25 | 67 | 7 | 63 | 12 | 4 | 9 | 5 |
| 2 | IIA | 15 | 67 | 8 | 55 | 13 | 7 | 14 | 3 |
| 3 | IIA | 10 | 55 | 10 | 50 | 9 | 9 | 14 | 6 |
| 4 | IIIA | 25 | 60 | 3 | 42 | 2 | 3 | 20 | 29 |
| 5 | IVA | 25 | 65 | 3 | 40 | 2 | 3 | 16 | 36 |

[a] According to Hernandez[6]

[b] RRT, 1·00, 1·02, 1·47, 1·80, 2·64 and 6·03 respectively under conditions of programming (100–200°; 8°/min); column: 300 cm × 0·5 cm, packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh); gas flow: 70 ml $H_2$/min.

GLC component (5) and (6) were best obtained from experiments using weaker silica gel (Table 1, experiments 4,5). Chromatography furnished GLC component 6 as a crystalline solid, m.p. 155–156°. This product was recognised as *trans*-sobrerol (pinolhydroate: VI)[8] from its spectral characteristics (IR: OH 3280, 920 $cm^{-1}$. PMR in $CDCl_3$: two  $\underline{H}_3C{-}\underset{\textstyle C}{\overset{\textstyle C}{\overset{|}{\underset{|}{C}}}}{-}O$, 3H singlets at 70, 73 c/s; vinylic Me, 3H broad s at 109 c/s; $C\underline{H}OH$, 1H ill-resolved tr at 241 c/s; $-\underset{|}{C}{=}C\underline{H}$, 1H, ill-resolved tr at 336 c/s) and comparison with an authentic sample[9] obtained by the action of $H_2SO_4$aq on pinene epoxide.

GLC component 5 was obtained as a liquid (90% pure) from the above chromatography and in view of its spectral characteristics (IR: OH 3350, 1058 and 1030 $cm^{-1}$; $-\underset{|}{C}{=}CH_2$ 1640 and 890 $cm^{-1}$. PMR: two vinylic Me's, 6H broad s at 104 c/s; $-\overset{|}{\underset{|}{C}}\underline{H}OH$, 1H, m centered at 231 c/s; $-\underset{|}{C}{=}CH_2$, 2H broad s at 279 c/s; $-\underset{|}{C}{=}CH-$, 1H, m centered at 326 c/s) was considered to be *trans*-carveol (VII); IR and PMR spectra of which have been recorded in literature.[10] Identification was completed by its $CrO_3$ oxidation to carvone (PMR).

The two minor components 3 and 4 could not be obtained pure, though GLC component 4 is suspected from its retention time (mixed GLC with authentic sample[11]) to be isopinocamphone (VIII).

(+)-3α,4α-*Epoxycarane* (IX)[1] on exposure to silica gel furnished a product (recovery ~ 60%), the composition of which was dependent on the silica gel-substrate ratio (Table 2). The various components were separated by preparative GLC. GLC component 5 was readily identified (GLC, IR, PMR) as the unchanged epoxide and, understandably its concentration fell to a negligible level with a higher silica gel-substrate ratio. The various products of this reaction have been identified as the hydrocarbons X, XI, XII and *p*-cymene and, the aldehyde XIII.

GLC component 1 (RRT = 1) was recognised from its spectral characteristics ($\lambda_{max}$ 266 mμ, $\varepsilon = 3310$. IR: no OH or C=O; conj. C=C 1630, 1614 and 1550 $cm^{-1}$; gem-dimethyl 1360 and 1380 $cm^{-1}$; PMR: two quaternary $C\underline{H}_3$, 6H, s at 60 c/s; one vinylic $C\underline{H}_3$, 3H, somewhat broad s at 120 c/s; vinylic protons, 2H, m located between 295–310 c/s, and 3H, m located between 344–380 c/s. Mass spectrum: $M^+$, $m/e = 134$; $M\text{-}15^+$, $m/e = 119$, base peak) as 3,7,7-trimethyltropilidene (X)[12], the spectral data agreeing well with that reported in the literature recently.[13]

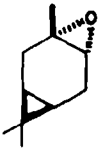
GLC component 2 (RRT = 1·11) was revealed from its PMR spectrum to be a mixture, but the mixture could be readily analysed by close scrutiny of its PMR and mass spectrum. The minor component (~ 20%) of the mixture was identified as 1-methyl-4-isopropenylbenzene (XI) (mass spectrum: $m/e = 132, 127, 91$); signals in the PMR spectrum at 126 c/s (d, $J = 1$ c/s; vinylic $C\underline{H}_3$), 139 c/s (s, $C\underline{H}_3$ on aromatic ring), 297, 313 c/s (s, $-C{=}C\underline{H}_2$) and 429 c/s (quartet, AB type, *p*-disubstituted

TABLE 2. REARRANGEMENT OF 3,4-EPOXYCARANE OVER SILICA GEL[a]

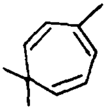
| GLC component | RRT[b] | Structure | % of Total product (by GLC) | |
|---|---|---|---|---|
| | | | silica gel/substrate ratio 25 | 50 |
| 1 | 1·0 | X | 12·0 | 21·6 |
| 2 | 1·11 | XI, XII | 13·0 | 12·1 |
| 3 | 1·47 | p-cymene | 3·9 | 9·4 |
| 4 | 2·39 | XIII | 33·5 | 52·7 |
| 5 | 3·16 | IX | 33·1 | 4·1 |

[a] Activity, IIA; solvent, hexane; temp. ~25–30°

[b] Column 300 cm × 0·8 cm packed with 30% diethyleneglycol polysuccinate on 30–60 mesh Chromosorb W; temp. 135°C; gas flow, 100 ml $H_2$/min.

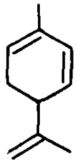


IX

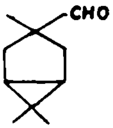


X

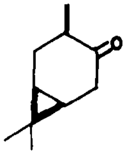
XI



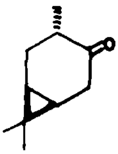
XII



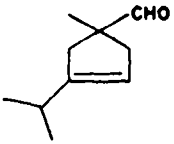
XIII



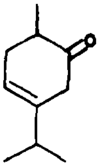
XIV



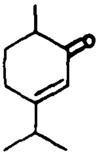
XV



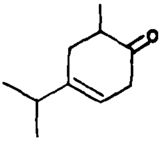
XVI



XVII



XVIII



XIX

benzene) are fully consistent with the PMR spectrum of XI described recently.[14] The major component ($M^+$, $m/e = 134$. IR: $-\underset{|}{C}=CH_2$ 890, 1650 $cm^{-1}$. PMR: two vinylic Me, 6H, broad s at 105 c/s; $-\underset{|}{C}=C\underline{H}_2$, broad s at 288 c/s; three more vinylic protons, m located between 315–350 c/s) is considered to be XII, in view of mechanistic considerations (*vide supra*) and a comparison of the PMR data with that reported[14] recently for XII.

GLC component 3 (RRT = 1·47) was easily recognised (IR, PMR) as *p*-cymene contaminated (IR) with some <5% m-cymene.

The major product of epoxycarane-silica gel reaction (GLC component 4, RRT = 2·39) was found (GLC, IR, PMR) to be the aldehyde XIII, recently described (see below) by us in connection with the rearrangement of epoxycarane on active $Al_2O_3$. The identification was completed by its oxidation ($Ag_2O$) to the corresponding acid and comparison (IR, PMR) of the derived methyl ester with an authentic sample[1].

As already stated the aldehyde XIII was prepared earlier in connection with our work on alumina-induced oxirane rearrangement.[1] The aldehyde was obtained as one of the products from epoxycarane–$ZnBr_2$ rearrangement, a reaction first inconclusively studied by Arbuzov.[13] Since completion of our earlier work,[1] the reaction of epoxycarane with $ZnBr_2$ has been investigated by three other groups of workers[16–18] who corroborate the formation of aldehyde XIII (for stereochemistry, see below). However, there is some confusion regarding the composition of the ketonic products. Having access, now, to a preparative GLC equipment, we have reinvestigated this reaction and the results have been summarised in Table 3. GLC

TABLE 3. REARRANGEMENT OF 3,4-EPOXYCARANE WITH ZINC BROMIDE[a]

| GLC component | RRT[b] | % of total product (GLC) | Remarks | Results of other workers (% yield) | | |
|---|---|---|---|---|---|---|
| | | | | Ref. 16 | Ref. 17[c] | Ref. 18[d] |
| 1 | 0·57 | 3·5 | ? | — | — | — |
| 2 | 0·82 | 3·0 | ? | — | — | — |
| 3 | 1·00 | 13·0 | p-cymene | 14·0 | — | — |
| 4 | 1·74 | 4·0 | aldehyde, XVI | — | — | — |
| 5 | 2·00 | 19·0 | aldehyde, XIII | 20·0 | 20·0 | 25·0 |
| 6 | 2·64 | 10·0 | unchanged oxide. | — | — | — |
| 7 | 4·05 | 9·0 | ketone, XVII | — | — | — |
| 8 | 4·33 | 7·0 | isocaranone XIV | 62·0 | 10·0 | — |
| 9 | 4·71 | 30·5 | caranone, XV | | 50·0 | 75·0 |
| 10 | 6·52 | 1·0 | ? | — | — | — |

[a] In refluxing benzene; reaction conditions comparable to those in Ref. 16 and 18. French workers[17] employ $ZnBr_2$ in dibutyl ether at 60°.

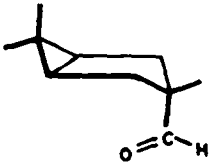
[b] Column: 300 cm × 0·8 cm, packed with 30% diethylene glycol polysuccinate on 30–60 mesh Chromosorb W; temp.: 135°; gas flow: 100 ml $H_2$/min.

[c] Product analysis after removal of hydrocarbons; carvenone (XVIII), to the extent of 20%, was also isolated.

[d] Authors report that from the reaction mixture, these two products could be isolated in a ratio of 1 : 3.

components 3, 5, 8 and 9 were readily identified (GLC, IR, PMR) as *p*-cymene (with some 3–5% m-isomer), bicyclic aldehyde XIII, isocaranone (XIV) and caranone (XV) respectively, as already described[1]. GLC components 4 and 7 have not been reported by earlier workers.[1, 16–18] The component 4 has been characterised as XVI, a product of ring cleavage of cyclopropane in the bicyclic aldehyde XIII; the structure XVI is in complete accord with its spectral characteristics (IR, $\mathrm{CHCl_3}$: $\underset{|}{\mathrm{HC}}{=}\mathrm{O}$ 1710, 2680 $\mathrm{cm^{-1}}$. PMR: 3H, s at 60, 67 and 73 c/s; vinylic H, 1H, tr centered at 310 c/s, $J = 3$ c/s; $\underset{|}{\mathrm{\underline{H}C}}{=}\mathrm{O}$, 1H, s at 563 c/s). The GLC component 7, a ketone (IR: C=O 1710 $\mathrm{cm^{-1}}$), shows in its PMR spectrum signals assignable to: $-\underset{|}{\mathrm{HC}}-\mathrm{C\underline{H}_3}$ (doublet centered at 66 c/s, $J = 7{\cdot}5$ c/s), $-\underset{|}{\mathrm{HC}}\ \mathrm{(C\underline{H}_3)_2}$ (6H, d centered at 62·5 c/s, $J = 7$ c/s), $-\underset{|}{\mathrm{C}}{=}\mathrm{CH}-$ (1H, m centered at 333 c/s); a 2H signal at 170 c/s (essentially a broad s with a minor shoulder) is attributed to the grouping $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{C\underline{H}_2}-\mathrm{C}{=}\mathrm{C}-$.* These structural features, considered along with its genesis from epoxycarane, dictate structure XVII for this compound; the only other alternative, XIX, stands clearly ruled out by the observed multiplicity of the $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{C\underline{H}_2}-\mathrm{C}{=}\mathrm{C}-$ signal.

Based on the fact that the two geminal-methyls in the bicyclic aldehyde XIII (and the corresponding acid Me ester) have the same chemical shift, we have earlier[1] assigned the stereochemistry XX to this aldehyde, as in the alternate configuration XXI, one (*endo*) of the geminal-methyls must be influenced by the anisotropy of the carbonyl group. On the other hand. Teisseire *et al.*[17] prefer the latter stereochemistry (XXI) apparently on mechanistic considerations, assuming the rearrangement to be concerted. However, it must be pointed out that if a concerted mechanism is conceded, the derivation of stereochemistry XXI by Teisseire *et al.*[17] is in error, as the product from 3α,4α-epoxycaranae (XXII) should be XX and not XXI.



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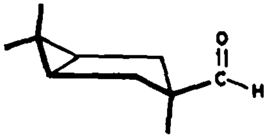
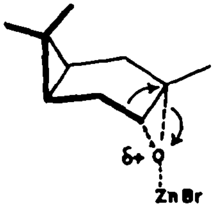


XXI



XXII

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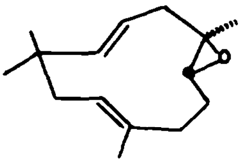
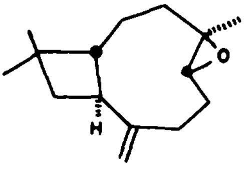
* e.g. this unit occurs in some pseudoguaianolides, which display this methylene resonance at ~ 2·85 ppm.[19]

This again would suggest stereochemistry XX for the bicyclic aldehyde.

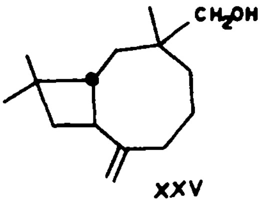
*Humulene epoxide*-II (XXIII)[20] *and* (−)-*caryophyllene oxide* (XXIV).[21] Both of these compounds remained essentially unchanged on exposure (52 hrs) to active silica gel (silica gel/substrate ratios: 25 and 50) in hexane at ~25–30°.



XXIII



XXIV



XXV

## DISCUSSION

Silica gel[22] is considered to be an acidic[23] catalyst; however, not much information is available as to the nature of the acidic sites, though considerable data on the acidic sites of silica-alumina are available.[24] Most of the reactions described above are typical reactions of these epoxides when in contact with suitable Lewis acids. Thus, in these reactions[*] active silica gel behaves as a *matrix* with electron acceptor sites, and this concept suffices to rationalise the products observed. For example, products from exposure of 2α,3α-epoxycarane (IX) to active silica gel can be rationalised as shown in Fig 1. With silica gel of lesser activity (more "hydrated" sites) more and more acidic centres tend to acquire protonic acid character and this will explain the shift towards sobrerol (VI) and carveol (VII) at the expense of α-campholene aldehyde (V), when epoxypinane is treated with silica gel of lower activity (Table 1).

It was rather surprising to see the essential inertness of humulene epoxide-II and caryophyllene epoxide towards active silica gel. One side reaction observed[32] with caryophyllene epoxide on exposure to active $Al_2O_3$, is the formation of ring-contracted alcohol XXV, a typical carbonium ion rearrangement product (after a subsequent Cannizzaro reaction)[1] and this was expected to be the major reaction on silica gel. The inertness of these oxides to silica gel may have origin in their absorption on silica gel in a conformation unsuitable, from stereoelectronic factors, for rearrangement.

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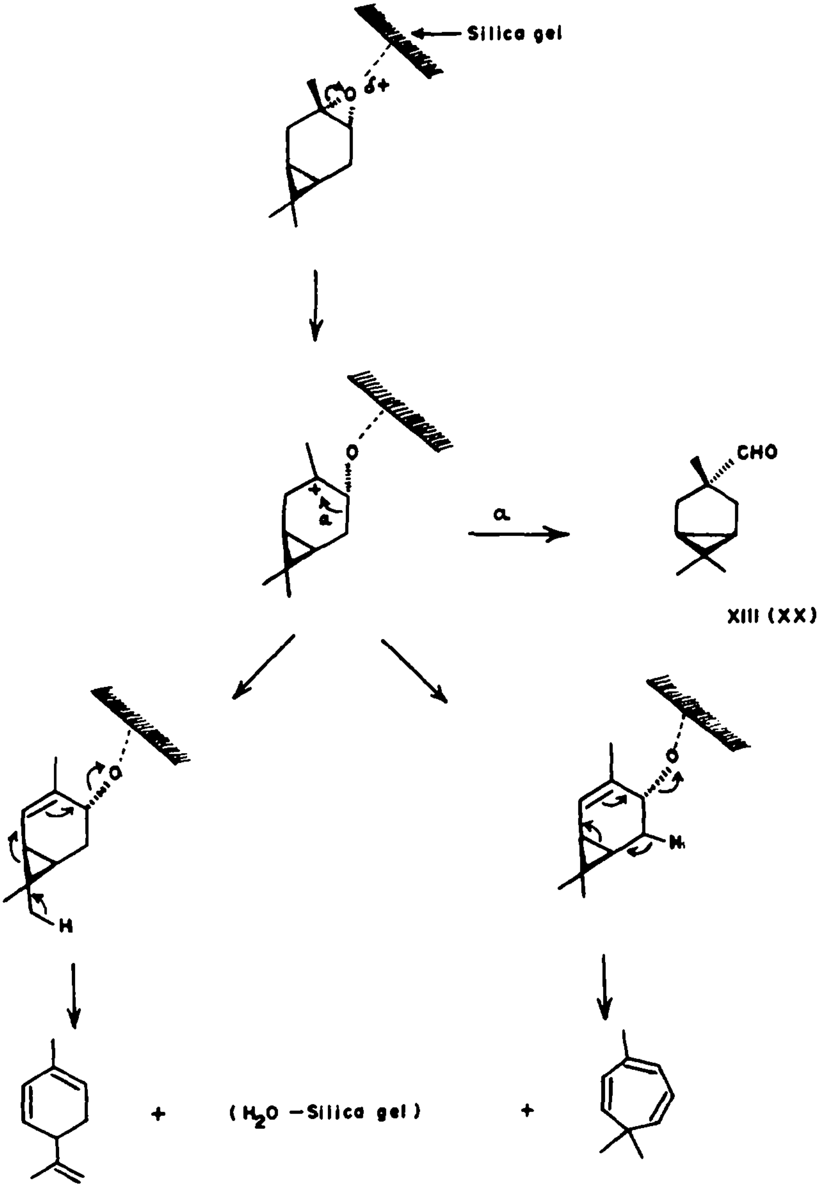
[*] There does not appear to be any record of similar epoxide-silica gel reactions earlier, though a number of secondary reactions caused by silica gel during chromatography have been noted and, these include: shifting of ethylenic linkages[25, 26] cleavage of cyclopropanes,[27] elimination-rearrangement,[28] and isomerization of enol acetate epoxides[29, 30] and anhydrosugars.[31]



XIII (XX)

XII

X

Fig. 1

## EXPERIMENTAL

For general remarks see Part II of this series.

*Silica gel.* Commercial chromatography grade silica gel (−100, +200 mesh) was slurried with hot, distilled water and washed repeatedly by decantation till essentially neutral (pH ~ 7), filtered, washed with distilled water, then liberally with EtOH, air dried and finally activated at 125–130° to activity I-IIA[6] (~7 hr).

*Standard procedure for reaction with silica gel.* The epoxide is added to a slurry of silica gel suspended in hexane (45 ml for every 25 g of silica gel) in a suitable, stoppered flask, flushed with $N_2$, and shaken mechanically for 6 hr and then kept aside for another 18 hr. The hexane is filtered and the silica gel washed with 5% MeOH in $Et_2O$ (800 ml for 1 g of epoxide; added in several portions). The combined solvent filtrates are carefully fractionated to remove solvent and the residue distilled *in vacuo*.

*Action of silica gel on 1-methyl-1,2-epoxycycloheptane.* The epoxide[1] (2·0 g) was treated with silica gel (100 g) in hexane according to the standard procedure to afford a liquid (1·5 g, b.p. 90–92°/40 mm), showing two major components, with RRT's of 1 (75%) and 2·43 (25%) on GLC (column: 300 cm × 0·5 cm, packed with 20% diethylene glycol polysuccinate on chromosorb W of 60–80 mesh; temp: 110°; gas flow: 70 ml $H_2$/min). The two components were separated by preparative GLC.

*1-Formyl-1-methylcyclohexane.* The major product (RRT = 1) had b.p. 80° (bath)/26 mm, $n_D^{25}$ 1·4465. (Lit.[2a] b.p. 120°/546 mm, $n_D^{21}$ 1·4490). (Found: C, 76·47; H, 11·33. Calcd. for $C_8H_{14}O$: C, 76·17; H, 11·18%). *2,4-Dinitrophenylhydrazone* ($H_2SO_4$ method), yellow needles, from EtOH, m.p. 156–157° (Lit.[2a] m.p. 154–155°). (Found: C, 55·34; H, 6·04. Calcd. for $C_{14}H_{18}O_4N_4$: C, 54·91; H, 5·89%).

The aldehyde (0·4 g) in EtOH (5 ml) was added to a slurry obtained by mixing 0·36 g $AgNO_3$ in 1·6 ml $H_2O$ with NaOHaq (0·17 g in 1·6 ml $H_2O$). The reaction mixture was left aside at room temp for 24 hr, then worked up in the usual manner to an acid (300 mg), which was esterified ($CH_2N_2$) to give methyl ester (180 mg), b.p. 90° (bath)/36 mm; IR: C═O 1740 cm$^{-1}$; PMR: $\underline{Me}—\overset{|}{\underset{|}{C}}—COOMe$, 3H, s at 68 c/s; $COO\underline{Me}$, 3H, s at 218 c/s.

*2-Methylcycloheptanone.* The minor product (RRT = 2·43) had b.p. 120° (bath)/26 mm, $n_D^{25}$ 1·4565; IR: C═O 1700 cm$^{-1}$; PMR: $C\underline{H}_2—\underset{|}{C}H—$, 3H, d centered at 64 c/s, $J$ = 7 c/s. 2,4-Dinitrophenylhydrazone ($H_2SO_4$ method), yellow needles (EtOH) m.p. 123–124° (Lit.[5b] m.p. 119–121°).

*Action of silica gel on 2α,3α-epoxypinane* (IV)

(a) *Silica gel of activity* I-IIA. α-Pinene epoxide[1] (1·0 g) was exposed to silica gel (25 g) suspended in hexane under the standard conditions. The crude product, after solvent removal, was distilled, b.p. 93–102°/25 mm, yield 0·66 g. This product (GLC, Table 1) displayed its PMR and IR spectra essentially similar to that of pure α-campholene aldehyde (V) (*vide infra*).

(b) *Silica gel of activity* IIIA. α-Pinene epoxide (4·4 g) was treated with silica gel (110 g) in hexane under the usual conditions. The crude product (3·0 g) slowly crystallised out and, in one experiment, the solid was collected by filtration, recrystallised from acetone to furnish white plates, m.p. 155–156° and identified as (+)-trans-sobrerol (*vide infra*).

In order to separate the various products of reaction, the total crude product (3·0 g) was subjected to inverted-dry-column-chromatography[33] (IDCC) on silica gel (250 g, grade IIA; 3·3 cm × 35 cm; solvent: 74 parts$C_6H_6$, 25·5 parts EtOAc and 0·5 part EtOH) and each fraction screened by GLC (for conditions see footnote to Table 1):

| | | |
|---|---|---|
| Fraction 1 | 0·6 g | lowermost band (0–2·5 cm from origin), GLC component 6 |
| Fraction 2 | 0·19 g | next band (2·5–3 cm), essentially GLC component 6 |
| Fraction 3 | 0·11 g | next band (3–6 cm), rejected |
| Fraction 4 | 0·44 g | next band (17–21 cm), essentially GLC component 5 |
| Fraction 5 | 0·14 g | next band (21–22·5 cm), mix of GLC components 5 and 3 |
| Fraction 6 | 0·81 g | uppermost band (22·5–31 cm), essentially GLC component (3) |

Fraction 1 was recrystallised from acetone to give white plates of (+)-*trans-sobrerol* (VI), m.p. 155–156°, $[\alpha]_D$ +147·1 (EtOH, *c* 2·2%) (Lit.[8] m.p. 150° $[\alpha]_D$ + 150°).

Fraction 4 was redistilled to give trans-*carveol* (VII) b.p. 90° (bath) 3 mm, $[\alpha]_D$ +62·5 (Lit.,[10a] b.p. 80–80·5°/4 mm, $[\alpha]_D^{20}$ +217·1). The product (96 mg) in ether (1 ml) was oxidised with $Na_2Cr_2O_7$aq (70 mg in 0·35 ml $H_2O$ and 0·05 ml $H_2SO_4$) for ~ 3 hr at room temp (25–30°) to give a product (66 mg) identified as carvone by PMR (Lit.[34]: PMR).

Fraction 6 was distilled to give *α-campholene aldehyde* (V)[7], b.p. 105–107°/30 mm; IR: $\mathrm{HC{=}O}$ 2705, 1730 $cm^{-1}$; PMR: two quaternary Me's, 47 and 60 c/s; one vinylic Me, 3H, broad s at 98 c/s; one olefinic proton, 1H, broad s at 313 c/s; $\mathrm{\underline{H}C{=}O}$, 1H, tr at 584 c/s (Lit.[7b]: PMR).

*Action of silica gel on* 3α,4α-*epoxycarane* (IX)

The epoxide[1] (5·2 g) was treated with silica gel (260 g) in hexane according to the standard procedure to yield a liquid (3·1 g, b.p. 80–110°/30 mm) showing five components on GLC (Table 2). Preparative GLC afforded these components.

GLC component 1 (Table 2) was distilled to give X, b.p. 95° (bath)/25 mm (Lit.[12] b.p. 62°/20 mm).

GLC component 2 (mixture of XI and XII) had b.p. 95° (bath)/25 mm. GLC component 3 (IR: 1120, 1090, 830 $cm^{-1}$) was recognised as essentially *p*-cymene.

The major product (GLC component 4, Table 2) was distilled to give XIII, b.p. 110° (bath)/40 mm, $n_D^{25}$ 1·4722 (Lit.[16] b.p. 70–72°/9 mm, $n_D^{20}$ 1·4644); IR: $\mathrm{HC{=}O}$ 2700, 1730 $cm^{-1}$; PMR: three quaternary Me's (9H, s at 60 c/s), $\mathrm{\underline{H}C{=}O}$ (1H, s at 575 c/s). (Found: C, 78·98; H, 10·81. Calcd. for $C_{10}H_{16}O$ C, 78·94; H, 10·52%).

3,6,6-*Trimethyl*-3-*carbomethoxy-bicyclo*[3.1.0]*hexane*. The above aldehyde (0·20 g) in EtOH (2·5 ml) was oxidised with a $Ag_2O$ slurry obtained by mixing 0·18 g $AgNO_3$ (in 0·8 ml $H_2O$) with NaOH aq (90 mg in 0·8 ml $H_2O$), as described earlier, to furnish an acid (150 mg) which was esterified ($CH_2N_2$) to yield its Me ester (125 mg): b.p. 160° (bath)/25 mm, $n_D^{20}$ 1·4549; IR: $\mathrm{C{=}O}$ 1724 $cm^{-1}$; PMR: quaternary Me's at 59, 59 and 69 c/s; $\mathrm{O\underline{Me}}$ (3H, s at 220 c/s). (Found: C, 71·94; H, 9·99. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%).

*Action of* $ZnBr_2$ *on* 3α,4α-*epoxycarane* (IX)

Freshly distilled epoxide (5·0 g) in $C_6H_6$ (25 ml) was refluxed and half of the solvent was distilled off to remove traces of moisture. To the remaining soln $ZnBr_2$ (0·1 g) was added and the reaction mixture refluxed for 1 hr. The reaction mixture was cooled, washed with water (5 ml × 3), dried and stripped off the solvent to yield, after distillation, a colourless liquid (3·33 g), b.p. 90–125°/40 mm (GLC, Table 3). The various components were separated by preparative GLC. Some relevant data is given below:

Aldehyde XVI, b.p. 110° (bath)/40 mm.

Isocaranone (XIV): b.p. 140° (bath)/40 mm, $n_D^{25}$ 1·4685 IR: $\mathrm{C{=}O}$ 1720 $cm^{-1}$; PMR: two quaternary Me's at 51·5 and 63 c/s; $\mathrm{C\underline{H}_3{-}CH}$ (3H, d centred at 55 c/s, $J$ = 6 c/s).

Caranone (XV): b.p. 140° (bath)/40 mm, $n_D^{25}$ 1·4690. IR: $\mathrm{C{=}O}$ 1720 $cm^{-1}$; PMR: two quaternary Me's at 57 and 65 c/s; $\mathrm{C\underline{H}_3{-}CH}$ (3H, d centered at 72 c/s, $J$ = 6 c/s).

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