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CYCLISATION OF OPTICALLY ACTIVE DIHYDROMYRCENES (2,6-DIMETHYL-2,7-OCTADIENE)

A STEREOSPECIFIC RING CONTRACTION

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Abstract—The isomeric (+) and (−)-dihydromyrcene cyclise in organic acids through a stereospecific ring contraction process to give the esters of α-(*S*)-(+)-1-(α-hydroxyethyl)-3,3-dimethylcyclohexane and α-(*R*)-(−)-1-(α-hydroxyethyl)-3,3-dimethylcyclohexane respectively. Small amounts of enantiomeric *cis*- and *trans*-tetrahydroeucarvyl esters are also formed. The absolute configuration of the chiral carbinol centres has been determined using Horeau's method. Also, the synthesis of both optical isomers of 3,3-dimethylcyclohexanol has been achieved for the first time.

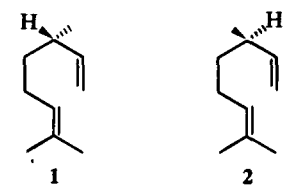
INTRODUCTION

Previously we described the preparation of the optically active ester (4) and its enantiomer from the (+) and (−)-dihydromyrcene.[1] The ring contraction during the cyclisation of the isomeric olefins by treatment with acetic acid containing a catalytic amount of mineral acids or with formic acid without a catalyst generated interest because of its stereospecific nature. It was of interest to determine the stereochemistry and configuration of the chiral centres involved. While this work was in progress, Hall and Lala[2] reported the cyclisation of the above diene, but without dealing with the stereochemistry and the optical isomerism of the reaction products isolated. This prompts us now to report our own findings on this reaction.

RESULTS

Both (+) and (−)-dihydromyrcenes (1 and 2) are readily obtainable from the corresponding α- and β-pinenes.[3] Treatment of (+)-dihydromyrcene with acetic acid containing a catalytic amount of sulphuric acid at room temperature did not effect cyclisation and the product was mainly the known acyclic acetate (3). However, when refluxed for 6–8 hr, the acyclic acetate disappeared and instead three optically active saturated cyclic acetates (4, 6 and 8) were obtained in a ratio of 80:16:4 respectively. The corresponding alcohols (5, 7 and 9) formed on hydrolysis were isolated by preparative GLC (20% carbowax 20 M on celite or 10% Apiezon L columns, 9′ × 0·25″ at 150°) and the structures as shown were assigned on the basis of chemical and spectroscopic evidence.

The alcohol α-(*S*)-(+)-1-(α-hydroxyethyl)-3,3-dimethylcyclohexane (5; R=H), α_D^{20} + 12·1 (neat liquid) showed the gem-dimethyl group as two singlets centred at δ 0·91 and δ 0·98 (3H,3H), a doublet at δ 1·19 (J = 6·0 Hz) due to the side chain Me group, one OH proton at δ 3·74 and a quintet at δ 3·42 (J = 6·0 Hz) resulting from equal coupling of the α-carbinol proton with four adjacent protons.



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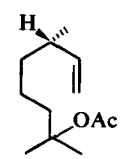

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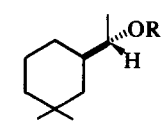

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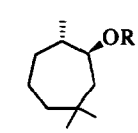

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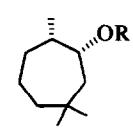

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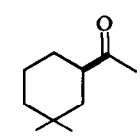

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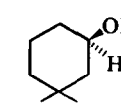
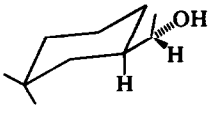


11: R = Ac
12: R = H

The α-carbinol centre of 5 was assigned (*S*) configuration on the basis of the mechanism of its formation and finally confirmed by the application of Horeau's method.[4] The alcohol was esterified with (±)-α-phenylbutyric anhydride and the unchanged α-phenylbutyric acid isolated was found to be laevorotatory, thus establishing (*S*) configuration for the alcohol. In order to determine the stereochemistry at C-1 of the cyclohexane ring bearing the side chain, the alcohol (5) was oxidised with chromic acid to (+)-1-acetyl-3,3-dimethylcyclohexane (10) which when subjected to Baeyer-Villiger reaction with peracetic acid generated (+)-3,3-dimethylcyclohexyl acetate (11).[5] The reaction of peracids with ketones is well known for its stereospecific nature and was expected to

give the product with the retention of configuration. The acetate was hydrolysed to (−)-3,3-trimethylcyclohexanol (12) of high optical purity.[6] Horeau's method for the determination of configuration showed a low stereospecificity with this alcohol and the optical yield was almost nil. However, its NMR spectrum showed the α-carbinol proton coupled to two axial and two equatorial protons at δ 3·62 (m, Jaa 10·6 Hz and Jae 4·2 Hz) thus confirming the equatorial conformation for the OH group.[7] This is further borne out by the examination of Drieding models of both alcohol (5) and ketone (10), which indicate the chair form with the equatorial side chain being the most stable conformation. It is also interesting to note that the NMR study of the 1,3 syn-axial interaction in 3,3-dimethylhalocyclohexanes by Bailey *et al.* indicated the presence of unobservably small amount of axial conformer, thus suggesting substantially larger syn-axial interaction making axial conformation unfavourable.[8]



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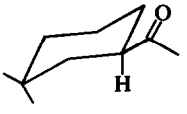

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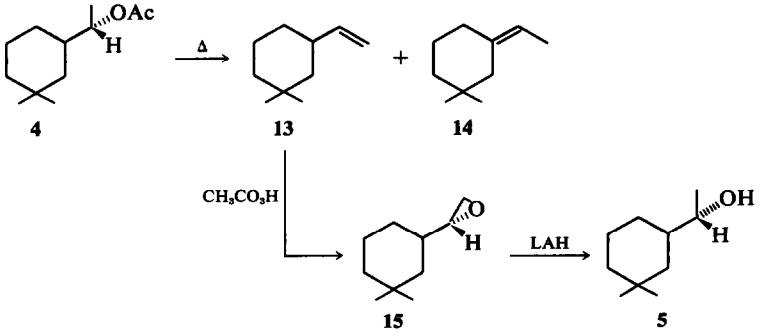
The ketone (10) underwent a highly stereoselective LAH reduction to generate the original alcohol (5). According to Cram's rule[9] which states that the reduction with a reagent such as LAH of a CO function adjacent to an asymmetric C atom leads to the predominant formation of the diastereoisomer obtained by the attack of metal hydride from the side of the smallest group (1-hydrogen in this case). Thus the preponderance of one isomer is to be expected but, surprisingly, in this case the other diastereoisomer could not be detected even by analysing the reduction product on several high efficiency GLC columns.

The alcohol 5 was also obtained by a stereospecific synthesis. The acetate 4 was pyrolysed at 500° to (+)-3,3-dimethyl-1-vinylcyclohexane (13) contaminated with the isomeric 1-ethylidene-3,3-dimethylcyclohexane (14). The former which showed the characteristic vinyl band at 912^{cm-1} in its IR spectrum and molecular weight 138 from its mass spectrum, was epoxidised with peracetic acid to give 1-(3,3-dimethylcyclohexyl)-1,2-epoxyethane (15). The LAH reduction of the epoxide gave mainly the dextrorotatory alcohol (5) with superimposable IR spectrum with the product derived from the original cyclisation of (+)-dihydromyrcene. Based on the established configuration of the alcohol, one can derive the configuration of the epoxide as shown in the scheme below.

The by-product alcohols (7 and 9) of the original cyclisation of (+)-dihydromyrcene were found to be (+)-*trans* and (+)-*cis*-tetrahydroeucarvols respectively. The structures were established by comparing the IR, NMR, mass spectrum and relative retention time on GLC with authentic samples of (±)-*trans*-and *cis*-tetrahydroeucarvols prepared from eucarvone. This ketone was reduced with sodium in ethanol to a 90 : 10 mixture of *trans*- and *cis*-α,β-dihydroeucarvols (16 and 17). This result is consistent with the findings of other workers on Na/EtOH reduction of several monocyclic α,β-unsaturated terpenoid ketones yielding predominantly the thermodynamically more stable *trans*-isomer.[10] Further hydrogenation of the dihydroeucarvol mixture, followed by preparative GLC gave *trans*-tetrahydroeucarvol (7). For practical purposes the *cis*-isomer was obtained by LAH reduction of tetrahydroeucarvone (18)[2] which gave *trans*- and *cis*-isomers in a ratio of 30 : 70. The NMR and IR spectra of the two isomers were consistent with the assigned structures (Experimental).

Cyclisation of (−)-dihydromyrcene (2) under the conditions applied to the enantiomeric diene led to the formation of active esters which on hydrolysis gave α-(*R*)-(−)-(α-hydroxyethyl)-3,3-dimethyl cyclohexane (19), (−)-*trans*-tetrahydroeucarvol (20) and (−)-*cis*-tetrahydroeucarvol (21). The configuration of the carbinol centre in 19 was established by following the sequence of reactions applied to the (+)-isomer.



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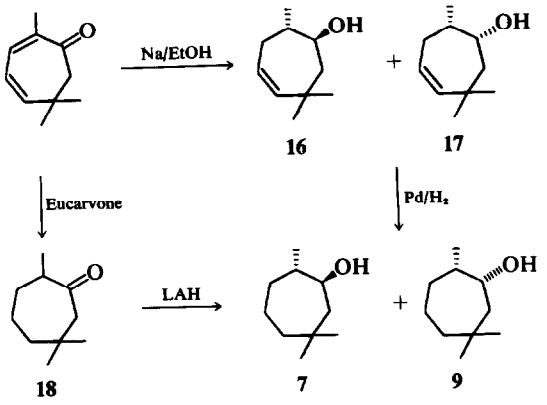
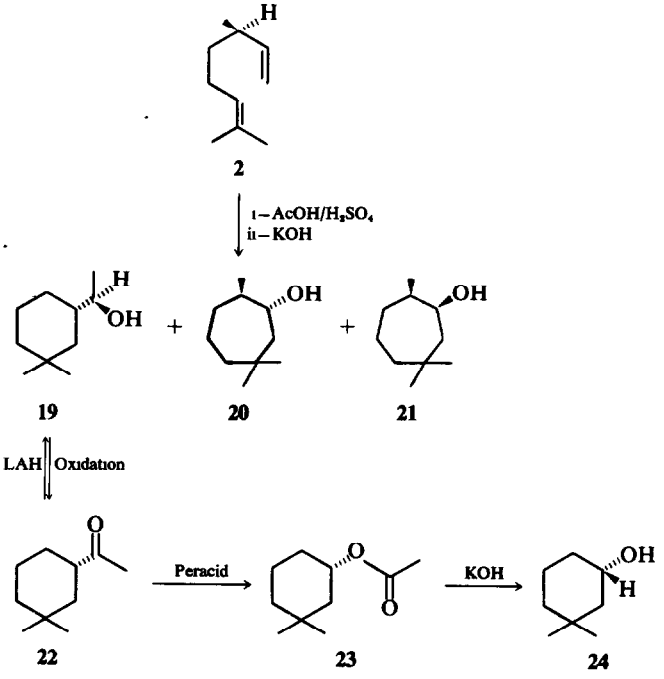


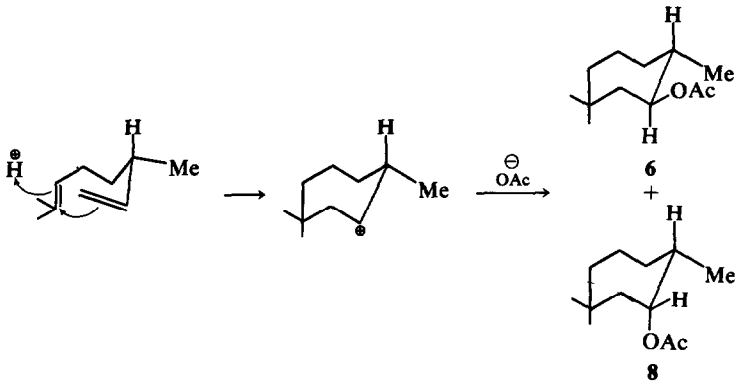
is finally attacked by the acetoxy anion to give mainly the thermodynamically more stable and sterically more favoured *trans*-ester (equatorial).

However, a similar mechanism where an intermediate cycloheptyl carbonium ion is postulated cannot account for the formation of optically active cyclohexane derivatives configurationally pure at both asymmetric centres. It was tempting to suggest that the first formed *trans*- and *cis*-tetrahydroeucarvol esters could be the precursors of the ring contraction product. The solvolysis of the cycloheptyl acetate or the formate in the given organic acid could be concerted with the breaking of the 6,7-bond to form the cyclohexane derivative with the retention of configuration. And indeed

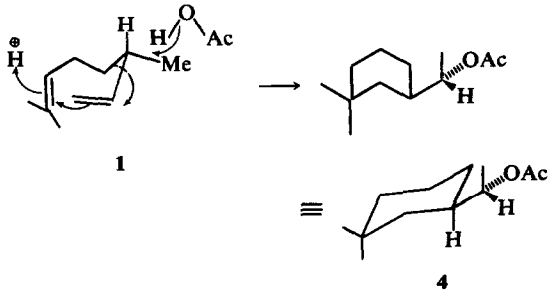


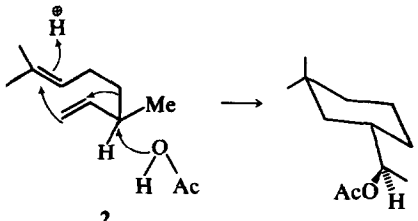
DISCUSSION

The cyclisation of acyclic terpenoids involves the initial protonation of 2,3-double bond followed by a concerted or non-concerted attack by other double bonds suitably situated. This process is well documented for the 2,6-dienes resulting in six membered ring compounds.[11] Therefore, the cyclisation of (+) and (−)-dihydromyrcenes (2,7-dienes) was expected to furnish cycloheptyl derivatives. However, the cyclisation gave these only as a by-product, the main reaction product being a ring contraction compound formed via a stereospecific process. The formation of *trans*- and *cis*-tetrahydroeucarvyl esters can be explained by postulating an initial protonation of the 2,3-double bond followed by the ring closure involving the 7,8-double bond to generate the carbonium ion which such a concerted process can be postulated for the *trans*-tetrahydroeucarvyl ester where the geometry of the molecule is just right as the 6,7-bond electrons are antiperiplanar to the leaving ester function. However, such a concerted process cannot be considered for the *cis*-tetrahydroeucarvyl ester where the geometry is unfavourable. This ester can only undergo the ring contraction reaction via a carbonium ion and hence the formation of a racemate at the C-1 centre of the cyclohexane ring. But the evidence we have gathered so far indicates a high degree of optical purity at this centre. Another argument against this mechanism is the fact that the independently synthesised *trans*- and *cis*-tetrahydroeucarvyl acetate mixture (90:10) isomerised to the cyclohexane ester extremely slowly (30% in 24 hr), whereas dihydromyrcenes



cyclise and rearrange smoothly in 5–6 hr under these conditions. A kinetic run also indicated that the ratio of the cyclohexane and the cycloheptane esters remained constant throughout the reaction. Therefore, in order to explain these results a completely concerted process initiated by the protonation of the 2,3-double bond of dihydromyrcene should be postulated in which the (+)-diene arranges itself in a quasi-chair form (of an incipient cycloheptane) during the transition state with the 6-Me group tending to acquire the more desirable quasi-equatorial position as depicted in Scheme 2. This conformation places the electrons of C(-5)-C(-6) bond of the olefin in a favourable position to attack the developing positive charge at C-7. Rearward attack of acetic acid at C-6 synchronous with the breaking of the C(-5)-C(-6) bond should afford the *S*-(+)-acetate with the retention of configuration. The (−)-dihydromyrcene is expected to acquire inverted quasi-chair form in order to avoid strong 1,4 interaction between the 6-Me and the gem-dimethyl function during the transition state. This further provides the ideal geometry for the molecule to undergo the ring contraction reaction in addition to offering a more stable equatorial conformation to the bulky side chain. Such a mechanism indicates (*R*)-configuration at the carbinol centre of the (−)-acetate. The assigned configurations were finally confirmed by the application of Horeau's method. Certain features of this mechanism are consistent with the observations of Cocker *et al.* on the concerted ring contraction reaction during the deamination of ceran-4-amine.[12]





EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 457 grating infra red spectrophotometer, NMR spectra were recorded on a Varian HA-1000 NMR spectrometer; the values are given in units downfield from TMS as internal standard. Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer, GLC analyses were performed on a Pye Unicam model 104 gas chromatograph. B.ps are uncorrected.

Cyclisation of (+)-dihydromyrcene (1)

(a) A mixture of dihydromyrcene (138 g) AcOH (360 g) and conc H_2SO_4 (25 g) was refluxed for 12 hr. Thereafter NaOAc (50 g) was added and excess AcOH was removed under reduced pressure. The crude product was washed with water, dried (Na_2SO_4) and distilled to yield the cyclic acetate mixture boiling in a range of 60–65° at 1 mm. Efficient fractionation gave (+)-acetate with the following properties: $\alpha_D^{20} + 10{\cdot}37$, n_D^{20} 1·4478; IR (neat liquid) 1735 (C=O), 1245 (—O—), 1071, 1038, 972 and 949$^{cm^{-1}}$ (Skeletal bands); NMR (CCl_4), δ 0·875 and 0·90 (2 s's, gem-dimethyl) δ 1·14 (d, $\underline{CH_3}CHOAc$, $J = 6$ Hz) δ 2·02 (s, acetate Me), δ 4·68 (qu, side chain methine $J = 6{\cdot}0$ Hz); mass spectrum: *m/e* 198. (Molecular ion).

(b) (+)-Dihydromyrcene (138 g) and 98% formic acid (184 g) were stirred at 90° for 6 hr. The reaction mixture was poured into water and extracted with benzene. Removal of the solvent followed by fractional distillation of the crude product gave the formate mixture: b.p. 55° at 1 mm, n_D^{20} 1·4520, $\alpha_D^{20} - 1{\cdot}94$ (neat liquid).

The acetate mixture prepared as in (a) was hydrolysed by refluxing with 2N ethanolic KOH (300 ml) for 2 hr. The mixture was poured into water and extracted with ether, dried (Na_2SO_4) and distilled to give a mixture of alcohols 5, 7 and 9 (70 g) in a ratio of 80:16:4. The hydrolysis of the formate also led to the same mixture of alcohols. The individual alcohols were obtained by preparative GLC (9′ × 0·25″, 20% Carbowax 20 M on celite at 180°).

The alcohols had the following properties:

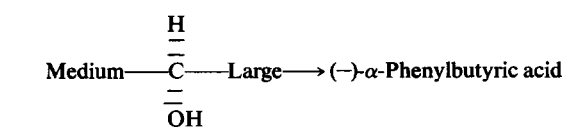
α-(S)-(+)-1-(*α-Hydroxyethyl*)-3,3-*dimethylcyclohexane* (**5**), α_D^{20} + 12·1 (neat liquid; IR bands at 3350 (OH), 1070 (C—O), 1381, and 1364^{cm-1} (gem-dimethyl); NMR (CCl_4) δ 0·91 and 0·98 (2 s's, gem-dimethyl), δ 1·19 (d, $\underline{CH_3}$CHROH), δ 3·42 (qu, α-carbinol proton), δ 3·74 (s, OH proton); mass spectrum, *m/e* 156 (molecular ion), base peak *m/e* 69.

(+)-trans-*Tetrahydroeucarvol* (**7**) *ca* 90% pure. α_D^{20} + 4·2 (*c* 15·5 in MeOH); IR bands at 3330 (OH), 1020 (C—O) 1385 and 1364 (gem-dimethyl), important skeletal bands distinguishing it from the *cis*-isomer: 1260, 1180, 1145, 955, 890 and 870^{cm-1}; NMR (CCl_4) δ 0·90 and 0·94 (s's, gem-dimethyl), δ 0·98 (d, *J* 2·4 Hz, 2-Me), δ 1·73 (s, OH proton) and 3·22 (m, α-carbinol proton); mass spectrum, *m/e* 156 (molecular ion).

(+)-cis-*Tetrahydroeucarvol* (**9**). α_D^{20} + 18·4 (*c* 14·4 in MeOH), IR bands at 3330 (OH), 1382 and 1362 (gem-dimethyl), important skeletal bands distinguishing it from the *trans*-isomer: 1325, 1185, 1170, 1155, 1090, and 880 cm^{-1}; NMR (CCl_4) δ 0·94 (s, gem-dimethyl), δ 0·88 (d, *J* 3·2 Hz, 2-Me), δ 1·70 (s, OH proton) and δ 3·78 (m, α-carbinol proton; mass spectrum *m/e* 156 (molecular ion).

Application of Horeau's method for the determination of configuration of alcohols (**5** *and* **19**)

The method applied was essentially the one by Cocker and co-workers in their work on the configuration of Caranols.[12] To a soln of 100 mg of **5** in 5 g pyridine was added racemic α-phenylbutyric anhydride (600 mg) and left overnight at room temp, water (2 ml) was added and and the mixture was warmed on stream bath for 30 min. The mixture was washed into a flask with a little water and titrated with 0·05 N-NaOH to measure the extent of reaction. An excess (5 ml) NaOH was added and the mixture extracted twice with benzene to remove the ester and the unchanged alcohol. The aqueous soln was acidified (IN HCl) and extracted with benzene. The benzene extract was dried (Na_2SO_4) and the solvent evaporated to constant weight. The α-phenylbutyric acid thus obtained was dissolved in benzene (5 ml) and the optical rotation was measured to indicate the presence of 1-α-phenylbutyric acid and hence (*S*)-configuration at the carbinol centre according to the scheme given below:-



The esterification of (−)-alcohol (**19**) gave (+)-α-phenylbutyric acid and hence (*R*)-configuration for the alcohol.

Oxidation of **5** *to* (+)-1-*acetyl*-3,3-*dimethylcyclohexane* (**10**)

To a soln of 15·6 g of **5** in gl AcOH (25 ml) was added a soln of sodium dichromate (15 g) in AcOH (50 ml) with cooling and left overnight at room temp. The mixture was poured into water and extracted with ether. The ether extract was washed twice with water and then with dil Na_2CO_3 aq. The solvent was evaporated and the oil was distilled to give 12 g of **10**: α_D^{20} + 5·34 (neat liquid); IR bands at 1702 (C=O), 1386, 1367 (gem-dimethyl), 1190, 1169, 972 and 848 cm^{-1} (skeletal); NMR (CCl_4) δ 0·92 and 0·94 (2 s's, gem-dimethyl), δ 2·2 (s, $\underline{CH_3}$C=O), δ 2·4 (>$\underline{CH}$—COMe); mass spectrum, *m/e* 154 (molecular ion.

Preparation of (+)-3,3-*dimethylcyclohexyl acetate* (**11**)

A soln of 15·4 g of **10** in chloroform (100 ml) was treated with commercially available 36% soln of peracetic acid (30 ml) buffered with NaOAc and left overnight at room temp. The mixture was poured into water and extracted with ether. The ethereal soln was washed several times with dil Na_2CO_3 aq, dried (Na_2SO_4) and distilled to yield **11**: b.p. 69° at 3·5 mm, lit. b.p. 196–98° at 750 mm; α_D^{22} + 9·6 (neat liquid); IR bands at 1720 (C=O), 1240 (C—O), 1850 and 1030 cm^{-1}; NMR (CCl_4) δ 0·96 (s, gem-dimethyl, 3H,3H), δ 1·92 (s, $\underline{CH_3}$COO—), and a m at δ 4·86 (C-1 proton, Jaa = 10·5 Hz, Jae = 4·2 Hz).

Hydrolysis of acetate (**11**) *to* (−)-3,3-*dimethylcyclohexanol* (**12**)

The acetate (19·8 g) was refluxed with KOH (7 g) dissolved in EtOH (50 ml) for 3 hr. The mixture was poured into water and extracted with ether, dried (Na_2SO_4) and distilled to give (−)-3,3-dimethylcyclohexanol (14 g) which had the following properties: b.p. 47° at 1 mm (lit. b.p. 80–1 at 16 mm),[6] α_D^{20} − 0·95 (neat liquid); IR showed bands at 3330 (OH) 1382 and 1362 (gem-dimethyls) 1060 (C—OH), 1020, 970, 940, 920 and 900 cm^{-1} (skeletal); NMR (CCl_4) δ 0·88 and 0·94 (2 s's, gem-dimethyl), δ 2·67 (s, OH proton) and δ 3·62 (m, Jaa 10·6 Hz, Jae 4·2 Hz, α-carbinol proton).

Lithium aluminium hydride reduction of ketone (**10**)

To a stirred suspension of LAH (2·0 g) in ether (50 ml) were slowly added 15·4 g of **15** dissolved in ether (50 ml) and then refluxed the mixture for 2 hr. 5% NaOH aq was slowly added over 30 min. The product was filtered and the oil thus obtained was distilled to afford **5**: α_D^{20} + 11·7; IR and the GLC retention time being identical with the original alcohol derived from the cyclisation reaction of (+)-dihydromyrcene.

Synthesis of alcohol (**5**) *from* (+)-3,3-*dimethyl*-1-*vinylcyclohexane* (**13**)

(+)-Acetate-**4** (50 g) was pyrolysed by passing through a glass tube (4′ × 0·25″) at 500°. The crude pyrolysate was washed with 10% Na_2CO_3 aq and the oil was distilled to give 26 g of a mixture of **13**, α_D^{20} + 7·27 (neat liquid) IR bands at 1630 (C=C), 1380, 1360 (gem-dimethyl) and 912 cm^{-1} (vinyl); mass spectrum *m/e* 138, (Molecular ion) and **14** in a ratio of 60:40. A pure sample of **13** was obtained by fractional distillation.

The olefin (18·0 g) in dichloromethane (50 ml) was epoxidised with 36% peracetic acid (20 ml) at 40° over 6 hr. The epoxide **15** thus obtained in 80% yield was reduced with LAH to give **5**, whose IR and retention time were identical to the alcohol derived from the cyclisation of (+)-dihydromyrcene.

Preparation of (±)-trans-*tetrahydroeucarvol*

Eucarvone (12 g) which was prepared by the method of Corey *et al.*[13] was dissolved in abs EtOH (130 ml). Na (10 g) was then added in small portions at a rate allowing gentle refluxing. After all the Na had been added, the contents were refluxed for a further hr. The mixture was worked up by removing EtOH by distillation and steam

distilling the oil (5 g) which consisted of *trans*-16 (90%) and *cis*-17 (10%). This mixture in EtOH (25 ml) was further hydrogenated with Pd/H_2 to furnish *trans*- and *cis*-tetrahydroeucarvols respectively. The pure *trans*-isomer was obtained by preparative GLC. The IR spectrum and the GLC retention time of this alcohol were identical to 7 obtained as by-product of the dihydromyrcene cyclisation.

Preparation of (±)-cis-*tetrahydroeucarvol*[2]

A soln of tetrahydroeucarvone (1·5 g) in ether (20 ml) was added to a stirred suspension of LAH (0·5 g) in ether (20 ml) and refluxed for 2 hr. The usual work up with 1N NaOH and extraction with ether followed by distillation under reduced pressure gave a mixture of *trans*- and *cis*-tetrahydroeucarvols in a ratio of 30:70. The *cis*-isomer was obtained in pure form by preparative GLC minor component 9 formed during the cyclisation of (+)-dihydromyrcene. The above mixture of alcohols had b.p. 65° at 2 mm.

Cyclisation of (−)-*dihydromyrcene* (2)

The olefin was cyclised under the conditions applied to the enantiomeric (+)-dihydromyrcene, and the mixture of cyclic esters obtained was hydrolysed to the corresponding alcohols which were isolated with the help of preparative GLC. The optical rotations of various compounds of this series are summarised below.

Compound	α_D^{20}
α-(*R*)-(−)-1-(α-Hydroxyethyl)3,3-dimethylcyclohexane	−11·62
(−)-1-Acetyl-3,3-dimethylcyclohexane	−4·88
(−)-3,3-Dimethylcyclohexyl acetate	−10·1
(+)-3,3-Dimethylcyclohexanol	+1·01
(−)-*trans*-Tetrahydroeucarvol (*ca* 80% pure)	−7·88 (*c* 20·3, MeOH)
(−)-*cis*-Tetrahydroeucarvol	−18·29 (*c* 12·3, MeOH)

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