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FLUOROSULFONIC ACID INDUCED RING OPENING OF PINANONES: PINANE CHIRALITY IN SYNTHESIS†

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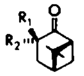
Abstract—The acid-catalysed ring opening of a number of substituted nopinones to give 4-(2-propyl)cyclohex-2-enones is described. In an application of this reaction use has been made of pinane chirality in the synthesis of *R*-*o*-mentha-2,4-diene (**13**) by fluorosulfonic acid-catalysed rupture of *cis*-verbanone (**8**) to (4*S*,5*R*)- and (4*R*,5*R*)-5-methyl-4(2-propyl)cyclohex-2-enone (**9** and **10**) followed by reduction–elimination.

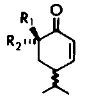
The molecular rearrangements of carbocations in solvolytic and strong acid media are one of the most well-studied classes of organic transformations.[1] Skeletal changes induced by acid-catalysed reactions of carbonyl containing compounds have been known for many years[2] and spectral studies of carbonyl compounds in strong acid media have been reported.[3] Much of the charge of a protonated carbonyl group is delocalized onto the carbonyl carbon,[4] this being equivalent to a resonance contributor which has the structure of a hydroxy-substituted carbocation, and may therefore undergo molecular rearrangements analogous to those of classical carbocations.[2] The reaction of the protonated carbonyl would be expected to be particularly facile in the presence of a strained α-cyclobutane as is the case in the substituted nopinones reported in this study.

The often complex nature of thermal[5,6] and acid-catalysed[7–9] ring-opening reactions of readily available optically active pinane derivatives has limited the use of such reactions in synthesis. Despite this a number of natural product syntheses have utilized acid-catalysed ring openings of pinane derivatives in key steps.[10–13] Although the literature contains many reports of terpenoid rearrangements induced by strong acids, such as fluorosulfonic acid, there have been few such studies of pinane derivatives.[14] In this paper we report our exploration of the reactions of pinanones with strong acid reagents and describe new applications of pinanes to asymmetric synthesis.

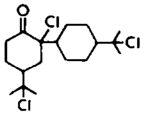
RESULTS AND DISCUSSION

In marked contrast to the thermolysis of nopinone (**1a**)[15,16] the reaction of this substrate with fluorosulfonic acid is surprisingly clean. In fact the ^{1}H-NMR spectrum of a sample prepared at −70° and observed at room temperature showed the presence of a single product which is stable under these conditions and which after neutralization was isolated and identified as cryptone (**2a**), a known natural product.[17] Protonated cyclohexenones have previously been studied under stable ion conditions[18] and reported to undergo ring contraction at higher temperatures.[19] In the course of reaction to form cryptone (**2a**) the chirality of C5 in the pinane nucleus is lost. The C1—C6 bond rupture is facilitated by ring strain and the optical inactivity of the product suggests the intermediacy of cation **3** or epimerization of the product under the reaction conditions (Scheme 1). This reaction has been reported to occur with ethylaluminium dichloride[20] and we have found that it can also be effected with aluminium chloride. In contrast with these results when the reaction is conducted with hydrogen chloride gas dimerization and formation of the trichloride (**4**) is observed. This reaction was first reported[21] to give a dimeric trichloro compound **5** the structure of which was later[9] revised to **6** and the relative stereochemistry (**4**) determined by X-ray crystallography.[22] The racemic nature of product **4** obtained from optically active (+)-nopinone (**1a**) is consistent with the reaction involving the intermediacy of achiral 4-[2-chloro-2-propyl]cyclohexanone (**7**) which subsequently undergoes an intermolecular aldol condensation and stereospecific addition of HCl (Scheme 2). This is supported by the isolation of **7** from the reaction and its conversion with HCl to **4**.





	R_1	R_2	
(1a)	H	H	(2a)
(1b)	CH_3	H	(2b)
(1c)	H,D	D	(2c)



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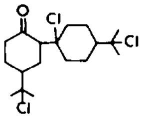

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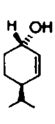

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The loss of optical activity in the rearrangement of nopinone with acid does not necessarily exclude the chirality of the pinane nucleus being utilized in related reactions for use in chiral synthesis.[23,24] For example

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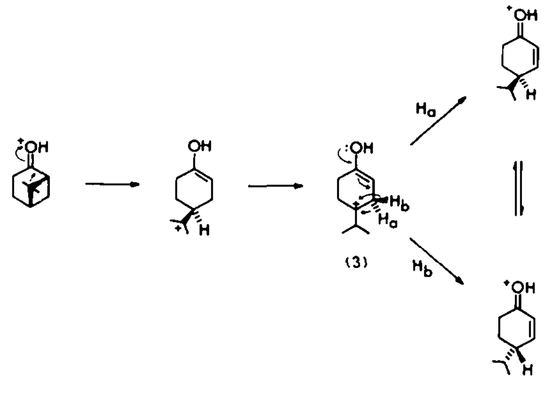
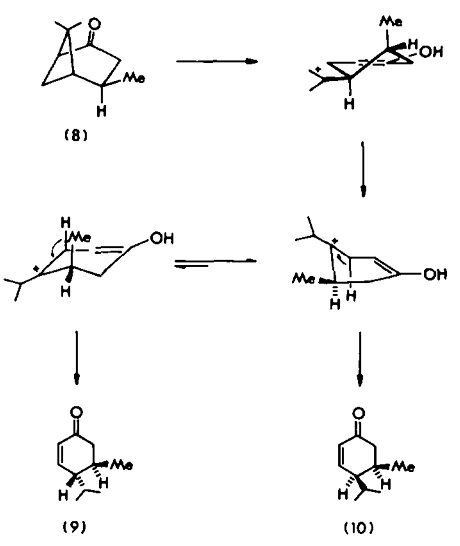
† Parts of this work were reported by P.J.S. at the 7th IUPAC Conference on Physical Organic Chemistry, Auckland, 20–24 August 1984.



Scheme 1.

stereospecific substitution at C4 of optically pure nopinone and subsequent ring opening would be expected to give chiral products since the chirality at C4 should be retained in the reaction as this site is β to the carbonyl (Scheme 3).

Thus acid-catalysed reaction of *cis*-verbanone (**8**) with fluorosulfonic acid produces a mixture of two products, seen both in the ^{1}H- and ^{13}C-NMR spectra of the reaction mixture. These products can be isolated and were identified as the (4*S*,5*R*) (*trans*) and (4*R*,5*R*) (*cis*) enones (**9** and **10**). The ^{1}H-NMR spectrum shows the olefinic protons as an AB quartet and the infrared spectrum shows the presence of the α,β-enone. The relative stereochemistry of the methyl and 2-propyl substituents was deduced from the chemical shift of the C5Me carbon: δ_C13.2 *cis* and 17.3 *trans* isomer. Reaction of *cis*-verbanone with aluminium chloride did not give the equilibrium mixture (*ca* 1 : 2) of *cis* and *trans* isomers (**10** and **9**) obtained from the fluorosulfonic acid reaction. Instead the *cis* isomer dominated (*ca* 2 : 1). The kinetic preference for the *cis* product (**10**) may be accounted for in Scheme 3 which shows the conformational equilibrium of the intermediate cations, with methyl pseudo axial and equatorial, and with the axial hydrogens suitably aligned for reaction to the *trans*-**9** and *cis*-**10** isomers.



Scheme 3.

Reduction of cryptone (**2a**) with lithium aluminium hydride or sodium borohydride in the presence of $CeCl_3$ affords predominantly the *trans* alcohol (**11**) with stereoselectivity being enhanced[25] by the use of sodium borohydride in the presence of $CeCl_3$. Similar reduction of the mixture of *cis*- and *trans*-**10** and **9** gave a mixture of stereoisomers, the composition of which depended on the reaction conditions. When the reaction with sodium borohydride and $CeCl_3$ was carried out at 40° there was *ca* 90% of one stereoisomer produced. The stereoisomers were not separated but detailed ^{13}C-NMR analysis suggests the major stereoisomer in all the reactions is stereoisomer **12**. Reaction of the alcohol mixture with 2,4-dinitrobenzenesulfenyl chloride[26] in triethylamine followed by heating gave *R*-*o*-mentha-2,4-diene (**13**). This reaction (Scheme 4) sequence proceeds[27] by a [2,3]sigmatropic rearrangement and stereospecific *syn*-elimination, which therefore requires a *trans* relationship between the hydroxy and propyl groups in the precursor alcohol. Optically active *o*-mentha-2,4-diene is of interest for its chiroptical properties[28] and the strong positive Cotton effect suggests it to have a right-handed P helicity (cf. M) (Fig. 1) in which the steric interaction between the methyl and propyl groups is minimized.

This reaction sequence represents an example of the reproduction of chirality[29] in which a specific chirality, which is subsequently destroyed, is used to control the formation of a new chiral centre. Thus, in principle, a single starting material, e.g. (−)-verbenone, can be converted selectively into either of the two enantiomers of the diene via the isomeric *cis*- and *trans*-verbanones (Scheme 5).

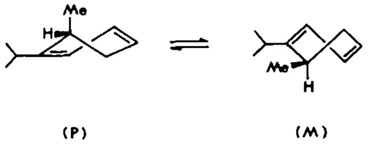
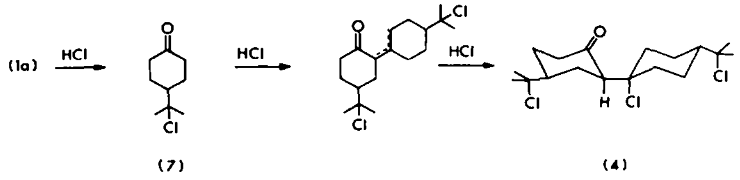
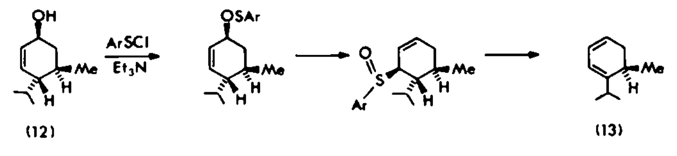


Fig. 1.

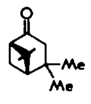


Scheme 2.



Scheme 4.

Reaction of fluorosulfonic acid with *cis*-3-methylnopinone (**1b**) gave a mixture of *cis* and *trans* isomers (**2b**) but the conformational flexibility of the system and the similarity of the ^{13}C-NMR data did not allow a simple identification of the stereoisomers. The same mixture of isomers was obtained when aluminium chloride was used and in a separate experiment it was shown that this was the thermodynamic mixture. 2-Methylverbanone (**14**) with fluorosulfonic acid gave 5,5-dimethyl-4-(2-propyl)cyclohex-2-enone (**15**). The reaction of *trans*-3-methyl-*cis*-verbanone (**16**) under the same conditions gave almost a single 5,6-dimethyl-4-(2-propyl)cyclohex-2-enone (**17**) (90%) different from the two stereoisomers (**18**) obtained from *cis*-3-methyl-*cis*-verbanone (**19**) and this result suggests that under the reaction conditions epimerization does not occur at C3(**16, 19**) C6(**17, 18**). This seemed surprising in view of the highly acidic conditions, although α,β-unsaturated ketones are known[30] to preferentially enolize at the γ-carbon rather than the α′-carbon. The lack of epimerization at C3 was tested by reaction of 3-deuteronopinone (**1c**) with fluorosulfonic acid. This gave 6-deuterocryptone with no loss of deuterium, even after several hours at room temperature in fluorosulfonic acid (Scheme 1). The retention of deuterium at the α′-carbon is consistent with the retention of configuration at the C3 chiral centre in the reaction of *cis*- and *trans*-3-methyl-*cis*-verbanone (**19** and **16**) with fluorosulfonic acid.



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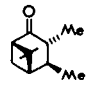

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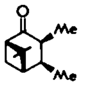

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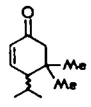

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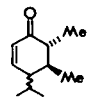

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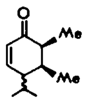

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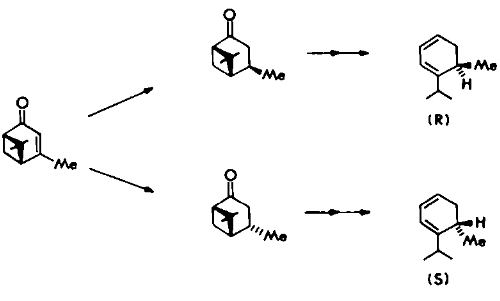

Scheme 5.

The multifunctionality and optical purity of the cryptone derivatives obtained from reaction of 3- and 4-substituted nopinones with fluorosulfonic acid suggests further potential uses for this reaction in the preparation of chiral monocyclic synthons.

EXPERIMENTAL

IR and UV spectra were recorded on Shimadzu IR27G and Varian DMS 100 spectrophotometers, respectively. ^{1}H- and ^{13}C-NMR spectra were recorded on Varian T60 and CFT 20 spectrometers, respectively, for $CDCl_3$ solns with Me_4Si as internal standard. Mass spectra were recorded on an A.E.I. MS902 spectrometer. Optical measurements were made with a Jasco ORD/UV5 spectrophotometer.

The starting ketones **1a–c, 8, 14, 16,** and **19** were prepared by lit. procedures.[31–35] Their ^{13}C-NMR spectra are listed in Table 1 and were assigned by comparison with lit. values.[36]

Reactions of pinanones with (a) *fluorosulfonic acid* (b) *aluminium chloride* (c) *hydrogen chloride* (i) *nopinone*

(a) (+)-**1a** (1 g, $[\alpha]_D$ 32°), prepared from (β)-pinene, was cooled to −70° and fluorosulfonic acid (3 ml) added. The mixture was stirred and allowed to warm to room temp over 30 min. In a separate experiment the reaction was followed in the ^{1}H-NMR spectrometer and shown to be complete in 5 min. Ice water was added dropwise and the product extracted with ether, washed with sodium bicarbonate until neutral and dried. The solvent was removed to give (*R,S*)-**2a** as an oil (830 mg), $[\alpha]_D - 2.6°$ (EtOH), ν_{max} 1685 cm^{-1} (lit. cit.[20] (*R*)-4-(2-propyl)cyclohex-2-enone (*R*-cryptone) $[\alpha]_D - 119.3°$ (EtOH)). ^{1}H-NMR δ_H (CCl_4) 0.98, J 6.5 Hz, C4′Me_2; 5.93, $J_{2,3}$ 10 Hz, $J_{2,4}$ 2 Hz, H2; 6.90, $J_{3,2}$ 10 Hz, $J_{3,4}$ 1.0 Hz, H3. ^{13}C-NMR δ_C 199.3, C1; 129.8, C2; 153.8, C3; 42.7, C4; 25.6, C5; 37.4, C6; 31.7, C4′; 19.6, C4′$\underline{Me_2}$. 4-(2-Propyl)cyclohex-2-enone was shown to be stable under the reaction conditions for a period of days.

(b) To a soln of (+)-**1a** (90 mg) in dichloromethane (5 ml) was added $AlCl_3$ (150 mg) and the soln stirred for 3 hr at 25°. The product was extracted with ether, washed with $NaHCO_3$ aq,

Table 1. ^{13}C-NMR chemical shifts of methyl-substituted nopinones

	1a^a	**1c**	**8**^{a}	**1b**^{b}	**14**	**16**	**19**
C1	57.9	57.9	56.0	57.7	58.2	58.4	58.1
C2	214.4	^{c}	214.0	216.7	214.0	^{c}	^{c}
C3	32.8	32.4^d	41.4	37.1	48.3	46.8	46.6
C4	21.4	21.3	31.1	30.9	^{c}	41.3	41.0
C5	40.5	40.5	47.5	41.1	53.8	48.0	47.7
C6	41.1	41.1	40.2	43.0	41.2	40.1	40.5
C7	25.2	25.2	28.4	25.6	25.5	28.9	28.7
C8	25.9	26.0	27.0	26.3	27.3	27.0	26.8
C9	22.1	22.1	24.6	22.0	25.9	24.1	23.9
Me			21.1	14.1	29.2	19.8	19.5
					32.2	20.0	19.8

[a] Previously reported, ref. 36.
[b] Previously reported, ref. 6.
[c] Not observed.
[d] Triplet, J = 19 Hz.

dried and the solvent removed to give (*RS*)-**2a** as an oil (88 mg), $[\alpha]_D$ 5.4°. ^{1}H- and ^{13}C-NMR spectra as above.

(c) Dry HCl gas was passed through a soln of **1a** (500 mg) in MeOH (10 ml) until such time as a ppt had formed. The mixture was extracted with ether and washed with water, dried and after removal of solvent the product was crystallized from MeOH to give (2*RS*,4*RS*)-*cis*-**4** (260 mg), m.p. 142–146° (lit. cit.[9] m.p. 148°). ^{1}H-NMR δ_H (CCl_4) 1.56, Me's, 6H; 1.62, Me's, 6H. ^{13}C-NMR δ_C 209.5, C1; 60.0, C2; 37.5, C3; 49.1, C4; 29.2, C5; 42.2, C6; 72.7, C4′; 76.8, C1*; 34.2, 31.2, C2*, C6*; 23.5, 23.7, C3*, C5*; 49.1, C4*; 74.3, C4*′; 30.2, 30.6, 30.7, 30.8, Me's (asterisks indicate the chlorocyclohexyl ring). The mother liquor was shown to contain 4-[2-chloroprop-2-yl]-cyclohexanone (**7**). ^{1}H-NMR δ_H 1.6, C$\underline{\text{Me}}_2$. ^{13}C-NMR δ_C 211, C1; 40.4, C2, C6; 27.7, C3, C5; 48.6, C4; 73.0, C4′; 30.6, C4′$\underline{\text{Me}}_2$. Reaction of **7** with dry HCl gas as above gave **4**.

(ii) cis-*Verbanone*

(a) *cis*-**8** (1.0 g) was reacted as above with fluorosulfonic acid to give a mixture (2:1) of (4*S*,5*R*)-*trans*- and (4*R*,5*R*)-*cis*-**9** and **10** (870 mg), ν_{max} 1685 cm^{-1}. ^{1}H-NMR δ_H (CCl_4) 1.0, $W_{1/2}$ 10 Hz, Me; 5.99, $J_{2,3}$ 11 Hz, H2; 6.84, $J_{3,2}$ 11 Hz, H3. (Found: M$^+$ 152.1202; $C_{10}H_{16}O$ requires M$^+$ 152.1201.) (4*S*,5*R*)-**9**, ^{13}C-NMR δ_C 200.1, C1; 129.9, C2; 151.7, C3; 49.4, C4; 32.5, C5; 45.7, C6; 27.6, C4′; 19.6, 21.4, C4′Me$_2$; 17.3, C5Me. (4*R*,5*R*)-**10**, ^{13}C-NMR δ_C n.o., C1; 129.3, C2; 150.9, C3; 47.3, C4; 31.5, C5; 46.0, C6; 28.3, C4′; 20.8, 20.7, C4′Me$_2$; 13.2, C5Me.

(b) *cis*-**8** (100 mg) was reacted in CH_2Cl_2 for 16 hr as above and gave a mixture (1:2) of (4*S*,5*R*)- and (4*R*,5*R*)-**9** and **10**, as an oil (95 mg), ^{1}H- and ^{13}C-NMR spectra as above.

(iii) cis-3-*Methylnopinone* (**1b**)

(a) *cis*-**1b** (137 mg) was reacted as above with fluorosulfonic acid (1 ml) to give a mixture of *cis*- and *trans*-**2b**[37] as an oil, ν_{max} 1685 cm^{-1}. ^{1}H-NMR δ_H(CCl_4) 0.96, J 6 Hz, C7Me$_2$; 1.07, J 6 Hz, C6Me; 5.88, $J_{2,3}$ 10 Hz, H2; 6.68, $J_{3,2}$ 10 Hz, H3. (Found: M$^+$ 152.1195; $C_{10}H_{16}O$ requires M$^+$ 152.1201.) Major isomer: ^{13}C-NMR δ_C n.o., C1; 129.6, C2; 153.2, C3; (39.3), C4; 34.1, C5; (43.5), C6; 31.7, C4′; 19.4, 19.1, C4′$\underline{\text{Me}}_2$; 15.1, C6$\underline{\text{Me}}$. Minor isomer: ^{13}C-NMR δ_C n.o., C1; 128.5, C2; 153.1, C3; (37.4), C4; 32.3 C5; (41.7), C6; 31.4, C4′; 20.2, 20.3, C4′$\underline{\text{Me}}_2$; C6$\underline{\text{Me}}$, 15.8. To this mixture (2:1) of isomers (35 mg) in dry benzene (2 ml) was added NaOEt (70 mg) and the mixture stirred at room temp for 17.5 hr. The product, isolated by means of ether, shows no change in isomer ratio.

(b) *cis*-3-Methylnopinone (**1b**) was reacted as above with $AlCl_3$ for 16 hr to give an identical mixture of isomers to that produced from fluorosulfonic acid (^{1}H- and ^{13}C-NMR).

(iv) 2-*Methylverbanone*

Compound **14** (51 mg) was reacted as above with fluorosulfonic acid (0.3 ml) to give **15** (40 mg) as an oil, ν_{max} 1680 cm^{-1}. ^{1}H-NMR δ_H 0.8–1.3, Me's; 2.2, $W_{1/2}$ 3.5 Hz, 6H$_2$; 6.07, $J_{2,3}$ 10 Hz, ^{4}J 2 Hz, H2; 6.8, $J_{3,2}$ 10 Hz, $J_{3,4}$ 3 Hz, H3; ^{13}C-NMR δ_C 199.7, C1; 129.4, C2; 150.1, C3; 52.3, C4; n.o., C5; 52.2, C6; 30.1, C4′; 18.6, (23.9), C4′Me's; (24.1), C5$\underline{\text{cMe}}$; 27.2, C5$\underline{\text{tMe}}$. (Found: M$^+$ 166.1348; $C_{11}H_{18}O$ requires M$^+$ 166.1358.) In a separate experiment the reaction was shown by ^{1}H-NMR to be rapid and the product 5,5-dimethyl-4-(2-propyl)cyclohex-2-enone stable under the reaction conditions for a period of days.

(v) trans-3-*Methyl*-cis-*verbanone*

trans-3-*Methyl*-*cis*-verbanone **16** (37.1 mg) was reacted as above with fluorosulfonic acid (0.3 ml) to give **17** (26 mg) as an oil, ν_{max} 1680 cm^{-1}. ^{1}H-NMR δ_H 1.1, 1.05, 1.0, 0.75, J 6.5 Hz, Me's; 5.92, $J_{2,3}$ 10 Hz, ^{4}J 2 Hz, H2; 6.64, $J_{3,2}$ 10 Hz, H3. The ^{13}C-NMR showed the product to be >90% a single stereoisomer. ^{13}C-NMR δ_C n.o., C1; 129.8, C2; 149.7, C3; (47.9), C4; 39.1, C5; (49.6), C6; 27.2, C4′; (17.0), 21.4, C4$\underline{\text{Me}}_2$; (12.1), C5Me; (16.5), C6Me. (Found: M$^+$ 166.1334; $C_{11}H_{18}O$ requires M$^+$ 166.1358.) The minor isomer of the mixture was distinguished by δ_C 149.4, C2; 127.9, C3.

(vi) cis-3-*Methyl*-cis-*verbanone*

cis-3-Methyl-*cis*-verbanone **19** (120 mg) was treated as above with fluorosulfonic acid (1 ml) to give a mixture (*ca* 1:1) of two stereoisomers of **18** (90 mg), ν_{max} 1680 cm^{-1}. ^{1}H-NMR δ_H 1.06, $W_{1/2}$ 12 Hz, Me's; 5.89, $J_{2,3}$ 10.8 Hz, H2; 6.69, $J_{3,2}$ 10.8, H3. ^{13}C-NMR δ_C 204.0, 202.4, C1; 129.1, 128.4, C2; 150.4, 149.1, C3; 49.9, 47.9, 47.1, 44.5, 38.2, 35.5, 28.5, 28.1, 21.7, 21.1, 21.0, 18.5, 15.5, 12.3, 11.0, 6.6. (Found: M$^+$ 166.1385; $C_{11}H_{18}O$ requires M$^+$ 166.1358.) These products were different from both the major and minor stereoisomers obtained from *trans*-3-methyl-*cis*-verbanone (**16**).

(vii) 3-*Deuteronopinone*

3-Deuteronopinone (500 mg) (D content from mass spectrometry: D_2 40, D_1 45, D_0 15%) was treated as above with fluorosulfonic acid and aliquots taken after reaction for 0.5, 1, 3 and 18 hr at room temp. These were quenched and worked up as above and analysed by mass spectrometry for the D content. In each case there was no significant loss of the deuterium in the product, **2c**. ^{13}C-NMR δ_C 129.9, C2; 154.1, C3; 42.7, C4; 25.3, C5; 31.7, C4′; 19.5 and 19.7, C4′$\underline{\text{Me}}_2$. M$^{+\cdot}$ (%): 140 (42), 139 (46), 138 (12).

Reduction of 4-(2-*propyl*)*cyclohex*-2-*enone*

(a) To a soln of **2a** (50 mg) in ether (1.5 ml) was added LAH (90 mg) and the mixture stirred at room temp for 0.5 hr. $NaSO_4 \cdot 10H_2O$ was added followed by water and the product extracted with ether to give *trans*-**11**.[38] ^{1}H-NMR δ_H 0.88, C4′$\underline{\text{Me}}_2$; 4.05, $W_{1/2}$ 14 Hz, H1; 5.5–5.75, H2, H3. ^{13}C-NMR δ_C 67.4, C1; 131.4, C2; 132.8, C3; 41.8, C4; 23.6, C5; 32.6, C6; 32.0, C4′; 19.2, 19.5, C4′$\underline{\text{Me}}_2$ containing *ca* 13% *cis*-4-(2-propyl)cyclohex-2-enol,[38] ^{13}C-NMR δ_C 64.1, C1; 128.9, C2; 135.1, C3; 42.0, C4; 19.7, 20.1, C4′$\underline{\text{Me}}_2$. (Found: M$^+$ 140.1202; $C_9H_{16}O$ requires M$^+$ 140.1201.)

(b) A mixture of **2a** (57 mg), $CeCl_3 \cdot 6H_2O$ (123 mg), $NaBH_4$ (20 mg) in MeOH (2 ml) was reacted at 0° for 0.5 hr. The product was isolated in the usual manner to give *trans*-4-(2-propyl)cyclohex-2-enol contaminated with less than 10% of the *cis* isomer and identical in all respects to the above sample.

(c) A mixture of **2a** (50 mg), $CeCl_3 \cdot 6H_2O$ (128 mg), $NaBD_4$ (16 mg) in MeOD (1 ml) at 0° gave 1-deuterio-4-(2-propyl)cyclohex-2-en-1-ol (51 mg) which showed the absence of H1 in the ^{1}H-NMR spectrum (δ 4.05). ^{13}C-NMR δ_C n.o., C1; 131.2, C2; 133.1, C3; 41.8, C4; 23.6, C5; 32.5, C6; 32.0, C4′; 19.2, 19.6, C4′Me$_2$. (Found: M$^+$ 141.1243; $C_9H_{15}OD$ requires M$^+$ 141.1264.)

Preparation of (R)-o-*mentha*-2,4-*diene* (**13**)

A mixture (2:1) of (4*S*,5*R*)- and (4*R*,5*R*)-**9** and **10** (75 mg), $CeCl_3 \cdot 6H_2O$ (160 mg), $NaBH_4$ (21 mg) in MeOH (2.6 ml) was stirred at 40° for 30 min. The mixture was brought to neutrality by careful addition of HCl and the product extracted into ether, washed and dried. Removal of solvent gave an almost pure sample of a single **12** (70 mg) (>85%). ^{1}H-NMR δ_H 5.5–5.8, H2, H3. ^{13}C-NMR δ_C 67.6, C1; 129.0, C2; 132.5, C3; 49.0, C4; 30.4, C5; 42.1, C6; 27.4, C4′; 20.1, 20.6, C4′$\underline{\text{Me}}_2$; 16.6, C5Me. At lower temps or with LAH varying mixtures of epimeric alcohols, always with the above isomer dominating, were obtained. To a soln of **12** (55 mg) in Et_3N (0.2 ml) and 1,2-dichloroethane (5 ml) was added 2,4-dinitrobenzenesulfenyl chloride (220 mg) and the mixture heated under reflux for 2.5 hr. The soln was poured into pentane (50 ml), filtered, and the solvent removed to give an oil which was adsorbed onto silica gel (20 g). Elution with pentane gave *R*-**13** as a colourless oil (10.7 mg), $[\alpha]_D$ 146° ($CHCl_3$), λ_{max} 265.6, CD λ 256 nm, $\Delta\varepsilon$ 4.83 ν_{max} 2950 cm^{-1}. ^{1}H-NMR δH 0.95, J 8 Hz, 1.07, J 8 Hz, 1.19, J 7 Hz, CH$\underline{\text{Me}}$; 5.55 $W_{1/2}$ 6 Hz, 5.82, $W_{1/2}$ 10 Hz, H2, H3, H4. ^{13}C-NMR δ_C 124.1, C5; 121.7, C4; 114.7, C3; 151.3, C2; 29.4, 32.7, C1, C2′; 31.3, C6; 17.3, 21.3, 23.1, C1$\underline{\text{Me}}$, C2′$\underline{\text{Me}}_2$. (Found: M$^+$ 136.1244; $C_{10}H_{16}$ requires M$^+$ 136.1258.)

REFERENCES

[1] M. Saunders, J. Chandrasekhar and P. von R. Schleyer, *Rearrangements in Ground and Excited States* (Edited by P.

de Mayo), Vol. 1, p. 1. Academic Press, New York (1980).

[2] A. Fry, *Mechanisms of Molecular Migrations* (Edited by B. S. Thyagarajan), Vol. 4, p. 113. Wiley-Interscience, New York (1971).

[3] G. A. Olah, A. M. White and D. H. O'Brien, *Chem. Rev.* **70**, 561 (1970).

[4] E. M. Arnett, J. V. Carter and R. P. Quirk, *J. Am. Chem. Soc.* **92**, 1770 (1970) and refs therein.

[5] J. M. Coxon and P. J. Steel, *Terpene Chemistry* (Edited by J. Verghese), p. 119. Tata–McGraw-Hill, New York (1982).

[6] Y. Bessière, M. Barthélémy, A. F. Thomas, W. Pickenhagen and C. Starkemann, *Nouv. J. Chim.* **2**, 365 (1978).

[7] N. Lander and R. Mechoulam, *J. Chem. Soc. Perkin Trans. I* 484 (1976).

[8] D. Whittaker, *Chemistry of Terpenes and Terpenoids* (Edited by A. A. Newman), p. 60. Academic Press, London (1972).

[9] K. G. Lewis and G. J. Williams, *Aust. J. Chem.* **21**, 2467 (1966).

[10] T. Inokuchi, G. Asanuma and S. Torii, *J. Org. Chem.* **47**, 4622 (1982).

[11] T. Yanami, M. Miyashita and A. Yoshikoshi, *J. Org. Chem.* **45**, 607 (1980).

[12] J. E. McMurry, J. H. Musser, M. S. Ahmad and L. C. Blaszczak, *J. Org. Chem.* **40**, 1829 (1975).

[13] A. Van der Gen, L. M. Van der Linde, J. G. Witteveen and H. Boelens, *Rec. Trav. Chim. Pays-Bas* **90**, 1034 (1971).

[14] D. Whittaker, *Terpene Chemistry* (Edited by J. Verghese), p. 96. Tata–McGraw-Hill, New York (1982).

[15] J. M. Coxon, R. P. Garland and M. P. Hartshorn, *Aust. J. Chem.* **25**, 2409 (1972).

[16] C. F. Meyer and J. K. Crandall, *J. Org. Chem.* **35**, 2688 (1970).

[17] A. F. Thomas, *The Total Synthesis of Natural Products* (Edited by J. ApSimon), Vol. 2, p. 97. Wiley-Interscience, New York (1973). For recent examples of natural product syntheses using cryptone as starting material see: S. L. Schreiber and C. Santini, *J. Am. Chem. Soc.* **106**, 4038 (1984); A. Hosomi, H. Iguchi, J. Sasaki and H. Sakurai, *Tetrahedron Lett.* **23**, 551 (1982).

[18] G. A. Olah, Y. Halpern, Y. K. Mo and G. Liang, *J. Am. Chem. Soc.* **94**, 3554 (1972).

[19] H. Hogeveen, *Rec. Trav. Chim. Pays-Bas* **87**, 1295 (1968).

[20] B. B. Snider, D. J. Rodini and J. von Straten, *J. Am. Chem. Soc.* **102**, 5872 (1980).

[21] O. Wallach and A. Blumann, *Justus Liebigs Ann. Chem.* **356**, 227 (1907).

[22] J. M. Coxon, G. J. Hydes and P. J. Steel, *Acta Crystallogr., Sect. C* **40**, 1037 (1984).

[23] S. F. Lee, M. Edgar, C. S. Pak, G. Barth and C. Djerassi, *J. Am. Chem. Soc.* **102**, 4784 (1980).

[24] J. P. Konopelski and C. Djerassi, *J. Org. Chem.* **45**, 2297 (1980).

[25] A. L. Gemal and J.-L. Luche, *J. Am. Chem. Soc.* **103**, 5454 (1981).

[26] R. Tang and K. Mislow, *J. Am. Chem. Soc.* **92**, 2100 (1970).

[27] H. J. Reich and S. Wollowitz, *J. Am. Chem. Soc.* **104**, 7051 (1982) and refs therein.

[28] D. A. Lightner, T. D. Bouman, J. K. Gawronski, K. Gawronska, J. L. Chappuis, B. V. Crist and A. E. Hansen, *J. Am. Chem. Soc.* **103**, 5314 (1981).

[29] D. Seebach, M. Boes, R. Naef and W. B. Schweizer, *J. Am. Chem. Soc.* **105**, 5390 (1983).

[30] A. J. Waring, *Comprehensive Organic Chemistry* (Edited by D. Barton and W. D. Ollis), Vol. 1, p. 1031. Pergamon Press, Oxford (1979).

[31] J. M. Coxon, R. P. Garland and M. P. Hartshorn, *Aust. J. Chem.* **23**, 1069 (1970).

[32] A. F. Regan, *Tetrahedron* **25**, 3801 (1969).

[33] Y. Bessière-Chrétien and B. Meklati, *C.R. Acad. Sci. Paris* **C269**, 1315 (1969).

[34] Y. Bessière-Chrétien and C. Grison, *Bull. Soc. Chim. Fr.* 3103 (1970).

[35] J. M. Coxon, R. P. Garland and M. P. Hartshorn, *Aust. J. Chem.* **25**, 947 (1972).

[36] J. M. Coxon, G. J. Hydes and P. J. Steel, *J. Chem. Soc. Perkin Trans. 2* 1351 (1984).

[37] W. M. B. Könst, L. M. Van der Linde and J. G. Witteveen, *Int. Flavours Food Addit.* **6**, 121 (1976).

[38] D. T. C. Gillespie and A. K. Macbeth, *J. Chem. Soc.* 1531 (1939).