The Chemistry of Terpenes. Part XIV.[1] Syntheses of (±)- and (+)-Fenchone, and (+)-*cis*-2,2,5-Trimethyl-3-vinylcyclopentanone, a Photoisomer of (−)-*trans*-Caran-4-one

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Treatment of (+)-α-2,3-epoxypinane or (−)-*trans*-pinocarveol with hydrogen bromide gives a mixture in which (−)-2-*endo*-bromo-6-*exo*-hydroxy-1,3,3-trimethylbicyclo[2,2,1]heptane is the major product. With silver acetate this affords (−)-2,2,4-trimethylcyclopent-3-enylacetaldehyde, which gives (−)-4-(2-hydroxyethyl)-1,3,3-trimethylcyclopentene on reduction. The alcohol reacts with peracetic acid giving an almost quantitative yield of (−)-β-1,2-epoxy-4β-(2-hydroxyethyl)-1,3,3-trimethylcyclopentane, which with boron trifluoride yields (+)-*cis*-3-(2-hydroxyethyl)-2,2,5-trimethylcyclopentanone. Treatment of the corresponding chloro-ketone with base affords (+)-fenchone.

Pyrolysis of (+)-*cis*-3-(2-acetoxyethyl)-2,2,5-trimethylcyclopentanone yields (+)-*cis*-2,2,5-trimethyl-3-vinylcyclopentanone, a photoisomer of (−)-*trans*-caran-4-one.

(±)-Fenchone is synthesised from 2,2,4-trimethyl-3-oxocyclopentanecarboxylic acid by chain extension to the largely *cis*-1-acetic acid, diborane reduction of which gives solely, (±)-*cis*-3-(2-hydroxyethyl)-2,2,5-trimethylcyclopentanone. The corresponding chloro-ketone affords (±)-fenchone on treatment with base.

In 1968, the structure (1) was assigned by two groups of workers[2,3] to the major photoproduct of (−)-*cis*-caran-4-one (2) on the basis of chemical evidence and mechanistic considerations. In seeking a synthesis of the *trans*-ketone (1), it appeared to us that 2,2,4-trimethylcyclopent-3-enylacetaldehyde (4) would be an attractive starting material. In fact, as described here, we synthesised (+)-*cis*-2,2,5-trimethyl-3-vinylcyclopentanone (3) from this aldehyde.

The enantiomorph of the aldehyde (4) had previously been obtained[4] by treatment of that of the bromo-alcohol (5) with silver acetate in acetic acid, the bromo-alcohol being described as the sole product of the treatment of (+)-*trans*-pinocarveol [enantiomorph of (6)] with ethereal hydrogen bromide. In our hands, however, repetition of the last step with (−)-*trans*-pinocarveol (6) led to the formation of six compounds, although the bromo-alcohol (5) predominated. We then found that treatment of the more readily available (+)-α-2,3-epoxypinane (7) with ethereal hydrogen bromide gave a similar mixture of compounds, a result which would be expected if the common carbonium ion (8) is formed from both (−)-*trans*-pinocarveol (6) and (+)-α-2,3-epoxypinane (7).

Chromatography of the mixture of products derived from (6) and (7) afforded *p*-cymene (9), (−)-2,2,3-trimethylcyclopent-3-enylacetaldehyde (10), (+)-pinocamphone (11) and (+)-isopinocamphone (12), (−)-2-*endo*-bromo-6-*endo*-hydroxy-1,7,7-trimethylbicyclo-[2,2,1]heptane (13), and (−)-2-*endo*-bromo-6-*exo*-hydroxy-1,3,3-trimethylbicyclo[2,2,1]heptane (5), in this order of elution. The yields of these products obtained from (6) and (7) are given in the Table. The carbonium ion (8) is probably an intermediate in the formation of *p*-cymene (9), and (−)-2,2,3-trimethylcyclopent-3-enylacetaldehyde (10) may be formed by rearrangement of the ion (8) to the less strained ion (14), which can collapse to (10) with loss of a proton.

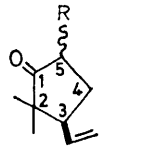
(+)-Pinocamphone (11) and (+)-isopinocamphone (12) are formed in the ratio 9 : 1, identical with that

[1] Part XIII, P. H. Boyle, W. Cocker, R. L. Gordon, and P. V. R. Shannon, preceding paper.
[2] D. C. Heckert and P. J. Kropp, *J. Amer. Chem. Soc.*, 1968, **90**, 4911.
[3] M. S. Carson, W. Cocker, S. M. Evans, and P. V. R. Shannon, *Tetrahedron Letters*, 1968, 6153.
[4] M. P. Hartshorn and A. F. A. Wallis, *J. Chem. Soc.*, 1964, 5254.

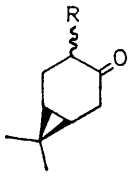
Products of the reaction of (−)-*trans*-pinocarveol (6) and (+)-2,3-epoxypinane (7) with hydrogen bromide

Starting compound	Products (%)				
	(5)	(9)	(10)	(11 + 12)	(13)
(6)	69·9	3·8	7·5	3·8	15·0
(7)	60·0	5·0	10·0	5·0	20·0

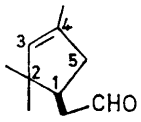
obtained by base-catalysed equilibration of authentic (+)-isopinocamphone (12). These compounds are no



(1) R = α-Me
(3) R = β-Me



(2) R = β-Me
(31) R = α-Me



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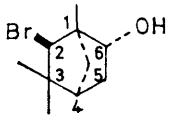

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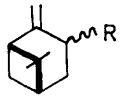
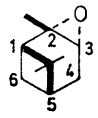


(6) R = α-OH
(15) R = β-OH



(7)

doubt formed by loss of a proton from the ion (8); their formation in relatively small amounts suggests that loss of a proton from this ion is less efficient than its rearrangement to (14). The enantiomorphs of these epimeric pinocamphones have been obtained[4] from (−)-*cis*-pinocarveol [enantiomorph of (15)] by treatment with acidic reagents.

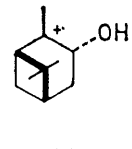
(−)-2-*endo*-Bromo-6-*endo*-hydroxy-1,7,7-trimethylbicyclo[2,2,1]heptane (13) is a new compound. The *endo*-configuration of the bromine atom is assigned by analogy with that of (5);[4,5] confirmation of the configuration of (13) is provided by its oxidation to (16), the enantiomorph of the bromo-ketone previously derived from the enantiomorph of the bromo-alcohol (17).[4] Debromination of the bromo-ketone (16) with zinc and acetic acid yielded (−)-camphor (18), and dehydrobromination of (13) with silver acetate in acetic acid afforded (−)-2,2,3-trimethylcyclopent-3-enylacetaldehyde (10).

The n.m.r. spectrum of the bromo-alcohol (13) (see Experimental section) agrees with its structure. A feature of its i.r. spectrum (Nujol) is the presence of the hydroxy-stretching vibration as two strong peaks at 3550 and 3440 cm^{-1}. The latter band is absent from the spectrum of a dilute solution, which shows a single, sharp band at 3560 cm^{-1} indicating that the bromo-alcohol (13) undergoes intermolecular association at high concentrations.[6]

The bromo-alcohol (13) may be formed, by a concerted reaction, from the ion (8), or it may be formed by attack of bromide ion on the carbonium ion (14), preferentially on the *endo*-side.

[5] P. P. Williams, *Chem. and Ind.*, 1964, 1583.
[6] K. Nakanishi, 'Infrared Absorption Spectroscopy,' Holden-Day and Nankodo, 1962, p. 32.
[7] H. Schmidt, M. Muehlstadt, and P. Son, *Chem. Ber.*, 1966, **99**, 2736.

The major product of the reaction between hydrogen bromide and (−)-*trans*-pinocarveol or (+)-α-2,3-epoxypinane is (−)-2-*endo*-bromo-6-*exo*-hydroxy-1,3,3-trimethylbicyclo[2,2,1]heptane (5). We found this compound to be laevorotatory, in agreement with other authors,[7] but in contrast to an earlier report[4] which claims that a laevorotatory product is formed from (+)-*trans*-pinocarveol.



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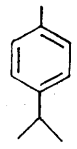
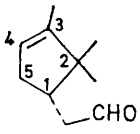


(9)



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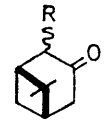
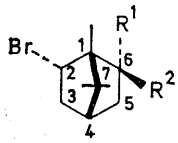
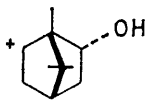


(11) R = α-Me
(12) R = β-Me



(13) R^1 = OH, R^2 = H
(16) R^1R^2 = O
(17) R^1 = H, R^2 = OH



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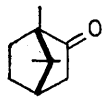

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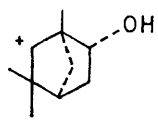

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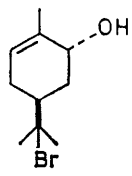


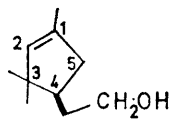
(20)

The products formed on treating (+)-α-2,3-epoxypinane (7) with hydrogen bromide differ from those resulting when the epoxide is treated with either hydrogen fluoride[8] or boron trifluoride–ether complex.[9] Although the aldehyde (4) is a major product in the last two cases,[8,9] it could not be detected in the first. It appears therefore that the formation of (5) by the reaction of bromide with the carbonium ion (19), derived from the initial ion (8), is preferred to the collapse of (19) to give the aldehyde (4). None of the monocyclic bromo-alcohol (20) was found amongst the reaction products of (7) with hydrogen bromide, although its fluoro-analogue is formed in 50% yield when the epoxide (7) is treated with hydrogen fluoride.[8]

The slight quantitative differences in the yields of products obtained from (−)-*trans*-pinocarveol (6) and (+)-α-2,3-epoxypinane (7) are paralleled in similar systems,[10] and may result from subtle geometric factors.

Attention was next turned to the synthesis proper. Reduction of (−)-2,2,4-trimethylcyclopent-3-enylacetaldehyde (4) with lithium aluminium hydride afforded the alcohol (21) with physical properties in good agreement with those recently described.[11] Peracetic acid epoxidation of the alcohol (21) gives a single product in

[8] M. G. Farges, *Bull. Soc. chim. France*, 1962, 1266.
[9] M. P. Hartshorn, D. N. Kirk, and A. F. A. Wallis, *J. Chem. Soc.*, 1964, 5494.
[10] D. V. Banthorpe and D. Whittaker, *Quart. Rev.*, 1966, **20**, 381.
[11] D. J. Goldsmith and R. C. Joines, *J. Org. Chem.*, 1970, **35**, 3572.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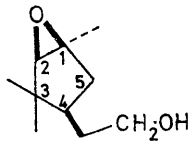
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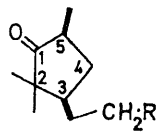
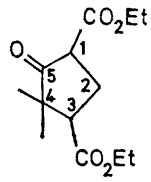

(23) R = OH
(28) R = OAc
(29) R = Cl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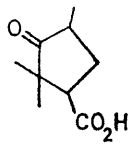
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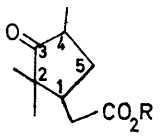
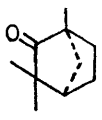

(26) R = Me
(27) R = H


(30)


(32)

high yield. Since its i.r. spectrum exhibits intramolecular hydrogen bonding in dilute solution, the new epoxide is assigned the β-configuration shown in (22). It seems likely that the hydroxyethyl group is responsible for the unidirectional attack by the peracid.[12] The epoxide (22) was smoothly converted by boron trifluoride–ether complex [13] into (+)-*cis*-3-(2-hydroxyethyl)-2,2,5-trimethylcyclopentanone (23).

Since the hydroxy-ketone (23) was a key intermediate, its structure was established by synthesis of its racemic form from diethyl (±)-4,4-dimethyl-5-oxocyclopentane-1,3-dicarboxylate (24).[14] This was methylated at C-1 and then hydrolysed and decarboxylated giving the acid (25),[15] which was subjected to chain extension by the Arndt–Eistert method, giving the keto-ester (26). This ester was also obtained in dextrorotatory form from the aldehyde (4) by oxidative hydroboronation to give the unisolated keto-acid (27) followed by esterification with diazomethane. In both instances the keto-ester (26) was found (n.m.r.) to be a mixture of isomers with the *cis*-form predominant (67%). The corresponding acid (27), obtained by alkaline hydrolysis of the ester (26), was formed with the *cis*-isomer highly predominant (90%),[16] and the alcohol (23) and its acetate (28) were formed solely as the *cis*-isomers.

Hydrolysis of the (±)-ester (26) and selective reduction of the crude acid (27) with diborane, yielded, after chromatography, (±)-*cis*-3-(2-hydroxyethyl)-2,2,5-trimethylcyclopentanone, identical in its spectra with the dextrorotatory product (23) obtained as already described from (+)-α-2,3-epoxypinane (7).

It was expected that substitution of a better leaving group for the hydroxy-function of (23) would make possible the synthesis of the bicyclo[2,2,1]heptane system. This expectation was realised by brief treatment of the keto-alcohol with thionyl chloride in pyridine, giving the chloro-ketone (29), which on treatment with sodium ethoxide gave a good yield of (+)-fenchone (30). Since we have synthesised the racemic keto-alcohol (23), the subsequent elaboration of this compound completes a formal total synthesis of fenchone.

Acetylation of the (+)-keto-alcohol (23) gave the acetate (28) which, on pyrolysis at 480°, was efficiently converted into (+)-*cis*-2,2,5-trimethyl-3-vinylcyclopentanone (3).

It was earlier suggested on mechanistic grounds [2] that the *cis*-ketone (3) should be formed on photolysis of (−)-*trans*-caran-4-one (31), although full experimental verification was lacking. We have now established that the *cis*-ketone (3) is indeed a major photoisomer of (−)-*trans*-caran-4-one (31).

The fact that the *trans*-ketone (1) was not formed by the pyrolysis of the keto-acetate (28), under conditions which must surely lead to the formation of the more thermodynamically stable isomer, was initially surprising to us. Earlier work [3] seemed to indicate that the *trans*-ketone was unaffected by base. We now find that in fact this ketone is converted by treatment with sodium methoxide into an equilibrium mixture consisting of 20% *trans*- and 80% *cis*-ketone. The *cis*-form (3) is therefore the more stable, a result which is supported by stereochemical considerations. Thus in the half-chair conformation, the *trans*-ketone (1) has two pseudo-equatorial and two pseudo-axial substituents, whereas the *cis*-ketone (3) has three pseudo-equatorial groups and one pseudo-axial.

Further convincing evidence for the assignment of the *cis*-configuration (3) to the more stable ketone was supplied by o.r.d. measurements. It has been shown [17] that the molecular amplitude of the Cotton effect exhibited by an optically active *cis*-2,2,3,5-cyclopentanone is greater than that of its *trans*-counterpart. The observed amplitudes of the *cis*-ketone (3) (+66·8) and the *trans*-ketone (1) (+50·8) confirm the assignment of their configurations. The corresponding *cis*- and *trans*-oxocyclopentaneacetic acids (27; β-Me, β-CH_2·CO_2H) and (27; α-Me, β-CH_2·CO_2H) show amplitudes of (+96) and (+27) respectively.[17]

A recent report [11] claims the formation of a 2,2,5-trimethyl-3-vinylcyclopentanone of unspecified configuration, by the isomerisation of the epoxide (32) with tin(IV) chloride. The n.m.r. data given [11] for the product agree with those obtained by us for the *trans*-ketone (1). There is, however, no obvious reason why the more stable *cis*-ketone (3) should not result under the reaction conditions employed, and indeed we find that brief treatment of the *trans*-ketone (1) with tin(IV) chloride in benzene gives an equilibrium mixture of the *trans*- and

[12] H. B. Henbest, *Proc. Chem. Soc.*, 1963, 159.
[13] H. B. Henbest and J. I. Wrigley, *J. Chem. Soc.*, 1957, 4596.
[14] C. S. Gibson, K. V. Hariharan, and J. L. Simonsen, *J. Chem. Soc.*, 1927, 3009.
[15] P. Hirsjarvi, *Ann. Acad. Sci. Fennicae* [A], 1952, **11**, 7.
[16] M. Harispe, D. Méa, A. Horeau, and J. Jacques, *Bull. Soc. chim. France*, 1963, 472.
[17] C. Ouannes and J. Jacques, *Bull. Soc. chim. France*, 1965, 3611.

cis-ketones in which the latter predominates. It is therefore not clear why the *cis*-ketone (3) apparently resulted from the isomerisation of (32).[11]

EXPERIMENTAL

I.r. spectra were measured for liquid films (L), Nujol mulls (N), or solutions in carbon tetrachloride. Unless otherwise stated n.m.r. spectra were measured for solutions in deuteriochloroform and optical rotations in carbon tetrachloride. O.r.d. measurements were made on solutions in ethanol with a JASCO instrument. Column chromatography was carried out on Merck silica gel (0·05—0·20 mm) with light petroleum containing varying quantities of ether as eluant.

(+)-α-2,3-Epoxypinane (7) was prepared by the peracetic acid oxidation of (+)-α-pinene ($[\alpha]_D^{20}$ +17° [*c* 2·76 in $CHCl_3$]) by the method used for the peroxidation of (+)-car-3-ene (*cf.* ref. 18). The epoxypinane had b.p. 29—31° at 0·25 mmHg, $[\alpha]_D^{21}$ +55° (*c* 0·2), n_D^{19} 1·4681.

Reaction of Ethereal Hydrogen Bromide with (+)-α-2,3-*Epoxypinane.* (−)-2-endo-*Bromo*-6-exo-*hydroxy*-1,3,3-*trimethylbicyclo*[2,2,1]*heptane* (5).—Hydrogen bromide was passed into an ice-cold solution of the epoxide (7) (33 g) in ether (200 ml) until the latter was saturated, and the mixture was kept at 0° for 12 h. It was added to ice (200 g), the organic layer was separated, and the aqueous phase was extracted with ether (2 × 100 ml). The extract was washed with water (3 × 200 ml) and with sodium hydrogen carbonate (5%; 2 × 100 ml), and dried. Removal of solvent gave a viscous oil which rapidly solidified; the product was crystallised twice from light petroleum giving (−)-2-*endo*-bromo-6-*exo*-hydroxy-1,3,3-trimethylbicyclo[2,2,1]heptane (5) (26 g) as needles, m.p. 114—115° (lit.,[4] 118—119°), $[\alpha]_D^{21}$ −6° (*c* 0·3), $\nu_{max.}$ (N) 3240, 2920, 2865, 1460, 1377, 1365, 1340, 1308, 1290, 1271, 1248, 1228, 1206, 1196, 1170, 1137, 1100, 1066, 1021, 997, 960, 943, 928, 914, 860, 790, and 723 cm^{-1}, τ 6·05 (1H, q, *J* 4 and 7 Hz, 6-H), 6·18 (1H, s, 2-H), 8·04 (1H, s, exch. D_2O, OH), and 8·88, 8·95, and 9·01 (each 3H, s, Me). Chromatography of the crude product (50 g) obtained from (7) (33 g) on silica gel (800 g) gave a clean separation into *p*-cymene (9) (2·5 g), (−)-2,2,3-trimethylcyclopent-3-enylacetaldehyde (10) (5 g), a mixture of (+)-pinocamphone (11) and (+)-isopinocamphone (12) (2·5 g), (−)-2-*endo*-bromo-6-*endo*-hydroxy-1,7,7-trimethylbicyclo[2,2,1]heptane (13) (10 g) and (−)-2-*endo*-bromo-6-*exo*-hydroxy-1,3,3-trimethylbicyclo[2,2,1]-heptane (5) (30 g), which were eluted in this order.

p-Cymene (9) was identified by i.r., n.m.r., and g.l.c. comparison with an authentic specimen.

(−)-2,2,3-Trimethylcyclopent-3-enylacetaldehyde (10) distilled as an oil, b.p. 32—33° at 0·15 mmHg, $[\alpha]_D^{21}$ −11° (*c* 0·2), n_D^{19} 1·4702, $\nu_{max.}$ 3020, 2950, 2708, 1724 (C=O), 1653 (C=C), 1460, 1442, 1408, 1383, 1360, 1298, 1284, 1210, 1170, 1137, 1117, 1086, 1032, 1018, 1006, 965, 943, 920, 820 (R_2C=CHR), and 802 cm^{-1}, τ 0·18 (1H, m, HC=O), 4·78 (1H, m, 4-H), 8·36 (3H, m, 3-Me), and 9·0 and 9·20 (each 3H, s, Me_2C).

The mixture of pinocamphones distilled as an oil, b.p. 46—48° at 1·1 mmHg, $[\alpha]_D^{21}$ +8° (*c* 0·4), identical (i.r., n.m.r., and g.l.c.) with an authentic mixture prepared from (+)-α-pinene.

(−)-2-endo-*Bromo*-6-endo-*hydroxy*-1,7,7-*trimethylbicyclo*[2,2,1]*heptane* (13) was obtained as a pale yellow solid which was distilled (b.p. 83—85° at 0·2 mmHg) and rechromatographed on silica; m.p. 110—111°, $[\alpha]_D^{21}$ −13° (*c* 0·2), $\nu_{max.}$ (N) 3550 (free OH), 3440 (intermolecularly bonded OH), 2945, 1452, 1391, 1374, 1291, 1260, 1205, 1160, 1121, 1063, 1035, 1020, 998, 966, 942, 920, 874, 842, 763, and 662 cm^{-1}, $\nu_{max.}$ (1·25% in CCl_4) 3560 cm^{-1} (sharp, OH), τ 5·4—6·0 (2H, overlapping ms, 2-H and 6-H), 7·01 (1H, s, exch. D_2O, OH), 8·21 (1H, t, *J* 5 Hz, 4-H), and 8·96, 9·07, and 9·12 (each 3H, s, Me) (Found: C, 51·8; H, 7·3. $C_{10}H_{17}BrO$ requires C, 51·5; H, 7·3%).

Conversion of (−)-2-endo-*Bromo*-6-endo-*hydroxy*-1,7,7-*trimethylbicyclo*[2,2,1]*heptane* (13) *into* (−)-2,2,3-*Trimethylcyclopent*-3-*enylacetaldehyde* (10).—The bromo-alcohol (0·5 g) in glacial acetic acid (5 ml) was heated on a water-bath for 1 h with silver acetate (0·5 g). The mixture was filtered through Celite, diluted with water, and extracted with ether. The product (10) (0·2 g), $[\alpha]_D^{20}$ −12° (*c* 0·2), was identical (i.r., n.m.r., and g.l.c.) with the aldehyde already described, obtained from (7).

Oxidation of (−)-2-endo-*Bromo*-6-endo-*hydroxy*-1,7,7-*trimethylbicyclo*[2,2,1]*heptane* (13). (−)-2-endo-*Bromo*-1,7,7-*trimethylbicyclo*[2,2,1]*heptan*-6-*one* (16).—The bromo-alcohol (0·5 g), in ether (10 ml), was stirred for 1 h at 20° with sodium dichromate dihyrate (0·35 g) in water (5 ml) containing sulphuric acid (0·24 ml). Ether (50 ml) was added and the organic layer was separated. It was washed with sodium hydrogen carbonate (5%; 3 × 10 ml) and water (2 × 10 ml) and dried. Removal of solvent gave (−)-2-*endo*-bromo-1,7,7-trimethylbicyclo[2,2,1]heptan-6-one (16) which crystallised as needles (from light petroleum), m.p. 130—131° (lit.,[4] 133—134°), $[\alpha]_D^{21}$ −20° (*c* 0·3), $\nu_{max.}$ (N) 2920, 2865, 1752 (C=O), 1458, 1419, 1393, 1378, 1324, 1296, 1243, 1219, 1192, 1055, 1012, 921, 860, 789, and 726 cm^{-1}, τ 5·78 (1H, q, *J* 4 and 10 Hz, 2-H), 9·03 (s, 2Me), and 9·10 (3H, s, Me).

Conversion of (−)-2-endo-*Bromo*-1,7,7-*trimethylbicyclo*-[2,2,1]*heptan*-6-*one* (16) *into* (−)-*Camphor* (18).—The bromo-ketone (0·1 g) was heated on a water-bath for 12 h with zinc dust (0·25 g) and acetic acid (5 ml), and the product was isolated with ether. The solvent was removed, the residue was distilled in steam, and the solid product was sublimed, giving (−)-camphor (18) (40 mg), m.p. 175—177°, $[\alpha]_D^{20}$ −25° (*c* 0·4), identical (i.r. and g.l.c.) with an authentic specimen of (+)-camphor.

(−)-trans-*Pinocarveol* (6).—This compound, b.p. 42—44° at 0·3 mmHg, $[\alpha]_D^{19}$ −32° (*c* 0·2), was prepared from (+)-α-2,3-epoxypinane (7) by a described route.[19]

Reaction of (−)-trans-*Pinocarveol* (6) *with Hydrogen Bromide.*—The alcohol (35 g), in ether (200 ml), was treated with hydrogen bromide as described for the similar reaction with (+)-α-2,3-epoxypinane (7). The mixture of products was chromatographed on silica gel (800 g), yielding *p*-cymene (9) (2 g), the aldehyde (10) (4 g), a mixture of pinocamphones (11 and 12) (2 g), the bromo-alcohol (13) (8 g), and the bromo-alcohol (5) (36 g), in this order of elution.

(−)-2,2,4-*Trimethylcyclopent*-3-*enylacetaldehyde* (4).—The bromo-alcohol (5) (12 g) was treated with silver acetate (12 g) in acetic acid (60 ml) as previously described,[4] giving the aldehyde (4) (7·4 g) as an oil, b.p. 35—36° at 0·5 mmHg, $[\alpha]_D^{21}$ −14° (*c* 0·2), n_D^{19} 1·4592, $\nu_{max.}$ (L) 3040, 2975, 2740, 1726 (C=O), 1659 (C=C), 1465, 1448, 1410, 1383, 1362, 1317,

[18] W. D. P. Burns, M. S. Carson, W. Cocker, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1968, 3073.

[19] J-P. Monthéard and Y. Chrétien-Bessière, *Bull. Soc. chim. France*, 1968, 336.

1283, 1262, 1210, 1172, 1128, 1108, 1080, 1040, 1000, 964, 950, 936, 880, and 830 (R_2C=CHR) cm^{-1}, τ (CCl_4) 0·34 (1H, m, HC=O), 4·95 (1H, m, 3-H), 7·66 (2H, m, 5-H), 8·37 (3H, m, 4-Me), and 8·99 and 9·20 (each 3H, s, Me_2C).

(−)-4-(2-*Hydroxyethyl*)-1,3,3-*trimethylcyclopentene* (21).—The aldehyde (4) (10 g) in ether (150 ml) was slowly treated with lithium aluminium hydride (1·3 g). After stirring for 0·5 h, a saturated solution of ammonium chloride was added and the product was collected in ether. The alcohol (21) was obtained as an oil (9 g), b.p. 53—54° at 0·1 mmHg, $[\alpha]_D^{21}$ −15° (*c* 0·2), n_D^{20} 1·4662, $\nu_{max.}$ (L) 3320 (OH), 3010, 2910, 1654 (C=C), 1442, 1379, 1360, 1312, 1207, 1160, 1128, 1058, 1038, 1018, 1006, 961, 918, 880, 827 (R_2C=CHR), and 761 cm^{-1}, τ 4·86br (1H, s, 2-H), 6·39 (2H, t, *J* 6·5 Hz, CH_2·OH), 7·93br (2H, m, 5-H), 8·0 (1H, s, exch. D_2O, OH), 8·38br (3H, s, 1-Me), and 9·0 and 9·19 (each 3H, s, Me_2C).

(−)-β-1,2-*Epoxy*-4β-(2-*hydroxyethyl*)-1,3,3-*trimethylcyclopentane* (22).—Hydrogen peroxide (100 vol.; 20 ml) was concentrated under reduced pressure to 8 ml and then added dropwise to ice-cold acetic anhydride (20 g) during 0·25 h. After being stirred for 1 h at 0° the mixture was added dropwise to an ice-cold solution of the alcohol (21) (6·5 g) in methylene chloride (100 ml) containing anhydrous sodium acetate (15 g). After 50 h at 0—10°, the mixture was added to ice and extracted with ether; the extract was washed with water, 5% sodium hydrogen carbonate, and water. The product (6·3 g), which contained (t.l.c.) one major and one minor component was chromatographed on silica. The *epoxide* (22) was obtained as a viscous oil, b.p. 81—83° at 0·3 mmHg, $[\alpha]_D^{21}$ −22° (*c* 0·2), $\nu_{max.}$ (L) 3370 (OH), 2940, 2870, 1464, 1428, 1385, 1379, 1367, 1308, 1245, 1126, 1081, 1056, 1030, 1008, 967, 950, 909, 879, and 840 (epoxide) cm^{-1}, $\nu_{max.}$ (1% in CCl_4) 3640, 3420br,s (bonded OH) cm^{-1}, τ 6·44 (2H, t, *J* 6·2 Hz, CH_2·OH), 7·13 (1H, s, 2-H), 7·27 (1H, s, exch. D_2O, OH), 8·59 (3H, s, 1-Me), and 8·98 and 9·24 (each 3H, s, Me_2C), *m/e* 170 (M^+). The minor product (0·1 g) eluted from the column before the epoxy-alcohol was found to be an epoxy-acetate, probably the acetate of (22). It was not further investigated.

(+)-cis-3-(2-*Hydroxyethyl*)-2,2,5-*trimethylcyclopentanone* (23).—A stirred solution of the epoxy-alcohol (22) (5 g) in anhydrous ether (250 ml) was treated at 0° with boron trifluoride–ether complex (15 ml) and the mixture was kept at 0° for 0·75 h. It was diluted with ether (200 ml), washed with saturated ammonium chloride solution, and dried. Removal of solvent gave a crude product (5 g), which was distilled yielding the *ketone* (23) (3·5 g, 70%) as an oil, b.p. 92—94° at 0·2 mmHg, $[\alpha]_D^{21}$ +7·0° (*c* 0·2), $\nu_{max.}$ 3415 (OH), 2960, 2940, 2875, 1734 (C=O), 1460, 1380, 1326, 1295, 1250, 1208, 1180, 1125, 1074, 1055, 1016, 969, 953, 905, and 881 cm^{-1}, τ 6·27 (2H, t, *J* 6 Hz, CH_2·OH), 8·1 (1H, s, exch. D_2O, OH), 8·9 (3H, d, *J* 6 Hz, 5-Me), and 8·97 and 9·14 (each 3H, s, Me_2C), *m/e* 170 (M^+).

(±)-cis-3-(2-*Hydroxyethyl*)-2,2,5-*trimethylcyclopentanone* [*Racemic Form of* (23)]. *Diethyl* (±)-4,4-*Dimethyl*-5-*oxocyclopentane*-1,3-*dicarboxylate* (24).—Ethyl 2,3-dicyano-3-methylbutyrate [$\nu_{max.}$ (L) 2975, 2920, 2225 (CN), 1743 (ester), 1460, 1394, 1365, 1320, 1252, 1200, 1146, 1122, 1090, 1020, 945, 935, and 845 cm^{-1}] was prepared by the published method.[20] It was condensed with acrylonitrile, hydrolysed, and re-esterified giving diethyl 3-ethoxycarbonyl-2,2-dimethyladipate as an oil, b.p. 142—144° at 0·6 mmHg, $\nu_{max.}$ (L) 2985, 1735 (ester), 1455, 1445, 1370, 1300, 1250, 1170, 1126, 1097, 1030, 922, 862, and 775 cm^{-1}. A forerun was identified as diethyl 2,2-dimethylsuccinate (*cf.* ref. 21), b.p. 67—69° at 0·6 mmHg, n_D^{19} 1·4218, $\nu_{max.}$ (L) 2995, 1734 (ester), 1472, 1445, 1386, 1368, 1342, 1304, 1256, 1212, 1182, 1148, 1130, 1097, 1034, 950, 863, and 776 cm^{-1}, τ (C_6H_6) 5·99 (2H, q, *J* 7 and 12·3 Hz, O·CH_2·CH_3), 6·08 (2H, q, *J* 7 and 12·3 Hz, O·CH_2·CH_3), 7·54 (2H, s, CH_2), 8·79 (6H, s, Me_2C), 8·97 (3H, t, *J* 7 Hz, CH_2·CH_3), and 9·0 (3H, t, *J* 7 Hz, CH_2·CH_3). Diethyl 3-ethoxycarbonyl-2,2-dimethyladipate was cyclised according to the published procedure,[14] except that toluene was used as solvent, giving the diester (24) as an oil, b.p. 124—126° at 0·5 mmHg, $\nu_{max.}$ (L) 2945, 1747, 1718, 1655 (enol?), 1610, 1458, 1360, 1340, 1323, 1292, 1270, 1246, 1194, 1145, 1088, 1057, 1034, 1010, 968, 920, 894, 856, and 776 cm^{-1}. It gave a strong purple colour reaction with iron(III).

(±)-2,2,4-*Trimethyl*-3-*oxocyclopentane*-1-*carboxylic Acid* (25).—The keto-ester (24) (25·6 g) in ethanol (20 ml) was added dropwise during 0·25 h to an ice-cold solution of sodium (2·3 g) in ethanol (250 ml). After 10 min, methyl iodide (15 g) in ethanol (20 ml) was slowly added; the mixture was kept at 0° for 12 h and then refluxed for 2 h. It was added to ice (200 g), the product was extracted with ether (3 × 150 ml), the extract was washed with water (3 × 100 ml) and dried, and the solvent was removed giving diethyl 1,4,4-trimethyl-5-oxocyclopentane-1,3-dicarboxylate as a yellow oil (22 g), $\nu_{max.}$ (L) 2960, 1747, 1730, 1460, 1370, 1346, 1290, 1264, 1217, 1186, 1117, 1090, 1050, 1013, 950, 898, 886, 858, 810, 780, and 726 cm^{-1}. It gave no colour with iron(III). The crude diester was refluxed for 8 h with sulphuric acid (5%; 500 ml), the cooled solution was extracted with ether (4 × 100 ml), and the extract was washed with water and dried. Removal of solvent gave the acid (25) as an oil (13 g) which quickly solidified. It crystallised from light petroleum as needles, m.p. 63—64° (lit.,[15] 61—63°), $\nu_{max.}$ (N) 3020, 2900, 2830, 1728 (keto), 1700 (CO_2H), 1453, 1396, 1370, 1278, 1246, 1194, 1166, 1133, 1075, 1032, 1004, 981, 894, 860, 786, 765, 730, and 670 cm^{-1}, τ 8·73 (3H, s, *gem*-Me), 8·82 (1H, d, *J* 7 Hz, *trans*-4-Me), 8·87 (2H, d, *J* 7 Hz, *cis*-4-Me), and 9·04 (3H, s, *gem*-Me). The 4-methyl signals correspond roughly to 33% *trans*- and 67% *cis*-isomers.

(±)-*Methyl* 2,2,4-*Trimethyl*-3-*oxocyclopentylacetate* (26).—The acid (25) (3·5 g) was refluxed for 1 h with thionyl chloride (6 ml). Excess of thionyl chloride was removed in a vacuum and the resulting acid chloride was dissolved in anhydrous ether (15 ml). This solution was added dropwise to a stirred, ice-cold solution of diazomethane [from nitrosomethylurea (7 g)] in anhydrous ether (100 ml). The resulting mixture was kept at 0° for 0·5 h and then at room temperature for 12 h. The solvent and excess of diazomethane were removed, giving the crude diazo-ketone as a yellow syrup. Dissolved in dry methanol (60 ml), it was treated with a slurry of freshly prepared silver oxide (2 g) in methanol (5 ml); the mixture was refluxed for 4 h, boiled with charcoal (0·5 g) for 10 min, and filtered through Celite. The solvent was removed by distillation and the pale yellow residue was chromatographed on silica gel (150 g), giving (*a*) the methyl ester of the keto-acid (25) (0·2 g) followed by (*b*) the required (±)-*methyl* 2,2,4-*trimethyl*-3-*oxocyclopentylacetate* (26) (1·5 g), as an oil, b.p. 69—71° at

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[21] G. Stork and F. H. Clarke, *J. Amer. Chem. Soc.*, 1961, **83**, 3114.

0·25 mmHg, $\nu_{max.}$ (L) 2980, 2960, 1738 (ketone and ester), 1460, 1438, 1384, 1362, 1337, 1298, 1255, 1220, 1200, 1168, 1136, 1063, 1042, 1005, and 900 cm^{-1}, τ 6·33 (3H, s, MeO), 8·86 (3H, d, J 6 Hz, 4-Me), 8·96 (3H, s, *gem*-Me), 9·11 (1H, s, *gem*-Me), and 9·20 (2H, s, *gem*-Me) [the signals at τ 9·11 and 9·20 are derived from *trans*- (33%) and *cis*- (67%) isomers in a mixture], *m/e* 198 (M^+) (Found: C, 66·8; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%).

(+)-*Methyl* 2,2,4-*Trimethyl*-3-*oxocyclopentylacetate* (26).—(−)-2,2,4-Trimethylcyclopent-3-enylacetaldehyde (4) (1 g) in tetrahydrofuran (25 ml) was slowly treated with diborane [generated from sodium borohydride (2 g) and boron trifluoride–ether complex (6 ml) in diglyme (20 ml)], carried in a stream of nitrogen. After stirring for 1 h at 20°, sodium hydroxide (3M; 5 ml) was added dropwise, followed by hydrogen peroxide (100 vol.; 5 ml). After 1 h, the mixture was diluted with water (50 ml) and extracted with ether (3 × 50 ml); the extract was dried and the solvent was removed under reduced pressure giving a viscous oil (1 g). This, in ether (20 ml), was stirred for 1 h with a mixture of sodium dichromate dihydrate (2·8 g), water (40 ml), and sulphuric acid (1·9 ml). Work-up gave the crude keto acid as a syrup, which was methylated with diazomethane giving the *ester* (0·5 g),[16] b.p. 68—70° at 0·2 mmHg, $[\alpha]_D^{19}$ +7° (*c* 0·2), identical (i.r. and n.m.r.) with the racemic ester already described.

Methyl (±)-2,2,4-*Trimethyl*-3-*oxocyclopentane*-1-*carboxylate*.—Esterification of the racemic acid (25) in ether with diazomethane gave the ester as an oil, $\nu_{max.}$ (L) 2975, 2890, 1738, 1460, 1438, 1364, 1260, 1238, 1214, 1177, 1142, 1127, 1086, 1044, 1027, 1000, 986, 952, 934, 894, 810, 787, and 748 cm^{-1}, identical with the product already mentioned under (*a*).

(±)-2,2,4-*Trimethyl*-3-*oxocyclopentylacetic Acid* (27).—The methyl ester (26) (1 g) was refluxed for 2 h with methanolic potassium hydroxide (10%; 20 ml); the mixture was then diluted with water (100 ml) and the product was extracted with ether. The acid was obtained as a gum.

(±)-cis-3-(2-*Hydroxyethyl*)-2,2,5-*trimethylcyclopentanone* [*Racemic Form of* (23)].—The acid (27) (0·7 g) in tetrahydrofuran (20 ml) was slowly treated at 0° with a saturated solution of diborane in tetrahydrofuran (15 ml). After 10 min the mixture was treated with sodium hydroxide (3M; 40 ml) and stirring was continued for 1 h. The mixture was diluted with water (100 ml) and the product was collected in ether. The crude product (23) (0·4 g) was chromatographed on silica gel giving the racemic form of the keto-alcohol (23) (0·3 g) as an oil which was identical in spectra with the optically active form already described.

(+)-*Fenchone* (30).—Freshly distilled thionyl chloride (1 ml) was added dropwise to (+)-*cis*-3-(2-hydroxyethyl)-2,2,5-trimethylcyclopentanone (23) (0·5 g) in dry pyridine (5 ml). After 20 min, water (20 ml) was added, and the mixture was extracted with ether (3 × 20 ml). The extract was washed with hydrochloric acid (2%; 3 × 20 ml) and water (3 × 20 ml), dried, and evaporated, giving the chloro-ketone (29) (0·5 g) as a pale yellow oil, $\nu_{max.}$ (L) 2960, 2875, 1735 (C=O), 1460, 1385, 1370, 1291, 1250, 1208, 1072, 1010, 990, 942, 906, 882, 835, 808, and 721 cm^{-1}. The crude chloro-ketone, in ethanol (2 ml) was added slowly to a stirred solution of sodium (0·1 g) in ethanol (3 ml); the mixture was set aside for 4 h, diluted with water (20 ml), and extracted with ether (3 × 15 ml). Removal of solvent gave an oil which was chromatographed on silica gel (10 g), yielding (+)-fenchone (30) (0·2 g), $[\alpha]_D^{21}$ +48° (*c* 0·2), n_D^{20} 1·4618, $\nu_{max.}$ (L) 2965, 2885, 1740 (C=O), 1460, 1385, 1363, 1337, 1316, 1292, 1268, 1240, 1214, 1170, 1156, 1107, 1072, 1017, 1002, 995, 960, 946, 936, 894, 836, and 824 cm^{-1}, τ 8·88 (3H, s, Me) and 8·98 (6H, s, 2Me). A more polar, chlorine-free fraction (40 mg), probably resulting from displacement of the chloro-substituent by ethoxide was also obtained [$\nu_{max.}$ (L) 1730 (C=O) and broad absorption in the 1100—1200 cm^{-1} range] but it was not further investigated.

(+)-cis-3-(2-*Acetoxyethyl*)-2,2,5-*trimethylcyclopentanone* (28).—The keto-alcohol (23) (5 g) was dissolved in pyridine (20 ml), acetic anhydride (5 g) was added, and the mixture was set aside for 5 h. Water (100 ml) was added, the mixture was extracted with ether (3 × 100 ml), the extract was washed with water (5 × 100 ml) and dried, and the solvent was removed. The crude product (5·1 g) was distilled giving the *acetate* (28) as an oil, b.p. 90—92° at 0·2 mmHg, $[\alpha]_D^{21}$ +7° (*c* 0·2), n_D^{22} 1·4537, $\nu_{max.}$ (L) 2965, 2880, 1735, 1460, 1368, 1240, 1042, 905, and 806 cm^{-1}, τ 5·85 (2H, t, J 6·5 Hz, CH_2·OAc), 7·96 (3H, s, O·COMe), 8·89 (3H, d, J 6 Hz, 5-Me), and 8·98 and 9·13 (each 3H, s, Me_2C), *m/e* 212 (M^+).

Pyrolysis of the Acetate (28). (+)-cis-2,2,5-*Trimethyl*-3-*vinylcyclopentanone* (3).—The acetate (5 g) was introduced into an S-shaped empty glass column (160 cm × 4 mm) heated at 480°. The liquid was rapidly vaporised and carried forward in a stream of nitrogen. Condensation of the effluent yielded a red oil which was collected in ether (20 ml), washed with sodium hydrogen carbonate solution (5%; 4 × 20 ml), and dried. Removal of solvent gave a crude product (3 g) of 80% purity (g.l.c.). Chromatography on silica gel (30 g) gave (+)-cis-2,2,5-*trimethyl*-3-*vinylcyclopentanone* (3) (2 g) as an oil contaminated with its *trans*-isomer (1) (10%) (n.m.r.), $[\alpha]_D^{22}$ +25° (*c* 0·2), n_D^{21} 1·4540, $\nu_{max.}$ (L) 3080, 2960, 2875, 1736, 1640, 1460, 1424, 1380, 1362, 1317, 1280, 1240, 1198, 1162, 1130, 1100, 1068, 1030, 1019, 1000, 978, 919, 896, 800, and 720 cm^{-1}, τ (CCl_4) 4·3 (1H, m, C*H*=CH_2), 4·85br (1H, s, vinyl H *trans* to ring), 5·06 (1H, m, vinyl H *cis* to ring), 8·86 (3H, d, J 7 Hz, 5-Me) and 9·00 and 9·26 (each 3H, s, Me_2C) [the highest field methyl signal for the *trans*-isomer (see later) occurred at τ 9·18, all the other signals being virtually coincident], *m/e* 152 (M^+).

Epimerisation of the Photoproduct (1) *from* (−)-cis-*Caran*-4-*one* (2).—(−)-*cis*-Caran-4-one (2), $[\alpha]_D^{20}$ −140° (*c* 0·2), n_D^{19} 1·4683, was prepared as described previously.[22] After photolysis,[3] (+)-*trans*-2,2,5-trimethyl-3-vinylcyclopentanone (1), was obtained pure by a single passage of the product through silica gel. It had $[\alpha]_D^{19}$ +40° (*c* 0·2), n_D^{19} 1·4553, $\nu_{max.}$ (L) 3019, 2980, 1895, 1739, 1642, 1463, 1422, 1384, 1294, 1260, 1204, 1170, 1152, 1136, 1070, 1023, 1004, 980, 921, 880, and 978 cm^{-1}, τ (CD_3·OD) 4·16 (1H, m, *H*C=CH_2), 4·81 (1H, m, vinyl H *trans* to ring), 5·03 (1H, m, vinyl H *cis* to ring), 8·93 (3H, d, J *ca.* 7 Hz, 5-Me), and 9·01 and 9·18 (each 3H, s, Me_2C). This ketone (1) (0·12 g), in methanol (0·5 ml) was added to a solution of sodium (30 mg) in methanol (3 ml). After 10 min the mixture was diluted with water and worked up in the usual way, giving (+)-*cis*-2,2,5-trimethyl-3-vinylcyclopentanone (3) (0·1 g), $[\alpha]_D^{20}$ +52° (*c* 0·2), identical in spectra with the synthetic product already described.

(−)-trans-*Caran*-4-*one* (31).—This was obtained as

[22] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.* (*C*), 1967, 485.

follows (*cf.* refs. 23 and 24). (+)-α-3,4-Epoxycarane [18] (24 g) was gradually added to a solution of aluminium chloride (13·8 g) and lithium aluminium hydride (1·2 g) [25] in dry ether and the mixture was refluxed for 3 h. It was worked up in the usual way giving (g.l.c.) (−)-*cis*-caran-*trans*-3-ol (60%) and (−)-*trans*-caran-*trans*-4-ol (40%). The mixture of alcohols, in ether (100 ml), was stirred for 1 h at 0° with sodium dichromate dihydrate (7 g) in water (100 ml) and sulphuric acid (5 ml), poured into water, and extracted with ether. Removal of solvent from the washed and dried extract gave (g.l.c.) a mixture of (+)-*cis*-caran-*trans*-3-ol (60%), (−)-*trans*-caran-*trans*-4-ol (5%), and (−)-*trans*-caran-4-one (31) (35%). The mixture was chromatographed on silica gel, giving the pure ketone (31) as an oil, $[\alpha]_D^{20}$ −75° (*c* 0·1) (*cf.* refs. 23 and 24), n_D^{19} 1·4705, $\nu_{max.}$ (L) 2946, 1717 (C=O), 1460, 1410, 1380, 1330, 1300, 1242, 1138, 1084, 1042, 1017, 986, and 960 cm^{-1}, τ 8·77 (3H, d, *J* 7 Hz, 3-Me) and 8·93 and 9·08 (each 3H, s, Me_2C). The initial mixture of alcohols obtained from the epoxycarane when subjected to preparative g.l.c. on a 3 m × 9·5 mm Carbowax 20M column at 155 °gave (+)-*cis*-caran-*trans*-3-ol, m.p. 32—33°, $[\alpha]_D^{20}$ +31·6° (*c* 0·24) (lit.,[23] m.p. 32°, $[\alpha]_D^{20}$ +21·4°), $\nu_{max.}$ (N) 3420, 2948, 2880, 1463, 1377, 1270, 1222, 1148, 1129, 1074, 1060, 1018, 975, 958, 942, 921, 900, 861, and 790 cm^{-1}, τ 8·23 (s, exch. D_2O, OH), 8·85, 9·0, and 9·11 (each 3H, s, Me), and 9·2—9·5 (2H, overlapping ms, 1-H and 6-H); and (−)-*trans*-caran-*trans*-4-ol, $[\alpha]_D$ −16° (*c* 0·25) (lit.,[23] −13·8)°, $\nu_{max.}$ (L) 3360, 2940, 1455, 1390, 1377, 1324, 1212, 1140, 1121, 1067, 1053, 1035, 1006, 986, 963, 940, 928, 870, 823, 790, and 760 cm^{-1}, τ 6·47 (1H, m, 4-H), 8·23 (s, exch. D_2O, OH), 8·99 (3H, s, *gem*-Me), 9·08 (3H, d, *J* 5·5 Hz, 3-Me), 9·10 (3H, s, *gem*-Me), and 9·25—9·55 (2H, overlapping ms, 1-H and 6-H).

Photolysis of (−)-trans-*Caran-4-one* (31).—This was irradiated under similar conditions to those described for the photolysis of (2).[3] Comparative kinetic studies indicated that the rates of isomerisation of the *cis*- (2) and *trans*- (31) ketones were in the ratio 1 : 3. (+)-*cis*-2,2,5-Trimethyl-3-vinylcyclopentanone (3) was isolated by chromatography on silica gel as an oil, $[\alpha]_D^{20}$ +56·2° (*c* 0·26), n_D^{20} 1·4540. Its i.r. and n.m.r. spectra were coincident with those of the synthetic specimen. The $[\alpha]_D$ value of the *cis*-ketone (3), obtained by photolysis of *trans*-caran-4-one (31) and by epimerisation of the *trans*-ketone (1) obtained by photolysis of *cis*-caran-4-one (2), is higher than that of the product obtained by pyrolysis of (28). This results from differences in the optical purity of the car-3-ene and pinene employed as starting materials.

O.r.d. Measurements.—Measurements were made on the *trans*- (1) and *cis*- (3) cyclopentanones in ethanolic solutions at *c* 0·15 and 0·25 respectively, giving the following results: *trans*-ketone (1) $[\phi]_{360}$ +500°, $[\phi]_{322}$ +2280°pk, $[\phi]_{310}$ +1000°, $[\phi]_{304}$ 0°, $[\phi]_{300}$ −1000°, $[\phi]_{290}$ −2400°, $[\phi]_{280}$ −2800°tr, and $[\phi]_{260}$ −2200° (*a* +50·8); *cis*-ketone (3) $[\phi]_{360}$ +750°, $[\phi]_{323}$ +3300°pk, $[\phi]_{308}$ +750°, $[\phi]_{305}$ 0°, $[\phi]_{300}$ −1350°, $[\phi]_{290}$ −3075°, $[\phi]_{283}$ −3375°tr, and $[\phi]_{260}$ −2400° (*a* +66·7).

Epimerisation of (+)-trans-2,2,5-*Trimethyl*-3-*vinylcyclopentanone* (1) *with Tin*(IV) *Chloride.*—The ketone (50 mg) in benzene (2 ml) was stirred for 0·5 h with tin(IV) chloride (20 mg) and the mixture was then diluted with water. The product, collected in ether, gave an oil (40 mg), $[\alpha]_D^{19}$ +50° (*c* 0·2) containing (i.r.) both (1) and (3). The specific rotation suggests that the composition of the mixture is *cis*-ketone (63%) and *trans*-ketone (37%). The i.r. spectrum of the mixture is similar to that of the *cis*-ketone except that peaks at 1240, 1100, and 1000 cm^{-1} are less intense than in the spectrum of the pure compound.

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