The Chemistry of Terpenes. Part XI.[1] Volatile Products of the Photolysis of (+)-*cis*-Caran-5-one

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Irradiation of (+)-*cis*-caran-5-one in ether, through quartz, affords the following volatile products: (−)-*cis*-*m*-menth-8-en-5-one, (−)-*cis*-*m*-menthan-5-one, (−)-*m*-menth-3-en-5-one, (−)-*cis*-*m*-menthan-*cis*-5-ol, (−)-*cis*-*m*-menthan-*trans*-5-ol, and *cis*-*m*-menth-8-en-*cis*-5-ol. In n-hexane, even after considerable periods of irradiation, only the three ketones are formed, and in benzene, (−)-*m*-menth-3-en-5-one is the sole volatile product.

IRRADIATION of caran-2-one (I) gives *p*-menth-3-en-2-one (II), as the main product, and 3,3-dimethylocta-4,6-dienal (III).[2] (−)-*cis*-Caran-4-one (IV) similarly affords (+)-*trans*-1,1,3-trimethyl-5-vinylcyclopentan-2-one (V)[3,4] and a mixture of *cis*- and *trans*-2-(1,1-dimethylallyl)-4-methylcyclobutanone (VI).[3]

In furtherance of our studies of the chemistry of the carenes and their derivatives we have irradiated solutions in ether, n-hexane, and benzene of (+)-*cis*-caran-5-one (VII) in quartz glass vessels. In ether, three volatile ketones were formed: (−)-*cis*-*m*-menth-8-en-5-one (VIIIa) in up to 37% yield,† its dihydro-derivative, (−)-*cis*-*m*-menthan-5-one (VIIIb), and (−)-*m*-menth-3-en-5-one (IX). Three volatile alcohols: (−)-*cis*-*m*-menthan-*cis*-5-ol (Xa), (−)-*cis*-*m*-menthan-*trans*-5-ol (Xb), and *cis*-*m*-menth-8-en-*cis*-5-ol (Xc), were identified. There was some g.l.c. evidence for the existence of very minor amounts of *cis*-*m*-menth-8-en-*trans*-5-ol (Xd) in the photolysis mixture. The composition of the photolysis mixture after different periods of irradiation is expressed in the Figure. Unidentified non-volatile products (32%) † were also formed. On g.l.c. the volatile compounds were eluted in the order (VIIIb), (VIIIa), (Xb), unchanged (+)-*cis*-caran-5-one (VII), (Xa), (IX), and (Xc).

In n-hexane, after irradiation for 30 hr., the volatile products were entirely ketonic, consisting of unchanged (+)-*cis*-caran-5-one (VII) (66%), (−)-*cis*-*m*-menth-8-en-5-one (VIIIa) (13%), (−)-*cis*-*m*-menthan-5-one (VIIIb) (12%), and (−)-*m*-menth-3-en-5-one (IX) (9%). Non-volatile unidentified compounds (11%) were also formed. In benzene, after the same period, the only volatile compounds present were (−)-*m*-menth-3-en-5-one (IX) (32%) and the starting material (VII). Non-volatile, unidentified compounds (8%) were also present.

3,3,6-Trimethylhepta-4,6-dienal (XI) was not found (*cf.* ref. 2) after irradiation of (VII) in any of the three solvents.

In most cases, the components of the mixtures of photoproducts were separated by preparative g.l.c., and identified spectroscopically and by analytical g.l.c. comparison with authentic components prepared by other routes.

The products formed from the irradiation of (+)-*cis*-caran-5-one in ether were extensively investigated, and the products formed in n-hexane and benzene were compared with them. We only describe here our work

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† The yields of volatile products are expressed as percentages of the total volatile products, including recovered starting material. The non-volatile substances are expressed as percentages of starting material.

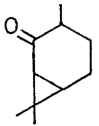
[1] (*a*) Preliminary communication, *Chem. Comm.*, 1969, 726; (*b*) Part X, M. S. Carson, W. Cocker, D. H. Grayson, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1969, 2220.

[2] W. G. Dauben and G. W. Shaffer, *Tetrahedron Letters*, 1967, 4415.

[3] D. C. Heckert and P. J. Kropp, *J. Amer. Chem. Soc.*, 1968, **90**, 4911.

[4] M. S. Carson, W. Cocker, S. M. Evans, and P. V. R. Shannon, *Tetrahedron Letters*, 1968, 6153.

on the irradiations in ether. The mixed photoproduct consisting of alcohols and ketones was oxidised by Brown and Garg's method,[5] giving the three ketones (VIIIa), (VIIIb), and (IX), as well as unchanged caranone, the close relationship of the alcohols and ketones thus being established.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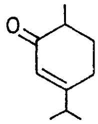
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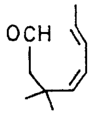

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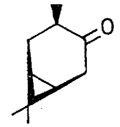
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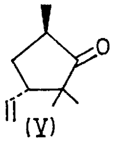
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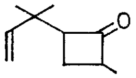
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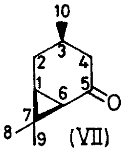

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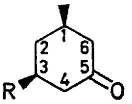
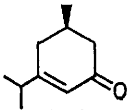


(VIII)

a; $R = CMe{=}CH_2$
b; $R = CHMe_2$
c; $R = CMe_2{\cdot}OEt$
d; $R = CMe_2{\cdot}OH$
e; $R = CMe_2Cl$
f; $R = CMe_2{\cdot}OAc$
g; $R = CMe_2{\cdot}CHO$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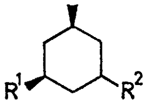
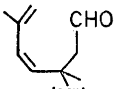
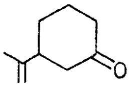


(X)

a; $R^1 = CHMe_2$, $R^2 = \beta$-OH
b; $R^1 = CHMe_2$, $R^2 = \alpha$-OH
c; $R^1 = CMe{=}CH_2$, $R^2 = \beta$-OH
d; $R^1 = CMe{=}CH_2$, $R^2 = \alpha$-OH
e; $R^1 = CHMe_2$, $R^2 = \beta$-OEt
f; $R^1 = CHMe_2$, $R^2 = \alpha$-OEt



(XI)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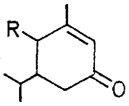
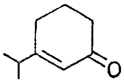


(XIII)

a; $R = CO_2Et$
b; $R = H$


(XIV)

(—)-*cis-m*-Menth-8-en-5-one (VIIIa), the principal photoproduct, showed i.r. maxima at 3067 ($C{=}CH_2$), 1712 (C=O), 1645 (C=C), and 890 ($C{=}CH_2$) cm.$^{-1}$; its n.m.r. spectrum (carbon tetrachloride) showed signals at τ 5·2 (s, $C{=}CH_2$), 7·76 (m, $CH_2{\cdot}CO{\cdot}CH_2$), 8·25 (s, MeC=C), and 8·95 (d, *J* 6 Hz, MeC). These spectra are similar to those of 3-isopropenylcyclohexanone (XII).[6] The photoproduct (VIIIa) exchanged four protons when treated with sodium deuteroxide in tetradeuteriomethanol, thus establishing the environment of its keto-group.

Hydrogenation of the principal photoproduct (VIIIa) over palladised charcoal gave the second photoproduct, (—)-*cis-m*-menthan-5-one (VIIIb) as the sole product. This ketone showed an i.r. maximum at 1718 cm.$^{-1}$ (C=O), and n.m.r. signals at τ 7·6—8·8 (9H), 8·98 (d, *J* 6 Hz, MeC), and 9·09 (d, *J* 6 Hz, Me_2C). It was identical (g.l.c. and i.r. and n.m.r. spectra) with (±)-*m*-menthan-5-one obtained when (±)-*m*-menth-6-en-5-one (XIIIb) was reduced over palladised charcoal.[7]

The third ketonic product, (—)-*m*-menth-3-en-5-one (IX) was never isolated pure from the photochemical reaction; it was always contaminated with about 30% of the minor photoproduct, *cis-m*-menth-8-en-*cis*-5-ol (Xc). However, the unsaturated ketone (IX) was obtained pure by an alternative method (see later). It showed u.v. maxima at 234 (log ε 4·05) and 310 (1·6) nm., and i.r. maxima at 1664 (C=C–C=O), 1621 (C=C), and 890 cm.$^{-1}$. The spectra are similar to those of (±)-*m*-menth-6-en-5-one (XIIIb) (*cf.* ref. 7) (see Experimental section), and those of 3-isopropylcyclohex-2-en-one (XIV).[6] (—)-*m*-Menth-3-en-5-one (IX) and (±)-*m*-menth-6-en-5-one (XIIIb) show a strong i.r. peak at 880—890 cm.$^{-1}$, whereas (±)-ethyl -5-oxo-*m*-menth-6-en-2-carboxylate (XIIIa) (see later) lacks this maximum, which is normally associated with the $C{=}CH_2$ group. The n.m.r. spectrum of (—)-*m*-menth-3-en-5-one (IX) displayed signals at τ 4·28 (s, C=CH), 7·3—8·4 (6H), and 8·87 (d, *J* 6 Hz, 3 × Me).

Reduction of the unsaturated ketone (IX) over palladised charcoal gave (—)-*cis-m*-menthan-5-one (VIIIb) as the only product, identical with the corresponding photoproduct. We have confirmed that (±)-*m*-menth-6-en-5-one (XIIIb) is reduced over palladised charcoal to a single product, (±)-*cis-m*-menthan-5-one.[7] Thus the hydrogenation product of (—)-*m*-menth-3-en-5-one (IX) probably has the *cis*-configuration (VIIIb) also. When the mixture of ketonic photoproducts was hydrogenated over palladised charcoal, the sole product was (VIIIb).

Independent support for the identities of the three ketonic photoproducts, (VIIIa and b) and (IX) was obtained as follows. Treatment of (+)-*cis*-caran-5-one (VII) with boron trifluoride–ether complex afforded (—)-*m*-menth-3-en-5-one (IX) in 98% yield, and the other unsaturated ketonic photoproduct, (—)-cis-*m*-menth-8-en-5-one (VIIIa). Treatment of the latter with boron trifluoride gives (—)-*m*-menth-3-en-5-one (IX) almost quantitatively, in a reaction analogous to the conversion of dihydrocarvone into carvenone by the same reagent.[8] Reaction of (+)-*cis*-caran-5-one (VII) with boron trifluoride–ether complex in ethanol gave (—)-8-ethoxy-*cis-m*-menthan-5-one (VIIIc). With 50% sulphuric acid, (+)-*cis*-caran-5-one gave the ketol, 8-hydroxy-*cis-m*-methan-5-one (VIIId) in the greater yield, and (—)-*m*-menth-3-en-5-one (IX). However, with concentrated hydrochloric acid, or (better) with hydrogen chloride in ether, the product was (+)-8-chloro-*cis-m*-menthan-5-one (VIIIe).

We portray these acid-catalysed reactions as shown in Scheme 1, though the free carbonium ion may not exist. Synchronous reactions may be involved in forming (VIIIa, c, d and e).

Reduction of (+)-*cis*-caran-5-one (VII) with lithium in liquid ammonia, gave a mixture of ketone and alcohol

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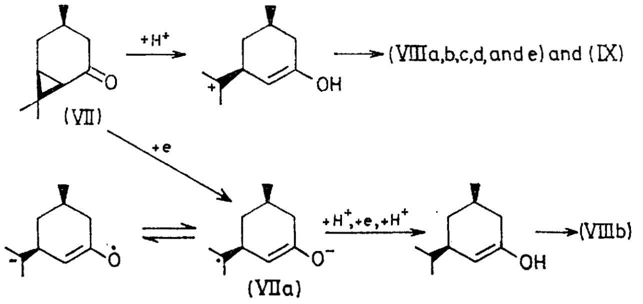
[5] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

[6] H. O. House, R. A. Latham and C. D. Slater, *J. Org. Chem.*, 1966, **31**, 2667.

[7] E. L. Eliel and F. J. Biros, *J. Amer. Chem. Soc.*, 1966, **88**, 3334.

[8] J. C. Fairlie, G. L. Hodgson, and T. Money, *Chem. Comm.*, 1969, 1196.

which on oxidation afforded (—)-*cis*-*m*-menthan-5-one (VIIIb) as the sole product. The reduction can be formally expressed as in Scheme 1.



SCHEME 1

The chloro-ketone (VIIIe) showed u.v. maxima at 285 nm. (log ε 1·25) and i.r. peaks at 1715 (C=O) and 817 (C–Cl) cm.$^{-1}$. Its n.m.r. spectrum (carbon tetrachloride) displayed signals at τ 7·5—8·7 (8H), 8·40 and 8·46 (two s, Me_2C), and 8·9 (d, *J* 5 Hz, MeC). Its configuration was established by its quantitative reconversion with methanolic potassium hydroxide, into (+)-*cis*-caran-5-one (VII). Stirred with zinc and acetic acid, the chloro-ketone gave a mixture of (—)-*cis*-*m*-menth-8-en-5-one (VIIIa), (—)-*cis*-*m*-menthan-5-one (VIIIb), (—)-*m*-menth-3-en-5-one (IX) and, predominantly, (+)-8-acetoxy-*cis*-*m*-menthan-5-one (VIIIf). The acetoxy-ketone had i.r. maxima at 1738 (Ac), 1720 (C=O), and 1250 (C–O) cm.$^{-1}$, and it displayed n.m.r. signals at τ 7·5—8·7 (8H), 8·07 (s, Ac), 8·57 (s, Me_2C), and 8·9 (d, *J* 5 Hz, MeC). With zinc and formic acid, the chloro-ketone gave six compounds (g.l.c.), the principal product being (+)-8-formyloxy-*cis*-*m*-menthan-5-one (VIIIg). When heated with sodium iodide in acetone, the chloro-ketone gave (t.l.c. and i.r. spectrum) *m*-menth-3-en-5-one (IX) as the principal product, together with a number of minor products.

The formation of the two ketonic photoproducts, (VIIIb) and (IX), from the chloro-ketone (VIIIe) supports their structures.

We now consider the alcoholic photoproducts, (—)-*cis*-*m*-menthan-*cis*-5-ol (Xa), (—)-*cis*-*m*-menthan-*trans*-5-ol (Xb), and *cis*-*m*-menth-8-en-*cis*-5-ol (Xc). Their close relationship with the ketonic photoproducts has already been established (see before). Reduction of (—)-*cis*-*m*-menthan-5-one (VIIIb) with lithium aluminium hydride afforded two alcohols, one of them in 97% yield. In view of the nature of the reducing agent this must be the more stable (—)-*cis*-*m*-menthan-*cis*-5-ol (Xa). The minor alcohol must be its 5-epimer (Xb). These alcohols were identical (g.l.c. and i.r. spectrum) with the corresponding photoproducts.

The structures of the two alcohols (Xa) and (Xb) were confirmed as follows. (±)-*cis*-*m*-Menthan-5-one (see before)[7] was reduced with platinised charcoal in alcohol, giving a mixture of (±)-*cis*-*m*-menthan-*cis*-5-ol and its 5-epimer in the ratio 55 : 45. Earlier workers[7] found that Adams catalyst in acetic acid gave these alcohols in the ratio 65·5 : 35·5. They were identical (g.l.c.) with the photoproducts (Xa) and (Xb) and with the lithium aluminium hydride reduction products of (—)-*cis*-*m*-menthan-5-one. When the mixture of racemic alcohols and unchanged ketone was passed through a column of neutral alumina, partial equilibration, in which the ketone presumably played a part, took place, giving a mixture containing 83% of the more stable (±)-*cis*-*m*-menthan-*cis*-5-ol. The latter was obtained pure by careful chromatography on alumina. The previous workers[7] showed that equilibration, with mixed hydride, of the mixture of racemic alcohols afforded 97·6% of the *cis*-5-ol.

Reduction of (—)-*m*-menth-3-en-5-one (IX) in ethanol over 5% palladised charcoal, made sometime previously, gave only (—)-*cis*-*m*-menthan-5-one (VIIIb), which was further reduced over 5% platinised charcoal to the epimeric alcohols (Xa) and (Xb). However, reduction of the ketone (IX) in ethanol over a commercial brand of palladised charcoal gave a mixture of (—)-*cis*-*m*-menthan-5-one (VIIIb) (37%), the *cis*- and *trans*-5-ols (Xa) (12%) and (Xb) (18%), and the corresponding *cis*- and *trans*-ethyl ethers (Xe) (11%) and (Xf) (22%). Further reduction of this mixture, in ethanol, over platinised charcoal increased the quantity of the *cis*-5-ol (Xa), but afforded no increase in the yields of the ethers. Reoxidation of the mixture of alcohols and ethers afforded the ketone (VIIIb) and the ethyl ethers (Xe) and (Xf). The alcohols and ethers were separated and purified by preparative g.l.c. The alcohols were then found to be identical in g.l.c. characteristics and similar in i.r. spectrum to the respective photoproducts and the reduction products of (±)-*cis*-*m*-menthan-5-one.[7]

The scope of this reductive etherification reaction is being investigated. However, we have shown that the alcohols (Xa) and (Xb) are not the precursors of the ethers since the former are recovered unchanged when stirred with the catalyst in ethanol in an atmosphere of hydrogen. However, under these conditions, (—)-*cis*-*m*-menthan-5-one (VIIIb) affords (g.l.c.) the corresponding *cis*- (Xa), and *trans*-5-ol (Xb) and their ethyl ethers, (Xe) and (Xf), as well as some unchanged ketone (VIIIb) (23, 28, 18·5, 28·4, and 2%), and cyclohexanone similarly affords cyclohexanol and its ethyl ether. We have some evidence that hemiacetals, and possibly enol ethers, are intermediates in these reductions.

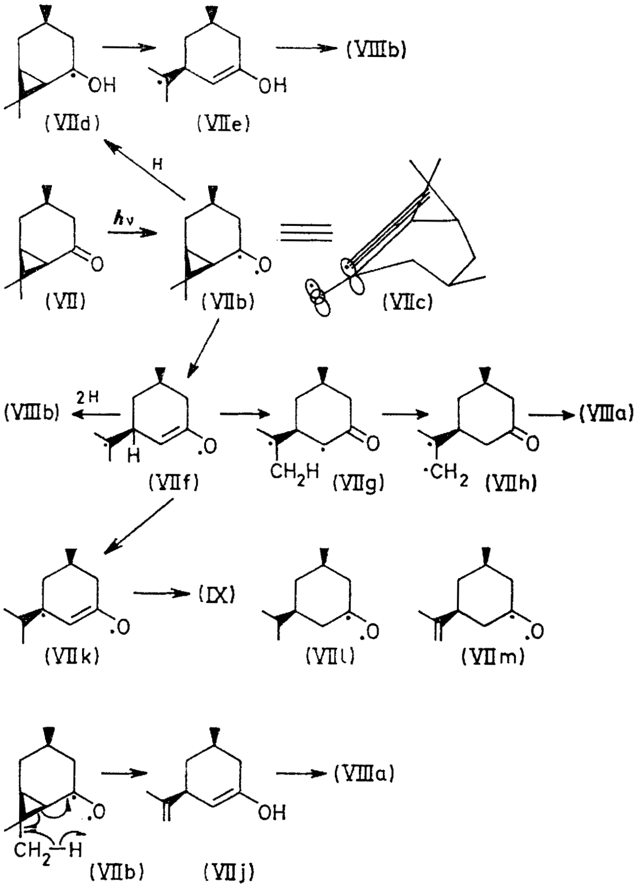
The stereochemistry of the alcohols (Xa) and (Xb) and of their ethers (Xe) and (Xf) can also be demonstrated from their n.m.r. spectra. The *cis*-alcohol (Xa) in deuteriochloroform shows a broad multiplet centred at τ 6·35 ($w_{\frac{1}{2}}$ 31 Hz), assigned to the α-carbinol proton, whereas in dimethyl sulphoxide the carbinol proton band is at τ 6·5 ($w_{\frac{1}{2}}$ 29 Hz). In the case of the ether (Xe), in deuteriochloroform, the former α-carbinol proton signal is centred at τ 6·96 ($w_{\frac{1}{2}}$ 26 Hz). The *trans*-alcohol (Xb) in deuteriochloroform shows its α-carbinol proton signal at τ 5·80 ($w_{\frac{1}{2}}$ 13 Hz), whereas in dimethyl sulphoxide the signal is centred at τ 6·02 ($w_{\frac{1}{2}}$ 13 Hz). The *trans*-ether (Xf) in deuteriochloroform shows a former α-carbinol proton at τ 6·41 ($w_{\frac{1}{2}}$ 12 Hz). These data indicate that (Xa) has an equatorial hydroxy-group and that (Xe) is its ethyl ether, and (Xb) and (Xf) are, respectively, the epimeric alcohol and ether. We have confirmed the configuration of (Xf) by treatment of its alcohol (Xb) with ethyl iodide and silver oxide.

cis-m-Menth-8-en-*cis*-5-ol (Xc) was not isolated pure. It was identified by comparison (g.l.c.) with the principal reduction product of (—)-*cis-m*-menth-8-en-5-one (VIIIa) with lithium aluminium hydride. In this reduction, (Xc) was formed in 91% yield (g.l.c.), the other product presumably being *cis-m*-menth-8-en-*trans*-5-ol (Xd), but the latter was obtained in quantities too small to be identified. However, the mixture of alcohols (Xc) and (Xd) enhanced the intensities of two peaks in the g.l.c. of the photo-product. The larger of these peaks corresponded to the major reduction product (Xc), and the minor photoproduct peak corresponded to the minor reduction product.

The Figure illustrates the progress of the irradiation in ether. In the early stages (—)-*cis-m*-menth-8-en-5-one (VIIIa) and its dihydro-derivative (VIIIb) are the only significant products. They are formed at about the same rate. However, after about 4 hr. the speed of formation of the latter declines, whereas that of the former remains fairly constant. After 6—7 hr. the actual amount of (—)-*cis-m*-menthan-5-one (VIIIb) in the photolysis mixture progressively diminishes, and the content of (—)-*cis-m*-menthan-*cis*-5-ol (Xa) increases. It seems therefore that this alcohol is formed by the photoreduction of (—)-*cis-m*-menthan-5-one (VIIIb). The αβ-unsaturated ketone (IX) is formed only slowly in the initial stages of the reaction, but the amounts of this compound and the alcohol (Xc) always associated with it on g.l.c., increase more rapidly in the later stages of the photolysis. The Figure suggests that the αβ-unsaturated ketone is not a photoproduct from which the others are derived; this was confirmed by its irradiation in ether. None of the other volatile photoproducts was formed, but the unsaturated ketone was rapidly used up; a solid compound (probably dimeric) and other non-volatile products were obtained. These will be the subject of further study in another connection.

Since in benzene, (—)-*m*-menth-3-en-5-one (IX) is the only volatile product, whilst in ether and in n-hexane (—)-*cis-m*-menthan-5-one (VIIIb) is formed, it seems that the last two solvents act as a source of hydrogen. The formation of alcohols in ether, a better hydrogen donor than n-hexane, (*cf.* ref. 9) supports this suggestion. The photoreduction of αβ-unsaturated ketones is, in fact, a general process in the presence of alcoholic or ethereal solvents.[9,10] The further photoreduction of (—)-*cis-m*-menthan-5-one (VIIIb), in ether, is likely to take place preferentially from the less hindered α-side of the molecule so as to give the *cis*-alcohol (Xa). Similarly, reduction of (—)-*cis-m*-menth-8-en-5-one (VIIIa) would be likely to give *cis-m*-menth-8-en-*cis*-5-ol (Xc) as major product.

The course of the photochemical reaction can be portrayed as in Scheme 2. Presumably the initial stage will involve the formation of the triplet biradical (VIIb), which can be represented in the delocalised form (VIIc) (*cf.* ref. 11). This radical may abstract hydrogen from the solvent, ether or n-hexane, to give the radical (VIId), from which the radical (VIIe) may subsequently be formed. Hydrogenation of the latter will give (—)-*cis-m*-menthan-5-one (VIIIb). We have not found any *cis*-caran-5-ol in the photolysis mixture. It is therefore unlikely that either (VIIb) or (VIId) is further hydrogenated before rearrangement.



SCHEME 2

An alternative rearrangement of (VIIb) would afford (VIIf), hydrogenation of which would again yield (—)-*cis-m*-menthan-5-one (VIIIb). However, the biradical (VIIf) could rearrange to (VIIg) [again, a possible precursor of (VIIb)], and this by a 1,4-hydrogen shift could give (VIIh), from which the main photoproduct (VIIIa) would be formed. A further possibility (*cf.* ref. 9) is that the initially formed radical (VIIb) could itself undergo a 1,5-hydrogen shift with concomitant

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[9] W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, 1969, **34**, 1849.

[10] P. J. Kropp, 'Organic Photochemistry,' ed. O. L. Chapman, Arnold, London, 1967, vol. 1, p. 77, where references are given.

[11] W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, 1969, **34**, 2512.

opening of the cyclopropane ring, to give the enol (VIIj) from which (VIIIa) would again be formed. The geometry would not be unfavourable for such a change if the molecule were to assume a boat form.

The formation of the αβ-unsaturated ketone (IX) probably takes place *via* production of the biradicals (VIIb) and (VIIf), followed by a rearrangement of the latter, which involves a 1,2-hydrogen shift, to (VIIk). The low yields of the ketone are almost certainly a result of the formation of non-volatile substances, probably dimeric.

Finally, the alcohols are probably formed *via* the biradicals (VIII) and (VIIm), which can acquire hydrogen from the solvent, ether.

Reduction of (+)-*cis*-caran-5-one (VII) with lithium in liquid ammonia, which involves the radical ion (VIIa) (Scheme 1), affords (−)-*cis*-*m*-menthan-5-one (VIIIa) and the corresponding alcohols, whereas catalytic reduction of (VII) and the corresponding alcohol, (+)-*cis*-caran-*cis*-5-ol, affords[12] (+)-*cis*-*m*-menthane.

The pyrolysis of the caranones is the subject of further study. However, in preliminary experiments we have found that on heating (+)-caran-*cis*-5-one (VII) in a sealed ampoule at 440°, a complete conversion into (VIIIa) (11%), (XI) (62%), *m*- or *p*-cymene (11%) (these isomers are not resolved on the g.l.c. columns used), and several minor products, takes place.

EXPERIMENTAL

The general experimental conditions were those described earlier.[1b] Analytical g.l.c. was carried out at 150° on Carbowax (3 m.) and at 130° on 80% Carbowax–20% Castorwax (2 m.) columns. Preparative g.l.c. was carried out at 153° on Carbowax (20 ft. × $\frac{3}{8}$ in.) columns. Optical rotations were measured for solutions in chloroform, u.v. spectra for solutions in ethanol, and i.r. spectra for liquid films unless stated otherwise. Photochemical reactions were performed in a Hanovia photochemical reactor (1 l.) with transparent fused-quartz sleeves, with a 125 w medium-pressure mercury lamp. The light petroleum used in chromatography had b.p. 40—60°.

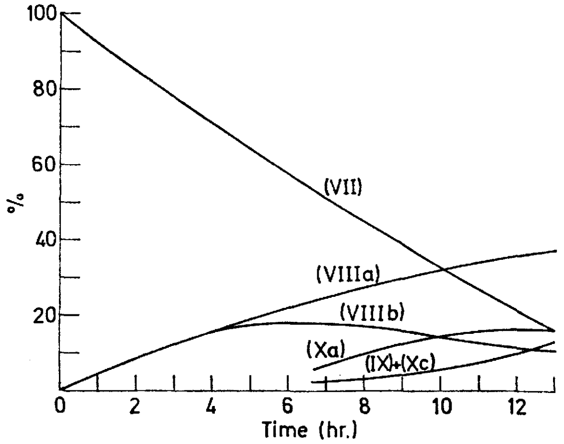
Photolysis.—(+)-*cis*-Caran-5-one (VII) (5 g.) in sodium-distilled ether (1 l.) was stirred and irradiated under nitrogen; the products were monitored from time to time by g.l.c. Tetradecane was used as an internal standard. The course of the reaction is illustrated in the Figure. The photolysis reactions carried out in n-hexane and benzene were similarly performed and are not further described.

The reaction was stopped after 13 hr. at which time the products began to proliferate. They were isolated by preparative g.l.c. and their purities were checked by analytical g.l.c. With the exception of (−)-*cis*-*m*-menth-3-en-5-one (IX), which was obtained in 70% purity, contaminated with *cis*-*m*-menth-8-en-*cis*-5-ol (Xc), each was pure as judged by analytical g.l.c.

(−)-cis-m-*Menth*-8-*en*-5-*one* (VIIIa) was an *oil*, $[\alpha]_D^{20}$ −2·1° (*c* 0·8), n_D^{20} 1·4701 (Found: C, 78·2; H, 10·35. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Its *semicarbazone* (needles from ethanol) had m.p. 166—167°, $[\alpha]_D^{20}$ +2·5° (*c* 0·22), $\lambda_{max.}$ 230 nm. (log ε 4·04), $\nu_{max.}$ 3413, 3175 (NH), 1672 (CO·NH), 1639 (C=C and C=N), and 881 (C=CH$_2$) cm.$^{-1}$ (Found: C, 63·1; H, 9·2; N, 20·2. $C_{11}H_{19}N_3O$ requires C, 63·1; H, 9·15; N, 20·1%).

(−)-cis-m-*Menthan*-5-*one* (VIIIb).—(*a*) As obtained by photolysis of (VII), this was an *oil*, $[\alpha]_D^{20}$ −2·01° (*c* 0·6), n_D^{20} 1·4543 (Found: C, 77·0; H, 12·0. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%). Its *semicarbazone* (needles from methanol) had m.p. 170—171°, $[\alpha]_D^{20}$ −11·0° (*c* 0·23), $\lambda_{max.}$ 229 nm. (log ε 4·083), $\nu_{max.}$ 3448, 3175, 1672, and 1647 cm.$^{-1}$ (Found: C, 62·3; H, 9·9; N, 19·5. $C_{11}H_{21}N_3O$ requires C, 62·5; H, 10·0; N, 19·9%).

(*b*) (−)-*cis*-*m*-Menth-8-en-5-one (VIIIa) (50 mg.) was hydrogenated in ethanol (10 c.c.) over 10% palladised charcoal (30·5 mg.), giving the required ketone (32 mg.), identical (i.r. spectrum and g.l.c.) with (−)-*cis*-*m*-menthan-5-one obtained by photolysis.



Photolysis of (+)-*cis*-caran-5-one in ether; composition of the mixture of volatile products

(−)-m-*Menth*-3-*en*-5-*one* (IX).—This was obtained from the photolysis mixture as an oil of about 70% purity by taking a fine cut from the preparative g.l.c. peak (a flat peak with a shoulder) which contained this ketone and the alcohol (Xc). The ketone then gave a sharp peak with a small shoulder.

Isomerisation of (+)-cis-*Caran*-5-*one with Acids*.—(*a*) Ice-cold (+)-*cis*-caran-5-one (904 mg.) was added slowly to ice-cold boron trifluoride–ether complex (1·01 g.). After 12 hr., the mixture was poured into ice and ammonium chloride and extracted with ether, giving a yellow oil (885 mg.) which (g.l.c.) contained (−)-*m*-menth-3-en-5-one (IX) (98%) and (−)-*cis*-*m*-menth-8-en-5-one (VIIIa); each peak was enriched by the corresponding photoproduct. Reduction of the mixture of (VIIIa) and (IX) (58 mg.) in ethanol (10 c.c.) over 10% palladised charcoal (50 mg.) gave (−)-*cis*-*m*-menthan-5-one (VIIIb) (g.l.c. and i.r. spectrum) as the only product.

(*b*) (+)-*cis*-Caran-5-one (366 mg.) in ethanol (5 c.c.) was added to a cold solution of boron trifluoride–ether complex (1 c.c.) in ethanol (3 c.c.), and the mixture was kept overnight. It was worked up as in (*a*), giving a mobile oil (500 mg.) consisting (g.l.c.) substantially (97%) of (−)-8-*ethoxy*-cis-m-*menthan*-5-*one* (VIIIc) with entrained ethanol. The ketone was chromatographed on silica, and eluted with light petroleum–ether (9 : 1) as an oil

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

(468 mg.), $[\alpha]_D^{20}$ 0° (*c* 0·6), $[\alpha]_{436}^{20}$ −2·4°, $[\alpha]_{365}^{20}$ −26·8°, (*c* 1·26), n_D^{20} 1·4568, $\nu_{max.}$ 1710 and 1070 cm.$^{-1}$ (C–O), τ 6·65 (q, *J* 7 Hz, O·CH$_2$), 7·4—8·7 (8H, CH$_2$ and CH), 8·9 (s, CMe$_2$), and 8·7—9·2 (6H, CH$_3$ and O·CH$_2$·C*H*$_3$) (Found: C, 72·0; H, 11·4. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·2%).

(*c*) (+)-*cis*-Caran-5-one (765 mg.) was stirred for 6·5 hr. with sulphuric acid (50%, w/v; 5 c.c.) and set aside overnight. The mixture was poured into water (10 c.c.) and extracted with ether, from which an oil (720 mg.) was isolated. G.l.c. and i.r. spectroscopy revealed the presence of (−)-*m*-menth-3-en-5-one (IX) and the ketol (VIIId). The mixture was chromatographed on silica gel; (−)-m-*menth*-3-*en*-5-*one* (IX) (300 mg.) was eluted with light petroleum–ether (4 : 1) as an oil, $[\alpha]_D^{20}$ −70° (*c* 0·74), n_D^{20} 1·4910 (Found: C, 79·0; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). It was homogeneous on analytical g.l.c., and had u.v., i.r. and n.m.r. spectra similar to those of the photoproduct (IX) of 70% purity. Its *semicarbazone* (needles from methanol) had m.p. 167°, $\lambda_{max.}$ 267 nm. (log ε 4·22). The ketol, (−)-8-*hydroxy*-cis-m-*menthan*-5-*one* (VIIId) (350 mg.) was eluted with light petroleum–ether (1 : 1), as a colourless oil, $[\alpha]_D^{20}$ −6·3° (*c* 0·6), $\nu_{max.}$ 3390 (OH), 2940, 1701 (C=O), 1449, 1418, 1366, 1330, 1261, 1218, 1174, 1147, 1131, 1085, 1064, 990, 966, 955, 929, 893, 870, and 769 cm.$^{-1}$, τ (CCl$_4$) 8·86 (s, Me$_2$C), 8·95 (d, *J* 5 Hz, MeC), 7·4—8·6 (8H, m, CH$_2$ and CH), and 7·7 (OH, exchangeable). Its 3,5-*dinitrobenzoate* (prisms from aqueous methanol) had m.p. 98—99°, $\nu_{max.}$ (Nujol) 1709, 1626, 1590, and 1541 (NO$_2$) cm.$^{-1}$ (Found: C, 55·7; H, 5·5; N, 7·7. $C_{17}H_{20}N_2O_7$ requires C, 56·0; H, 5·5; N, 7·7%).

(*d*) Hydrogen chloride was passed into an ice-cold solution of (+)-*cis*-caran-5-one (525 mg.) in ether (30 c.c.), until saturated, and the mixture was set aside overnight. It was poured on ice, the ether layer was separated, and the aqueous layer was extracted with ether (2 × 10 c.c.). The combined ether extract was washed with water and 5% sodium hydrogen carbonate and dried, giving a solid (540 mg.), m.p. 45·5—50°. It crystallised with difficulty from aqueous methanol, but was readily sublimed under reduced pressure giving (+)-8-*chloro*-cis-m-*menthan*-5-*one* (VIIIe), m.p. 50—51°, $[\alpha]_D^{20}$ +17° (*c* 0·05), $\nu_{max.}$ (Nujol) 2915, 1706, 1447, 1414, 1362, 1332, 1282, 1266, 1252, 1230, 1220, 1200,1190, 1136, 1119, 1096, 1065, 990, 937, 910, 889, 862, and 813 (C–Cl) cm.$^{-1}$, τ (CCl$_4$) 8·95 (d, *J* 6 Hz, MeC), 8·4 and 8·45 (s, Me$_2$C), and 7·55—8·7 (8H, m, CH$_2$ and CH) (Found C, 63·1; H, 8·9; Cl, 18·1. $C_{10}H_{17}ClO$ requires C, 63·7; H, 9·01; Cl, 18·6%).

(*e*) (+)-*cis*-Caran-5-one (5·47 g.) was stirred at room temperature for 26 hr. with concentrated hydrochloric acid (4·55 g.). The mixture was poured into water and extracted with ether, from which an oily solid was obtained. It was collected at the pump, giving the chloro-ketone (VIIIe) (4·5 g.), m.p. 48° after sublimation. The filtrate, extracted with ether gave an oil (378 mg.) which when chromatographed on silica gave the chloro-ketone (VIIIe) (216 mg.), the $\alpha\beta$-unsaturated ketone (IX) (61·5 mg.), and the ketol (VIIId) (80 mg.).

Conversion of (−)-cis-m-*Menth*-8-*en*-5-*one* (VIIIa) *into* (−)-m-*Menth*-3-*en*-5-*one* (IX).—The ketone (VIIIa) (43 mg.) was set aside for 12 hr. with boron trifluoride–ether complex (70 mg.). The product was poured on ice and ammonium chloride, extracted with ether, and washed with water, and dried. Evaporation gave a yellow oil (36 mg.) consisting solely of (−)-*m*-menth-3-en-5-one (IX), identical (g.l.c. and u.v. and i.r. spectra) with the product already described.

Reconversion of the Chloro-ketone (VIIIe) *into* (+)-cis-*Caran*-5-*one* (VII).—A mixture of chloro-ketone (144 mg.), potassium hydroxide (125 mg.), and methanol (2 c.c.) was set aside for 12 hr. It was then diluted with ether (20 c.c.), washed with water (2 × 10 c.c.), and dried, giving (+)-*cis*-caran-5-one (120 mg.) identical (i.r. spectrum and g.l.c.) with an authentic specimen.

Reduction of (+)-cis-*Caran*-5-*one* (VII) *with Lithium in Liquid Ammonia*.—Lithium (175 mg.) was added slowly to a stirred solution of (+)-*cis*-caran-5-one (520 mg.) in liquid ammonia (50 c.c.), and stirring was continued for 2 hr. The product was a pale yellow oil (452 mg.) containing both alcohol and ketone (i.r. spectrum and g.l.c.). It was oxidised with a mixture of chromium trioxide (1·33 g.), concentrated sulphuric acid (1·24 c.c.), water (5 c.c.), and acetone (25 c.c.), giving (−)-*cis*-*m*-menthan-5-one as a single product, $[\alpha]_D^{20}$ −0·48° (*c* 0·19), identical (g.l.c. and i.r. and n.m.r. spectra) with the photoproduct (VIIIb). Its semicarbazone had m.p. and mixed m.p. 170—171° (see before), $[\alpha]_D^{20}$ −13·8° (*c* 0·31) (Found: C, 62·0; H, 9·8; N, 19·5%).

Action of Zinc on the Chloro-ketone (VIIIe).—(*a*) A mixture of the ketone (870 mg.), acetic acid (10 c.c.), water (2 c.c.), and zinc dust (5 g.) was stirred for 24 hr. It was filtered, the solid residue was washed with ether (20 c.c.), and the filtrate was extracted with ether (2 × 20 c.c.). The combined extract was washed with water (2 × 10 c.c.), 1% sodium hydrogen carbonate (3 × 10 c.c.), and water (10 c.c.), and dried, giving an oil (337 mg.) which contained (t.l.c.) four compounds. It was chromatographed on silica gel (17 g.) and eluted with light petroleum–ether (gradient; 9 : 1 to 1 : 1). The following compounds were thus obtained: (i) an unidentified ketone (5 mg.), $\nu_{max.}$ 1706 and 1667 infl. cm.$^{-1}$, (ii) a mixture (80 mg.) of (−)-*cis*-*m*-menth-8-en-5-one (VIIIa) and (−)-*cis*-*m*-menthan-5-one (VIIIb) in the proportion (g.l.c.) 3 : 2, (iii) unchanged chloro-ketone (VIIIe) (35 mg.), (iv) (−)-*m*-menth-3-en-5-one (IX) (24 mg.), and (v) (+)-8-*acetoxy*-cis-m-*menthan*-5-*one* (VIIIf) (100 mg.), as an oil, $[\alpha]_D$ +7·4° (*c* 0·5), $\nu_{max.}$ 2915, 1738 (ester), 1720 (keto), 1449, 1418, 1379, 1361, 1333, 1250 (acetate), 1227, 1205, 1190, 1174, 1149, 1125, 1093, 1065, 1015, 971, 947, 925, 901, 885, 863, 826, and 763 cm.$^{-1}$, τ (CCl$_4$) 8·91 (d, *J* 5 Hz, MeC), 8·57 (s, Me$_2$C), 8·07 (s, AcO), and 7·4—8·7 (8H, m, CH$_2$ and CH) (Found: C, 67·5; H, 9·0. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%).

(*b*) A mixture of the chloro-ketone (123 mg.), formic acid (12 c.c.), and zinc dust (1 g.) was stirred for 12 hr. The product was worked up as in (*a*), giving a thick yellow oil (100 mg.). It was chromatographed as in (*a*), giving (+)-8-*formyloxy*-cis-m-*menthan*-5-*one* (VIIIg) (50 mg.), which was eluted with light petroleum–ether (3 : 2); $[\alpha]_D^{20}$ +12·5° (*c* 0·92), $\nu_{max.}$ 1730 (ester), 1710 (keto), and 1190 (formate) cm.$^{-1}$, τ (CCl$_4$) 2·13 (s, CHO), 7·5—8·4 (8H, C*H*$_2$ and C*H*), 8·53 (6H, Me$_2$C), and 8·93 (d, *J* 5 Hz, MeC) (Found: C, 66·9; H, 9·15. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%).

(±)-*Ethyl* 5-*Oxo*-m-*menth*-6-*en*-2-*carboxylate* (XIIIa).—This compound was prepared from isobutyraldehyde (56·2 g.) and ethyl acetoacetate (210 c.c.) according to the method described for an analogous compound [13] (*cf.* ref. 7). The ester was obtained as an oil (84·6 g.), b.p. 106—110°/

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[13] E. C. Horning, M. Denekas, and R. Field, *Org. Synth.*, 1955, Coll. Vol. III, p. 317.

0·3—0·4 mm., n_D^{20} 1·4788 (homogeneous on g.l.c. and t.l.c.) (*cf.* ref. 7), $\lambda_{max.}$ (EtOH) 233 nm. (log ε 4·05), $\lambda_{max.}$ (EtOH containing 5% N-NaOH) 233 (log ε 3·87), 283 (3·27), and 396 (3·19) nm., $\nu_{max.}$ 1724 (ester), 1667 (C=O), 1629 (C=C), and 815 $R_2C{=}CHR$ cm.$^{-1}$, τ (CCl_4) 4·16 (s, =CH), 8·06 (s, MeC=C), 9·05 and 9·1 (dd, *J* 7 Hz, Me_2C), 7·75 (d, *J* 3 Hz, $CH_2\cdot CO$), 8·58, 8·7, and 8·81 (t, $C\mathit{H}_3\cdot CH_2\cdot CO$), 5·61, 5·75, 5·86, and 5·99 (q, $CH_3\cdot C\mathit{H}_2\cdot CO$), and −2·1 (exchangeable, minor enolic OH). A second fraction (3·6 g.), b.p. 110—115°/0·3—0·4 mm. consisted substantially (t.l.c.) of the required ester.

(±)-m-*Menth*-6-*en*-5-*one* (XIIIb).—Compound (XIIIa) (50 g.) was decarboxylated by the method earlier described,[13] giving the ketone (XIIIb) (21·5 g.), b.p. 120—122°/12 mm., n_D^{20} 1·4834, $\lambda_{max.}$ 234 (log ε 4·08) and 303 (1·68) nm., $\nu_{max.}$ 1658 and 1629 (C=C–C=O) and 883 ($R_2C{=}CHR$) cm.$^{-1}$. Its *semicarbazone* (microneedles from methanol) had m.p. 172—173°, $\lambda_{max.}$ 266 nm. (log ε 4·39) (Found: C, 62·7; H, 9·0; N, 20·3. $C_{11}H_{19}N_3O$ requires C, 63·1; H, 9·15; N, 20·1%).

(±)-cis-m-*Menthan*-5-*one*.—The unsaturated ketone (XIIIb) (10 g.) was reduced in ethanol (15 c.c.) with 5% palladised charcoal (1 g.) giving the ketone (VIIIb) (8·2 g.), b.p. 102°/10 mm., n_D^{20} 1·4522 (*cf.* ref. 7), $\lambda_{max.}$ 282 nm. (log ε 1·46), $\nu_{max.}$ 1718 cm.$^{-1}$. Its *semicarbazone* (needles from ethanol) had m.p. 182°, $\lambda_{max.}$ 229 nm. (log ε 4·15), $\nu_{max.}$ 3448, 3145, 1669, and 1645 cm.$^{-1}$ (Found: C, 62·0; H, 9·7; N, 19·9. $C_{11}H_{21}N_3O$ requires C, 62·5; H, 10·0; N, 19·9%).

(±)-cis-m-*Menth*-cis-5-*ol and* (±)-cis-m-*Menth*-trans-5-*ol*.—(±)-*cis*-*m*-Menthan-5-one (2·26 g.) was reduced in ethanol (15 c.c.) over 5% platinised charcoal (0·5 g.) during 24 hr. The product (2·24 g.) showed peaks (g.l.c.) corresponding to unreduced ketone (24%), the *cis*-alcohol (42%), and the *trans*-alcohol (33%) (*cf.* ref. 7). It was chromatographed on neutral alumina (Merck grade 1; 90 g.) in light petroleum-ether (4 : 1) containing increasing amounts of ether. Unchanged ketone was eluted first, followed by the *trans*-alcohol, which was contaminated with the *cis*-alcohol, and finally the *cis*-alcohol, a sample of which was obtained pure. G.l.c. of the total alcohol fraction (1·4 g.) after chromatography showed the presence of *trans*-alcohol (17%), and *cis*-alcohol (83%). The *cis*-alcohol (70 mg.) had n_D^{20} 1·4596. It was similar in i.r. spectrum and identical in g.l.c. characteristics with the optically active alcohol (Xa) described later. The mixture of racemic *cis*- and *trans*-alcohols enriched the appropriate g.l.c. peaks of the photoproduct and also of a mixture of the active alcohols (Xa) and (Xb).

(−)-cis-m-*Menthan*-cis-5-*ol* (Xa) *and* (−)-cis-m-*Menthan*-trans-5-*ol* (Xb).—(*a*) (−)-*cis*-*m*-Menthan-5-one (VIIIb) (19 mg.) was reduced in ether (8 c.c.) with lithium aluminium hydride (12 mg.) giving a mixture (15 mg.) containing (g.l.c.) (−)-*cis*-*m*-menthan-*cis*-5-ol (Xa) (97%) and its 5-epimer (Xb) (3%), $\nu_{max.}$ (of mixture) 3335, 2933, 1453, 1383, 1362, 1299, 1266, 1250, 1221, 1178, 1164, 1139, 1095, 1042, 1020, 1001, 970, 950, 910, 870, 854, 820, and 755 cm.$^{-1}$, τ (CCl_4), 9·12 (d, *J* 5 Hz, MeC), 9·08 and 9·02 (Me_2C), 7·98—8·8 (m, CH_2 and CH), 6·5 (m, $C\mathit{H}\cdot OH$), and 8·0 (exchangeable, OH).

(*b*) (+)-*cis*-Caran-5-one (VII) (3·15 g.) was converted into (−)-*m*-menth-3-en-5-one (IX) (3·16 g.) by treatment with boron trifluoride–ether complex (4 c.c.) as already described, and then hydrogenated over 5% palladised charcoal (Johnson Matthey) (1 g.), in ethanol (10 c.c.). The product (2·93 g.) contained (g.l.c.) (−)-*cis*-*m*-menthan-5-one (VIIIb) (37%), the epimeric alcohols (Xa) (12%) and (Xb) (18%), and the ethers (Xe) (11%) and (Xf) (22%). [In a second experiment the yields of products were (VIIIb) (63%), (Xa) (9%), (Xb) (18%), (Xe) (6%), and (Xf) (11%).] The mixture was further reduced over 5% platinised charcoal (1 g.) in ethanol giving a product (2·65 g.) containing (g.l.c.) the alcohols (Xa) (35%) and (Xb) (32%), and the ethers (Xe) (11%) and (Xf) (22%). The products were separated by preparative g.l.c., being eluted in the order (Xf), (Xe), (VIIIb), (Xb), and (Xa).

(−)-cis-m-*Menthan*-cis-5-*ol* (Xa) was an oil, $[\alpha]_D^{20}$ −0·98° (*c* 0·5), n_D^{20} 1·4592, $\nu_{max.}$ 3350, 2900, 1450, 1430, 1388, 1370, 1328, 1312, 1279, 1248, 1230, 1184, 1170, 1150, 1117, 1105, 1048, 1029, 1001, 975, 955, 918, 850, 824, and 808 cm.$^{-1}$, τ ($CDCl_3$) 6·1—6·67 ($C\mathit{H}\cdot OH$), 8·19 (OH), 7·8—9·2 (9H, CH_2 and CH), 9·05 (d, *J*, 5 Hz, MeC), and 9·02, 9·09, and 9·18 (Me_2C) (Found: C, 77·4; H, 12·9. $C_{10}H_{20}O$ requires C, 76·9; H, 12·9%). Its 3,5-*dinitrobenzoate* (needles from methanol) had m.p. 82—83° [lit.,[7] for (±)-3,5-dinitrobenzoate, 105—106°], $[\alpha]_D^{20}$ −13·5° (*c* 0·515), $\nu_{max.}$ 3077, 2874, 1718, 1629, 1595, 1543, 1453, 1368, 1335, 1282, 1176, 1163, 1152, 1089, 1074, 1040, 1030, 1000, 980, 961, 951, 935, 925, 894, 862, 845, 821, 806, 774, and 724 cm.$^{-1}$, τ ($CDCl_3$) 0·86 (3H, ArH), 4·9 ($C\mathit{H}\cdot O\cdot CO\cdot R$), 9·0 (d, *J* 5 Hz, MeC), and 9·04 and 9·15 (Me_2C) (Found: C, 58·3; H, 6·3; N, 8·05. $C_{17}H_{21}N_2O_6$ requires C, 58·45; H, 6·3; N, 8·3%).

(−)-cis-m-*Menthan*-trans-5-*ol* (Xb) was an oil, $[\alpha]_D^{20}$ −5·3° (*c* 0·53), n_D^{20} 1·4597, $\nu_{max.}$ 3350, 2950, 1452, 1428, 1385, 1369, 1330, 1310, 1288, 1240, 1182, 1170, 1148, 1119, 1109, 1048, 1030, 1008, 988, 950, 900, 859, 822, 800, and 700 cm.$^{-1}$, τ ($CDCl_3$) 5·7—5·9 ($C\mathit{H}\cdot OH$), 8·34 (OH), 8·17—8·9 (9H, CH_2 and CH), and 9·08, 9·1, and 9·17 (3 × Me) (Found: C, 76·8; H, 12·9. $C_{10}H_{20}O$ requires C, 76·9; H, 12·9%). Its 3,5-*dinitrobenzoate* (needles from ethanol) had m.p. 130° [lit.,[7] for (±)-3,5-dinitrobenzoate, 115—116°], $[\alpha]_D^{20}$ +2·35 (*c* 0·51), $\nu_{max.}$ 3100, 2900, 1720, 1628, 1598, 1546, 1458, 1375, 1348, 1292, 1265, 1250, 1230, 1180, 1140, 1115, 1090, 1074, 1045, 990, 981, 943, 925, 920, 860, 830, 810, 770, 738, 720, and 680 cm.$^{-1}$ (Found: C, 58·3; H, 6·7; N, 8·05. $C_{17}H_{21}N_2O_6$ requires C, 58·45; H, 6·3; N, 8·3%).

(−)-cis-m-*Menthan*-cis-5-*ol ethyl ether* (Xe) was an oil, $[\alpha]_D^{20}$ −3·06° (*c* 0·62), n_D^{20} 1·4444 $\nu_{max.}$ 2940, 2870, 2795, 2740, 2620, 1458, 1440, 1380, 1366, 1350, 1339, 1309, 1270, 1251, 1230, 1180, 1164, 1146, 1110, 1084, 1062, 1045, 1038, 972, 948, 940, 916, 890, 859, 848, and 840 cm.$^{-1}$, τ ($CDCl_3$) 6·6 (q, 2H, *J* 7 Hz, $O\cdot CH_2$), 6·8—7·1 (CH·OR), 8·89 (t, *J* 7 Hz, $O\cdot CH_2\cdot C\mathit{H}_3$), 9·0 (d, *J* 5 Hz, MeC), and 9·08 and 9·18, (Me_2C), *m*/*e* 184 (M^+), 141 ($M^+ - Me_2CH$), 45 (EtO^+), and 43 (Me_2CH^+).

(−)-cis-m-*Menthan*-trans-5-*ol ethyl ether* (Xf) was an oil, $[\alpha]_D^{20}$ −10·8° (*c* 0·62), n_D^{20} 1·4439 $\nu_{max.}$ 2930, 2900, 2850, 2775, 2700, 2650, 2560, 1460, 1448, 1395, 1380, 1361, 1342, 1309, 1296, 1257, 1234, 1164, 1123, 1109, 1080, 1061, 1044, 1029, 1000, 952, 895, 868, 845, 800, and 684 cm.$^{-1}$, τ ($CDCl_3$) 6·41 (m, CH·OR), 6·66 (q, *J* 7 Hz, $O\cdot CH_2$), 8·87 (t, *J* 7 Hz, $O\cdot CH_2\cdot C\mathit{H}_3$), 9·15 (d, *J* 5 Hz, MeC), and 9·1 and 9·2 (Me_2C), *m*/*e* 184 (M^+) and other fragments as in (Xe) (Found: C, 78·7; H, 12·8. $C_{12}H_{24}O$ requires C, 78·2; H, 13·1%). This ether (Xf) was also prepared as follows. A mixture of the alcohol (Xb) (78 mg.), ethyl iodide (468 mg.), tetrahydrofuran (5 c.c.), and freshly prepared silver oxide (464 mg.) was refluxed for 30 hr., cooled, and filtered. The solvent was removed giving an oil, which on g.l.c. showed the presence of unchanged alcohol (Xb), the ether (Xf), and several other compounds. [When tetrahydrofuran, ethyl iodide, and silver oxide were refluxed together, a mixture containing (g.l.c.) these other compounds was obtained.] The relative yields of alcohol (Xb) and ether (Xf) were 84 and 16%.

Hydrogenation of (−)-cis-m-*Menthan*-5-*one* (VIIIb).—The ketone (56 mg.) in ethanol (5 c.c.) was stirred under hydrogen with 5% palladised charcoal (0·1 g.) for 18 hr. The alcohol was carefully removed, leaving an oil (43 mg.), g.l.c. of which showed the presence of the following compounds eluted in the order given: (−)-*cis*-*m*-menthan-*trans*-5-ol ethyl ether (Xf) (28·4%), its 5-epimer (Xe) (18·5%), unchanged menthanone (VIIIb) (2%), (−)-*cis*-*m*-menthan-*trans*-5-ol (Xb) (28%), and its 5-epimer (Xa) (23%).

cis-m-*Menth*-8-*en*-cis-5-*ol* (Xc).—(−)-*cis*-*m*-menth-8-en-5-one (VIIIa) (52·7 mg.) was reduced with lithium aluminium hydride (26 mg.) in ether (15 c.c.). The product, obtained in quantitative yield, showed (g.l.c.) one main peak (91%) and one minor peak (9%), $\nu_{max.}$ (of mixture) 3333, 3077, 2924, 2857, 1642 (C=C), 1449, 1433, 1368, 1351, 1299, 1271, 1235, 1209, 1152, 1136, 1112, 1085, 1021, 1006, 973, 952, 911, 890 ($C=CH_2$), and 855 cm.$^{-1}$. The main product, *cis*-*m*-menth-8-en-*cis*-5-ol (Xc), enhanced the intensity of the appropriate g.l.c. peak of the photoproduct mixture.

Pyrolysis of (+)-cis-*Caran*-5-*one* (VII).—This was carried out, with ketone (15 mg.) at 440° in a sealed, evacuated ampoule heated in a metal bath; the products were investigated by g.l.c. (see Discussion section).

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