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A review of some investigations of the chemistry of carene

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Synopsis—The HYDROGENATION, HYDROBORONATION, PYROLYSIS, AMINATION, OXIDATION, and the PHOTOCHEMICAL ISOMERISATION of (+)-CAR-3-ENE, a potential raw material for the fine chemical industry, have been performed, and are here reviewed. CARANOLS, CARANONES, CARANAMINES and their rearrangement products have been SYNTHESISED.

The bicyclic terpene, carene, exists in nature as (+)-car-2-ene (formula 1) and (+)-car-3-ene (formula 2). Both are present in Indian and in Baltic (1) oils of turpentine, (+)-car-3-ene (formula 2) being the more abundant. Both are however found in sufficient quantity to make them potentially valuable as starting points for the synthesis of terpenoids. Although a considerable amount of investigation was carried out in the early nineteen twenties, particularly by the late Sir John Simonsen and his collaborators (2), the advent of the techniques of chromatography and spectroscopy has made a re-examination of the chemistry of this bicyclic monoterpene a profitable exercise, with a view to its economic use, as well as the uncovering of some interesting chemistry. We started on this work some five years ago.

There is a considerable body of evidence based upon conformational analysis and n.m.r. spectra (3) that the configuration and preferred conformation of (+)-car-3-ene is the boat form (formula 3) rather than the upturned boat form (formula 4).

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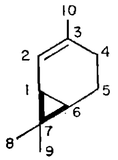

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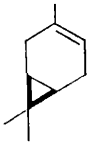

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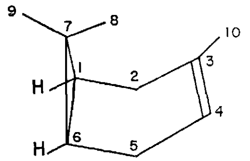

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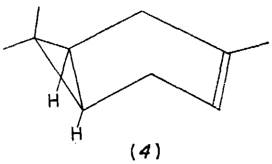


(4)

This is particularly revealed by the 8- methyl signal (τ 9.24) which shows diamagnetic shielding by the double bond. (+)-Car-2-ene (formula 1) similarly takes up a boat form. Thus the α- side of the double bond seemed ripe for elaboration.

HYDROGENATION (4)

Catalytic hydrogenation of (+)-car-3-ene (formula 2) was expected to take place preferentially from the α- side, giving (—)-*cis*-carane (formula 5). Little (+)-*trans*-carane (formula 6) was expected, and none was found in any catalytic hydrogenation experiments. In the event it was found that the products varied widely according to reaction conditions. Using 5% platinised charcoal, ethanol as solvent, hydrogen at 10.1 MN m^{-2} pressure, and at room temperature, (—)-*cis*-carane (formula 5) was obtained almost quantitatively in at least 98% purity (glc on a 3 m, 20% squalene-*Chromosorb W* column). However at 101 KN m^{-2} pressure, using 5% palladised charcoal and ethanol as solvent, (—)-*cis*-carane (formula 5) represented only about 50% of the product. The other product was 1,1,4-trimethylcycloheptane (formula 7). The proportions of these two products varied widely with reaction conditions. Thus using 5% palladised charcoal, 101 KN m^{-2} of hydrogen, and propionic acid as solvent, 1,1,4-trimethylcycloheptane was always the major product, and the yield of this increased with increasing temperature, until at 65° it was the only product.

The 1,1,4-trimethylcycloheptane (formula 7) was identified (a) by its lack of optical activity, and (b) by its nmr spectrum which showed signals at τ 9.12 (singlet, 6H, *gem*-dimethyl protons) and 9.12 (doublet, J 5.5Hz, CH_3-10). (—)-*cis*-Carane showed signals in its nmr spectrum at τ 9.2-9.8 (2 cyclopropane protons), 9.07 and 9.02 (each 3H, *gem*-dimethyl protons) and 9.18 (doublet, J 5Hz, CH_3-10).

Table I.
Effect of temperature on the hydrogenation of (+)-car-3-ene in propionic acid using palladised charcoal as catalyst

Temperature	% *cis*-Carane	% 1,1,4-Trimethyl-cycloheptane
0°	35.5	64.5
8	33.0	67.0
20	26.0	74.0
33	18.5	81.5
48	7.0	93.0
61	3.0	97.0
73	0	100.0
90	0	100.0
106	0	100.0
126	0	100.0

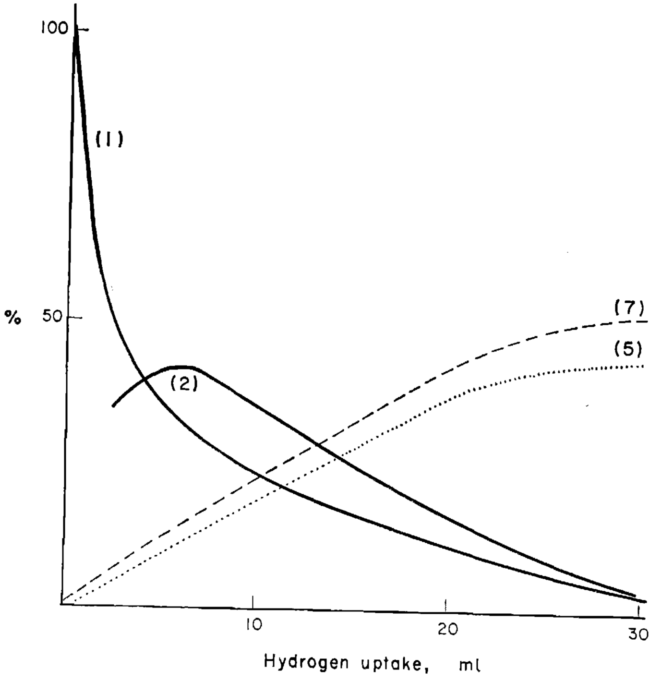


Figure 1. Percentage composition of reaction mixture during hydrogenation of (+)-car-2-ene (formula 1) [(formula 2) (+)-Car-3-ene, (formula 5) (—)-*cis*-Carane, (formula 7) 1,1,4-trimethylcycloheptane]

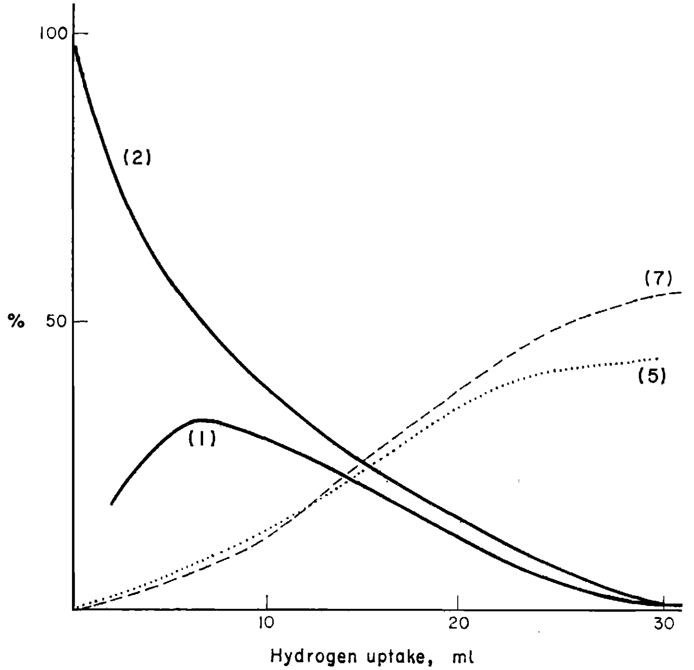
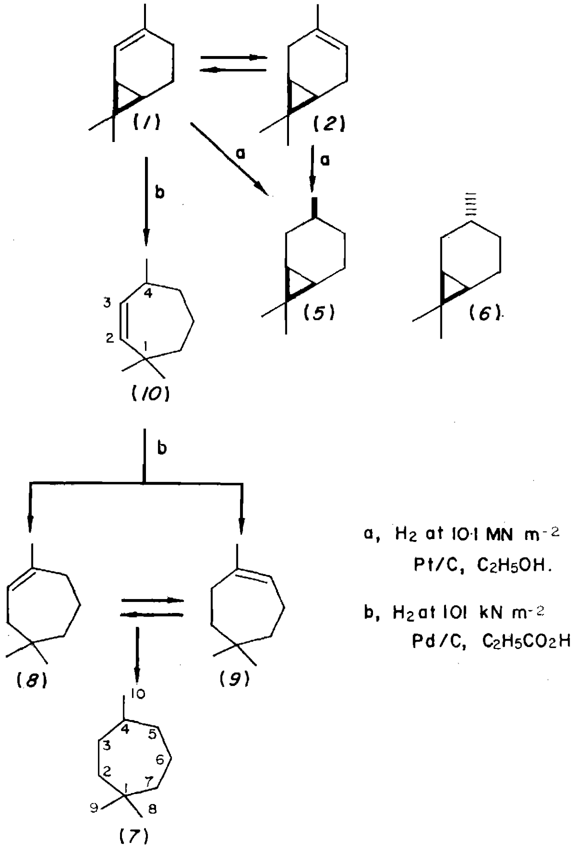


Figure 2. Percentage composition of reaction mixture during hydrogenation of (+)-car-3-ene (formula 2) [(formula 1) (+)-Car-2-ene, (formula 5), (—)-*cis*-Carane, (formula 7), 1,1,4-trimethylcycloheptane]

The formation of 1,1,4-trimethylcycloheptane from (+)-car-3-ene (formula 2) can be ascribed to the intermediate production of (+)-car-2-ene (formula 1), having a 'conjugated' system in which the cyclopropane ring simulates a double bond. That this is the case is shown by the absorption of (+)-car-2-ene (formula 1) in the ultraviolet region which displays a band, in ethanol, at 221 nm (log ε 3.6). We have shown that (+)-car-3-ene (formula 2) and (+)-car-2-ene (formula 1) can be equilibrated in presence of palladised charcoal saturated with hydrogen; no equilibration takes place in the absence of hydrogen. The two compounds can be separated by chromatography on silica impregnated with 25% silver nitrate. Catalytic hydrogenation of (+)-car-2-ene (formula 1) in propionic acid, using 5% palladised charcoal gave final results similar to those obtained from (+)-car-3-ene (formula 2). However, the rate of formation of 1,1,4-trimethylcycloheptane (formula 7) was substantially higher at the start of the reduction of (+)-car-2-ene than of (+)-car-3-ene. *Figs. 1* and *2* illustrate this point.



a, H_2 at 10·1 MN m^{-2}
Pt/C, C_2H_5OH.

b, H_2 at 101 kN m^{-2}
Pd/C, $C_2H_5CO_2H$

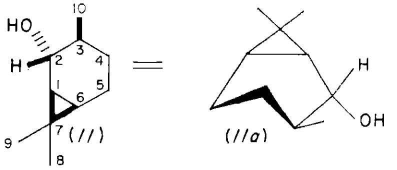
Again, when (+)-car-3-ene (formula 2) was refluxed with 5% palladised charcoal it gave a mixture of *m*- (20%) and *p*- cymene (30%), 1,1,4-trimethylcyclohept-3-ene (formula 8) (25%), and 1,1,4-trimethylcyclohept-4-ene (formula 9) (25%), which were separated by preparative glc on a 6 m, 30% *Castorwax-Chromasorb W* column. 1,1,4-Trimethylcyclohept-3-ene (formula 8) absorbed in the ir (liquid film) at 1 650 (C=C), 1 383, 1 362 (*gem*-dimethyls), and 808 cm^{-1} ($R_2C{=}CHR$), and its nmr spectrum displayed signals at τ 9.08 (singlet, 6H, *gem*-dimethyl protons), 8.37 (broad singlet, 3H, $CH_3C{=}C$), and 4.7 (doublet, J 6.5Hz, 1H, $C{=}CH$). Its isomer (formula 9) absorbed (liquid film) at 1 650, 1 375, 1 355, and 856 cm^{-1} in the ir and in its nmr spectrum it resonated at τ9.14 (singlet, *gem*-dimethyl protons), 8.30 (broad singlet, $CH_3C{=}C$), and 4.73 (triplet, J 6Hz, $C{=}CH$). Both cycloheptenes afforded 1,1,4-trimethylcycloheptane (formula 7) on catalytic hydrogenation.

The experimental evidence described above leads us to suggest that the hydrogenation of the carenes proceeds by the following reaction sequence.

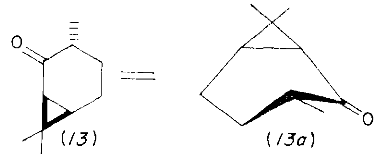
In the first stage of the reaction, (+)-car-2-ene (formula 1) undergoes 1,4- addition of hydrogen to the 'conjugated' system thus forming 1,1,4-trimethylcyclohept-2-ene (formula 10). This could not be isolated from the reaction mixture, presumably because of its rapid isomerisation to its more stable isomers (formulae 8 and 9), whose double bonds are stabilised by the attached methyl groups. The second stage of the reaction involves the saturation of the double bonds in these cycloheptenes. The chemistry of these compounds has not been investigated.

OXIDATIVE HYDROBORONATION

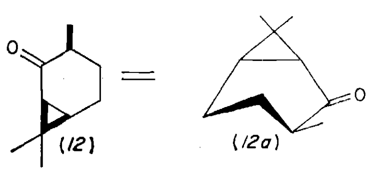
Reaction of boron hydride with alkenes is known to take place by cis-addition of $H(^-)$ and $(^+)BH_2$, in an anti-Markownikoff manner, to the less hindered side of the double bond (5). Moreover the boranes, thus formed, undergo isomerisation at elevated temperatures with migration of boron to sterically preferred positions (6). This has been demonstrated in particular for the hydroboronation products of α-(4) and β-(7) pinenes. Furthermore, boranes undergo oxidation with alkaline hydrogen peroxide giving alcohols having the same configuration as their precursors. We have applied these reactions to (+)-car-2-ene (formula 1) and (+)-car-3-ene (formula 2), (8).



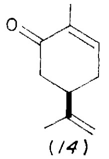
(11) (11a)



(13) (13a)



(12) (12a)



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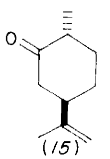
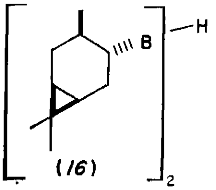


(15)

(+)-*Car-2-ene*

(+)-Car-2-ene (formula 1) was expected to hydroboronate on the α-side of the double bond giving, after oxidation,(—) -*cis*-caran-*trans*-2-ol (formula 11). In accordance with expectation this alcohol was produced in 85% yield, and its hydroxyl configuration was established by a study of its nmr spectrum, after deuterium exchange. This showed the pseudoaxial α-carbinol proton (H at C-2) as a broad doublet at τ 7.06 (J 8Hz). Oxidation of the alcohol, using a two phase system of chromic acid-dilute sulphuric acid and ether (9), gave (—)-*cis*-caran-2-one (formula 12), which in the ultra-violet region shows ε = 1 900 at 210 nm, and in the ir region absorbs at 1 689 cm^{-1}, indicative of conjugation of the C=0 and cyclopropyl systems. Equilibration of the ketone (formula 12) with ethoxide afforded (—)-*trans*-caran-2-one (formula 13), identical with an authentic specimen prepared (10) from (—)-carvone (formula 14). We have shown (11) that (+)-dihydrocarvone (formula 15), an intermediate in Baeyer's synthesis (10), is conveniently obtained in high yield by reduction of (—)-carvone with lithium in liquid ammonia.



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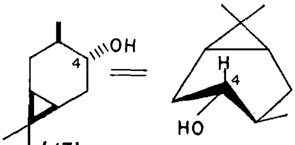
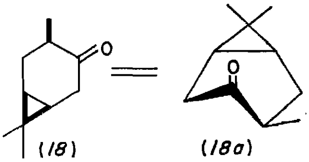
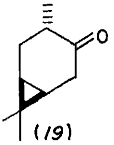


(17) (17a)



(18) (18a)



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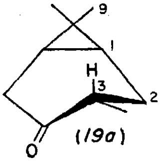
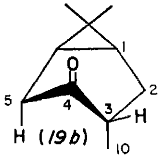
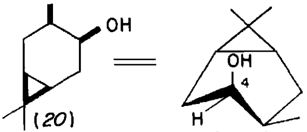


(19a)



(19b)



(20) (20a)

(+)-Car-3-ene

Hydroboronation of (+)-car-3-ene (formula 2) in diglyme at 20° gave *cis*-caranyl-*trans*-4-borane (formula 16) which on alkaline peroxide oxidation afforded (—)-*cis*-caran-*trans*-4-ol (formula 17). The identity of this alcohol was confirmed, by (a) reduction of its toluene *p*- sulphonic ester with lithium aluminium hydride to (—)-*cis*-carane (formula 5) (12), (b) its nmr spectrum which shows a complex multiplet in the region of τ 7.0. However, deuteriation removed a broad singlet at τ 6.96 (O*H*) revealing a multiplet centred on τ 7.04 derived from the α- carbinol proton (H4) which has two axial-axial (J 9Hz) and one axial-equatorial (J 6Hz) couplings. This accords with the half-chair conformation (17a) in which both hydroxyl and 10- methyl groups are equatorial.

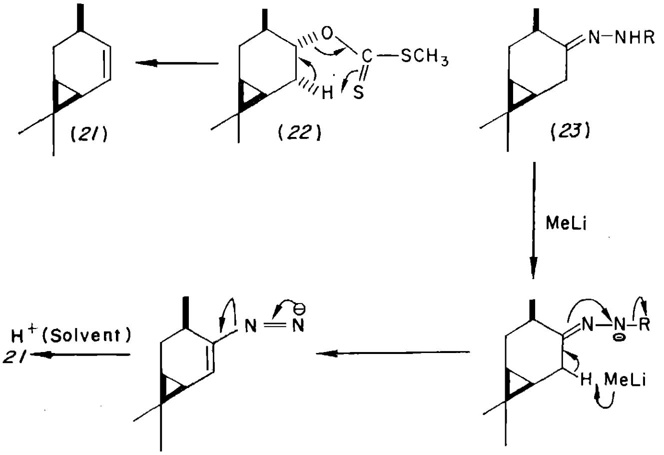
Oxidation of (—)-*cis*-caran-*trans*-4-ol (formula 17) by Brown and Garg's method (9) gave (—)-*cis*-caran-4-one (formula 18) which was virtually unchanged when treated with sodium ethoxide. This initially surprising behaviour is consistent with the compound (formula 18) being a stable ketone (13). However, the solvent shifts (14, 15) for the 10-methyl doublet, $\Delta^{CDCl_3}_{C_6H_6}$ and $\Delta^{CCl_4}_{C_5H_5N}$ are $+0.03$ and—0.07 respectively thus suggesting that this ketone exists as conformer (formula 18a). Models show that it is likely to be more stable than the *trans*-isomer (formulae 19a, b). Thus in (formula 19a), there is an additional H3/9-methyl interaction, whilst in (formula 19b) an additional H5/10- methyl interaction exists.

Catalytic hydrogenation of (—)-*cis*-caran-4-one (formula 18) over Adams's platinum catalyst gave a mixture of (—)-*cis*-caran-*trans*-4-ol (formula 17) (1 part) and its epimer (+)-*cis*-caran-*cis*-4-ol (formula 20) (9 parts). The predominance of the less stable, axial alcohol in this reaction is to be expected (16). The half-chair conformation of the alcohol (formula 20=20a) is shown by the signal of the equatorial H4 at τ 6.35 (doublet, J 6Hz) compared with the multiplet at τ 7.04 (J 9Hz) for its epimer (formula 17=17a).

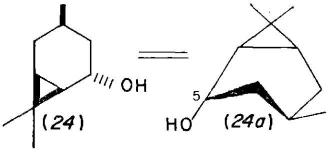
Reduction of (—)-*cis*-caran-4-one (formula 18) with lithium aluminium hydride gave a mixture of the epimeric alcohols (formulae 17 and 20), in which the more stable, equatorial alcohol (formula 17) predominated in the ratio 7:3 (13). The major alcohol (—)-*cis*-caran-*trans*-4-ol (formula 17) was isolated *via* its toluene p- sulphonic ester. The properties of the alcohols (formulae 17 and 20) and their ketone (formula 18) agree well with those described by Gollnick *et al* (17-19).

(—)-*cis-Car-4-ene*

We initially prepared (—)-*cis*-car-4-ene (formula 21) by the pyrolysis



$R = p\text{-}CH_3C_6H_4SO_2$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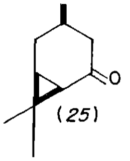
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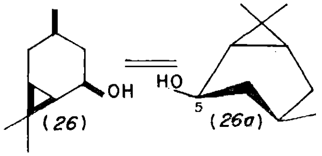
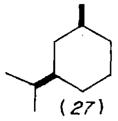

(26) (26a)


(27)

(17) of the methyl xanthogenate (formula 22) of (—)-*cis*-caran-*trans*-4-ol (formula 17), a reaction which is known to take place by *cis*-elimination. Yields were only moderate. We have recently found (20) that (—)-*cis*-car-4-ene (formula 21) is formed quantitatively from the toluene *p*- sulphonylhydrazone (formula 23) of (—)-*cis*-caran-4-one (formula 18) by treatment with methyl lithium (21). It is now possible to obtain substantial quantities of car-4-ene by this route.

Steric hindrance to approach of boron hydride to the β- side of (—)-*cis*-car-4-ene is not so evident, from a study of models, as it is in the cases of the car-2- and 3-enes. In addition, since the double bond may be considered to be symmetrical, the boron atom can appear at either C4 or C5, leading, after oxidation to both caran-4- and 5-ols. In the event, (—)-*cis*-car-4-ene (formula 21) gave a mixture of (—)-*cis*-caran-*trans*-4-ol (formula 17) (20%) and (—)-*cis*-caran-*trans*-5-ol (formula 24)

(80%). We were unable to separate them by glc on any available column, but the 5-ol was isolated from the mixture *via* its 3,5-dinitro-benzoate. A complete separation of the epimers was however effected by oxidation to the corresponding ketones (formula 18) and (+)-*cis*-caran-5-one (formula 25) (which were readily separated by chromatography on silica gel), followed by reduction (see below).

The conjugated nature of (+)-*cis*-caran-5-one (formula 25) is clear from its ultraviolet spectrum which shows $\varepsilon = 3\ 279$ at 210 nm, and its ir spectrum which displays a carbonyl group maximum at 1 685 cm^{-1}.

Reduction of (+)-*cis*-caran-5-one (formula 25) with lithium aluminium hydride afforded a mixture of the pseudo-equatorial alcohol, (+)-*cis*-caran-*cis*-5-ol (formula 26) as major product and its pseudo-axial epimer (formula 24), from which the former was isolated by crystallisation from methanol. Reoxidation of the mixture of alcohols afforded the single ketone (formula 25), thus demonstrating the presence of the intact cyclopropane group in the alcohols. Their configurations were based (a) upon the known steric characteristics of lithium aluminium hydride as a reducing agent, (b) the nmr signals of the 5H (α- carbinol proton) which for the *trans*-5-ol (formula 24) was a poorly resolved doublet (J 4.5Hz) centred at τ 6.0 and for the *cis*-5-ol (formula 26) was a multiplet at τ 5.5-6.1. These are respectively the characteristics expected of equatorial or pseudo-equatorial and axial or pseudo-axial 5- hydrogen atoms.

In passing, it is of interest to note that reduction of (+)-*cis*-caran-5-one (formula 25) over platinum afforded predominantly (+)-*cis*-*m*-menthane (formula 27) (12), a hydrogenolysis product also obtained from (+)-*cis*-caran-*cis*-5-ol (formula 26) using the same catalyst. It is clear that caran-5-ol is here simulating an allylic alcohol.

The configurations and conformations of the caranols described above were confirmed (22) in a number of ways.

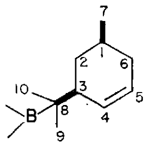
(a) Comparison of the dihedral coupling constants of the hydroxy-protons with the α- carbinol protons in their nmr spectra measured in dimethyl sulphoxide (23) distinguishes between axial and equatorial hydroxy groups.

(b) Similarly, comparison of the rates of oxidation of the alcohols with chromate makes a distinction between conformers, it being well known that axial alcohols are more rapidly oxidised than their equatorial counterparts (24-27). Changes in chromate concentration were measured spectroscopically.

(c) Comparison of the rates of alkaline hydrolysis of the 3,5-dinitrobenzoates shows that the more sterically hindered axial esters are more slowly hydrolysed than their equatorial counterparts (24, 28).

(d) Horeau's method (29), in which the preferred enantiomer of α-phenylbutyric anhydride consumed in the esterification of the caranols is determined, leads to a knowledge of the configuration at the carbinol centre.

By these methods we arrived at the configurations shown in the formulae (11a, 17a, 20a, 24a, and 26a) for the caranols discussed above.



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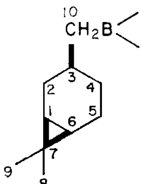

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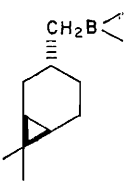

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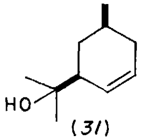
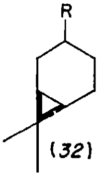


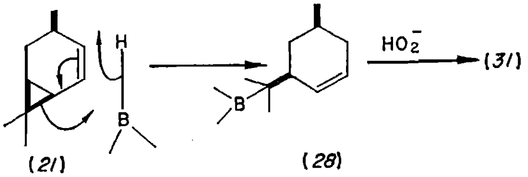
(31)



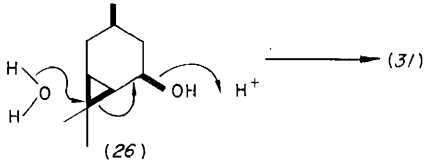
(32)

The methods used for the preparation of the caranols are effective but tedious. It therefore appeared appropriate to apply Brown's isomerisation reaction (6) to the readily formed *cis*-caranyl-*trans*-4-borane (formula 16) with a view to the formation of an equilibrium mixture of the 2-, 4-, and 5-boranes. In the event we found (8) that when the 4-borane (formula 16) was heated, it rapidly isomerised giving a mixture of the boranes mentioned, together with *cis*-*m*-menth-4-enyl-8-borane (formula 28) and, if the temperature reached 140°, *cis*- and *trans*-caranyl-10-boranes (formulae 29, 30) were also formed. Oxidation of the mixture of borane isomers with alkaline peroxide gave a mixture of (—)-*cis*-caran-*trans*-2-ol (formula 11), (—)-*cis*-caran-*trans*-4-ol (formula 17), (—)-*cis*-caran-*trans*-5-ol (formula 24), (—)-*cis*-*m*-menth-4-en-8-ol (formula 31), and a mixture of *cis*- and *trans*-caran-10-ols (formula 32; R, β-, α- CH_2OH). The results of these experiments are shown graphically in *Fig. 3*. The speeds of formation of the boranes (identified as their alcohols) are shown in *Fig. 4*.

The formation of the unsaturated monocyclic borane (formula 28) probably takes place by 1,4- addition of boron hydride to the α, β- unsaturated cyclopropane system of (—)-*cis*-car-4-ene (formula 21) formed as intermediate, as portrayed below. A similar 1,4- hydroboronation occurs with α- gurjunene (30).



The identity of (—)-*cis*-*m*-menth-4-en-8-ol (formula 31) was confirmed by its preparation from (+)-*cis*-caran-*cis*-5-ol (formula 26), by pyrolysis (11, 31) and by reaction with 0.1N hydrochloric acid (8). The acid catalysed reaction takes place as shown below.



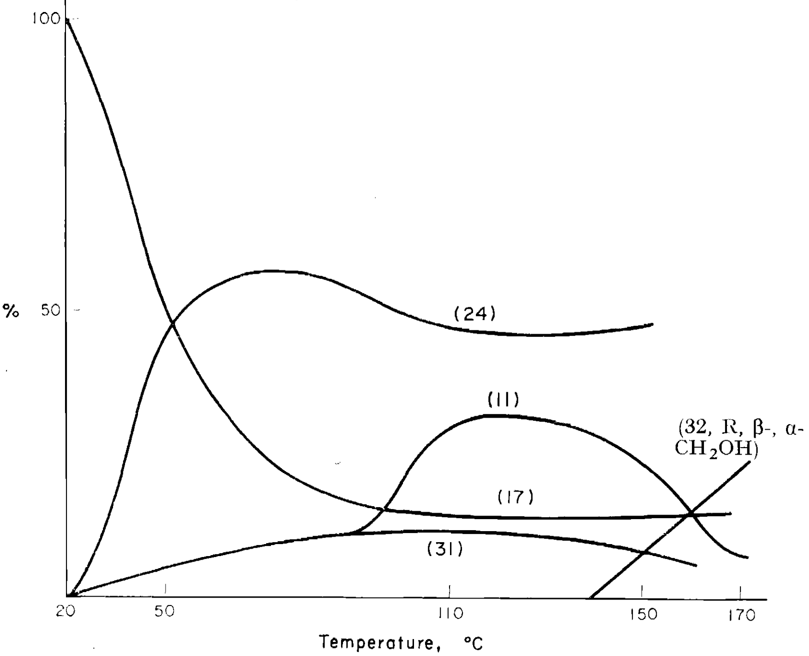


Figure 3. Approximate compositions of the alcohol mixtures from the oxidative hydroboronation of (+)-car-3-ene (formula 2) at different temperatures.

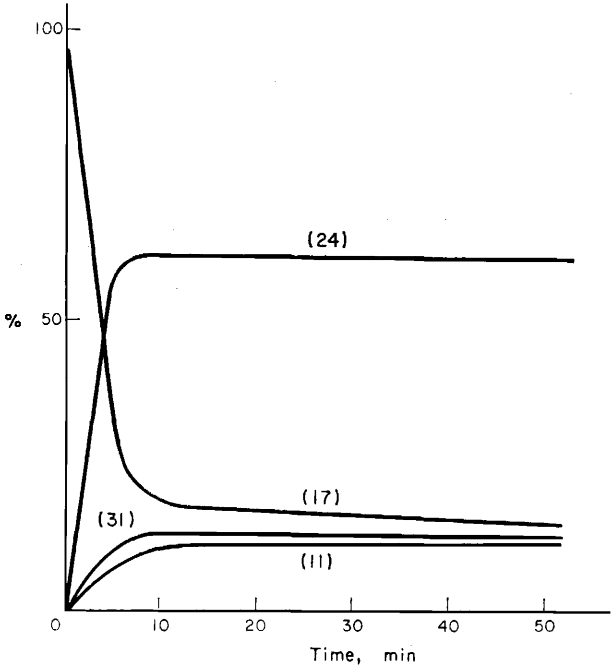


Figure 4. Percentage of alcohols (formulae 11, 17, 24 and 31) formed as a function of time at 100°. [(formula 11) (—)-*cis*-caran-*trans*-2-ol, (formula 17) (—)-*cis*-caran-trans-4-ol, (formula 24), (—)-*cis*-caran-trans-5-ol, (formula 31) (—)-*cis*-m-menth-4-en-8-ol]

The *cis*- and *trans*-caran-10-ols (formula 32, R, β-, α-CH_2OH) were not separable by glc nor through their 3,5-dinitrobenzoates, nor was there any evidence from the nmr spectrum of their mixture that more than one component was present. This spectrum showed a multiplet at τ 9.2-9.6 (cyclopropane protons), singlets at τ 9.04 and 9.6 (*gem*-dimethyl groups), a doublet at τ 6.70 (J 5.5Hz; CH_2-10), and a singlet at τ 6.6 (OH) removed by deuteriation. We were not surprised by the difficulties in separation of these 10-ols, for earlier (12) we had shown that the closely related hydrocarbons, (—)-*cis*- (formula 5) and (+)-*trans*-carane (formula 6) were inseparable by glc since they are quasi-enantiomeric. Nevertheless, these hydrocarbons showed small, but quite distinct differences in their ir and nmr spectra (12). We made use of these facts in assessing the composition of the mixture of the 10-ols. Thus reduction of their mixed toluene *p*- sulphonates with lithium aluminium hydride gave a mixture of equal quantities of *cis*- (formula 5) and *trans*-carane (formula 6). The formation of the *cis*- and *trans*-caran-10-ols (formula 32; R, β-, α-CH_2OH) must proceed *via* the intermediacy of car-3 (10)-ene (formula 33).

Whilst elevated temperature hydroboronation of (+)-car-3-ene did not offer an attractive route to the caran-2- or 10-ols, it did however afford a simple method of obtaining (—)-*cis*-caran-*trans*-5-ol (formula 24) in good yield. *Fig. 4* shows that in 10 min at 100°, *cis*-caran-*trans*-4- is converted into about 60% of *cis*-caran-*trans*-5-borane. Its predominance may result from the electronic effects of the polarisation of the conjugated system of car-4-ene (formula 21), formed as an intermediate, towards the cyclopropane ring.

Pyrolysis

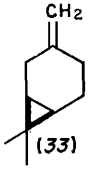
(+)-*Car-3-ene*

The pyrolysis of β- pinene (formula 34) is the first stage in the manufacture of a range of perfumery substances (32). Under favourable conditions, it gives myrcene in up to 90% yield. In furtherance of our plan to study the chemistry of carene, it seemed appropriate (11) to study its pyrolysis. Liquid (+)-car-3-ene (formula 2) was dropped into a packed, heated tube and carried forward as vapour in a current of nitrogen. The cracking took place in the vapour phase since the extent of pyrolysis at a given temperature did not alter when the surface area of the column packing was increased fortyfold. The products were condensed, isolated by column chromatography and preparative glc, and identified by their spectral and other physical characteristics, and by comparison with authentic materials. The column was packed with glass beads, or with a catalyst, e.g. a potassium aluminosilicate.

Car-3-ene is relatively stable to pyrolysis. Thus, whilst, in our apparatus, without catalyst such as aluminosilicate, β- pinene was completely isomerised at 325°C, car-3-ene began to isomerise only at about 450°C. (+)-Car-2-ene (formula 1) was however somewhat more readily decomposed than (+)-car-3-ene (33).

Table II shows the effects of temperature on the products of pyrolysis of (+)-car-3-ene. It shows quite clearly that whilst at 480°, car-3-ene is decomposed to the extent of only one third, at 560° it is completely decomposed giving almost entirely aromatic products.

This resistance of the cyclopropyl ring to thermal cracking may be traced to the difficulty of formation of the free radicals (formulae 35 and 36). These have not the resonance stabilisation of the radicals (formulae 37, 38 and 39 respectively) derivable from β-pinene, α- pinene, and car-



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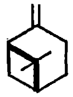

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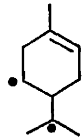

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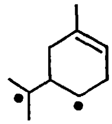

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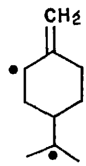

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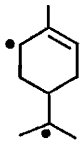

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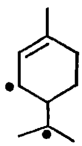
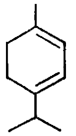


(39)

2-ene. Indeed, car-3-ene (formula 2) may be considered to have quasi-aromatic character; the bonds allylic to the double bond are in fact quasi-vinylic with respect to the three membered ring. Hence under the conditions of pyrolysis and flow-rate that we employed, the high temperature necessary to effect cracking of (+)-car-3-ene militated against the formation of acyclic products. Indeed we found that at these temperatures both β- pinene and myrcene afford aromatic products.



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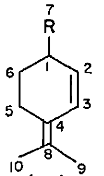

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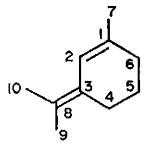

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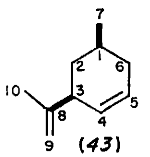

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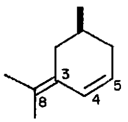


(44)

Cracking of (+)-car-3-ene started at a lower temperature (300°C) when the column was packed with a potassium aluminosilicate catalyst. At 400°C it was completely transformed giving *m*- cymene (8.2%), *p*- cymene (10.9%), α- terpinene (formula 40) (21%), (±)-*p*-mentha-2,4(8)-diene (formula 41; R, CH_3) (14%) and *m*-mentha-1, 3(8)-diene (formula 42) (34)

Table II

Products % of pyrolysis, without catalyst, of (+)-car-3-ene at different temperatures

Temperature °C	Benzene	Toluene	*m*- and *p*-Xylenes	Styrene	*m*-Cymene	*p*-Cymene	*m*- and *p*-Methylstyrenes	Dehydro- *m*-cymene	Dehydro- *p*-cymene	Carene
480	0	5.0	4.9	0	10.4	6.3	0	0	0	65.7
510	1.5	16.4	12.9	6.2	18.4	10.0	3.4	5.3	3.4	9.9
560	4.8	22.4	16.2	5.8	11.2	6.0	11.6	6.1	4.4	0
600	9.4	25.0	13.5	5.0	6.9	5.0	12.8	6.1	3.1	0
640	14.4	32.0	20.5	3.9	2.8	1.5	14.8	4.1	2.7	0
675	16.4	37.5	20.5	1.3	1.1	1.0	11.2	2.6	1.6	0

Table IV

Spectral characteristics of menthadienes

[(Formula 41; R, α-Me) (+)-*p*-mentha-2,4(8)-diene, (formula 42) *m*-mentha-1, 3(8)-diene, (formula 43) (—)-*cis*-*m*-mentha-4, 8-diene, (formula 44) (+)-*m*-mentha-3(8)-4-diene, (formula 46) (+)-*trans*-*p*-mentha-2, 8-diene]

	Formulae				
Spectrum	(41; R, α-CH_3)	(42)	(43)	(44)	(46)
Uv nm (log ε). (EtOH)	244(3.93)[35]	245 (4.11)	End absorption only	243.5 (4.28)	End absorption only
Ir (liquid)	731 (*cis* CH=CH)	1630 (C=C)	888 ($R_2C=CH_2$) 731 (*cis* CH=CH)	1680 (C=C) 726 (*cis* CH=CH)	1642 (C=C) 885 ($R_2C=CH_2$) 728 (*cis* CH=CH)
nmr (CCl_4)	9.02 (d, J 7Hz, $CH_3$7) 8.29 [s, 6H, $(CH_3)_2C=C$] 4.55 (d, J 11Hz, H2) 3.68 (d, J 11Hz, H3)	8.29 (s, 9H, $CH_3C=C$) 3.9 (s, 1H, H2)	9.02 (d, J6Hz, CCH_3) 8.32 (s, $CH_3C=C$) 5.31 (s, $CH_2=C$) 4.42 (s, CH=CH)	9.02 (d, J 6Hz, CCH_3) 8.24 [s, 6H, $(CH_3)_2C=C$] 4.44 (m, 1H, H5) 3.65 (d, J 10Hz, H4)	9.05 (d, J 7Hz, CCH_3) 8.32 (s, $CH_3$10) 5.32 (s, $CH_2$9) 4.52 (s, H2, H3)

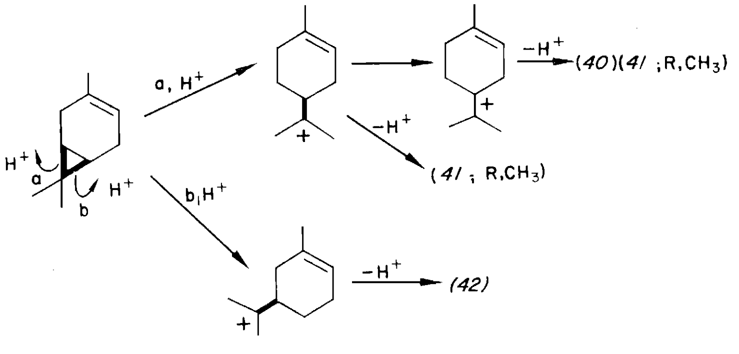
Table III

Products % from heating (+)-*cis*-caran-*cis*-5-ol (formula 26) with acetic acid at various temperatures

Temperature °C	Formulae		
	(43)	(44)	(31)
180	71.7	12.2	16.7
210	74.5	13.3	11.6
300	61.8	21.7	3.4

(14.4%). The ultraviolet spectrum of (±)-*p*-mentha-2,4(8)-diene (formula 41; R, CH_3) showed a maximum at 244 nm (log ε 3.93) (35) and at 731 cm^{-1} (*cis* CH=CH) (36) in the infra-red. Signals at τ 9.02 (d, J 7Hz, 3H, CH_3-7), 8.29 [s, 6H, $(CH_3)_2C{=}C$], 4.55 (d, J 11Hz, H2) and 3.68 (d, J 11Hz, H3) in the nmr spectrum are in complete agreement with its structure. *m*-Mentha-1,3(8)-diene (formula 42) likewise showed a conjugated diene maximum at 245 nm (log ε 4.11) in the ultraviolet, and at 1 630 cm^{-1} in the infra-red. Its nmr spectrum showed peaks at τ 8.29 (s, 9H, vinylic CH_3 groups) and at 3.9 (s, 1H, H2), in agreement with its structure.

We portray the formation of these dienes, which is acid catalysed, in the following manner.



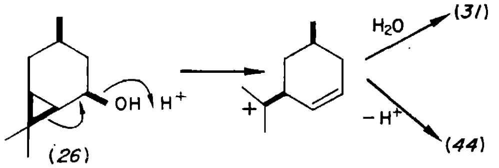
(+)-*cis-Caran-cis-5-ol*

We next pyrolysed (+)-*cis*-caran-*cis*-5-ol (formula 26), without catalyst, at about 480°C, in the vapour phase, with the object of obtaining other menthadienes. In the event the product consisted largely of (—)-*cis*-*m*-mentha-4, 8-diene (formula 43) (80%) (17) and the previously unknown (+)-*m*-mentha-3(8), 4-diene (formula 44). When the caran-5-ol (formula 26) was heated with a catalytic amount of acetic acid (*Table III*), the dienes (formulae 43 and 44) were formed along with (—)-*cis*-*m*-menth-4-en-8-ol (formula 31) (8). This is an interesting result for unlike the pyrolysis of (+)-car-3-ene, the alcohol (formula 26) gave only *meta* menthane derivatives.

The structures of the menthadiene (formula 43) and its conjugated isomer (formula 44) were assigned spectroscopically and chemically. Both consumed two molar proportions of hydrogen, the former giving *cis-m*-menthane and the latter giving a mixture of *cis*- and *trans-m*-menthanes. It should be remembered, however, that the configurations of the menthane products of hydrogenation cannot be used as an indication of the configurations of the starting dienes. It has been our experience that the more stable *o*-, *m*-, or *p*-menthanes are obtained predominantly regardless of the configurations of the dienes.

The spectra of the menthadienes (formulae 41-44 and 46) are given in *Table IV* and they fully substantiate the assigned structures. The configurations of the two alkyl groups of (—)-*cis-m*-mentha-4, 8-diene (formula 43) are those of (+)-*cis*-caran-*cis*-5-ol (formula 26) since the centres at C1 and C3 are not involved in the pyrolysis reaction.

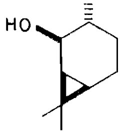
Although the alcohol (—)-*cis-m*-menth-4-en-8-ol (formula 31) may be obtained from (+)-*cis*-caran-*cis*-5-ol (formula 26) by pyrolysis it is more conveniently obtained by treating this alcohol with 0.1N hydrochloric acid at 20°C. The yield of the alcohol (formula 31) depends upon the concentration of the acid. With higher concentrations of acid, dehydration and isomerisation take place giving *m*-menth-3(8),4-diene (formula 44).



(—)-*cis-m*--Menth-4-en-8-ol (formula 31) shows nmr resonances at τ 9.02 (d, J 5Hz, CH_3-7), 8.91 and 8.86 (singlets, CH_3-9, 10), 8.5 (s, OH), 4.25 (s, 2H, H4, H5). There was no signal in the τ 5-7.5 region, indicating the tertiary character of the alcohol. In the infra-red, peaks at 3268 (OH), 1 642 (C=C), and 735 (*cis* CH=CH) cm^{-1} support the structure. Confirmation comes from its mass spectrum which shows peaks at m/e 154 (M^+), 59 [$(CH_3)_2COH^+$], and 44 (CH_3COH^+). Finally dehydration of the alcohol (formula 31) with phosphoryl chloride gave a mixture of the dienes (formulae 43 and 44).

(—)-*trans-Caran-cis-2-ol*

Pyrolysis, at 410°C in the vapour phase, of (—)-*trans*-caran-*cis*-2-ol (formula 45) which was obtained by the lithium aluminium hydride reduction of (—)-*trans*-caran-2-one (formula 13), gave (+)-*trans*-*p*-mentha-2,8-diene (formula 46) (85%) and (+)-*p*-mentha-2,4(8)-diene (formula 41, R, α- CH_3) (15%).



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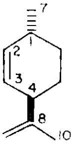

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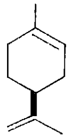

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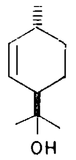


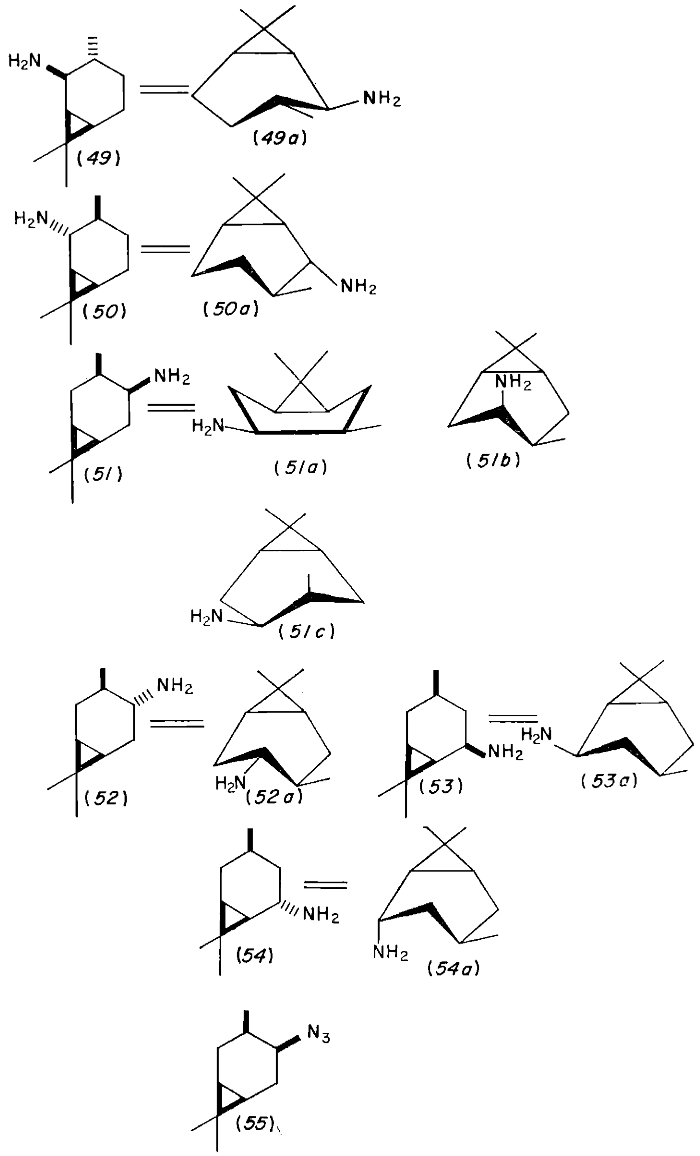
(48)

On heating (—)-*trans*-caran-*cis*-2-ol (formula 45) with a little acetic acid in a sealed tube at 210°C, (+)-*trans*-*p*-mentha-2,8-diene (formula 46) was again the predominant product. Its spectra (*Table IV*) and the fact that on hydrogenation it affords *trans*-*p*-menthane largely settle its structure. However the configuration of the 7- methyl group follows from the configuration of the alcohol (formula 45), since this methyl takes no part in the reaction. If it did, the pyrolysis product would be *p*-mentha-1,8-diene (formula 47). The minor product of the acid-catalysed thermal isomerisation was (+)-*trans*-*p*-menth-2-en-8-ol (formula 48) (33) an analogous alcohol to (—)-*cis*-*m*-menth-4-en-8-ol (formula 31) similarly formed from (+)-*cis*-caran-*cis*-5-ol (formula 26). The infra-red spectrum of the menthenol (formula 48) showed peaks at 3350 (OH), 1 650 (C=C), and 728 (*cis* CH=CH) cm^{-1}, whilst its nmr spectrum had signals at τ 9.04 (d, J 6Hz, CCH_3), 8.86 and 8.91 [singlets, $C(CH_3)_2$], 8.23 (s, OH) and 4.38 (s, H2,3). Its mass spectrum was similar to that of its isomer (formula 31) (see above). These spectra confirm its structure.

Larger yields (85%) of (+)-*trans*-*p*-menth-2-en-8-ol (formula 48) were obtained when (—)-*trans*-caran-*cis*-2-ol (formula 45) was treated with 3N hydrochloric acid. *a*- Terpinene (formula 40) (5%) and (+)-*p*-menth-2,4(8)-diene (formula 41; R, α-CH_3) (15%) are other products of this reaction.

CARANAMINES

Only one caranamine was known, when we commenced our work (37), namely a dextrorotatory caran-4-amine (38). However during the course of the work a preparation of (+)-*trans*-caran-*cis*-2-amine, presumably Baeyer's amine (38), was described (39). We have therefore worked out (37) stereospecific routes to the following: (—)-*trans*-caran-*cis*-2-amine (formula 49) (the enantiomorph of Baeyer's amine), (—)-*cis*-caran-*trans*-2-amine (formula 50), (+)-*cis*-caran-*cis*-4-amine (formula 51), (—)-*cis*-caran-



trans-4-amine (formula 52), (+)-*cis*-caran-*cis*-5-amine (formula 53) and (—)-*cis*-caran-*trans*-5-amine (formula 54). With suitable elaboration these amines might give compounds of useful physiological properties. They are in fact strong bases which rapidly form carbonates with atmospheric carbon dioxide.

(—)-*cis*-Caran-*trans*-4-amine (formula 52) was obtained in two ways, (a) from the oxime of (—)-*cis*-caran-4-one (formula 18) by reduction with sodium in ethanol; under these conditions the more stable amine is formed, and, (b) from *cis*-caran-4α-borane (formula 16) by treatment with hydroxylamine *o*- sulphonic acid, a reaction which is known to take place with configurational retention (40).

(+)-*cis*-Caran-*cis*-4-amine (formula 51) was also obtained in two ways,

(a) the toluene *p*-sulphonate of (—)-*cis*-caran-*trans*-4-ol (formula 17) was reacted with lithium azide (41) in methanol, giving the azide (formula 55) with inverted configuration at C4. This was reduced with retention of configuration to the *cis*-4-amine (formula 51).

(b) The oxime of (—)-*cis*-caran-4-one (formula 18) was reduced in acetic acid over platinum, though very slowly, to a mixture of (+)-*cis*-caran-*cis*-4-amine (formula 51) (3 parts) and its 4- epimer (formula 52) (1 part), already described. This reduction followed stereochemically the course of that followed in the reduction of the ketone itself. The all *cis*-amine (formula 51) was separated from its epimer (formula 52) through its more sparingly soluble toluene *p*-sulphonic acid salt. The reverse separation is possible with the hydrochlorides.

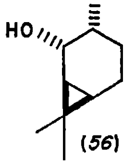
The preparation of the remaining caranamines mentioned above was accomplished (37) by a combination of the methods described above. Suffice it to say that (+)-*cis*-caran-*cis*-5-amine (formula 53) formed a sparingly soluble tartaric acid salt and its 5- epimer (formula 54) formed a sparingly soluble oxalate. (—)-*cis*-Caran-*trans*-2-amine (formula 50) was also isolated *via* its oxalate whilst (—)-*trans*-caran-*cis*-2-amine (formula 49) formed a sparingly soluble toluene *p*- sulphonate. The difference in the solubilities of the amine salts proved of great value in their isolation in a pure state.

We arrived at the preferred conformations of the amines by several methods. Thus (a) we used conformational analysis, (b) we compared the actual with the theoretical band-width of the nmr signal of the —C *H* (NH_2) proton (42) calculated from the Karplus equation (43, 44). The calculated band widths are only approximate (45), nevertheless there is sufficient difference between these values for alternative conformers to make the calculations meaningful, (c) we compared the specific rotations of the caranamines with those of the corresponding alcohols. On the basis of these data we assign the conformations (formulae 49a, 50a, 51a, 52a, 53a and 54a) to the caranamines described above. In the case of (+)-*cis*-caran-*cis*-4 amine (formula 51), which has the preferred boat form (formula 51a), the possible half-chair forms (formulae 51b and c) are eliminated since in these there will be considerable interaction between the *gem*-dimethyl group and the amino (formula 51b) or 10-methyl (formula 51c) groups. It should be noted that there is a divergence between the specific rotations of (+)-*cis*-caran-*cis*-4-ol (formulae 20=20a) ($[\alpha]_{\mathrm{D}}^{20}+49°\mathrm{C}$) and (+)-*cis*-caran-*cis*-4-amine (formula 51a) ($[\alpha]_{\mathrm{D}}^{20}+27.3°\mathrm{C}$). This may be explained on the basis of the difference in conformation of the alcohol and amine which is a result of the greater conformational energy of the amino than the hydroxy group (46).

Table V.
Products of deamination of caranamines
[The products are given by formulae numbers. These are followed by yields (%)]

Amine	*Product*
(49)	(56-14), (45-19), (46-41), (48-24)
(50)	(11-26), (11, β-OH-21), (57-49)
(51)	(17-12), (20-12), (60; R^1, α-CH_3, R^2, β-OH-14), (60; R^1, β-CH_3, R^2, α-OH-4), (61-14), (2-29), (21-8.5), (63-1). Uncharacterised substances (5.5)
(52)	(17-18), (20-15), (60; R^1, α-CH_3, R^2, β-OH-7), (60; R^1, β-CH_3, R^2, α-OH-2), (61-12), (2-21) (21-13), (63-8).
(53)	(24-7), (26-7), (31-81), (2+21-5)
(54)	(24-7), (26-7), (31-81), other hydrocarbons (5)

Having obtained a variety of caranamines of established configuration we examined their deamination with nitrous acid (47). All the caramines (formulae 49-54) when reacted with nitrous acid at 0°C under standard conditions afforded appreciable quantities (see *Table V*) of the corresponding alcohols of both configurations. To exemplify this we might mention the conversion of (—)-*trans*-caran-*cis*-2-amine (formula 49) to (+)-*trans*-caran-*trans*-2-ol (formula 56) (14%) and (—)-*trans*-caran-*cis*-2-ol (formula 45) (19%).



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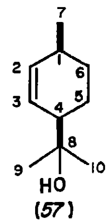
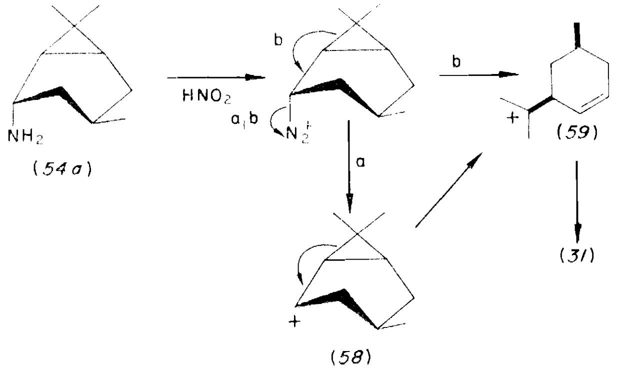


(57)

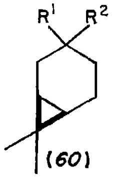
These alcohols arise from attack of water at the carbonium ion, or developing carbonium ion, derived from the diazonium ion. The differences in yield of the epimeric 2-, 4- and 5- caranols are not such as to suggest a conclusive detailed mechanism of the reaction.

However in the deamination of the caran-2- and 5-amines the major products have lost their cyclopropane rings (*Table V*). Thus, for example, (—)-*trans*-caran-*cis*-2-amine (formula 49) affords a 41% yield of (+)-*trans*-*p*-menth-2,8-diene (formula 46) and 24% of its hydration product (+)-*trans*-*p*-menth-2-en-8-ol (formula 48). Similarly (—)-*cis*-caran-*trans*-2-amine (formula 50) affords a 49% yield of the epimeric menthenol, (—)-*cis*-*p*-menth-2-en-8-ol (formula 57) the 1- epimer of (+)-*trans*-*p*-menth-2-en-8-ol (formula 48) (33) previously obtained by the acid-catalysed thermal isomerisation of (—)-*trans*-caran-*cis*-2-ol (formula 45). Deaminations of (—)-*cis*-caran-*trans*-5-amine (formula 54) and (+)-*cis*-caran-*cis*-5-amine (formula 53) in a similar fashion afforded (—)-*cis*-*m*-menth-4-en-8-ol (formula 31), previously obtained by the acid catalysed rearrangement of (+)-*cis*-caran-*cis*-5-ol (formula 26).

The formation of these menthadienes and menthenols can formally be explained as follows, using the deamination of (—)-*cis*-caran-*trans*-5-amine (formula 54) as example.



Mechanism (a) is similar to that suggested for the acid-catalysed rearrangement of the corresponding alcohol (formula 26), the carbonium ions (formulae 58 and 59) being possible intermediates in each case. It should,



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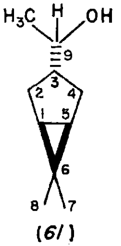

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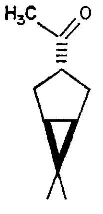

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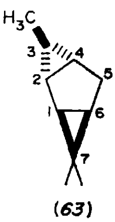


(63)

however, be remembered that a carbonium ion formed by deamination (sometimes known as a hot carbonium ion) frequently behaves differently from one produced by solvolysis or by protonation of the hydroxy group. There is one further point, the formation of formula 31 by deamination may be a synchronous process as in route (b).

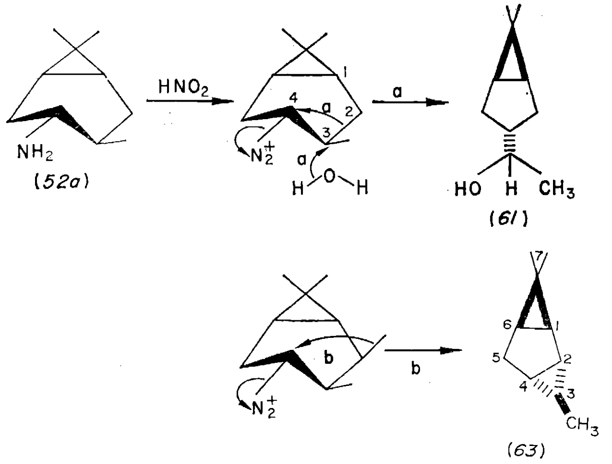
The deamination of the *cis*-caran-4-amines (formulae 51 and 52) proved to be most interesting because of the diversity of their products. Thus both afforded eight products, in each case, two being the epimeric 4-ols (formulae 17=17a and 20=20a). In addition, however, the epimeric 3-ols, (+)-*trans*-caran-*cis*-3-ol (formula 60, R_1, α-Me; R_2, β-OH) and (+)-*cis*-caran-*trans*-3-ol (formula 60; R_1, β-Me; R_2, α-OH) (48) were formed in minor quantities. These are formed from a carbonium ion at C3, resulting from hydride transfer from C3 to C4, and subsequent attack of water at the former centre. The higher yield of the former alcohol suggests product development control, but there is no other evidence in support of this suggestion.

Ring rearrangements also took place in the deamination of the caran-4-amines. One of the products was the previously unknown alcohol R(—)-*trans*-3-[1-hydroxyethyl]-6, 6-dimethylbicyclo[3,1,0]hexane (formula 61). It was obtained in a pure condition by careful chromatography on alumina followed by preparative glc on *Castorwax*. The identity of this alcohol was based on its properties and its nmr spectrum which showed the *gem*-dimethyl group as a singlet at τ 9.05 (6H), the side-chain methyl as a doublet at 8.95, an obscured multiplet at 8.9-9.28 derived from the two cyclopropyl protons and a broad signal at 8.2-8.36 (5H) derived from the four equivalent methylene protons and one hydroxyl group. The α- carbinol proton appeared as a quintet at τ 6.6 (J 6Hz) resulting from its almost equal coupling with the adjacent protons. The *trans*-configuration of the cyclopropyl group and hydroxyethyl side-chain follow from the fact that there is only very small nmr deshielding (*ca.* 1Hz) in pyridine of the *gem*-dimethyl signals which are coincident in carbon tetrachloride. The less stable *cis*- arrangement should give a large (*ca.* 16Hz) deshielding of the nearer *gem*-dimethyl group to the carbinol grouping (49).

Oxidation of the alcohol (formula 61) gave the optically inactive symmetrical ketone, *trans*-3-acetyl-6, 6-dimethylbicyclo[3,1,0]hexane (formula 62) whose maximum in the infra-red at 1 704 cm^{-1}, at τ 9.02[$(CH_3)_2C$] and 7.96 (CH_3CO) in its nmr spectrum, and at m/e 152 (M^+), 109[M^+—CH_3CO and/or M^+—$(CH_3)_2CH$] (base peak) and 43[CH_3CO^+ and/or $(CH_3)_2CH^+$] in its mass spectrum established its structure. It was unaffected by base, thus confirming the *trans*- arrangement of groups, but it was reconverted to the racemic form of the alcohol (formula 61) with lithium aluminium hydride. A racemic form of the alcohol (formula 61) having an unspecified configuration at C3 has been obtained (50) by treatment of car-3-ene dibromide with silver oxide, giving the ketone (formula 62; configuration at C3 unspecified) followed by lithium aluminium hydride reduction of the latter.

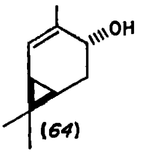
The configuration at the carbinol centre of our alcohol (formula 61) was derived by the use of Horeau's reaction (29).

The other ring rearranged deamination product was the very volatile hydrocarbon (formula 63), namely (+)-3β,7,7-trimethyl-*anti-cis-anti*-tricyclo[$4,1,0,0^{2,4}$]heptane. In its nmr spectrum it showed no olefinic hydrogen or vinylic methyl group resonances, but it displayed a methyl doublet at τ 9.05, two methyl singlets at 8.97 and 9.11, a saturated methylene signal at 8.21 (2H) and cyclopropyl protons (5H) at 8.91-9.65. Its mass spectrum displayed ions at m/e 136 (M^+), 107 ($M^+ - CH_3CH_2$), and 93[$M^+ - (CH_3)_2CH$] (base peak). The loss of CH_3CH_2 and $(CH_3)_2CH$ from the substituted cyclopropane rings is characteristic of these groups and, together with the nmr spectrum, these features establish the structure of the tricyclic hydrocarbon (formula 63).



The formation of these rearrangement products may be portrayed as above, using the diazonium ion from (—)-*cis*-caran-*trans*-4-amine (formula 52a) as example.

In the example quoted, the reaction may be synchronous but in the case of the epimeric 4-amine, the geometry does not pertain. There is no



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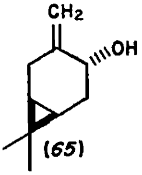

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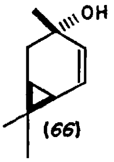

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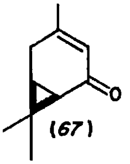

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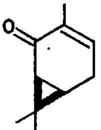

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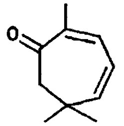

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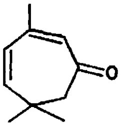

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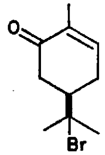

(71)

other evidence to support a concerted reaction in the initial stages. However in the formation of the alcohol (formula 61), rearward attack of water on the carbonium ion at C3 must be synchronous with the breaking of the C2-C3 bond so as to afford the R- configuration at the chiral centre.

OXIDATION

The oxidation of (+)-car-3-ene (2) at its allylic centres with gaseous oxygen has been the subject of recent investigation (18). The products were (+)-car-2-en-*trans*-4-ol (formula 64), (—)-car-3(10)-en-*trans*-4-ol (formula 65), and (—)-*cis*-car-4-en-*trans*-3-ol (formula 66). Earlier Semmler and Schiller (51) isolated what was believed to be car-3-en-5-one (formula 67) from the oxidation products of (+)-car-3-ene with permanganate. This unsaturated ketone (formula 67) was regarded (52) as a very unstable entity and its isomer car-3-en-2-one (formula 68) as being incapable of separate existence because of its ready isomerisation into eucarvone (formula 69). Initially we decided to reinvestigate the oxidation of (+)-car-3-ene (formula 2) using (a) potassium permanganate (53) and, (b) chromium trioxide (54). When (+)-car-3-ene was stirred in acetone at room temperature with potassium permanganate, a complex mixture was obtained, 10% of which consisted of neutral volatile oxidation products, in addition to recovered (+)-car-3-ene. After distillation, the volatiles were separated by a combination of column chromatography on silica-gel and preparative glc on *Carbowax* columns. The principal oxidation product was (—)-car-3-en-5-one, having the absolute configuration shown in (formula 67) and this represented 75% of the total neutral volatile oxidation products*. Its

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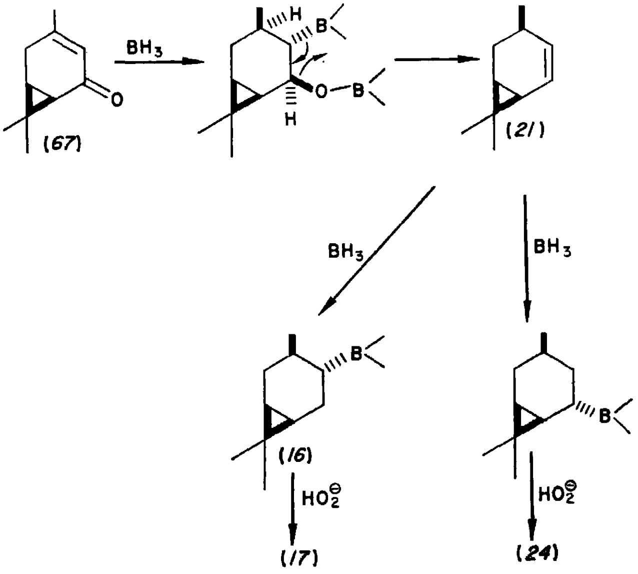
*The yield of each oxidation product is expressed as a percentage of the total volatile oxidation products.

structure was defined by (a) its mass spectrum (m/e 150, M^+), (b) its nmr spectrum which showed the presence of the *gem*-dimethyl group at τ 8.99 (s, 6H), the two cyclopropyl protons at 8.60 (m, 2H), 8.13 (s, 3H, $CH_3C{=}C$), and 4.33 (s, 1H, $HC{=}C$), (c) its ir spectrum (liquid phase) which had peaks at 1 695 and 1 658 ($C{=}C{-}C{=}O$ and possibly $C{=}O$ conjugated with cyclopropyl) cm^{-1} and (d) its ultraviolet spectrum which showed a maximum, in ethanol, at 229 nm (log, ε 4.11). Its semicarbazone which showed a maximum, in ethanol, at 272 nm (log ε 4.36) supported the structure we assigned. Finally, catalytic hydrogenation of the carenone over palladised charcoal furnished (+)-*cis*-caran-5-one (formula 25). Thus this elusive ketone was fully characterized.

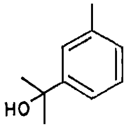
Hydroboronation of the carenone (formula 67) followed by peroxide oxidation of the borane, afforded a mixture of (—)-*cis*-caran-*trans*-4-(formula 17) and (—)-*cis*-caran-*trans*-5-ol (formula 24), whose formation can be rationalised (55) as shown below.



The instability of the carenone (formula 67) can be judged from the fact that on treatment with ice-cold acid or alkali, or even with warm sodium acetate, it is converted into 1,1,4-trimethylcyclohepta-2,4-diene-6-one (formula 70), an isomer of eucarvone (formula 69). These 7-membered ring ketones were present in yields of 3.5% and 1% in the oxidation product of (+)-car-3-ene.

We also isolated (+)-car-3-en-2-one (formula 68) (2%) whose very existence was doubted by some earlier workers (52). However, van Tamelen, McNary, and Lornitzo (56) claimed its intermediate formation in the synthesis of eucarvone (formula 69) from carvone hydrobromide (formula 71), but we were unable to repeat this work. There is little doubt that (+)-car-3-en-2-one (formula 68) is unstable, but it can be kept for long periods in a neutral environment. However, even cold sodium acetate will convert it to eucarvone (formula 69). We attribute its stability, under the alkaline conditions of oxidation of (+)-car-3-ene, to its absorption on the surface of the manganese dioxide formed in the oxidation.

(+)-car-3-en-2-one (formula 68) showed m/e 150 (M+) in its mass spectrum, maxima at 227 and 254 nm in ethanol, and at 221 and 244 nm in hexane. Whilst these maxima are at longer wavelengths than forecast by Woodward's rules (58), the nmr spectrum of the ketone (formula 68) with signals, τ 8.91 and 8.78 (singlets, 6H *gem*-dimethyls), 8.52 (m, 2H, cyclopropyl protons), 8.3 (s, 3H, $CH_3C{=}C$), 7.46 (m, 2H, H5), and 3.75 (m, 1H, $\underline{H}C{=}C$) leaves no doubt as to its identity. On hydrogenation it afforded (—)-*cis*-caran-2-one (formula 12).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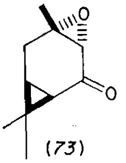
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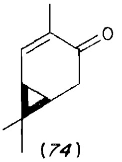
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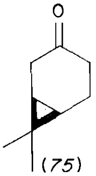
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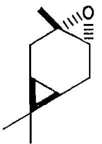
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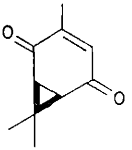
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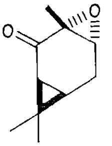
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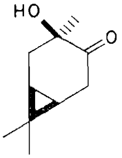
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Other oxidation products were 8-hydroxy-*m*-cymene (formula 72) (3%), (—)-α-3,4-epoxycaran-5-one (formula 73) (2%), (+)-car-2-en-4-one (formula 74) (1.5%), (+)-nor-caran-3-one (formula 75) (2.5%), (+)α-3,4,-epoxycarane (formula 76) (18) (2%), (—)-car-3-ene-2, 5-dione (formula 77) (58) (5%), and (+)-α-3,4-epoxycaran-2-one (formula 78) (2%). Each oxidation product was identified by its spectrum and by comparison with an authentic specimen prepared by unambiguous methods.

Whilst the oxidation procedures described gave valuable products, yields were low and separation of the products was tedious. Attempts were therefore made to improve yields by the use of chromium trioxide in acetone, with and without base (54). Using chromium trioxide alone, the major oxidation product was 8-hydroxy-*m*-cymene (formula 72) representing some 45% of the total neutral volatiles. (—)-Car-3-ene-5-one (formula 67) (8.2%) was again found, but (+)-car-3-en-2-one (formula 68) was only present in traces. All the other products formed in the permanganate oxidation were found in minor quantities and in addition (+)-3 hydroxy-*trans*-caran-4-one (formula 79) (10%) was formed.

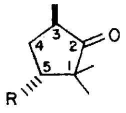
When chromium trioxide in acetone with added sodium acetate, or chromium trioxide in pyridine were used as oxidants no single product was formed in large quantities. With sodium acetate as base, the major product was (+)-α-3,4-epoxycarane (formula 76) (24%) whilst in pyridine two products, namely (—)-car-3-en-5-one(formula 67) (25%) and 1, 1, 4-trimethyl cyclohepta-2,4-dien-6-one (formula 70) (28%) stood out in yield. In any case the overall yield of volatile products was never greater than 20% though unoxidised carene was recovered in substantial quantities.

Using tertiary butylchromate (59) in benzene as oxidant, (+)-car-3-ene gave a 35% overall yield of volatile neutral oxidation products. We have not yet sought for the optimum oxidation conditions for this reaction, but it has promising possibilities. Thus, four main products were obtained, namely, (—)-car-3-en-2,5-dione (formula 77), (11%), (+)-car-3-en-2-one (formula 68) (11.4%), 8-hydroxy-*m*-cymene (formula 72) (27%), and (—)-car-3-en-5-one (formula 67) (46%). Minor oxygenated products (0.8%) and hydrocarbons (3.8%) completed the mixture of volatile products. The yield of the dione (formula 77) increased with length of the reaction. This method of oxidation made it possible to prepare substantial quantities of (+)-car-3-en-2-one and (—)-car-3-en-5-one required for our photochemical experiments on these compounds.

Photolysis (60—62)

The caranones seemed to us to be suitable ketones for submission to photochemical reaction, since they contain the cyclopropyl ring, which in the case of the 2- and 5- ones is conjugated with the keto group. We irradiated an ether solution of (—)-*cis*-caran-4-one (formula 18) through quartz, with light from a medium pressure mercury lamp (60). A 50% yield of photo-products was obtained, which, after repeated chromatography on Kieselgel using a mixture of light petroleum (95%)—ether (5%)

as solvent, afforded (+)-*trans*-1,1,3-trimethyl-5-vinylcyclopentan-2-one (formula 80; R, $CH=CH_2$) as the main product. Heckert and Kropp (61), carrying out a similar photochemical reaction also isolated this substituted cyclopentanone, but in addition they isolated a mixture of *cis*- and *trans*-2-methyl-2(3-methyl-2-oxocyclobutyl)but-3-ene (formula 81).



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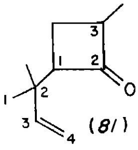
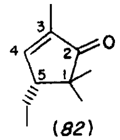


(81)

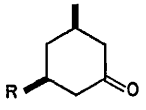


(82)

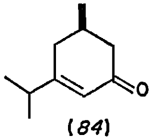
We identified our ketone (formula 80; R, $CH=CH_2$) as follows. It absorbed one mole of hydrogen to give *trans*-5-ethyl-1,1,3-trimethylcyclopentan-2-one (formula 80; R, C_2H_5). It also exchanged one proton for deuterium using sodium deuterioxide in deuterioxide thus showing the environment of the keto group. The deuteriated ketone displayed nmr signals at τ 4-5.1 ($C\underline{H}=C\underline{H}_2$), 8.86 (s, 3H, $CH_3$3), 8.97 and 9.2 [singlets, each 3H, $(CH_3)_2C$]. Before deuteriation there was an additional signal at τ 7-8.4 (1H, H3). As expected the ketone (formula 80; R, C_2H_5) reacted with one mole of bromine in acetic acid giving a monobromo compound, which on refluxing with pyridine afforded the unsaturated ketone (formula 82). This compound showed a maximum at 227 nm in the ultraviolet, peaks at 1 706 and 1 639 cm^{-1} in the infra-red, and signals at τ 2.92 (s, 1H, H4), 8.25 (s, 3H, $CH_3C=C$), and 8.96 and 9.09 [singlets, $(CH_3)_2C$] in its nmr spectrum which identified it conclusively. We assign the *trans*-arrangement of methyl and vinyl groups in (formula 80; R, $CH=CH_2$) on theoretical grounds.

Photolysis, through quartz, of (+)-*cis*-caran-5-one (formula 25) in ether gave an abundance of products (62), the yield of volatile products being 65%. The products were (—)-*cis*-*m*-menth-8-en-5-one (formula 83; R, $CH_3C=CH_2$) (37%), its dihydro compound (—)-*cis*-*m*-menthan-5-one [formula 83; R, $(CH_3)_2CH$] (12%), (—)-*m*-menth-3-en-5-one (formula 84) (15%), (—)-*cis*-*m*-menthan-*cis*-5-ol [formula 85; R, $(CH_3)_2CH$; R^1, β-OH] (15%), (—)-*cis*-*m*-menthan-*trans*-5-ol [formula 85; R, $(CH_3)_2CH$; R^1, α-OH] (1-2%) and *cis*-*m*-menth-8-en-*cis*-5-ol (85; R, $CH_3C=CH_2$; R^1 β-OH) (trace). Irradiation in hexane afforded only the ketones and in benzene the only volatile product was the α,β- unsaturated ketone (formula 84) (32%).

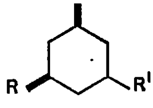
The identities of the ketones were established as follows:— Reaction of



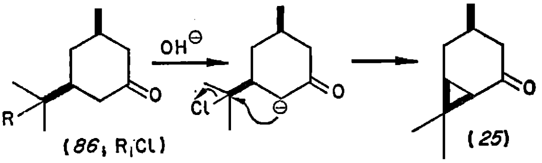
(83)



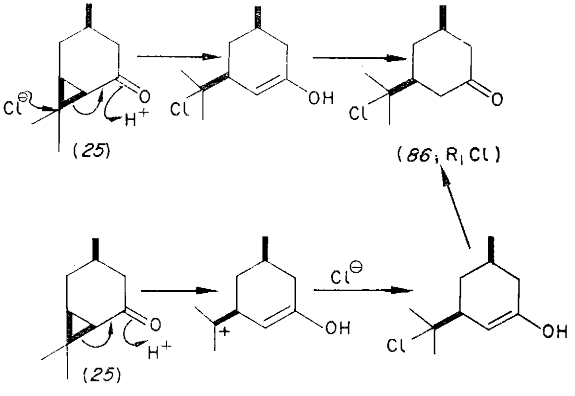
(84)



(85)



(+)-*cis*-caran-5-one (formula 25) with hydrogen chloride in ether afforded (+)-8-chloro-*cis*-*m*-menthan-5-one (formula 86; R, Cl) which was reconverted quantitatively to (+)-*cis*-caran-5-one (formula 25) on treatment with methanolic potash. Thus the configuration of the chloro-compound (formula 86; R, Cl) was established. Alternative mechanisms of the formation of the chloroketone are shown below. One of these is concerted.



When the chloro-compound was stirred with zinc in acetic acid, it gave a mixture of three of the photolysis products, namely (—)-*cis*-*m*-menthan-5-one (formula 83; R, $(CH_3)_2CH$), (—)-*m*-menth-3-en-5-one (formula 84) and (—)-*cis*-*m*-menth-8-en-5-one (formula 83; R,$CH_3C{=}CH_2$) and in addition, as principal product, (+)-8-acetoxy-*cis*-*m*-menthan-5-one (formula 86; R, CH_3COO). Since the principal photoproduct (—)-*cis*-*m*-menth-8-en-5-one (formula 83; R, $CH_3C{=}CH_2$) was reduced over palladised charcoal, with uptake of one mole of hydrogen, to (—)-*cis*-*m*-menthan-5-one [formula 83; R, $(CH_3)_2CH$] their relationship is clear.

Likewise (—)-*m*-menth-3-en-5-one (formula 84), the other ketone photo-product was reduced to (—)-*cis*-*m*-menthan-5-one. The spectra of these unsaturated ketonic photo-products are in accord with their structures. We give as an example the spectra of the principal photo-product, (—)-*cis*-*m*-menth-8-en-5-one (formula 83; R, $CH_3C{=}CH_2$). In the infra-red region this absorbed at 3 067 ($C{=}CH_2$), 1 712 ($C{=}O$), 1 645 ($C{=}C$), and 890 ($C{=}CH_2$) cm^{-1}, whilst in its nmr spectrum, in carbon tetrachloride, it displayed signals at τ 5.2 (s, $C{=}CH_2$), 7.76 (m, CH_2COCH_2), 8.25 (s, $CH_3C{=}C$), and 8.95 (d, J 6Hz, CH_3C).

The formation of the dihydro ketone, (—)-*cis*-*m*-menthan-5-one [formula 83; R, $(CH_3)_2CH$] during the photolysis is clearly the result of intervention by the solvent. When either ether or hexane is employed as solvent this saturated ketone is formed, whereas in benzene only the α, β- unsaturated ketone (formula 84) is produced. There is ample precedent, at any rate in the case of ether (63), for the solvent acting as hydrogen donor. Hexane could also act as hydrogen donor, but benzene is most unlikely to assume this role. It is also significant that alcohols are formed only when ether, the best hydrogen donor of the three solvents, is employed.

ACKNOWLEDGMENTS

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DISCUSSION

DR. E. T. THEIMER: You stated that there was convincing evidence that both 2- and 3-carene had a "boat" configuration and therefore give exclusively *cis*-carane on hydrogenation. Have you investigated the behaviour of 2,10-carene on hydrogenation? One might expect a more stretched out configuration leading to substantial amounts of *trans*-carane.

THE LECTURER: Are you referring in particular to what we all call *beta* carene; the car-3,10ene?

DR. E. T. THEIMER: Yes.

THE LECTURER: We have hydrogenated car-3,10-ene, and as you surmise, we get almost equal quantities of *cis*- and *trans*- caranes. The double bond is placed so that there is not much more hindrance to attack on the top side than the bottom side.

We have also hydrogenated car-4-ene (formula 21). This is recent work which I was unable to include in the paper. Based upon the hydrogenation of car-2-ene, hydrogenation of car-4-ene across the 4,7- positions might be expected. In fact, during this hydrogenation the double bond migrates out of conjugation with the cyclopropane ring giving initially car-3-ene which is converted to car-2-ene and thence to 1,1,4-trimethylcycloheptane. Incidentally, the reduction of car-4-ene is much slower than that of either car-2- or car-3-ene. If the reaction is monitored, the initial formation of car-3-ene can be recognised, and this is converted to car-2-ene followed by its disappearance and the formation of 1,1,4-trimethylcycloheptane.

DR. E. T. THEIMER: Does this take place independently of the catalyst used?

THE LECTURER: Yes, under the same conditions of hydrogenation as described for the hydrogenation of car-3-ene. I have no doubt, however, that if we hydrogenated at 10.1 MN m^{-2} pressure of hydrogen, *cis*-carane would result. It is a question of the relative speeds of addition of hydrogen to the double bond and migration of the double bond. I believe that under pressure direct hydrogenation across the double bond would be faster than either double bond migration or 1,4- addition of hydrogen to give 1,1,5-trimethylcyclohept-2-ene.

DR. E. T. THEIMER: Did you use a palladium on carbon catalyst? We know that it is an extremely rapid isomerisation catalyst for double bonds. In the case of β-pinene, you can go to α-pinene with that system in about 5 min at 160-170°. If, however, you were to use say, nickel or something that was not so good an isomerising agent, I wonder whether it would be possible to get 1,4- addition of hydrogen to give 1,1,5-trimethylcyclohept-2-ene.

THE LECTURER: I think that under such conditions 1,1,5-trimethylcyclohept-2-ene would result. It is, however, strange that car-4-ene fails to undergo a similar reaction to car-2-ene with palladised charcoal and hydrogen. Both show the same sort of conjugation in their uv and ir spectra arising from overlap of π-systems.

DR. G. P. MOSS: Have you tried the hydrogenation of carenes with homogeneous catalysis? It is well known that this method does not normally encourage isomerisations.

THE LECTURER: No, though we have it very much in mind.

MR. J. MCIVER: I saw no mention about the odour value of the numerous compounds produced in this extensive work. Has any work been carried out on the odour of the materials; are any of these compounds particularly useful to perfumers?

THE LECTURER: We have not done anything of this sort, though we have passed on materials for evaluation to some of our friends. To us, who are not perfumers, the caranols have modified menthol odours. Likewise the ketones have modified menthone odours. I think that many of our products would merit professional evaluation.

MR. MCIVER: Do any show promise at all?

THE LECTURER: I have not received any information about our products. Evaluation, for perfumery purposes, is something which was outside the scope of our work and I have left it to others to carry out these evaluations.