The Chemistry of Terpenes. Part VI.† Pyrolysis and Acid-catalysed Rearrangements of (+)-Car-3-ene and Some Derivatives ‡

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Under otherwise similar conditions, (+)-car-3-ene requires higher temperatures to promote its vapour-phase pyrolysis than are required for the pinenes. Without catalyst (+)-car-3-ene gives principally aromatic products, but in the presence of a potassium aluminosilicate catalyst it affords hydroaromatic products by an ionic mechanism. The products of pyrolysis and acid-catalysed rearrangement of (−)-cis-caran-cis-5-ol and (−)-trans-caran-cis-2-ol, similarly dependent upon conditions, are described.

THE pyrolysis of β-pinene (I) is the first stage in the manufacture of many perfumes.[1] Under favourable conditions it gives myrcene in up to 90% yield, and from the latter linalo-ol, geraniol, and citral are obtained. Similarly α-pinene affords allo-ocimene. In continuation of our study [2] of the chemistry of the carenes and their derivatives, we have investigated the thermal cracking of (+)-car-3-ene (II) and its two derived alcohols, (+)-cis-caran-cis-5-ol (III) [2] and (−)-trans-caran-cis-2-ol (IV).[3]

Liquid carene was dropped into a packed, heated tube and carried forward as vapour in a current of nitrogen. The identity of the products (Table 1) which were isolated by preparative gas–liquid chromatography (g.l.c.), was established by analytical g.l.c., by their spectra, and by other physical characteristics, with authentic substances as standards. The relative quantities of the products were obtained from the areas under the peaks of the chromatograms; the authenticity of the method

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† Part V, W. Cocker, A. C. Pratt, and P. V. R. Shannon, preceding Paper.

‡ For a preliminary report see *Tetrahedron Letters*, 1966, 4547.

[1] B. Dudley Sully, *Chem. and Ind.*, 1964, 263.

[2] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc. (C)*, 1967, 915.

[3] S. P. Acharya and H. C. Brown, *J. Amer. Chem. Soc.*, 1967, **89**, 1925.

was previously established by use of these products as standards. The dehydrocymenes were catalytically hydrogenated (uptake of hydrogen 1 mol.) to the cymenes. The g.l.c. trace of the mixture of *m*- and *p*-methylstyrenes was identical with that of a synthetic specimen of the *p*-isomer. The infrared and n.m.r. spectra of the mixture showed bands coincident with those present in the spectra of the *p*-isomer. Other bands in the spectra of the mixture were attributable to the *m*-isomer.

Under our conditions of pyrolysis, (+)-car-3-ene began to decompose at about 450°. At 480° it was cracked to the extent of only about one third (Table 1). In the same apparatus with the same flow rate, β-pinene (I) was completely decomposed at 325°. (+)-Car-2-ene (V) also decomposes more readily than (+)-car-3-ene.[4]

Indeed, under these conditions we have found that both β-pinene and myrcene afford only aromatic products.

Table 1 shows that *m*- and *p*-cymene are the main products of pyrolysis at the lowest temperatures used. Higher temperatures favour the formation of simpler aromatic compounds; toluene and the xylenes are formed to a greater extent than benzene. Their formation is a primary process, since the cymenes were relatively unaffected when heated at these higher temperatures. They did however lose hydrogen to give the 8-dehydrocymenes (*ca.* 20% at 550°). Benzene, toluene, and the xylenes likewise were unaffected by heating to the higher temperature.

The extent of the pyrolysis at a given temperature did not alter appreciably when the effective surface area of the column was increased about forty-fold by packing with
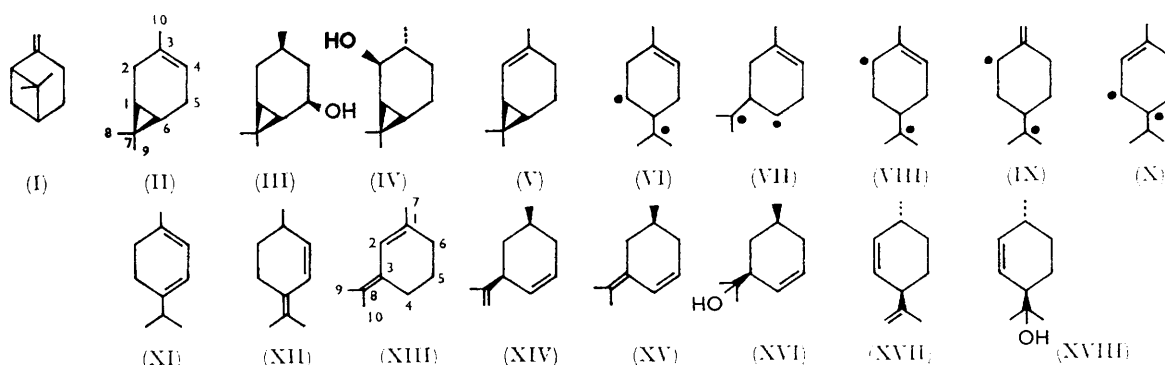

TABLE 1

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

Product (%)

Temp.	Benzene	Toluene	*m*- and *p*-Xylenes	Styrene	*m*-Cymene	*p*-Cymene	*m*- and *p*-Methylstyrenes	Dehydro-*m*-cymene	*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

Propene, isoprene, and other minor unidentified products were also formed.

The resistance of the cyclopropane ring in (+)-car-3-ene to thermal cracking may be traced to the absence in the initial free diradicals (VI) and (VII) of a resonance-stabilised allylic system such as is present in the diradicals (VIII), (IX),[5] and (X), derivable from α-pinene, β-pinene, and car-2-ene respectively. Cracking of the allylic bonds in car-3-ene is evidently inhibited by their pseudo-vinylic character produced by the cyclopropane ring. This is borne out by the virtual absence of retro-Diels–Alder fission in the mass spectrum.[6] Under our conditions of pyrolysis and flow rate, the high temperatures necessary to effect cracking of (+)-car-3-ene preclude subsequent formation of any acyclic products.

glass-wool. This confirmed that the carene decomposition occurred in the vapour-phase.

In the presence of potassium aluminosilicate, (+)-car-3-ene vapour began to crack at about 300°. At 400° it was completely transformed into five main products. These were *m*-cymene (8·2%), *p*-cymene (10·9%), α-terpinene (XI) (21%), (±)-*p*-mentha-2,4(8)-diene (XII) [7a] (14%), and *m*-mentha-1,3(8)-diene (XIII) [8] (14·4%). Catalyst ageing prevented quantitative product variation with temperature to be investigated, but at higher temperatures the quantity of cymenes increased in proportion as would be expected (see Table 1).

The α-terpinene (XI) and *p*-mentha-2,4(8)-diene (XII)

[4] K. Gollnick and G. Schade, *Tetrahedron*, 1966, **22**, 123.
[5] R. L. Burwell, *J. Amer. Chem. Soc.*, 1951, **73**, 4461.
[6] J. W. Cornforth, personal communication.
[7] I. H. Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 4th edn., 1965, vol. 3, (*a*) p. 1941; (*b*) p. 1731; (*c*) vol. 4, p. 2115.

[8] (*a*) I. I. Bardyshev, *Doklady Akad. Nauk S.S.S.R.*, 1953, **90**, 1035; (*b*) R. Y. Levina, D. G. Kim, E. N. Smirnova, N. D. Orlova, and E. G. Treshchova, *Zhur. obshchei Khim.*, 1957, **27**, 1779, (*Chem. Abs.*, 1958, **52**, 4518b); (*c*) G. A. Rudakov and A. T. Marchevskii, *Sbornik Statei obshchei Khim.*, 1953, **2**, 1432 (*Chem. Abs.*, 1955, **49**, 5390e).

were hydrogenated over palladised charcoal, with the uptake of two molar proportions of hydrogen, to give in each instance a mixture of *cis*- and *trans*-*p*-menthanes which are readily distinguishable from the *m*-menthanes by g.l.c.[9] *m*-Mentha-1,3(8)-diene (XIII) likewise gave a mixture of *cis*- and *trans*-*m*-menthanes. α-Terpinene showed spectroscopic properties (u.v., i.r., and n.m.r.) (cf. refs. 10 and 11) and g.l.c. characteristics identical with those of authentic material. (±)-*p*-Mentha-2,4(8)-diene (XII)[7a] showed a maximum at 2440 Å (log ε 3·93)[12] in the ultraviolet and a band at 731 (*cis*-RCH=CHR)[13] cm.$^{-1}$ in the infrared. In its n.m.r. spectrum it showed peaks at τ 9·02 (3H, d, $J = 7$ c./sec., 1-Me), 8·29 (6H, s, C=CMe$_2$) 4·55 [1H, d, $J = 11$ c./sec., C(2)H], and 3·68 [1H, d, $J = 11$ c./sec., C(3)H]. *m*-Mentha-1,3(8)-diene (XIII)[8] showed a maximum in the ultraviolet at 2450 Å (log ε 4·11) in good agreement with the calculated value for this conjugated diene, and a band at 1630 cm.$^{-1}$ in the infrared. In its n.m.r. spectrum it showed peaks at τ 8·29 (9H, s, vinylic methyls) and at 3·9 [1H, s, C(2)H]. The cymenes could not be separated by preparative g.l.c., but the *m*–*p* mixture was isolated in this way and identified by analytical g.l.c. and infrared spectrum.

A similar range of products, obtained in similar proportions, was produced when (+)-car-3-ene was heated in a sealed tube with the aluminosilicate catalyst for 4 hours at 200°. Without this catalyst, car-3-ene was recovered unchanged.

Since the catalyst is acidic, the readiness of (+)-car-3-ene to isomerise when heated at lower temperatures than are required without a catalyst is no doubt a result of carbonium ion formation. The products are all conjugated, unlike the dienes obtained by non-acidic pyrolysis (see below).
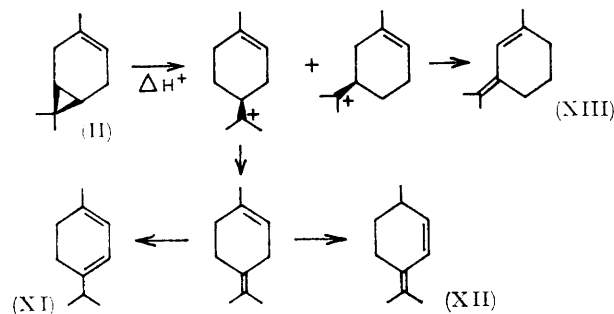

When car-3-ene is heated with metatitanic acid it apparently affords[8c] dipentene, (−)-limonene, terpinolene, α-terpinene, and *m*-mentha-1,3(8)-diene as well as other products.

(+)-*cis*-Caran-*cis*-5-ol (III)[2] was pyrolysed in the vapour phase at about 480° to give (−)-*cis*-*m*-mentha-

4,8-diene (XIV)[14] (80%) and the previously unknown (+)-*m*-mentha-3(8),4-diene (XV) (15%). When the alcohol (III) was heated in a sealed tube with acetic acid, the hydrocarbons (XIV) and (XV) were formed along with (−)-*cis*-*m*-menth-4-en-8-ol (XVI).[2,7b] Table 2 shows the composition of the product obtained at different temperatures. No trace of *para*-isomers was observed; the reaction was specific in cyclopropane bond breaking.

TABLE 2

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

Temp.	Product (%)		
	(XIV)	(XV)	(XVI)
180°	71·7	12·2	16·7
210	74·5	13·3	11·6
300	61·8	21·7	3·4
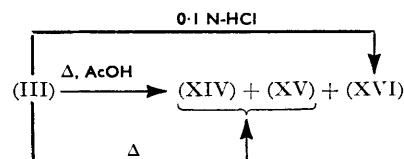
The structure of the menthadiene (XIV)[14] was deduced as follows: (*a*) hydrogenation * consumed 2 molar proportions of hydrogen to give predominantly *cis*-*m*-menthane; (*b*) the n.m.r. spectrum of (XIV) showed the presence of one saturated ring-methyl at τ 9·02 (3H, d, $J = 6$ c./sec.), one MeC=C group at τ 8·32 (3H, s), one CH$_2$=C group at τ 5·31 (2H, s), and two disubstituted olefinic hydrogens at τ 4·42 (2H, s); and (*c*) the u.v. spectrum showed only end absorption, but bands occurred at 888 (R$_2$C=CH$_2$) and 731 (*cis*-RCH=CHR) cm.$^{-1}$ in the infrared spectrum. These facts leave only two alternative structures, with the ring double-bond in either the 4,5- or the 5,6-position. The resonance of the 1-proton was shown to be at τ 8·37 by collapse of the 1-methyl doublet on double resonance, so that the ring double-bond must be in the 4,5-position. The configurations at C-1 and C-3 follow, since these centres are not involved during the pyrolysis of the alcohol (III). (+)-*m*-Mentha-3(8),4-diene (XV) showed a maximum at 2435 Å (log ε 4·28) in the ultraviolet, which indicates a conjugated diene system. In the infrared it displayed bands at 1680 and 726 (*cis*-RCH=CHR) cm.$^{-1}$. Its n.m.r. spectrum indicated a saturated ring methyl (τ 9·02, 3H, d, $J = 6$ c./sec.), two vinylic methyls (τ 8·24, 6H, s), and two olefinic hydrogens [τ 4·4, 1H, m, C(5)H and τ 3·65, 1H, d, $J = 10$ c./sec., C(4)H]. Hydrogenation of the diene (XV), with uptake of 2 molar proportions of hydrogen, afforded a mixture of *cis*- and *trans*-*m*-menthanes. These facts lead to an unambiguous

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* The configurations of the products of hydrogenation over palladised charcoal cannot be used as an indication of the configurations of the starting menthadienes because it appears that the more stable isomer is obtained predominantly regardless of the configuration of the diene. This has been demonstrated[9] for *ortho*-, *meta*-, and *para*-menthanes when prepared from the appropriate menthenes or menthadienes.

[9] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.* (*C*), 1966, 946.
[10] H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1940, 1453.
[11] Cf. H. Farnow and F. Porsch, *Dragoco Report*, 1964, **11**, 3.
[12] Cf. H. Komae, *J. Sci. Hiroshima Univ.*, 1960, *A*, 24, 699.
[13] Cf. F. Porsch, H. Farnow, and H. Winkler, *Dragoco Report*, 1963, **10**, 263.
[14] K. Gollnick, *Tetrahedron Letters*, 1966, 327.

structural assignment for (XV). Again the configuration at C-1 follows because of its non-participation in the pyrolysis; otherwise the compound would be racemic.

The alcohol (XVI) is produced more conveniently and in higher yield from (+)-*cis*-caran-*cis*-5-ol (III) by treatment with 0·1N-hydrochloric acid at 20°.[2] A more detailed study of this reaction has indicated that the products depend upon the acid concentration. Thus at very low acidity after 12 hours the tertiary alcohol is the main product, but at higher acidity dehydration and isomerisation take place to give the conjugated hydrocarbon (XV) as sole product (see Figure 1).
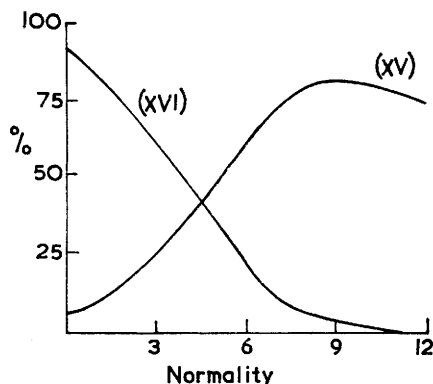

FIGURE 1 Effect of varying strengths of acid on (+)-*cis*-caran-*cis*-5-ol (III)

The spectroscopic evidence for the structure of (—)-*cis*-*m*-menth-4-en-8-ol (XVI) has been quoted briefly in a previous publication.[2] The alcohol shows in its n.m.r. spectrum a poorly resolved doublet at τ 9·02 [$J = 5$ c./sec., C(7)H$_3$], singlets at 8·91 and 8·86 [C(9 and 10)H$_3$], a broad singlet at 8·5 (exchangeable, OH), and a singlet at 4·25 [2H, C(4 and 5)H]. Absence of a signal in the region τ 5—7·5 indicates that the compound is a tertiary alcohol. The infrared spectrum shows bands at 3268 (OH), 1642 (C=C), and 735 (*cis*-RHC=CHR) cm.$^{-1}$. The mass spectrum shows peaks at m/e 154 (M^+), 59 (Me$_2$COH$^+$), and 44 (MeCOH$^+$), which confirm the dimethyl carbinol structure. The alcohol, when treated with phosphoryl chloride in pyridine gave a mixture of hydrocarbons (XIV) and (XV) which were identified by g.l.c. and their infrared spectra. The *meta*-orientation and configuration of the ring substituents, and the position of the 4,5-double bond in (XVI) are thus assured.

(—)-*trans*-Caran-*cis*-2-ol (IV), the configuration of which has recently been established,[3] * was prepared by reduction with lithium aluminium hydride of (—)-*trans*-caran-2-one prepared by Baeyer's method.[15] The stage involving the reduction of (—)-carvone to (+)-dihydrocarvone was improved by the use of lithium in liquid ammonia. The yields of *cis*- and *trans*-dihydrocarvone were 14 and 86%, respectively (g.l.c.).

In an analogous way to the caran-5-ol, (—)-*trans*-

caran-*cis*-2-ol (IV), when heated at 410° in the vapour phase, gave the hydrocarbons (+)-*trans*-*p*-mentha-2,8-diene (XVII) [4] (85%) and (+)-*p*-mentha-2,4(8)-diene (XII; α-Me) [7a] (15%). When heated in a sealed tube at 210° with acetic acid, the alcohol gave two main products; the more abundant was the hydrocarbon (XVII), which on hydrogenation afforded predominantly *trans*-*p*-menthane. It showed only end absorption in the ultraviolet. However, bands in the infrared at 1642 (C=C), 885 (R$_2$C=CH$_2$), and 728 (*cis*-RCH=CHR) cm.$^{-1}$, and signals in the n.m.r. spectrum at τ 9·05 [3H, d, $J = 7$ c./sec., C(7)H$_3$], 8·32 (3H, s, C(10)H$_3$], 5·32 [2H, s, C(9)H$_2$], and 4·52 [2H, C(2 and 3)H], together with the evidence given above, lead only to structure (XVII). The configuration of the 7-methyl group is as shown; this follows from the configuration of the alcohol (IV).†

The second product was (+)-*trans*-*p*-menth-2-en-8-ol (XVIII).[4] Its infrared spectrum showed peaks at 3350 (OH), 1650 (C=C), and 728 (*cis*-RCH=CHR) cm.$^{-1}$, and its n.m.r. spectrum revealed a saturated ring-methyl (τ 9·04, d, $J = 6$ c./sec.), two tertiary methyl groups [τ 8·86, s, and 8·91, s, C(9 and 10)H$_3$], an OH group (τ 8·23, s, exchangeable), and two olefinic hydrogens [τ 4·38, 2H, s, C(2 and 3)H]. Its mass spectrum confirmed the dimethylcarbinol structure with peaks at m/e 154 (M^+), 96 (C$_7$H$_{12}^+$), and 59 (Me$_2$COH$^+$). Finally the alcohol was dehydrated with phosphoryl chloride and pyridine to a mixture of (XVII) (80%) and (XII) (20%). The configuration of C-7 in (XVIII) is as shown for the same reasons as advanced for compound (XVII).

(IV)

Δ, 410°   H$^+$, 20°   AcOH, 210°

(XVII) (XII; α-Me)   (XI)   (XVIII) (XVII)
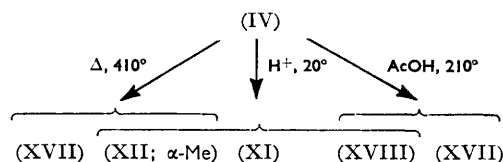
(—)-*trans*-Caran-*cis*-2-ol (IV) was treated with hydrochloric acid of strengths varying from 0·1N to 12·5N to give mixtures of α-terpinene (XI), (+)-*trans*-*p*-menth-2-en-8-ol (XVIII), and (+)-*p*-mentha-2,4(8)-diene (XII; α-Me) (see Figure 2). No *m*-disubstituted cyclohexenes were found when the alcohol (IV) was heated alone or treated with acid.

The structural assignment of (+)-*p*-mentha-2,4(8)-diene (XII; α-Me) follows from its hydrogenation to a mixture of *trans*- (90%) and *cis*-*p*-menthane (10%). Its ultraviolet, infrared, and n.m.r. spectra were identical with those already described for the racemic diene obtained by pyrolysis of (+)-car-3-ene. The configuration of the 7-methyl is α as in the parent alcohol (IV); the optical activity of the hydrocarbon (XII; α-Me) indi-

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† If the 1-carbon atom participates as a carbonium ion in the rearrangement, which is unlikely, the expected arrangement of alkyl groups would still be *trans*, since then both methyl and isopropenyl substituents of the cyclohexene would occupy the most stable pseudo-equatorial dispositions. Involvement of the 1-carbon atom in this way would however lead to the more stable mentha-1,8-diene.

[15] A. Baeyer, *Ber.*, 1894, **27**, 1915.

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* Additional evidence for the structure (IV), in particular the configuration at C-1, was adduced by us through oxidation of (IV) to (—)-*trans*-caran-2-one [15] with α-7-methyl.

cates that the centre of chirality at C-1 was undisturbed during the formation of the hydrocarbon.

Acid-catalysed dehydration of the caran-2- and -5-ols yields conjugated dienes, whilst high temperature dehydration affords unconjugated dienes. There is thus evidence for two distinct reactions involving the cyclopropane ring-opening and dehydration of the alcohol,
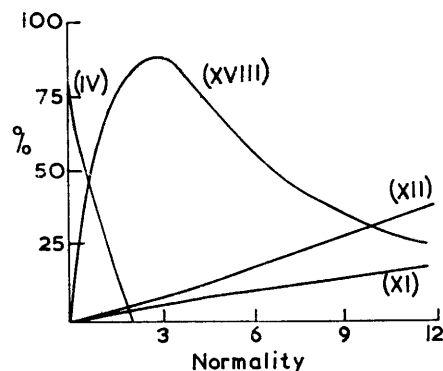

FIGURE 2   Effect of varying strengths of acid on (−)-*trans*-caran-*cis*-2-ol (IV)

namely (*a*) a non-ionic reaction at high temperatures and (*b*) an ionic reaction at low temperatures in the presence of mineral acid. A similar duality of mechanism undoubtedly exists in the (+)-car-3-ene pyrolysis: (*a*) a vapour phase, free radical reaction, and (*b*) an ionic, aluminosilicate (acid) catalysed reaction.

We advance tentative schemes (A and B) for these two distinct routes, with the alcohol (III) as an example.
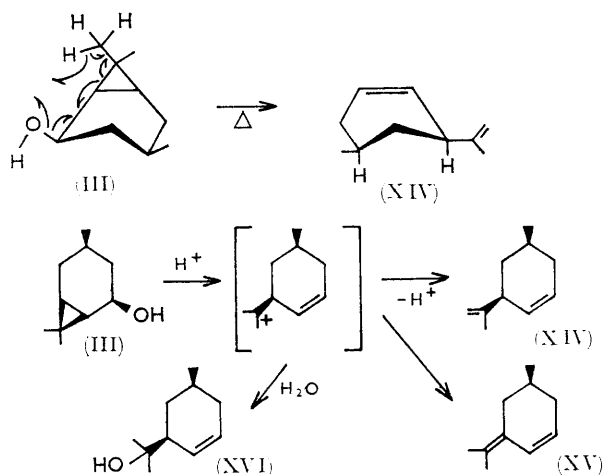
The proximity of the β-methyl and 5-β-hydroxy-groups in (III) is such as to allow a synchronous concerted elimination of water and cyclopropane ring-opening. This possibility is currently being investigated.

EXPERIMENTAL

General experimental conditions are as described in Part I.[16] Ultraviolet spectra were measured with alcohol

K K

as solvent, with a Unicam SP 800 spectrophotometer. Optical rotations were measured with a Perkin-Elmer automatic polarimeter, model 141. Except where otherwise stated, rotations were for chloroform solutions.

Apparatus.—Vapour phase pyrolyses were carried out in a vertical 'Pyrex' glass tube (30 × 3 cm.) packed with either hollow glass beads (1 cm. diam.) or a catalyst, and lagged with asbestos. The tube was heated by a winding of Nichrome wire (15 ft.; 6 ohms per metre) to which 65—95 v were applied from a Variac transformer. The reactor was fitted with a dropping funnel and nitrogen inlet. A water-cooled condenser was fitted at the bottom of the reactor tube and the products were collected in ice-cooled traps.

The apparatus was calibrated for temperature, with a standard thermocouple, at the tube position of maximum temperature. For this purpose voltages at 5 v intervals between the extremes stated were chosen. The apparatus was heated, with nitrogen flowing for 2 hr., before use so as to ensure a steady temperature.

Pyrolysis of (+)-Car-3-ene (II) *without Catalyst.*—(*a*) This compound was dropped at *ca.* 200 mg./min. into the reactor and carried down as vapour by oxygen-free nitrogen at 50 c.c./min. (this gave a contact time of *ca.* 1 min.). Table 1 gives the reactor temperatures used. The products were analysed by g.l.c. [20% Castorwax column (3 m.) at 113°] and were eluted in the order, propylene, isoprene, benzene, toluene, *m*- and *p*-xylenes, styrene, carene, *m*-cymene, *p*-cymene, *m*- and *p*-methylstyrenes, and dehydro-*m*- and dehydro-*p*-cyemes. The aromatic products were identified after preparative g.l.c. by comparison with authentic specimens. The dehydro-compounds were hydrogenated in ethanol over palladised charcoal, with the uptake of hydrogen (1 mol.) to the corresponding cymenes, which were characterised as described above. Isolation of the cymenes was only possible at low temperatures at which *m*- and *p*-methylstyrenes (see Table 1) were not present, since these overlapped the cymenes in the preparative chromatogram. At the low temperatures necessary, considerable amounts of unchanged carene remained (see Table 1) and consequently the pyrolysate had to be recycled 3 times at 480° to increase the quantities of cymenes to reasonable proportions. For the same reason, the *m*- and *p*-methylstyrenes could be isolated free from the cymenes only at high temperatures, when the latter were present in small amounts.

In a typical experiment, (+)-car-3-ene (30 g.) pyrolysed at 560° gave a crude product (28 g.) which was distilled to give fractions (A) (4 g.), b. p. <96°, (B) (10 g.), b. p. 96—126°, (C) (3 g.), b. p. 126—165°, and (D) (4·5 g.), b. p. 165—180°, and a residue (6·5 g.). Preparative g.l.c. of each fraction on a 30% Castor wax column (6 m. × 0·63 m.) at 110—130° (nitrogen flow rate 200 c.c./min.) with ice-cooling of the receiver afforded pure specimens of the compounds mentioned above, which showed i.r. and n.m.r. spectra and analytical g.l.c. properties identical with those of authentic compounds. Propene and isoprene were identified only by g.l.c. comparison with authentic compounds. Benzene was collected by use of solid carbon dioxide as coolant.

At 480°, at which temperature about 60% of the (+)-car-3-ene remained unchanged, an increase in the surface area of the inside of the pyrolysis tube with glass wool (about forty-fold) did not change the extent of decomposition.

p-Methylstyrene.—*p*-Methylacetophenone [7c] (25 g.) in dry

[16] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.* (*C*), 1966, 41.

ether (250 c.c.) was added dropwise during 30 min. with ice-cooling to a stirred suspension of lithium aluminium hydride (3 g.) in ether (100 c.c.). Stirring was continued for 3 hr. and the excess of lithium aluminium hydride was then destroyed with moist ether and ice. The ethereal layer was washed with water (3 × 20 c.c.), dried, and distilled, to give *p*-(1-hydroxyethyl)toluene (20 g.), b. p. 70°/0·6 mm., $\nu_{max.}$ 3295 (OH), 1530 (RC=CR), and 817 (1,4-benzenoid substitution) cm.$^{-1}$. The alcohol (5 g.) in benzene (5 c.c.) was pyrolysed in the vapour phase (see above) at 420°. The products consisted of unchanged alcohol and *p*-methylstyrene in the ratio of 2 : 1 (g.l.c.). *p*-Methylstyrene, obtained by preparative g.l.c. on a 30% Castorwax column (6 m.) at 140°, had n_D^{20} 1·5410, $\nu_{max.}$ 1505 (RC=CR), 903 (C=CH$_2$), and 824 (1,4-benzenoid substitution) cm.$^{-1}$, τ 7·7 (s, Me), 4·9 (d,d $J_{\alpha\beta} = 11$, $J_{\beta\beta} = ca.$ 1 c./sec., *cis*-β-H), 4·42 (d,d $J_{\beta\alpha} = 17$, $J_{\beta\beta} = ca.$ 1 c./sec., *trans*-β-H), and 2·67—3·77 (aromatic protons and α-H). The mixture of *m*- and *p*-methylstyrenes obtained by preparative g.l.c. as described above showed analytical g.l.c. identical with, and n.m.r. compatible with the authentic *p*-methylstyrene. In addition to the bands in the i.r. shown by the authentic hydrocarbon, the mixture showed peaks at 792 and 714 cm.$^{-1}$, due to the *m*-isomer.

Pyrolysis of β-Pinene and Myrcene without Catalyst.—β-Pinene was pyrolysed as previously described for (+)-car-3-ene. At 410°, the main product was myrcene, identification confirmed by comparison with authentic material (i.r. and g.l.c.). At 600°, the main products were benzene, toluene, and xylene (comparison with authentic materials on g.l.c.). On pyrolysis under conditions identical with those used for (+)-car-3-ene at 560°, myrcene likewise yielded benzene, toluene, and xylene.

Stability of Simple Aromatic Compounds to Pyrolysis without Catalyst.—Benzene, pyrolysed in the usual way at 600°, was completely unaffected (analytical g.l.c.), as were toluene and *p*-xylene. *p*-Cymene yielded *p*-dehydrocymene (20%) and traces of benzene, toluene, and xylene when similarly treated.

Pyrolysis of (+)-Car-3-ene in the Presence of a Catalyst.—(*a*) The reaction column was packed with a pelletised molecular sieve (potassium aluminosilicate; B.D.H. type 3A; 100 g.) which was dried before use at 200° for 3 hr. in a current of nitrogen. In a typical experiment, (+)-car-3-ene (50 g.) was dropped at *ca.* 200 mg./min. (nitrogen flow 60 c.c./min.) into the column kept at 400°, and the products were analysed on a 20% Castorwax column (3 m.) at 145°. α-Terpinene, *m*-cymene, *p*-cymene, (±)-*p*-mentha-2,4(8)-diene (XII),[7a] and *m*-mentha-1,3(8)-diene (XIII)[8] * were eluted in this order. They were separated by preparative g.l.c. on a 30% Castorwax column (6 m. × 0·63 cm.) at 110°. α-Terpinene had n_D^{22} 1·4530 (Found: C, 88·2; H, 11·6. Calc. for C$_{10}$H$_{16}$: C, 88·2; H, 11·8%), i.r., n.m.r., and g.l.c. properties identical with those of the authentic compound. *p*-Mentha-2,4(8)-diene (XII) had n_D^{20} 1·5068, $[\alpha]_D^{20}$ 0° (*c* 0·5). Its spectroscopic properties are described in the Discussion. *m*-Mentha-1,3(8)-diene (XIII) had n_D^{20} 1·5132, $[\alpha]_D^{20}$ 0°, spectroscopic properties described above (Found: C, 87·6; H, 11·9. C$_{10}$H$_{16}$ requires C, 88·2; H, 11·8%).

(*b*) (+)-Car-3-ene (30 mg.) was heated at 200° for 4 hr. with the above catalyst (7 mg.). The products were analysed by g.l.c. and found to be the same as in (*a*). With-

out catalyst (+)-car-3-ene was unaffected under these conditions.

Pyrolysis of (+)-*cis-Caran-cis-5-ol* (III).[2]—(*a*) This alcohol (3 g.) was heated in a sealed tube at, *e.g.,* 300° (see Table 2) for 4·5 hr. with acetic acid (7 mg.). The product, collected in ether, was washed with sodium carbonate, dried, and separated into three components on a 30% Apiezon column (6 m. × 0·94 cm.) at 140°. The products were eluted in the order (—)-*cis-m*-mentha-4,8-diene [14] (XIV), (+)-*m*-mentha-3(8),4-diene (XV), and (—)-*cis-m*-menth-4-en-8-ol [2,7b] (XVI), and represented an 85% yield, estimated from g.l.c. standard. (—)-cis-m-*Mentha*-4,8-*diene* (XIV) had n_D^{22} 1·4659, $[\alpha]_D^{20}$ —101·26° (*c* 0·65), $\nu_{max.}$ (film) 3080, 3020, 2990, 2910, 2870, 1775, 1640, 1445, 1425, 1360, 1275, 1260, 1210, 1150, 1125, 1065, 980, 913, 888, 874, 811, 731, and 704 cm.$^{-1}$ (Found: C, 88·2; H, 11·8. C$_{10}$H$_{16}$ requires C, 88·2; H, 11·8%). (+)-m-*Mentha*-3(8)-4-*diene* (XV) had n_D^{20} 1·4885, $[\alpha]_D^{20}$ +144° (*c* 0·625), $\nu_{max.}$ (film) 3080, 2990, 2940, 1680, 1640, 1620, 1460, 1430, 1370, 1330, 1290, 1270, 1250, 1210, 1170, 1130, 1080, 989, 952, 922, 873, 845, 792, and 726 cm.$^{-1}$ (Found: C, 88·1; H, 11·6. C$_{10}$H$_{16}$ requires C, 88·2; H, 11·8%). (—)-*cis-m*-Menth-4-en-8-ol (XVI) had $[\alpha]_D^{22}$ —11·1° (*c* 0·4) (cf. ref. 2), $\nu_{max.}$ 3268, 3010, 2924, 1642, 1455, 1395, 1370, 1325, 1290, 1220, 1200, 1180, 1160, 1140, 1130, 1080, 1060, 989, 958, 920, 897, 874, 845, 788, and 735 cm.$^{-1}$.

The alcohol (XVI) (140 mg.) in pyridine (3 c.c.) was kept with phosphoryl chloride (165 mg.) for 48 hr. The hydrocarbons were collected in ether; g.l.c. on a 20% Castorwax column (3 m.) at 120° gave 2 peaks (*ca.* 1 : 2) which were unresolved from authentic specimens of (XIV) and (XV) respectively. The residue after removal of ether showed $\nu_{max.}$ 1634, 1595, 992, 893, 877, and 730 cm.$^{-1}$, attributable to a mixture of (XIV) and (XV).

(*b*) A solution of (+)-*cis*-caran-*cis*-5-ol (10%; 5 c.c.) in benzene was admitted at *ca.* 0·2 c.c./min. into the reactor tube kept at 480° (nitrogen flow-rate 70 c.c./min.). The products, and mixtures with authentic compounds, were analysed by g.l.c. on a 20% Castorwax column (3 m.) at 140°. They consisted of (—) *cis-m*-mentha-4,8-diene (XIV) (80%), (+)-*m*-mentha-3(8),4-diene (XV) (15%) and other minor products.

Effect of Hydrochloric acid of Various Concentrations on (+)-*cis-Caran-cis-5-ol* (III).—A modification of our preparative method [2] was used. Samples of the alcohol (III) (10 mg.) were thoroughly shaken for 15 min. with hydrochloric acid (30 mg.) (0·1N, 1N, 2·5N, 5N, 7·5N, 10N, and 12·5N), and then set aside for 24 hr. The organic material was extracted with ether (1 c.c.) and the extract was washed successively with water (0·25 c.c.), 10% sodium hydroxide (0·25 c.c.), and water (1 c.c.), and dried (MgSO$_4$). The products, and mixtures with authentic compounds, were analysed by g.l.c. on a Castorwax column (3 m.) at 150° (see Figure 1).

(—)-*trans-Caran-cis-2-ol* [3] (IV).—This alcohol was prepared by a modification of Baeyer's method.[15] (+)-Dihydrocarvone was prepared as follows: (—)-carvone (60 g.) in anhydrous ether (300 c.c.) was added dropwise with stirring to liquid ammonia (1 l.) during 15 min., and lithium (8 g.) was added slowly, in small pieces (3 mm.), during 20 min. with stirring; the mixture turned dark blue. Stirring was continued for a further 2 hr., then ethanol (80 c.c.) was added dropwise during 1 hr., and the mixture became brown. Ether (400 c.c.) was added, followed by water (200 c.c.) added dropwise during 1 hr. The ethereal

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* Neither ref. 8*a* nor 8*b* gives a full description of the hydrocarbon; ref. 8*c* gives no details of physical properties.

layer was washed with water and concentrated to 300 c.c. A solution of sodium dichromate dihydrate (50 g.) and sulphuric acid (27 c.c.) in water (250 c.c.) [17] was then added during 1 hr. with ice-cooling and stirring, and the mixture was stirred overnight. It was worked up in the usual way to give (+)-dihydrocarvone (48 g.), b. p. 60°/1 mm., $[\alpha]_D^{23}$ +13·21° (c 1·9), n_D^{23} 1·4693. It gave a single peak on a 20% Castorwax column (3 m.) at 170°, but on a 20% Carbowax column (3 m.) at 132° it gave 2 peaks, probably corresponding to trans-dihydrocarvone (86·2%) and its cis-isomer (13·8%). (+)-Dihydrocarvone (20 g.) was converted into (−)-trans-caran-2-one (17 g.), b. p. 60°/1 mm., $[\alpha]_D^{19}$ −162·9° by Baeyer's method.[15] (−)-trans-Caran-2-one (20 g.) in dry ether (200 c.c.) was treated carefully with ice-cooling and stirring with lithium aluminium hydride (3 g.) during 30 min. Stirring was continued for 3 hr. The excess of lithium aluminium hydride was destroyed with moist ether, and the product, collected in ether, gave (−)-trans-caran-cis-2-ol (IV) [3] (17 g.), b. p. 56°/0·5 mm., $[\alpha]_D^{19}$ −54·3° (c 2·0) (lit.,[3] −60·9°).

Oxidation of the Alcohol (IV) *to* (−)-trans-*Caran-2-one*. —The above alcohol (1·5 c.c.) in ether (15 c.c.) was treated with a solution of sodium dichromate dihyrate (1·7 g.) and sulphuric acid (1·1 c.c.) in water (7 c.c.), added dropwise during 5 min. with stirring and ice-cooling. Stirring was continued for 3 hr. and the product was collected in ether and gave (−)-trans-caran-2-one (1 g.), $[\alpha]_D^{20}$ −147·9° (c 2·6) [lit.,[18] −153° (c 5·0)], i.r. and n.m.r. spectra identical with those of authentic material [(−)-cis-caran-2-one has $[\alpha]_D^{20}$ −81° (c 4·0)].[18]

Pyrolysis of (−)-trans-*Caran*-cis-2-ol (IV).—The alcohol (IV) (1 g.) was heated with acetic acid (50 mg.) in a sealed tube at 210° for 1·25 hr. When cool, the mixture, which consisted of two layers, was treated with ether (15 c.c.), and the organic layer was washed (a) with sodium hydroxide solution until the washings were alkaline, and (b) with water (2 × 20 c.c.). The ether layer was dried, and solvent was removed to leave a mixture (0·75 g.) of (+)-trans-p-mentha-2,8-diene (XVII) (51·2%), n_D^{20} 1·4669, $[\alpha]_D^{20}$ +205·1° (c 0·4 in benzene) [lit.,[4] n_D^{20} 1·4660, $[\alpha]_D^{25}$ +221·2° (c 2·4 in benzene)], $\nu_{max.}$ (film) 2941, 2882, 1785, 1642, 885, and 728 cm.$^{-1}$ (Found: C, 88·7; H, 12·2. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%), and (+)-trans-p-menth-2-en-8-ol (XVIII) [4] (27·2%) (see below). A g.l.c. standard confirmed that these products alone represent the observed yield.

The hydrocarbon (XVII) is readily autoxidised and must be analysed immediately after preparation.

Effect of Hydrochloric Acid of Various Concentrations on (−)-trans-*Caran*-cis-2-ol (IV).—(a) Samples of alcohol (10 mg.) were treated with hydrochloric acid (30 mg.) as described for (+)-cis-caran-cis-5-ol. The results, established by analytical g.l.c. on a Castorwax column (3 m.) at 150°, are shown in Figure 2.

(b) (+)-trans-p-*Menth-2-en-8-ol* (XVIII).[4]—The alcohol (IV) (5 g.) was shaken with 2N-hydrochloric acid (5 c.c.) for 15 min. and set aside overnight. The organic layer was extracted into ether (2 × 25 c.c.), washed with water

(2 × 10 c.c.), 10% sodium hydroxide solution (2 × 10 c.c.), and water (2 × 10 c.c.), and dried ($MgSO_4$). Removal of solvent left a clear liquid (4·5 g.), which when repeatedly fractionated under reduced pressure gave the alcohol (XVIII) [4] (1·5 g.), b. p. 43°/0·25 mm., n_D^{23} 1·4745, $[\alpha]_D^{22}$ +92·3° (c 1·3 in benzene), 95% pure (g.l.c.) [lit.,[4] n_D^{20} 1·4759, $[\alpha]_D^{20}$ +105·3° (c 2·3 in benzene)], i.r. spectrum identical with that reported,[4] n.m.r. spectrum reported in the Discussion.

The alcohol (XVIII) (320 mg.) in pyridine (6 c.c.) was kept with phosphoryl chloride (420 mg.) at 20° for 12 hr. The product was collected in ether, and analysed by g.l.c. on a Castorwax column (3 m.) at 150°. Two peaks (1 : 4) corresponded to authentic samples of (XII) and (XVII) respectively.

(c) α-*Terpinene* (XI) *and* (+)-p-*Mentha-2,4(8)-diene* (XII; α-Me).—The alcohol (IV) (5 g.) was treated with 12·5N-hydrochloric acid (5 c.c.) and kept overnight at 20°. The product, analysed by g.l.c. on the Castorwax column at 143°, contained α-terpinene (XI) (19%), (+)-p-mentha-2,4(8)-diene (XII; α-Me) (38%), and (+)-trans-p-menth-2-en-8-ol (XVIII) (22%). Distillation gave a hydrocarbon fraction, b. p. 20—31°/0·65 mm. which was subjected to preparative g.l.c. on a 30% Castorwax column (6 m.) at 110° to give α-terpinene (XI), spectroscopic and g.l.c. properties identical with those of the authentic compound, and (+)-p-mentha-2,4(8)-diene (XII; α-Me), $[\alpha]_D^{20}$ +53·06° (c 0·83 in ethanol) (lit.,[7a] $[\alpha]_D$ +49·11°), spectroscopic and g.l.c. properties identical with those of the racemic compound described above.

Hydrogenation of the Dienes (XI)—(XVII) *and* (XII; α-Me).—Hydrogenations of the dienes (ca. 20 mg.) were carried out with ethanol (3 c.c.) as solvent over 5% palladised charcoal (ca. 40 mg.) at 1 atm. and 20°. The saturated products were identified by g.l.c., with authentic cis- and trans-m- and p-menthanes as standards, on a 30% Castorwax column (3 m.) at 110°. A mixture of authentic m- and p-menthanes was thus clearly resolved into four peaks. The results are tabulated below:

	Uptake of hydrogen (c.c.)	Uptake required for 2 mols of hydrogen
(XI)	9·4	9·9
(XII)	6·6	7·4
(XIII)	11·4	11·6
(XIV)	14·6	14·2
(XV)	13·1	12·5
(XVII)	4·2	4·3
(XII; α-Me)	4·3	4·3

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

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