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PRODUCTS OF THE PYROLYSIS OF (+) CAR-3-ENE AND RELATED COMPOUNDS

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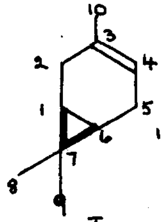
Earlier investigations[eg.1,2] of the pyrolysis of car-3-ene have suggested that m- and p- cymene, and dipentene are commonly products of this reaction, but the products were not rigorously isolated.

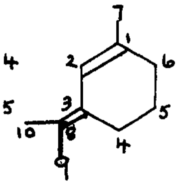
We have now shown that pyrolysis of (+) car-3-ene (I) vapour in glass at 550° gives, as the main product, a mixture of the following volatile aromatic hydrocarbons which are present in the mixture in the proportions (%) shown: - benzene, (4.8), toluene (17.7), m- and p- xylene mixture (14.8), styrene (6.3), m- cymene (11.4), p- cymene (7.2), 8(9)dehydro- m- cymene (5.6), and 8(9)dehydro- p- cymene (4.4). The cymenes are not the source of benzene or toluene for under the reaction conditions the cymenes are not converted to these substances. At higher temperatures however, the proportions of m- and p- cymenes decrease.

We have found that pyrolytic fission of the six-membered ring of car-3-ene is markedly more difficult to accomplish than that of β- pinene. The latter affords[3] high yields of myrcene at relatively low temperatures and we have confirmed this result. The stability of car-3-ene can be attributed to the partial double bond character of the carbon-carbon bonds of the six-membered ring, arising from the juxtaposition of the double bond and the cyclopropane ring. This is supported by the mass spectrum of car-3-ene which shows very little 'retro Diels-Alder type' fission.

In the presence of potassium alumino silicate at 400°, vapour phase pyrolysis of car-3-ene in glass gives a mixture in which non-aromatic conjugated hydrocarbons predominate. These are m-mentha-1,3(8)diene (II. 14.4%), (±) p-mentha-2,4(8)diene (III; 14.4%), and α- terpinene (IV; 21%). In addition m- and p- cymene in 8.2% and 10.9% proportions are formed. The proportions of all these compounds vary with changes in the reaction temperature.



I



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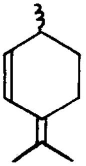

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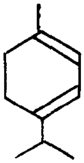

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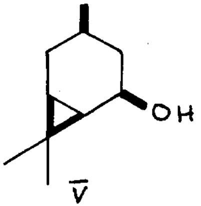

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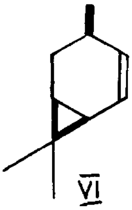
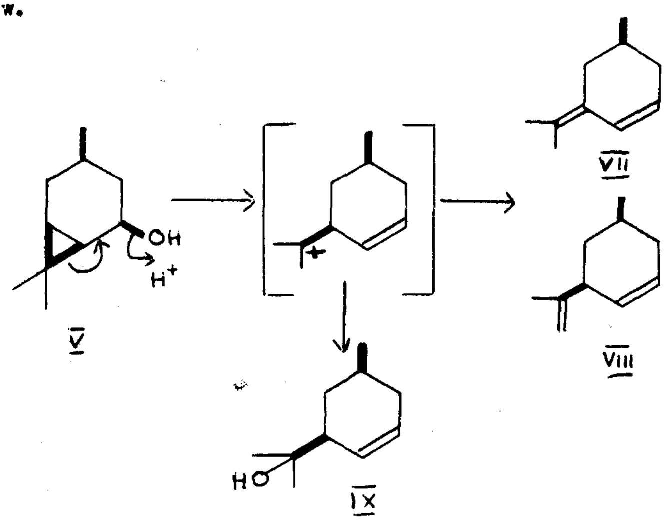


VI

We have also investigated the acid catalysed pyrolysis, in glass, at 200-300° of (+) *cis* caran-5-*cis*-ol (V) which we have prepared[4] from (+) car-3-ene (I) and from (-) *cis* car-4-ene (VI). The major products of pyrolysis are the (+) m-mentha-3(8),4-diene (VII; 13.3%), $[\alpha]_D$+ 144°, and (-) *cis* m-mentha-4,8(9)diene[5] (VIII; 74.5%), $[\alpha]_D$- 50.6°. Additionally, small variable yields (3-16%) of the alcohol, (-) m-mentha-4-ene-8-ol (IX), $[\alpha]_D$-11.1° were isolated. It was converted to a mixture of (VII) and (VIII) at higher temperatures than were typical of the pyrolyses.

Formation of these compounds may be portrayed as shown below.



All the above compounds were isolated by preparative g.l.c. and their structures deduced, where necessary, by microhydrogenation to *cis* and *trans* m- and p- menthanes,[6] and/or by ultraviolet, infrared, n.m.r. and mass spectroscopy.

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5. c.f. K. Gollnick, Tetrahedron Letters, No. 3, 327 (1966).

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