

The Pyrolysis of *cis*-Verbanone

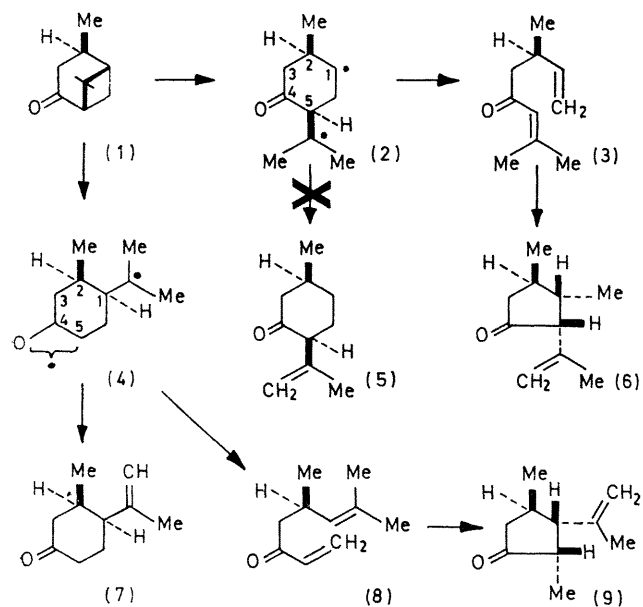
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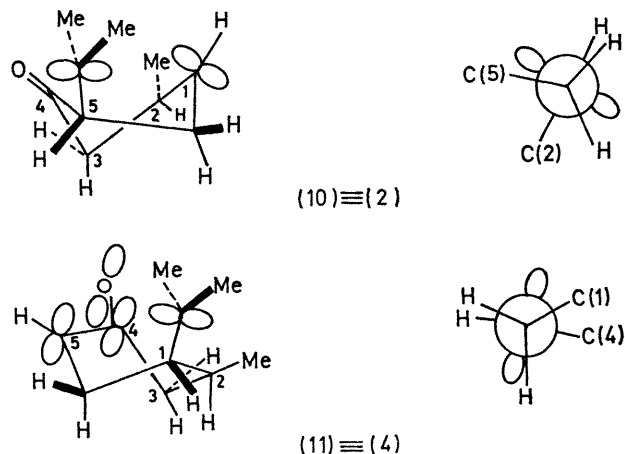
Summary The pyrolysis of *cis*-verbanone (1) gives dienes (3) and (8), and ketones (6), (7), and (9); monocyclic primary products are formed from pinane derivative pyrolysis when the 1,4-diradical intermediate is stabilised by π -delocalisation.

PYROLYSIS of *cis*-verbanone (1)¹ on passage through a stainless-steel tube at 580° (contact time 0.1s) gave a crude product shown (g.l.c.) to consist of six major components. These were identified by i.r., u.v., and n.m.r. spectra as *cis*-

verbanone (1) (17%), diene (3) (15%), isomeric diene (8) (15%), cyclopentanones (6) (7.5%) and (9) (13%), and the cyclohexanone (7) (20%). While the dienes, (3) and (8), and the cyclohexanone (7) were primary pyrolysis products, the cyclopentanones (6) and (9) were formed (control experiments) by cyclisation of dienes (3) and (8) respectively (Scheme). The absence of (<0.5%) of the isomeric cyclo-



SCHEME



hexanone (5) from among the pyrolysis products of *cis*-verbanone (1) is noteworthy.

The pyrolysis of the pinane derivative *cis*-verbanone (1) to give the acyclic primary products, (3) and (8), involves the cleavage of two C-C bonds of the cyclobutane ring, probably *via* the 1,4-diradical intermediates (2) and (4), respectively. The cleavage of the second C-C bond will occur most readily when the singly occupied orbitals of the 1,4-diradical (2) are eclipsed with that C-C bond. For the

1,4-diradical (2), in which the carbon atoms adjacent to the secondary radical are sp^3 -hybridised, reaction can occur in conformation (10) to give acyclic products, and no monocyclic primary products are isolated. This type of product composition has been found for other pinane derivatives in which both C-2 and C-4 are sp^3 -hybridised.^{2,3}

In contrast for the 1,4-diradical (4) with an sp^2 -carbon atom adjacent to the secondary radical, the stereochemical requirements for π -delocalisation of the secondary radical impose conformational constraints on the system (11). Consequently cleavage of the second C-C bond is relatively

disfavoured and 1,5-hydrogen transfer from a methyl group of the isopropyl radical becomes a competing reaction path leading to a monocyclic product. For pinane derivatives^{3,4} where the 1,4-diradical formed has the secondary radical adjacent to the sp^2 carbon at C-2 or C-4, both monocyclic and acyclic primary products are obtained.

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