Thermal Rearrangement of a Homofulvene to a Cyclopentadiene

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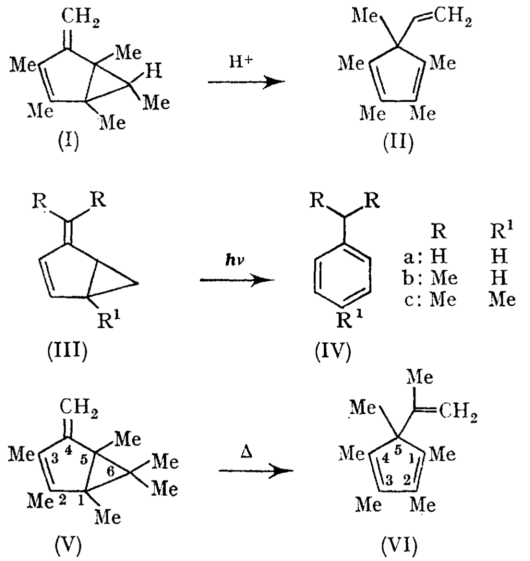
The acid-catalyzed rearrangement of homofulvene (I) to cyclopentadiene (II) has recently been described by two groups,[1,2] but the homofulvenes (III) were reported[3] to be unchanged upon being heated in the absence of solvent until they polymerized. Compounds (IIIb) and (IIIc), however, were photochemically aromatized to (IVb) and (IVc) respectively, possibly *via* a 1,7-suprafacial[4] hydrogen shift. We now report on the thermal rearrangement of the hexamethylhomofulvene (V) (which cannot aromatize) to the cyclopentadiene (VI), and describe experiments with labelled (V) which are pertinent to the reaction mechanism.

When the injector port was too hot, in the v.p.c. purification of (V),[5] a new product was observed. The reaction proceeded cleanly and essentially quantitatively above 200°; the product was a colourless oil to which structure (VI) is assigned on the basis of spectral and chemical properties: (VI) had a λ_{max} (95% EtOH) 248 nm. (ϵ 4250) and i.r. bands (neat) at 1640 (conj. C=C) and 885 cm.$^{-1}$ (term. $C=CH_2$).[6] Its n.m.r. spectrum (CCl_4) showed a quartet at τ 5·25 (vinyl protons) allylically coupled with one methyl group, a triplet at τ 8·93, J *ca.* 1·0 Hz. This methyl, though allylic, is strongly shielded by the



conjugated π-system.† The remainder of the spectrum consists of two quartets at τ 8·27 and 8·45 (6H each, J 0·7 Hz) for the C(1)–C(4) and C(2)–C(3) methyls respectively and a singlet at τ 9·03 for the C(5) methyl.

The cyclopentadiene (VI) and maleic anhydride gave adduct (VII), m.p. 183·5—185°, and with tetracyanoethylene, adduct (VIII), m.p. 154—155°. Hydrogenation of (VI) (Pt–ethanol) gave 5-isopropylpentamethylcyclopentadiene which, with tetracyanoethylene, gave the adduct (IX), m.p. 142—143°.‡

Mechanistic paths for the reaction (V) → (VI) can be envisioned in which the bond that breaks in the three-membered ring of (V) is either C(1)–C(6) or C(5)–C(6). Examples are concerted paths (A or B, both 1,5-sigmatropic H-shifts) or diradical paths C and D.

To distinguish between these alternatives, $[^2H]$(V)[5] was pyrolyzed. At 200° the reaction was clean; in the n.m.r. spectrum of the product, the peaks at τ 8·27 and 8·45 integrated for only three hydrogens each, and were still homoallylically coupled. The product is $[^2H_2]$(VI–B), and only the C(1)–C(6) bond in (V) breaks. At 275°, however, appreciable label scrambling occurred.

Further study of the reaction mechanism is in progress.

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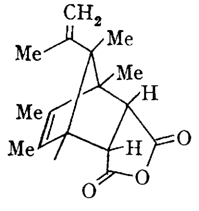
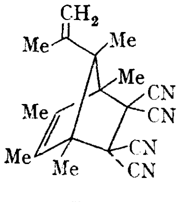
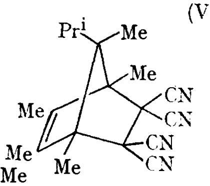


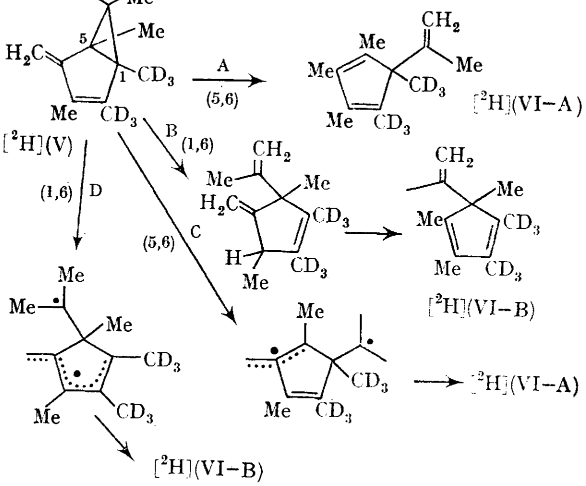
(VII)



(VIII)



(IX)



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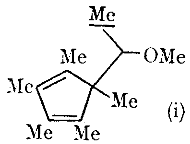
† For a similar effect, note that the indicated methyl in (i) appears at τ 9·45 (ref. 2).



(i)

‡ Elemental analyses and spectral properties agree with the proposed structures.

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[6] Similarly substituted cyclopentadienes have comparable spectral properties. For examples, see L. DeVries *J. Org. Chem.*, 1960, **25**, 1838; S. Mclean and P. Haynes, *Tetrahedron*, 1968, **21**, 2343, and ref. 2.