Thermal Isomerization of 2-Methylbicyclo[2,1,0]pent-2-ene to 1-Methylcyclopentadiene

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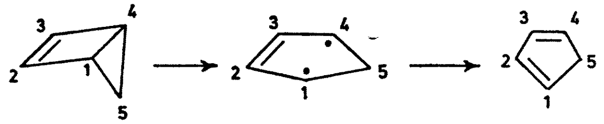
Summary The thermal rearrangement of 2-methylbicyclo[2,1,0]pent-2-ene gives 1-methylcyclopentadiene, rather than the 2-methylcyclopentadiene required by the usually assumed diradical mechanism for this valence isomerization.

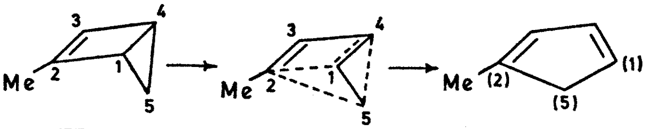
THERMAL conversion of bicyclo[2,1,0]pent-2-ene (I) into *cis*, *cis*-cyclopentadiene (II)[1] must, it would seem, be a disrotatory, symmetry-forbidden, and diradical two-step process.[2] This view, based on the tacit assumption that the rearrangement is a valence isomerization involving the C(1)–C(4) single bond and the C(2)–C(3) double bond, has not been disparaged by gas-phase kinetic[3,4] and isotopic labelling results.[5] Both the activation parameters[3,4] and deuterium labelling experiments establishing the durability of the C(5) methylene unit throughout the rearrangement[5] are interpretable through the diradical hypothesis.



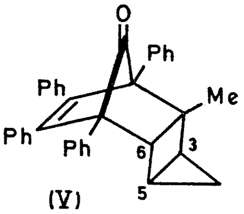
(I) (II)

We now report that 2-methylbicyclo[2,1,0]pent-2-ene (III) rearranges thermally to 1-methylcyclopentadiene (IV), thus revealing the process as one ascribable to a valence isomerization involving C(1)–C(2) and C(4)–C(5) bonds, a symmetry-allowed [$\sigma^2s + \sigma^2a$] cycloreaction.

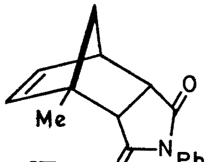
A tetrahydrofuran solution of 2-methylbicyclo[2,1,0]pent-2-ene[6] from the photolysis of 2-methylcyclopentadiene[7] was freed from unconverted diene and divided. Half of the solution was combined with tetraphenylcyclopentadienone to form the corresponding Diels–Alder adduct (V), $\tilde{\nu}_{max}$ 1765 cm^{-1}, m.p. 197—198° (dec) from diethyl ether; n.m.r.: τ 3·0 (m, 20 H), 7·29 (d, J 2 Hz, 1 H), 8·05 (m, 2 H), 9·05 (m, 2 H), and 9·11 (s, 3 H) assigned, respectively, to aromatic, C(6)-H, C(3) and C(5) methine, methylene, and methyl protons.[8]† No trace of an isomeric adduct was detectable spectroscopically or by t.l.c.



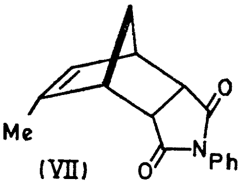
(III) (IV)



(V)



(VI)



(VII)

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† Further characterized through decarbonylation to 2-methyl-3,4,5,6-tetraphenylbicyclo[6,1,0]nona-2,4,6-triene.

The second half of the solution was added to a tetrahydrofuran solution of an excess of *N*-phenylmaleimide, a dienophile unreactive toward bicyclopentenes[5] but an efficient trap for derived rearrangement product(s); the Diels–Alder process competes effectively against hydrogen shifts in the diene product(s) equilibrating 1- and 2-methylcyclopentadienes.[9,10]‡§ At 43°, the rearrangement of 2-methylbicyclo[2,1,0]pent-2-ene in the presence of *N*-phenylmaleimide led to a single adduct, m.p 178—179°, identical with one (VI) obtained from authentic 1-methylcyclopentadiene. No trace of the adduct (VII), m.p. 118—119·5°, stemming from 2-methylcyclopentadiene was seen by t.l.c. analysis under conditions known to separate (VI) and (VII).

This conversion, though readily treated as a $[\sigma^2s + \sigma^2a]$ concerted process, could possibly go in two steps, through initial 1,3-sigmatropic isomerization with inversion at C(5) to give 1-methylbicyclo[2,1,0]pent-2-ene, followed by the diradical ring-cleavage; but we view this alternative as less likely and probably an insecure refuge for steadfast diradical partisans. The rearrangement with 1,4- or 2,3-dideuteriobicyclopentene should and will be done to remove this residual uncertainty.

The steric prohibition against the normally favoured conrotatory concerted process for thermal cyclobutene isomerizations is seen, in the conversion (III) → (IV), to bring not a nonconcerted but an alternative, usually noncompetitive, concerted route to the fore. This fact spoils the usually assumed either/or concerted/nonconcerted mechanistic dichotomy, and urges experimentation to gauge the relative kinetic advantages of various concerted versions of a rearrangement type. The $[\sigma^2s + \sigma^2a]$ mechanism has, we feel, considerable potential applicability for other hydrocarbon rearrangements, and suitable labelling work is in progress.

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‡ At 47° in the absence of a trapping agent, McLean and Findlay[6] observed the thermal conversion of (III) to methylcyclopentadienes.

§ In separate experiments *N*-phenylmaleimide was observed to add instantaneously to both 1- and 2-methylcyclopentadiene; the resulting Diels–Alder adducts were stable under the reaction conditions.

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[6] First prepared and identified by S. McLean and D. M. Findlay, *Canad. J. Chem.*, in the press.

[7] Using our technique developed for bicyclopentene: A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, jun., submitted for publication in *Org. Synth.*

[8] Compare the n.m.r. data with those for the cyclopentadiene–bicyclopentene Diels–Alder adduct: J. E. Baldwin and R. K. Pinschmidt, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 5247.

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