# Photoisomerization of 1-Methylenecyclohexa-2,5-dienes

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PHOTOISOMERIZATION of 1-methyl-4,4-diphenylcyclohexa-2,5-diene (I) occurs, *via* its singlet state with phenyl migration, to give (II).[1] It was of interest to study systems where the 4-substituents were alkyl rather than aryl, and we now report on the photochemistry of 1-methylene-2,3,4,4,5,6-hexamethylcyclohexa-2,5-diene (III) and related compounds.[2,3]

Direct irradiation through Vycor of [$^1$H](III)[4] in ether (2·5—5% solution) for 20 hr. with a 450 w Hanovia lamp gave 29% of unchanged (III), 31% of the photoisomer [$^1$H](IV), 5% of an unidentified volatile product, and 35% of nonvolatile material. In ether-penta-1,3-diene (9 : 1), these yields were 34, 38, 8, and 20%. Irradiation through Pyrex of [$^1$H](III) in acetone failed to give (IV).

The structure of (IV) follows from its spectral properties and thermal isomerization[5]: it had a $\lambda_{max}$ (95% EtOH) 253nm. ($\epsilon$ 11,300) and i.r. bands (neat) at 1625 (conj. C=C) and 850 cm.$^{-1}$ (term. C=CH$_2$).[6] The n.m.r. spectrum (CCl$_4$) showed two vinyl hydrogens ($\tau$ 5·32 and 5·47), two allylic methyl groups [$\tau$ 8·34 and 8·44, C(2) and C(3) respectively, broadened by homoallylic coupling] and one methyl singlet at high field ($\tau$ 9·35), the *endo*-C(6) methyl shielded by the $\pi$-electrons of the double bonds. The other methyls appeared at $\tau$ 8·97 [*exo*-C(6)] and $\tau$ 8·89 [C(1) and C(5)].

Rearrangement (III) ⟶ (IV) might occur either by a "bond crossing" mechanism or by methyl migration. To distinguish between these alternatives, [$^2$H](III)† was irradiated. "Bond crossing" should give [$^2$H](IV), whereas methyl migration would give a mixture of [$^2$H](V) and [$^2$H](VI). The n.m.r. spectrum of the photoproduct of [$^2$H](III) showed a decrease in the peak at $\tau$ 8·89 to three protons, consistent only with [$^2$H](IV), and not with a mixture of [$^2$H](V) and [$^2$H](VI). The spectrum also lacked the peak at $\tau$ 8·34, and that at $\tau$ 8·44 was sharpened as expected. We conclude that, in contrast with (I), (III) photoisomerizes by a "bond-crossing" mechanism, but also most probably from a singlet excited state.

Methyl substituents influence the reaction course. Thus (VII) and (VIII) were relatively

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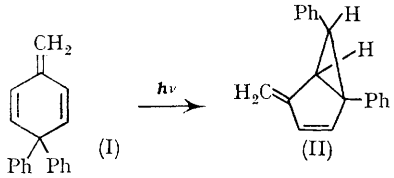
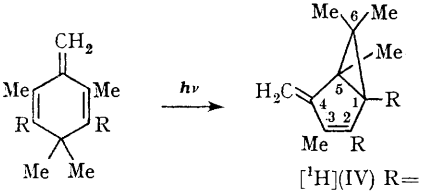
† Prepared from 3,5-bistrideuteriomethyl-2,4,4,6-tetramethylcyclohexa-2,5-dienone (ref. 4).

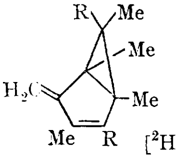


(I) (II)

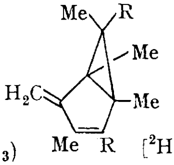


[$^1$H](III) R=Me
[$^2$H](III) R=$CD_3$

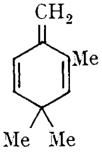
[$^1$H](IV) R=Me
[$^2$H](IV) R=$CD_3$

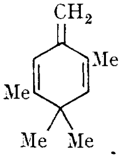

[$^2$H](V)

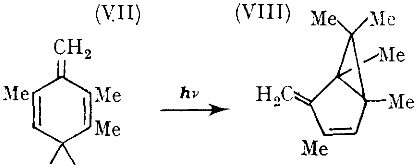
(R=$CD_3$)


[$^2$H](VI)

inert to irradiation under conditions identical to those used with (III). However (IX) did photoisomerize to (X) and other products which are being further investigated.


(VII)


(VIII)



(IX) (X)

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[1] H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *J. Amer. Chem. Soc.*, 1967, **89**, 5973.

[2] A very preliminary report, but without labelling experiments which define the mechanistic path, was given some years ago; H. Hart, A. J. Waring, P. Collins and R. Lange, Abstracts, American Chemical Society 149th Meeting Detroit, 1965, 51P.

[3] Irradiation of protonated (III), to give the heptamethylbicyclo[3,1,0]hexenyl cation has recently been described; R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, in the press.

[4] Prepared by the acid-catalyzed dehydration of the alcohol obtained from hexamethylcyclohexa-2,5-dienone (H. Hart and D. W. Swatton, *J. Amer. Chem. Soc.*, 1967, **89**, 1874) and methylmagnesium bromide.

[5] See H. Hart and J. D. DeVrieze, following Communication.

[6] Elemental analysis was satisfactory. For spectral data of closely related homofulvenes, see M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Letters*, 1968, 3583; L. A. Paquette and G. R. Krow, *ibid.*, p. 2139; L. A. Paquette, *ibid.*, p. 2133; H. Hogeveen and H. C. Volger, *Chem. Comm.*, 1967, 1133; R. Criegee and H. Grüner, *Angew. Chem. Internat. Edn.*, 1968, **7**, 467; W. Schäfer and H. Hellmann, *ibid.*, 1967, **6**, 518; L. deVries, *J. Amer. Chem. Soc.*, 1960, **82**, 5242; D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 1958, 688; D. H. R. Barton, R. Bernasconi, and J. Klein, *ibid.*, 1960, 511.