Internal Photocycloaddition of 6-Phenylhex-2-ene[1]

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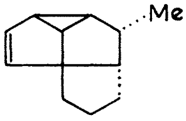
Summary Photolysis of 6-phenylhex-2-ene leads to the formation of internal cycloadducts, possibly through the intermediate formation of a singlet exciplex.

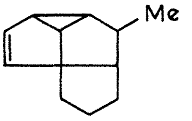
THE mechanism of product formation in the intermolecular 1,3-cycloaddition of olefins to the aromatic ring[2,3] has caused considerable speculation.[4–6] We report now on the first intramolecular analogue of this cycloaddition reaction.

In the photolysis of the title compound, we anticipated that initial excitation of the phenyl group would be followed by intersystem crossing and subsequent triplet-energy transfer to the olefin; the observable consequence, by analogy with the photochemistry of 1-phenylbut-2-ene,[7] would be isomerization of the double bond. In fact, irradiation of a cyclopentane solution of *cis*-6-phenylhex-2-ene using a Vycor-enclosed, low-pressure mercury lamp, does result in *cis–trans* isomerization; the major product, however, is a mixture of isomers resulting from internal 1,3-cycloaddition to the aromatic ring. Thus, the v.p.c. purified product is isomeric with the starting material,† has one double bond (perphthalic acid), and can be reduced to a dihydro- (CCl_4)[8] or tetrahydro- (EtOH) product with 10% Pd–C. The n.m.r spectrum (60 MHz, CCl_4) is characterized by the appearance of two vinyl hydrogens but the complete absence of aryl hydrogens. The u.v. spectrum (cyclopentane) contains an absorption maximum at 213 nm. (ϵ 3500) characteristic of a vinyl cyclopropane chromophore.[3,8] As mentioned above the product is a (thus far, inseparable) mixture of isomers, partial resolution having been achieved by capillary v.p.c. Though a completely unambiguous set of individual structural assignments is not yet possible,‡ we believe that the reaction is indeed an internal 1,3-cycloaddition:[9] (*a*) internal photocycloaddition of the phenylhexene proceeds largely with retention of stereochemical integrity, *e.g.* the *trans*-isomer photolyzes to give a product readily resolved by v.p.c. from the product derived from the *cis*-isomer. A comparable result has been suggested in one instance of intermolecular cycloaddition.[3] (*b*) Quantum yields for product formation from the *cis*-olefin are: 0·24, 0·26, 0·27, and 0·28. The quantum yield reported[10] for 1,3-cycloaddition of cyclopentene to benzene (cyclopentene solvent) is 0·25. (*c*) The internal cycloaddition reaction is inefficiently quenched by *cis*-penta-1,3-diene (slope *ca.* 4·5 l.mole^{-1}) with comparable quenching of phenylhexene fluorescence by the diene also observed. (*d*) Oxygen saturation of *cis*-phenylhexene solutions quenches cycloaddition and fluorescence with equal effectiveness ($\phi_0/\phi = 1{\cdot}4$). (*e*) Even though cycloaddition is relatively efficient, photoisomerization of *cis*-phenylhexene to the *trans*-isomer proceeds at a reasonable rate ($\phi_{c\rightarrow t} =$ 0·05 compared with $\phi_{c\rightarrow t}$ 0·16 for 1-phenylbut-2-ene[7]). (*f*) Photolysis of a solution of *cis*-phenylhexene and benzophenone with light >330 nm. produces *cis–trans* isomerization but none of the cyclo-adduct. (*g*) Relative fluorescence yields for toluene, 1-phenylhexane, 1-phenylbut-2-ene and 6-phenylhex-2-ene are 1·0 : 0·96 : 0·72 : 0·05 respectively, *e.g.* a pronounced diminution in fluorescence is observed for the substrate which undergoes internal cycloaddition.

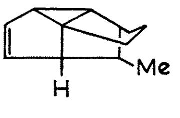
These data suggest that the internal cycloaddition is directly analogous to the intermolecular cycloaddition reactions previously reported, proceeds through the intermediacy of a phenyl singlet state (or a derivative thereof,



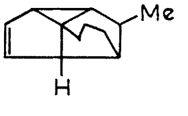
(I)



(II)



(III)



(IV)

† Analysis: Calc. for $C_{12}H_{16}$: C, 89·93; H, 10·07. Found: C, 89·97, H, 10·20%. Molecular ion: 160 *m/e*.

‡ A detailed analysis of n.m.r. absorption and decoupling data (with benzene as solvent) and a consideration of models for the possible isomers, lead us to favour structures (i)—(iv) as the probable components of the mixture.

see below), and can co-exist with intersystem crossing of the phenyl group. Bryce-Smith and Longuet-Higgins have proposed a diradical ("prefulvene") precursor for 1,3-cycloaddition.[4,6] However, an alternate possibility would be an intermediate complex of the excited phenyl group and olefin ("exciplex");§ such a complex might either go on to give the product or dissociate to the ground state (thus giving rise to the remarkably efficient¶ internal fluorescence quenching observed for the phenylhexene.) Analogy may be found in the exciplexes recently proposed to explain photocycloaddition and fluorescence quenching of aromatics by dienes[11] and ketones by olefins.[12]. A further logical extension would be the excimers postulated as intermediates leading to photodimerization and self-quenching.[13] Although the fluorescence data lead us to favour the exciplex hypothesis, a decision between the two mechanisms is not yet possible and, in fact, both are conceivably compatible. An expanded correlation between internal fluorescence quenching and internal cycloaddition in aryl olefins is presently in progress. It is noteworthy that marked fluorescence quenching is observed in that olefin (6-phenylhex-2-ene) which can achieve coplanarity between double bond and aryl ring; the correlation with Hirayama's observations[14] on excimer formation in diphenylalkanes is striking (excimer formation is optimized when the phenyl groups are three methylenes apart).

We are grateful to the National Science Foundation and the National Cancer Institute of the Public Health Service for support of this research.

(*Received, November 4th*, 1968; *Com.* 1491.)

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§ We are grateful to Kaplan and Wilzbach for suggesting this possibility to us.

¶ Fluorescence quenching of benzene by olefins *in solution* has been observed by Kaplan and Wilzbach (personal communication) and comparable studies on the toluene–2-hexene system have been carried out in our laboratories (R. Peiffer, unpublished data). A 0·8M solution of *trans*-2-hexene reduces the fluorescence of toluene (4×10^{-3}M) by 22%.

[1] Considered as part of the series, "Organic Photochemistry", for previous Part see H. Morrison, R. Brainard, and D. Richardson, *Chem. Comm.*, 1968, 1653.

[2] D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512.

[3] K. S. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 2066.

[4] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[5] K. Kraft and G. Koltzenburg, Preprints of the International Conference on Photochemistry, Munich, 1967, p. 439.

[6] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

[7] H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, 1968, **90**, 3428.

[8] O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, 1964, **86**, 2660.

[9] A second mode of addition originally reported by Srinivasan and Hill (*J. Amer. Chem. Soc.*, 1965, **87**, 4654) is now in question (see ref. 6).

[10] K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *J. Amer. Chem. Soc.*, 1968, **90**, 1116.

[11] K. Kraft and G. Koltzenburg, *Tetrahedron Letters*, 1967, 4723; L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 1968, **16**, 125.

[12] N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, 1968, **90**, 3274.

[13] For example, see H. Morrison, H. Curtis, and T. McDowell, *J. Amer. Chem. Soc.*, 1966, **88**, 5415.

[14] F. Hirayama, *J. Chem. Phys.*, 1965, **42**, 3163.