Photosensitized Cyclization Reaction of 2-Phenylhexa-1,5-diene

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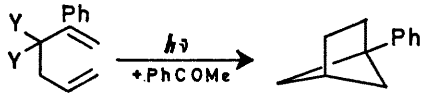
Summary 2-Phenylhexa-1,5-diene undergoes efficient photosensitized internal cycloaddition to give 1-phenylbicyclo[2,1,1]hexane.

WE report a case of efficient internal photocyclization of a substituted styrene, directly in contrast to the lack of examples in the literatures of intra- or inter-molecular cycloaddition reactions of simple acyclic styrenes.[1]



(I) Y = H
(Ia) Y = D

(II)

U.v. irradiation of a benzene solution of 2-phenylhexa-1,5-diene (I) in the presence of acetophenone as photosensitizer with a medium-pressure mercury lamp (Pyrex filter) led to quantitative conversion of the olefin into a single product ($\Phi = 0{\cdot}048$).† The compound (II) can easily be isolated by passing the irradiated solution over neutral alumina, or by preparative g.l.c. Molecular weight determination (by mass spectroscopy) indicates that the product is isomeric with (I). Its structure is clearly indicated by the 60 MHz ^{1}H n.m.r. spectrum,‡ which shows the absence of signals attributable to vinyl protons. The low-field signal consists of a singlet at δ 7·03 (5H, phenyl group). The structure of the high-field signals closely resemble that of 1-vinylbicyclo[2,1,1]hexane:[2] a quartet (AA′ part of an AA′BB′ pattern) centred at δ 1·37 (2H), a singlet (δ 1·73) superimposed with a high-field shoulder accounting altogether for six protons, and a broad signal at δ 2·44 (1H). The high-field quartet is characteristic of the *endo*-methano-hydrogens in bicyclo[2,1,1]hexyl systems,[2] and not expected for the reasonable alternative structure, 1-phenylbicyclo[2,2,0]hexane, for the photoproduct. Furthermore, that this group of signals is not affected in the photoproduct derived from photosensitized irradiation of 2-phenyl-3,3-dideuteriohexa-1,5-diene (Ia) further negates the possibility of a bicyclo[2,2,0]hexyl structure. The photoproduct, therefore, is 1-phenylbicyclo[2,1,1]hexane, (II). The u.v. and i.r. spectra are also consistent with the assignment.

The selectivity and high quantum yield of this reaction of (I) makes it synthetically useful. Preliminary studies with 2-phenylhepta-1,6-diene, an homologue of (I), showed that direct irradiation led to an isomeric product of still unidentified structure, while sensitized irradiation did not lead to efficient cyclization. Direct irradiation of an ether solution of (I) gives, instead of (II), several lower-boiling products of as yet unknown structure.

This project was partially supported by a PRF Research Grant.

(*Received, May* 29*th*, 1970; *Com.* 829.)

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† The reaction can also be sensitized by triphenylene, albeit at reduced efficiency. On energy grounds (67 and 71 kcal/mole for the respective triplet-state energies of triphenylene and styrene) the low efficiency is expected.

‡ Solvent CCl_4; Me_4Si as internal standard.

[1] Examples of photocycloaddition of cyclic styrenes and derivatives with hetero-atom substituents (possible presence of a low-lying $n \rightarrow \pi^*$ state) are known. See, *e.g.*, O. L. Chapman and G. Lenz, *Org. Photochem.*, 1967, **1**, 283, and D. J. Trecker, *ibid.*, 1969, **2**, 63.

[2] R. S. H. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, **1967**, **89**, 4936.