result of a gain in resonance energy and some loss of strain energy.

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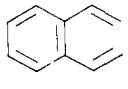
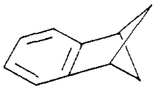
Photoisomerization of *o*-Divinylbenzene[1]

Sir:

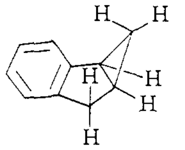
Research on the photochemistry of 1,3,5-hexatrienes[2] has led us to study the photochemistry of *o*-divinylbenzene (I), a related system in which the central double bond is replaced by a benzene ring. We expected as one possible photoreaction of I a head-to-tail cycloaddition between the two vinyl groups to give benzobicyclo[2.1.1]hexene (II), a nucleus which was unknown until most recently.[3,4]



I



II

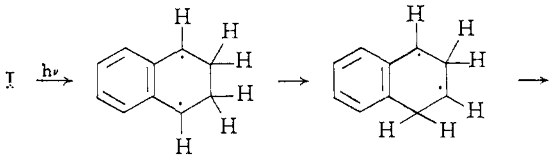


III

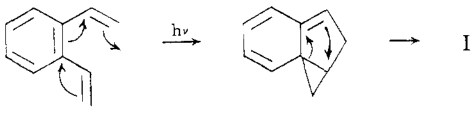
Irradiation of a 0.2% ethereal solution of I with a 450-w Hanovia high-pressure mercury lamp, through a Corex filter, proceeded with the appearance of a single, volatile product as determined by glpc analysis. In a typical experiment using 2.0 g of I, the starting material was completely consumed after 4.5 hr of irradiation, and a 30% yield of the volatile product (estimated by glpc) had formed. Distillation of the reaction mixture afforded a pure sample of this material, which was established to be 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (III),[5] rather than II, on the basis of the following evidence.

The infrared spectrum of III showed absorption maxima at 3030 (m), 2900 (w), 1600 (w), 1475 (s), 805 (m), 790 (m), 758 (s), and 720 (s) cm^{-1}. In its nmr spectrum, III showed complex mutliplets centered at τ 10.0 (*endo* cyclopropyl proton), 9.1 (*exo* cyclopropyl proton), 8.3 and 7.8 (homobenzylic and benzylic bridgehead protons), 7.1 (benzylic methylene protons), and 3.1 (aromatic protons), in a ratio of 1:1:1:1:2:4.[6] These spectra, clearly excluding structure II, were found to be identical with those of authentic III, synthesized previously by Goodman and Eastman.[7]

An interesting feature of this photoisomerization is the necessity of either a hydrogen atom migration, such as that shown in eq 1, or a carbon skeleton rearrangement. An attractive version of the latter might be based on the initial cyclization of I to IV, closely analogous to one mode of 1,3,5-hexatriene cyclization,[2] followed by a vinylcyclopropane–cyclopentene rearrangement which restores the aromatic ring (see eq 2). Deuterium tracer studies described below have now excluded mechanism 1 and similar hydrogen atom rearrangements, but are in accord with expectations based on mechanism 2.



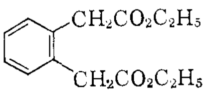
(1)



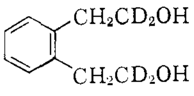
(2)

I IV

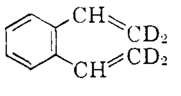
Reduction of ethyl *o*-phenylenediacetate (V) with lithium aluminum deuteride gave diol VI, which was dehydrated over potassium hydroxide at 180–200° (60 mm)[8] to give $\beta,\beta,\beta',\beta'$-tetradeuterio-*o*-divinylbenzene (VII) in 47% over-all yield. The mass spectrum of VII showed its parent peak at *m/e* 134 and indicated that the product was at least 97% d_4 labeled. The nmr spectrum of VII showed no discernable β-proton absorption.



V

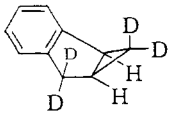


VI



VII

Irradiation of VII, carried out as described above, gave deuterated 1,1a,6,6a-tetrahydrocycloprop[*a*]indene, isolated in 29% yield by careful distillation. The nmr spectrum of this product showed *only* aromatic absorption at τ 3.1 and the two bridgehead protons in their previously observed positions as an AB quartet ($J \cong 7$ cps). This spectral evidence establishes unambiguously the labeling pattern shown in formula VIII, as required by mechanism 2. Deuterium or hydrogen atom rearrangements are excluded.



VIII

Further experiments have indicated that similar isomerizations occur with *o*-divinylbenzene derivatives bearing substituents on the olefinic carbon atoms, and we are now engaged in a more detailed investigation of these novel reactions.

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[1] The partial support of this research by National Science Foundation Research Grant GP-4128 is acknowledged with pleasure.

[2] For leading references and a review of this area of photochemistry see J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2850 (1966); H. Prinzbach, H. Hagemann, J. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

[3] H. Tanida and Y. Hata, *J. Am. Chem. Soc.*, **88**, 4289 (1966).

[4] M. Pomerantz, *ibid.*, **88**, 5349 (1966).

[5] A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

[6] These assignments were made on the basis of chemical shifts and coupling constants; *cf.* W. G. Danben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

[7] We wish to thank Professor Eastman for providing us with the infrared and nmr spectra of authentic III.

[8] J. O. Halford and B. Weissmann, *J. Org. Chem.*, **17**, 1646 (1952).

[9] National Institutes of Health Postdoctoral Fellow, 1965–1967.

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