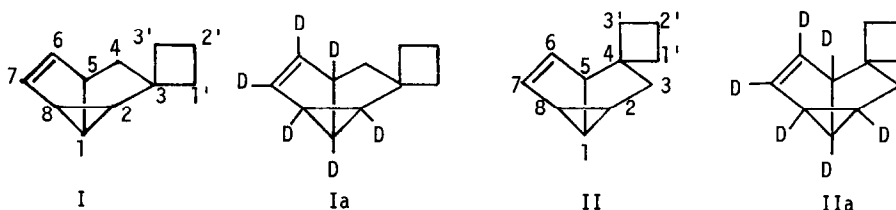


THERMAL REARRANGEMENTS OF THE PHOTOCHEMICAL 1,3-ADDUCTS
OF BENZENE TO METHYLENECYCLOBUTANE

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(Received in USA 24 May 1974; received in UK for publication 24 June 1974)

The 1,3-photoadducts I and II of benzene to methylene cyclobutane are of interest from two



points of view. First, the addition reaction by which they may be produced would constitute a rare example of the photochemical 1,3-addition of benzene to an exocyclic double bond¹ to yield a spiro ring product. Secondly, these products should exhibit unusual thermal rearrangements since they possess a dihydrosemitubular skeleton coupled to a cyclobutane ring. In I, the (2'-vinylcyclopropyl) cyclobutane group which in other examples² has been shown to give rise to a characteristic rearrangement is peculiarly constrained by the spiro-fusion of the cyclobutane moiety.

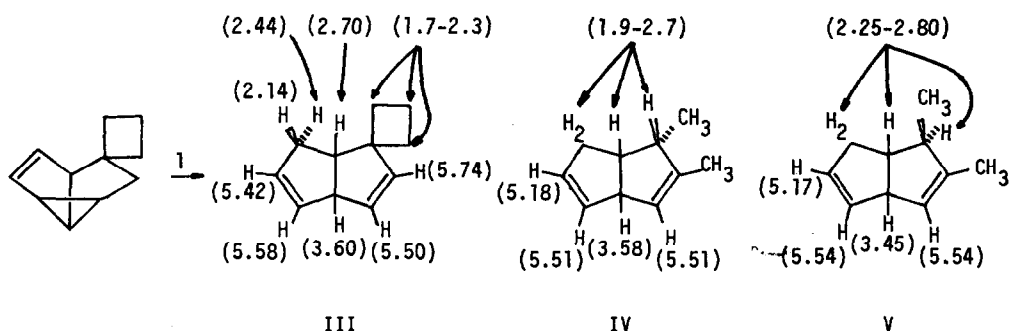
Irradiation of a solution (25%) of methylenecyclobutane in benzene at 254 nm for 40 hours gave a poor yield (5% isolated) of two major products (I, II) in equal amounts. These could be separated from each other with difficulty by vapor phase chromatography (silicone column 8', 125°). I analyzed to a 1:1 adduct of benzene to the olefin and showed absorptions in its infrared (3010 and 1590 cm^{-1}), ultraviolet ($\lambda_{\text{sh}}^{\text{pentane}}$ 216 nm; ϵ_{sh} 2070) and nmr spectra (δ , 5.48-1H; 5.23-1H; 2.98-1H; 2.48-1H; 2.39 to 1.50-10H) which were typical of the endo-1,3-photoadducts of benzene to olefins^{3,4}. The nmr absorption of the proton at C_5 was of interest since it was coupled strongly to two protons (presumably H_1 and H_4 -endo) and weakly to one (H_6). This showed that the spiro-ring was not adjacent to C_5 and therefore at C_3 .

Product II also analyzed to a 1:1 adduct of benzene to the olefin and displayed absorptions (IR: 3010, 1580 cm^{-1} ; UV: $\lambda_{\text{max}}^{\text{pentane}}$ 218 nm; ϵ_{max} 2580; NMR: δ , 5.48, 5.37, 2.84, 2.34 and 1.50-1H each; 2.23 to 1.64-9H) that were typical of the endo-1,3-adducts of benzene to

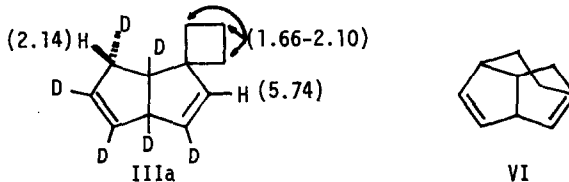
olefins⁵. The nmr spectra of the partially deuteriated compounds, Ia and IIa, (made from deuteriobenzene) were used to supplement these identifications.

Pyrolyses were carried out in Pyrex tubes (~ 7 ml) into which the sample (2-10 μ l) was sealed in a vacuum and heated to the desired temperature in an oil-bath.

I was stable to heating to 300° for 20 minutes. Under the same conditions, II was decomposed completely to an isomeric product III (Mol. wt. by mass spectrometry: 146; other important peaks at 118, 117, 103 and 91) in 50% yield as well as to a mixture of C₅ and C₆ compounds. It was anticipated that II would undergo a 1,5-hydrogen shift (reaction 1) to give III. This constitutes a homo [1,5] sigmatropic shift⁶ that is common to many other



tricyclo [3.3.0.0^{2,8}] octenes⁷ as well. Structure II for the product was fully substantiated by comparing the nmr spectrum of this compound to those of IV and V which have been described in the literature⁸. The similarity between the chemical shifts of the protons on the bicyclo [3.3.0] octadiene moiety in these three compounds is striking. A further confirmation for the course of reaction (1) was obtained from the pyrolysis of IIa which was expected to give IIIa. The eight proton resonances in the product

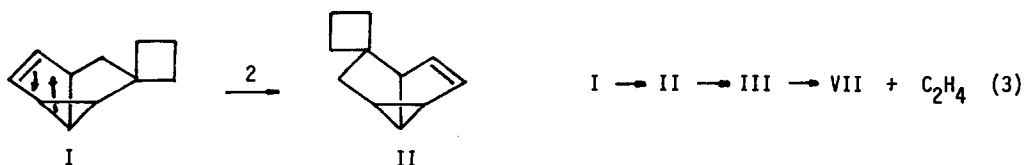


are seen to be consistent with the proposed mechanism.

The thermal stability of I under these conditions is readily explicable. On one hand, it cannot undergo a homo [1,5] shift of a hydrogen⁶ because the C₃ position is bonded to four other carbon atoms. The possibility of a (2'-vinylcyclopropyl) cyclobutane rearrangement² is excluded by the severe strain which would exist in the hypothetical product (VI).

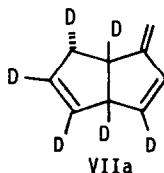
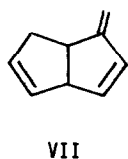
It points out that the presence of a cyclobutane ring at C₄ in these photochemical 1,3-adducts is a necessary but not a sufficient condition for this type of rearrangement to occur.

Pyrolysis of I at 320° for 40 min resulted in its decomposition with the formation of a single liquid product, VII (80%) with a molecular weight of 118 (C₉H₁₀). Subsequently, it was found that at the same temperature, pyrolysis of either II or III also gave the same C₉H₁₀ compound as the major liquid product. It is known from earlier work on the pyrolysis of certain 1,3-photoadducts of alkylbenzenes^{8,9} that in the absence of competing decomposition pathways, a vinylcyclopropane rearrangement will take place at > 300°. In the case of I,



this reaction (2) would yield II. Since it was shown above that the primary product from the decomposition of II is III, it is reasonable to deduce that the chain of reactions shown in (3) operates in the pyrolysis of I.

The infrared spectrum of VII showed strong absorptions at 3090, 1640, and 868 cm⁻¹ which were indicative of a >CH_2 group¹⁰. Its ultraviolet spectrum ($\lambda_{\text{max}}^{\text{pentane}}$ 238 nm; ϵ_{max} 8400) showed the presence of a semicyclic 1,3-diene chromophore.¹¹ Its nmr spectrum (Fig. 1) showed that it possessed ten unique protons which consisted of two singlets (δ , 4.89, 4.77-1H each) which could be attributed to the exocyclic methylene group. The remaining four olefinic protons fell into two pairs one of which must be in conjugation with the exocyclic bond. Of the midfield absorptions, the ones at δ 2.84 and 2.34 were mutually coupled strongly ($J = 16.5$ Hz) and the former to the proton at δ , 3.43 ($J = 10$ Hz) as well. The former can be identified as a geminal pair on a methylene group. These considerations when coupled to the observation that VII is formed from III by the loss of an ethylene molecule suggests the following bicyclic structure. Its formation (from III) constituted a typical



decomposition of a cyclobutane ring into two olefinic compounds.¹⁰ Further support for this

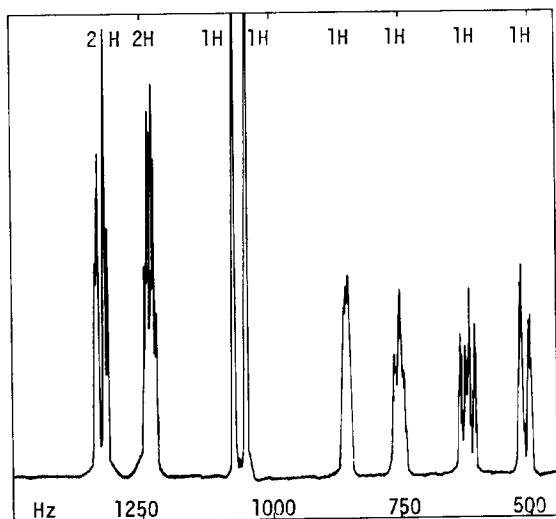


Fig. 1 Proton NMR Spectrum of VII

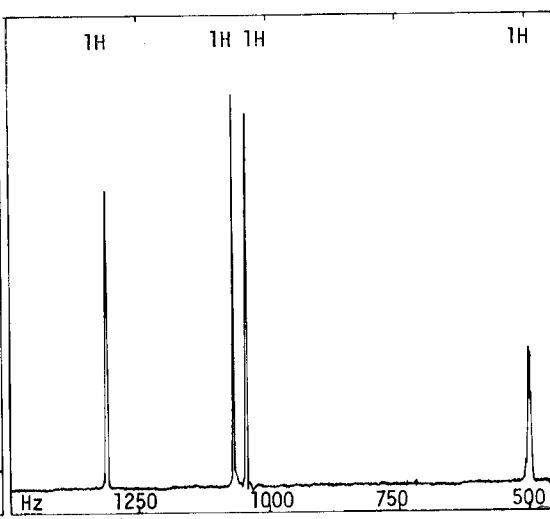


Fig. 2. Proton NMR Spectrum of VIIa

Frequencies at 220 MHz downfield from TMS as internal reference. Solvent: CCl_4 .

scheme was obtained from the pyrolysis of IIa at 320° which gave VIIa of the deuterium distribution that is shown (Fig. 2). The fact that the pyrolysis of Ia also led to VIIa with an identical distribution of deuterium atoms confirms the validity of reaction scheme 3.

Acknowledgment: The Author wishes to thank the Air Force Office of Scientific Research (AFSC), U.S. Air Force for Contract No. F44620-72-C-0024 under which this work was carried out.

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