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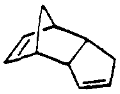
Organic Photochemistry with 6.7-eV Photons: Bicyclo[4.1.0]hept-3-ene. Internal Transfer and Carryover of Electronic Energy

Sir:

In studies on the solution-phase photochemistry at 185 nm of cyclic monoolefins[1-3] and cyclic diolefins (both conjugated[4] and unconjugated[5]), it was found that the lifetimes of the electronically excited state that was involved were too short to promote bimolecular processes in which an electronically excited molecule was a reactant. Even intramolecular transfer of electronic energy was not observed to influence the photochemistry of a compound such as 4-vinylcyclohexene.[5] In more rigid bichromophoric molecules such as **1**, an internal [2 + 2] addition is a major reaction at 185 nm,[5] but this may not be related to an actual transfer of electronic energy between the double bonds. In this communication, results on the photochemistry of bicyclo[4.1.0]hept-3-ene (**2**, hereafter BCH) at 185 nm are reported. These demonstrate that the incident photon is most probably absorbed by the π bond while the reactions that are observed are mostly those of the cyclopropyl group.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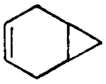
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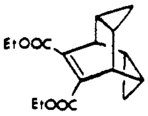
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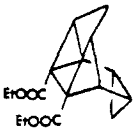
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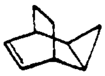

5


6

The ring system **2** is incorporated in numerous compounds which were studied by Prinzbach and his co-workers.[6] Typically, they found that **3** on triplet sensitization gave **4** as a major product. This reaction can be duplicated at 185 nm in the solution-phase irradiation of **5** which gives a nearly quantitative yield of **6**.[7] These observations will be referred to later.

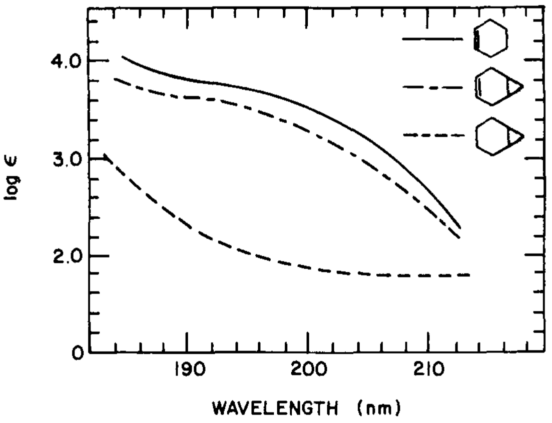
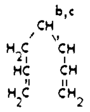
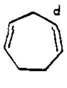


Figure 1. Ultraviolet absorption spectra of bicyclo[4.1.0]hept-2-ene and model compounds. Spectrum of cyclohexene was taken in hexane,[8] the rest in pentane.

Table I. Photolysis of Bicyclo[4.1.0]hept-3-ene in Solution (Solvent, Pentane; Concn, 2×10^{-2} M; Time, 30 Min)

Product					
7	8(a+b)	9	10	unknown	% Conversion w.r.t. starting material
 [a]	 [b,c]	 [c]	 [d]		
Yield %					
8.3	36.1	16.7	30.6	8.3	16.8

[a] W. Kirmse and K. Pöhlmann, *Chem. Ber.*, **100**, 3564 (1967). [b] Consisted of 1:2 trans:cis. [c] Identified by comparison with authentic material. [d] E. A. Hill, R. J. Theissen, C. E. Cannon, R. Miller, R. B. Guthrie, and A. T. Chen, *J. Org. Chem.*, **41**, 1191 (1976).

The solution-phase ultraviolet spectrum of a highly purified sample of BCH is shown in Figure 1 along with the spectra of cyclohexene[8] and bicyclo[4.1.0]heptane.[9] The resemblance between the spectra of the first two compounds and the absence of any feature that would be indicative of any mixing between the excited states of the olefin and cyclopropyl groups is noteworthy. Of course, this does not *prove* the absence of such an interaction.

Photolysis of BCH in pentane solution[10] gave five isomeric products in significant yield which together accounted for 92% of the material that disappeared. The identities of the products and relevant kinetic data are given in Table I.[11] The remaining 8% was made up of three products which were not identified. The mass balance was 100% within the experimental uncertainty (±5%) up to 16% conversion, but beyond that point secondary photolysis of the initial products was evident. The rate of disappearance of the reactant was 1.2 (±0.2) relative to the rate of cis → trans isomerization of cyclooctene.[2]

The formation of **7** from BCH is a typical reaction of the cyclohexene ring in solution phase photochemistry at 185 nm.[1,3,12] It can be represented to proceed via a carbene intermediate (eq 1). 1,3,6-Heptatriene and 1,4-cycloheptadiene are

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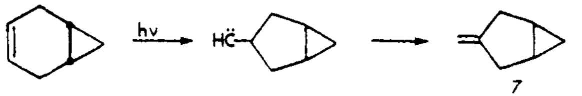
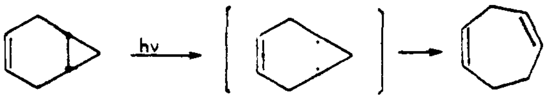
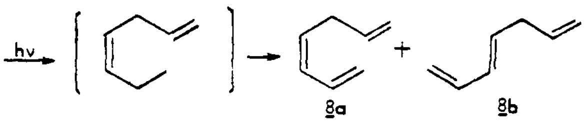


7 (1)

the expected products of the irradiation of a bicyclo[*n*.1.0]alkane at 185 nm.[9] Thus formal cleavage of one and two bonds of the cyclopropane ring in BCH can be represented as shown in eq 2 and 3. The origin of bicyclo[4.1.0]hept-2-ene is of considerable interest.



10 (2)

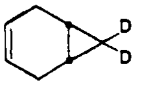


8a 8b (3)

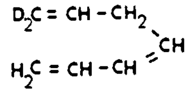
It can come directly from BCH by a 1,3-H migration (eq 4), but such a process has not been observed in the photochemistry of cyclohexene itself.[13] It is more reasonable to assume that it originates in 1,4-cycloheptadiene by a di-π-methane rearrangement.

9 (4)

In order to establish this, the photolysis of bicyclo[4.1.0]hept-3-ene-*7,7-d*$_2$ (**11**) was undertaken. This compound, if it undergoes reactions 2 and 3, should give **12** and **13**, respectively. In an actual experiment, after 50% conversion of **11**, the recovered starting material showed no evidence of scrambling of the deuterium.

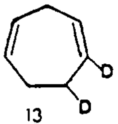


11



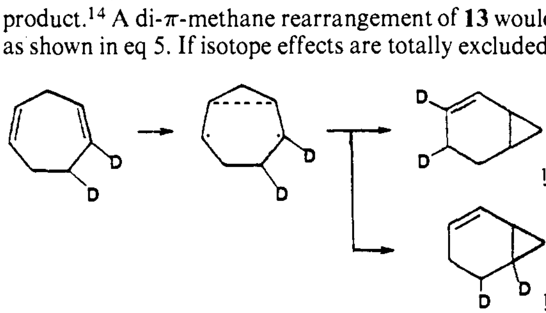
$$\begin{array}{l} D_2C=CH-CH_2 \\ \qquad\qquad\qquad\quad \diagdown CH \\ H_2C=CH-CH \nearrow \end{array}$$

12



13

The NMR spectrum of the 1,3,6-heptatriene-*d*$_2$ showed δ 2.9 (1.80 H), 4.7-6.8 (6.20 H). This is consistent with structure **12**, considering that a certain degree of scrambling of deuterium accompanies this reaction.[9] The NMR spectrum of the 1,4-cycloheptadiene-*d*$_2$ showed δ 2.25 (3.1 H), 2.85 (1.8 H), and 5.65 (3.1 H) which would agree with structure **13**. In the NMR spectrum of bicyclo[4.1.0]hept-2-ene obtained from the irradiation of **11**, the cyclopropyl protons at δ 0.70 integrated to 2 H so that reaction 4 can be ruled out as the source of this product.[14] A di-π-methane rearrangement of **13** would proceed as shown in eq 5. If isotope effects are totally excluded, **14a** and **14b** would be formed in equal amounts and the NMR spectrum of this mixture would have all of the absorptions of **9** but the intensities would be δ 6.0-5.0 (1.5 H), 1.85 (3 H), and 1.40-0.40 (3.5 H).



14a (5a)
14b (5b)

The product that was isolated had absorption intentities of 1.52, 3.00, and 3.48, respectively.[15] A detailed analysis of the spectrum at 220 MHz showed that one of the deuterium atoms could be placed at the olefinic absorption at δ 5.45 (C-3) and not at δ 5.90 (C-2) which would be in agreement with reaction 5a.

Two significant conclusions can be drawn from this study. These are the following. (1) The cyclopropyl group is the preferred reaction site although its absorption is 10-fold weaker than that of the olefinic group. It may be naive to look upon these two chromophores as being independent centers for the absorption of a photon, but it is difficult to assume mixing of the two states exists when they are separated by methylene groups. The behavior of BCH contrasts with that of the more rigid tricyclic molecule, **5**. It is conceivable that the flexibility of the BCH system is an important factor in the activation of the cyclopropyl group. The importance of this result lies in the possibilities that it opens up in far-ultraviolet photochemistry by demonstrating that a strongly absorbing chromophore can be used to "pump" energy to a reaction site in a molecule much as carbonyl groups have been used at longer wavelengths. (2) There are two examples here of secondary products being formed by the carryover of the excitation energy to the initial product. Thus, in the formation of 1,3,6-heptatriene, the cis isomer is the logical initial product. However the ratio of cis to trans was constant at 2:1 from 1 to 16% conversion which showed that the trans was *not* formed by the secondary *photolysis* of the cis compound but from a stereoisomerization from a "hot" initial product. The second example is even more clear-cut. Bicyclo[4.1.0]hept-2-ene (**9**) must come from an electronically "hot" 1,4-cycloheptadiene since, even at 1% conversion of BCH, the ratio of **9** to **10** was the same as at 16% conversion. Again, up to 20% conversion, the yield vs. time plots for **9** and **10** do not show any departure from linearity which would be indicative of the existence of more than one route for the formation of **9** (i.e., secondary photolysis of **10**). Since di-π-methane rearrangements are known to occur only from electronically excited states of 1,4-dienes,[16] this is almost certainly an example of the carryover of electronic excitation.

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(9) R. Srinivasan and J. A. Ors, *J. Am. Chem. Soc.*, **100**, 7089 (1978).
(10) Photolyses were carried out in spectroscopic grade pentane solution (2 × 10^{-2} M) using a low pressure mercury resonance lamp and Suprasil windows. For kinetic studies, a band-pass filter was used to isolate the 185-nm radiation.
(11) The identities of the products were established by comparison with authentic material (**8** and **9**) or from spectroscopic data (**7** and **10**).
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(13) This is known from the photolysis of cyclohexene-*2,2,6,6-d*$_4$. See ref 3.
(14) The same argument can be applied to more involved hydrogen migrations in succession with opening and reclosing of the cyclopropane ring.
(15) This agreement is closer than one could have hoped for on the basis of uncertainties in the integration.
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