surprising. However, the observation that the one-electron approximation correctly predicts the relative $S_0 \rightarrow T_1$ oscillator strengths with respectable accuracy must be considered somewhat of a triumph. The following salient conclusions can be made with reference to Table XIV.

(1) The principal perturbing singlet is the second excited π,π^* state as was found for formaldehyde.[26] The mixing of this singlet into T_1 accounts for roughly 65% of the total oscillator strength calculated.

(2) The oscillator strength of the $S_0 \rightarrow S_2(\pi,\pi^*)$ transition is the most influential variable in determining the oscillator strength for the $S_0 \rightarrow T_1$ transition. The fact that these oscillator strengths could be observed experimentally contributed greatly to the success of these calculations.

(3) Because of the large ground-state dipole moment of the propenals, mixing of S_0 into T_1 is quite important and cannot be neglected. For example, in crotonaldehyde this term alone contributes 1.52×10^{-7} to the oscillator strength, which is equivalent to the *total oscillator strength* calculated by Sidman for the $S_0 \rightarrow T_1$ transition in formaldehyde.[26]

(4) Mixing of T_1 into S_0 is relatively unimportant and contributes only about 5% to the total $S_0 \rightarrow T_1$ oscillator strength calculated.

(5) Mixing of singlet states higher than $S_2(\pi,\pi^*)$ into T_1 is quantitatively insignificant and could have been safely ignored.

Acknowledgments. We are grateful for the advice and criticism of Dr. T. R. Evans and Professor N. J. Turro in the preparation of this manuscript. We are also indebted to Professors K. B. Wiberg and W. B. Hammond for their assistance with the molecular orbital calculations and Professor W. C. Pringle for helpful discussions on the spin-orbit coupling calculations. We also wish to thank the U. S. Army Research Office (Durham) for partial financial support and the Connecticut Research Commission for support of special instrumentation.

[26] J. W. Sidman, *J. Chem. Phys.*, **29**, 644 (1958).

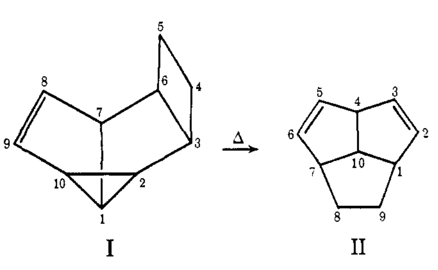
Stereochemistry of the (2′-Vinylcyclopropyl)cyclobutane Rearrangement. Photochemical 1,3 Addition of Benzene to 3,4-Substituted Cyclobutenes

R. Srinivasan

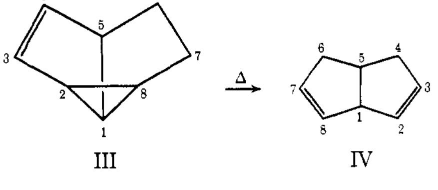
Contribution from the Thomas J. Watson Research Center, Yorktown Heights, New York 10598. *Received May 9, 1972*

Abstract: Thermal isomerization of *cis*-4,5-dimethyl-*endo*-tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8 (IX) at 300° gave rise to *endo,cis*-8,9-dimethyltricyclo[5.2.1.0^{4,10}]deca-2,5-diene (XII) as the major isomeric product. The reaction, which is a typical (2′-vinylcyclopropyl)cyclobutane rearrangement, thus proceeds with retention of the stereochemistry at the migrating σ bond. Arguments are presented to show that this rearrangement is distinct from the homo [1,5] sigmatropic shift which in the tricyclo[3.3.0.0^{2,8}]octene-3 systems involves the migration of hydrogen atoms only. It is also distinct from, although related to, the vinylcyclopropane rearrangement. The use of the (2′-vinylcyclopropyl)cyclobutane rearrangement in synthesis is exemplified by the preparation of *endo*-tetracyclo[8.2.1.0^{2,6}.0^{7,13}]trideca-3,8,11-triene (VII) from benzene and 1,3,5-cycloheptatriene in three steps.

In an earlier publication[1] it had been shown that the endo-photochemical 1,3 adduct of benzene to cyclobutene (I) which incorporates a (2′-vinylcyclopropyl)cyclobutane function, on pyrolysis, is transformed into II in 50% yield. Superficially, this reaction may appear to be a special instance of the homo [1,5] sigmatropic shift[2] that is observed in tricyclo[3.3.0.0^{2,8}]octene-3.[3] In reality, reaction 2 fails to occur when the 7 position does not have a hydrogen in an endo orientation. Thus, the *cis*-6,7-*endo*-dimethyl derivative of III shows no tendency to isomerize to a 4,6-dimethyl derivative of IV.[4] Polycyclic derivatives



(1)



(2)

of III which do not contain a (2′-vinylcyclopropyl)cyclobutane function, on pyrolysis, either give rise to a homo [1,5] sigmatropic shift of *hydrogen*[5] or fragment to

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[1] R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970).

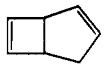
[2] A summary of the literature references to this reaction may be found in R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 132. See, in particular, R. N. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).

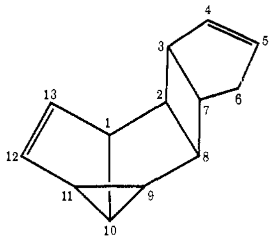
[3] W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965).

[4] R. Srinivasan, *Tetrahedron Lett.*, 4551 (1971).

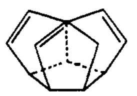
smaller molecules.[6] It follows that the stereochemistry of reaction 1 cannot be inferred from our knowledge of reaction 2.

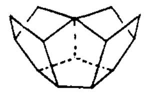
In this article, we report on the photochemical 1,3 addition of benzene to *cis*-3,4-dimethylcyclobutene and the pyrolysis of the compound that resulted. On the basis of the knowledge that was gained from this reaction, we have also carried out the photochemical 1,3 addition of benzene to bicyclo[3.2.0]hepta-2,6-diene (V) to give VI which we were able to transform pyrolytically to VII. In view of the recent interest[7] in the ring system VIII, the potential of VII and its derivatives as suitable intermediates to VIII is noteworthy.


V



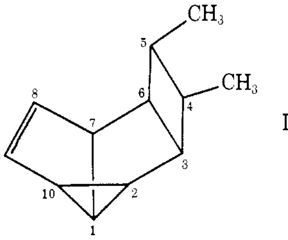
VI


VII

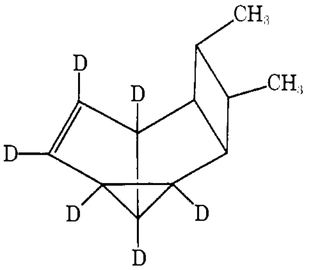

VIII

Results

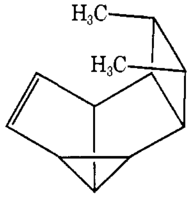
The photochemical addition of benzene to *cis*-3,4-dimethylcyclobutene was carried out with 253.7-nm radiation using a 20% solution of the latter in benzene. The photochemical efficiency of the reaction was comparable to that of benzene and cyclobutene at the same wavelength.[8] There were two addition products which were formed in 20 and 5% yields, respectively, along with very minor amounts of other products. As in the photoaddition of benzene to cyclobutene,[8] the major product was found to be a single 1,3 adduct from the following data. Both the molecular weight and the elementary analysis of the compound indicated that it was a 1:1 adduct of benzene to *cis*-3,4-dimethylcyclobutene. Its infrared spectrum showed absorptions at 3050 and 1600 cm^{-1} (cyclopentene) and at 1375 cm^{-1} (CH_3). Its ultraviolet spectrum showed an absorption maximum at 217.5 nm (ϵ_{max} 2500) which is indicative of a vinylcyclopropane chromophore.[9] The nmr spectrum of the material showed the presence of two olefinic protons (δ5.61) and two methyl groups (δ 0.92, 0.82; doublets, J = 7 Hz). The compound that was prepared similarly from C_6D_6 and *cis*-3,4-dimethylcyclobutene showed no absorption which would correspond to olefinic protons while the absorptions due to the methyl groups remained intact. These data which are typical of other 1,3 photoadducts of benzene to olefins[8,9] suggested that the compound on hand had a similar structure (IX). The compound derived from C_6D_6 would be IXa. The 220-MHz nmr spectrum of the compound (detailed in the Experimental Section) displayed near correspondence of the chemical shifts and coupling pattern of the ring protons to the spectra of the 1,3 photoadducts of benzene to 2-butene[9] and cyclobutene.[8] thus confirming the proposed tetracyclic structure. The stereochemistry at C_3 and C_6 was established to be endo from the observation that the compound underwent the (2′-vinylcyclopropyl)cyclobutane rearrangement (see below). This conforms to earlier work[1,10] which had shown that the major 1,3 photoadducts of benzene and several alkylbenzenes to cyclobutene possessed an endo orientation of the cyclobutane ring to the rest of the molecule. It seemed likely that the orientation of the two methyl groups would be outward (as in structure IX) since the alternative inward orientation (as in X) would crowd them into the double bond and greatly strain the system. Thus Dreiding models show that in X the centers of C_9 and the methyl carbon on C_4 are only 1.25 Å part.



IX



IXa



X

In a nuclear Overhauser experiment,[11] saturation of the proton signal from the methyl groups in IX failed to show even a 1% enhancement of the signal due to the olefinic protons. While such a negative result may not have a unique interpretaton, it certainly does not conflict with the stereochemistry shown in IX.

The second photoadduct from this reaction was quite labile and difficult to purify. It was, however, determined from its mass spectrum that it was a 1:1 adduct. Its nmr spectrum strikingly resembled the spectrum of the 1,4 adduct of benzene to cyclobutene[8] especially in the characteristic pattern of the four olefinic protons (δ 3.75) which formed two strongly coupled doublets of doublets. This olefinic absorption, as well as the broad absorption (2 H) at δ 3.6, was missing from the nmr spectrum of the corresponding photoadduct of C_6D_6 to *cis*-3,4-dimethylcyclobutene which suggested that the compound was the 1,4 adduct (XI), while the partially deuterated derivative would be XIa. Confirmatory evidence was obtained by heating the compound to 200° in a nmr sample tube when the spectrum of the material disappeared and was replaced by the nmr spectra of benzene and *cis,trans*-2,4-

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(5) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

(6) R. Srinivasan, *J. Phys. Chem.*, **76**, 15 (1972).

(7) P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).

(8) R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971).

(9) K. S. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966).

(10) R. Srinivasan, *ibid.*, **93**, 3555 (1971).

(11) We thank Dr. E. B. Whipple of the Union Carbide Research Center, Tarrytown, N. Y., for carrying out these experiments.

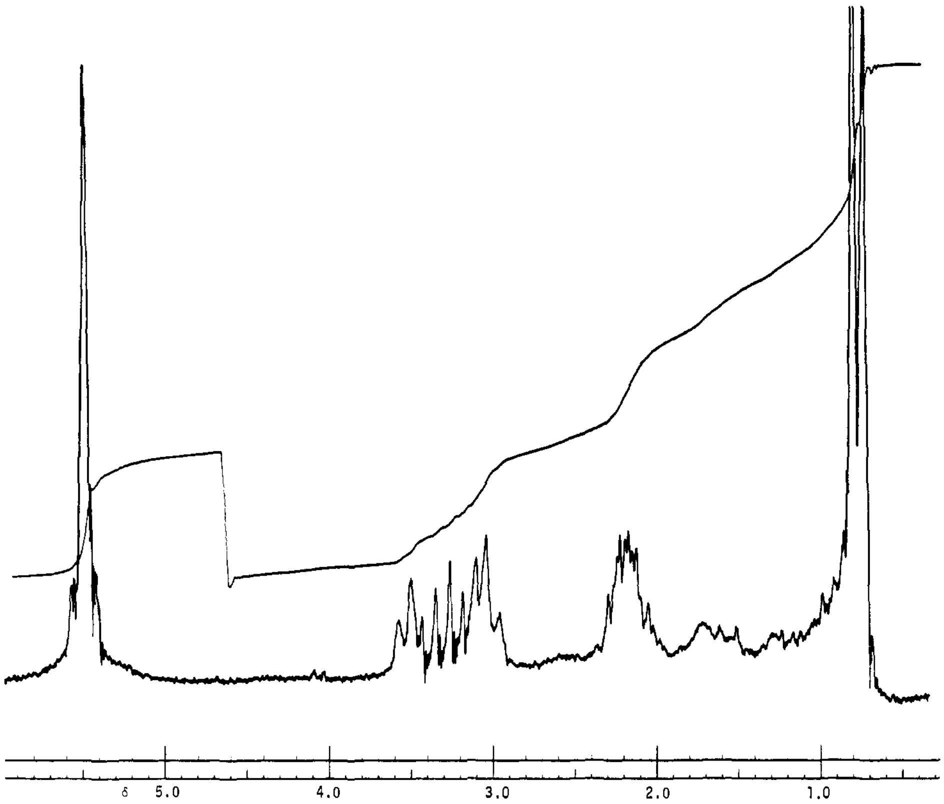
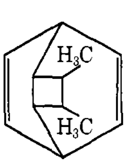
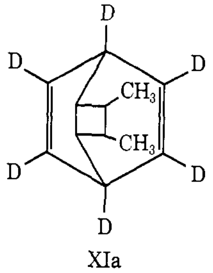


Figure 1. Nuclear magnetic resonance spectrum (100 MHz) of XII.



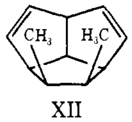
XI



XIa

hexadiene. It has been noted before[8] that the 1,4 adduct of benzene to cyclobutene underwent decomposition with similar facility to give benzene and 1,3-butadiene.

Pyrolysis of IX was carried out at 300° in the vapor phase at low (<10 Torr) pressure in sealed Pyrex tubes. The products consisted of small amounts of C_6 compounds (which indicated that the material had partly split up to the starting materials), five isomeric compounds (as determined by mass spectrometry), and some polymer. The distribution of the isomers was reminiscent of the pattern that had been seen in the pyrolysis of I.[1] The major (38%) compound among the isomers analyzed to the formula $C_{12}H_{16}$. Its infrared spectrum showed strong absorptions at 3040 (cyclopentene) and 1380 cm^{-1} (CH_3). The nmr spectrum of this compound (Figure 1) was quite similar to that of II which indicated that it was the 8,9-dimethyl derivative of II as shown in structure XII. Of particular interest was the region from δ 3.1 to 3.6.



XII

A detailed analysis of the spectrum of II has shown[1] that these absorptions are made up of a broad doublet (1 H) at δ 3.6 from the proton on C_4 and a quartet (J = 8 Hz) at δ 3.3 (1 H) which is due to the single proton on C_{10} which is coupled equally to H_1, H_4, and H_7. These two absorptions are identical in XII. The absorption due to the two protons at C_1 and C_7 is resolved as a broad triplet in XII in contrast to II because there is only one proton each at C_8 and C_9 in the former instance.

The occurrence of the absorption due to the six methyl protons in XII as a doublet (J = 7 Hz) both at 60 and 100 MHz indicated that the two methyl groups were identical and therefore cis to each other. This also shows that the stereochemistry of these groups in IX is carried over to XII. A search was made among the other isomeric products to see if the *trans*-8,9-dimethyl isomer of XII was also formed. No evidence for its formation was obtained. An upper limit of 1% of the total yield of isomers can be placed on its formation.

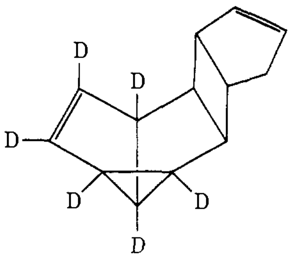
The orientation of the methyl groups in XII was determined by a nuclear Overhauser experiment on the compound. Saturation of the signal due to the methyl protons was found to cause an 8.7% increase in the absorption due to the olefinic protons. The conditions that were used were identical with those in the NOE experiment on IX which gave no detectable enhancement. Hence, the two methyl groups must be endo oriented as shown in structure XII.

The photochemical addition of benzene to bicyclo-[3.2.0]hepta-2,6-diene (V) was carried out by the irradiation of a 15% solution of the latter in benzene at 253.7 nm. As with other cyclobutenes,[8,10] it was found advantageous not to carry the reaction to more than 20% conversion in a single irradiation since the photoadducts seemed to undergo (photosensitized?) decomposition. There were two major addition products which were isolated by distillation followed by preparative glc. The isolated yields were: major adduct, 30%; minor adduct, 15%. The photochemical efficiency of the reaction was comparable to the 1,3 photoaddition of benzene to cyclobutene.[8]

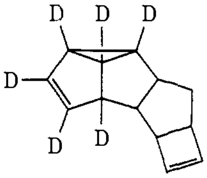
Both the major and minor adducts analyzed to the formula $C_{13}H_{14}$ and had molecular weights of 170 so that they were 1:1 adducts of the two reactants. The infrared spectrum of the major adduct showed absorptions at 3020 (s) and 1590 (m) cm^{-1} while the minor adduct had absorptions at 3030 (s) and 1600 (w) cm^{-1}. The ultraviolet spectrum of both adducts showed a pronounced shoulder at ~220.0 nm (ϵ 2000). The 60-MHz nmr spectrum of both adducts showed the presence of four olefinic protons in each compound, the remaining absorptions being between δ 1.3 and 3.7 in a complex pattern. These data suggested that each of these adducts was pentacyclic in nature.[12] The absorption at 220 nm in the uv spectrum indicated that both compounds may be 1,3 photoadducts, the absorption being due to the presence of a vinylcyclopropane chromophore.[9]

The 1,3 photoaddition of benzene to bicyclo[3.2.0]hepta-2,6-diene can be expected to occur at either of the two double bonds in the diene. Depending upon the geometry (exo or endo) at the point of addition, the orientation of the cyclobutane ring with respect to the cyclopentane ring in the bicycloheptane moiety, and the location of the methylene group in the cyclopentane ring (of the bicycloheptane), 16 stereoisomers are possible. The two adducts on hand were sorted out by analyzing the nmr spectra of the partially deuterated compounds that were obtained by the photochemical addition of C_6D_6 to bicyclo[3.2.0]hepta-2,6-diene.

The spectrum of the major product showed the presence of only two olefinic protons at δ 5.78 while the absorption due to two more olefinic protons at δ 5.85 which was present in the undeuterated compound was missing. The upfield protons in the partly deuterated adduct extended only to δ 2.0, the absorption due to two protons at δ 1.8 in the undeuterated compound being absent. In the case of the minor adduct also, the partly deuterated compound had only two olefinic proton absorptions in its spectrum. However, in contrast to the major adduct, these were the downfield (δ 6.18) component, the pair that was originally at δ 5.60 being missing. At the upfield end of the spectrum, the minor adduct had two protons at δ ~1.6 which were present in both the deuterated and undeuterated adducts.



VIa

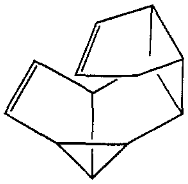


XIII

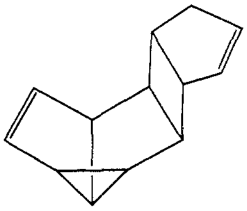
Structures VIa and XIII correspond to one isomer each of the 1,3 adducts of C_6D_6 to the cyclobutene and cyclopentene rings of bicyclo[3.2.0]hepta-2,6-diene. In comparing the nmr spectra of these compounds, the lowest field proton would be the olefinic proton in the cyclobutane ring of XIII. This compound would also have the highest field proton absorptions from the CH_2 group in the cyclopentane ring. It is hence possible to identify the major and minor adducts as the 1,3 photoadducts of benzene to the cyclobutene and cyclopentene rings of bicyclo[3.2.0]hepta-2,6-diene. The pyrolytic behavior of these compounds (see below) further substantiates this assignment.

Although the infrared (at low resolution) and 60-MHz nmr spectra of both adducts consisted of sharp lines indicative of single compounds, the shapes of their gas chromatographic elution peaks suggested the possibility that they were both mixtures. Therefore the proton-decoupled, C_{13} spectra of both adducts were determined. The spectra were quite similar in that, in each case, they consisted of eight lines centered at 130 ppm downfield from TMS (olefinic protons) and 18 lines in the region 50 ± 15 ppm also downfield from TMS. This showed clearly that each adduct was made up of two and only two closely related isomers. On this basis it was possible to analyze the 220-MHz proton spectra of the adducts of C_6D_6 to bicyclo[3.2.0]hepta-2,6-diene and calculate that the major adduct was a 2:1 mixture and the minor adduct, a 1:1 mixture of two components.

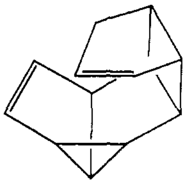
Arguments outlined earlier in this article on the 1,3 addition of benzene to *cis*-3,4-dimethylcyclobutene suggest that in the corresponding addition of benzene to the cyclobutene ring in bicyclo[3.2.0]hepta-2,6-diene, endo addition will predominate. Of these endo adducts (VI, XIV, XV, and XVI), XIV and XVI, in which the cyclopentene ring points toward the benzene part of the molecule, can be excluded on a stereochemical basis analogous to that used to rule out structure X. The crowding of the C_{12}–C_{13} carbons by the cyclopentene ring should be an even more serious problem in this instance since Dreiding models show that the centers of both C_5 and C_6 will be only 1.5 Å away from the centers of C_{13} and C_{12}, respectively. It is therefore reasonable to conclude that the major adduct was a mixture of VI and XV. It may be noted in passing that these two isomers are interconvertible by a vinylcyclopropane rearrangement.



XIV



XV



XVI

In the 1,3 addition of benzene to cyclopentene, endo orientation is believed to be favored although the selectivity is less than in cyclobutene.[13] In the absence of definite stereochemical data, it is possible to represent

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[12] The ^{13}C spectra of these products (which are discussed later) eliminated the possibility that they may have contained tetrasubstituted double bonds.

[13] K. S. Wilzbach and L. Kaplan, private communication.

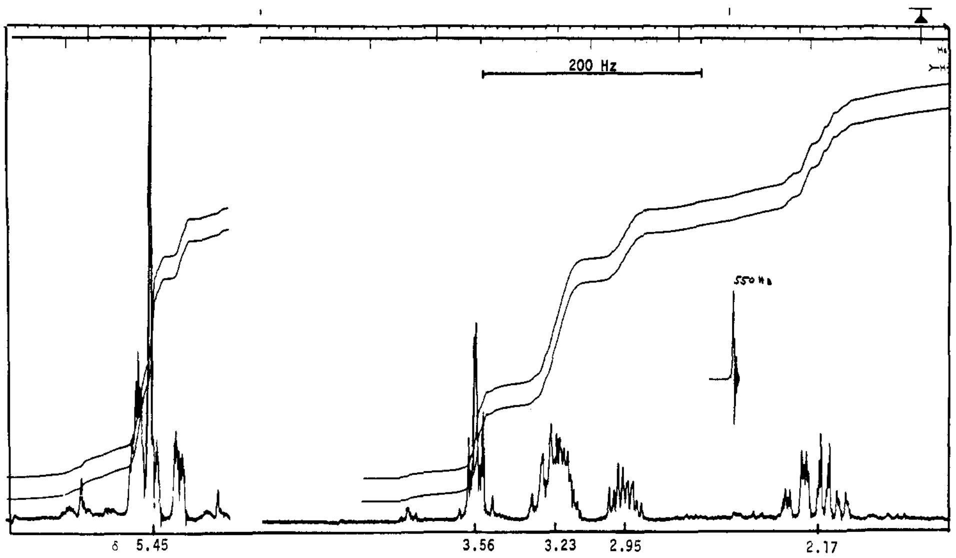


Figure 2. Nuclear magnetic resonance spectrum (220 MHz) of VII.

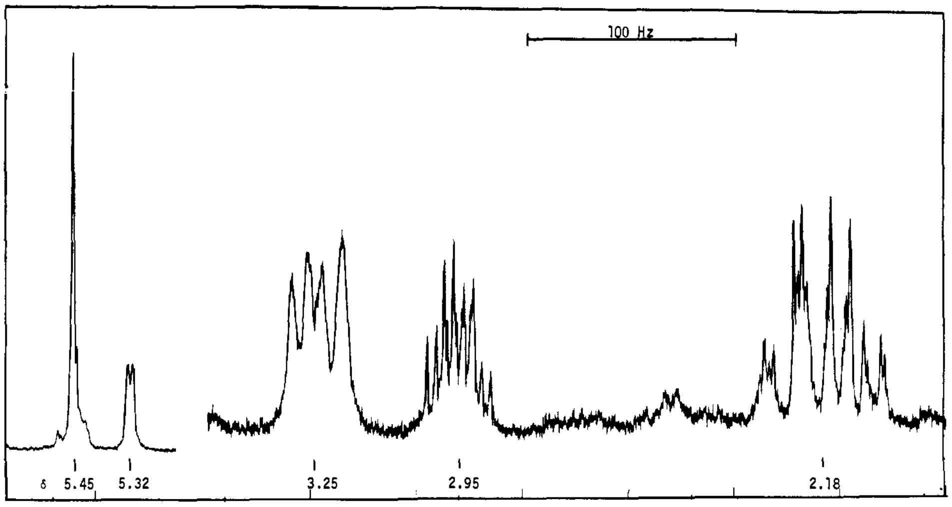
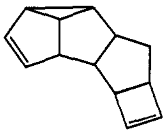
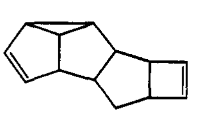


Figure 3. Nuclear magnetic resonance spectrum (220 MHz) of the hexadeuterio derivative of VII (structure as in XVII or XVIII; see text).

the two components of the minor adduct only by structures XIIIa and b.



XIIIa



XIIIb

The pyrolysis of each of these adducts was carried out under the same conditions as those described for IX. The minor adduct gave only one isomeric product in 50% yield. Since this compound showed only two olefinic protons in its nmr spectrum, it cannot result from a (2′-vinylcyclopropyl)cyclobutane rearrangement or a homo [1,5] sigmatropic shift. Therefore, the presentation of these results will be deferred to a future publication.

The major adduct underwent pyrolysis even at 230° to give a major product in 50% yield. This compound analyzed to the formula $C_{13}H_{14}$ and had a mass spectral molecular weight of 170. It was therefore isomeric to the starting material. Its infrared spectrum showed an intense absorption at 3030 cm^{-1} (cyclopentene). Its ultraviolet spectrum showed only end absorption (ϵ_{220} 1800; ϵ_{210} 6700). Its nmr spectrum and the spectrum of the partly deuterated product that was correspondingly derived from the major photoadduct of C_6D_6 to bicyclo[3.2.0]hepta-2,6-diene are shown in Figures 2 and 3. The C_{13} (proton decoupled) spectrum showed six lines close together from 840 to 760 Hz downfield from CCl_4, six lines from 850 to 1050 Hz upfield from CCl_4, and a single line 1390 Hz upfield from CCl_4.

These spectra clearly show that this compound is a single isomer with six olefinic carbons. It must possess a tetracyclic structure with three double bonds, no two of which are in conjugation. The product that can be expected from either VI or XV *via* a (2′-vinylcyclopropyl)cyclobutane rearrangement will have the structure VII which fits all of these data well. The partly deuterated compound VIa will correspondingly give XVII while the isomer XV, if partly deuterated, will lead to XVIII.[14] Thus a comparison of the nmr

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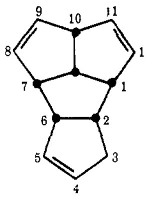
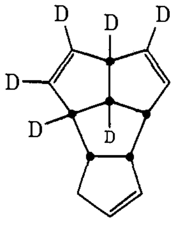
[14] The 1,3-addition reaction creates an asymmetric group which when added to an asymmetric molecule such as V can give rise to two

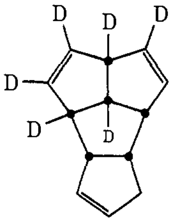
spectra of VII, II, and XII shows that in all three compounds, the protons at 8, 9, 11, and 12 (numbering as in VII) occur as a strongly coupled AB pair at *ca.* δ 5.5 and that three of these (8, 9, and 11) are missing in the spectra of the partly deuterated compounds made from C_6D_6. The narrow absorption at δ 5.45 in VII which is attributable to the olefinic protons 4 and 5 is unchanged on partial deuteration.



VII



XVII



XVIII

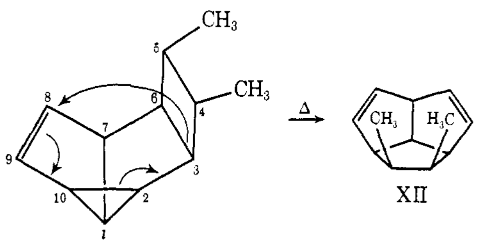
From the spectra of II and XII, it is known that the protons corresponding to 1, 7, 10, and 13 (numbering as in VII) occur at chemical shifts from δ 3.1 to 3.6. Of these, 10 and 13 are farthest downfield and occur (in the case of VII) together at δ 3.56, the quartet (J = 7 Hz) formed by H_{13} being superimposed on the absorption due to H_{10}. In the spectrum of the partially deuterated compound, these absorptions as well as one out of the trio at δ 3.22 are seen to be missing.

The absorptions due to H_2, H_3, $H_{3'}$, H_4, and H_5 can be expected to be least affected by partial deuteration. This is not impressive to see in H_4 and H_5 which are only weakly coupled but is strikingly evident in H_2 and the AB pair formed by the methylene group at C_3. The last two protons are obviously strongly (J = 17.5 Hz) coupled to each other and also to the adjacent bridgehead proton by J = 4 and 8 Hz, respectively. H_2 is strongly coupled (J = 16.5 Hz) to H_6 as well. The entire pattern is unchanged in the partly deuterated compound.

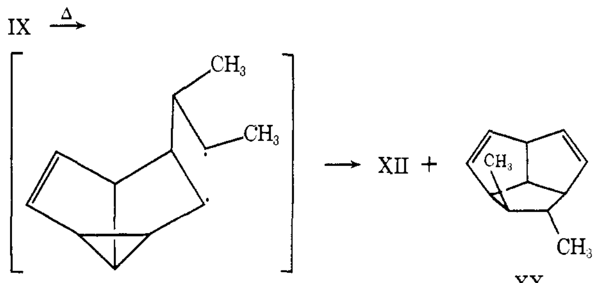
Two further points which concern the structure of VII are the following: (i) The stereochemistry at the 2,6 bond is believed to be cis and endo as portrayed in the structural formula. This follows by analogy from the results on XII. (ii) Whether the partly deuterated derivative of VII has structure XVII or XVIII or is actually a mixture of both is of considerable interest. The observation that the nmr pattern of the bridgehead proton adjacent to the methylene group is unchanged on partial deuteration may be taken as evidence that this proton does not adjoin a deuterium atom. This would favor structure XVIII, but if the coupling between H_2 and H_1 is weak, which seems to be the case, this argument would not be valid. The chemical shift of the lone proton at C_{12} which is farthest upfield of the four olefinic protons consisting of H_8, H_9, H_{11}, and H_{12} may be interpreted to mean that this proton faces the double bond as in structure XVII. The possibility that the product is a mixture seems unlikely from the appearance of the 220-MHz spectrum.

Discussion

The rearrangement of IX to XII which we have used as a test for the stereochemical course of the (2′-vinylcyclopropyl)cyclobutane rearrangement can be expected to occur in one of two ways. Apart from a concerted pathway which is represented by reaction 3, the reaction may proceed *via* a diradical (XIX) which can undergo stereoisomerization at C_4 before rearranging to a mixture of XII and XX. The observation that there was no detectable amount of XX in the system may be interpreted to mean that the diradical (XIX), if it is formed at all, leads to products other than tricyclo[5.2.1.0^{7,10}]deca-2,5-dienes. The argument that the diradical preferentially leads to XII rather than XIX seems implausible since any equilibration in the diradical state may be expected to favor the less hindered and therefore more stable XX over XII.

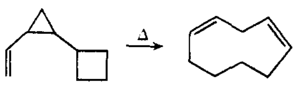


IX XII (3)

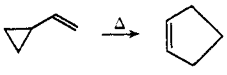


XIX XX (4)

It has already been pointed out that the (2′-vinylcyclopropyl)cyclobutane rearrangement which, in a general sense, can be represented by reaction 5 bears no relationship to the homo [1,5] sigmatropic shift in related systems. Of more interest is a comparison of (5) to the simple vinylcyclopropane rearrangement (6). There appears to be agreement[15–17] that this rearrangement, when it occurs in monocyclic systems, proceeds by a diradical mechanism. Data on a bicyclic system[18] also seem to favor a similar mechanism. There has been a recent report[19] of an exceptional example of a bicyclic system in which the reaction tends to be stereospecific although it may proceed *via* a diradical intermediate, presumably because of the lim-



(5)



(6)

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dl pairs. Note that in VI and XV, the stereochemistry of the benzene moiety is identical but the bicyclo[3.2.0]hepta-2,6-diene is portrayed in two ways. The difference is noncritical in structure VII but may lead to some confusion in the structures XVII and XVIII for the partially deuterated pyrolysis product.

(15) C. S. Elliott and H. M. Frey, *Trans. Faraday Soc.*, **61**, 345 (1965).

(16) R. M. Willcott and W. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4310 (1969).

(17) P. H. Mazzochi and H. J. Tamburin, *ibid.*, **92**, 7221 (1970).

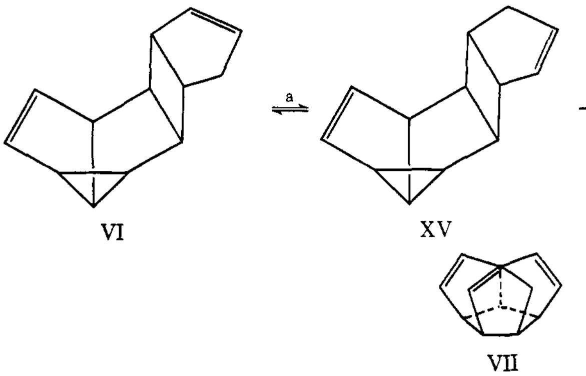
(18) W. E. von Doering and J. B. Lambert, *Tetrahedron Lett.*, **19**, 1989 (1963).

(19) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971).

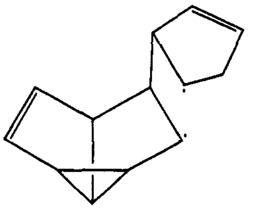
ited rotational freedom that is present in the intermediate. The stereochemical selectivity that is evident in the (2′-vinylcyclopropyl)cyclobutane rearrangement seems to set it apart from the vinylcyclopropane rearrangement, although the results must be viewed with some caution. Thus, IX may turn out to be an isolated example. In any case, this class of rearangements must be studied in many more instances before a generalization may be acceptable.

There are two points of interest concerning the synthesis of VII. In the photochemical 1,3 addition of benzene to bicyclo[3.2.0]hepta-2,6-diene (V), it is seen that addition occurs twice as efficiently to the cyclobutene ring as to the cyclopentene ring. This is in accord with quantitative data published previously[6,8,9] on similar addition reactions to 2-butene, cyclobutene, and norbornene which showed that the photochemical efficiency of the reaction increased with increasing strain in the olefin. The present instance further points out that the local strain at the olefinic group is an important factor. It suggests a method to control the site of addition in a relatively complex molecule.

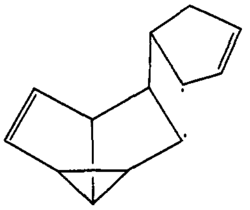
A second point of interest is the identity of the isomer (VI or XV or both) which undergoes rearrangement to give VII. If it is assumed that the vinylcyclopropane rearrangement (reaction 7a) between VI and XV is rapid before reaction 7b occurs,[14] the identification of the precursor to VII becomes academic. We have to assume that this is actually the case because the mixture of partially deuterated VI and XV seemed to give only one partially deuterated derivative of VII, *i.e.*, XVII. This would mean that the equilibrium between VI and XV would favor VI. It may be noted that if a diradical mechanism is considered for this isomerization, the intermediate XXI from VI would be less likely to be stabilized by allylic resonance than the intermediate XXII from XV.



VI XV VII (7)



XXI



XXII

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMS-4 mass spectrometer. Ultraviolet spectra were measured on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra at 60 and 220 MHz were run on a JEOLCO Minimar and on a Varian HR-220 spectrometer, respectively. The latter was operated by the Consortium at The Rockefeller University, New York. ^{13}C spectra were run on a Bruker HFX-10 spectrometer. Microanalyses were carried out by Schwarzkopf Microanalytic Laboratories, Woodside, N. Y., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

***cis*-3,4-Dimethylcyclobutene** was prepared by the photoisomerization of *trans,trans*-2,4-hexadiene.[20]

Bicyclo[3.2.0]hepta-2,6-diene (V) was prepared by the photoisomerization of 1,3,5-cycloheptatriene[21] in pentane solution (15%) using 253.7-nm radiation. When approximately 25% of the starting material had disappeared, the rate of the reaction seemed to slow down by an order of magnitude. The irradiation was stopped, and the solution was distilled through an 18-in. spinning-band column. After all of the solvent had distilled over, bicyclo-[3.2.0]hepta-2,6-diene (95% purity), bp 96–98°, was collected. The unreacted 1,3,5-cycloheptatriene was also recovered by distillation. When the recovered starting material was taken into consideration, the yield of bicyclo[3.2.0]hepta-2,6-diene was nearly quantitative. The poor yield that is obtained when ether is used as the solvent[21,22] was found to be due to attack on the solvent.

Photoaddition of Benzene to *cis*-3,4-Dimethylcyclobutene. The reaction was carried out in a manner identical with that used for the addition of benzene to cyclobutene.[8] The products were isolated by gas chromatography on a UCON-550X column (9 ft) at 125°. The isolated yields of IX and XI were 20 and 5%, respectively.

***cis*-4,5-Dimethyl-*endo*-tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8 (IX):** infrared spectrum (neat liquid) 3050 (m), 2940 (s), 1600 (w), 1375 (m), 917 (m), 820 (s), 787 (m), 738 (s), 725 (s), and 685 (m) cm^{-1}; ultraviolet spectrum (pentane) max 217.5 nm (ϵ 2500 l. mol^{-1} cm^{-1}); nmr spectrum (CCl_4 solution; TMS as internal reference) 220-MHz spectrometer, frequencies (Hz) indicated from TMS = 0, H_1, 563; H_2, 353; H_3, ~607; H_4, 507; H_5, 367; H_6, ~607; H_7, 798; H_8, 1327; H_9, 1336; H_{10}, 397; CH_3, 191 and 201, J = 7; J_{12}, 7; J_{23}, 7; J_{78}, 2; J_{89}, 5; J_{910}, 2; J_{210}, 7; J_{110}, 7; J_{17}, ~6.

Anal. Calcd for $C_{12}H_{16}$: C, 89.90; H, 10.09. Found: C, 89.70; H, 10.27.

3,4-Dimethyltricyclo[4.2.2.0^{2,5}]deca-7,9-diene (XI): nmr spectrum (CS_2 solution, TMS as internal reference) δ 6.38 (1 H) doublet of doublets; 6.20 (1 H) doublet of doublets; ~3.6 (2 H) broad; 1–2 (6 H) complex; 0.9 (6 H) broad singlet.

Pyrolysis of IX. A sample of IX (0.1 g, 0.63 mmol) was placed in a 250-ml Pyrex flask which was then evacuated to 0.1 Torr and sealed. The flask was heated to 300° for 20 min. After cooling to room temperature, the contents of the flask were washed out with pentane and separated by glc under the same conditions as for IX and XI. The major isomeric product was XII, 0.038 g (38%). There were four other isomeric products which together amounted to 0.05 g.

Pyrolysis at a higher pressure of IX gave a poorer yield of XII. Addition of benzene vapor as an inert diluent had no effect on the yield of XII.

***endo,cis*-8,9-Dimethyltricyclo[5.2.1.0^{4,10}]deca-2,5-diene (XII):** mass spectrum parent peak 160, major peaks at 131, 104, and 40; infrared spectrum (CCl_4) 3040 (s), 2850 (vs), 1440 (s), 1380 (2), 1360 (m), and 880 (s) cm^{-1}; nmr spectrum, see Figure 1.

Anal. Calcd for $C_{12}H_{16}$: C, 89.90; H, 10.09. Found: C, 89.61; H, 10.80.

Photoaddition of Benzene to Bicyclo[3.2.0]hepta-2,6-diene (V). A solution of V (4.0 g, 43 mmol) in benzene (24 g, 308 mmol) was irradiated in a quartz tube with 253.7-nm radiation from three modules of a Rayonet Type RS RPR-208 reactor.[23] After 40 hr, the solution was distilled and the distillate reirradiated. From eight such successive irradiations, the residues were collected. After any unreacted benzene and V were removed by distillation at atmospheric pressure, the residue was subjected to a bulb-to-bulb distillation at *ca.* 1 Torr to remove polymeric material. This distillate (~4 g), which was light yellow, was separated by preparative glc on a UCON-550X column (9 ft) at 155°. Minor adduct: retention time 36 min, 1.1 g (15%). Major adduct: retention time

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[20] R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

[21] W. G. Dauben and R. L. Cargill, *Tetrahedron Lett.*, **12**, 186 (1961); R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 3432, 4141 (1962).

[22] Adducts of ether to 1,3,5-cycloheptatriene were actually isolated from this reaction.

[23] Supplied by The Southern New England Ultraviolet Co., Middletown, Conn. 06459.

46 min, 2.2 g (30%). The yields were poorer when a mixture of benzene–V of 1:5 was used.

Major Adduct. Mixture of Pentacyclo[8.3.0.0^{2,8}.0^{3,7}.0^{9,11}]trideca-4(or 5),12-dienes (VI and XV): mass spectrum parent peak 170, other intense peaks at 155, 105, 104, 91, and 76; infrared spectrum (liquid film) 3020 (s), 2900 (vs), 1590 (w), 1345 (m), 826 (s), 786 (m), 730 (vs), and 710 (vs) cm^{-1}; ultraviolet spectrum (pentane) shoulder at 220 nm (ϵ 2000); nmr spectrum (CCl_4 solution), TMS as internal reference, see text.

Anal. Calcd for $C_{13}H_{14}$: C, 91.73; H, 8.29. Found: C, 91.45; H, 8.17.

Minor Adduct. Mixture of Pentacyclo[9.2.0.0^{2,9}.0^{3,7}.0^{6,8}]trideca-4,12-diene (XIIIa) and Pentacyclo[9.2.0.0^{3,10}.0^{4,8}.0^{7,9}]trideca-5,12-diene (XIIIb): mass spectrum parent peak 170, other intense peaks at 155, 129, 105, 104, 92, 91, 90, and 39; infrared spectrum (liquid film) 3030 (s), 2900 (vs) 1600 (w), 1350 (m), 855 (m), 775 (s), 752 (vs), and 732 (vs) cm^{-1}; ultraviolet spectrum (pentane) shoulder at 223 nm (ϵ 2080); nmr spectrum (CCl_4 solution), TMS as internal reference, see text.

Anal. Calcd for $C_{13}H_{14}$: C, 91.73; H, 8.29. Found: C, 91.80; H, 8.09.

Pyrolysis of the Major Adduct (VI and XV). The reaction was carried out in exactly the same way as the pyrolysis of IX except that the temperature was maintained at 230° for 90 min. The products were separated by preparative glc at 155°. VII (retention time 34 min) was collected as a colorless liquid (50%).

***endo*-Tetracyclo[8.2.1.0^{2,6}.0^{7,13}]trideca-3,8,11-triene (VII)**: mass spectrum parent peak 170, other intense peaks at 155, 105, 104, 76, 75, and 39; infrared spectrum (liquid film) 3030 (s), 2860 (vs), 1600 (w), 1445 (m), 1350 (m), 848 (m), 830 (m), 743 (vs), 723 (vs), and 705 (s) cm^{-1}; ultraviolet spectrum (pentane) 230 nm (ϵ 240) 220 (1800), and 210 (6700); nmr spectrum (CCl_4 solution, TMS as internal reference) see Figures 2 and 3.

Anal. Calcd for $C_{13}H_{14}$: C, 91.73; H, 8.29. Found: C, 91.42; H, 8.19.

Acknowledgment. The author wishes to express his gratitude to the Air Force Office of Scientific Research (AFSC), U. S. Air Force, for Contract No. F 44620-72-C-0024 under which this work was carried out. He also thanks Dr. J. N. C. Hsu for many useful discussions.

Stereochemical Aspects of Ether Oxygen Participation. VIII. Kinetic, Polarimetric, and Deuterium Isotope Effect Analysis of Oxygen Lone-Pair Involvement during Solvolysis of 8-Oxabicyclo[3.2.1]octan-2-yl Derivatives[1]

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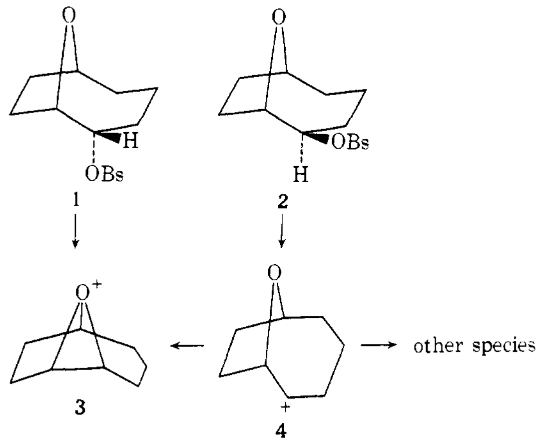
Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210. *Received April 12, 1972*

Abstract: Upon solvolysis in buffered acetic acid, *endo*-8-oxabicyclo[3.2.1]octan-2-yl brosylate gives rise uniquely to the corresponding endo acetate. The endo acetate arising from acetolysis of chiral endo brosylate, $[\alpha]_{365}^{25°}$ $+54.7°$, is completely racemic. Titrimetric and polarimetric rate measurements of these reactions have been made. These studies indicate the operation of R_2O-3 neighboring group participation to give a symmetrical oxonium ion which partitions itself between racemic acetate (22%) and racemic internally returned brosylate (78%). Subjection of (+)-*exo*-2-deuterio-*endo*-8-oxabicyclo[3.2.1]octan-2-yl brosylate to the same reaction conditions allows for the determination of the α-deuterium isotope effect of this ionization process. The low fractionation factor (k_H/k_D = ~1.08) is particularly compatible with the proposed high degree of internal nucleophilic assistance in the rate-determining step. The products of acetolysis of *exo*-8-oxabicyclo[3.2.1]octan-2-yl brosylate are derived exclusively from carbon skeletal rearrangement. The markedly divergent fates of the epimeric brosylates are discussed in the light of the above data.

In an earlier paper of this series[3] it was shown that acetolysis of *endo*-9-oxabicyclo[4.2.1]nonan-2-yl brosylate (**1**) proceeds with direct intervention of oxonium ion **3**. Comparable solvolysis of **2** also results in appreciable formation of **3**, although stereochemical, kinetic, and product development considerations attest to the formation of **4** prior to covalent bonding of the neighboring oxygen atom in this instance.[3] The dominating influence of oxonium ion intervention in the [4.2.1] bicyclic series is reflected particularly in the almost complete lack of 1,2-carbon migration (*cf.* **5** and **6**), especially during ionization of **2**. These observations contrast with those reported by Martin and Barlett for hydrolysis of the isomeric 7-oxanorbornyl



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[1] For part VII of this series, see L. A. Paquette and M. K. Scott, *J. Amer. Chem. Soc.*, **94**, 6760 (1972).

[2] American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969; National Science Foundation Graduate Fellow, 1966–1968.

[3] L. A. Paquette and P. C. Storm, *J. Amer. Chem. Soc.*, **92**, 4295 (1970).