Anal. Calcd for $C_6H_{10}IP$: C, 30.02; H, 4.20; I, 52.87; P, 12.91. Found: C, 30.15; H, 4.39; I, 52.63; P, 12.63.

Reaction with Iodine. An ether solution containing VI and 1-methyl-3-phospholene (V) was treated with a solution of iodine in ether. The course of the reaction was followed by gas chromatography at 65°; results are in Table IV. Iodine decolorization was very rapid, but at 0.5 ml of iodine the color persisted.

Reaction with Bromine. A solution of 8.69 mmol of VI in 21.4 ml of isooctane was treated with a solution prepared from 1 ml (18 mmol) of bromine in 100 ml of carbon tetrachloride. After 60 ml had been added, the color of the bromine persisted, indicating that about 10 mmol had reacted. The mixture contained much yellow solid, which was filtered off and washed with isooctane. The solid was dissolved in water and neutralized with sodium bicarbonate. The solution was saturated with potassium sulfate and extracted several times with chloroform. Extracts were combined, dried over Drierite, and evaporated to leave 0.932 g of solid. The crude product contained residual bromide ion (positive test with aqueous silver nitrate). It reduced potassium permanganate solution. Its infrared spectrum showed stretching bands for C=C (1570 cm^{-1}), olefinic C—H (3030 cm^{-1}), and phosphoryl (1200 cm^{-1}).

Reaction with Oxygen. The absorbance at 284 mμ of a saturated water solution of VI in a quartz cell sealed with wax was measured over a period of 6.5 hr. The log of the absorbance decreased in a roughly linear fashion from 0.1858 to 0.1098. When the stopper was removed from a solution of log *A* 0.1098, the absorbance dropped much more rapidly and vanished on long standing. Only end absorption was present in the spectrum.

The Barrelene to Semibullvalene Transformation. Correlation of Excited-State Potential Energy Surfaces with Reactivity. Mechanistic and Exploratory Organic Photochemistry. XLIV[1]

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Abstract: A photochemical transformation of barrelene was observed, wherein a C_8H_8 isomer is produced as the major product; cyclooctatetraene was obtained as a minor product. The structure of the C_8H_8 isomer was elucidated as that of bullvalene minus one vinyl bridge, and the compound was named "semibullvalene." The process was demonstrated to proceed *via* the triplet of barrelene in a process subsequently shown to be general. The irradiation of semibullvalene afforded cyclooctatetraene. It was found that semibullvalene undergoes degenerate valence tautomerism at a faster rate than any previously studied system. Barrelene was labeled at all vinyl positions with deuterium, leaving only the bridgehead positions still bearing hydrogen. The method developed for deuteration of barrelene involved treatment with lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine; the method promises to be generally useful for preparing deuterated compounds. The location of the hydrogen label in the semibullvalene photolysis product was investigated and found to fit one of two reasonable mechanisms. The reaction mechanism was shown to proceed *via* a unique bicyclic, allylic, triplet biradical having finite lifetime. The rearrangement was considered from a theoretical viewpoint with the use of three-dimensional Hückel theory, and the results were used to correlate the excited-state potential energy surface with observed photochemical behavior.

Interest in our laboratory has been heavily focused on exploratory and mechanistic organic photochemistry. Consequently, when reasonable quantities of barrelene[2] became available,[2,3] the enticing problem of the photochemistry of barrelene presented itself.

Exploratory Studies of the Photochemistry of Barrelene. Our initial efforts dealt with the direct irradiation of barrelene (*i.e.*, without sensitizer). However, cyclooctatetraene appeared to be the only product, as shown by ir, nmr, and vpc analysis, and our attention turned to the sensitized irradiation. Because of the volatility of barrelene, isopentane was chosen as a solvent, and acetone was selected as a sensitizer; this allowed later solvent removal.

Indeed, the sensitized irradiation of barrelene led to an interesting product, whose development could be followed by nmr. Additionally, cyclooctatetraene was formed in lesser quantity. However, separation of the new product proved unusually difficult because of overlap with the cyclooctatetraene on a large variety of vpc columns. Finally, a method of separation was developed which involved liquid–liquid partition chromatography with a stationary aqueous silver nitrate phase.

The cyclooctatetraene was identified by ir, nmr, and vpc retention time comparison with an authentic sample.

The major product was a colorless, volatile liquid with a strong odor, whose nmr consisted of three multiplets at τ 4.92, 5.83, and 7.03 in a 2:4:2 ratio. The nmr and ir spectra are given in Figure 1. The compound was found to be isomeric with barrelene (C_8H_8) by elemental analysis, and the parent ion of mass 104 found in the mass spectrum confirmed the molecular weight.

There are 16 possible C_8H_8 isomers, of which barrelene,[2,3] cubane,[4] and cyclooctatetraene are known. Interestingly, bonding between atoms 5 and 7, 3 and 6,

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(1) (a) For paper XLIII of the series note H. E. Zimmerman, *Angew. Chem.*, 81, 45 (1969); (b) paper XLII, H. E. Zimmerman, *Photochem. Photobiol.*, 7, 519 (1968).

(2) H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960).

(3) H. E. Zimmerman G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, 91, 2330 (1969).

(4) P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 3157 (1964).

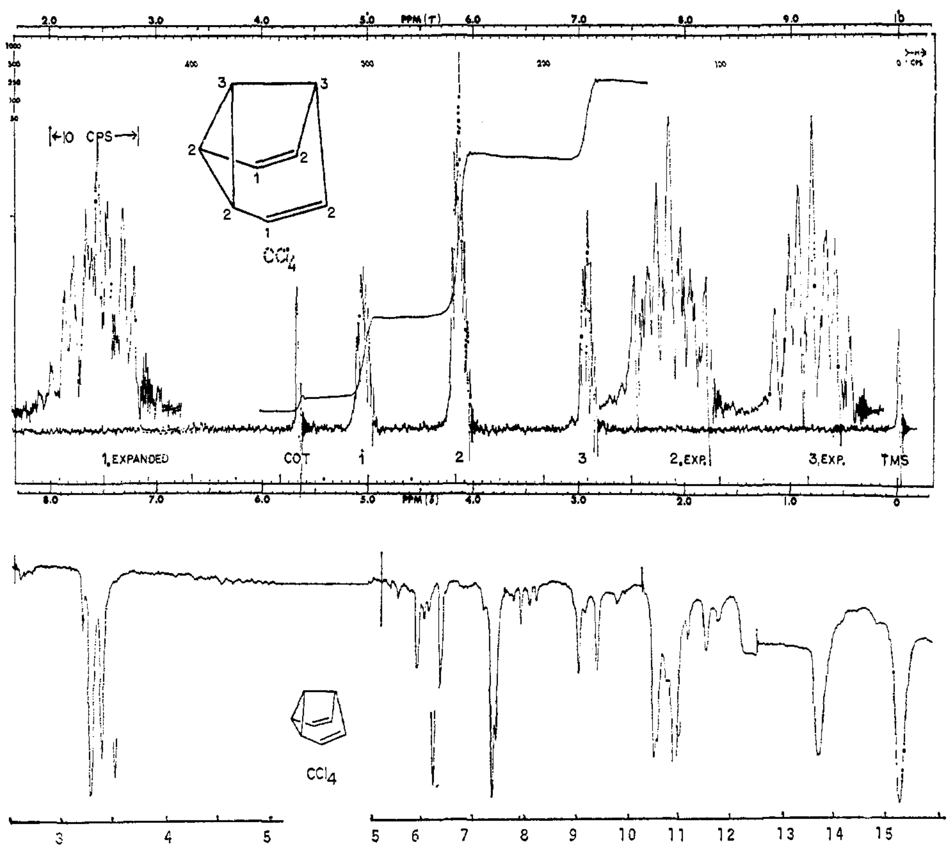
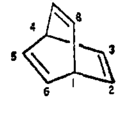
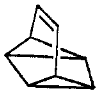


Figure 1. (a, top) Nmr spectrum of semibullvalene. (b, bottom) Infrared spectrum of semibullvalene (CCl_4).

and 2 and 8 would lead to cubane. However, the nmr spectrum of the major product limited consideration markedly. *A priori* one might consider structure **2** in direct analogy to the known photochemical rearrangement of norbornadiene to quadricyclene.[5] However,



1

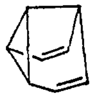


2

(1a)

this structure, as well as most of the other C_8H_8 isomers, is not consistent with the nmr spectrum. The 2:4:2 ratio of protons observed for the new product and consideration of the known chemical shifts of some related strained systems (*e.g.*, quadricyclene cyclopropyl protons at τ 8.59,[6] nortricyclene cyclopropyl hydrogens at τ 8.99,[6] bicyclo[2.2.0]hexane protons at τ 7.0–8.3,[7] bicyclobutane hydrogen at τ 8.6–9.6[8]) rule out most of the possibilities. In the case of **2**, the structure is not consistent with the highest field absorption's being a two-hydrogen peak and does not fit the chemical shifts. Remaining are the two structures **3** and **4**.

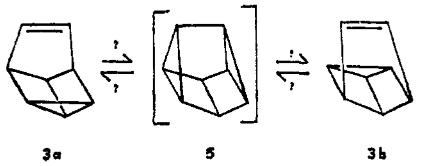
3



4

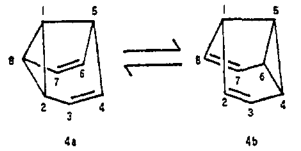
(1b)

Compound **3** could give the observed spectrum of the photoproduct only by undergoing the valence tautomerism outlined in eq 2. This involves a four-center process *via* species **5**. This is cyclobutadienoid (*i.e.*, "Hückel-like" and $4N$) and thus[1b,9,10] "forbidden." Such valence tautomerism should be too slow to result in time averaging.



(2)

Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**4**) appeared more promising as a structure for the new photoproduct, since the valence tautomerism available to it (eq 3) is similar to that shown by the bullvalene analogs, and the observed nmr spectrum is very similar to those reported[11,12] for barbaralone (**6**) and dihydrobullvalene (**7**) (see Table I). This valence tautomerism involves a Hückel-like transition state in a $4N + 2$ electron system and is allowed and understandably rapid.



(3)

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[5] G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961).

[6] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[7] D. M. Lemal and K. S. Shim, *J. Amer. Chem. Soc.*, **86**, 1550 (1964).

[8] D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963).

[9] H. E. Zimmerman, *Science*, **153**, 837 (1966).

[10] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1566 (1966).

[11] W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963).

[12] R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964).

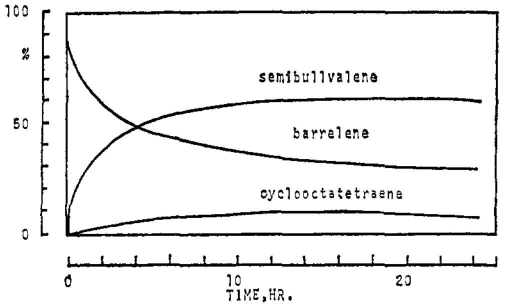
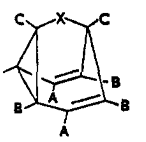


Figure 2. Plots of product distribution *vs.* time in sensitized irradiation of barrelene.

It is seen that hydrogens 2, 4, 6, and 8 become equivalent in **4**, as do 1 and 5, while the set of 3 and 7 remains unchanged but equivalent. By using nortricyclene as a reasonable model for the cyclopropyl hydrogens (τ 8.99)[6] and norbornadiene for the vinyl hydrogens (τ 3.35),[13] we can estimate an average value of τ 6.17 expected for the 2, 4, 6, and 8 protons. This compares well with the observed τ 5.83.

Table I. Nmr Data for Semibullvalene, Barbaralone, and Dihydrobullvalene

Type H	Compd	τ^a	Ref
A	**4**	4.92^b	This work
	6	4.3^c	11
	7	4.37^d	12
B	**4**	5.83^b	This work
	6	5.8^c	11
C	**7**	6.32^d	12
	**4**	7.03^b	This work
	6	7.3^e	11
	7	8.1^d	12
		4 X = zero carbon bridge **6** X = carbonyl bridge **7** X = CH_2CH_2 bridge	

[a] Multiplets in each case. [b] CCl_4. [c] No solvent given. [d] CS_2. [e] Acetone-d_6.

The uv spectrum of the photoproduct showed only a shoulder at 225–235 nm (ϵ 2400) which is quite similar to that reported[14] for **7**: shoulder at 230 nm (ϵ 3400).

Conclusive evidence that the photoproduct did indeed have the structure **4** was obtained by catalytic hydrogenation (note eq 4) with platinum oxide in ether, which afforded three products. The major product was the known[15] tricyclo[3.3.0.0^{2,8}]octane (**8**), which was formed in 67% yield. The structure of **8** was shown by comparison with an authentic sample, using ir, nmr, and vpc retention time. Authentic **8** was prepared by hydrogenation of **10**, which is one of the known photoisomers[16–18] of 1,3,5-cyclooctatriene (**9**) (eq 4).

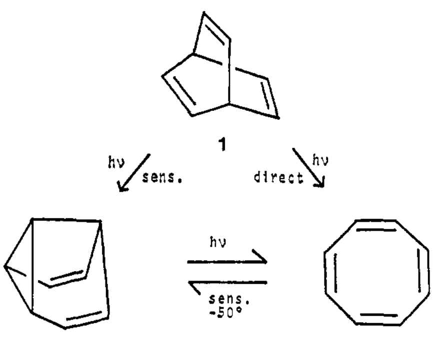


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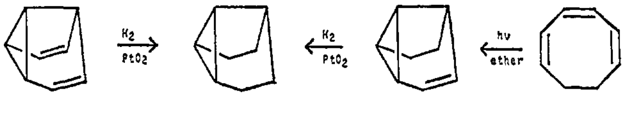
Figure 3. Photochemical interconversions of barrelene, semibullvalene, and cyclooctatetraene.



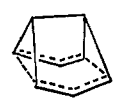
4 **8** **10** **9**

(4)

It was of interest to determine whether the barrelene to semibullvalene conversion was reversible. An acetone-sensitized irradiation of semibullvalene containing 4% cyclooctatetraene produced a mixture containing 14% cyclooctatetraene but no barrelene. When a solution of barrelene with acetone sensitizer was irradiated until the solution was opaque, a limiting product distribution was obtained, containing 35.3% barrelene, 61.3% semibullvalene, and 3.4% cyclooctatetraene. The concentration was adjusted so that acetone was absorbing 99% of the incident radiation. A plot of the product distribution *vs.* time is given in Figure 2. The photochemical interconversions of the C_8H_8 isomers shown in this work and subsequent work performed in this laboratory[19] are summarized in Figure 3.

Valence Tautomerism in Semibullvalene. The nmr spectrum of semibullvalene was studied over a temperature range of −110 to +117° at 60 Mc, and no change was noted in either chemical shift or integration values (within experimental error of the latter) of the three multiplets. At 117° some decomposition was noted. The spectra obtained at several representative temperatures are shown in Figure 4. It will be noted that, in order to go to the lower temperatures, sacrifice of resolution was necessary. Thus the HR60 spectra have less definition than the A60 runs which went only to −50°. Nevertheless, all spectra seem temperature invariant.

The lack of change in the nmr spectrum at low or high temperature raised the intriguing possibility that **4a** and **4b** are resonance contributors to an electron-delocalized, symmetrical species **4′**. Such a species would be a



4′

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(13) G. V. D. Tiers, "Tables of τ-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

(14) G. Schröder, *Chem. Ber.*, **97**, 3131 (1964).

(15) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(16) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964).

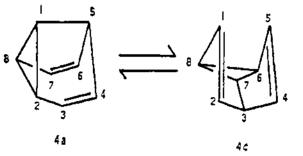
(17) W. R. Roth and B. Peltzer, *Angew. Chem.*, 76, 378 (1965).

(18) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

(19) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **90**, 4763 (1968).

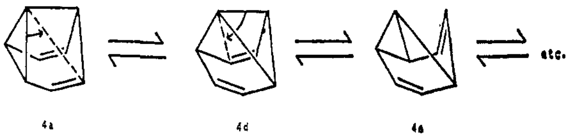
cyclic, six-electron, Hückel-like[9] entity. However, the uv spectrum (*vide supra*) and the lack of a ring current, as evidenced by the nmr, seems to rule out this consideration. But semibullvalene does exhibit a more rapid degenerate Cope rearrangement than any of the previously reported compounds, since these did show a change in the nmr spectrum at temperatures above −110°.

At least two other types of valence tautomerism were considered but were ruled out by the nmr. The type of isomerization shown in eq 5 was conceivable, since hydrogens 3 and 7 of semibullvalene were at somewhat high field (τ 4.92), compared to the vinyl protons of dihydrosemibullvalene (**10**) (τ 4.53 and 4.71). Such a process would move the 3 and 7 protons to higher field by partially equilibrating them with the pair 1 and 5. This would fit a slightly low-field absorption by protons 1 and 5. Although bizarre, this type of valence tautomerism was not unreasonable, since the atomic nuclei at the top and bottom of semibullvalene are nearly equivalently located. Such tautomerism would lead in the extreme to two nmr peaks. The absence of nmr temperature dependence up to 117° ruled out this form of tautomerism.



(5)

Another type of valence tautomerism which was envisioned as a possibility was the vinyl–cyclopropane tautomerization first considered by Viehe[20] and shown in eq 6. When coupled with the observed tautomerism of eq 3, this vinyl–cyclopropane tautomerization could lead to a single line in the nmr spectrum. However, the tautomerism of eq 6 involves a four-center, four-electron, "cyclobutadienoid"[9,21] transition state (all front lobes overlapping) and should be energetically unfavorable.



(6)

Having established the existence of the bizarre rearrangement of barrelene (**1**) to semibullvalene (**4**), we were interested in the mechanism of the process. Two mechanisms seemed especially reasonable, and these are outlined in Chart I. The problem of elucidation of the correct mechanism for the transformation was especially intriguing, since mechanism I is dependent on all three ethylenic bridges of **1**, while mechanism II involves only two ethylenic linkages of **1** and should be applicable to the numerous other systems having a divinylmethane moiety.

Since, as can be seen from Chart I, the two pathways lead to different predictions for the placement of these bridgehead positions in semibullvalene (**4**) product, an approach utilizing labeled barrelene was needed. The method chosen substituted the vinyl positions with deuterium atoms.[22] Hexadeuteriobarrelene (**11**) was prepared by treatment of **1** with lithium N-deuteriocyclo-

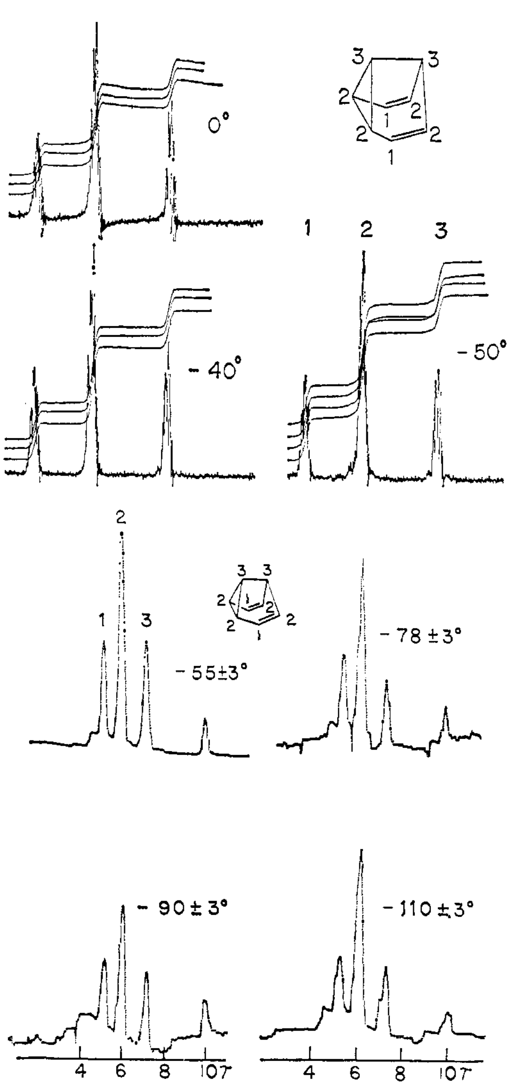
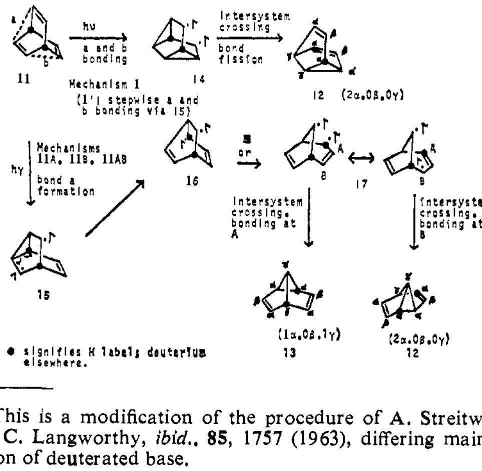


Figure 4. (a, top) Nmr spectra of semibullvalene with A-60 spectrometer at 0, −40, and −50°. (b, bottom) nmr spectra with HR60 spectrometer at −55, −78, −90, and −110°.

Chart I. Possible Mechanisms for the Barrelene to Semibullvalene Interconversion



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(20) H. G. Viehe, *Angew. Chem.*, 77, 768 (1965); structure 4 was cited as one of a series of compounds which could be considered as vinylogs of benzvalene, and the collective name "octavalenes" was suggested.

(21) This is a 1,3-suprafacial migration and could be predicted to be slow on the highest occupied MO basis considered by R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 2511 (1965) equally well.

(22) This is a modification of the procedure of A. Streitwieser, Jr., and W. C. Langworthy, *ibid.*, **85**, 1757 (1963), differing mainly in the utilization of deuterated base.

Table II. Summary of Hydrogen Distribution in Semibullvalene Product

Mechanism	Run 1[a,b,e] (12.5 ± 0.5% residual vinyl H) α	β	γ	Run 2[c,d,e] (10.3 ± 0.1% residual vinyl H) α	β	γ
I	0.818 (±0.013)	0.091 (±0.005)	0.091 (±0.005)	0.843 (0.002)	0.079 (0.001)	0.079 (0.001)
IIA	0.500 (0.011)	0.091 (0.005)	0.409 (0.006)	0.500 (0.002)	0.079 (0.001)	0.421 (0.002)
IIB	0.818 (0.013)	0.091 (0.005)	0.091 (0.005)	0.843 (0.002)	0.079 (0.001)	0.079 (0.001)
IIAB	0.659 (0.012)	0.091 (0.005)	0.250 (0.006)	0.671 (0.002)	0.079 (0.001)	0.250 (0.002)
Observed	0.647 (0.020)	0.093 (0.005)	0.258 (0.021)	0.665 (0.015)	0.082 (0.005)	0.254 (0.012)

[a] 60-Mc nmr in 1:1 acetone–isopentane, using acetone as internal standard. [b] Hydrogen distribution normalized to a total of 2.75 hydrogens as determined by nmr analysis. [c] 60-Mc nmr in CCl_4, using TMS as internal standard. [d] Hydrogen distribution normalized to 2.62 hydrogens as determined by nmr analysis. [e] Errors represent scatter of nmr integrations.

hexylamide in N,N-dideuteriocyclohexylamine at room temperature in three passes. Nmr and mass spectral analyses revealed the extent of vinyl deuteration (see Experimental Section for details). The mass spectrum confirmed the assumption that only six hydrogens had been exchanged; only 0.1 ± 0.1% contribution from D_7 and 0% from D_8 species were found.

In mechanism I the bridgehead hydrogens of barrelene are found at the α positions of semibullvalene (**4**) (*vide supra*). Mechanism II leads to three different hydrogen-label distributions in **4**, depending upon the final bond closure. The distribution 1α, 0β, 1γ results, if the final bond formation is concerted with bond fission and if there is preference for bond formation and fission at the same carbon (labeled A in Chart I). This variation is pathway IIA. If bond formation is concerted with bond fission but with a preference for bond formation at the carbon allylic (labeled B in Chart I) to bond fission, the result is 2α, 0β, 0γ: pathway IIB. In process IIAB there is a symmetrical allylic biradical **17** which has a finite existence. Closure at carbon atoms A and B becomes equally probable, neglecting possible secondary deuterium isotope effects, and the result is 1.5α, 0β, 0.5γ.

Determination of Mechanistic Pathway by Photolysis of Bridgehead-Labeled Barrelene. Two samples of hexadeuteriobarrelene (**11**) containing 12.5 ± 0.5% and 10.3 ± 0.1% residual vinyl hydrogens, respectively, were irradiated in isopentane with acetone as a sensitizer. The same products were observed as in the photolysis of nondeuterated barrelene. In the first run the reaction was monitored by nmr. The starting barrelene remained unchanged in per cent vinyl deuteration as determined by integration, and the width at half-height of the broad singlet attributed to the bridgehead hydrogens of **11** remained constant. In the second irradiation, the residual barrelene was separated from semibullvalene by vpc. The normalized integration values for hexadeuteriosemibullvalene found in the two runs are given in Table II, along with the values predicted by each mechanism.

Inspection of Table II shows that the hydrogen distribution resulting is quite different from that required for mechanisms I, IIA, and IIB. However the hydrogen distribution is very close to that expected for mechanism IIAB.

The nearness of the product distribution to a 1:1 ratio of hexadeuteriosemibullvalenes labeled as in **12** and **13** strongly supports the absence of an appreciable secondary isotope effect. A fortuitous combination of mechanism I and mechanism IIA could also afford the observed product distribution. However, this would require that the barrelene triplet state has two structurally different pathways available to it leading to the same product with identical quantum yields and is not reasonable.

It is of interest that the same general mechanism occurs in the rearrangement of benzobarrelene to benzosemibullvalene.[23] This supports the view that, although the π system of the third bridge is involved in excitation, the third bridge does not participate structurally in the mechanism.

Discussion of Results. The potential energy surfaces of ground and excited states were explored using three-dimensional Hückel calculations[24] in an attempt to understand the factors controlling the mechanism leading from barrelene to semibullvalene and favoring pathway II.

The *x*, *y*, and *z* coordinates of each atom, carbon and hydrogen, were derived from direct measurement of a Prentice-Hall Framework Molecular Model of each species along the reaction coordinate. This included barrelene (**1** ≡ **11**), the biradicals **14**, **15**, and **16**, and semibullvalene (**4** equivalent to **12** and **13**). For species along the reaction coordinate with geometries intermediate between these, the *x*, *y*, and *z* coordinates were interpolated and then checked with approximate models. The results are given in Figure 5 for mechanisms I and II of Chart I. Also, the results are given for mechanism I′ which is a variant of mechanism I in which the two transannular bridging processes occur in two discrete steps.

The drawings in Figure 5 can be considered to depict different cross sections of the general potential energy surface interconnecting the C_8H_8 isomers and leading from barrelene to semibullvalene.

Mechanism I (Figure 5a) leads on excitation to a triplet which requires an appreciable activation energy to bridge doubly and give biradical **14**. Interestingly, this species does not correspond to a ground-state minimum. In any case, faced with such an activation

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(23) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

(24) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

barrier it is not unexpected that the excited state does not utilize mechanism I.

A slight variation, mechanism I′, circumvents the large excited state barrier with stepwise bridging and shows the singly bridged excited state to be a low energy point. Additionally, with this geometry there is a close approach of excited and ground states which should facilitate intersystem crossing to ground state. However, the energy minimum (Figure 5b) for mechanism I′ can be seen to be positioned largely over the portion of the ground-state curve leading back to barrelene. Hence again we find a mechanism not likely to afford semibullvalene product.

Finally, in the case of mechanism II the excited state formed on vertical excitation is on an energy slope sufficiently high to allow the molecule to pass over the modest barrier separating excited reactant from excited allylic biradical.

Within a few vibrations the energy well at **17** would be populated. Furthermore, we note that this allylic biradical is at an energy minimum both as a ground state and as an electronically excited state species. A high population of this energy well is to be expected as is intersystem crossing to ground state by the excited allylic biradical. The latter results from the nearness of the excited- and ground-state surfaces with allylic biradical geometry. Of the two barriers surrounding the ground-state allylic biradical **17**, the one interposed between reactant barrelene and **17** is considerably higher than that between this ground-state intermediate and product semibullvalene. Hence the successful operation of mechanism II in leading from barrelene to semibullvalene can be understood in terms of this partial exploration of the potential energy surface. Furthermore, the strong experimental evidence for a finite lifetime of the symmetrical allylic biradical **17** accords with the calculations.

This description of the potential energy surface, despite its success, should be recognized as being valid only for semiquantitative and qualitative purposes.[25]

It is of interest to consider the mechanism from some other vantage points. First, we might attempt to write correlation diagrams. However, symmetry is not maintained throughout all pathways with the result that the noncrossing rule cannot be utilized in deciding which MO's correlate in every instance.

Another approach which is more successful is that of Zimmerman and Mariano.[26] It was noted that there is a cyclic array of six orbitals with one sign discontinuity in the divinylmethane rearrangement, and that this leads to a photochemically allowed process.[27]

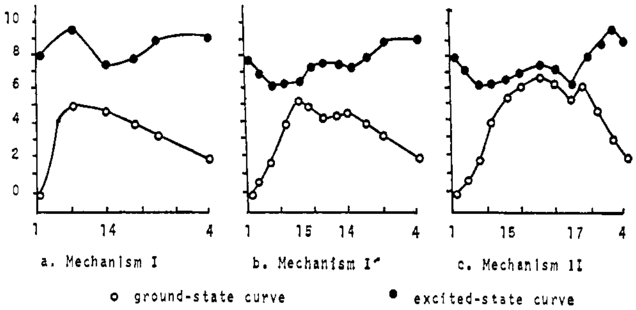
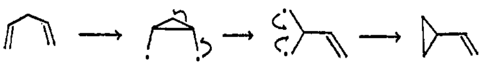


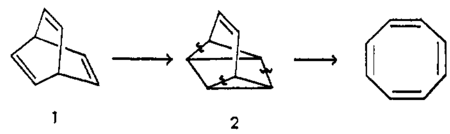
Figure 5. Potential energy *vs.* reaction coordinate for three mechanisms.

Finally, we conclude that despite the availability of three bridges in barrelene, only two are involved directly in the photochemical rearrangement to semibullvalene. The mechanism utilized is that of the very general[26] di-π-methane (or divinylmethane) rearrangement.



18 19 20 21 (7)

As noted by Zimmerman and Mariano[26] the di-π-methane rearrangement seems to utilize a triplet mechanism for bicyclic systems and this is in agreement with the present results. Direct irradiation afforded the singlet which proceeds instead to cyclooctatetraene which may be pictured as



1 2 (8)

in analogy to the case of benzobarrelene whose singlet has been shown by Zimmerman, Givens, and Pagni[23] to give benzocyclooctatetraene by a similar mechanism.

Experimental Section[28]

Bicyclo[2.2.2]-2,5,7-octatriene (Barrelene). Barrelene was prepared by the synthesis that we reported earlier.[2,3]

Direct Irradiation of Barrelene. A Vycor tube containing a solution of 250 mg of barrelene in 10 ml of methylcyclohexane (Eastman Kodak, Spectral Grade) was degassed, sealed under vacuum, strapped to a quartz immersion well containing a 450-W medium pressure Hanovia mercury lamp, and irradiated for 16 hr with external ice-water cooling. The photolysis mixture was subjected to preparative vpc on a 200 × 2.5 cm column packed with 15% Diisodecyl phthalate on Apiezon G at 64° and 25 psi helium to give 50 mg of cyclooctatetraene (retention time 36 min), identified by ir, nmr, and vpc retention time comparison with an authentic sample, and a very minor peak with the retention time (6.25 min) of benzene. A solution of 50 mg of barrelene in 0.5 ml of methylcyclohexane was sealed in a quartz tube and irradiated for 4 hr with a 450-W Hanovia medium-pressure mercury lamp through 6 nm of a solution of 0.1 *M* $CoSO_4 \cdot 7\ H_2O$ and 0.4 *M* $NiSO_4 \cdot 6\ H_2O$ (10% transmittance at 213 nm) to give a mixture containing 7.4% benzene, 21.4% cyclooctatetraene, and 71.2% barrelene as assayed by nmr.

Acetone-Sensitized Irradiation of Barrelene. A Vycor tube containing a solution of 654 mg of barrelene and 2.011 g of acetone in

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(25) The energies obtained were too large. However, it is important to test the value of extended Hückel theory by experiment.

(26) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(27) (a) The cyclic system of orbitals is the array sp^2 (at atom 5), sp^3 (atom 4), p (atom 7), p (atom 8), p (atom 5), p (atom 6) (note structure **1** for numbering). Since the p orbital at 5 is involved in forming a new σ bond to carbon 8 and the sp^2 orbital at 5 is becoming a p orbital overlapping with that at 6, it is convenient to picture the p + sp^2 pair at atom 5 as two sp^5 orbitals. These both overlap with the p orbital at C-6, thus completing the cyclic array. Independent of the way in which the basis set (*i.e.*, the definitional set) of orbitals is chosen, there will be an odd number of sign discontinuities around the cycle; this then becomes a Möbius system with six electrons and the reaction is ground-state forbidden but excited-state allowed. (b) Although these electronic considerations predict the energetics to be favorable, quick collapse by bonding of atoms 4 and 7 is discouraged by the unpaired spins of the triplet. Hence formation of the allylic biradical as an open, discrete intermediate can be understood. (c) A more naive viewpoint would picture a cyclic array of just the four orbitals of the 4,5-σ bond and the 7,8-π bond. This, too, would fit our Möbius–Hückel treatment and might be simply termed an addition of a single bond across a double bond. But this attributes no role to the second double bond and seems less realistic.

(28) All melting points were taken on a hot stage calibrated with known compounds.

50 ml of isopentane (Phillips 99%) was degassed, sealed under vacuum, strapped to a quartz immersion well containing a 450-W medium-pressure Hanovia lamp, and the solution was photolyzed for 50 min with external cooling by an ice-water bath. The solution was concentrated to *ca.* 5 ml through a 25 cm × 15 mm column packed with helical coils (Helipak). Preparative vpc on a 2 m × 2.5 cm column packed with 15% Apiezon L on Chromosorb P (acid washed, 60-80 mesh) at 75° and 15 psi helium afforded: peak 1, 285 mg of barrelene, retention time 38 min; peak 2, 218 mg of a mixture of tricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene (semibullvalene) and cyclooctatetraene, 51 min. The mass balance was 77%. Nmr analysis showed the second peak to contain 6% cyclooctatetraene.

Semibullvalene and cyclooctatetraene showed the same retention time on the following 200 × 0.65 cm analytical vpc columns: 20% TCP on Celite, 20% diisodecyl phthalate on Fluoropack, 5% Dow Corning 710 Silicon Oil on Chromosorb P, 10% Monsanto Polyphenyl Ether on HMDS Chromosorb P, and 15% Apiezon L on Chromosorb P (all run at 75° and 20 psi of helium). A mixture of the two compounds could be separated on a 1 m × 0.65 cm column packed with 0.07 *M* $AgNO_3$ in glycerol, 40% by wt on Chromosorb P (60-80 mesh);[29] however, the column packing decomposes semibullvalene after use for 2-3 hr at 54°.

In two portions, 196 mg of a mixture of semibullvalene and cyclooctatetraene was applied to a 1.5 m × 2.4 cm column packed with a 15% aqueous solution of silver nitrate on 70% by wt Celite (Celaton-FW-80, Eagle-Pitcher Co.) and elution with 40-ml fractions of ether (reagent grade) saturated with water gave: fractions 1-47, nil; 48-64, cyclooctatetraene; 62-110, semibullvalene. The corresponding fractions were, 43-59 and 57-112, respectively, in the second chromatogram. The eluent was passed through a 3.20-mm quartz cell in a Beckman DU spectrometer with the wavelength at 232 nm and the optical density read on a strip recorder. Fractions 65-110 and 60-112 from the two portions were dried, concentrated through a 25 × 1.5 cm Helipak column to *ca.* 5 ml, and separated by preparative vpc on a 2 m × 2.5 cm column packed with 15% Apiezon L on Chromosorb P (acid washed, 60-80 mesh) at 76° and 20 psi of helium. Collection in a U tube cooled in a Dry Ice-methanol bath afforded 100 mg of pure semibullvalene as shown by the lack of cyclooctatetraene in the nmr spectrum. This represents a 30% yield based on unrecovered barrelene and a 50% loss during separation. The spectral data for semibullvalene were: ir (CCl_4) 3.20, 3.27, 3.39, 5.93, 6.08, 6.18, 6.39, 7.21, 7.40, 7.47, 7.95, 8.12, 8.26, 9.08, 9.44. 10.56, 10.60, 10.69, 10.97, 11.20, 11.57, 11.80, 13.75, and 15.32 μ; in CS_2 also: 12.32, 12.50, 12.72, 13.10, 13.50, and 13.63 μ; nmr (CCl_4) τ 4.92 (m, 2 H, 3,7 vinyls), 5.83 (m, 4 H, 2,4,6,8 C*H*CH=), 7.03 (m, 2 H, 1,5 methines); uv max (95% ethanol) 225-235 nm sh (ϵ 2400); mass spectrum (70 eV) parent ion 104.

Anal. Calcd for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.73.

The cyclooctatetraene fractions from silver nitrate liquid-liquid chromatography of several photomixtures were combined to give 11.2 mg of cyclooctatetraene (1%), which was identified by comparison of vpc retention time and ir and nmr spectra with an authentic sample.

A solution of 100 mg of barrelene in 350 mg of acetone and 4 ml of isopentane was irradiated for 60 min with a 450-W Hanovia lamp. An nmr spectrum of the mixture showed 43% barrelene, 46% semibullvalene, and 11% cyclooctatetraene by integration.

Hydrogenation of Semibullvalene. To a stirred suspension of 136 mg of platinum oxide in 5.0 ml of anhydrous ether, which had been equilibrated overnight under 1 atm of hydrogen, was added 63.2 mg (0.605 mmol) of semibullvalene in 2.0 ml of ether. After 20 min, 1.60 equiv (67.60 ml, 742.9 mm, 22.2°) had reacted and no further uptake was observed. Analytical vpc on 200 × 0.65 cm column packed with 15% Ucon oil LB 550X on Chromosorb P at 75° and 20 psi of helium gave peaks with retention times of 17 min (29% by peak area), 19 min (4%), and 25 min (67%). Concentration to *ca.* 3 ml with the Helipak column followed by preparative vpc on a 2 m × 2.5 cm column packed with 15% Ucon oil LB 550X on Chromosorb P at 75° and 20 psi of helium yielded 6.2 mg of the first two peaks and 16.6 mg of tricyclo[3.3.0.$0^{2,8}$]octane by comparison of vpc retention time and ir and nmr spectra with an authentic sample. Neither minor component was identified further. The lack of thermal rearrangement was established by nmr analysis before vpc work-up.

Tricyclo[3.3.0.$0^{2,8}$]octane.[30] Tricyclo[3.3.0.$0^{2,8}$]octane was prepared by platinum oxide hydrogenation in ether of tricyclo[3.3.-0.$0^{2,8}$]-3-octene. The ir spectrum (CS_2) showed bands at 3.29, 3.31, 3.42, 3.50, 7.35, 7.55, 7.67, 7.79, 7.89, 7.98, 8.30, 9.35, 9.91, 10.04, 10.19, 10.52, 10.69, 10.95, 12.81, 13.27, 14.35, and 14.78 μ; nmr (CCl_4) τ 7.45 (m, 1 H) and 7.8-8.9 (m, 11 H).

Tricyclo[3.3.0.$0^{2,8}$]-3-octene. Following the method of Chapman,[16] tricyclo[3.3.0.$0^{2,8}$]-3-octene was prepared by irradiation of 1,3,5-cyclooctatriene for 9 hr under nitrogen with a 450-W Hanovia medium-pressure mercury immersion lamp using a Vycor filter. The 1,3,5-cyclooctatriene was prepared by the method of Cope.[31]

The spectral data for tricyclo[3.3.0.$0^{2,8}$]-3-octene were: ir (CCl_4) 3.29, 3.39, 3.50, 6.29, 6.93, 7.40, 7.58, 7.71, 9.39, 9.53, 10.03, 10.11, 10.40, 10.51, 10.99, 11.06, 11.45, 11.95, 13.84, 14.24, 14.88, 15.22 μ; nmr (CCl_4) τ 4.6 (m, 2 H, CH=), 6.96 (m, 1 H), 7.58 (quartet, 1 H), and 8.0-8.7 (m, 6 H) which was identical with the spectrum given in ref 16.

Acetone-Sensitized Photolysis of Semibullvalene. A solution of 164 mg of semibullvalene (4% cyclooctatetraene by nmr integration) in 525 mg of acetone and 45 ml of isopentane was sealed in a quartz tube under vacuum, strapped to a water-cooled immersion well containing a 450-W Hanovia medium-pressure mercury lamp and irradiated for 60 min. Concentration *in vacuo* followed by preparative vpc using a 2 m × 2.5 cm column packed with 15% Apiezon L on Chromosorb P at 75° and 20 psi of helium afforded 71 mg of semibullvalene, which now contained 14% cyclooctatetraene by nmr analysis.

Nmr Monitored Photolysis of Barrelene. A tightly capped nmr tube containing 65 mg of barrelene, 250 mg of acetone, and 0.20 ml of isopentane was strapped to an immersion well containing a 450-W Hanovia lamp and irradiated for 20.5 hr. Periodically the nmr spectrum was recorded and the relative amount of barrelene, semibullvalene, and cyclooctatetraene present were determined by integration.

The photolysis solution slowly turned a deep brown in 6.5 hr and polymeric material was noticed on the walls of the tube after 4.6 hr. A very small amount (1%) of benzene was present after 20.5 hr.

Low-Temperature Nmr Spectrum of Semibullvalene. The nmr spectrum of a 15% solution of semibullvalene (containing 4% cyclooctatetraene) in carbon disulfide with TMS as an internal standard was recorded at 25.0, 0.0, −21.0, −39.0, and −49.5°. No change in the chemical shift or shape of the semibullvalene multiplets was observed and the integration values remained constant within experimental error. A Varian HR-60 instrument was used to record the spectrum at temperatures to −110° and no change in the spectrum was apparent.

High-Temperature Nmr Spectrum of Semibullvalene. The nmr spectrum of semibullvalene was unchanged at temperatures up to 117° except for the appearance of decomposition products.

Preparation of Photolysis Grade Pentane. Commercial pentane was stirred overnight with 30% fuming sulfuric acid. The mixture was separated and the hydrocarbon layer washed with sodium bicarbonate solution and then washed three times with water. The liquids were distilled through a Vigreux column from phosphorus pentoxide and the bp 34-36° fraction collected.

N,N-Dideuteriocyclohexylamine. A solution of 45 ml of cyclohexylamine (bp 131-132°) and 18 ml of deuterium oxide (Merck Sharp and Dohme, 99.7% D minimum) was stirred for 1 hr under a dry nitrogen blanket. The water was then removed from the upper phase by distillation with 210 ml of dry benzene (azeotrope bp 69°, 8.9% water). Another 18 ml of deuterium oxide was added and after 1 hr of stirring, the water was removed from the organic layer by distillation with 210 ml of dry benzene. After a third washing with 18 ml of deuterium oxide and benzene azeotrope, the cyclohexylamine was distilled at 130-132° to give 28 ml. The cyclohexylamine was redistilled to afford 20 ml of colorless N,N-dideuteriocyclohexylamine (bp 132-133°), which was stored under dry nitrogen until used. Traces of benzene and nondeuterated amine (5%) at τ 8.88 (NH_2) were seen in the nmr (CCl_4).

Deuteration of Barrelene. To 20.0 ml of freshly prepared N,N-dideuteriocyclohexylamine under dry nitrogen was added 3.0 ml of hexane containing 2.375 *M* butyllithium[32] (Alfa Inorganics) by

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[29] M. A. Muhs and J. P. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

[30] J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

[31] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Amer. Chem. Soc.*, **72**, 2510 (1950).

[32] The butyllithium was standardized by the method of Gilman and Haubein.[33]

syringe through a serum cap. The clear solution of lithium N-deuteriocyclohexylamide was stirred magnetically for 1 hr and a solution of 0.7678 g of barrelene in 2.0 ml of pentane (Photolysis Grade) was added by syringe and the mixture stirred at room temperature for 24 hr. The reaction was quenched with 0.50 ml of deuterium oxide, cooled to 0°, and then neutralized with 5% hydrochloric acid. The barrelene was extracted with 100 ml of pentane, dried, and carefully concentrated to *ca.* 5 ml through a 25 cm × 1.5 cm Helipak column. Separation by preparative vpc on a 2 m × 25 mm column packed with 15% Apiezon L on Chromosorb P (60–80 mesh) at 76° and 20 psi of helium afforded 0.4915 g (64% recovery) of barrelene (retention time 12.5 min) by collection in a U tube cooled in a Dry Ice–methanol bath. Nmr analysis showed 72 ± 1% vinyl deuteration (assuming no bridgehead exchange). This sample was combined with 0.2840 g of barrelene showing 65 ± 0.5% vinyl deuteration and was added in 3.0 ml of pentane to a solution of 3.0 ml of 2.375 *M* butyllithium in hexane and 25 ml of N,N-dideuteriocyclohexylamine which had been stirred under nitrogen for 1 hr. The clear solution was stirred at room temperature for 16 hr, cooled, and quenched with 1.0 ml of deuterium oxide. On work-up there was obtained 0.4409 g of barrelene showing 80 ± 1.2% vinyl deuteration.

This sample was then combined with 0.1360 g of barrelene which had been brought to 84% vinyl deuteration in two similar exchanges and was exchanged a third time with 40 ml of freshly prepared N,N-dideuteriocyclohexylamine containing 3.0 ml of hexane 2.375 *M* in butyllithium for 14 hr at room temperature. Work-up afforded 0.3623 g of barrelene whose nmr indicated 89.7 ± 0.1% deuteration at the vinyl positions.

Mass Spectrum of Deuterated Barrelene.[34] The assumption of little or no bridgehead deuterium incorporation was confirmed by mass spectral analysis. Ionization voltages of 70, 17.5, 15, 12.5, and 10.0 eV were used, and it was observed that the ratio of mass 110 to mass 109 increased from 1.00 at 70 eV to 1.20 at 10.0 eV, indicating that higher ionization voltage favors loss of a hydrogen atom to give greater M − 1 contribution. The threshold voltage for barrelene is 7.95 ± 0.16 eV[35] but due to instrument problems no usable spectra could be obtained for ionization voltages below 10.0 eV. The mass spectrum consisted of a series of peaks from mass 107 through 111 which contained contributions from protio and deuterio ^{12}C and ^{13}C molecules, but negligible barrelene with less than two deuterium atoms. The corrected peak height *P* for mass M is obtained by subtracting the M + 1 and M + 2 ^{13}C contributions from lower mass units from observed peak height *P* and then adding its own M + 1 and M + 2 ^{13}C contributions.[36] This gives the peak heights for the various masses as if all carbon atoms were ^{12}C and gives direct indication of the per cent deuterium content. The absence of mass 111 and 112 (D_7 and D_8) indicates absence of bridgehead exchange, and one obtains a value of 87.8 ± 0.8% in the vinyl positions with the following contributions from the various masses: mass 107, 3.0 ± 0.1%; mass 108, 13.6 ± 0.1%; mass 109, 36.7 ± 0.2%; and mass 110, 46.7 ± 0.4%.

Acetone-Sensitized Irradiation of Deuterated Barrelene. A solution of 61 mg of barrelene (87.5 ± 0.5% vinyl deuterated) in 0.20 ml of acetone and 0.20 ml of 2-methylbutane (Baker Grade, J. T. Baker Chemical Co.) was irradiated for 3 hr in an nmr tube using a 450-W, medium-pressure Hanovia mercury source. The reaction was monitored by nmr at 30, 60, 120, and 180 min. The nmr indicated 88 ± 0.5% vinyl deuteration throughout the irradiation and the width at half-height of the bridgehead peak remained constant at 4.5 Hz.

A solution of 330 mg of barrelene (89.7 ± 0.1% vinyl deuterated) in 0.775 g of acetone and 25 ml of 2-methylbutane was placed in a 20 × 1.5 cm quartz tube, degassed, and sealed under vacuum. The tube was strapped to the cooling jacket of a 450-W Hanovia lamp, wrapped with aluminum foil and irradiated for 30 min using unfiltered light. The tube was opened and the photolysis mixture concentrated to *ca.* 5 ml using a Helipak column and separated by preparative vpc (Apiezon L column at 76°). This afforded 57 mg of a mixture of semibullvalene and cyclooctatetraene (31 min retention time) and 33 mg of barrelene (24.5 min). The semibullvalene was washed into an nmr tube with carbon tetrachloride and the nmr spectrum was the same as in the nonisolated irradiation (*vide supra*).

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[33] H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

[34] We thank Mr. R. McKelvey for running the mass spectrum.

[35] J. L. Franklin, Rice University, personal communication, 1967.

[36] The corrections used in the calculation were: (a) probability that all carbon atoms are ^{12}C = 0.9176;[37] (b) P_{M+1}/P_M and P_{M+2}/P_M for eight carbon atoms are 0.08772 and 0.003381, respectively.[38]

[37] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 296.

[38] J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1963, p 12.