with light of wavelengths above 2700 A did not yield any detectable triplet species.[3] When benzophenone was added and the sample irradiated with 3650-A light, a 9-kMc epr absorption near 8300 gauss was immediately observed. The zero-field parameters D and E obtained from analysis of the spectra are: IIa, $D = 1.625$, $E = 0.00$; IIb, $D = 1.626$, $E = 0.00$; and IIc, $D = 1.606$, $E = 0.003$ cm^{-1}.[4] Qualitatively D measures the magnitude of the spin–spin interaction of the unpaired electrons and E its deviation from cylindrical symmetry. The identification as II is justified by the proximity of the parameters to those of nitrenes obtained from alkyl monoazides under similar conditions; *e.g.*, triphenylmethylnitrene, $D = 1.660$, $E = 0.00$; and diphenylmethylnitrene, $D = 1.636$, $E = 0.00$ cm^{-1}. The parent methylnitrene with $D = 1.595$, $E = 0.00$ cm^{-1} is readily observed from sensitized photolysis of methyl azide.[5] Previous attempts to obtain alkylnitrenes without sensitization at 77°K were unsuccessful, although weak signals were observed at 4°K.[6] Once prepared, the alkylnitrenes, including the azidonitrenes II, are stable for days at 77°K without further irradiation. Clearly at 77°K ground-state II cannot undergo decomposition to III in the matrix, although the expulsion of two molecules of nitrogen is possible.

Under continued irradiation at 3650 A the concentration of II levels off after its initial rise and then decreases slightly. Associated with the maximum is the rapid rise of the absorptions characteristic of III. There is no evidence for a triplet or quintet dinitrene as an intermediate. In six different environments, including crystalline benzophenone and glassy MTHF, the methylenes have the same epr spectra as those obtained from the corresponding diazo compounds.

The desirability of obtaining III from a precursor other than IV arose from the observation that little reorientation of the developing methylene occurred during expulsion of the nitrogen molecule. Decomposition of diazo compounds with polarized light gave highly oriented triplets in a rigid matrix, suggesting that the cage about the precursor severely restricted molecular motion.[7] However, in the observations in the preceding paragraph the initial angles for the two routes should be approximately 110 and 120° for I and IV, respectively. The methylene angle in III is 145–155°.[1,8] While the absolute value in III is somewhat uncertain, the predicted sensitivity of the epr spectrum to changes in the angle[1,9] allows us to conclude that the difference for III prepared by the two routes is less than 1–1.5°. With the corresponding angles of I and IV differing by ~10°, it appears that there is sufficient freedom for different precursor geometries to yield the same final geometry, a conclusion which should be valid regardless of the detailed mechanism of the transformations involved.[10] Such constancy of the structure of III is compatible with the observed geometry being the preferred structure of the methylene independent of the particular environment.

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[3] Hydrolysis of the dihalomethane precursor to the ketone or aldehyde can produce a sensitizer which will generate a triplet. No triplet is observed if any ketone or aldehyde is thoroughly removed.

[4] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[5] K. Schueller, unpublished results.

[6] E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964).

[7] E. Wasserman and W. A. Yager, *J. Phys. Chem.*, 71, 201 (1967).

[8] R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchinson, Jr., B. E. Kohler, and R. Silbey, *J. Chem. Phys.*, **43**, 2006 (1965).

[9] J. Higuchi, *ibid.*, **39**, 1339 (1963).

[10] Diphenylmethylene produced by low-temperature photolysis of tetraphenylethylene oxide also has the same geometry. Here the angle in the precursor about the future divalent carbon may well be similar to that in diphenyldiazomethane (A. M. Trozzolo, H. Kristinsson, and G. Griffin, unpublished results).

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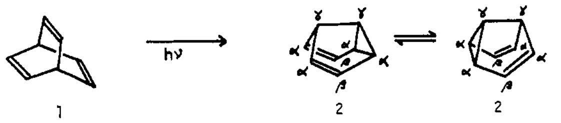
Mechanistic Organic Photochemistry. XXIV.[1] The Mechanism of the Conversion of Barrelene to Semibullvalene. A General Photochemical Process

Sir:

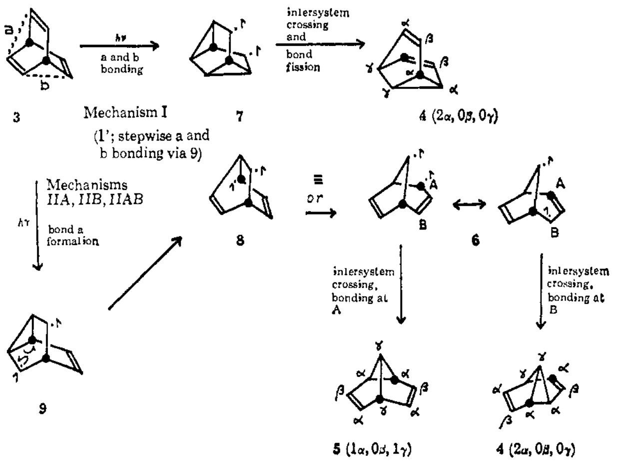
Previously we reported the photosensitized barrelene (**1**) to semibullvalene (**2**) transformation.[2]



(1)

Two fundamentally different mechanisms[3] seemed *a priori* possibilities. These are presented in Chart I. The simpler mechanism was tentatively chosen,[2] and efforts were initiated to determine which was correct.

Chart I. Possible Mechanisms for the Barrelene to Semibullvalene Interconversion



• signifies H label; deuterium elsewhere.

Hexadeuteriobarrelene (**3**) was prepared by treatment of barrelene with lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine[4] at room

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[1] For paper XXIII of the series see H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

[2] H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

[3] R. W. Binkley, Ph.D. Thesis, University of Wisconsin, 1966.

[4] (a) We thank Professor A. Streitwieser for helpful comments on the method. (b) The general method for deuterium removal by this base is given by A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, **85**, 1757 (1963).

temperature. Nmr analysis revealed 87.5 and 89.7% vinyl deuteration in two runs, and mass spectral analysis revealed the same extent of total deuteration within experimental error and little or no d_7 species. This means that relatively little bridgehead exchange is taking place.

Semibullvalene (**2**) has only three types of hydrogens (α, β, and γ in a ratio of 4:2:2) as a result of rapid valence tautomerism (eq 1). Hence the two bridgehead hydrogens of vinyl-deuterated barrelene (**3**) will be distributed among the α, β, and γ locations, detectable by nmr, in a way dependent on mechanism. Process I of Chart I requires both of the two hydrogen atoms to appear in the α positions (*i.e.*, 2α, 0β, 0γ). Process II gives the distribution 1α, 0β, 1γ if the final bond formation (note Chart I) is concerted with bond fission and with a preference for bond formation and fission at the same carbon (process IIA). Alternatively, if the preference is for bond formation at the allylic carbon (process IIB), then the distribution 2α, 0β, 0γ is expected. Finally, if the symmetrical allylic biradical **6** has appreciable existence (mechanism IIAB), closures A and B become equally probable except for potential secondary deuterium isotope effects, and the intermediate distribution 1.5α, 0β, 0.5γ should result.

Irradiation of the deuterated barrelene (**3**) in two separate runs, using 50 and 4% acetone in isopentane, afforded semibullvalene (vpc isolation in run 2) with the hydrogen distributions 1.52α, 0β, 0.48γ (run 1) and 1.48α, 0β, 0.52γ (run 2), after correction for residual vinyl hydrogen in the reactant. The uncorrected results along with expected values are collected in Table I.

Table I. Summary of Hydrogen Distribution in Semibullvalene Product

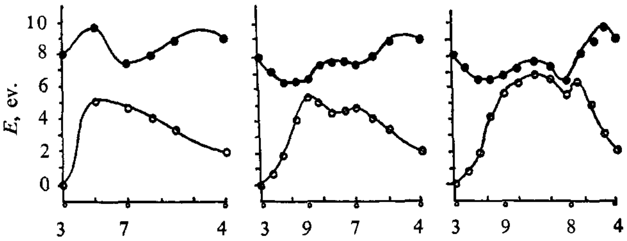
Mechanism	Run 1 (12.5% residual vinyl H)			Run 2 (10.3% residual vinyl H)		
	α, %	β, %	γ, %	α, %	β, %	γ, %
I[a]	81.8	9.1	9.1	84.3	7.9	7.9
IIA[a]	50.0	9.1	40.9	50.0	7.9	42.1
IIB[a]	81.8	9.1	9.1	84.3	7.9	7.9
IIAB[a]	65.9	9.1	25.0	67.1	7.9	25.0
Observed	65.5	10.0	24.5	66.5	8.1	25.4

[a] Calculated using known residual vinyl hydrogen content.

The results clearly support mechanism IIAB. No evidence for an appreciable secondary isotope effect is found; this is reasonable in view of the exothermicity of the biradical ring-closure step. Interestingly, the simplest mechanism thus proved not to be correct.

In an attempt to understand the factors controlling the mechanism, the potential energy surfaces of ground and excited states were explored using the general method of Lipscomb and Hoffmann.[5] The results are given for the different mechanisms in Figure 1.

In the present study Prentice–Hall models were used for each species along the reaction coordinate and the x, y, z coordinates for each carbon and hydrogen atom were obtained by measurement. The drawings in Figure 1 can be considered to be different cross sections of the general potential energy surface leading from reactant barrelene (**1** or **3**) to semibullvalene (**2**, **4**, or **5**).



a. Mechanism I b. Mechanism I′ c. Mechanism II

Figure 1. Potential energy *vs.* reaction coordinate for three mechanisms: ○, ground-state curve, ●, excited-state curve.

Mechanism I (Figure 1a) leads on excitation to an electronically excited species requiring an appreciable activation energy (note the minimum available to excited **3** as seen in Figure 1b) to bridge concertedly to give diradical **7**. Interestingly, a slight variation (mechanism I′), in which bridging of the excited state occurs stepwise, circumvents the large barrier; see Figure 1b. However, the main excited-state minimum is positioned above the barrelene surface and vertical demotion should lead back to reactant. The surfaces for mechanism II are such that vertical excitation affords a species with sufficient vibrational energy to surmount the barrier leading to the main excited-state minimum, and this lies above an electronic ground-state minimum which leads preferentially to semibullvalene product. We conclude that this partial exploration of the potential energy surfaces is in accord with the experimental observation of mechanism II.

We also point out that the barrelene to semibullvalene conversion is one example of a general type of excited-state transformation in which a divinylmethane moiety is converted into a vinylcyclopropane group. Some examples are the dibenzobarrelene to dibenzosemibullvalene transformation,[6a] the benzonorbornadiene to tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene reaction,[6b] the 5,5-dimethyl-1,3,6-heptatriene conversion,[6c] the 1,3,6-cyclooctatriene to bicyclo[5.1.0]-2,5-octadiene photolysis,[6c,d] the 1,3-diphenylpropene to 1,2-diphenylcyclopropane irradiation,[6e] and the bicyclo[4.2.2]-2,4,7,9-decatetraene to bullvalene reaction.[6f]

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(5) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); (b) *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963). (d) The energies obtained are too large and carry only qualitative significance. It is of importance, nevertheless, to provide experimental tests of the value of the extended Hückel method.

(6) (a) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 2882 (1966); (b) J. R. Edman, *ibid.*, **88**, 3454 (1966); (c) W. B. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); (d) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964); (e) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (f) M. Jones and L. T. Scott, *ibid.*, **89**, 150 (1967).

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Atomic Silicon. Reaction with Trimethylsilane

Sir:

Silicon chemistry has been studied by the nuclear-recoil technique employing the reactions $^{31}PH_3$ +