tion environment of each iron atom is octahedral with the cyclopentadienyl group occupying three coordination sites; the tin and two carbonyls are located at the three remaining sites. The bonding in the [π-C_5H_5-$Mo(CO)_3$] moiety is similar to that in [π-$C_5H_5Mo(CO)_3]_2$[6] and [(π-$C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4$][7] in which the metal atom is a seven-coordinated atom with the cyclopentadienyl group occupying three coordination sites.

Bond lengths and interatomic angles are given in Table I. The tin–molybdenum bond length of 2.891 A is the first such bond distance reported. It is considerably shorter than the expected distance of 3.00 A based on the sum of the covalent radii of tin (1.39 A)[8] and molybdenum (1.61 A).[6,7] The two tin–iron bond lengths agree well with other bond distances between these two metals.[2] The tin–chlorine bond length is exceptionally long and exceeds the distance of 2.43 A found in $Cl_2Sn[\pi$-$C_5H_5Fe(CO)_2]_2$.[2] The interatomic angles associated with the coordination environment of the tin atom are distorted considerably from the tetrahedral value. The greatest amount of tetrahedral angle distortion involves the lighter and less bulky chlorine atom. The Cl–Sn–M angle is decreased in each case in order to permit the M–Sn–M′ angles to increase. The orientations of the two cyclopentadienyl ligands bonded to the two iron atoms in this compound are almost identical with each other and are similar to the ring orientation observed in $Cl_2Sn[\pi$-$C_5H_5Fe(CO)_2]_2$.[2] The orientation of the cyclopentadienyl ligand bonded to the molybdenum atom is distinctly different from that found in [π-$C_5H_5Mo(CO)_3]_2$[6] and [π-$(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4$];[7] the ring is rotated approximately 36° from the orientation observed in the latter two compounds.

Table I. Bond Distances and Interatomic Angles and Their Estimated Standard Deviations[a]

Bond	Distance, A	Angle	Degrees
Sn–Mo	2.891 (5)	Mo–Sn–Fe_1	115.8 (2)
Sn–Fe_1	2.583 (7)	Mo–Sn–Fe_2	117.9 (2)
Sn–Fe_2	2.598 (7)	Mo–Sn–Cl	98.4 (3)
Sn–Cl	2.50 (1)	Fe_1–Sn–Fe_2	115.6 (2)
Mo–$C_{(ring)}$	2.35 (5)[b]	Fe_1–Sn–Cl	107.4 (3)
Mo–$C_{(CO)}$	1.96 (4)[b]	Fe_2–Sn–Cl	97.2 (3)
C–O	1.19 (5)[b]	Mo–C–O	173 (3)[b]
C–C	1.46 (7)[b]	C–C–C	106 (4)[b]
Fe_1–$C_{(ring)}$	2.14 (6)[b]	Sn–Fe_1–$C_{(CO)}$	91 (2)[b]
Fe_1–$C_{(CO)}$	1.68 (6)[b]	Fe_1–C–O	176 (4)[b]
C–O	1.20 (6)[b]	C–C–C	106 (5)[b]
C–C	1.45 (8)[b]	Sn–Fe_2–$C_{(CO)}$	87 (2)[b]
Fe_2–$C_{(ring)}$	2.12 (6)[b]	Fe_2–C–O	174 (5)[b]
Fe_2–$C_{(CO)}$	1.79 (6)[b]	C–C–C	107 (5)[b]
C–O	1.17 (6)[b]		
C–C	1.47 (8)[b]		

[a] Estimated standard deviations in the least significant figures are given in parentheses. [b] Indicates an average value.

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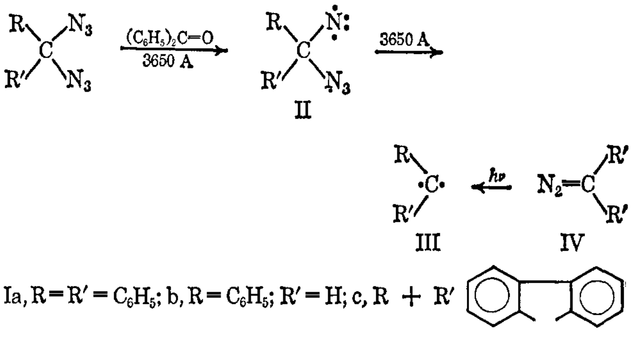
Generation of Methylenes from Geminal Diazides *via* Excited Nitrenes

Sir:

We have observed that sensitized photolysis of geminal diazides (I) at 77°K in rigid matrices yields the corresponding methylenes (III). By use of epr spectroscopy we find that the α-azidonitrenes (II) form initially and are then photolyzed to III. The epr spectra of IIIa–c, which should be very sensitive to the geometry of the methylenes, are identical with those obtained from the corresponding diazo compounds IVa–c in a variety of environments,[1] indicating that the observed structure is an intrinsic property of the methylene, independent of the geometry of the precursor. The I → II transformation is an example of the general preparation of ground-state triplet alkylnitrenes by sensitized photolysis of the corresponding azides, a procedure which has allowed the first observation of the parent methylnitrene.



Ia, R = R′ = C_6H_5; b, R = C_6H_5; R′ = H; c, R + R′

The diazides were prepared by treating the corresponding dihalomethanes with an alkali azide, usually in acetonitrile. Typically, Ia was prepared as follows: 0.01 mole of diphenyldichloromethane in 60 ml of dry acetonitrile was added dropwise to a stirred suspension of 0.05 mole of sodium azide in 30 ml of acetonitrile under dry nitrogen at −35°. The reaction mixture was allowed to warm to ambient temperature overnight. The acetonitrile was removed under vacuum at 30°. The solid residues were extracted with *n*-hexane, filtered, and dried over anhydrous potassium carbonate. The solvent was evaporated under reduced pressure at 25°, yielding a white solid, mp 42–44° (88% yield). *The products should be handled with catuion as a 50-mg sample of Ib detonated when it came into contact with a hot glass surface during the sealing of an ampoule.*

Irradiation of a purified sample[2] of I in Fluorolube, tetrahydro-2-methylfuran, or other solvents at 77°K

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(6) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27, 809 (1957).

(7) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 87, 2576 (1965).

(8) D. H. Olson and R. E. Rundle, *Inorg. Chem.*, 2, 1310 (1963).

(1) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray *J. Chem. Phys.*, 40, 2408 (1964); A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964).

(2) The sample of Ic available was less than 25% diazide. However, its behavior was completely parallel to that of the pure samples of Ia and Ib.

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

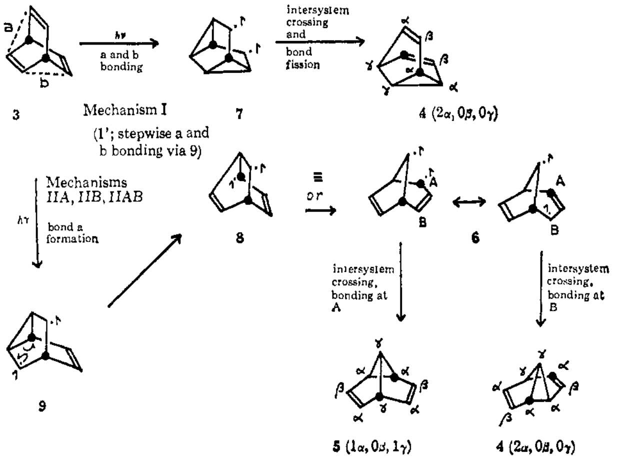
Sir:

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

1 2 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).