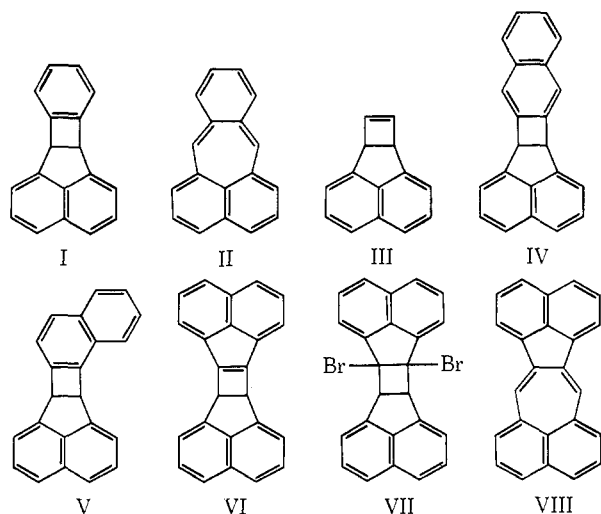


**Energy Barriers in Photochemical Reactions.**  
**Photochemical Conversion of**  
**6b,12c-Dihydrocyclobuta[1,2-a:3,4-a']bisacenaphthylene**  
**(Dehydroheptacyclene) to**  
**Dinaphth[de-1,2,3:d'e'-5,6,7]azulene**

Sir:

It has been reported<sup>1</sup> that the photochemical ring opening of I to II does not proceed after absorption of a



single photon but occurs when the metastable triplet state absorbs another photon. The observation was interpreted in terms of unreactive  $S_1$  and  $T_1$  states, separated by energy barriers in the excited hypersurfaces from product geometries. The triplet barrier can be overcome using energy of the second photon. Simple MO theory permitted a rationalization of the presence of such barriers in terms of correlation diagrams and predictions of some related molecules in which symmetry-imposed barriers should be present (III–V) and others in which they should be lower or absent altogether (e.g., VI).<sup>2</sup> The predicted occurrence of the two-photon process has already been verified<sup>3</sup> for III–V.

If the concept of energy barriers intervening in the singlet and triplet photochemical processes  $I \rightarrow II$  is correct, it might be possible to induce a change in the reaction mechanism by using shorter wavelength radiation. When the photon energy is sufficient to bring the molecule over the barrier in the singlet hypersurface, there may be finite probability that the molecule will overcome the barrier before it loses the additional energy by internal conversion and thermal equilibration with the medium. Since the latter process is fast, travel across the barrier would also have to be fast in order to compete successfully, but such an exceedingly fast photochemical process occurs in the triplet manifold<sup>1,3</sup> and thus would not be surprising in the singlet state.

(1) J. Michl and J. Kolc, *J. Amer. Chem. Soc.*, **92**, 4148 (1970).

(2) (a) J. Michl and J. Kolc, presented at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, Switzerland, July 12–18, 1970; J. Michl, *J. Amer. Chem. Soc.*, **93**, 523 (1971); *Mol. Photochem.*, **4**, 287 (1972); (b) J. Michl in "Chemical Reactivity and Chemical Paths," G. Klopman, Ed., Wiley, New York, N. Y., Chapter 8, in press.

(3) (a) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970); (b) J. Kolc, A. Manzara, and J. Michl, presented at International Symposium on Organic Chemistry of the Excited State, Reading, Great Britain, July 24–27, 1972; J. Kolc and J. Michl, Abstracts, First Rocky Mountain Regional Meeting of the American Chemical Society, Fort Collins, Colo., June 30–July 1, 1972, p 32; (c) J. Kolc and J. Michl, *J. Amer. Chem. Soc.*, **95**, 7391 (1973).

We wish to report an observation of such a change in mechanism for I and for VI, which we have synthesized for the purpose of this study.

Irradiation of an equimolar mixture of acenaphthylene and 1,2-dibromoacenaphthylene in a benzene-pentane solvent under  $N_2$  to low conversions (ca. 15 hr, medium-pressure Hg arc, Pyrex filter) gave 14% isolated yield of a mixed dimer (VII), mp 230° dec. Heptacyclene and tetrabromoheptacyclene were not formed in significant amounts.<sup>4</sup> Elemental analysis and spectra confirm the expected structure VII and slightly favor cis stereochemistry by comparison with the heptacyclenes:  $m/e$  460 ( $M^+$ );  $uv_{max}$  (dioxane), 293 ( $\epsilon$  13,000), 220 nm (140,000); nmr (chloroform- $d$ , 100 MHz)  $\tau$  4.67 (s, 1 H), 2.6–2.9 (m, 6 H). Debromination of VII with zinc in tetrahydrofuran at room temperature afforded yellow somewhat unstable VI in 75% yield. Its structure was secured by spectroscopy:  $m/e$  302 ( $M^+$ ); nmr (chloroform- $d$ , 100 MHz),  $\tau$  4.46 (s, 1 H), 2.2–2.8 (m, 6 H);  $uv_{max}$  (dioxane), 343 nm ( $\epsilon$  5300 sh), 323 (13,000), 224 (115,000), shape close to sum of acenaphthene and acenaphthylene.

In agreement with our previous report,<sup>1</sup> irradiation of solutions of I in EPA glass at  $-196^\circ$  with monochromatic radiation of wavelengths 254 nm and longer (metallic vapor lamps, interference filters) causes no detectable reaction. Simultaneous irradiation with visible light of wavelengths above 360 nm, known to be absorbed by naphthalene triplet, causes easily detectable formation of II (the visible light alone has no effect). On the other hand, monochromatic irradiation with 229 nm and particularly 214 nm light causes similarly rapid formation of II without irradiation by visible light, and the initial rate of formation of II is proportional to the first power of light intensity. Thus, the photochemical reaction of the molecule possessing excess energy is able to compete successfully with return to thermally equilibrated  $S_1$  and  $T_1$  states. Such return, however, occurs as well, as shown by an observed increase in the initial rate of formation of II when visible irradiation is added to short-wavelength monochromatic irradiation.

Under the same conditions, irradiation of rigid solutions of VI with monochromatic light of wavelengths 277 nm and longer causes no detectable reaction. Simultaneous irradiation with visible light has no detectable effect, which is compatible with the fact that phosphorescence of VI is extremely weak or absent altogether (cf. acenaphthylene phosphorescence<sup>5</sup>). Monochromatic irradiation at 254 nm and shorter wavelengths leads to appearance of the highly distinctive<sup>3c</sup> absorption spectrum of VIII, identified by comparison with an authentic sample prepared according to ref 6. The

(4) Photocycloadditions of acenaphthylene triplet to olefins are now well known. See ref 3a; B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970); W. Hartmann and H. G. Heine, *Angew. Chem., Int. Ed. Engl.*, **10**, 272 (1971); J. E. Shields, D. Gavrilovic, and J. Kopecký, *Tetrahedron Lett.*, 271 (1971); ref 5. We presume that 1,2-dibromoacenaphthylene triplet is efficiently formed (internal heavy atom effect, cf. ref 5) and reacts similarly. As ascertained in a separate experiment, 1,2-dibromoacenaphthylene dimerizes extremely inefficiently, possibly for steric reasons. This was noted independently by D. A. Herold (M. S. Thesis, University of North Carolina, Chapel Hill, N. C., 1972). Absence of large amounts of heptacyclene in our reaction mixture suggests that energy transfer to 1,2-dibromoacenaphthylene is very efficient.

(5) W. I. Ferree, Jr., and B. F. Plummer, *J. Amer. Chem. Soc.*, **95**, 6709 (1973).

(6) H. J. Bestmann and D. Ruppert, *Angew. Chem., Int. Ed. Engl.*, **7**, 637 (1968).

initial rate of formation of VIII depends linearly on light intensity indicating a normal one-photon mechanism.

The barrier in the photochemical process VI  $\rightarrow$  VIII is higher than had been expected from simple theory.<sup>2</sup> In terms of correlation diagrams, this may be related to the fact that the MO's of acenaphthylene involved, although of correct nodal properties, have relatively small expansion coefficients at the double bond where their assistance is needed during the reaction.<sup>2b</sup>

Further work along these lines as well as exploration of synthetic possibilities opened by the availability of VI and VII are in progress.

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### Stereochemistry of Chloride Displacement from Silacyclobutanes

Sir:

The stereochemistry of reactions at asymmetric silicon atoms has been studied in a number of different chiral organosilane systems with results which have indicated that the stereochemical outcome depends on the nature of entering and leaving groups and sometimes the solvent but not normally on organosilane structure.<sup>1</sup> The first significant deviation from this type of behavior was recently reported.<sup>2,3</sup> In the 1-phenyl-1-silaacenaphthene ring system, both inversion and retention are reasonable stereochemical possibilities, but only retention is observed, even in reactions which proceed with predominant or complete inversion of configuration at Si in other chiral organosilanes. Sommer postulated<sup>2</sup> that the stereochemical crossover is associated with angle strain at Si. This observation demands confirmation in other angle strained systems. We now wish to report the stereochemistry of reactions in the strained 1,2-dimethyl-1-silacyclobutane ring system.

Dubac, *et al.*, have reported<sup>4</sup> the displacement of *tert*-butoxide from 2-methyl- and 3-methyl-1-silacyclobutanes by methylmagnesium iodide or *n*-butyllithium or LiAlH<sub>4</sub>, all of these reactions being proposed to be stereospecific with retention. However, similar reactions involving displacement of alkoxide in nonstrained systems also proceed with retention.<sup>1a,b,5</sup> The same authors reported the reduction of 1,2-dimethyl-1-chloro-1-silacyclobutane by LiAlH<sub>4</sub> to be nonstereoselective.<sup>4</sup>

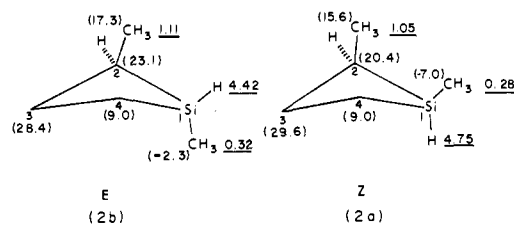
(1) (a) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965; (b) R. Corriu and J. Massé, *Bull. Soc. Chim. Fr.*, 3491 (1969); (c) H. Sakurai and M. Murakami, *J. Amer. Chem. Soc.*, **94**, 5080 (1972).

(2) D. N. Roark and L. H. Sommer, *J. Amer. Chem. Soc.*, **95**, 969 (1973).

(3) Certain resonance-stabilized organolithium and magnesium reagents are reported to give different results in cyclic systems for reasons unrelated to those under discussion here: R. Corriu and J. Massé, *J. Organometal. Chem.*, **34**, 221 (1972).

(4) J. Dubac, P. Mazerolles, and B. Serres, *Tetrahedron Lett.*, 3495 (1972).

(5) R. Corriu and G. Royo, *Bull. Soc. Chim. Fr.*, 1497 (1972); R. Corriu and J. Massé, *J. Organometal. Chem.*, **35**, 51 (1972).



**Figure 1.** <sup>1</sup>H (underlined) and <sup>13</sup>C (in parentheses) chemical shifts for (*E*)- and (*Z*)-1,2-dimethyl-1-silacyclobutane, in CDCl<sub>3</sub> relative to TMS.

We have reinvestigated this latter reaction and find it to be greater than 95% stereospecific.

Silacyclobutane ring closure by the method of Damrauer<sup>6</sup> afforded in 75% yield a 60:40 mixture, **1a** and **1b**, respectively, of the two isomers of 1,2-dimethyl-1-chloro-1-silacyclobutane. The ratio of the two isomers was determined from the relative intensities of the SiMe protons in the nmr (CCl<sub>4</sub>), **1a** ( $\delta$  0.55) and **1b** ( $\delta$  0.62). Enrichment to an 80:20 mixture was accomplished by careful distillation on a 7-cm Vigreux column. Reduction of the 80:20 mixture of **1a** and **1b** with LiAlH<sub>4</sub> in diethyl ether gave an 80:20 mixture, **2a** and **2b**, respectively, of the two isomers of 1,2-dimethyl-1-silacyclobutane, as determined by glpc.<sup>7</sup> Similarly, reduction of the original 60:40 mixture of **1** gave a 60:40 mixture of **2** indicating the reaction is stereospecific.

In order to determine the stereochemistry of the reaction, **2a** and **2b** were separated by preparative glpc.<sup>8</sup> The structures of **2a** and **2b** were assigned from <sup>1</sup>H and <sup>13</sup>C chemical shifts (Figure 1).<sup>9</sup> No attempt has been made to judge the relative stabilities of silacyclobutane conformers. The silacyclobutane ring is known to be puckered but also to be flipping extremely rapidly on an nmr time scale.<sup>10</sup> In many substituted cycloalkanes, substituents exert an influence on the chemical shifts of protons on an adjacent carbon that is stereospecific and greater when the substituent and proton are cis to one another than when they are trans.<sup>11</sup> Methyl groups generally show the effect of shielding cis protons on adjacent carbons,<sup>12</sup> and, in the *E* isomer in our system, shielding of the proton on Si by the cis C<sub>2</sub>-Me gives rise to a resonance at substantially higher field ( $\delta$  4.42) than the Si-H of the *Z* isomer ( $\delta$  4.75). Also, the Si-Me and C<sub>2</sub>-Me protons appear at higher field (slightly, but consistently) in the *Z* isomer where they are cis to one another. The proton on C<sub>2</sub> could not be resolved from

(6) R. Damrauer, R. A. Davis, M. T. Burke, R. A. Karn, and G. T. Goodman, *J. Organometal. Chem.*, **43**, 121 (1972).

(7) Glpc analysis was carried out using a 16 ft  $\times$  1/8 in. column of 15% Apiezon L on 60-80 mesh Chromosorb W at 85°.

(8) Preparative glpc was carried out on a Perkin-Elmer Model 21 using a 5 ft 4 in.  $\times$  3/4 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W operating at a temperature of 85° and a carrier gas flow rate of 270 ml/min.

(9) Nmr spectra were obtained on approximately 25% CDCl<sub>3</sub> solutions employing Varian HA-100 and CFT-20 spectrometers for pmr and cmr determinations.

(10) L. V. Vilkov, V. S. Mastryukov, Yu. V. Baurava, V. M. Vdovin, and P. L. G. Grinberg, *Dokl. Akad. Nauk SSSR*, **117**, 1084 (1967); J. Laane and R. C. Lord, *J. Chem. Phys.*, **48**, 1508 (1968); W. C. Pringle, Jr., *ibid.*, **54**, 4979 (1971).

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(12) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 747 (1962); E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Lett.*, 741 (1962); H. Booth, *Tetrahedron*, **22**, 615 (1966); R. C. Fort and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).