consideration of the reaction's mechanism, then, will necessarily await the unambiguous identification of the boron-containing byproducts.

Registry No. n-$B_{18}H_{22}$, 21107-56-2; $Me_4NB_9H_{12}$, 67537-67-1.

Dimethylsilylene: Its Optical Absorption Spectrum and Reaction Kinetics[1]

A. S. Nazran, J. A. Hawari, and D. Griller*

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

I. S. Alnaimi and W. P. Weber*

Department of Chemistry
University of Southern California
*Los Angeles, California 90007*
Received May 21, 1984

Photolysis of dodecamethylcyclohexasilane[2] (I) has been used as a convenient source of dimethylsilylene (II) in solution[3-9] and in the gas phase[10] (eq 1). The reaction has also been used to

$$c\text{-}(Me_2Si)_6 \xrightarrow{h\nu} c\text{-}(Me_2Si)_5 + Me_2Si: \qquad (1)$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
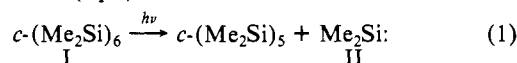
generate the silylene in hydrocarbon and argon matrices so that its infrared,[11] UV–visible[12] (λ_{max} = 450 nm), and fluorescence spectra[12] could be recorded. In fact, irradiation in the UV–visible band at 450 nm has been used to induce rearrangements of II which have been monitored by infrared spectroscopy.[11] We report results which show that this system is more complicated than the current literature suggests and which demonstrate that the UV–visible spectrum of II has been incorrectly assigned or that there is a substantial shift ($\sim$100 nm) in its absorption maximum in going from matrices to solution.

Laser flash photolysis[13] (λ = 308 nm, pulse width 8 ns, power 80 mJ per pulse) of I (10^{-4} M), in 3-methylpentane or cyclopentane solvent at 293 K, gave an absorption band at 350 nm. This transient grew with a lifetime of 74 ns and decayed in 8 μs. No band was detected at 450 nm.

Quenching experiments suggest that the transient absorption at 350 nm was due to dimethylsilylene (II). Addition of triethylsilane, an effective silylene scavenger,[4,9] quenched the transient absorption (eq 2). The rate constant for this reaction, k_2, was

$$Me_2Si: + Et_3SiH \rightarrow Et_3SiSi(Me)_2H \qquad (2)$$
$$\text{III}$$
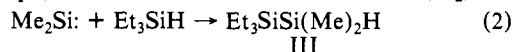
measured by monitoring the pseudo-first-order rate constant, k_{obsd}, for the disappearance of the transient as a function of substrate concentration, eq 3, where k_0 describes the decay of the transient

$$k_{obsd} = k_0 + k_2[Et_3SiH] \qquad (3)$$

in the absence of the quencher. It was found that $k_2 = 2.0 \times 10^6$ M^{-1} s^{-1} in cyclopentane solvent.

In similar vein, methanol quenched the absorption spectrum at 350 nm (eq 4), although the reaction kinetics were a little

$$Me_2Si: + MeOH \rightarrow MeOSi(Me)_2H \qquad (4)$$
$$\text{IV}$$
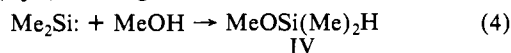
unusual. In cyclopentane as solvent and at methanol concentrations below 0.05 M, the rate constant for quenching, k_4, was found to be 3.1×10^7 M^{-1} s^{-1} while above this concentration it was 5.7×10^6 M^{-1} s^{-1}. Similar effects have been observed in competition studies of the insertion reactions of dimethylsilylene into Si–H and O–H bonds.[9] They are presumably related to changes in the distribution of methanol monomers and oligomers that occur when the alcohol concentration is varied. However, we were unable to account for the sharp change in reaction kinetics by quantitative analysis of the data in these terms, although such an approach was successful for arylchlorocarbenes.[14]

The methanol quenching experiment was repeated in tetrahydrofuran as solvent, which was chosen for its ability to prevent oligomerization of the methanol.[15] The absorption spectrum was "blue shifted" by the solvent such that λ_{max} = 300 nm. In the absence of methanol the absorption grew with a lifetime of 30 ns and decayed with one of 8 μs. The rate constant for reaction with methanol was found to be 3.1×10^7 M^{-1} s^{-1}. As expected, tetrahydrofuran eliminated the unusual kinetic behavior, and the rate constant measured in this solvent was quite similar to that observed at low methanol concentrations in cyclopentane.

Product studies were carried out by photolyzing I (0.05 M) and triethylsilane (2.5 M) in cyclopentane in a photochemical reactor (300 nm). Analysis by GC/MS showed that III had been formed in 85% yield at 64% conversion of I. In addition, product studies were carried out in cyclopentane solution with methanol (0.38 M) as substrate. While the simple insertion product IV was formed in >95% yield V and VI were detected in yields of 1% and 2%,

$$MeO(Me_2Si)_3H \qquad MeO(Me_2Si)_4H$$
$$\text{V} \qquad\qquad \text{VI}$$

respectively, at 43% conversion of I. Similar results were obtained when decamethylcyclopentasilane was used as the dimethylsilyene source.[16]

To confirm that the absorption spectrum at 350 nm was indeed due to dimethylsilylene, we carried out a competition study by photolyzing a mixture of I (0.04 M), methanol (0.27 M), and triethylsilane (0.22 M) in cyclopentane to 80% conversion of I. Product analysis indicated that the ratio k_4/k_2 was 2.1 whereas the laser flash photolysis results (vide supra) gave 2.4.

While we were unable to detect the 450-nm absorption previously assigned[12] to dimethylsilylene by photolysis at 308 nm, we were able to detect an absorption at a similar wavelength by photolysis with much higher energy radiation (249 nm, pulse width 8 ns, power up to 250 mJ per pulse). Under these conditions, a band at 470 nm was detected along with the 350-nm band. The former was present immediately after the laser flash and decayed in 192 ns and could not be quenched by methanol (0.2 M) or triethylsilane (0.15 M).

Product studies carried out in methanol as solvent, with photolysis of I at 250 nm, revealed no new products, which was consistent with this observation and suggests that the 470-nm transient was a species, present in low concentration, that gave insignificant yields of chemical products *or* that it decomposed to give dimethylsilylene.

(1) Issued as NRCC-23768.
(2) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1963**, *28*, 1651.
(3) See, for examples, ref 4–9.
(4) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.
(5) Sakurai, H.; Murakami, M. *J. Am. Chem. Soc.* **1972**, *94*, 5081. Ando, W.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1979**, 655. Tzeng, D.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1451. Gu, T.-Y. Y.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1641. Tortorelli, V. J.; Jones, M., Jr. *J. Chem. Soc., Chem. Commun.* **1980**, 785; *J. Am. Chem. Soc.* **1980**, *102*, 1425. Chihi, A.; Weber, W. P. *J. Organomet. Chem.* **1981**, *210*, 163; *Inorg. Chem.* **1981**, *20*, 2822.
(6) Gu, T-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7.
(7) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095.
(8) Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981**, *20*, 1302.
(9) Steele, K. P.; Tzeng, D.; Weber, W. P. *J. Organomet. Chem.* **1982**, *231*, 291 and references therein.
(10) Davidson, I. M. T.; Lawrence, F. T.; Ostah, N. A. *J. Chem. Soc., Chem. Commun.* **1980**, 859. Davidson, I. M. T.; Ostah, N. A. *J. Organomet. Chem.* **1981**, *206*, 149.
(11) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845. Arrington, C. A.; Klingensmith, K. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 525.
(12) Drahak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427.
(13) For a detailed description, see: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.
(14) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.
(15) Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974.
(16) These results are similar to those found by Ishikawa and Kumada who concluded that such materials were secondary products derived from photolysis of octamethylcyclotetrasilane.[4] When 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene was used as a source of dimethylsilylene, only the monoinsertion product was detected.[17]
(17) Hawari, J. A.; Griller, D. *Organometallics* **1984**, *13*, 1123.

The present results imply that the photolysis of I gives dimethylsilylene, which has an absorption spectrum at 350 nm in solution. The large difference in absorption maxima for the spectra reported in solution and in matrices (450 nm) point either to a very large matrix effect or to an incorrect assignment.

Parent Azulvalene and Dewar Azulene. Syntheses and Isomerizations of Tetracyclo[5.3.0.0²,⁴.0³,⁵]deca-6,8,10-triene and Tricyclo[5.3.0.0²,⁵]deca-3,6,8,10-tetraene[1]

Yoshikazu Sugihara,* Takashi Sugimura, and Ichiro Murata*

Department of Chemistry, Faculty of Science Osaka University, Toyonaka, Osaka 560, Japan
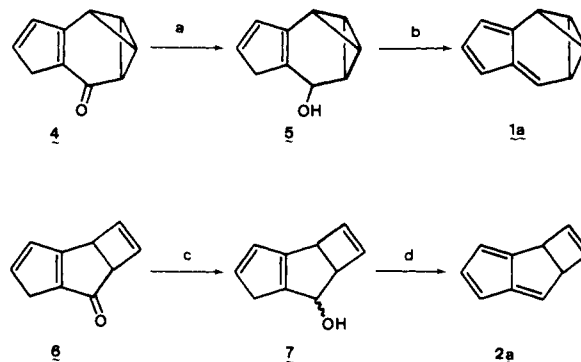
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It is well-known that the synthetic achievement of the valence isomers of benzenoid hydrocarbons promoted a better understanding not only of their unique strained structures but also of the potential energy surfaces between these isomers.[2] Nonalternant hydrocarbons[3] hold the complementary position to alternant hydrocarbons as far as the nature of aromatic hydrocarbons is concerned. Therefore, the valence isomers of these nonalternant molecules are of interest especially in the study on their mutual interconversions and isomerizations. While some derivatives of azulvalene (**1b**),[4] Dewar azulene (**2b**),[5] and Dewar heptalene (**3**)[6] have recently been synthesized by us, the methoxy

1a, X = H
1b, X = OCH$_3$

2a, X = H
2b, X = OCH$_3$

3
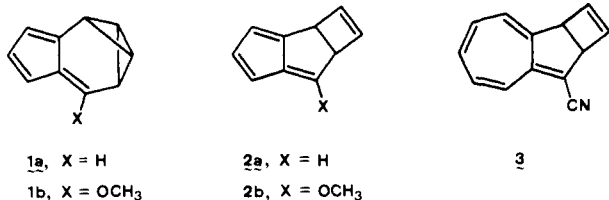
substitution in **1b** and **2b** causes some perturbation of the electronic structure intrinsic to the azulene isomers. To eliminate this complication the syntheses of the parent compounds **1a** and **2a** have been intended.

After previous unsuccessful approaches toward their syntheses,[7] **1a** and **2a** have now been prepared following a formal 1,6-dehydration sequence (Scheme I).[8] Tetracyclic dienone **4**[4,9] was

(1) Taken in part from: Sugimura, T. Ph.D. Thesis, Osaka University, Japan, 1984.

(2) For reviews, see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. van Tammelen, E. E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 738. Burger, U. *Chimia* **1979**, *33*, 147.

(3) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961. Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966.

(4) Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1981**, *103*, 6738.

(5) Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1982**, *104*, 4295.

(6) Sugihara, Y.; Wakabayashi, S.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 6718.

(7) All attempts to convert **1b** and **2b** into parent hydrocarbons by way of hydride reduction failed (cf.: Strum, E.; Hafner, K. *Angew. Chem.* **1964**, *76*, 862. Pauson, P. L.; Sandhu, M. A.; Watts, W. E. *J. Chem. Soc. C* **1968**, 860).

Scheme I[a]

reduced to give the alcohol **5**, which was extracted with dichloromethane and used in the next step without purification. To a solution of **5** and 4-(dimethylamino)pyridine in dichloromethane, acetyl chloride was added dropwise at 0 °C. After 2 h the product was extracted into pentane, washed with water, and dried (MgSO$_4$). The solution was filtered through a short column of silica gel (deactivated with 20% H$_2$O, pentane) to afford **1a**[10] as an acid- and air-sensitive orange oil (25% yield).

Tricyclic ketone **6**[11] was reduced to yield the alcohol **7**. Treatment of **7** in a mixture of dichloromethane and carbon tetrachloride with tri-n-butylphosphine at 0 °C for 0.5 h produces **2a**[12] as an air-sensitive yellow oil in 40% yield, which can be isolated virtually pure through chromatography on a short column of silica gel (deactivated with 20% H$_2$O, pentane).

On thermolysis, **1a** undergoes quantitative isomerization to azulene with first-order kinetics.[13] From an Arrhenius plot (r = 0.9995) of the data, the activation parameters, $\Delta H^{\ddagger}$ = 27.5 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = −4.8 ± 1.1 eu, E_a = 28.6 ± 0.5 kcal/mol, and log A = 12.3 ± 0.3, are obtained. **2a** was also converted (60–80%) thermally to azulene with partial decomposition. From the several runs the activation energy for the process was roughly estimated to be ∼32 kcal/mol, deduced from the decay rate of **2a**.[13] The activation energy for the thermolysis of **1a** is substantially smaller than that of **1b**.[4] Furthermore comparison of the activation energies for **1a** and **2a** shows that **1a** directly

(8) All the reactions were carried out in argon atmosphere. All solvents used for the reactions and workup were deaerated by bubbling with argon and distilled under argon before use. It should be noted that the synthetic methods described in the text provide azulene-free **1a** and **2a**. This makes the purification of these labile molecules easier. **1a** and **2a** were too unstable to allow their combustion analyses; however, these structures were unequivocally established by their characteristic NMR spectra.[10,12]

(9) **4** is now available conveniently from 9-chlorotetracyclo[5.3.0.0²,⁴.0³,⁵]dec-1(7)-en-6-one, colorless needles, mp 55.5–56.6 °C, which can be stored in a refrigerator without decomposition.[1]

(10) ¹H NMR (100 MHz, CDCl$_3$) δ 6.67 (dd, 1 H, J = 4.8, 1.7 Hz, H-6), 6.31 (dd, 1 H, J = 5.3, 2.0 Hz, H-9), 5.90 (m, 1 H, H-10), 5.83 (ddd, 1 H, J = 5.3, 1.1, 0.8 Hz, H-8), 3.47 (t, 2 H, J = 2.4 Hz, H-3,4), 3.03 (dtd, 1 H, J = 3.9, 2.4, 0.8 Hz, H-2), 2.49 (m, 1 H, H-5); ¹³C NMR (22.5 MHz, CDCl$_3$) δ 137.4, 133.2, 121.3, 116.9, 40.1, 38.5, 36.0; UV (cyclohexane) λ$_{max}$ 281 (ε 11 000), 400 nm (370).

(11) **6** was obtained from tricyclo[5.3.0.0²,⁵]dec-9-en-6-one[4] through allylic bromination with NBS/ABIBN/CCl$_4$ followed by dehydrobromination with KO-t-Bu in ether.[1]

(12) ¹H NMR (100 MHz, CDCl$_3$) δ 6.83 (dd, 1 H, J = 4.8, 2.0 Hz, H-6), 6.81 (dd, 1 H, J = 5.2, 2.1 Hz, H-9), 6.48 (dd, 1 H, J = 2.4, 0.8 Hz, H-4), 6.41 (dm, 1 H, J = 2.4 Hz, H-3), 6.13 (dd, 1 H, J = 5.2, 0.8 Hz, H-8), 6.04 (m, 1 H, H-10), 4.48 (m, 1 H, H-5), 4.00 (m, 1 H, H-2); ¹³C NMR (22.5 MHz, CCl$_4$) δ 140.9 (2 carbons), 140.7, 139.7, 116.9, 113.3, 64.1, 46.2; UV (cyclohexane) λ$_{max}$ 270 (ε 17 000), 384 nm (1400).

(13) A solution of **1a** or **2a** in toluene-d_8 in the presence of a small amount of TMEDA was degassed and sealed in vacuo in an NMR tube, and thermolyses were performed in an NMR cavity. The disappearance of **1a** and the appearance of azulene were monitored by NMR integration. First-order rate constants for **1a** are k^{363} = 1.78 × 10⁻⁵, k^{373} = 4.85 × 10⁻⁵, k^{383} = 1.44 × 10⁻⁴, and k^{393} = 3.44 × 10⁻⁴ s⁻¹. For the thermolysis of **2a**, half-lives are found to be 10 h (393 K), 2 h (403 K), and 50 min (413 K).