Synthesis, Characterization, and Flash Vacuum Pyrolysis Studies of *anti*-[2.2](1,6)Azulenophane

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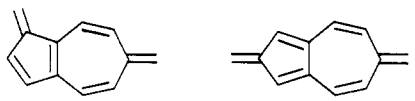
Two short synthetic pathways affording *anti*-[2.2](1,6)azulenophane (3) via fluoride-induced 1,8-eliminations from trimethylsilyl-tetraalkylammonium salts are described. The structural assignment of the title compound 3 is based on spectral data. Results from flash vacuum pyrolysis experiments suggest that 3 fractures at 620 °C to generate the corresponding monomer, 1,6-azulylene (1), a highly reactive polyene.

Introduction

The description of low-lying electronic states of polyenes is an area of intense activity for both theorists and spectroscopists.[1] Our interest in this area[1a] led us to the family of azulylenes. Two of the Kekulē isomers of this set are 1,6-azulylene (1) and 2,6-azulylene (2). Such polyenes are



1 2

reactive intermediates but can in principle be generated by a number of methods. We recently communicated[2] preliminary results on the generation of 2 by flash vacuum pyrolysis (fvp) of its [2.2](2,6)azulenophane dimers.[3,4] [2.2](1,6)Azulenophane (3) is likewise an obvious choice for a fvp precursor of 1. A further incentive for choosing this precursor was the fact that azulenophane 3 was unknown at the outset of this work and syntheses and spectroscopic properties of cyclophanes are interesting in their own right.[4a] Herein we would like to report the successful preparation of *anti*-[2.2](1,6)azulenophane from two different trimethylsilyl-tetraalkylammonium salts. The structural assignment of this compound is based on spectral data.[5] Also described are the results of fvp studies which suggest that 3 fractures cleanly at 620 °C to afford the transient 1. This work therefore lays the groundwork for detailed spectroscopic and kinetic studies of the polyenic transient 1.

Two [2.2]azulenophanes containing two azulene decks have been described in the literature.[6] [2.2](2,6)Azulenophane had been synthesized independently by two groups with a 1,8-Hofmann elimination of the 6-functionalized tetraalkylammonium hydroxide as the cyclophane-generating step[7,8] previous to our results[2] on the 2-functionalized isomer. The known [2.2](1,3)azulenophane was assembled by first coupling the two azulene units to the dithiacyclophane followed by photochemical sulfurextrusion ("sulfur route").[9] Neither of these methods appeared to be applicable to the synthesis of 3[10] but the fluoride-induced trimethylsilyl chloride or trimethylsilyl-tetraalkylammonium salt elimination[11] seemed promising. The fluoride ion promoted eliminations proceed under mild reaction conditions, and the cyclophane yields are relatively high. These results obviously suggest that 1,6-trimethylsilyl-tetraalkylammonium bisfunctionalized azulenes might be well suited precursors for the synthesis of cyclophane 3. The assembly of the 1-(trimethylsilyl-6-methylazulene structure was envisoned to proceed in a regioselective manner using the Hafner azulene synthesis.[12] A method for the functionalization of the 6-methyl group in 6-methylazulene has been worked out in these laboratories,[13] therefore providing, at least in principle, access to the required 1,6-bisfunctionalized trimethylsilyl-tetraalkylammonium azulenes. Two regioisomeric routes suggested by this reasoning are summarized in Scheme I.

Synthesis

[(Trimethylsilyl)methyl]cyclopentadiene was prepared from sodium cyclopentadienide and commercially available (iodo- or (chloromethyl)trimethylsilane in 47% yield.[14] When this product was treated with *N*-butyl-4-methylpyridinium bromide, a 3:1 mixture of 1,6- and 2,6-disubstituted azulenes 4 was obtained in 52% yield. Formation of the 2,6-disubstituted azulene was surprising since exclusive formation of 1-alkylated azulenes had previously been observed when monoalkylated cyclopentadienes were reacted with pyridinium salts under similiar conditions.[12,15] All attempts to separate these two isomers on a preparative scale by column chromatography (silica gel, various impregnated silica gels, alumina (neutral, basic, acidic)), thin-layer chromatography, or fractional distillation at low

(1) (a) Koenig, T.; Wielesek, R. A.; Snell, W.; Balle, T.; Imre, D.; Southworth, S.; Klopfenstein, C. E. *J. Am. Chem. Soc.* **1983**, *105*, 2256 and references cited therein. (b) Schulz, R.; Schweig, A.; Zittlau, W. *J. Am. Chem. Soc.* **1983**, *105*, 2980. (c) Balle, T.; Nitsche, S.; Roth, K.; Haselbach, E. *J. Am. Chem. Soc.* **1984** *106*, 3927. (d) Herrick, D. R. *J. Chem. Phys.* **1981**, *74*, 1239. (e) Spanget-Larsen, J. *Croat. Chim. Acta* **1984**, *57*, 991. (f) Chadwick, R. R.; Gerrity, D. P.; Hudson, B. S. *Chem. Phys. Lett.* **1985**, *115*, 24.

(2) Koenig, T.; Rudolf, K.; Chadwick, R.; Geiselmann, H.; Patapoff, T.; Klopfenstein, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 5024.

(3) (a) Wiersum, U. E. *Aldrichimica Acta* **1984**, *17*, 31. (b) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic: New York, 1980.

(4) Koenig, T.; Southworth, S. *J. Am. Chem. Soc.* **1977**, *99*, 2807. Koenig, T.; Wielesek, R.; Snell, W.; Balle, T. *J. Am. Chem. Soc.* **1975**, *97*, 3225. Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem.* **1971**, *93*, 5034. Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436. (a) For different aspects of cyclophane chemistry, see: Vogtle, F., Ed. *Topics in Current Chemistry*; Springer Verlag: Berlin, 1983; Vols. 113, 115.

(5) Part of this work has been previously communicated, see: Rudolf, K.; Koenig, T. *Tetrahedron Lett.* **1985**, 4835.

(6) For a review on azulenophanes, see: Ito, S.; Fujise, J.; Fukazawa, J. *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vol. II, pp 485-520.

(7) Luhowy, R.; Keehn, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 3797.

(8) Kato, N.; Fukazawa, J.; Ito, S. *Tetrahedron Lett.* **1976**, 2045.

(9) Fukazawa, J.; Aoyagi, M.; Ito, S. *Tetrahedron Lett.* **1979**, 1055.

(10) The acidity of the methyl hydrogens in *N*-[(1-methyl-6-azulyl)-methyl]-*N*,*N*,*N*-trimethylammonium hydroxide is expected to be unusually low due to the dipolar character of azulenes. *N*-[(6-methyl-1-azulyl)methyl]-*N*,*N*,*N*-trimethylammonium hydroxide is expected to be unstable at the temperatures required for Hofmann eliminations.

(11) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 1043.

(12) Hafner, K. *Angew. Chem.* **1958**, *70*, 419.

(13) (a) Robinson, R.; Rudolf, K.; Koenig, T. *J. Org. Chem.* **1985**, *50*, 5871. (b) McDonald, R. N.; Petty, H. E.; Wolfe, N. L.; Pankstelis, J. V. *J. Org. Chem.* **1974**, *36*, 1877.

(14) Kira, M.; Watanabe, M.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5201.

(15) We have found that mixtures of 1,6- and 2,6-disbustituted azulenes are also obtained when other cyclopentadienes are used under these conditions: Rudolf, K.; Koenig, T., unpublished results.

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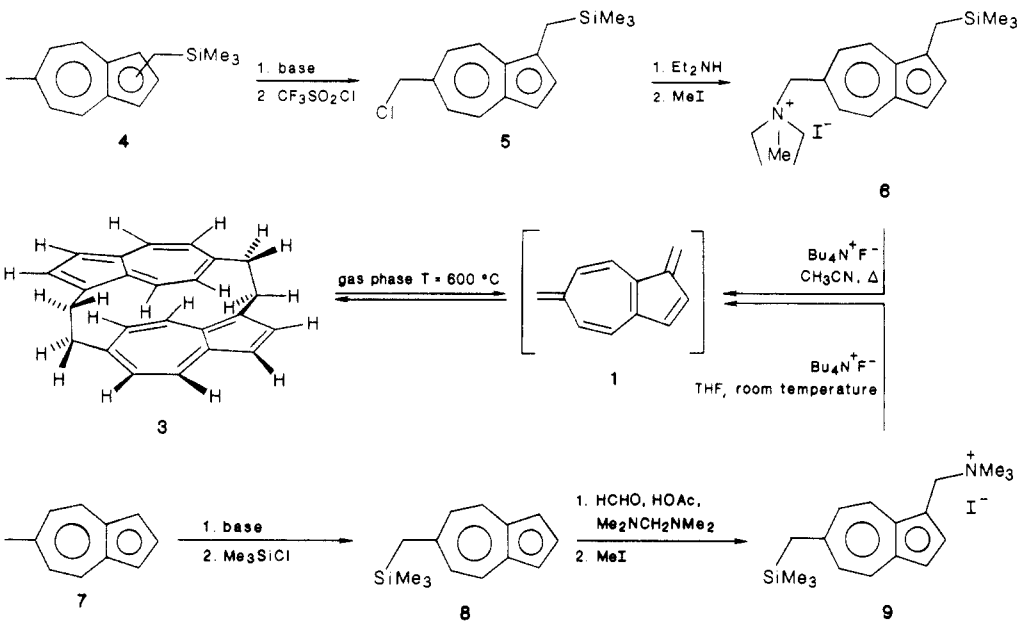
Scheme I

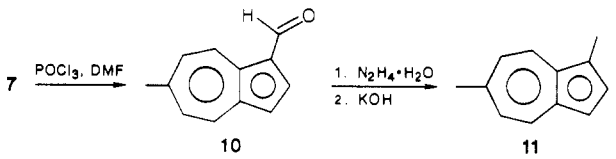


pressure were unsuccessful. The isomeric mixture was therefore chlorinated by using sodium *N*-methylanilide to form the anion followed by treatment with trifluoromethanesulfonyl chloride.[13] Careful column chromatography on sodium borate impregnated silica gel afforded the 6-chloromethyl derivative **5** as a pure compound in 46% yield. The corresponding 2,6-isomer could not be isolated from the reaction mixture. As expected, **5** was easily converted to the corresponding quaternary ammonium–trimethylsilyl salt **6** (Scheme I) but only in 27% yield due to base-induced trimethylsilyl group cleavage under the reaction conditions. Upon treatment of **6** with tetrabutylammonium fluoride in refluxing acetonitrile the target cyclophane **3** was formed in 17% yield (Scheme I). While this route succeeds in yielding **3**, the fact that it involves an inseparable mixture of regioisomers **4** and that the yields are rather poor for the transformation **5** to **6** caused us to seek a more efficient synthetic pathway.

The superior regioselective pathway for the synthesis of [2.2](1,6)-azulenophane (**3**) begins by treatment of 6-methylazulene (**7**) with the conveniently prepared lithium tetramethylpiperidine base. This very easily yields solutions of the lithium 6-methylazulenate salt. The salt formation can be observed by ^{1}H NMR spectroscopy, which proves it to be clean and quantitative.[13a] Subsequent addition of trimethylsilyl chloride gives the silylated azulene **8** in 68% yield. Introduction of the 1-(dimethylamino)methyl group was effected in a regioselective manner analogous to previously published procedures,[16] modified to avoid acid promoted trimethylsilyl group cleavage. Quaternization with methyl iodide proceeds smoothly to give **9** in 79% yield. The iodide salt **9** proved to be thermally unstable in refluxing acetonitrile, and the best conditions that we found for performing the elimination reaction were with tetrabutylammonium fluoride at 22 °C in tetrahydrofuran, which afforded **3** in only 10% yield.

In spite of the low yield in the last step, this procedure is a very short and convenient synthesis of **3**. Starting with the easily available 6-methylazulene, the azulenophane precursor **9** is obtained in 54% overall yield and the azulenophane **3** itself in 5.4% overall yield (for the four steps).

Scheme II



It is important for our purposes that all the synthetic transformations leading to **9** can be scaled-up without any problems.

1,6-Dimethylazulene (**11**) was needed here as monomeric reference compound for the dimeric cyclophane **3**. It has been previously synthesized,[17] but a more convenient pathway was found (Scheme II) in an approach analogous to the one used by Hafner and co-workers.[18]

Spectral Characterization

The new azulenophane **3** was characterized first by combustion analysis and high-resolution mass spectrometry. The mass spectrum (70 eV) shows a molecular ion peak at *m/e* 308.156 (calculated for $C_{24}H_{20}$: 308.156) and a base peak at *m/e* 154, associated with the cleavage of the two ethano bridges. The infrared spectrum shows strong absorptions at 1560 and 1387 cm^{-1}, typical for azulenic compounds. Figure 1 displays the ^{1}H NMR spectrum of **3** which was the same for the material obtained from either **6** or **9**. The structural assignments of **3** rests on ^{13}C NMR and ^{1}H NMR data. The ^{13}C spectrum shows ten aromatic carbon resonances including four quaternary carbons and two aliphatic resonances as required for a [2.2](1,6)azulenophane possessing either a C_2 symmetry axis or a center of inversion. All aromatic signals in the ^{1}H NMR spectrum are split into doublets. These observations confirm 1,6-disubstitution on both of the azulene units.

There are six isomers of the same ethano–azulene connectivity as **3** when both conformations and regioisomers are considered (Figure 2). First, there are two regioisomers, one with ethano bridges connecting the 1,1′- and 6,6′-positions of the azulene rings (syn regioisomers **3b** and

(16) Anderson, A. G.; Anderson, R. G.; Fujita, T. S. *J. Org. Chem.* **1962**, *27*, 4535.

(17) Scott, L. T.; Minton, M. A.; Kirms, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 6311.

(18) Hafner, K.; Bernhard, C. *Ann.* **1959**, *625*, 108.

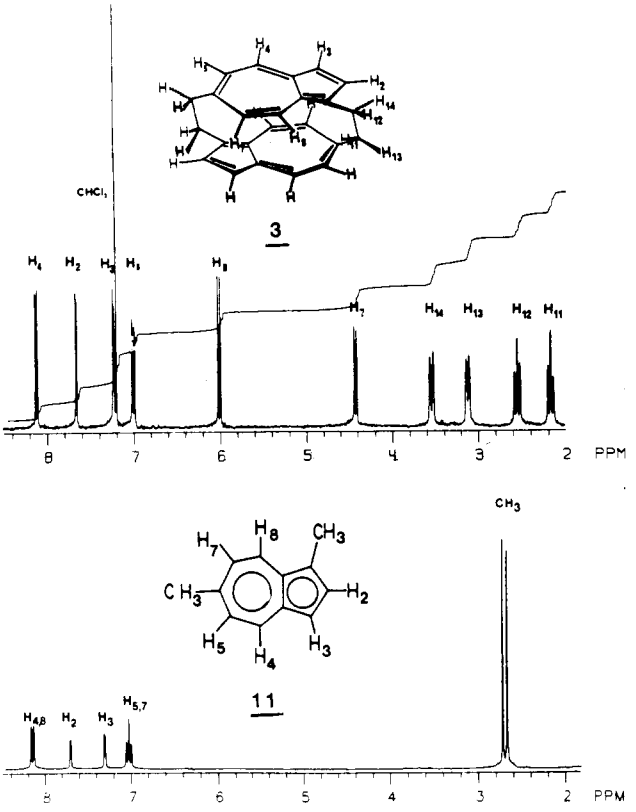


Figure 1. ^{1}H NMR spectra of [2.2](1,6)azulenophane (**3**) and 1,6-dimethylazulene (**11**).

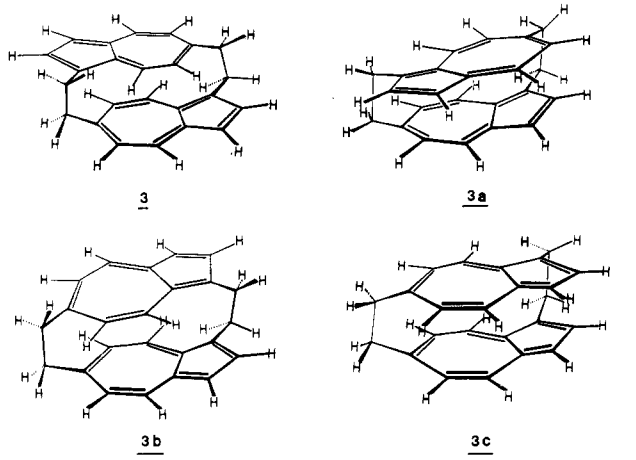


Figure 2. Possible configurational and conformational isomers of [2.2](1,6)azulenophane (**3**).

3c), the other with the bridges connecting 1,6′- and 6,1′-positions of the azulene rings (anti regioisomers **3** and **3a**). Each of these two configurational ([1,1';6,6']) isomers can exist as either a syn or anti conformation. The anti conformations (**3**, **3b**) show a "stepwise structure" for the aromatic planes. The syn conformations (**3a**, **3c**) feature "face-to-face" stacking of the aromatic planes. Furthermore, the syn configurational isomer possessing the anti conformation **3b** and the anti configurational isomer possessing the syn conformation **3a** are dissymmetric and can exist as enantiomers.

Both of the conformational isomers of the [1,1′;6,6′] (syn) configurational isomer (**3b**, **3c**) should display two distinct AA′BB′ patterns for the two bridging ethano groups, whereas both of the conformational isomers of [1,6′;6,1′] (anti) diastereomer (**3**, **3a**) should show first-order splitting into a ddd for each of the four distinctly nonequivalent methylene bridges in the two ethano bridges. The upfield part of the ^{1}H NMR spectrum clearly shows the first-order behavior and splitting into ddd establishing that the compound obtained here is one of the conformational isomers of the [1,6′;6,1′] (anti) configuration (**3**, **3a**). The upfield portion of the ^{1}H NMR spectrum (2.2–3.8 ppm) can be simulated with the set of coupling constants presented in Table I.

Table I. ^{1}H Chemical Shifts (δ, Diagonal Values), Coupling Constants (J_{ij}, Hz) of the Bridging Methylene Hydrogens and Estimated Dihedral Angles (θ_{ij}) for 3

		J_{ij}		
proton (i,j)	H_{11}	H_{12}	H_{13}	H_{14}
H_{11}	2.17 ppm	11.93 Hz	11.99 Hz	3.00 Hz
θ_{ij} H_{12}	ca. 180°	2.55 ppm	2.82 Hz	13.41 Hz
θ_{ij} H_{13}	J_{gem}	ca. 60°	3.12 ppm	4.59 Hz
θ_{ij} H_{14}	ca. 90°	J_{gem}	ca. 60°	3.54 ppm

The distinction between the two conformations of the [1,6′;6,1′] (anti) configurational isomer (**3**, **3a**) is possible considering interdeck magnetic anisotropy effects. As indicated in Figure 1, two signals assignable to aromatic protons show large upfield shifts (4.4, 6.0 ppm) compared to 1,6-dimethylazulene. The positions of the remaining aromatic resonances are within 0.05 ppm of those for the monomeric reference compound 1,6-dimethylazulene. The anti conformational isomer **3** is expected to display large upfield shifts for the pair of two (H_7, H_8) proton sets related by the inversion center and negligible small changes in chemical shifts for the remaining aromatic signals. The syn conformational isomer **3a** would be expected to show a large upfield shift of one aromatic signal and moderate shifts for several of the others. Therefore, the ^{1}H NMR data are only compatible with formation of the anti conformational isomer **3**, and it is the only cyclophane isolated from either of the two synthetic routes.

The assignment of the individual aliphatic proton resonances was possible with the aid of decoupling experiments. Selective irradiation of the methylene hydrogens proved that the signals at 3.54 and 2.55 ppm are due to protons attached to the further upfield of the two aliphatic carbons. Available ^{13}C NMR data for 6-methylazulene and 1-methylazulene[19] suggest that the further downfield of the two sp^3 carbons is attached to the C-6 position of the azulene ring. The two hydrogens (H_{11}, H_{12}) in close proximity to an adjacent aromatic plane (see Figure 1) are assumed to be upfield from their respective geminal hydrogens (H_{13}, H_{14}), which are further removed from the adjacent aromatic rings. These considerations lead to the suggested assignment (Figure 1, Table I). This assignment is also consistent with rules for the dependence of coupling constants on the dihedral angle between the coupled vicinal hydrogens.

The visible part of the electronic spectra of **3**[5] shows some slightly broadened vibrational structure with a maximum at 613 nm, 18-nm red-shifted when compared to **11**. These features, broadening of the bands and a bathochromic shift of the absorption maximum for the first absorption band, are commonly observed for [2.2]-cyclophanes. Compound **3** shows two bands without counterpart in the spectrum of **11** which appear at 462 and 495 nm. Similar bands were observed in [2.2](1,3)azulenophane and ascribed to "transannular π-electron interaction between two facing azulene rings". [2.2](2,6)Azulenophane (**12**) does not show such additional structured bands in the visible region.[7]

(19) Braun, S.; Kinkeldei, J. *Tetrahedron* **1977**, *33*, 1827.

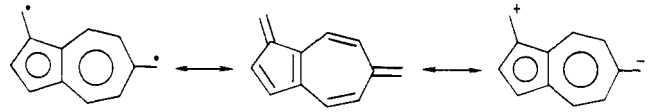
A qualitative evaluation of the first two electronic transitions in [2.2]azulenophanes is possible using the concepts of "through-space" (TS) and "through-bond" (TB) interactions.[20] The TS interaction between the two decks in a cyclophane leads to a splitting of the (Π) basis molecular orbitals giving rise to a new set of + or − combinations.[21a] For azulenophanes, the basis orbitals of initial interest are ϕ_5 (HOMO) and ϕ_6 (LUMO), and we designate the through-space combination orbitals as $\psi_5(\pm)$ and $\psi_6(\pm)$. In our notation,[21a,22] $\psi_i(-)$ designates the combination with a node between the decks.

The most important point is that only two of the four possible one-electron transitions involving $\psi_5(\pm)$ promotion to $\psi_6(\pm)$ are symmetry allowed if the cyclophanes are assumed to be frozen in their average point groups (C_{2h} for **12** and C_i for **3**). In systems in which the TS interaction dominates, the $\psi_5(-)$ to $\psi_6(+)$ (bu ← ag) transition, which would most clearly reveal the transannular interaction, is forbidden. The two allowed transitions in **12**, which is dominated by the TS interaction,[23] are nearly degenerate so that the absorption spectrum does not obviously reveal the fact that two distinct transitions are present in the longest wavelength region. [2.2]1,6-Azulenophane (**3**) and [2.2]1,3-azulenophane are "metacyclophane-like". The TS and TB interactions are not so simple in such instances.[22] However, the qualitative expectation that the $\psi_5(\pm)$ gap should not be the same as the $\psi_6(\pm)$ gap does simply arise. The two allowed transitions involving $\psi_5(\pm)$ and $\psi_6(\pm)$ may thus be moved further away from the accidental coincidence in **12** and could rationalize the extra bands maxima (462 and 495 nm) in the spectrum of **3** that are without counterpart in the spectrum of 1,6-dimethylazulene (**11**) or **12**. These absorption bands would then be a result of "transannular π-electron interaction between the two facing azulene rings" as suggested[9] for [2.2]1,3-azulenophane.

We hasten to add that the density of electronic states in azulenophanes is much higher than this simple model admits, and it is by no means certain that the present one-electron argument is adequate to assign the origin of the new observed (462, 495 nm) bands. Many electron effects and a wider range of interacting substrates need to be considered, and a wider range of spectroscopic methods needs to be investigated before assignment is possible. The presently reported synthesis of **3** adds an additional dimension to the approach available for learning of the nature of the interdeck interactions in nonalternant systems. This makes the attempt to understand these interactions in general somewhat more feasible since more structural probes are now available.

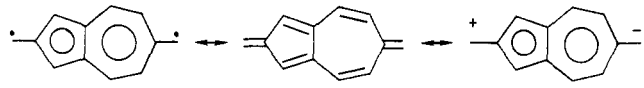
Reactive Intermediate 1: Flash Vacuum Pyrolysis

It is of interest to note that the two different precursors to **3** (**6** and **9**) both give the same isomer of the azulenophane **3** under different reaction conditions. This is in contrast to the [2.2](2,6)azulenophane case, where an approximately 1:1 mixture of syn and anti isomers is found.[2,23,24] One possible explanation for exclusive formation of **3** is that the dimer formation does not proceed through the intermediate 1,6-azulylene (**1**) but occurs via a nucleophilic displacement reaction. An alternative explanation is suggested considering the electronic structure of **1**. The dipolar character of azulene could result in



1a **1** **1b**

polarization of the external methylene groups as depicted in **1b**. The analogous dipolar structure for 2,6-azulylene (**2b**) should be less important for the description of the electronic structure of **2** since C_6 and C_2 possess comparable electron densities. The delocalization force for **2** might thus be better depicted by **2a**. The regioselectivity



2a **2** **2b**

in dimerization of **1** vs. the lack thereof in **2** can be rationalized by this difference. If **1** is actually best described through **1** and **1b** and **2** best by **2** with **2a**, formation of the actually isolated cyclophane isomers follows naturally from the dipolar selectivity implicit in the contribution from **1b** in the transition state. Better insight into such questions would be possible with direct observation of the intermediate (**1**) rather than of overall reactions such as those of Scheme I which might involve it. Since the 2,6-isomer **2** can be observed directly,[2] the same methodology (fvp) was applied to the generation of **1** from **3**.

The thermal reactivity of [2.2](1,6)azulenophane (**3**) was tested by flash vacuum pyrolysis/mass spectrometry (fvp–MS). When **3** was passed through a 620 °C hot pyrolysis oven attached to a mass spectrometer a prominent m/e 154 peak and no higher m/e peaks were observed, while the precursor **3** showed a rather large m/e 308 peak under the same ionization conditions. This result suggests clean thermal fragmentation of the dimer **3** to the polyenic transient **1**. The effluent from the identical pyrolysis (620 °C) device could be collected on a liquid nitrogen cooled (−196 °C) surface as a yellow-colored material. Upon warming to −78 °C, this material polymerized with concomitant color change from yellow to blue-green. The blue-green color suggests that this polymer is composed of azulene units and consequently that the m/e 154 product is **1**. The yellow pyrolysis product can be dissolved in 3-methylpentane (ca. −150 °C). The presence of a transient species is revealed in the absorption spectrum (Figure 3). The disappearance of this reactive intermediate follows second-order kinetics (Figure 3 insert), and the associated rate constant k_2 has boundary values from 3.1 L/(mol·s) to 21.5 L/(mol·s) depending on the exact value of the initial concentration. The spectral features of this absorption spectrum (Figure 3) are in reasonable agreement with the predictions of semiempirical molecular orbital methods for singlet transitions of **1**.[25] The re-

(20) (a) Gleiter, R. *Tetrahedron Lett.* **1969**, 4453. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1 and references therein.

(21) (a) Koenig, T. "Structure Representation Model" presented in part at the 16th Conference on Reaction Mechanisms, June 22–25, 1976. (b) Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314.

(22) Koenig, T.; Tuttle, M.; Wielesek, R. *Tetrahedron Lett.* **1974**, 2537.

(23) Kovac, B.; Mohraz, M.; Heilbronner, E.; Ito, S.; Fukazawa, Y.; Keehn, P. M. *J. Electr. Spectrosc. Relat. Phenom.* **1981**, 327.

(24) Kato, N.; Matsunaga, H.; Oeda, S.; Fukazawa, Y.; Ito, S. *Tetrahedron Lett.* **1979**, 2419.

(25) The CNDO/S-CI model[26] (only singly excited configurations are included in the CI calculations) predicts three singlet transitions above 300 nm (at 496, 321, 304 nm) for **1**. The HAM3-CI[27,28] model (singly *and* doubly excited configurations are included in the CI calculations) suggests four transitions above 300 nm where the second lowest transition (calculated at 532 nm) can be described as "doubly excited" in MO terminology. Important for the present purpose is the fact that both models agree in predicting at least three transitions in the 300–800 nm. The agreement between the measured singlet transitions and calculated spectra (Figure 3) support the suggestion that the transient is actually **1**.

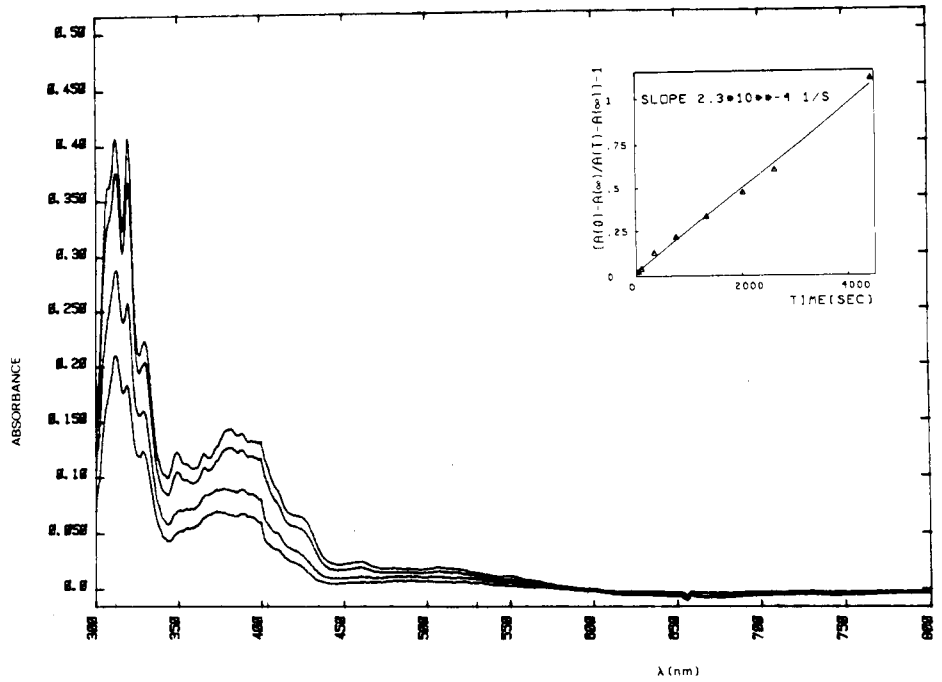


Figure 3. UV–vis spectrum of 1,6-azulylene (1) as a function of time.

activity of the transient obtained here is considerably higher than that of its 2,6-isomer **2**.[2] No NMR spectra have been obtained as yet due to the high rate of reaction of **1** at the relatively high concentrations required for NMR detection.

The present results suggest that azulenophane **3** is, as expected, an excellent thermal precursor for the gas-phase generation of **1**. Detailed spectroscopic and kinetic studies of the reactive intermediate which is certainly formed from **3** by fvp and which is probably **1**, are now possible. We hope to be able to provide the information on electronic structure which is implicit in these systems through studies of their spectral properties. The present results clearly establish that such spectral investigations are now feasible because of the easy synthesis of a good precursor (**3**) that is described here.

Experimental Section

General. Infrared spectra were recorded on a Sargent-Welch 3-200 infrared spectrometer or a Beckman IR 4240 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL-100, a Nicolet QE 300, or a Nicolet NT 360-MHz instrument and referenced to tetramethylsilane or chloroform. ^{13}C NMR spectra were taken on the Nicolet NT 360 MHz spectrometer. Absorption spectra were measured on a Beckman DU-7 or a Hewlett-Packard 8450 spectrophotometer. High-resolution mass spectra were obtained on a CEC-21-110B double focusing mass spectrometer and monitoring mass spectra on a Hewlett-Packard 5930A quadrupole instrument. Elemental analyses were carried out by MicAnal Organic Microanalysis (Tucson, Az). Melting points are determined on a Mel-Temp apparatus and are uncorrected.

6-Methylazulene (7).[29] Sodium hydride (14.61 g, 0.30 mol) and dry dimethylformamide (DMF) were placed in a 2-L flask, flushed with nitrogen and cooled to 0 °C. Cyclopentadiene (39.71 g, 0.6 mol) was added over 20 min and stirred for an additional 10 min. Then, 80.3 g (0.35 mol) of butyl-4-picolinium bromide was added to the cold solution and the solution stirred for 1 h followed by reflux for 3 h. The mixture was cooled to 55 °C and 300 mL of hexane added with 200 mL being decanted after mixing the heterogeneous system. This extraction was repeated with six additional 200-mL aliquots of hexane. The combined hexane extracts were washed with 1 L portions of water and dried. Solvent evaporation yielded 14.6 g of crude **7**. Flash chromatography using pentane over silica gel gave 80% recovery of **7**, which was pure by ^{1}H NMR ($CDCl_3$): δ 2.63 (s, CH_3), 7.05 (d, J = 10 Hz, $H_{5,7}$), 7.30 (d, J = 4 Hz, $H_{1,3}$), 7.78 (t, J = 4 Hz, H_2), 8.19 (d, J = 10 Hz, $H_{4,8}$).

6-[(Trimethylsilyl)methyl]azulene (8). 6-Methylazulene (**7**) (2.0 g, 14.1 mmol) was dissolved in 20 mL of dry tetrahydrofuran under positive nitrogen pressure. An ether solution (1.3 M) of 16.2 mmol of lithium 2,2,6,6-tetramethylpiperidine[13a] was added at 0 °C, and the resulting dark red mixture was allowed to stand at room temperature for 30 min, cooled with an ice bath, and then treated with 2 equiv of freshly distilled chlorotrimethylsilane (3.1 g, 28.2 mmol). After 10 min at 0 °C the blue mixture was allowed to warm to room temperature and poured over 300 mL of water. The ether extract (150 mL) was washed twice with 200 mL of 3% aqueous hydrochloric acid, repeatedly with water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left 2.80 g (93%) of a blue solid. The crude product was purified by sublimation [40 °C (0.05 torr)] to give 2.04 g (68%) 6-(trimethylsilyl)methyl]azulene as blue-purple crystals: mp 106–108 °C; ^{1}H NMR ($CDCl_3$) δ 8.38 (d, J = 10.0 Hz, 2 H, $H_{4,8}$), 7.93 (t, J = 3.5 Hz, 1 H, H_2), 7.30 (d, J = 3.5 Hz, 2 H, $H_{1,3}$), 7.11 (d, J = 10.0 Hz, 2 H, $H_{5,7}$), 2.60 (s, 2 H, CH_2SiMe_3), 0.27 (s, 9 H, $Si(CH_3)_3$); IR (CaF_2 $CDCl_3$; in cm^{-1}) 2958 (m), 2041 (w), 1590 (m), 1575 (s), 1399 (s), 1251 (m), 1163 (m), 1142 (m); UV–vis (cyclohexane) λ [nm] (log ϵ) 235 (4.06), 285 (4.83), 292 (4.80), 329 (3.50), 336 (3.62), 343 (3.61), 352 (3.72), 365 (3.47), 543 sh (2.41), 560 (2.49), 581 (2.45), 609 (2.45), 635 (2.14), 671 (2.10); mass spectrum, calcd for $C_{14}H_{18}Si$ 214.118, found 214.119. Anal. Calcd: C, 78.44; H, 8.46. Found: C, 78.84; H, 8.61.

1-[(*N*,*N*-Dimethylamino)methyl]-6-[(trimethylsilyl)methyl]azulene. Paraformaldehyde (71 mg, 2.36 mmol), bis(*N*,*N*-dimethylamino)methane (267 mg, 2.61 mmol), and 4.4 g of glacial acetic acid were heated until a clear solution was obtained and then cooled in an ice bath. This cold solution was added dropwise to a cold (0 °C) and stirred solution of 6-[(trimethylsilyl)methyl]azulene (0.975 g, 4.56 mmol) in 400 mL of dichloromethane and stirred for 2 h. The reaction mixture was poured over 200 mL of saturated aqueous sodium carbonate solution and the organic layer washed two times with 200 mL of

(26) Ellis, R. L.; Kuehnlenz, G.; Jaffe, H. H. *Theor. Chim. Acta* **1972**, *26*, 131 and references cited therein; "*Quantum Chemistry Program Exchange*"; Indiana University, Bloomington, IN; QCPE No. 174.
(27) Lindholm, E. *Lecture Notes in Chemistry*; Springer Verlag: Berlin, 1985; and references cited therein.
(28) As noted in ref 2, the HAM/3 HOMO-LUMO gap in **1** is much too low. A modified version of HAM is presently under development in these laboratories.
(29) Hafner, K. *Angew. Chem.* **1955**, *67*, 301.

saturated aqueous sodium carbonate solution and twice with water, dried, and concentrated under reduced pressure to yield 1.11 g (90%) of the desired product as a blue oil. ^{1}H NMR ($CDCl_3$) δ 8.27 (d, J = 10 Hz, 1 H, H_4 or H_8), 8.11 (d, J = 10 Hz, 1 H, H_8 or H_4), 7.66 (d, J = 4 Hz, 1 H, H_2), 7.21 (d, J = 4 Hz, 1 H, H_3), 6.87 (d, J = 10 Hz, 1 H, H_5 or H_7), 6.83 (d, J = 10 Hz, 1 H, H_7 or H_5), 3.83 (s, 2 H, CH_2N), 2.33 (s, 2 H, CH_2Si), 2.24 (s, 6 H, $N(CH_3)_2$), 0.02 (s, 9 H, $Si(CH_3)_3$); IR (CaF_2, CCl_4; in cm^{-1}) 2946 (m), 2799 (w m), 2754 (m), 1575 (s), 1444 (m), 1407 (s), 1250 (s m), 1160 (m), 1139 (m); mass spectrum, calcd for $C_{17}H_{25}SiN$ 271.176, found 271.176.

[2.2](1,6)Azulenophane (3). 1-[(*N*,*N*-Dimethylamino)-methyl]-6-[(trimethylsilyl)methyl]azulene (437 mg, 1.61 mmol) was dissolved in 15 g of hexane, 2.5 g of methyl iodide was added, and the mixture was stirred for 24 h in a nitrogen atmosphere. The flask was cooled with an ice bath and the quaternary ammonium salt **9** filtered (585 mg, 1.42 mmol, 88%). Dissolution of **9** in 160 mL of dry tetrahydrofuran and slow dropwise addition (2 h) of 1.5 mmol of tetrabutylammonium fluoride in 70 mL of tetrahydrofuran to the rapidly stirred solution under nitrogen resulted in a dark green colored mixture. Filtration followed by evaporation under reduced pressure left a solid residue, which was extracted with ether. Chromatography on neutral alumina eluting with hexane gave (22.9 mg, 10.5%) as a blue-green solid: mp >350 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.10 (d, J = 9.57 Hz, 2 H, H_4), 7.65 (d, J = 3.86 Hz, 2 H, H_2), 7.22 (d, J = 3.82 Hz, 2 H, H_3), 6.99 (dd, J = 9.60, 1.34 Hz, 2 H, H_5), 6.00 (d, J = 10.30 Hz, 2 H, H_8), 4.41 (dd, J = 10.30, 1.40 Hz, 2 H, H_7), 3.54 (ddd, J = 13.41, 3.00, 4.59 Hz, 2 H, H_{14}), 3.12 (ddd, J = 11.99, 4.59, 2.82 Hz, 2 H, H_{13}), 2.55 (ddd, J = 13.41, 11.93, 2.82 Hz, 2 H, H_{12}), 2.17 (ddd, J = 11.93, 11.99, 3.00 Hz, 2 H, H_{11}); IR (CaF_2, CCl_4; in cm^{-1}) 3060 (w), 3005 (w), 2915 (s), 2840 (m), 1560 (s), 1435 (m), 1423 (m), 1387 (s), 1294 (w), 1255 (w), 1183 (w); UV–vis (cyclohexane) λ [nm] (log ϵ) 257 sh (4.44), 275 (4.66), 301 sh (4.25), 360 (3.63), 462 (2.40), 495 (2.43), 594 sh (2.67), 613 (2.73), 637 (2.72), 668 (2.71), 696 sh (2.53), 740 (2.37); ^{13}C NMR ($CDCl_3$) δ 151.4 (m), 142.2 (m), 135.7 (d, J = 151.1 Hz), 135.6 (d, J = 159.9 Hz), 135.1 (m), 131.8 (d, J = 151.6 Hz), 128.8 (m), 126.7 (d, J = 159.3 Hz), 122.9 (d, J = 153.5 Hz), 115.4 (d, J = 167.9 Hz), 45.17 (t, J = 130.0 Hz), 31.4 (t, J = 128.7 Hz); mass spectrum, calcd for $C_{24}H_{20}$ 308.156, found 308.156. Anal. Calcd: C, 93.46; H, 6.54. Found: C, 93.01; H, 6.28.

[(Trimethylsilyl)methyl]cyclopentadiene.[14] (Iodomethyl)trimethylsilane (13.5 g; 63.1 mmol) was dissolved in 200 mL of dry tetrahydrofuran, the flask was flushed with nitrogen, and 1.1 equiv of sodium cyclopentadienide in 75 mL of tetrahydrofuran was added. The mixture was stirred at room temperature for 2 days. The mixture was filtered and the liquid "distilled" at room temperature (0.15 torr, dry ice cooled receiver) to give 4.50 g (29.6 mmol, 47%) of the desired product as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.0 (s, 9 H, $Si(CH_3)_3$), 1.80–1.92 (m, 2 H), 2.80–3.00 (m, 2 H), 5.80–6.45 (m, 3 H); IR (neat; in cm^{-1}) 3050 (m), 2945 (s), 2880 (s), 1600 (m), 1590 (m), 1512 (w), 1405 (w m), 1357 (m), 1344 (s), 1191 (m), 1149 (m), 975 (m), 943 (m), 891 (m), 840 (s).

6-Methyl-1-[(trimethylsilyl)methyl]azulene and 6-Methyl-2-[(trimethylsilyl)methyl]azulene (4). [(Trimethylsilyl)methyl]cyclopentadiene (12.0 g, 78.9 mmol) dissolved in 70 mL of tetrahydrofuran was placed in a flask under positive nitrogen pressure. After cooling (ice bath), 60 mL of a 1.3 M solution of methyllithium in ether was added via syringe to the stirred solution. After 2 h at ice bath temperature and 30 min at room temperature, an additional 15 mL of the 1.3 M methyllithium solution was added and stirring continued for 15 min. The reaction flask was cooled again in an ice bath and *N*-butylpicolinium bromide (27.2 g, 0.12 mol) added as a solid. The reaction mixture was kept for 1 h at room temperature and then added with stirring (under nitrogen) to 400 mL of *N*,*N*-diethylaniline at 180 °C. The tetrahydrofuran was allowed to distill off during the addition. After 1.5 h the dark reaction mixture was cooled and poured into ice-cold 5% aqueous hydrochloric acid and extracted three times with 200 mL of hexanes. The combined organic layers were washed twice with 5% aqueous hydrochloric acid and twice with water and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure, followed by a short-column distillation [89–91 °C (0.05 torr)] yielded 9.3 g (52%) of a blue oil. The blue oil consisted of an isomeric mixture of 6-methyl-1-[(trimethylsilyl)methyl]azulene and 6-methyl-2-trimethylsilyl)methyl]azulene in a ratio of 3:1, respectively, as determined by ^{1}H NMR: ^{1}H NMR ($CDCl_3$) [1,6-isomer] δ 8.05 (d, J = 10 Hz, 1 H, H_4 or H_8), 7.98 (d, J = 10 Hz, 1 H, H_8 or H_4), 7.54 (d, J = 4 Hz, 1 H, H_2), 7.06 (d, J = 4 Hz, 1 H, H_3), 6.90 (d, J = 10 Hz, 2 H, $H_{5,7}$) 2.62 (s, 3 H, CH_3), 2.53 (s, 2 H, CH_2Si), 0.07 (s, 9 H, $Si(CH_3)_3$), [2,6-isomer] δ 8.01 (d, J = 10 Hz, 2 H, $H_{4,8}$), 7.06 (d, J = 10 Hz, 2 H, $H_{5,7}$), 7.01 (s, 2 H, $H_{1,3}$), 2.64 (s, 3 H, CH_3), 2.49 (s, 2 H, CH_2Si), 0.10 (s, 9 H, $Si(CH_3)_3$); mass spectrum calcd for $C_{15}H_{20}Si$ 228.133, found 228.113.

6-(Chloromethyl)-1-[(trimethylsilyl)methyl]azulene (5). The silylated azulene mixture **4** (526 mg, 2.31 mmol) was dissolved in 7 mL of dry tetrahydrofuran under nitrogen and cooled to −10 °C. Sodium *N*-methylanilide (4.2 mL of a 0.7 M tetrahydrofuran solution) was added and the red-brown mixture stirred for 1 h. The sodium azulenate solution was then transferred (via syringe) into a second flask containing trifluoromethanesulfonyl chloride (0.32 mL, 3.01 mmol), which had previously been flushed with nitrogen, sealed, and cooled to 0 °C. After 30 min at 0 °C (occasional swirling) the dark green solution was poured over 250 mL of ice–water. The aqueous layer was extracted with ether, and the combined ether layers were washed twice with 1.5% aqueous hydrochloric acid solution and twice with water and dried over anhydrous sodium sulfate. The residue was chromatographed on 20 g of sodium tetraborate impregnated silica gel (4.8 g of sodium tetraborate was dissolved in a 300 mL of hot water; 104 g silica gel (40 μm) was added, the slurry stirred, and the water evaporated overnight at 90 °C). Hexane eluted first a small amount of unreacted starting material, which was followed by pure **5**. Evaporation of the solvent under reduced pressure gave 208 mg (0.80 mmol, 46%) of the desired product as a blue oil, which decomposed slowly, even when stored in a refrigerator: ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 10.0 Hz, 1 H, H_4 or H_8), 8.04 (d, J = 10.0 Hz, 1 H, H_8 or H_4), 7.63 (d, J = 3.5 Hz, 1 H, H_2), 7.30 (d, J = 3.5, 1 H, H_3), 7.01 (br d, J = 10 Hz, 2 H, $H_{5,7}$), 4.66 (s, 2 H, CH_2Cl), 2.49 (s, 2 H, CH_2Si), 0.00 (s, 9 H, $Si(CH_3)_3$); UV–vis (cyclohexane) λ [nm] (log ϵ) 242 (4.6), 292 (5.2), 346 sh (4.0), 359 (4.2), 376 (3.9), 604 sh (2.86), 628 sh (2.91), 647 (2.94), 674 sh (2.89), 712 (2.84), 755 sh (2.55), 799 (2.37), 848 sh (1.69); $M^{\cdot+}$ 264, 262 (relative intensity 1:2.6).

6-[(*N*,*N*-Diethylamino)methyl]-1-[(trimethylsilyl)-methyl]azulene. A solution of 6-(chloromethyl)-1-[(trimethylsilyl)methyl]azulene (105 mg, 0.40 mmol), 5 mL of dichloromethane, and 1.0 g of diethylamine was stirred for 18 h at room temperature under nitrogen. The mixture was concentrated under reduced pressure and the remaining oil taken up in ether and extracted with 200 mL of ice-cold 5% aqueous hydrochloric acid. The acidic extracts were washed once with ether and then carefully neutralized with 5% aqueous potassium hydroxide solution. The combined ether layers obtained from these extractions were dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Dissolution of the dark green residue in dichloromethane followed by chromatography on neutral alumina (dichloromethane as eluent) gave 32.3 mg (0.11 mmol, 27%) of the desired product as a blue oil: ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 10 Hz, 1 H, H_4 or H_8), 8.05 (d, J = 10 Hz, 1 H, H_8 or H_4), 7.58 (d, J = 4 Hz, 1 H, H_2), 7.26 (d, J = 4 Hz, 1 H, H_1), 7.11 (d, J = 10 Hz, 2 H, $H_{5,7}$), 3.67 (s, 2 H, $AzCH_2N$), 2.60 (q, J = 8 Hz, 4 H, NCH_2CH_3), 2.50 (s, 2 H, CH_2Si), 1.08 (t, J = 8 Hz, 6 H, NCH_2CH_3), 0.03 (s, 9 H, $Si(CH_3)_3$); mass spectrum, calcd for $C_{19}H_{29}NSi$ 299.207, found 299.209.

[2.2](1.6)Azulenophane (3). 6-[(*N*,*N*-Diethylamino)-methyl]-1-[(trimethylsilyl)methyl]azulene (32.3 mg, 0.11 mmol) was dissolved in 5 mL of ether, 2.0 g of methyl iodide was added, and the mixture was stirred under nitrogen for 1.5 days. The solution was concentrated under reduced pressure, taken up in 12 g acetonitrile, and placed in a three-necked flask equipped with stir bar, reflux condenser, nitrogen inlet tube, and constant addition funnel. The system was flushed with nitrogen and brought to reflux. Tetrabutylammonium fluoride (0.2 mmol) dissolved in 1.0 mL of tetrahydrofuran and 6.0 mL of acetonitrile was added dropwise during 25 min to the refluxing, vigorously stirred solution. Reflux was maintained for an additional 30 min and the mixture allowed to cool to room temperature. The dark green solution

was filtered and evaporated. The ether-soluble material in the residue was concentrated to leave 13 mg of a solid. Extraction with ligroin and column chromatography (silica gel (60–200 mesh)) using ligroin and then carbon tetrachloride gave 2.9 mg (0.009 mmol, 17%) of [2.2](1,6)azulenophane (**3**). For spectral characterization, see experimental procedure for the preparation of **3** from 1-[(*N*,*N*-dimethylamino)methyl]-6-[(trimethylsilyl)-methyl]azulene.

1,6-Dimethylazulene (11). Phosphorus oxychloride (1.69 g, 11.0 mmol) was added dropwise to 5 mL of ice-cold DMF. The mixture was stirred for 15 min and added to a vigorously stirred solution of 6-methylazulene (1.42 g, 10.0 mmol) in 10 mL of DMF. Stirring was continued for another 15 min. Ether was added and the mixture poured into 150 mL of ice–water. The aqueous layer was washed once with ether, then made alkaline with 10% aqueous potassium hydroxide solution, and repeatedly extracted with ether. The ether extracts were washed eight times with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 1.60 g (94.1%) of the aldehyde **10**, purple crytals: mp 52–53.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.30 (s, 1 H, CHO), 9.38 (d, J = 10 Hz, 1 H, H_4 or H_8), 8.32 (d, J = 10 Hz, 1 H, H_8 or H_4), 8.13 (d, J = 4 Hz, 1 H, H_2), 7.46 (d, J = 10 Hz, 2 H, $H_{5,7}$), 7.24 (d, J = 4 Hz, 1 H, H_3), 2.72 (s, 3 H, CH_3); IR (KBr; in cm^{-1}) 2805 (w), 2737 (w), 1642 (s), 1575 (m), 1497 (m), 1443 (m), 1413 (s), 1395 (s), 1310 (w), 1283 (m), 1231 (w), 1182 (m), 1021 (m), 911 (w), 830 (s), 798 (m), 786 (m), 724 (m), 683 (m), 647 (m); UV–vis (cyclohexane) λ [nm] (log ϵ) 630 (2.14), 603 sh (2.17), 572 (2.60), 549 sh (2.61), 528 (2.68), 516 sh (2.63), 390 (3.94), 376 (3.87), 312 (4.65), 303 sh (4.53), 294 sh (4.43), 266 (3.85), 237 (4.19), 218 (4.36); mass spectrum, calcd for $C_{12}H_{10}O$ 170.073, found 170.073.

Hydrazine hydrate (99%) [3.0 mL, 60 mmol] was added to a solution of **10** (1.4 g 8.2 mmol) in 10 mL of absolute ethanol. The mixture was stirred for 20 min, 50 mL of absolute ethanol was added, and the green blue solution was added dropwise during 1 h to a previously heated (180 °C) solution of 20 mL of diethylene glycol and 2.8 g of potassium hydroxide, allowing distillation of ethanol and the product. More ethanol was added until no more blue distillate could be observed. The blue-colored ethanol distillate was concentrated, the residue dissolved in hexanes, and the hexanes layer washed twice with water. Drying over anhydrous sodium sulfate, followed by evaporation, gave 0.77 g (60%) of 1,6-dimethylazulene as a blue oil: ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 9.5 Hz, 2 H, $H_{4,8}$), 7.62 (d, J = 3.5 Hz, 1 H, H_2), 7.23 (d, J = 3.5 Hz, 1 H, H_3), 6.94 (br d, J = ca. 10 Hz, 2 H, $H_{5,7}$), 2.64 (s, 3 H), 2.59 (s, 3 H). The UV–vis data agreed with the ones reported by Scott and co-workers.[17]

Flash Vacuum Pyrolysis. Apparatus. Gas-phase pyrolysis experiments were done in a flow system. The precursor was placed at the end of a quartz pyrolysis tube (38 cm long; 1.3 cm in diameter) and heated with a tubular oven to a temperature sufficient to ascertain a steady rate of sublimation. The precursor flowed through an adjacent reaction zone (17 cm long), where thermolysis occurred, and the reaction products were analyzed through a connected HP 5930 A quadrupole mass spectrometer.

Procedure. Typically 2–4 mg of sample was placed into the quartz tube, the temperature of the sublimation oven was set to a temperature at which the sample had sufficient vapor pressure, and the temperature of the reaction oven was raised slowly from room temperature to about 900 °C. The periodically measured mass spectra were analyzed for disappearance of starting material and formation of product by measuring the intensities of particular mass fragments as a function of the reaction zone temperature.

Isolation and Low-Temperature UV–vis Spectroscopy of 1,6-Azulylene (1) from Pyrolysis of [2.2](1,6)Azulenophane (3) at 620 °C. The starting material **3** (0.7 mg) was transferred into a small vial and the vial placed into the pyrolysis tube. The pyrolysis tube was connected to a cold trap for the low-temperature isolation of reactive intermediates,[30] and a vacuum (approximately 10^{-3} torr) was applied. The pyrolysis oven was brought to 620 °C and maintained at this temperature throughout the experiment. After 1 h, the cold trap was charged with liquid nitrogen, ca. 0.5 mL of 3-methylpentane was condensed onto the cold surface, and the sublimation oven was heated slowly to 150 °C. A yellow deposit developed on the surface of the predeposited 3-methylpentane.

After the pyrolysis had been completed the cold trap was warmed to ca. −100 °C through addition of dry ice–acetone slurry to the liquid nitrogen and the yellow-colored 3-methylpentane solution collected (at −78 °C) in an attached quartz cell (quarasil, NSG Precision Cells, Inc.; 1 cm × 1 cm × 4 cm). Another ca. 3 mL of solvent was condensed into the quartz cell and the sample sealed under vacuum. The yellow-colored (slight brownish tint) 3-methylpentane solution of **1** was examined with the Hewlett-Packard HP8450 spectrometer at −196 °C. The sample was warmed to room temperature, and the decomposition of **1** was monitored by periodically scanning the UV–vis spectrum. The final reading ($t \rightarrow \infty$) was taken as background and subtracted from each of the previously measured spectra. Disappearance of the peaks at $\lambda > 300$ nm (312, 320, 330, 349, 381, 400, 424, 462, 506 nm) followed second-order kinetics. For λ = 312 nm the absorbance time data were ($A_0 - A_\infty$, s) as follows: 0.424, 0; 0.413, 50; 0.407, 110; 0.375, 350; 0.348, 770; 0.318, 1340; 0.288, 2030; 0.264, 2630; 0.201, 4430.

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