s^{-1}. Also, we now find that the quantum yield for loss of N$_2$ from **1** is 0.95 ± 0.05. Since **1** has no obvious structural features that should make new intersystem crossing paths accessible, it is reasonable to apply to it the rate constant $\sim 10^6$ s^{-1}, which is observed in other saturated cyclic diazenes.[14] Therefore, at ordinary temperatures, intersystem crossing to the triplet of diazene **1** does not compete significantly with deazetation, essentially all of which occurs from the excited singlet **1** and gives diyl **2**.

Moreover, in contrast to some other diazenes, which show[15] decreases of 100-400% in the fluorescence intensity with change of temperature from -10 to 20 °C, the decrease for **1** is only 35%. Thus, the relative probabilities of the deactivation routes from the excited singlet of **1** are not markedly temperature dependent, and it is unlikely that at low temperature the mechanism changes completely to one which photochemically populates the diazene triplet state and hence the triplet diyl **3**.

We now measure a minimum value of the rate of appearance of the $\Delta m_s = 1$ ESR transitions of the triplet **3**,[2,3] generated with a roughly collimated 2500-W xenon flash lamp. One flash on a randomly oriented sample of **1** in a frozen 2-methyltetrahydrofuran matrix produces an easily detected ESR signal, which, for samples at 100 and 77 K, is monitored by display on a scanning oscilloscope synchronized with the lamp flash. At 4.2 K, the ESR signal-to-noise ratio with this system is less favorable because of saturation of the transitions, but the rise of the signal is readily observed with a chart recorder. The time resolutions of the two methods are about 10^{-3} and 7×10^{-2} s, respectively. The ESR spectrum is indefinitely stable at these temperatures and increases in intensity if the flashes are repeated. In each case, the signal rises without a time lag.

The time-resolution of the flash photolysis experiment requires any intermediate, e.g., diazenyl biradical **6** or bicyclic hydrocarbons **7** or **8**, that lies between the singlet excited state of **1** and the triplet diyl **3** to decompose with a rate constant $>6.9 \times 10^2$ s^{-1} at 77 K and >14 s^{-1} at 4.2 K. If we assume a preexponential term of 10^{13} s^{-1} for such a unimolecular decomposition, we calculate that E_a, which would represent the strength of the C-N bond in **6**, or the C(1)-C(4) or C(5)-C(6) bonds in **7** and **8**, could not be greater than about 3500 or 270 cal/mol, based upon the 77 and 4.2 K experiments, respectively.[16]

Arrhenius extrapolation to 300 K of the rate of formation of triplet diyl **3** from these "E_a" values leads to $k_{300} \sim 3 \times 10^{10}$ and 5×10^{13} s^{-1}. Thus, capture of the photolytically generated singlet at 300 K before it escaped by intersystem crossing to the triplet would require the trapping agent to react at rates 10-10^3 times the diffusion-controlled encounter frequency, $k_{\rm diff}$.[17] The preferred formulation for the capturable singlet in the cascade mechanism therefore is the true biradical **2**. Bicyclic hydrocarbons **7** and **8** nevertheless may be isolable substances and are valid targets for independent synthesis.

References and Notes

(1) The support of this work by the National Science Foundation (CHE-76-00416) is gratefully acknowledged. This paper is dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

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(16) The argument might be made that at 4.2 K, the very sensitive ESR method detects a small amount of a fast triplet-populating reaction that by-passes the slower normal cascade. However, this interpretation would require that the cascade, which clearly is the predominant pathway at 105 K, be *completely* suppressed at 4.2 K. Were any of the cascade mechanism to survive at 4.2 K, the ESR signal response would have a steep initial slope followed by a shallow exponential rise, rather than the sharp jump to a flat plateau actually observed.

(17) Relative reactivities of olefinic trapping agents for the singlet intermediate **2** range over 2–3 orders of magnitude.[8a] Hence, the absolute rates, at least of the less reactive olefins, must be much less than $k_{\rm diff}$.

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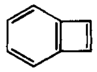
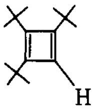
1,2-Bis(trimethylsilyl)benzocyclobutadiene, a Paratropic 8π-Electron System

Sir:

Cyclobutadiene (**1**) and benzocyclobutadiene (**2**) are pivotal molecules in the understanding of the electronic structure and chemical behavior of cyclic delocalized $4n\pi$-systems.[1,2] Their extreme reactivity with respect to oxidation and dimerization has necessitated the application of low temperature matrix techniques[3] in their isolation and the determination of infrared and electronic spectral data. These conditions have precluded the recording of proton magnetic resonance spectra which would provide important information regarding induced ring current effects and the possible (anti)aromatic character of **1** and **2**.[1,2] Stabilization of **1** and **2** by ring substitution has been achieved in a variety of cases[2,4] but only one example (e.g., **3**)[5] has contained protons directly bound to the π-nucleus. We wish to report the synthesis of 1,2-bis(trimethylsilyl)benzocyclobutadiene (**5**), the least substituted benzocyclobutadiene hitherto isolated, and the first benzocyclobutadiene in which the measured chemical shifts of the ring protons enable an estimate of ring current effects.

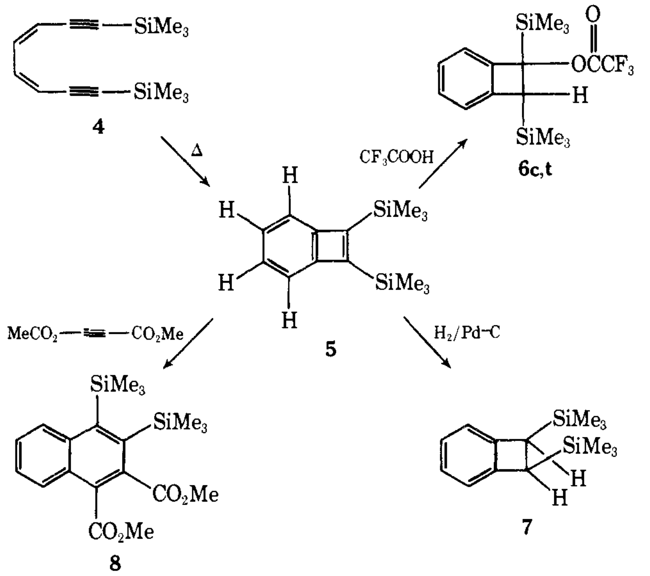

1


2



3

Vacuum transfer of *cis*, *cis*-dienediyne **4** or one of its other stereoisomers[6] through a hot quartz tube (650 °C/0.001 Torr) gave, in a remarkably clean transformation, an extremely air sensitive orange-red oil which was manipulated under vacuum or scrupulously clean, oxygen-free nitrogen.[7] Relevant spectra were taken using vacuum sealed apparatus, cells, and tubes. We assign structure **5** to this product on the basis of its spectroscopic and chemical properties. The NMR spectrum (toluene-d_8) is shown in Figure 1 and compared with that of starting material **4**. Solvent induced shifts appear negligible ($\tau_{\rm olefinic}$ 3.80, 4.37 in CCl$_4$; 3.70, 4.25 in CD$_3$CN). The mass spectrum showed a molecular ion at *m/e* 246.1260 (calcd for $C_{14}H_{22}Si_2$: 246.1259). The electronic spectrum had strong peaks at λ_{max} (ether) 236, 243 and a weak broad absorption at 404, 413 sh, 441 sh, 472 sh. Exposure to air gave a complex mixture of colorless oxidized materials, one of which was identified as phthalic acid.[8]



Benzocyclobutadiene, **5**, is remarkably thermally stable. Heating to 150 °C for several hours led to unchanged starting material, while extensive decomposition occurred above 180 °C. No dimer could be isolated. Similarly, irradiation with a medium-pressure Hg lamp gave recovered starting material. However, treatment with excess trifluoroacetic acid-CCl_4 resulted in the instant formation of the trifluoroacetate **6** (presumably a mixture of isomers) purified by PTLC.[9] Hydrogenation (Pd-C) smoothly converted **5** to the corresponding dihydroderivative **7**[9] an ideal model system with which to compare π-electronic effects. Angular cycloaddition occurred when **5** was treated with dimethylacetylene dicarboxylate to give the crystalline adduct **8**.[9] This adduct when reacted with CF_3COOH-H_2SO_4-CCl_4 (1:1:1) was smoothly converted into naphthalene-1,2-dicarboxylic acid anhydride (mp 163-165 °C, lit.[10] mp 167 °C) identified by its mass spectrum (*m/e* 198) and comparison of UV and IR spectra with published data.[11] An attempt to form a 2,4,7-trinitrofluorenone charge transfer complex with **5** was unsuccessful, presumably due to the steric bulk of the trimethylsilyl groups.

A small amount (4%) of an isomeric side product was formed consistently in the preparation of **5** and has been assigned structure **9** on the basis of spectral, analytical, and chemical data.[9] It is most easily isolated by exposing the products of the pyrolysis of **4** to air followed by PTLC. Treatment with methanolic KOH removed the acetylenic trimethylsilyl group (*m/e* 174; τ (CCl_4) 2.68 (m, 4 H), 6.93 (s, 1 H), 9.63 (s, 9 H)). Hydrogenation of **9** (Pd-C) followed by desilylation with H_2SO_4-CF_3CO_2H-CCl_4 (1:1:1) gave ethylbenzene. Control experiments showed that **9** seemed to be derived directly from starting diyne **4** and not from **5** by subsequent pyrolysis. A possible radical mechanism of its formation is shown in Scheme I. Its occurrence might be the result of the severe steric requirements of the trimethylsilyl groups destabilizing the electrocyclic pathway leading to **5** enabling effective competition of the radical path.

Comparison of the properties of benzocyclobutadiene **5** with those of benzocyclobutene **7** dramatically illustrate the effect of mixing-in a double bond symmetrically with the π-system of benzene. The 8π-electron structure **5** is extremely air sensitive, very reactive (though considerably kinetically stabilized), and has spectral properties consistent with the presence of very high lying HOMO's and low lying LUMO's in accord with theoretical expectations for a planar 4*n* π-system.[1,2,12] Most strikingly, the increased shielding of the unsaturated ring protons, when going from **7** to **5**, amounts to an average of 1.04 ppm, a convincing manifestation of strong paramagnetic ring current contributions to the induced ring current in **5**.[13] In addition, the characteristic high wavelength absorption in the electronic spectrum (λ_{max} 404) is a further indication of the unique electronic structure.[12] It is interesting to note, however, that the position of this band seems to shift considerably, depending on the substitution pattern (cf. 1,2-diphenyl-3,4,5,6-tetramethylbenzocyclobutadiene, λ_{max} 468 nm;[4c] 1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene: λ_{max} 372 nm;[4c] benzocyclobutadiene, λ_{max} 289 nm, tailing above 330 nm[3b]). Finally, it is clear that benzocyclobutadienes should be readily accessible and isolable as long as just the reactive four ring is sterically blocked and workup conditions are oxygen free. This finding should encourage approaches to other cyclobutadienoids thought to be unreachable synthetically.[2]

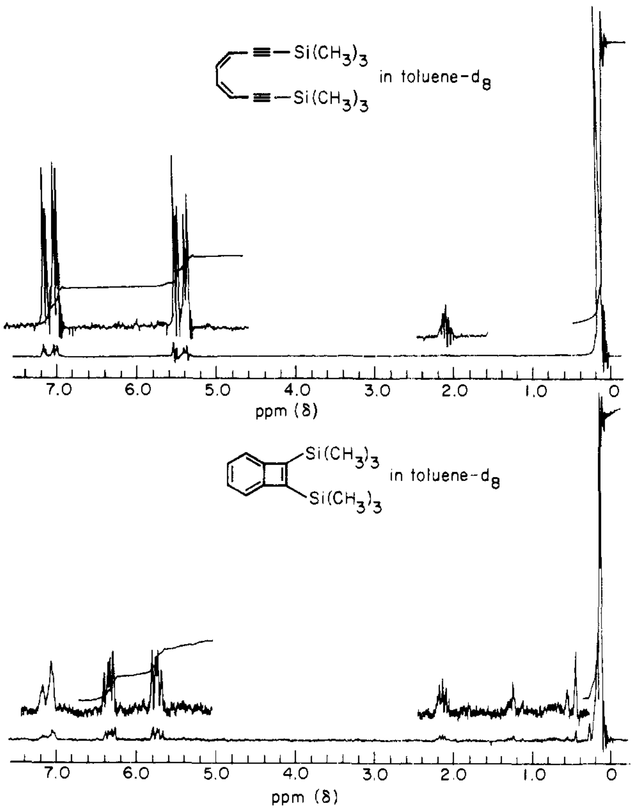
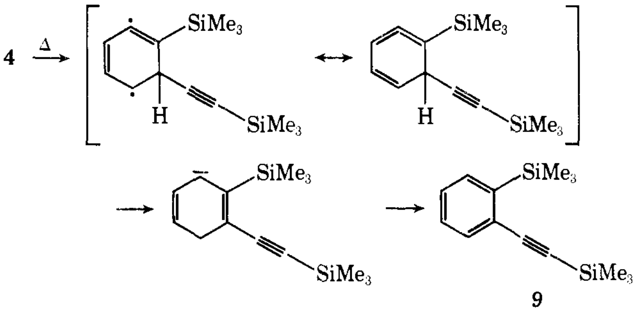


Figure 1. The 60-MHz ^{1}H NMR spectra of **4** and **5**. The spectrum of **5** contains solvent peaks at τ 2.90 and 7.85, and peaks due to side product **9** at τ 9.55 and 9.72.

Scheme I



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Reactions of Alkyl Substituted Bicyclo[3.1.0]hexatriene

Sir:

We recently reported aspects of the chemistry of bicyclo[3.1.0]hexatriene (I).[1,2] In this paper we discuss the chemical perturbation induced by substitution of an alkyl group at C_2 of I.

The precursor of 2-*tert*-butylbicyclo[3.1.0]hexatriene (IIa), 2-*tert*-butyl-4,6-dibromo-2-bicyclo[3.1.0]hexene (IIIa), was prepared from 6-bromo-3-bicyclo[3.1.0]hexen-2-one by reaction with *tert*-butyllithium followed by anhydrous HBr. Treatment of IIIa with 8 equiv of potassium *tert*-butoxide in 5 mL of THF at −70 °C for 15 h produced only one of the four possible *tert*-butyl-6-*tert*-butoxyfulvenes as judged by both ^1H NMR and ^{13}C NMR analysis.[3] Similarly, upon treatment of IIIa with 6 equiv of potassium *tert*-butoxide and 8 equiv of $HNMe_2$ in 5 mL of THF at −70 °C, a mixture of two *tert*-butyl-6-dimethylaminofulvenes, A and B, was obtained in a ratio of 3:1, respectively. This mixture of aminofulvene isomers slowly epimerized under the reaction conditions to yield a 1:1 mixture of both isomers.

These results suggest that only isomer A was initially formed as indicated by the formation of only one 6-*tert*-butoxy-*tert*-butylfulvene. From ^1H NMR of the 3:1 mixture of A:B, we knew which set of olefinic protons correlated with the initially formed isomer A and which arose from the epimer B.[4] The location of the *tert*-butyl group was established by treating the mixture of A and B with phenyllithium to form the 6-phenylfulvene followed by dimethyl acetylenedicarboxylate. The ^1H NMR of the Diels-Alder adduct, obtained in 70% overall yield, clearly indicated that the *tert*-butyl group was only present at C_2 (IV) and C_3 (V) of the original aminofulvene.[5]

However, it was not known whether structure IV or V corresponded to the initially formed isomer A. Exposure of a 1:1 mixture of A and B to a 3:1 mixture of $MeOD/CDCl_3$ at 42 °C resulted in the incorporation of 1.7 D over a 1.5-h period. By analogy to 6-dimethylaminofulvene,[6] the hydrogens at C_1 and C_4 were more easily exchanged. After deuteration, compound A possessed a singlet (1 H) at δ 6.39 ($CDCl_3$) and compound B possessed a singlet (1 H) at δ 6.62 ($CDCl_3$).

In the unsubstituted 6-dimethylaminofulvene, H_3 is upfield from H_2 by 0.20 ppm. CNDO/2 calculations predict the total electron densities on H_3 and H_2 of IV and V, respectively, to be equally perturbed by addition of a *tert*-butyl group to C_2 or C_3 of the parent compound. The anisotropic effect of the *tert*-butyl group exerted upon H_3 and H_2 should be the same for both IV and V. Therefore H_3 of IV should be upfield from H_2 of V by the same parts per million as H_3 is from H_2 for the parent aminofulvene. The correlation between the predicted