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References and Notes

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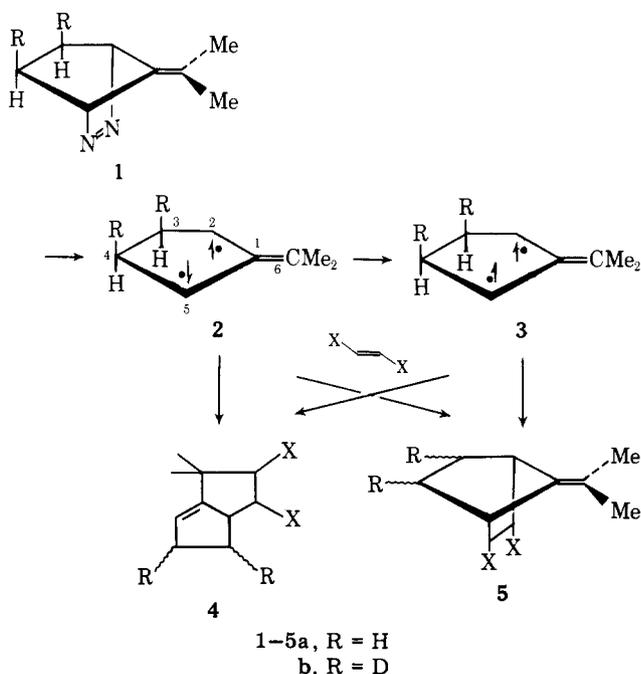
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On the Nature of the Capturable Singlet Trimethylenemethane Intermediate in the Decomposition of 7-Isopropylidene-2,3-diazanorbornene¹

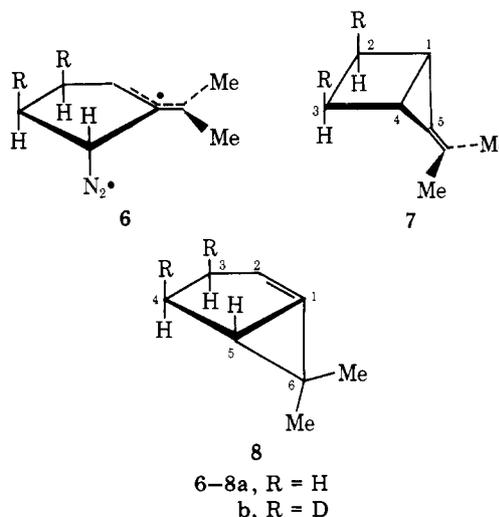
Sir:

The formation of the ground state triplet trimethylenemethane $3^{2,3}$ in thermal or direct photolytic decompositions of diazene **1** occurs by a sequential mechanism involving a proximate intermediate, which can be captured by olefins.⁴⁻⁸ Although it has been convenient to formulate this first intermediate as the singlet state of 2-isopropylidene-cyclopentane-1,3-diyl (**2**, Scheme I), the evidence so far has not excluded the possibility that the species might have quite a different structure, for example, a diazenyl biradical **6**⁹ or one of the bicyclic hydrocarbons, **7** or **8**. In this paper we report both stereo-

Scheme I



chemical and kinetic evidence that strongly favors the symmetrical singlet diyl **2** rather than **6**, **7**, or **8**.



Thermal decomposition at 50 °C of a CH_3CN solution of 2-2.5 M in fumaronitrile and 1 M in stereospecifically labeled **1b**⁵ gives (>90% yield, >98.5% regiospecific) two fused adducts **4b** (X = CN) which are separated preparatively by gas chromatography (GC). Both have the trans dicyano configuration and result from capture of the first intermediate.⁶ Although each adduct **4b** in principle could give two epoxides, *m*-chloroperbenzoic acid converts each predominantly to one member of the corresponding pair. Examination of the lanthanide shifted (LIS)¹⁰ NMR spectrum of the epoxide prepared from the **4b** (X = CN) isomer of lower GC retention time (XE-60 column, 185 °C) shows that the deuterium configuration of the product is at least 90% randomized. Similar results are observed in epoxides from **4b** derived by thermal decomposition of **1b** in the presence of O_2 and by photolysis, both in degassed and O_2 -saturated solutions.

For the sake of argument, the stereorandomization of the singlet adduct **4b** (X = CN), like that of the triplet adduct **5b** (X = CO_2Me) whose stereochemistry we reported earlier,⁵ may be assumed to result from static or time-averaged structural equivalence of two faces of the intermediate (rather than mere accidental equivalence of two competing cycloaddition rates). The capturable singlet intermediate then still could be either of the unsymmetrical bicyclic hydrocarbons **7** or **8**, but only if stereomutation by reversible cleavage of the weak bond, C_1 - C_4 of **7**² or C_5 - C_6 of **8**,¹¹ were rapid relative to capture. We are confronted, therefore, with the problem of distinguishing between a very weak bond, as in **7** or **8**, and no bond, as in the singlet diyl **2**.

We note first that the direct photolytic decompositions of **1** at 22 and 0 °C produce a species that seems to be the same as the first thermal intermediate. It adds stereospecifically to olefins,^{8,13} and although direct comparison of the fused/bridged product ratio (**4/5**, Scheme I) is difficult because the photolyses must be carried out at low temperature to avoid pyrolysis of **1**, the photolytic fused/bridged (F/B) ratios fall on a smooth curve of the thermal data as a function of temperature. Even at -168 °C (105 K in Et_2O -isopentane-ethanol), photolysis of **1** in the presence of acrylonitrile gives the high F/B product ratios characteristic⁸ of a large contribution of singlet-derived adduct.^{7b}

Some photophysical observations confirm the chemical evidence for persistence of the cascade mechanism at low temperatures. At or near room temperature, the observed fluorescence intensities of methanol solutions of **1** monitored at 420 nm suggest a fluorescence yield of the order of 0.1%, which means that the fluorescence rate constant must be $\sim 10^9$

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 show¹⁵ 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 $5 \times 10^{13} s^{-1}$. 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_{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

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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.^{5a} Hence, the absolute rates, at least of the less reactive olefins, must be much less than k_{diff} .

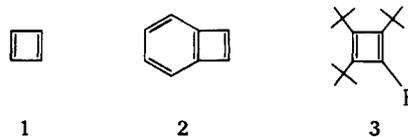
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1,2-Bis(trimethylsilyl)benzocyclobutadiene, a Paratropic 8π -Electron System

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 techniques³ 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.



Vacuum transfer of *cis*, *cis*-dienediyne **4** or one of its other stereoisomers⁶ 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 ($\tau_{olefinic}$ 3.80, 4.37 in CCl_4 ; 3.70, 4.25 in CD_3CN). The mass