Table II. Determination of ϵ for Triplet 1

meas	abs (506 nm)[a]	double integral[b]	[1],[c] M	ϵ,[c] M^{-1} cm^{-1}
1 UV-vis	0.575 ± 0.03			7820 ± 1600
1 EPR		366 ± 18	$2.10 (\pm 0.25) \times 10^{-4}$	
2 EPR		344 ± 17	$1.98 (\pm 0.24) \times 10^{-4}$	6100 ± 1000
2 UV-vis	0.423 ± 0.005			
3 EPR		253 ± 30	$1.45 (\pm 0.27) \times 10^{-4}$	7760 ± 1800
3 UV-vis	0.394 ± 0.004			

[a] The reported errors are standard deviations. [b] The reported errors represent ±5% except for the third, which reflects the disparity of the two measurements that were averaged. [c] The errors are the sums of the relative errors in the contributing values and thus represent conservative limits.

of $6 (\pm 2) \times 10^{-7}$ s^{-1}.[69] Rates measured with the other vibronic peaks were all within or near this range.

Photochemical Action Spectrum. A sample of **2** in MTHF was placed in the Oxford cryostat. The sample was cooled to 4 K, and photolyzed with 334-nm light from the 1000-W Xe arc lamp (ca. 20-nm monochrometer band pass) for 5–10 min to generate a sufficient concentration of **1**. The signal intensity was monitored at 3073 G (9.27 GHz, 0.5 mW) while the monochrometer wavelength was advanced 1 nm every 10 s with the slits set for a 2.75-nm band pass. The data were recorded digitally with a resolution of ca. 5.5 points nm^{-1}. With the aid of a FORTRAN program written for the IBM-PC/AT the curve was smoothed over a 25-point region by a least-squares procedure[110] and then differentiated by using a 35-point window, which also accomplished a second least-squares smoothing.[110] The lamp intensity correction was applied as a Gaussian function of lamp intensity data with a 2.5-nm fwhm to approximate the band pass, centered at each data point. The action spectrum of Figure 5 (a and b) was shifted by ca. 2 nm (into alignment with the absorption spectrum of Figure 5c) to compensate for an apparent miscalibration of the monochrometer (possibly caused by a slight misalignment of the optical arrangement). Attempts were made to detect a second biradical transition[3d] by scanning down to 260 nm (the practical limit for the Xe lamp used) but no decay of the EPR signal was observed.

Determination of Oscillator Strength. A sample of **2** in MTHF in a standard 5-mm-o.d. EPR tube was irradiated at 77 K for ca. 7 min with light from the 1000-W Xe arc lamp that had been directed through filter combination no. 1 (Table I). The sample tube was placed well away from the optical focal point and rotated during the photolysis to provide a uniform distribution of **1** throughout the MTHF matrix. The sample was stored at 77 K for 3 h prior to the analysis in order to avoid the faster portion of the nonexponential decay (see above). The effective path length of the EPR tube in the UV-vis spectrophotometer beam was measured as 0.35 ± 0.01 cm (roughly in accord with the inner diameter specified by the manufacturer) by comparison of a standard solution's absorbance in the tube with that in an ordinary 1-cm cell. The volume contraction of the solvent was measured as ca. 20% upon cooling from room temperature to 77 K. The EPR spin standard[111] consisted of a 5.48×10^{-4} M solution of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) in MTHF in a tube identical with that containing the biradical sample. The concentration at 77 K was $6.85 (\pm 0.4) \times 10^{-4}$ M, the estimated error being based primarily upon the uncertainty in the volume change. EPR spectra were recorded at 77 K by using 0.01-mW power for TEMPO spectra and both 0.01 and 0.1 mW for spectra of **1**, thereby avoding signal saturation in both cases. The digitized first-derivative spectra were numerically double-integrated by standard methods and scaled to a common receiver gain. The 506-nm absorbance of the sample was determined by recording five spectra as the sample tube was rotated in the finger Dewar with respect to the spectrophotometer beam. The absorbance was measured relative to a base line drawn between the edges of the spectrum with the aid of an HP-85A program. Three pairs of EPR and absorption measurements were made, at ca. 3, 6, and 9.5 h after photolysis (see Table II). The second member of the pair followed the first as closely as temporospacial constraints permitted, and the order of the two was reversed to compensate for the effects of both intrinsic and adventitious decay of the biradical. Absorbance values and double integrals for the three pairs of measurements on the sample of **1** are reported in Table II. The average of the three values for ϵ is 7200 M^{-1} cm^{-1}.

Magnetophotoselection. The photolysis setup consisted of, in series, the 1000-W Hg(Xe) arc lamp, the monochrometer, and two quartz lenses having 100- and 175-mm focal lengths. The first of these was adjusted to provide a parallel light beam and the second to reduce the image of the monochrometer exit slit to approximately the width of the sample at the point of incidence. An Oriel Model 27340 polymer sheet type near-UV/visible linear polarizer was placed between the two lenses and positioned appropriately with a rotatable mount. The monochrometer was found to polarize the light somewhat in the horizontal ($\mathbf{E} \| \mathbf{H}_0$) direction; therefore, for photolyses with unpolarized light, the assembly was replaced with the standard one, in which the (unpolarized) lamp output is directed through an appropriate series of filter glasses and focused into the EPR cavity. Spectra were recorded with 0.2-mW microwave power at ca. 9.25 GHz.

Acknowledgment. We thank the National Science Foundation for generous support of this work.

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(110) Savitzky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627–1639.

(111) When using a doublet signal as an intensity standard for a triplet, one must include a correction for the fact that triplet signals are inherently $^{4}/_{3}$ as intense per electron as doublet signals, or $^{8}/_{3}$ as intense per paramagnet. See, for example: Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358–2364.

2,4-Dimethylenebicyclobutane: Preparation, Characterization, and Relationship to the Non-Kekulé Isomer of Benzene

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Contribution No. 7847 from the Arnold and Mabel Beckman Laboratory of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125. Received September 22, 1988

Abstract: Thermolysis or direct photolysis of 5,6-dimethylene-2,3-diazabicyclo[2.1.1]hex-2-ene (**2**) in fluid solution produces 2,4-dimethylenebicyclo[1.1.0]butane (**3**), whose ^1H NMR spectrum (−80 °C, CD_2Cl_2) consists of singlets at δ 4.22 and 3.18 in a 2:1 ratio. Compound **3** is thermally unstable and dimerizes with second-order kinetics between −80 and −25 °C ($\Delta H^{\ddagger} = 6.8$ kcal/mol, $\Delta S^{\ddagger} = -28$ eu) by a novel mechanism involving direct combination of two molecules of **3** in the rate-determining step. This singlet-manifold reaction ultimately produces a mixture of two dimers, 3,8,9-trimethylenetricyclo[5.1.1.0^{2,5}]non-4-ene (**11**) and *trans*-3,10-dimethylenetricyclo[6.2.0.0^{2,5}]deca-4,8-diene (**12t**), with the former predominating. In contrast, triplet-sensitized photolysis of **2**, which leads to triplet 2,4-dimethylene-1,3-cyclobutanediyl (**1**), provides in addition to **11** and **12t**, a substantial amount of *trans*-5,10-dimethylenetricyclo[6.2.0.0^{3,6}]deca-3,8-diene (**13t**) and small amounts of two unidentified dimers. In addition, triplet biradical **1** ring closes to **3** in rigid media both thermally (77–140 K) and photochemically. In solution, **3** forms triplet **1** upon energy transfer from sensitizers having relatively low triplet energies. The implications of the thermal chemistry for the energy surfaces of the system are discussed.

In the preceding paper[2] we described the preparation of the non-Kekulé isomer of benzene, 2,4-dimethylene-1,3-cyclobutanediyl (**1**), by photolysis of diazene **2** under cryogenic conditions in rigid media. Triplet **1** was found to be quite amenable

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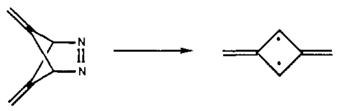


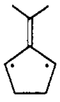
2 1

to characterization by EPR and electronic spectroscopy. These studies, however, did not provide spectroscopic information concerning either singlet **1** or the ring-closed isomers **3** and **4**. In the hope of generating and characterizing one or more of these species, we have studied this system under higher temperature, solution-phase conditions. We report herein that dimethylenebicyclobutane **3** is observable by low-temperature NMR spectroscopy. This very strained hydrocarbon dimerizes readily at low temperatures, and the mechanism of the process is quite novel. In addition, we describe the photochemical reactivity of both **1** and **3** and the unimolecular and bimolecular thermal reactivities of triplet **1** (^{3}**1**).

3

4

For most biradicals, formation of a new bond (ring closure) is a substantially exothermic process that occurs rapidly at all but the lowest temperatures.[3] However, structural features can be incorporated to offset the energetic advantage of bond formation. This has been beautifully demonstrated in a series of experiments by Berson and co-workers.[4] Thus, both the triplet and singlet states of trimethylenemethane (TMM) derivative **5** are independently trappable entities. These workers determined that the singlet encounters a barrier of 2.3 kcal/mol along its preferred closure pathway to the fully covalent form **6**. This kinetic barrier is apparently caused by the thermodynamic destabilization of the two possible closure products, **6** and **7**, relative to **5**. In fact, ring closure of ^{3}**5** to **6** is slightly *endothermic*. The situation is quite different with the parent TMM.[3,5,6] The ring closure to methylenecyclopropane (**9**) is calculated to be exothermic by ca. 15 kcal/mol,[7] and neither ^{1}**8** nor ^{3}**8** are readily trapped in fluid media.[6]



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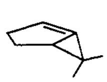

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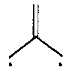
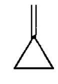


8 (TMM)



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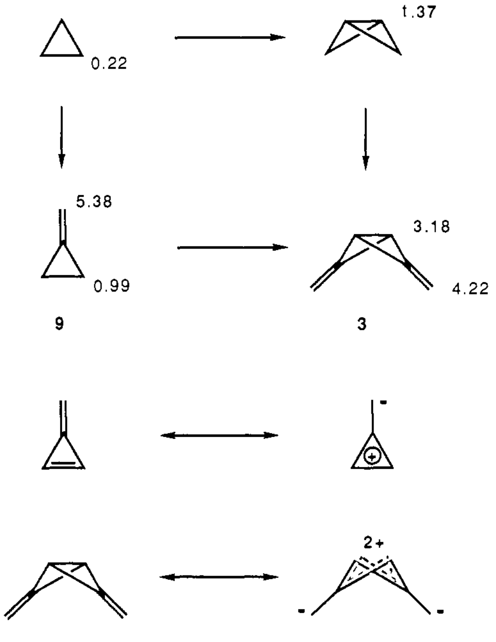
A thermochemical analysis of the ring closure of ^{3}**1** to provide dimethylenebicyclobutane **3** produces intriguing results. The roughly 80 kcal/mol gained by forming a new C–C bond[8] is offset by the loss of an estimated 41 kcal/mol of resonance energy[9] and an increase in strain energy. The strain energy of **1** is ca. 32 kcal/mol,[12] but that of **3** is more difficult to evaluate. A reasonable estimate would add 41 kcal/mol for each of the two methylenecyclopropane units[11] and another 9 as a result of their incorporation into a bicyclobutane ring system,[14] for a total of 91 kcal/mol. However, **3** is potentially a very unusual molecule, and its relative energy could be influenced by electronic interactions between the π-bonds and the transannular σ-bond. In fact, ab initio calculations by Schleyer[15] indicate that **3** is stabilized by such effects. Based on several types of isodesmic reactions calculated by Schleyer, an effective strain energy in the range of 76–82 kcal/mol would appear to be more appropriate. Using 79 kcal/mol for this value, we estimate the energy difference between ^{3}**1** and **3** to be 79 – (80 + 32 – 41) = 8 kcal/mol, with the triplet biradical being *more* stable than its covalent isomer. This is in acceptable agreement with ab initio calculations by Feller, Davidson, and Borden, which find **3** to be virtually isoenergetic with ^{3}**1**.[16,17] (The strain energy of bicyclo[2.1.0]pent-(1,2)-ene has been estimated as 123 kcal/mol,[18] disqualifying **4** as a viable participant in the

Scheme I



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(1) NSF Predoctoral Fellow, 1981–1984.

(2) (a) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.*, preceding paper in this issue. See also: (b) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774–1775; **1986**, *108*, 299–300.

(3) *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982.

(4) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446–453. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4, pp 151–194.

(5) Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799–807; *J. Am. Chem. Soc.* **1977**, *99*, 6438–6440.

(6) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242–248. Dowd, P.; Sengupta, G.; Sachdev, K. *J. Am. Chem. Soc.* **1970**, *92*, 5726–5727.

(7) Feller, D.; Davidson, E. R.; Borden, W. T. *Isr. J. Chem.* **1983**, *23*, 105–108.

(8) The bond dissociation energies for Et–Et, Et–nPr, Et–iPr, nPr–iPr, and iPr–iPr are all within 2 kcal/mol of 80: Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 309.

(9) At the Hückel level, the resonance energy (RE) of TMM is $(2(3)^{1/2} - 2)\beta = 1.46\beta$, while that of 1 is $((2(5)^{1/2} + 2) - 4)\beta = 2.47\beta$. The value of 41 kcal/mol is obtained by multiplying the TMM RE, 24 kcal/mol,[10] by the ratio of Hückel REs, 1.69.

(10) This estimate is obtained as follows: Upon going from ^{3}**8** to **9**, the energy gained by forming a C–C σ-bond, 80 kcal/mol,[8] is partly compensated by an increase in strain energy of 41 kcal/mol[11] and a loss of resonance energy (RE). Ab initio calculations find the ^{3}**8**–**9** energy difference to be 15 kcal/mol;[7] thus, the TMM RE is 80 – 41 – 15 = 24 kcal/mol. Note that the biradical RE is calculated relative to two localized radical centers and the appropriate number of isolated ethylene units.

(11) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322.

(12) This estimate derives from the observation that each sp^{2} center incorporated into a cyclobutane adds ca. 1.5 kcal/mol to the strain energy.[11,13]

(13) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386.

(14) The strain energy of bicyclobutane is taken to be 64 kcal/mol, 9 higher than that of two cyclopropanes.[11]

(15) Budzelaar, P. H. M.; Kraka, E.; Cremer, D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 561–567.

(16) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 1216–1218.

(17) (a) Feller, Davidson, and Borden[16] employed an STO-3G geometry optimization to find two minima corresponding to dimethylenebicyclobutane **3**, one with a 125° flap angle and a 1.64-Å transannular bond, the other with a 144° flap angle and a 1.88-Å central bond. The STO-3G/TCSCF-CI energies of these were found to be 2–4 kcal/mol higher and their SVP/TCSCF energies 4–5 kcal/mol lower than that of planar ^{3}**1**. (b) In contrast, Schleyer and co-workers,[15] by using 3-21G/TCSCF geometry optimization, find a single energy minimum for **3** with a 135° flap angle and a 1.78-Å transannular bond. These authors do not address the relative energies of **3** and ^{3}**1**, however. For comparison, at the same level of theory, bicyclobutane is calculated to have a flap angle of 120° and a 1.53-Å central bond.[15]

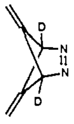
(18) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85–92. We are aware of no experimental evidence for the existence of a derivative of this ring system.

chemistry of **1**.) Thus, to the extent that thermodynamics govern the reactivity of such systems, the **1**–**3** pair should be more similar to the Berson system (**5**–**6**) than to the parent (**8**–**9**).

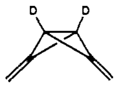
Dimethylenebicyclobutane **3** is an interesting structure in its own right. Ab initio calculations[15,16] have found geometries for **3** that are quite different from bicyclobutane itself, with the ring of **3** being considerably flattened and the central bond substantially lengthened.[17] Moreover, these calculations predict the bridgehead carbons of **3** to be highly inverted; that is, all four atoms bound to them lie on the same side of a plane. One might then describe the central bond as comprising the small lobes of sp^3-like hybrid orbitals.

Preparation of 3 and Characterization of Dimers

^{1}H NMR Spectroscopy of 3. Upon direct photolysis or thermolysis of diazene **2** in CD_2Cl_2 several ^{1}H NMR signals are observed that are attributed to stable dimeric ($C_{12}H_{12}$) products (see below). In addition, a thermally labile species is observed. This compound displays singlets at δ 4.22 and 3.18 in a 2:1 ratio; upon photolysis of **2**-d_2, only the δ 4.22 singlet is observed. These signals are assigned to 2,4-dimethylenebicyclo[1.1.0]butane (**3**) and its deuterated analogue **3**-d_2. These species are, in fact, the only reasonable sources of these NMR signals, given the manner in which they were produced and the chemistry to be described.



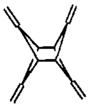
2-d$_2$



3-d$_2$

Scheme I shows ^{1}H NMR data for **3** and related compounds.[19] It is clear that the bridgehead protons of **3** are further downfield than one would expect, while the exocyclic methylenes are surprisingly upfield. A similar pattern is seen in methylenecyclopropene (Scheme I) and is rationalized in terms of the zwitterionic resonance structure shown, which includes an aromatic, 2π-electron ring. It is perhaps a greater leap to the analogous structure for **3** (Scheme I). However, as noted above, ab initio calculations indicate that **3** is considerably flattened relative to the parent bicyclobutane. This could signal contributions from the zwitterionic form.

Potential Dimers. Early in our studies we observed products from the decomposition of diazene **2** that we suspected were dimers of biradical **1**. We considered the five structures **10**–**14** to be the



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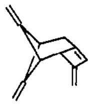

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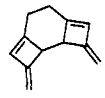

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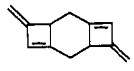

13

14

only reasonable candidates for these dimers. These structures are formally derived by simply making every sensible union of two biradicals **1** at their centers of unpaired electron density. The involvement of **3** (or for that matter **4**) in the dimerization should not introduce additional structures, and we have found no evidence to suggest that more structures need be considered (see below).

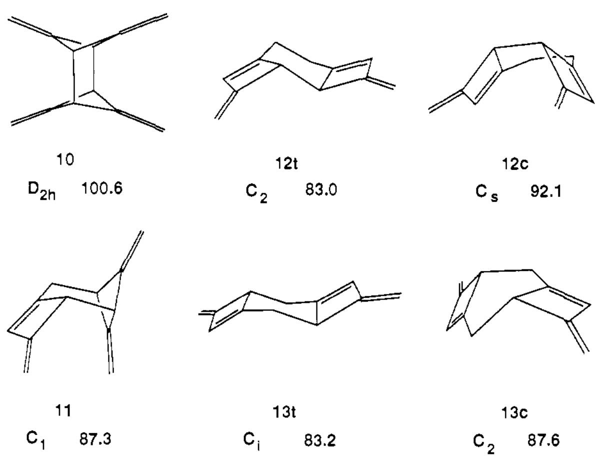

Figure 1. MM2 geometries and strain energies (kilocalories/mole) of dimers.

Table I. Product Mixtures from Thermal and Photochemical Decompositions of **2**

	product, %				
	11[a]	**12t**[a]	**13t**[a]	D_1[b]	D_2[b]
T, °C					
−78 °C	90	10	0[c]	0[c]	0[c]
+40 °C[d]	80[b]	20[b]	ca. 0.2[b]	ca. 0.1	tr
hν at −95 °C	90	10	ca. 0.1[b]	ca. 0.05	tr
^{3}*hν* at −78 °C					
0.01 M Ph_2CO	40	10	50	ca. 1	ca. 1
0.10 M Ph_2CO[e]	60	10	30	ca. 1	ca. 1

[a] By ^{1}H NMR unless otherwise noted. [b] By GC unless otherwise noted. [c] Estimated as <0.005% by GC. [d] The experiment was conducted by dropwise addition of a cold (−78 °C) solution of **2** to a 40 °C flask. [e] The composition of the product mixture early in the photolysis is reported.

In order to determine their geometries and relative energies, we carried out empirical force field (MM2)[20] calculations on **10**–**13**. Dimers **12** and **13** can exist as cis or trans stereoisomers, and thus, in all, six potential structures were considered. Figure 1 shows the calculated geometries of **10**–**13** and lists their MM2 strain energies and point group symmetries. While it is evident that all six species are energetically feasible, several are of relatively higher energy due to the presence of boat cyclohexane moieties and the attendant eclipsing interactions. Most notably, the cis isomers, **12c** and **13c** are of significantly higher energies than their trans counterparts, whose cyclohexane rings are locked into chair conformations. Compound **10** is found to have the highest strain energy for this reason.

The key to the potential existence of cyclobutadienophane **14**[21] is the notion that it might experience a stabilizing electronic interaction of the nominal NBMOs of the cyclobutadiene units. Such an interaction could then make **14** "three-dimensionally aromatic". Unfortunately, we have found no hint that **14** is among the dimeric products formed from **2**.

The solution-phase thermal chemistry and photochemistry of diazene **2** affords primarily three of the seven possible dimers, which we have identified by NMR spectroscopy (see below) as **11**, **12**, and **13**. Because of their bilateral symmetries, we have not been able to conclusively assign **12** and **13** the cis or trans stereochemistry. However, we favor the trans for each on the basis of the calculated strain energies (Figure 1) and the mechanistic

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(19) (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 258–261. (b) Wiberg, K. B. *Adv. Alicyclic Chem.* **1968**, *2*, 185–205. Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749–2769. (c) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698–3699. Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699–3700.

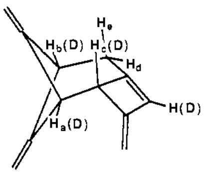
(20) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(21) See: Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; pp 176–177. A cobalt-capped relative of **14** has recently been reported: Gleiter, R.; Karcher, M.; Ziegler, M. L.; Nuber, B. *Tetrahedron Lett.* **1987**, *28*, 195–198.

analysis to follow. As such, we will present dimers **12** and **13** as the trans stereoisomers, but with the caveat that this assignment is not absolutely firm.

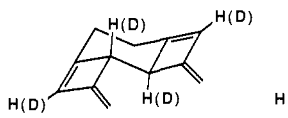
Dimerization in the Singlet and Triplet Manifolds. Spectroscopic Assignment of Dimers. Direct photolysis (≤−78 °C) or thermolysis (≥−78 °C) of diazene **2** in CD_2Cl_2 ultimately provides a quantitative yield of dimers **11** and **12** in ratios varying from ca. 9:1 to 4:1 depending on temperature (Table I; very small amounts of three other dimers are also detected by GC—their assignments are discussed below). These compounds are thermally stable to ca. 100 °C, but both are air sensitive—**11** especially so. That these species are, in fact, $C_{12}H_{12}$ hydrocarbons is confirmed by GC–MS analysis of the products from **2** (M^+, *m/e* 156) and from **2**-d_2 (M^+, *m/e* 160). The structural assignments are unambiguous from the 400-MHz ^1H NMR spectra of the protiated and deuterated species.

The major product displays five aliphatic and seven olefinic signals, one of which is attributable to a cyclobutene proton. It is therefore assigned as the only asymmetric dimer, **11**. Bridgehead protons H_a and H_b couple, while H_c appears as a slightly broadened singlet. The aliphatic methylene protons, H_d and H_e, give rise to an AB quartet, one member of which is split further by a 4-Hz coupling to H_b. That this is the only three-bond coupling observed is entirely consistent with the calculated (MM2) dihedral angles. The H_a–H_c and H_b–H_e dihedral angles are ca. 73°, while that between H_b and H_d is 50°. Accordingly, only the latter pair should couple significantly. This assignment is confirmed by the spectrum of **11**-d_4 and is additionally supported by ^{13}C NMR data.

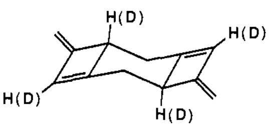


11 (-d4)

The spectrum of the minor isomer comprises six signals—three aliphatic and three olefinic—establishing it as either **12** or **13** by symmetry considerations. The key to its assignment as **12** is the observation that the bridgehead methines appear as a singlet, whereas those of **13** must couple with the neighboring methylene protons. Again, although we cannot distinguish **12t** from **12c**, we will refer to this product as **12t** (see below).



12t (-d4)



13t (-d4)

Triplet-sensitized photolysis of diazene **2** in CD_2Cl_2 affords three dimers that are easily observed by ^1H NMR and two others, D_1 and D_2, each in ca. 1% yield (Table I), which are seen by GC only. The three major products are **11**, **12t**, and a new dimer whose six-signal ^1H NMR spectrum, GC retention time, and GC–MS fragmentation pattern are very similar to those of **12t**. The distinguishing characteristic of the new dimer, however, is that the ^1H NMR signal of its bridgehead methines is split by coupling to the neighboring methylenes. This new product must therefore be **13** (we will refer to it as **13t**). Consistent with this assignment is the ^1H NMR spectrum of **13t**-d_4, in which the methylene proton multiplets have collapsed to doublets. With regard to the minor (1%) dimers, D_1 and D_2, we currently have no structural information except that the mass spectrum of D_1 is almost identical with that of **13t**, while D_2 displays a unique MS fragmentation pattern, but one more like that of **11** than **12t** or **13t**.[22a] Control experiments have demonstrated that neither **13t** nor the minor dimers D_1 and D_2 are produced upon sensitized photolysis of **11** and **12t**.

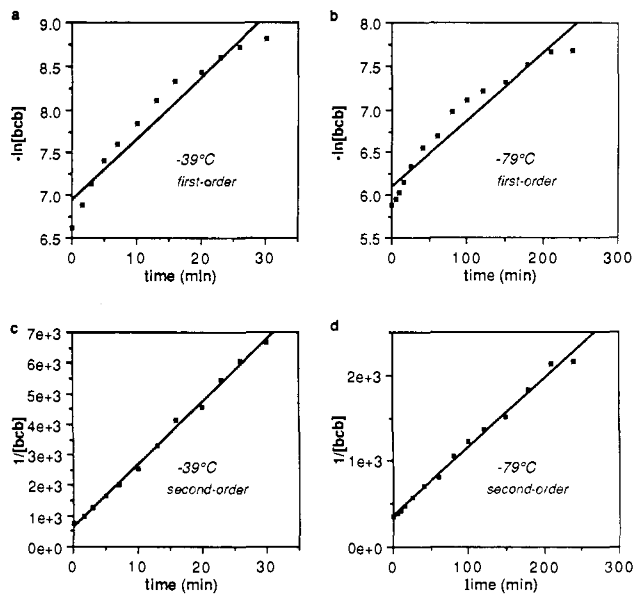


Figure 2. Concentration vs time data for the dimerization of dimethylenebicyclobutane **3**. Analysis of the data according to the first-order rate law provides the plots shown for (a) the −39 °C and (b) the −79 °C decay of **3**. These data are recast in second-order form to provide the 1/[3] vs *t* plots (c and d).

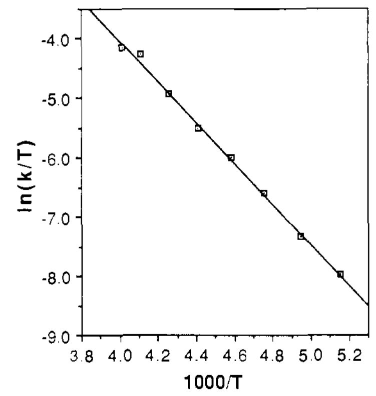


Figure 3. Eyring plot for the thermal dimerization kinetics of dimethylenebicyclobutane **3** between −25 and −80 °C in CD_2Cl_2. The activation parameters are $\Delta H^{\ddagger} = 6.8$ (±0.6) kcal/mol and $\Delta S^{\ddagger} = -28$ (±3) eu.

The addition of 0.8 atm O_2 completely shuts down dimer formation (although **2** is still destroyed) in the sensitized photolysis, while it has no effect on the thermal dimerization.[23] Oxygen is an excellent trap for triplet biradicals,[24] and these observations indicate that ^{3}**1** is an intermediate in the formation of dimers upon sensitized photolysis, but not upon thermolysis or direct photolysis of **2**. In addition, because **13t** is indigenous only to the product mixtures produced by the triplet photochemistry and is formed in substantial quantities, it is an excellent indicator of bimolecular ^{3}**1** chemistry. The virtual absence of **13t** among the products of thermolysis or direct photolysis of **2**, combined with oxygen's inability to perturb the reaction, demonstrates that ^{3}**1** is not involved.[25] Thermolysis and direct photolysis of **2** therefore provide

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[22] Snyder, G. J. Ph.D. Thesis, California Institute of Technology, 1988; (a) pp 236–238; (b) pp 273–274; (c) p 275; (d) pp 188–193; (e) pp 197–200; (f) pp 204–208.

[23] The rate constant for dimerization of **3** at −38 °C was also found to be unaffected by the addition of oxygen.

[24] See, for example: Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2225–2226. Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1982**, *115*, 1197–1208. Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929–935. See also: Ref. 4.

[25] In addition, we have observed no CIDNP in the ^1H NMR signals of **11** and **12t** produced by thermolysis of **2**. Cf. the observation of CIDNP in the dimerization of **5**: Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544–1546, and ref 4.

dimers **11** and **12t** by a mechanism *confined exclusively to the singlet manifold.*

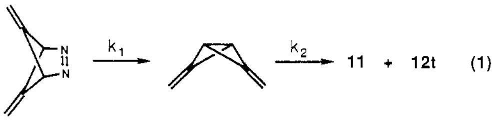
Dimerization in the Singlet Manifold

Dimethylenebicyclobutane Dimerization Kinetics. When a sample of **2** in CD_2Cl_2 is irradiated at −95 °C until no diazene remains, **3** is produced with a typical initial concentration of (1–3) $\times 10^{-3}$ M, along with **11** and **12t**. Bicyclobutane **3** is unstable at this temperature, and its decay can be monitored by ^1H NMR between −80 and −25 °C. The decay is cleanly *second order*, as illustrated in Figure 2. The Eyring plot of Figure 3 furnishes activation parameters $\Delta H^{\ddagger} = 6.8\ (\pm 0.6)$ kcal/mol and $\Delta S^{\ddagger} = -28\ (\pm 3)$ eu ($E_a = 7.3$ kcal/mol, log $A = 7.0$). Because bicyclobutanes are, in general, especially susceptible to electrophilic attack at the bridgehead positions,[19b,26] we were concerned that the observed decay of **3** might incorporate some component of acid catalysis. We therefore checked these activation parameters by using samples containing 0.02 M 2,6-lutidine to scavenge any adventitious acid and obtained values within the error limits specified above.

We have also measured the secondary deuterium kinetic isotope effect (KIE) on the dimerization rate by using samples of **3** and **3**-d_2. In the range −40 to −75 °C, k_H/k_D was found to be 1.3 (±0.1), corresponding to a k_H/k_D of 1.2 at room temperature.

Intermediacy of 3 in Formation of Dimers from 2. Several pieces of evidence indicate the intermediacy of **3** in the formation of **11** and **12t** and lead us to conclude that **3** is produced quantitatively upon both thermolysis and direct photolysis of **2**. The observation of approximately the same **11**/**12t** ratio from the thermal and photochemical decompositions of **2** at −78 °C (Table I) is consistent with the intervention of a common intermediate. Ideally, one would like to establish that **3** independently forms the same product mixture; however, the thermal lability of **3** makes such an experiment infeasible. When a typical (ca. 10^{-2} M) sample of diazene **2** in CD_2Cl_2 is irradiated at ≥−95 °C, ^1H NMR spectroscopy reveals a large amount of **11** and **12t** and a small amount of **3** (ca. 10%). Dimerization of **3** is known to occur at the temperature of the photolysis, consistent with its being the source of the large amount of dimers observed.[27] Although we cannot accurately measure the ratio of **11** to **12t** formed from decay of the small amount of **3** observed, this ratio is roughly the same as that present at the end of the photolysis. These observations are consistent with the postulate that photoexcited **2** produces dimers exclusively via **3**.

More compelling evidence that dimers **11** and **12t** originate entirely from **3** is provided by the course of the thermal decomposition of **2**. The diazene decomposes with strict first-order kinetics, as monitored by ^1H NMR between −45 and −65 °C, and with activation parameters, $E_a = 18.2\ (\pm 0.1)$ kcal/mol and log $A = 14.9\ (\pm 0.1)$.[28] As diazene **2** decays, the concentration of **3** first increases rapidly then decreases, while the concentrations of **11** and **12t** increase steadily (Figure 4). This behavior is what one would expect if the reaction proceeds via eq 1. Moreover,



(1)

2 3

if this mechanism represents the only pathway from **2** to **11** and **12t**, the time evolution of the concentration of **3** is quantitatively predictable, since k_2 is known, and k_1 is simply the rate of loss of diazene **2**.

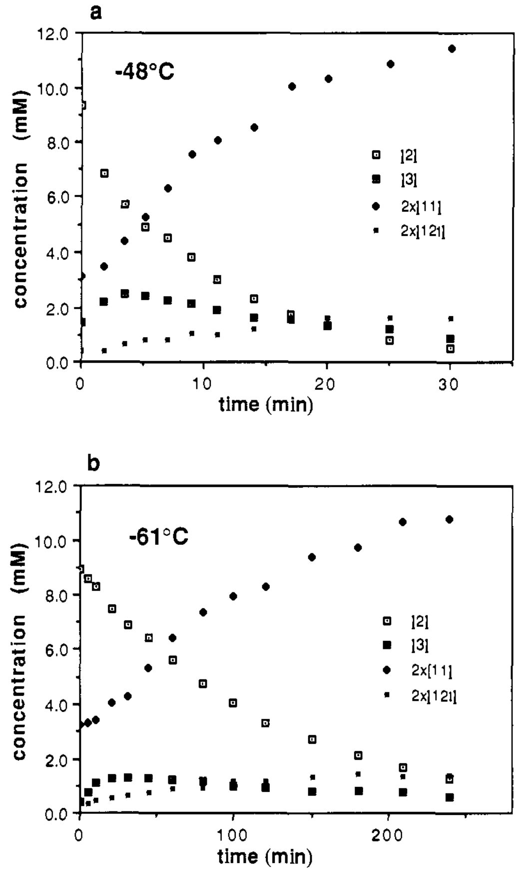


Figure 4. Concentrations of diazene **2**, dimethylenebicyclobutane **3**, and dimers during the course of the thermolysis of **2** in CD_2Cl_2 (a) at −48 °C and (b) at −61 °C.

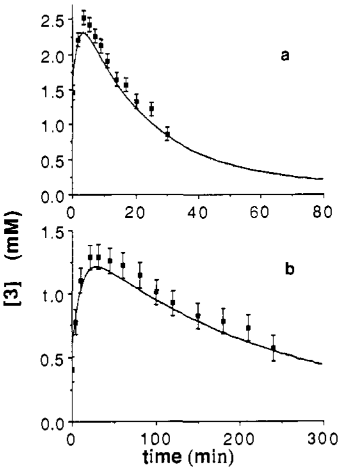


Figure 5. Time evolution of [**3**] during thermolysis of **2** (a) at −48 °C and (b) at −61 °C. The data points were obtained by ^1H NMR. The curves were calculated numerically as described in text.

Figure 5 shows the calculated [**3**] vs time curves, using the previously determined values of k_1 and k_2. Given the uncertainty in both k_2 and the measured concentrations, the experimental data follow the calculated curves quite well. We estimate that a 20–30% diversion of **2** from the route of eq 1 would produce a meaningful disparity between the calculated curves of Figure 5 and the experimental data points, so that rigorously, at least 70–80% of the diazene **2** that decays thermally produces **3**. However, we have no evidence to suggest that a second dimerization pathway bypassing **3** is involved, and so we invoke Occam's

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[26] Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128–136.

[27] The decay rate at −100 °C in ca. 10:1 CF_2Cl_2/CD_2Cl_2 is 0.01 M^{-1} s^{-1}.

[28] The substantial drop in E_a relative to the parent 2,3-diazabicyclo[2.1.1]hex-2-ene ($E_a = 34.4$; log $A = 15.5$)[29] is fully consistent with expectations based on analogous systems. In particular, the expected one-bond cleavage would produce a pentadienyl radical, which enjoys substantial (ca. 19 kcal/mol) resonance stabilization.[38] For detailed discussion, see: Reference 22, pp 165–168.

[29] (a) Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211–4217. (b) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092–4093.

Scheme II

a.

$$3 + 3 \xrightarrow{k_2} \text{Dimers}$$

b.

$$3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1$$

$$3 + 1 \xrightarrow{k_2} \text{Dimers}$$

c.

$$3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1$$

$$1 + 1 \xrightarrow{k_2} \text{Dimers}$$

razor[30a] and conclude that both thermally and photochemically, **3** is the exclusive source of **11** and **12t** in the singlet manifold.

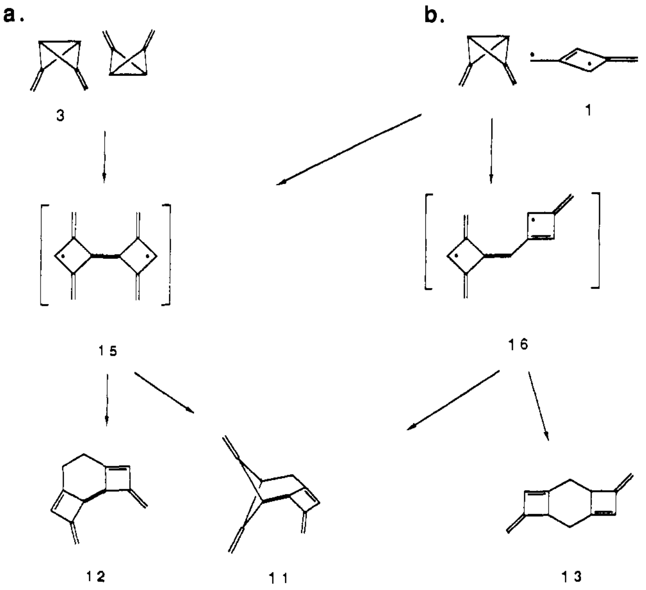
Dimerization Mechanism. One can imagine three reasonable mechanisms for the dimerization of dimethylenebicyclobutane **3**. These are presented in Scheme II. Of course, direct dimerization (mechanism a) gives rise to second-order kinetics. In addition, if singlet **1** (^{1}**1**) has a finite lifetime and is thermally accessible from **3**, it could also participate. The dimerization step could then involve either trapping of ^{1}**1** by **3** (mechanism b) or the reaction of two singlet biradicals (mechanism c). The rate law for mechanism b, derived by applying the steady-state approximation to the concentration of ^{1}**1**, is $-\mathrm{d}[3]/\mathrm{d}t = (2k_1k_2[3]^2)/(k_{-1} + k_2[3])$. This mechanism could lead to second-order decay of **3** if the dimerization step were rate-determining—that is, if $k_{-1} \gg k_2[3]$. The rate law for mechanism c is more complex; however, this mechanism can also lead to second-order kinetics.[31]

If ^{1}**1** is a participant in the dimerization mechanism, it should be possible to chemically intercept it, thereby shutting down the formation of the dimers. We therefore decided to test the effect of large concentrations of two electron-deficient olefins, fumaronitrile and maleic anhydride, which have been found to be excellent traps for ^{1}**5**.[4] When an 8.5×10^{-3} M solution of diazene **2** in acetone-d_6 is allowed to decompose thermally at −50 °C in the presence of 0.9 M fumaronitrile, dimers **11** and **12t** are formed in 70% yield. In the presence of 1.0 M maleic anhydride, a 30% yield of dimers is obtained. Although we have not been able to determine the fate of the rest of the material, the mechanistic analysis relies only on the yield of **11** and **12t**.

We will first analyze these results in terms of mechanism b (Scheme II). Because the rate constants for the formation and loss of **3** at −50 °C are known, we can calculate that during the thermolysis of 8.5×10^{-3} M **2** the maximum concentration of **3** present at any one time is 2×10^{-3} M. We will assume, for the sake of argument, that **3** is formed quantitatively under these conditions and all the **3** that does not appear as dimers has been trapped as ^{1}**1**. Then, if mechanism b is operative, ^{1}**1** is trapped competitively by **3** and the olefin with rate constants k_B and k_T, respectively. For 30% dimer formation in the presence of 1.0 M maleic anhydride, $k_B(2 \times 10^{-3}\ \mathrm{M}) > {}^3/_7k_T(1.0\ \mathrm{M})$, or $k_B > 200k_T$; similarly, for 70% dimers with 0.9 M fumaronitrile, $k_B > 1000k_T$.

We note that the less than quantitative yields of dimers formed in the presence of these olefins is not necessarily inconsistent with the dimerization proceeding entirely by mechanism a. Electron-deficient olefins are known to attack bicyclobutanes,[26] and the large strain energy of **3** might make it unusually reactive toward the olefins used. Furthermore, thermal deazetation of **2** could produce **3** via ^{1}**1**, which may be intercepted before it undergoes ring closure. Either of these reactions would be interesting; however, additional experiments are required to determine the fate of the missing material and its mechanistic implications.

Scheme III



Our best estimates of the olefin trapping rates come from a comparison to the extensively investigated chemistry of biradical **5**. Both maleic anhydride and fumaronitrile trap ^{1}**5** at or near the diffusion rate, k_d.[4,22b] If ^{1}**1** were also trapped at the diffusion rate, mechanism b would require that **3** react significantly faster than k_d and would consequently be eliminated. (Mechanism c of Scheme II is even more untenable in light of this result and will not be considered further.) Of course, the critical issue is the extent to which **5** is a good model for **1**. Certainly there are many structural similarities, and at present we can conceive of no reasons for dramatically different behaviors for the two.[32]

A second argument against the involvement of ^{1}**1** in the dimerization of **3** is based on the expected lifetime of such a singlet biradical. Taking 10^{10} M^{-1} s^{-1} as an upper limit on the diffusion rate in CH$_2$Cl$_2$ at −78 °C, reaction of ^{1}**1** with 10^{-3} M **3** (the maximum feasible concentration) would occur no faster than 10^7 s^{-1}. Intersystem crossing (ISC) to the triplet ground state of **1** would have to be at least 2 orders of magnitude slower than this to account for the lack of characteristic triplet-derived dimer **13t** in the −78 °C thermolysis of **2** (Table I). Based on precedent from a variety of systems,[33] an ISC rate constant of $\leq 10^5$ s^{-1} would be unusually small.

The final and perhaps strongest point that argues for the direct dimerization of **3** (Scheme IIa) is that it provides a mechanism that nicely rationalizes the product distribution. As shown in Scheme IIIa, a stepwise process involving initial bond formation at the bridgehead positions would produce biradical intermediate **15**. This step provides a pathway to **11** and **12t**, both of which contain a methine–methine connection, and excludes **13t**, which does not. As suggested in Scheme IIIb, any path involving the reaction of biradical ^{1}**1** with **3** would be expected to be much less selective. There is certainly spin density at the methylene groups of ^{1}**1**, and the formation of biradicals other than **15**, such as **16**, would seem to be quite favorable. It is difficult to imagine why **16** would close exclusively to **11**, with no formation of **13**. (This is especially so given the course of the triplet dimerization—see below.) Stated differently, if mechanism b of Scheme II is op-

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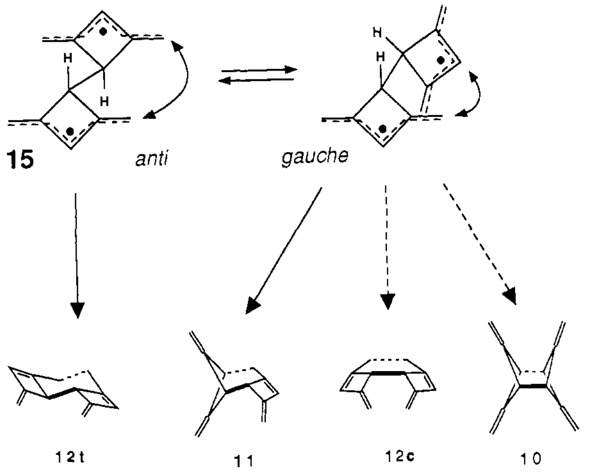
(30) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984; (a) p 3; (b) pp 96–97.

(31) The rate law is $-\mathrm{d}[3]/\mathrm{d}t = (k_1k_2[3][1])/(k_{-1} + k_2[1])$. The condition $k_{-1} \gg k_2[1]$ provides the expression $-\mathrm{d}[3]/\mathrm{d}t = k_1k_2[3][1]/k_{-1}$. If **3** and **1** are in equilibrium, $[1] = k_1[3]/k_{-1}$. Substituting this for [**1**] leads to a second-order expression.

(32) Cycloaddition of olefins to ^{1}**1** should be quite exothermic and does not occur with electron-rich olefins, as is the case for ^{1}**5**.[22c] A geometry change such as rotation of a CH$_2$ group of ^{1}**1** is ruled out by the identity of the singlet-manifold dimers, as discussed below.

(33) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 186.

Scheme IV



erative, one of two unrealistic constraints must be imposed: either ^{1}**1** and **3** combine to give only **15**, or **16** closes to give **11** but not **13**.

We conclude that the dimerization must involve *direct combination of two molecules of dimethylenebicyclobutane 3 as the rate-determining step.* Steric and electronic considerations suggest the geometrically specific line of approach shown in Scheme IIIa,[34] and the large, negative entropy of activation is quite consistent with a bimolecular, stepwise process of this type.[37] The activation enthalpy, 7 kcal/mol, would appear to be inordinately low for a reaction that involves cleavage of two σ-bonds to form a biradical in the rate-determining step. However, thermochemical estimates indicate that this reaction should be quite exothermic. Thus, the net loss of one C–C σ-bond, worth 80 kcal/mol,[8] is offset by the delocalization energy of the two pentadienyl systems of **15**, estimated as 19 kcal/mol[38] each, and a release of ca. 98 kcal/mol of strain. This difference in strain energies is determined by subtracting 60 kcal/mol for biradical **15**[12] from 2 × 79 for the strain of two dimethylenebicyclobutanes **3** (see above). Thus, the enthalpy change for the first step of the dimerization (Scheme IIIa) is –56 kcal/mol! The transition state must surely feel some of this energy release, and an unusually low activation enthalpy is therefore not unreasonable.

The secondary deuterium KIE observed, $k_H/k_D \simeq 1.2$ (298 K), is also consistent with this direct dimerization mechanism. On going from two molecules of **3** to biradical **15** (Scheme IIIa) two nominal sp^3 centers are converted to sp^2, leading to the expectation that $k_H/k_D > 1$.[30b] Of course, the bridgehead carbons of **3** participate in rather unusual bonding.[15,16] Nevertheless, the factor governing the magnitude of k_H/k_D is the reduction in the frequency of the vibrational mode that becomes the out-of-plane C–H bend at the radical centers of **15**. Regardless of what type of hybridization best describes the bridgehead carbons of **3**, the corresponding frequency—that of the C–H bend in the direction of the central bond—should be significantly higher than that of the out-of-plane sp^2 C–H bend.

There are four dimers with methine–methine bonds, **10**, **11**, **12t**, and **12c**, that could potentially be formed upon closure of intermediate **15**, but only two of these are observed. We analyze the product-determining step as illustrated in Scheme IV. The proposed line of approach requires that **15** be produced in the anti conformation. Formation of the second bond can then occur between neighboring methylene groups to produce either enantiomer of **12t**. Rotation of **15** to either C_2-symmetric gauche conformer followed by ring closure at the proximate radical centers provides enantiomeric forms of **11** (Scheme IV). On the other hand, the pathways to **10** and **12c** involve rotation of **15** toward the eclipsed conformation, which presumably disfavors formation of these dimers. The finding that, in fact, only **11** and one stereoisomer of **12** are formed, strongly supports this analysis. On this basis we assign the observed isomer of **12** the *trans* stereochemistry.

Given that intermediate **15** is likely formed in the anti conformation, the predominance of **11** over **12t** suggests that rotation is significantly faster than ring closure for singlet **15**. This is consistent with expectation,[39] especially considering that **15** is stabilized by delocalization of its unpaired electrons and also "strain-protected"[4] to some extent. Applying our usual thermochemical analysis, **15** suffers energetically from a missing C–C bond (80 kcal/mol[8]) and the strain present in the cyclobutyl rings (2 × 30 kcal/mol[12]), but some of this is offset by the pentadienyl delocalization energy (2 × –19 kcal/mol[38]). Ring closure produces dimers with approximately 85 kcal/mol of strain energy (Figure 1), making formation of the second bond exothermic by only ca. 17 kcal/mol [(80 + 60 – 38) – 85].

Dimerization in the Triplet Manifold

As mentioned above, sensitized photolysis of diazene **2** produces a new dimer, **13t**, as a major product along with **11**, **12t**, and very small amounts of two unidentified dimers (Table I). The reaction must involve biradical **1** in its triplet ground state. Not surprisingly, this dimerization is less selective than the coupling of two molecules of **3**, and so a more complex mixture results. The dimerization most likely occurs by both stepwise reaction of two triplet biradicals, and reaction of ^{3}**1** with **3** (presumed to arise via thermal or photochemical closure of ^{3}**1**—see below). Several C_{12} biradical intermediates, including **15** and **16**, may be involved. Preliminary experiments indicate that the product ratio depends on the *sensitizer* concentration (Table I; see Experimental Section). This could reflect a competition between the (^{3}**1** + ^{3}**1**) and (^{3}**1** + **3**) mechanisms.[22d]

Interconversions of ^{3}1 and 3

Photochemistry of ^{3}1 at 77 K. We reported previously[2] that triplet **1** displays a strong, spin-allowed electronic transition at 506 nm (with vibronic structure extending to near 400 nm). The biradical is destroyed rapidly and irreversibly upon visible excitation of this transition. We also noted that upon photolysis (at 4 or 77 K) the destruction of ^{3}**1** is accompanied by the appearance of no free-radical (or other) EPR signal.[2] This demonstrates that the photochemistry does not involve H-atom abstraction from the matrix material.[40] Because the biradicals are immobilized in distinct matrix sites the photochemical reaction must therefore be a unimolecular process. Ring closures to **3** or **4** come to mind immediately, at least as the initial step in the mechanism. Although closure to **4** appears less favorable, it cannot be ruled out a priori. The more likely potential photoproduct, **3**, is also formed upon adventitious thermolysis and direct photolysis of diazene **2** (and also almost certainly upon thermal decay of ^{3}**1**—see below). Consequently, simple product analysis is not sufficient to unambiguously assign the photoproduct. Identifying the photoproduct is therefore a matter of photolyzing enough ^{3}**1** that either (1) a

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(34) Stepwise, endo attacks on the transannular bonds of bicyclobutanes are well precedented[26,29a,35] and the line of approach shown in Scheme IIIa is required by the orbital topology of the "bent" bicyclobutane central bond.[36]

(35) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 1131-1 32.

(36) See, for example: Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767-773. Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1973; pp 203-205.

(37) While the observed activation parameters may appear to suggest a concerted dimerization, they are quite comparable to those seen in the stepwise dimerization of 2,3-dimethylene-2,3-dihydrofuran: Chou, C.-H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 4138-4144.

(38) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(39) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863-3870. See also: Dervan, P. B.; Dougherty, D. A. in ref 3, Chapter 3, pp 107-149.

(40) Such abstractions have been observed, for example, upon photolysis of triplet diphenylcarbene in alcoholic matrices at 77 K[41] and upon photolysis of triplet 1,3-cyclopentanediyl in cyclohexane at 5.5 K.[42]

(41) Leyva, E.; Barcus, R. L.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7786-7788.

(42) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688-4694.

product other than **3** and its dimers can be detected or (2) by the absence of such a new species, **3** can be established as the photoproduct.

We elected to use EPR to measure the amount of ^{3}**1** photolyzed and to analyze the product composition by low-temperature ^{1}H NMR. Accordingly, a sample consisting of **2** and 0.24 M acetophenone as a photosensitizer in 8:1 toluene-d_8/3-methylpentane was irradiated at 77 K in the EPR cavity with light of 340–390 nm—a region in which only the sensitizer absorbs. Under these conditions the signal intensity of ^{3}**1** was found to level off considerably after ca. 30 s of irradiation, presumably as a result of competitive secondary photolysis of the biradical by scattered and emitted light. This effect made it possible to generate only ca. 3.5×10^{-5} M ^{3}**1** from a given photolysis, as determined by spin-counting. Consequently, it was necessary to repeatedly generate and destroy the biradical in order to accumulate a detectable amount of photoproduct. The sample was therefore subjected to 150 cycles of a 30-s sensitized photolysis of **2** followed by a 10-s direct photolysis of ^{3}**1** at $\lambda > 450$ nm. Constant monitoring of the EPR signal intensity and intermittent spin-counting provided an estimate of the total amount of biradical photolyzed, in terms of an effective concentration at −78 °C, as 2.7 mM. Because the (presumably significant) quantity of biradical photolyzed adventitiously during generation of the EPR signal is not included in this estimate, the stated concentration represents a lower limit on the amount of photoproduct produced.

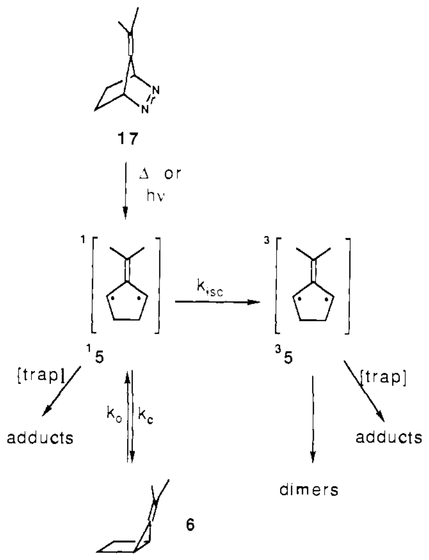
^{1}H NMR spectroscopy at −80 °C revealed that the initial mixture, 12.1 mM **2**, 1.8 mM **3**, and 3.3 mM dimers had been converted to a mixture of 5.2 mM **2**, 3.3 mM **3**, and 6.6 mM dimers **11** and **12t**. That all the material present before the photolysis was thus accounted for (within experimental error) among the compounds **2**, **3**, and the dimers provides good evidence that the photoproduct is **3** (which dimerized to some extent upon thawing the sample for NMR analysis). Moreover, the sample displayed no new ^{1}H NMR signals in the solvent "window" between δ 2.3 and 6.8, although a photoproduct present in a concentration of 2.7 mM would have been easily observable. We thus conclude that photolysis of ^{3}**1** with visible light cleanly produces **3**.

Photochemistry of Dimethylenebicyclobutane 3. Compound **3** is a hydrocarbon that lacks a long-wavelength chromophore in the traditional sense. Nevertheless, its unique structure and the likelihood of electronic interactions between the olefinic groups and the strained, transannular bond led us to wonder if **3** could be induced to ring-open to **1** photochemically. Indeed, we have found evidence that **3** is converted to ^{3}**1** upon photosensitization.

Samples of **3** in CH_2Cl_2 containing various triplet sensitizers were irradiated at −78 °C, warmed to room temperature, and analyzed by GC. Substantial amounts of **13t**, a clear indicator for the intervention of triplet **1**, were produced when benzophenone (triplet energy, E_T = 68.5 kcal/mol[43]), benzil (E_T = 53.7[43]), or fluorenone (E_T = 53.3[43]) were used as sensitizers. Smaller but still significant quantities of **13t** were found in samples containing the photosensitizers 9-methylanthracene, acridine, and phenazine, which have E_T = 41–45 kcal/mol,[44] as well as methylene blue, whose E_T is ca. 32 kcal/mol.[45] Control experiments demonstrated that, except of course in the case of Ph_2CO, **13t** is not formed upon photolysis of **2**, **11**, or **12t**, leaving **3** as its only source. Thus we conclude that **3** opens to ^{3}**1** upon energy transfer from the sensitizers used.

Given this result it should, in principle, be possible to generate and directly observe the triplet biradical by sensitized photolysis of **3** in a glass at 77 K. Unfortunately, in practice, such an experiment presents technical obstacles that we have not yet been able to overcome. Specifically, we have been unable to find a low-energy (E_T < E_T of **2**), nonemissive sensitizer that is sufficiently soluble at −78 °C in a suitable glass-forming solvent. If successful, this process, coupled with the photochemical conversion ^{3}**1** → **3**, would constitute a novel photochemical "switch" involving the interconversion of colored paramagnetic and colorless diamagnetic materials.

Scheme V



We have also attempted to photolyze **3** directly. Irradiation of a sample of **3** in MTHF at 77 K with 254-nm light failed to produce the absorption spectrum of ^{3}**1**. We suspect that the visible light scattered by the MTHF matrix rendered this experiment impractical;[46] the photochemical opening of **3** may have occurred under these conditions, but not efficiently enough to compete with the adventitious photolysis of ^{3}**1**. This experiment also may be viable under different conditions.

Thermal Decay of ^{3}1 in Rigid Media. Triplet **1** decays slowly and nonexponentially at 77–140 K in a variety of solvents to produce an EPR-silent species that we can confidently assign as **3**. We have performed a preliminary investigation of the temperature dependence of the decay rate in CH_2Cl_2 between 90 and 130 K. Most-probable rates obtained from a ln I vs $t^{1/2}$ analysis[47] are quite insensitive to temperature, but further study will be required before the significance of these observations can be ascertained.[22e]

Discussion

For most biradicals ring closure to a fully covalent structure is a very exothermic process. Ring closure is therefore normally quite facile from the triplet state and even more so from the singlet. However, in some cases the combined effects of resonance stabilization of the biradical and strain-induced destabilization of the covalent isomer can offset the energetic advantage of bond formation. This is the case for Berson's biradical, **5**. Experimentally, hydrocarbon **6** is found to be less stable than ^{3}**5**,[4] and ring closure of the triplet biradical is therefore not observed. In addition, ^{1}**5** encounters a finite barrier to ring closure, and this is also believed to be a consequence of the high strain energy of **6**.[4] Recall that, in contrast, triplet TMM (**8**), which lies ca. 15 kcal/mol higher in energy than **9**,[7] ring closes with only a 7 kcal/mol activation energy,[5] and ^{1}**8** has not been demonstrated to be a stable structure. Because our system was a priori expected to resemble Berson's energetically, much of the following discussion addresses similarities and dissimilarities in the behaviors of the two systems.

The Berson Cascade Mechanism. Partly as a consequence of the barrier to closure of ^{1}**5**, the chemistry of Berson's system is

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[43] Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537–4540.

[44] Engel, P. S.; Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 245–313.

[45] Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133–336.

[46] The intensity of the scattered light depends on λ^{-4}: Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976; p 27.

[47] Doba, T.; Ingold, K. U.; Siebrand, W. *Chem. Phys. Lett.* **1984**, 339–342. Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *J. Phys. Chem.* **1984**, *88*, 3165–3167. A linear ln I vs $t^{1/2}$ plot implies a distribution of rate constants, presumably arising from matrix site effects.

characterized by the sequential formation of the singlet and triplet biradicals upon photolysis or thermolysis of diazene **17**. This "cascade mechanism"[4] is summarized in Scheme V. The system displays three distinct behaviors in different temperature regimes.[4] At very low temperatures, e.g., 77 K, ISC dominates activated ring closure of ^{1}**5**, and the triplet biradical is the major product. At intermediate temperatures, passage over the 2.3 kcal/mol barrier to ring closure (k_c) occurs to the exclusion of ISC, and **6** is formed in quantitative yield. At high temperatures (>−50 °C), **6** can open (k_0) to regenerate ^{1}**5**, and the system eventually finds its thermodynamic sink—^{3}**5**.

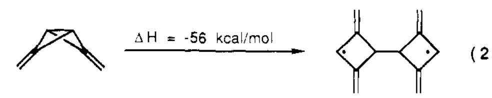
It is important to appreciate that in the high-temperature regime ring closure dominates both ISC and trapping. Thus, although the high-temperature reactivity of this system is characterized by the singlet–triplet cascade, entry onto the singlet surface is followed instantly by ring closure just as it is for "ordinary" biradicals.[3] In Berson's system the cascade is then established by reopening of **6**. This leads to a conclusion that is perhaps not widely appreciated: the Berson cascade mechanism depends not on the height of the barrier for closure of ^{1}**5** (as long as this barrier is finite) but on the height of the barrier for opening of **6**. The key is that the ring-opening barrier is low enough that **6** and ^{1}**5** can establish an equilibrium.

Concerning the Possibility of a Cascade Mechanism for 1. With this point in mind, we note that the absence of a singlet–triplet cascade for **1** does not necessarily mean that ^{1}**1** closes more easily than ^{1}**5**. Rather, it could simply signify that **3** is unable to return to the singlet biradical, presumably because of its facile dimerization rather than an inordinately large E_a for its ring opening. However, we have no direct evidence that ^{1}**1** intervenes in any of our chemistry or even exists at all as a true minimum on the potential energy surface.[22f,48]

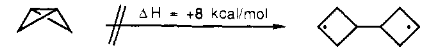
We have found that ^{3}**1** ring closes irreversibly to **3** in rigid media at ≥77 K. This indicates that **3** must lie lower in free energy than ^{3}**1**, at least at the temperatures of the EPR kinetic studies. The entropy term favoring the triplet biradical would be more important at higher temperatures and could place ^{3}**1** slightly below **3** at room temperature if the enthalpy of ^{3}**1** were no more than 1 kcal/mol higher than that of **3**.

To summarize, while we have no direct evidence for a cascade mechanism such as that observed in Berson's system, all the data can be interpreted in terms of such a mechanism. The vast difference in the behaviors of the two systems may simply result from **3** being removed from the picture via its facile dimerization faster than it can return to ^{1}**1** and thereby establish the cascade. In addition, we must emphasize that there is no direct evidence for a barrier to closure of ^{1}**1**, and such a structure might be only a transition state for inversion of **3**. The paucity of intersystem crossing in the chemistry of **3** could therefore indicate only that **3** has no good way to enter the triplet surface.

The Dimerization of 3. We have established that dimethylenebicyclobutane **3** undergoes an extremely facile and novel direct dimerization that involves rate-determining scission of two σ-bonds to form a biradical intermediate. Such a process is to our knowledge completely without precedent in bicyclobutane chemistry and virtually unprecedented in general. We cited the large exothermicity of the reaction (eq 2), estimated as $\Delta H = -56$ kcal/mol, to rationalize the unusually small activation enthalpy of 7 kcal/mol. It is instructive to compare ΔH for the dimerization of **3** to the analogous dimerization of the parent bicyclobutane (**18**) (eq 3). We estimate ΔH for this process to be +8 kcal/mol,[51] and the reaction has not been observed.[19b] It is quite evident that the large exothermicity of the dimerization of **3** results from a combination of its high strain energy and the delocalization of the unpaired electrons of **15**.

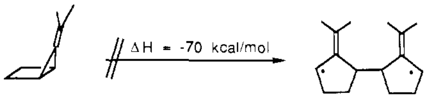


3 15 (2)



18 (3)

However, the exothermicity of the reaction cannot be the only reason that **3** dimerizes so easily, and the unusual structure of this species must also be a contributing factor. This point is nicely illustrated by the fact that an analogous dimerization of **6** (eq 4) should also be quite exothermic, with $\Delta H = -70$ kcal/mol![52] However, such a reaction is not observed for **6**, even at −78 °C, where its ring opening is extremely slow.[4] If such a dimerization had activation parameters comparable to ours, it should have been readily observable at this temperature. However, if E_a were just a few kcalories per mole higher than that for the dimerization of **3**, dimerization of **6** would be unable to compete with its facile ring opening. That such a bimolecular dimerization may be lurking just over the energetic horizon for **6** remains an intriguing possibility.



6 (4)

It would thus appear that structural features of **3** are partially responsible for its propensity to dimerize. Recall that calculations find **3** to be flattened relative to normal bicyclobutanes,[15,16] and our NMR data support this idea. Additionally, the bridgehead carbons of **3** are predicted to be substantially inverted.[15,16] One could easily envision such features as contributing to the ease of the dimerization.

Photochemistry of ^{3}1 and 3. Photolysis of the triplet biradical with light of 400–510 nm excites a $^3B_{2u} \rightarrow {}^3B_{1g}$ transition.[2,54] Ring closure to **3** could then occur, with ISC to the singlet surface either preceding or concomitant with puckering of the biradical. Torsion of an exocyclic methylene group could assist the spin flip in the first case.[55] Such a rotation is apparently involved in the photochemistry of biradical **5**,[4] which provides, to our knowledge, the only reported example of the photochemistry of a simple TMM derivative. Irradiation of ^{3}**5** at 77 K with 300-nm light excites a spin-allowed transition and produces enyne **19**, as shown in eq 5. In the case of ^{3}**1** there is no indication that the analogous ring closure to **4** (eq 6) plays any part in the photochemistry. Closure to **3** is certainly expected to be the preferred route in the ground state because of the enormous strain energy of **4**, and this should influence the excited-state energetics.

With regard to the mechanism of the photosensitization of **3** to form ^{3}**1** in solution, we can only speculate. Because opening of **3** to ^{3}**1** is promoted by sensitizers having extremely low triplet energies, an excited state of **3** is probably not involved. Specific chemical interactions between **3** and the sensitizer, such as reversible attack at a bridgehead carbon, appear unlikely, given that the reaction is promoted by a variety of aromatic ketones, hy-

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(48) Note that the small amounts of triplet-derived dimers formed upon direct photolysis of **2** at −95 °C (Table I) do not require the intervention of a ^{1}**1** → ^{3}**1** mechanism, since diazenes commonly encounter a barrier to nitrogen loss from S_1, enabling some ISC to T_1 before deazetation.[49] Such a barrier is indicated by the temperature-dependent photochemistry of the parent bicyclo[2.1.1]diazene.[50]

(49) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320–4322. Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435–6437. Mirbach, M. F.; Mirbach, M. J.; Liu, K.-C.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299–306.

(50) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333–2334.

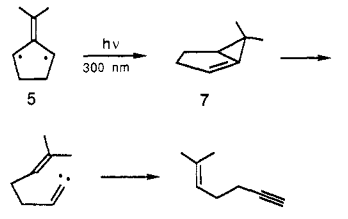
(51) Applying our usual thermochemical estimates, we subtract the strain energy of two molecules of **18**, 2 × 64 kcal/mol,[11] from 2 × 28[12] + 80[8] for the strain and "missing" C–C bond energy of the biradical.

(52) This value is obtained as 80[8] + 2 × 5[53] − 2 × 12 (allyl RE)[38] = 66 kcal/mol for the biradical, minus 2 × (27[11] + 41[11]) for **6**.

(53) The strain energy of **5** is taken as an average of those for methylenecyclopentane, 6 kcal/mol, and cyclopentene, 4 kcal/mol.[11]

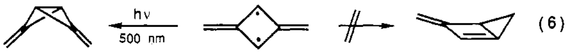
(54) Pranata, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 1621–1627.

(55) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.



5 7 19

(5)



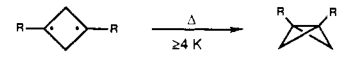
3 1 4

(6)

drocarbons, and heterocycles. Another possibility is electron transfer from the relatively high lying σ-orbital of the central bond of **3**. Since **3** and ^{3}**1** are predicted to be of comparable energies,[16] and **3** may also be significantly flattened relative to a "normal" bicyclobutane, the energy of the S–T surface crossing may be quite low. It is perhaps intuitively reasonable, therefore, that **3** is opened to ^{3}**1** by very low energy sensitizers. In addition, the gradual falloff in photosensitization efficiency appears to fit the Balzani model for energy transfer processes,[56] although a firm conclusion with regard to this point would require more quantitative experimental results.

Thermal Ring Closure of ^{3}1. Because technical limitations have prevented us from investigating the ring closure kinetics of ^{3}**1** under a variety of conditions, we hesitate to place too much emphasis on the preliminary results we have obtained. However, it is clear that the EPR signal of ^{3}**1** does decay at 77 K in a variety of solvents[2] (although these were unsuitable for higher temperature kinetics studies). For comparison, ^{3}**5** is indefinitely stable with respect to unimolecular reaction to near room temperature,[4] while ^{3}**8** closes to **9** at ca. 110 K and above.[5] Since ring closure of ^{3}**5** is endothermic, and closure of ^{3}**1** is exothermic (see above), it is not surprising that ^{3}**1** is less stable than ^{3}**5**. However, the finding that ^{3}**1** ring closes more easily than the parent TMM (^{3}**8**) is quite surprising. Certainly, the closure of ^{3}**1** is not nearly as exothermic as the closure of ^{3}**8** and other factors must then make ^{3}**1** exceptionally prone to ring closure.

A possible explanation of this result is that tunneling is involved in the decay of ^{3}**1**, allowing reaction to occur at lower temperatures than expected. The qualitative observation that the decay rates are quite insensitive to temperature is consistent with this proposition. We also note that heavy-atom tunneling has been observed in the ring closures of the closely related cyclobutanediyls, **20** (R = alkyl),[57] although it is, to our knowledge, unprecedented in the ring closure of a delocalized (non-Kekulé) biradical. The previously mentioned closeness of the energy surfaces of **3** and ^{3}**1** could certainly enhance a tunneling mechanism. Further experiments concerning this ring closure reaction are underway.



20

Experimental Section[58]

Solvents and Reagents. CD_2Cl_2 was obtained from Aldrich or MSD Isotopes and used without further purification unless otherwise noted. The CH_2Cl_2 used to make diazene solutions was Spectro-grade solvent that had been distilled from CaH_2 or P_2O_5 and stored under N_2. Mesitylene was distilled from Na; benzophenone was recrystallized from CH_2Cl_2/hexane. Other reagents and solvents were used as obtained commercially unless otherwise noted.

Sample Preparation. Freshly made samples of diazene **2**[2a] at −78 °C were dissolved in the appropriate solvent, and the solution was transferred via 30-gauge Teflon tubing to a sample tube. Alternatively, the solution was transferred to a graduated storage tube, from which it could be apportioned to several sample tubes. Typically, CD_2Cl_2 (1–3 mL) containing a known volume of mesitylene (ca. 2 μL) as an internal standard was used, and the mesitylene concentration at ca. −80 °C was calculated as the room-temperature concentration/0.9 to account for the ca. 10% volume contraction (see below) accompanying the temperature change. The sample tubes were Wilmad Glass 701-PQ 5-mm-o.d., 3.5-mm-i.d. quartz tubes, which had been based-washed, rinsed thoroughly with water and organic solvents, and dried. The samples were typically degassed by three freeze–pump–thaw cycles (liquid N_2–CO_2/Me_2CO), frozen, and sealed with an oxygen-gas flame. When oxygen was to be introduced, the sample was warmed to −95 °C (liquid N_2/MeOH) or −78 °C (CO_2/iPrOH), the appropriate amount of gas (<1 atm) was admitted, and (after a few minutes) the tube was sealed carefully with a flame. Samples were stored at −100 °C or at 77 K before use.

Table II. Transmittance Data for Filter Combinations

no.	filters[a]	trans range,[b] nm	λ_{max}(trans), nm
1	WG-305/KG-5/UG-11	$306 < \lambda < 386$	355 (0.35)
2	no. 1 + 334 int[c]	$326 < \lambda < 342$	335 (0.08)
3	WG-305 or -345/GG-375/[d] KG-5/UG-11	$352 < \lambda < 386$	368 (0.16)
4	WG-305/WG-360/KG-5/ UG-11	$342 < \lambda < 386$	365 (0.25)
5	WG-360/GG-455/KG-5	$446 < \lambda < 806$	490–600 (0.6)
6	WG-305/OG-570/KG-5	$557 < \lambda < 807$	594 (0.57)

[a] Obtained from Schott (3-mm thickness). [b] Cutoff values are defined as 1% transmittance. [c] A 334-nm interference filter obtained from Oriel. [d] A 1-mm thickness.

Photolysis. Samples were irradiated with light from an Oriel 1000-W "ozone-free" Hg(Xe) arc lamp (operated at 950–980 W) mounted in a housing equipped with an *f*/0.7 quartz lens assembly and a water filter. The light was directed through a series of filter glasses resting in a water-filled chamber. The filter combinations used and their transmittance data are listed in Table II.

NMR Experiments. Unless otherwise noted ^{1}H NMR experiments were performed on a JEOL GX-400 FT NMR spectrometer. Spectra were typically recorded at −80 °C with 64 scans and sufficient time between pulses (ca. 9 s) to ensure complete relaxation of all the protons in the species present (as determined by simply varying the pulse delay). For convenience, dimer concentrations are reported in terms of (monomer units)/2.

Spectroscopic Characterization of 2,4-Dimethylenebicyclo[1.1.0]butane (3). Direct photolysis of solutions of diazene **2** in various solvents at ≤−78 °C produces the characteristic singlets of **3**, identified by their thermal lability: ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ 4.22 (s, 4 H, olefinic methylenes), 3.18 (s, 2 H, bridgehead methines); ^{1}H NMR (400 MHz, C_7D_8, −80 °C) δ 4.34 (s, 4 H), 2.37 (s, 2 H).

Empirical Force Field (EFF) Calculations. MM2[20] calculations employed a version of N. L. Allinger's (*QCPE* 395) FORTRAN program that had been adapted for use on the IBM-PC by Serena Software. Parameters for conjugated dienes were developed that roughly reproduced the relative energies and geomerties of s-cis and s-trans rotomers of several butadienes as well as the E_a's for their interconversion, as determined by more sophisticated EFF calculations.[59] Thus, for the diene sp^2–sp^2 single-bond stretching constants we used $k = 5.0$, $r_0 = 1.46$ Å; for the torsional constants (defined in terms of the C–C–C–C dihedral angle), $V_1 = 1.7$, $V_2 = 7.0$, $V_3 = 0$ kcal/mol. Several conformations were considered for the various structures, but only those of Figure 1 were found to be energetically viable. The strain energies were obtained by subtracting the MM2 "strainless bond enthalpy" from the calculated heats of formation. Calculated $\Delta H_f°$ values are as follows: **10**, 151.6; **11**, 134.1; **12t**, 125.7; **12c**, 134.8; **13t**, 126.0; **13c**, 130.3 kcal/mol. The calculated bond lengths and angles are presented elsewhere.[22]

Characterization of Dimers. Because we have obtained the dimers only in relatively small quantities and have found them to be quite air sensitive (and seemingly more labile in the absence of solvent), we have made no serious attempt to separate them on a preparative scale. The ^{1}H NMR spectra reported here were obtained at −80 °C because the aliphatic methine and especially the cyclobutene protons of **11** and **12t** have severe relaxation problems at room temperature in both CD_2Cl_2 and C_7D_8 solutions (T_1 for the cyclobutene protons is ca. 0.5 min).

3,8,9-Trimethylenetricyclo[5.1.1.0^{2,5}]non-4-ene (11): ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ 6.11 (d, J = 1–2 Hz, 1 H, cyclobutene), 4.815,

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(56) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2163.

(57) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240–2252. Jain, R.; Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7294–7295.

(58) Additional observations concerning many methodological aspects of this work can be found elsewhere.[22]

(59) Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928–7932.

4.813, 4.78, 4.72, 4.48, 4.35 (6 s, 1 H each, olefinic methylenes[60]), 3.46 (d, $J_{1,7}$ = 5.9 Hz, 1 H, H-1), 3.38 (s, 1 H, H-2), 3.30 (pseudo-t, 1 H, H-7), 2.84 (dd, $J_{6,6}$ = 13.4 Hz, $J_{6,7}$ = 4.4 Hz, 1 H, H-6, cis to the cyclobutene ring), 2.77 (d, $J_{6,6}$ = 13.2 Hz, 1 H, H-6, trans to the cyclobutene ring);[61] (A decoupling experiment along with the spectrum of **11**-d_4 (see below) confirmed the assignments.) ^{13}C NMR (125 MHz, CD_2Cl_2)[64] δ 155.4, 151.0, 147.6, 146.8 (quaternary olefinic, C-3,5,8,9), 131.9 (cyclobutene, C-4), 102.9, 100.0, 94.9 (olefinic methylenes), 59.8, 55.7, 52.6 (aliphatic methine, C-1,2,7), 40.0 (aliphatic methylene, C-6). An INEPT pulse sequence confirmed the assignments of the methylene carbons and provided coupling constants of J_{CH} = 157 Hz for the olefinic and J_{CH} = 134 Hz for the aliphatic methylenes.

***trans*-3,10-Dimethylenetricyclo[6.2.0.0^{2,5}]deca-4,8-diene (12t)**: ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ 6.00 (d, J = 1 Hz, 2 H, cyclobutene), 4.45, 4.37 (2 s, 2 H each, olefinic methylenes), 2.81 (s, 2 H, H-1,2), 2.58 (m, major line separations ca. 7 and 3 Hz, 2 H, H-6,7[65]), 2.23 (m, major line separation ca. 7 Hz, 2 H, H-6,7[65]); (A decoupling experiment confirmed that the protons responsible for the last two signals are coupled to each other.) ^{13}C NMR (125 MHz, CD_2Cl_2)[64] δ 128.2 (cyclobutene, C-4,9), 94.4 (olefinic methylenes), 52.4 (aliphatic methines, C-1,2), 26.5 (aliphatic methylenes, C-6,7), the quaternary carbons, C-3,5,8,10, were not visible.

***trans*-5,10-Dimethylenetricyclo[6.2.0.0^{3,6}]deca-3,8-diene (13t)**: ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C; obtained by spectral subtraction of the signals of **11** and **12t**) δ 6.01 (d, J = 1–2 Hz, 2 H, cyclobutene), 4.45, 4.37 (2 s, 2 H each, olefinic methylenes), 2.83 (pseudo-t, line separation ca. 8 Hz, 2 H, H-1,6), 2.76 (dd, $J_{2,2}$ = 13 Hz, $J_{1,2eq}$ = 7 Hz, 2 H, H-2,7-equatorial), 2.13 (pseudo-t, line separation ca. 10 Hz, 2 H, H-2,7-axial).[65]

1,2,4,7-Tetradeuterio-11(11-*d*$_4$): ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ 4.814, 4.809, 4.78, 4.71 (4 s, 1 H each, olefinic methylenes), 4.47, 4.35 (2 d, J = 1 Hz, 1 H each, olefinic methylenes[60]), 2.83 (d, $J_{6,6}$ = 13.4 Hz, 1 H, H-6, cis to the cyclobutene ring), 2.76 (d, $J_{6,6}$ = 13.4 Hz, 1 H, H-6, trans to the cyclobutene ring).

1,2,4,9-Tetradeuterio-12t(12t-*d*$_4$): ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C) δ 4.45, 4.37 (2 s, 2 H each, olefinic methylenes), 2.59 (m, 2 H, H-6,7), 2.23 (m, 2 H, H-6,7).[65]

1,4,6,9-Tetradeuterio-13t (13t-*d*$_4$): ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C; obtained by spectral subtraction of the signals of **11**-d_4 and **12t**-d_4) δ 4.45, 4.37 (2 s, 2 H each, olefinic methylenes), 2.74 (d, $J_{2,2}$ = 13 Hz, 2 H, H-2,7-equatorial), 2.12 (d, $J_{2,2}$ = 13 Hz, 2 H, H-2,7-axial).[65]

GC and GC–MS Analysis of Dimers. GC analyses were performed on a Hewlett-Packard 5840A gas chromatograph equipped with a flame-ionization detector. The instrument had been modified for capillary capability and a J&W scientific 30-m, 0.25-μm Durabond-17 (bonded phenyl methyl silicone equivalent to OV-17) was used with H_2 as the carrier. Although retention times varied somewhat depending on flow rate and column age, typical retention times at 100 °C were as follows: **11**, 3.85; **12t**, 6.82; **13t**, 6.15; D_1, 8.37; D_2, 10.87 min. GC-MS analyses were performed by the U.C. Riverside Mass Spectrometry Lab with an equivalent column.[22a]

Thermal and Photochemical Reactions of Diazene 2. (a) Thermolysis and Direct Photolysis. A sample of diazene **2** in CD_2Cl_2 containing mesitylene as an internal standard was found by ^{1}H NMR to contain 22.8 mM **2**, 1.1 mM **3**, 5.9/2 mM **11**, and 0.7/2 mM **12t**, for a total of 30.5 mM monomer (C_6H_6) equivalents. After thermal decomposition at −78 °C, the sample was found to contain 30.6/2 mM **11** and 3.6/2 mM **12t**, for a total of 34.2 monomer equivalents (no insoluble material was observed after any thermal or photochemical decomposition), indicating quantitative formation of dimers from **2**, within experimental error. The decomposition of two additional diazene samples at −51 and −32 °C was analyzed in a similar fashion. At −51 °C, 31.4 mM **2**, 1.1 mM **3**, 16.7/2 mM **11**, and 2.4/2 mM **12t**, totaling 51.6 mM monomer equivalents, formed 43.9/2 mM **11** and 6.6/2 mM **12t**, or 50.5 mM monomer equivalents. At −32 °C, 36.7 mM **2**, 0.4 mM **3**, 9.8/2 mM **11**, and 1.2/2 mM **12t**, totaling 48.1 mM, produced 41.8/2 mM **11** and 7.5 mM **12t**, or 49.3 mM monomer equivalents.

Table III. Decay Kinetics of Diazene **2**[a]

T, K	k_1,[b] s^{-1}	t(final) h	half-lives
229.3	3.431 (±0.076) × 10^{-3}	0.3	4.8
225.1	1.603 (±0.026) × 10^{-3}	0.5	4.3
224.8	1.555 (±0.025) × 10^{-3}	0.5	4.2
220.5	6.964 (±0.21) × 10^{-4}	1.0	3.6
220.4	6.904 (±0.12) × 10^{-4}	1.0	3.7
216.5	3.174 (±0.029) × 10^{-4}	3.0	5.0
212.2	1.345 (±0.012) × 10^{-4}	4.0	2.8
208.2	6.009 (±0.075) × 10^{-5}	5.5	1.7

[a] In CD_2Cl_2. [b] Error limits represent standard deviations of the ln [**2**](rel) vs t plots.

Samples of diazene **2** and **2**-d_2 were photolyzed (using filter combination no. 1, Table II) at −95 °C and then thermolyzed at −75 °C. GC analysis of the product mixture (DB-17 capillary, 100 °C; see above) revealed the presence of ca. 0.1% **13t**, ca. 0.05% D_1, and a trace (<0.01%) of D_2, identified by their retention times. In contrast, analysis of several diazene samples that had undergone thermal decomposition at −78 °C showed no sign of these products (<0.005%). To test for CIDNP in the thermal dimerization, a sample of **2** in CD_2Cl_2 at ca. −95 °C was placed in the probe of a Varian EM-390 CW NMR spectrometer, which was at ambient temperature. The first scan showed the peaks of **2**, and these were replaced by the signals of **11** and **12t** as the sample warmed, but no unusual intensity effects were observed.

(b) Sensitized Photolysis. A sample of diazene **2** (ca. 8 mM) in CD_2Cl_2 containing 0.1 M benzophenone (Ph_2CO) and mesitylene as an internal standard was irradiated at −78 °C with filter combination no. 3 (Table II, λ 352–386 nm). The progress of the photolysis was monitored by ^{1}H NMR, initially at 5–15-s intervals and later less frequently, for a total of seven measurements spanning a photolysis time of 2 min. The spectra were recorded at −80 °C. Irradiation of **2** under these conditions (filter combination no. 3 or 4, Table II) in the absence of Ph_2CO causes no decomposition. In addition, control experiments reveal that no significant thermal decomposition of **2** occurs during such manipulations. The relative amounts of dimers **11**, **12t**, and **13t** formed early in the photolysis are presented in Table I. After ca. 125 s of photolysis, ca. 40% **11**, 10% **12t**, and 50% **13t** had been produced. The results of an experiment with 0.01 M Ph_2CO are also given in Table I. A control experiment was conducted to demonstrate that dimers **13t**, D_1, and D_2 do not result from secondary photolysis of **11** and **12t**. Thus, Ph_2CO was added to a sample of **11** and **12t** (which contained a trace of **13t**, D_1 and D_2) and the sample was degassed, sealed, and irradiated at −78 °C with filter combination no. 4 (Table II) for 30 s. GC analysis revealed no increase (or decrease) in the amounts of **13t**, D_1, and D_2 present.

(c) Effect of Oxygen. A sample of diazene **2** in CD_2Cl_2 under 0.8 atm O_2 was thermolyzed at −50 °C for 1.5 h. By ^{1}H NMR the thermolysis converted a mixture of 8.1 mM **2**, 2.5/2 mM **11**, and 0.4/2 mM **12t**, or 11.0 mM monomer equivalents to a mixture of 9.1/2 mM **11** and 1.5/2 mM **12t**, or 10.6 mM total, so that the conversion was quantitative within experimental error (no new signals appeared). A sample of ca. 8 mM **2** and 0.1 M Ph_2CO in CD_2Cl_2, identical with the first sample used in section b (above), was placed under 0.8 atm O_2. The sample was irradiated with filter combination no. 3 as described in section b (above) for ca. 2 min. The photolysis destroyed 80% of the diazene, but no **13t** was observed by ^{1}H NMR, and there was no detectable increase—and perhaps even a slight decrease—in the small amounts of adventitious **11** and **12t** present before the photolysis. In addition, new signals were found to grow in to a small extent during the reaction. These appeared as sharp peaks at δ 9.5–9.8 (six peaks), 8.9, 6.9, 6.7, 6.5 (two), 6.3 (three to four) and 5.0 (two).

Decomposition Kinetics of Diazene 2. Samples of ca. 10 mM **2** and ca. 5 mM mesitylene in CD_2Cl_2 were inserted in the NMR probe and allowed to equilibrate for ca. 5 min at the temperature of the experiment. Typically 12–16 spectra were recorded during each run over the time intervals listed in Table III, each spectrum being acquired with eight scans ca. 9 s apart. (The 229.3 K rate was obtained from only 10 points and with a shorter pulse delay.) The decays were all cleanly first order over several half-lives and the error attached to each rate constant listed in Table III represents the standard deviation of the slope of the −ln [**2**](rel) vs time plot. An Arrhenius plot [ln k = −9177(1/T) + 34.35] provided activation parameters log A = 14.9 (±0.1) and E_a = 18.2 (±0.1)

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[60] The last two are tentatively assigned to the C-3 (cyclobutene) methylene group by their proximity to the olefinic singlets of **12**t and **13t** (see below).

[61] The chemical shifts are in accord with those observed for model compounds. Specifically, 5,6-dimethylenebicyclo[2.1.1]hexane displays methylene and bridgehead proton signals at δ 4.33 and 3.03, respectively;[62] 3-methylenecyclobutene and 1-methyl-3-methylenecyclobutene display methylene signals at δ 4.3–4.5, while the olefinic (C-2) and allylic methylene protons appear at δ 6.2 and 2.8, respectively.[63]

[62] Martin, H.-D.; Eckert-Maksic, M.; Mayer, B. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 807–809.

[63] Wu, C. C.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 3529–3553.

[64] The peaks of **11** and **12t** were distinguished on the basis of the intensity differences between similar carbons in the two compounds.

[65] The δ 2.58 and 2.23 signals of **12**t and the δ 2.75 and 2.13 signals of **13t** are tentatively assigned as equatorial and axial, respectively for each compound. For **13**t the relative coupling constants expected on the basis of the dihedral angles clearly support this assignment: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 189, 206.

Table IV. Dimerization Kinetics of **3**[a]

T, K	k_2, $M^{-1}\ s^{-1}$	t(final), h	half-lives
249.4	3.99 (±0.27)	0.2	2.0
243.3	3.43 (±0.14)	0.3	3.1
235.0	1.70 (±0.03)	0.5	3.2
227.0	0.925 (±0.027)	1.0	3.4
218.4	0.548 (±0.008)	1.7	3.8
210.2	0.286 (±0.006)	1.8	2.9
202.2	0.132 (±0.005)	4.5	2.9
194.0	0.0666 (±0.0016)	4.0	2.6

[a] In CD_2Cl_2.

Table V. Sensitized Photolysis of **3**

sensitizer[a]	E_T,[b] kcal/mol	f(**13t**)[c]
benzophenone	68.5[d]	0.236
naphthalene	60.9[d]	0.002
benzil	53.7[d]	0.509[e]
fluorenone	53.3[d]	0.181
9-methylanthracene	41[f]	0.007
acridine	45.3[f]	0.039
phenazine	43.8[f]	0.042
methylene blue[g]	ca. 32[h]	0.015

[a] Ca. 0.04 M, in CH_2Cl_2. [b] Triplet energy. [c] By GC: **13t**/(**11** + **12t** + **13t**). [d] Reference 43. [e] The amount of **11** present was anomalously low (13%), presumably due to reaction with the sensitizer. [f] Reference 44. [g] Ca. 0.01 M. [h] Reference 45.

kcal/mol. The error limits represent standard deviations derived from the plots. Alternatively, an Eyring plot furnishes $\Delta H^{\ddagger} = 17.8$ (±0.1) kcal/mol and $\Delta S^{\ddagger} = 8.3$ (±0.3) eu.

Dimerization Kinetics of Dimethylenebicyclobutane 3. Samples of **2** (ca. 10 mM) were made by dissolving the solid diazene in a cold solution of mesitylene in CD_2Cl_2 and then dividing the solution among eight sample tubes. The standard solution consisted of 1.60 μL (1.38 mg, 11.5 mmol) of mesitylene in 2.80 mL of CD_2Cl_2, for a concentration of 4.11 mM at room temperature. In order to determine the concentration at low temperature, the solvent volume contraction was measured by the height of a sample of CH_2Cl_2 in an NMR tube. At −81 °C the volume was measured as 0.87 and at −29 °C 0.93 relative to that at room temperature, and the volume change was assumed to be linear with temperature. Each sample was irradiated at −95 °C (liquid N_2/MeOH bath) with filter combination no. 1 (Table II) for 20–30 min, the progress of the photolysis being monitored intermittently by UV spectroscopy. The samples were stored in liquid N_2 prior to the kinetics runs. The samples were inserted into the NMR probe and allowed to equilibrate for a few minutes at the desired temperature. The initial NMR spectra revealed the presence of ca. 3 mM **3** at the lower and ca. 1 mM **3** at the higher temperatures. A total of 10–14 spectra were recorded during each run, and each spectrum was obtained with eight scans ca. 7 s apart (ca. 60° pulses). (The 249.4 K rate was obtained from eight points and with four scans per spectrum.) The decays were all cleanly second order, as illustrated in Figure 2 for two runs, and the rates are reported in Table IV. The Eyring plot of Figure 3 [$\ln (k/T) = -3445\ (1/T) + 9.76$] provides activation parameters $\Delta H^{\ddagger} = 6.8$ kcal/mol and $\Delta S^{\ddagger} = -28$ eu. Although the standard deviations in the slope and intercept of the Eyring plot suggest that error limits of ±0.1 kcal/mol and ±1 eu be attached to these quantities, the inherent difficulty of these experiments and the potential effect of incomplete relaxation on the integrals of the ^1H NMR signals suggest the more conservative errors presented in text. Repeating the above experiment with five samples prepared with CD_2Cl_2 that had been distilled from CaH_2 and containing 0.02 M 2,6-lutidine (distilled from BaO) provided cleanly second-order decays and activation parameters $\Delta H^{\ddagger} = 7.4$ kcal/mol and $\Delta S^{\ddagger} = -25$ eu, in good agreement with the above results.

Secondary Deuterium Kinetic Isotope Effect. A stock solution of mesitylene in CD_2Cl_2 (distilled from CaH_2) was used to make two samples each of **2** and **2**-d_2, and the samples were irradiated as described above. Decay rates for **3** and **3**-d_2 were determined as described above at −38 and −71 °C. At −38 °C, k_H/k_D was determined to be 2.33 (±0.18) $M^{-1}\ s^{-1}$/1.89 (±0.07) $M^{-1}\ s^{-1}$ = 1.23 (±0.10); at −71 °C, 0.193 (±0.005) $M^{-1}\ s^{-1}$/0.137 (±0.010) $M^{-1}\ s^{-1}$ = 1.41 (±0.11). The experiment was later repeated at −49 °C to provide k_H/k_D of 1.104 (±0.036) $M^{-1}\ s^{-1}$/0.850 (±0.037) $M^{-1}\ s^{-1}$ = 1.30 (±0.07), and at −73 °C to provide a k_H/k_D of 0.144 (±0.003) $M^{-1}\ s^{-1}$/0.118 (±0.003) $M^{-1}\ s^{-1}$ = 1.22 (±0.04). All four k_H/k_D values are greater than unity to an experimentally significant extent. Extrapolated to a common temperature of −60 °C, these values become 1.26 (±0.10), 1.39 (±0.11), 1.32 (±0.07), and 1.21 (±0.04), for an average of 1.3.

Time Evolution of [3] and [Dimers] during Thermolysis of 2. Two samples were made by dissolving diazene **2** in a solution of CD_2Cl_2 containing 1.22×10^{-2} M mesitylene and 1.15×10^{-2} M 2-methoxynaphthalene (recrystallized from CH_2Cl_2/MeOH), both as internal standards. One sample was placed in the NMR probe and allowed to equilibrate at −48.4 °C, the other at −61.0 °C. ^1H NMR spectra were recorded with 8 scans at the higher temperature and 16 at the lower, and by using ca. 50° pulses 9 s apart. Twelve spectra were recorded over 30 min during the −48.4 °C thermolysis and 14 spectra spanned 4 h during the −61.0 °C thermolysis. The concentrations of **2**, **3**, **11**, and **12t** were determined by comparison of their integrated ^1H NMR signals with those of the internal standards and are plotted as Figure 4a and b.

Attempted Trapping of Singlet 1. Approximately 0.35 mL of a solution of diazene **2** and mesitylene in acetone-d_6 was added to each of two sample tubes, one containing 34.3 mg of maleic anhydride and the other 27.3 mg of fumaronitrile (recrystallized from CH_2Cl_2). The samples were degassed, the tubes were sealed, and with shaking, all the maleic anhydride dissolved, but a small amount of fumaronitrile remained undissolved. (Comparison of the ^1H NMR integrals for these compounds with that for mesitylene indicated that the concentrations of maleic anhydride and fumaronitrile were respectively 1.0 and 0.9 M.) The samples were analyzed by ^1H NMR, thermolyzed at −50 ± 5 °C for ca. 1 h, and then analyzed again to determine the amounts of dimers **11** and **12t** formed. In the maleic anhydride sample 8.18 mM **2**, 0.36 mM **3**, 1.35/2 mM **11**, and ca. 0.20/2 mM **12t** were converted, upon thermolysis, to 3.65/2 mM **11** and ca. 0.50/2 mM **12t**, so that 8.5 mM **2** + **3** formed 2.6/2 mM dimers for a 30% yield. In the fumaronitrile sample 8.69 mM **2**, 0.89 mM **3**, 1.79/2 mM **11**, and ca. 0.25/2 mM **12t** formed 8.15/2 mM **11** and 0.88/2 mM **12t**, so that 9.6 mM **2** + **3** was converted to 7.0/2 mM dimers, for a 70% yield. The estimated error in these values is ±10%.

Photochemistry of Triplet 1 at 77 K. A sample of diazene **2** was dissolved in a cold (−78 °C) solution of 0.85 mg of mesitylene, 20 μL of acetophenone (distilled), and 100 μL of 3-methylpentane (3-MP) in 750 μL of toluene-d_8, and ca. 500 μL of the solution was placed in a 5-mm-o.d., 3.5-mm-i.d. sample tube, degassed, and sealed. Applying the appropriate correction for volume contraction upon cooling, the concentration of mesitylene was 9.51×10^{-3} M at −78 °C. (The acetophenone concentration was ca. 0.24 M at 77 K.) ^1H NMR spectroscopy at −80 °C revealed that the diazene sample contained 12.1 mM **2**, 1.8 mM **3**, 5.7/2 mM **11**, and 0.9/2 mM **12t**, for a total of 20.5 mM monomer equivalents. A 4.27×10^{-4} M solution of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) in 12% 3-MP/toluene was placed in a sample tube to serve as an EPR spin standard. By correcting for contraction upon cooling, the concentration of TEMPO at 77 K was determined to be 5.08×10^{-4} M. EPR spectra were recorded at 77 K as described previously,[2a] the sample resting in a quartz finger Dewar mounted in the microwave cavity. The Dewar was positioned so that the hemispherical bottom of the tube was below the cavity. The cavity height was measured as 2.3 cm, so that the sample volume inside the cavity was 220 μL. The diazene sample was irradiated with light from the 1000-W Hg(Xe) arc lamp, which was directed alternately through filter combinations no. 4 (Table II) for 30 s to generate triplet **1** and no. 5 for 10 s to destroy it. The sample was subjected to 150 such cycles in 15–20-cycle sets, being thawed (ca. 1–2 s at −78 °C) between each set. The signal intensity was monitored at a single field setting during each photolysis cycle. The first and last spectra of each set were recorded and later numerically double-integrated[2a] and scaled to a common receiver gain. The average of the two double integrals (di) was multiplied by the number of cycles in the set, and the total di values for each set were combined to yield a relative di value of 1.86×10^4. Spectra of the standard TEMPO sample were recorded before and after the experiment, and di values of 640 and 665 were obtained. The instrument response factor for doublet (free-radical) signals, c_D = [TEMPO]/di = 7.79×10^{-7}. Triplet signals are inherently $^4/_3$ as intense per electron as doublet signals, or $^8/_3$ as intense per paramagnet.[66] Accordingly, the triplet response factor, $c_T = {}^3/_8 c_D = 2.91 \times 10^{-7}$. The total quantity of triplet **1** produced (and photolyzed), in terms of concentration within the 220-μL (see above) portion of the sample in the EPR cavity, is then given by [**1**] = c_T(di), or [**1**] = 5.43×10^{-3} M. Thus, 5.43×10^{-3} M × 0.220 mL, or 1.19×10^{-3} mmol of triplet **1** was photolyzed, which corresponds to a concentration of 2.7×10^{-3} M at −80 °C (the NMR temperature). Because this value is a lower limit, we have attached no errors to any of the numbers reported. ^1H NMR spectroscopy at −80 °C revealed the presence of 5.2 mM **2**, 3.3 mM **3**, 11.4/2 mM **11**, and 1.90/2 mM **12t**, for a total of 21.8 mM monomer equivalents, or a material balance within 6% of the original sample composition. No ^1H NMR signals besides those of **2**, **3**, **11**, and

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(66) Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358–2364.

12t were observed in the region from ca. δ 6.8 to 2.3.

Sensitized Photolysis of Dimethylenebicyclobutane (3). A ca. 1 mM solution of diazene **2** in CH_2Cl_2 (which had been placed under vacuum) was irradiated with light from the Hg(Xe) arc lamp, directed through filter combination no. 1 (Table II), at −95 °C until no diazene remained, as indicated by UV spectroscopy. The vessel was then pressurized with nitrogen, and the solution was quickly cannulated through 30-gauge Teflon tubing with ca. 400 μL being delivered to each of eight N_2-purged sample tubes. To each tube had been added the requisite amount of sensitizer to make a ca. 0.04 M solution (due to its large ε and low solubility, enough methylene blue was used to make a ca. 0.01 M solution). The sensitizers used and their triplet energies, E_T, are listed in Table V. The samples were immediately placed in liquid N_2 and later evacuated and sealed with a flame. Each sample, in turn, was thawed carefully, submerged in a CO_2/Me_2CO bath, withdrawn briefly, and shaken to dissolve all or most of the sensitizer, irradiated at −78 °C for 1 min with filter combination no. 3 (Table II), and finally warmed to room temperature. The methylene blue sample was irradiated instead for 2 min with filter combination no. 6. The solutions were analyzed by GC, and the fraction of total dimers constituted by **13t** is reported in Table V for each sensitizer used. In addition, a small, unidentified peak at retention time 7.37 min (relative to those reported above) was observed in each of the last five samples (the peak was quite large in the benzil sample). Control experiments demonstrated that this species is produced upon sensitized photolysis of a mixture of **11** and **12t**. Control experiments also established that the source of the **13t** observed was neither diazene **2** nor the dimers (**11** and **12t**).

Acknowledgment. We thank the National Science Foundation for generous support of this work.

Room-Temperature Phosphorescence from 1:1:1 Inclusion Compounds of β-Cyclodextrin with Brominated Alcohols and Acenaphthene

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Abstract: Acenaphthene (AN) has been found to form a 1:1:1 inclusion compound by complexing with a 1:1 inclusion compound of β-cyclodextrin (CDx) and alcohol. Of the primary alcohols examined, 1-propanol most easily associates with a 1:1 inclusion compound of CDx and AN. When brominated alcohol is included in the 1:1:1 inclusion compound, a room-temperature phosphorescence of AN is induced by a heavy-atom effect. From experiments on the AN phosphorescence quenching by $NaNO_2$, we have estimated a rate constant (k_3) for the association of AN with CDx, which already accommodates a 2-bromoethanol (BE) molecule, to be 1×10^{10} mol^{-1} dm^3 s^{-1} and a rate constant (k_4) for the dissociation of AN from the 1:1:1 inclusion compound including BE to be 8×10^4 s^{-1}. In the CDx–BE–AN system, k_3 is 2 orders of magnitude larger than the rate constant (k_1) for the association with free CDx into which BE is not incorporated, whereas k_4 is 1 order of magnitude smaller than the rate constant (k_2) for the dissociation from the 1:1 inclusion compound of CDx with AN. These findings indicate that a guest molecule (BE) inside the CDx cavity accelerates the association rate of AN with CDx and conversely decelerates the dissociation rate of AN from the 1:1:1 inclusion compound.

Room temperature phosphorescences of polynuclear aromatic hydrocarbons such as acenaphthene (AN), naphthalene, and pyrene are observed not only in micellar solutions containing Tl^+ as a heavy-atom perturber[1-4] but also in cyclodextrin solutions containing 1,2-dibromoethane.[4,5] As a phosphorescence-inducing mechanism in cyclodextrin solutions, Scypinsky and Cline Love have proposed the formation of a trimolecular complex among a luminophor, cyclodextrin, and 1,2-dibromoethane.[5] Using their technique with cyclodextrin, one can obtain reproducible, good-quality room-temperature phosphorescence spectra.

In a previous paper,[6] we have reported that a self-association occurs between two 1:1 inclusion compounds of β-cyclodextrin (CDx) with naphthalene. Subsequently, it has been found that a 1:1 inclusion compound of CDx with pyrene further associates with a primary or cyclic alcohol molecule to produce a 1:1:1 inclusion compound.[7] Because pyrene does not deeply enter the CDx cavity owing to the steric hindrance, the additional alcohol molecule can be incorporated into the void interior of the cavity which already accommodates pyrene. Since AN as well as pyrene is relatively bulky for the CDx cavity, it is expected that AN is shallowly bound to the CDx cavity and then complexes with an additional alcohol molecule to form a 1:1:1 inclusion compound. Thus, we studied the behavior of the inclusion compounds of AN. Since we found that brominated alcohol induces the room temperature phosphorescence of AN, we tried to determine a rate constant for the association of AN with a 1:1 inclusion compound of CDx–2-bromoethanol and a rate constant for the dissociation of AN from the 1:1:1 inclusion compound of CDx–2-bromoethanol–AN.

Experimental Section

Acenaphthene purchased from Tokyo Kasei and β-cyclodextrin from Nakarai were recrystallized three times from ethanol and water, respectively. Primary alcohols from methanol to 1-hexanol were purified by distillation under atmospheric or reduced pressure. 2-Bromoethanol (BE) and 2,3-dibromo-1-propanol were distilled under reduced pressure. Aqueous solutions of AN were prepared by using the same method as that for pyrene aqueous solutions.[7] Concentrations of AN were about 1.5×10^{-5} mol dm^{-3}. Aerated sample solutions were used except for measurements of the room-temperature phosphorescence, for which so-

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