

2.15 mmol). After 6 h of stirring, the mixture was filtered on silica gel, which was washed with ether. The filtrate was concentrated in vacuo and flash-chromatographed on silica gel (pentane \rightarrow ether/pentane, 1/10) to give **22** (250 mg, 70%). Data for **22**: IR (film) 3090, 1755, 1685, 895 cm^{-1} ; mass spectrum m/z 164 (18) (HRMS 164.1209, calcd for $\text{C}_{11}\text{H}_{10}\text{O}$ 164.1201), 149 (5), 122 (60), 107 (100). Data for exo isomer **22a** (from **17a**): ^1H NMR δ 4.90 (1, s), 4.73 (1, s), 2.29 (1, $1/2$ AB, $J = 17.4$ Hz), 2.1 (1, $1/2$ AB, $d, J = 3.2$ Hz), 2.04–1.87 (3, m), 1.31 (3, s), 1.10 (3, s), 0.88 (3, d, $J = 6.6$ Hz); ^{13}C NMR δ 214.58 (s), 159.11 (s), 99.12 (t), 60.12 (s), 53.40 (t), 44.82 (t), 43.34 (s), 34.42 (q), 17.61 (d), 16.99 (q), 7.74 (q). Data for endo isomer **22b** (from **17b**): ^1H NMR δ 4.66 (1, s), 4.58 (1, s), 2.08 (1, $1/2$ AB, $J = 17.4$ Hz), 1.97 (1, $1/2$ AB, $d, J = 1.96$ Hz), 1.96–1.74 (3, m), 1.19 (3, s), 1.05 (3, s), 0.82 (3, d, $J = 6.84$ Hz); ^{13}C NMR δ 212.6 (s), 162.0 (s), 95.6 (t), 61.2 (s), 54.1 (t), 44.6 (t), 43.1 (s), 38.6 (q), 16.8 (q or d), 16.6 (d or q), 8.9 (q).

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Registry No. **1**, 3168-90-9; **1-d₉**, 135773-75-0; **2**, 80638-72-8; **4**, 135773-67-0; **5**, 135773-68-1; **6**, 4752-31-2; **7a**, 625-35-4; **7b**, 97943-16-3; **7c**, 35660-94-7; **7d**, 83841-91-2; **7e**, 36278-22-5; **7f**, 59253-90-6; **8a**, 72233-31-9; **8a-d₉**, 135773-74-9; **8b**, 135773-69-2; **8b-d₉**, 135773-76-1; **8c**, 135773-70-5; **8d**, 135773-71-6; **8e**, 135773-72-7; **9**, 135773-73-8; **11a**, 30434-75-4; **11c**, 135773-77-2; **11d**, 135773-78-3; **12a**, 30434-70-9; **12b**, 135773-79-4; **12c**, 50506-54-2; **12c-d₆**, 135773-83-0; (**S^{*},S^{*}**)-**12d**, 135773-80-7; (**S^{*},R^{*}**)-**12d**, 135773-81-8; **12f**, 135773-82-9; **13**, 2614-88-2; **14**, 135773-84-1; **15**, 135773-88-5; **16**, 135773-85-2; **17a**, 135773-86-3; **17b**, 135773-87-4; **18**, 135773-89-6; **19**, 135773-90-9; **20**, 135773-91-0; **21**, 135773-92-1; **22a**, 135773-93-2; **22b**, 135773-94-3; AlCl_3 , 7446-70-0; CH_3COCl , 75-36-5; TiCl_4 , 7550-45-0; EtCOCl , 79-03-8; CuSO_4 , 7758-98-7; MeNO_2 , 75-52-5; $(\text{CH}_3)_2\text{CHEt}$, 78-78-4; $(\text{CD}_3)_2\text{CHEt}$, 77734-77-1; methylcyclopentane, 96-37-7; *cis*-decahydronaphthalene, 493-01-6; 1-methylcyclopentene, 693-89-0; cyclohexane- d_{12} , 1735-17-7; methylcyclohexane, 108-87-2; 2-methyl-2-butene, 513-35-9; 2,3-dimethylbutane, 79-29-8; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0.

A Carbene to Biradical Rearrangement: Reaction Paths from (8-Methyl-1-naphthyl)carbene to Acenaphthene

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Abstract: Photochemical nitrogen elimination from 1-(diazomethyl)-8-methylnaphthalene (**2**) yields acenaphthene (**3**) via the reactive intermediates (8-methyl-1-naphthyl)carbene (**a**) and 1,8-naphthoquinodimethane (**b**). The triplet biradical **b** was observed by absorption spectroscopy at 77 K and by laser flash photolysis at room temperature. The cyclization of triplet **b** to triplet **3** is forbidden by state symmetry. Two pathways for the reaction $\text{b} \rightarrow \text{3}$ have been identified: (1) intersystem crossing to the singlet ground state is rate-determining in the thermal decay of **b**, and (2) an adiabatic reaction yielding **3** in the lowest excited triplet state was observed upon photolysis of triplet **b** at 77 K. The carbene precursor of **b** was intercepted by methanol. This resulted in a reduced yield of transient **b** in acetonitrile. The trapping reaction did not obey a linear Stern–Volmer relationship.

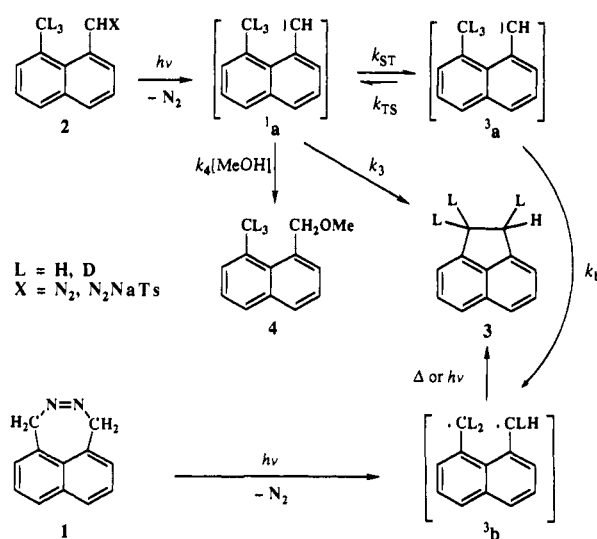
1,8-Naphthoquinodimethane (**b**, IUPAC name: 1,8-naphthalenediylbismethyl) has been identified by ESR spectroscopy as a non-Kekulé conjugated hydrocarbon biradical with a ground state of triplet multiplicity (^3b). It was generated by low-temperature photolysis of the azo compound 1,4-dihydro-naphtho[1,8-*de*][1,2]diazepine (**1**)¹ and of the diazo compound 1-(diazomethyl)-8-methylnaphthalene (**2**, $\text{X} = \text{N}_2$).² The high photochemical reactivity of 1,8-naphthoquinodimethane (^3b) has largely prevented its detection by spectroscopic techniques other than ESR when **1** was used as a precursor,^{1b} but several derivatives of ^3b have been extensively characterized by a variety of spectroscopic methods, both as transient intermediates at room temperature and as persistent species at low temperature.³ The hypothetical precursor of ^3b in the photolysis of the diazo compound (**2**, $\text{X} = \text{N}_2$), (8-methyl-1-naphthyl)carbene (**a**), has remained elusive.^{2b,4}

We now report that the electronic absorption of the triplet biradical **b** is readily observed both by low-temperature photolysis and by room temperature flash photolysis of the diazo compound **2** ($\text{X} = \text{N}_2$). Moreover, we have trapped the precursor carbene **a** with methanol in fluid solution, proving that it is a true intermediate (Scheme 1).

Results

Room Temperature Photolyses; Trapping of the Carbene a. Solutions of the diazo compound **2** were stable indefinitely at

Scheme 1



ambient temperature when kept in the dark. Irradiation of 10^{-4} M solutions of **2** ($\text{X} = \text{N}_2$) in degassed hexane or acetonitrile with

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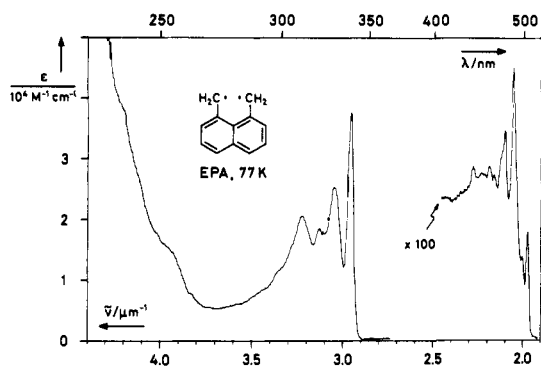


Figure 1. Absorption spectrum of triplet 1,8-naphthoquinodimethane (3b) in EPA glass at 77 K.

365-nm light filtered from a medium-pressure mercury arc lamp gave acenaphthene (**3**). UV monitoring indicated that some oxidation took place as a side reaction in aerated solutions. An additional product was formed in methanol; it was identified as 1-(methoxymethyl)-8-methylnaphthalene (**4**) by independent synthesis. This is the product expected if methanol intercepts the carbene intermediate **a**.

Quantitative analyses for the efficiency of methanol trapping of **a** were done by irradiation (Rayonet reactor with 12 RPR 350-nm lamps) of the tosylhydrazone **2** ($L = H$, $X = N_2$ NaTs) and its deuterated derivative ($L = D$) in MeONa/MeOH, since our attempts to purify the raw diazo compound **2** ($X = N_2$) had failed. Irradiation of the tosylhydrazones initially produced an orange color, indicating formation of the diazo compound, which disappeared upon prolonged photolysis. The material balance ($\geq 85\%$ by reference to an internal standard) and the product ratios **4/3** were determined by NMR from the intensities of the non-aromatic signals: 1H NMR **4** δ 2.9 (8- CH_3), 3.4 (OCH_3), 4.9 ppm (CH_2O), **3** δ 2.8 ppm (CH_2); 2H NMR **4** δ 2.7 ppm (8- CD_3), **3** δ 3.2 ppm (CD_2). The spectra of a pair of samples, of which one was sealed after purging with argon and the other left aerated during irradiation, were found to be indistinguishable by NMR. The following ratios of **4/3** were obtained: **2** ($L = H$, MeOH) 0.43 (1H NMR); **2** ($L = H$, MeOD) 0.47 (1H NMR); **2** ($L = D$, MeOH) 1.1 (1H NMR); **2** ($L = D$, MeOH) 1.3 (2H NMR).

Low-Temperature Photolyses; Absorption and Emission Spectra. The absorption spectrum shown in Figure 1 was observed after brief 365-nm irradiation of a solution of **2** ($L = H$, $X = N_2$) in EPA glass (ether/isopentane/alcohol 5:5:2 by vol), which was kept at 77 K in an optical quartz dewar. Due to the large (ca. 100-fold) intensity difference between the visible ($\lambda \leq 507$ nm) and UV ($\lambda \leq 337$ nm) absorption bands, the two parts of the spectrum had to be determined in separate experiments with different concentrations of starting material **2** (ca. 10^{-3} and 10^{-4} M, respectively). The positions of the peak maxima coincide exactly with the very weak features that were noted previously during low-temperature photolysis of **1**, which were tentatively attributed to the triplet biradical 1,8-naphthoquinodimethane (3b).^{1b} The spectrum persisted for hours when the glass was kept in the dark at 77 K but was quite sensitive to irradiation. Prolonged irradiation at 365 nm or brief irradiation with polychromatic light from a high-pressure mercury arc lamp led to a complete conversion to acenaphthene (**3**). On the basis of these observations, we assign the absorption spectrum shown in Figure 1 to 3b , which has

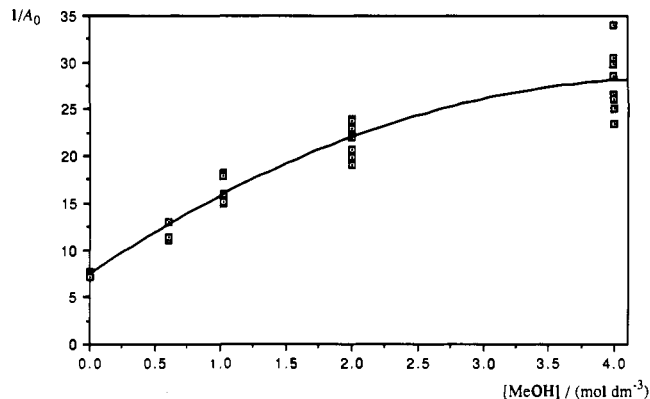


Figure 2. Stern-Volmer plot relating methanol concentration in acetonitrile to the inverse efficiency of formation of 1,8-naphthoquinodimethane. The latter was monitored by its absorbance at 337 nm shortly after laser flash photolysis of **2**.

previously been identified by EPR spectroscopy.^{1a,2} The spectrum of 3b is quite similar to the absorption spectra of bridged 1,8-naphthoquinodimethane triplet biradicals.³

With 365-nm irradiation at 77 K, the conversion of **2** ($X = N_2$) to 3b was much faster than the subsequent transformation to **3** because the absorbance of 3b is very low at this wavelength (Figure 1). The extinction of 3b at the 337-nm peak was nearly the same as that of the starting material **2** ($\epsilon \approx 20000$ M^{-1} cm^{-1}). Spectra recorded at the initial stages of the irradiation of **2** ($X = N_2$) indicated near-quantitative conversion to 3b with hardly any contribution from the final product **3**. Since extinction coefficients of **2** could not be determined accurately, the absolute extinction coefficients of 3b were estimated from the spectral changes observed in the subsequent photochemical conversion of 3b to the final product **3**.

A green emission appeared during the low-temperature photolysis of **2** with 365-nm light. This was not due to triplet-triplet fluorescence of 3b (expected to lie at $\lambda \geq 507$ nm, $\tau \leq 10^{-7}$ s),³ but was identical in spectral distribution [λ_{max}/nm (rel intensity): 479 (0.8), 491 (0.5), 513 (1), 528 (0.5), 553 (0.4)] and lifetime (2.9 ± 0.1 s) with the phosphorescence of acenaphthene (**3**). Using excitation by strictly monochromatic laser light of 353 nm (where **3** does not absorb), we have established that the emission did not arise from secondary excitation of the photoproduct **3**; reference samples containing only **3** did not detectably phosphoresce under these conditions. The green emission was also not detectable with the first laser pulse on a sample of **2** in frozen EPA that had been freshly prepared in the dark. Its intensity increased with further irradiation until the starting material was exhausted and subsequently decreased slowly as the biradical was converted to acenaphthene. These experiments prove that the phosphorescence of **3** was induced by excitation of the biradical 3b .

Flash Photolysis. 1,8-Naphthoquinodimethane (3b) was observed as a transient intermediate at ambient temperature (20 ± 2 °C) by nanosecond flash photolysis at 351 or 353 nm of solutions of **2** ($X = N_2$). The UV spectrum of the transient absorption was obtained by spectrographic detection in a time window from 100 to 140 ns after the laser pulse; it was clearly the same as that of 3b obtained at 77 K (cf. Figure 1). The decay kinetics of 3b were best monitored at 337 nm. At this wavelength, the strong absorbance of the starting material **2** is bleached by photolysis. The major part (ca. 85%) of the bleaching occurred within 100 ns (signal distortions by stray light from the laser pulse obscured the kinetics at shorter times). This was followed by a further slow decay of absorbance (ca. 15%) due to 3b . The decay of this transient obeyed first-order kinetics with a lifetime of 102 ± 5 μs in degassed hexane, which was reduced to 493 ± 13 ns in air-saturated hexane. The oxygen concentration in air-saturated hexane is 3.1×10^{-3} M;⁵ hence, the bimolecular rate constant for

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the oxygen quenching of triplet 3b is calculated as $(6.6 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

If 3b is formed by a 1,5-H shift from the short-lived carbene a, methanol trapping of a should compete with the formation of 3b . Indeed, the initial intensity of the transient absorbance by 3b at 337 nm, $A_0(^3b)$, was reduced when methanol was added to acetonitrile solutions of **2** ($X = N_2$). A plot of $1/A_0(^3b)$, obtained by 351-nm flash photolysis of **2** ($L = H, X = N_2$) in air-saturated acetonitrile, vs the concentration of added methanol is shown in Figure 2. The initial linear dependence at low methanol concentrations begins to curve and reaches a plateau at high concentrations of added methanol. Therefore, a more extensive set of data was obtained at methanol concentrations below 0.3 M where deviations from linearity were insignificant. Linear least-squares analysis of these data gave a slope of $14.3 \pm 1.0 \text{ M}^{-1}$ and an intercept of 9.5 ± 0.2 (errors are standard deviations, 26 data points). A similar series using the deuterated derivative **2** ($L = D, X = N_2$) gave $7.2 \pm 0.5 \text{ M}^{-1}$ and 4.6 ± 0.1 (21 data points). The ratios of slope to intercept were equal within the limits of error, $1.51 \pm 0.16 \text{ M}^{-1}$ for **2** ($L = H$) and $1.57 \pm 0.17 \text{ M}^{-1}$ for **2** ($L = D$).

In an attempt to determine the lifetime of a at reduced temperature, we performed flash photolysis of **2** in isooctane and pentane. Following flash photolysis of the deuterated diazo compound **2** ($L = D$), a time-resolved rise of a long-lived transient absorbance was observed at 370 nm with first-order growth kinetics ($k = 0.26 \times 10^7 \text{ s}^{-1}$ at ca. -64°C). The formation of this transient was suppressed by the addition of 10% toluene. Similar observations were made in the studies of 1-naphthylcarbene, which forms the 1-naphthylmethyl radical ($\lambda_{\text{max}} = 365 \text{ nm}$) by hydrogen abstraction from aliphatic hydrocarbons and is trapped by toluene.^{4,8} Hardly any of the 370-nm transient was seen with **2** ($L = H$), and its growth was not resolved ($k \geq 1 \times 10^7 \text{ s}^{-1}$). These results suggest that the lifetime of a ($L = D$) is ca. 400 ns at -64°C , whereas that of parent a ($L = H$) is less than 100 ns under these conditions.

Discussion

1-Naphthylcarbene has been studied extensively by EPR in rigid matrices⁷ and by flash photolysis in solution.^{4,8} We briefly summarize these results here, as the intermolecular reactivity of 1-naphthylcarbene provides an excellent reference for the competing intra- and intermolecular reactions of the carbene a. Trozzolo et al.^{7a} observed the triplet EPR spectrum of 1-naphthylcarbene down to 4 K, which indicates that its electronic ground state is a triplet. The reactions of 1-naphthylcarbene in solution have been interpreted in terms of a rapid equilibrium between the singlet and triplet state, with reactions occurring from both states. Analysis of these data suggested that the free energy gap between the singlet and triplet state of 1-naphthylcarbene is small ($0 < \Delta G_{\text{ST}} < 5.5 \text{ kcal mol}^{-1}$).⁴ Reactions attributed to the singlet state include the formation of a nitrile ylide by addition to acetonitrile ($k = 4.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in benzene),⁴ the addition of methanol ($k = 3.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile),⁴ and CH insertion reactions with hydrocarbons (e.g., $k = 8.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ with cyclohexane in 2,2,4-trimethylpentane).⁸ The last reaction exhibits a small kinetic isotope effect of 1.3 ± 0.2 ($k = 6.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ with perdeuterated cyclohexane in 2,2,4-trimethylpentane).⁸ The observed rates of the singlet reactions were interpreted as composite in nature due to preequilibrium between the singlet state and triplet ground state of the carbene, $k_{\text{obsd}} = k_{\text{singlet}}K_{\text{ST}}$. Hydrogen abstraction from hydrocarbons was attributed to the triplet state of 1-naphthylcarbene. This reaction was observed by the formation of 1-naphthylmethyl radical, which exhibits a sharp absorption peak at ca. 365 nm.^{4,8} In neat, reactive solvents such as carbon tetrachloride or acetone, a substantial fraction of the reaction products appeared to be formed directly from the photogenerated

singlet carbene, i.e., preceding equilibration between the singlet and triplet states.⁴ It was noted that flash photolysis of **2** ($X = N_2$) in acetonitrile did not produce any ylides, and it was proposed that the intramolecular reaction of the carbene in this case is too rapid for bimolecular acetonitrile addition to compete effectively.⁴

(8-Methyl-1-naphthyl)carbene Intermediate (a). The decay of the carbene a at room temperature escaped the time resolution of our nanosecond flash photolysis system. We also failed to detect the intermediate a by photolysis with UV monitoring at 77 K. In previous experiments, a was not observed by ESR upon photolysis of **2** at temperatures down to 4 K, even when the methyl hydrogens of **2** were replaced by deuterium.² Our flash photolysis experiments set an upper limit of 100 ns to the lifetime of the carbene a at ambient temperature. It is, however, sufficiently long-lived to undergo intermolecular trapping at room temperature; the formation of **4** upon photolysis of **2** in the presence of methanol provides clear evidence for the existence of the carbene a as a true reaction intermediate. Indeed, flash photolysis of **2** ($X = N_2$) in isooctane at -64°C indicated that the lifetime of 3a ($L = D$) was about 400 ns under these conditions, whereas 3a ($L = H$) was still too short-lived for detection ($< 100 \text{ ns}$).

The kinetic analysis of the reaction mechanism (Scheme I) accounts for two kinetically distinguishable reactive carbene intermediates, the singlet state 1a and the triplet state 3a . By analogy to the behavior of 1-naphthylcarbene, it would seem natural to assume a rapid equilibrium between 1a and 3a , to attribute the formation of 3b to hydrogen abstraction occurring from 3a , and the formation of acenaphthene (**3**) by CH insertion as well as the trapping by methanol to competing reactions occurring from 1a . The kinetic analysis of this scheme is based on the assumptions that 1a is the primary product of the direct photolysis of **2** and that the buildup of 3b is much faster than its decay. The latter assumption is known to hold since the lifetime of 3a is less than 100 ns at -64°C , and hence will be much less than the lifetime of 3b in aerated acetonitrile at ambient temperature (ca. 400 ns). This leads to the prediction that the inverse of the yield of 3b , and hence of the absorbance $A_0(^3b)$ observed immediately after the laser flash, should be linearly related to the concentration of the trapping agent methanol,

$$1/A_0(^3b) = \text{const}\{1 + (k_3 + k_4[\text{MeOH}])(k_{\text{TS}} + k_b)/(k_{\text{ST}}k_b)\} \quad (1)$$

where k_{ST} and k_{TS} are the rate constants of intersystem crossing of the carbene a, k_b and k_3 are the rate constants for the reaction of 3a to 3b and of 1a to **3**, respectively, and k_4 is the second-order rate constant for the trapping of 1a by methanol. Equation 1 holds irrespective of whether or not the equilibrium between 1a and 3a is established on the time scale of the reactions to 3b , **3**, and **4**. Furthermore, the ratio of the final products is predicted to be equal to the ratio of the slope and the intercept of the linear eq 1 multiplied by the concentration of methanol

$$4/3 = k_4[\text{MeOH}]/\{k_3 + k_{\text{ST}}k_b/(k_{\text{TS}} + k_b)\} \quad (2)$$

In fact, pronounced curvature was observed in plots of $1/A_0(^3b)$ vs $[\text{MeOH}]$ (Figure 2), and the ratios of slope to intercept of about 1.5 M^{-1} , found at low methanol concentrations ($< 0.3 \text{ M}$) for both the deuterated ($L = D$) and undeuterated ($L = H$) compound, are inconsistent with the product ratio $4/3 \approx 1$, found by product analysis following photolysis in neat MeOH; the product ratio, as predicted with eq 2 by extrapolation of the data obtained at low methanol concentrations to neat methanol ($[\text{MeOH}] = 25 \text{ M}$), amounts to ca. 37. Such behavior has been noted previously in related systems.⁶ Various ad hoc assumptions may be proposed to account for these findings: intersystem crossing of the excited diazo compound may be responsible for the carbene being (in part) formed in the triplet state, concentration-dependent oligomerization of methanol by hydrogen bonding may affect the reactivity of 1a toward methanol, solvent polarity changes in the acetonitrile/methanol solvent mixture used may affect the singlet-triplet equilibrium of the carbene or, finally, hydrogen abstraction from the 8-methyl group may in part occur from the excited state of the diazo compound **2**. A study of this system at higher time

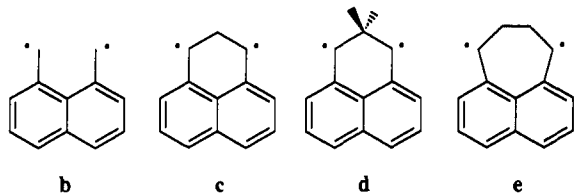
(7) (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1981**, *103*, 5503. (c) Wright, B. B.; Platz, M. S. *Ibid.* **1984**, *106*, 4175.

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resolution might distinguish between these possibilities. The formation of $^3\mathbf{b}$ at 4 K indicates that the 1,5-H shift from $^3\mathbf{a}$ to $^3\mathbf{b}$ occurs by tunneling at low temperature. It would be of interest to determine the temperature dependence and kinetic isotope effects of this reaction rate by time-resolved absorption or EPR spectroscopy.

1,8-Naphthoquinodimethane Intermediate ($^3\mathbf{b}$). The absorbance of $^3\mathbf{b}$, formed by 365-nm photolysis at 77 K, was nearly the same as that of the starting material $\mathbf{2}$ at 337 nm ($\epsilon \approx 20000 \text{ M}^{-1} \text{ cm}^{-1}$). On flash photolysis of $\mathbf{2}$ in acetonitrile or isooctane at room temperature, the change of absorbance at 337 nm was dominated by fast bleaching (ca. 85%), followed by a transient decay of ca. 15% arising from the decay of $^3\mathbf{b}$. Hence, the formation of $^3\mathbf{b}$ is a minor reaction at room temperature. If the major pathway for acenaphthene formation proceeds by intramolecular hydrogen transfer from $^1\mathbf{a}$ via the singlet biradical $^1\mathbf{b}$, we should expect a strong kinetic isotope effect. More probably, acenaphthene is formed from the singlet carbene by a concerted CH insertion with only moderate sensitivity to isotopic substitution at the methyl group ($L = \text{H/D}$). Indeed, the deuterated compound $\mathbf{2}$ ($L = \text{D}$) gave a somewhat but not much higher yield of $^3\mathbf{b}$ (about 25% of the bleaching at 337 nm). Similarly, the yield of the trapping product $\mathbf{4}$ increased about 2-fold upon deuteration of $\mathbf{2}$.

The absorption spectrum of $^3\mathbf{b}$ (Figure 1) is remarkably similar to those of alkane-bridged derivatives of $^3\mathbf{b}$, 1,3-perinaphthadiyl ($^3\mathbf{c}$)^{3a} and 2,2-dimethyl-1,3-perinaphthadiyl ($^3\mathbf{d}$),^{3c} which are known^{3d} to be planar, and 1,4-perinaphthadiyl ($^3\mathbf{e}$),^{1b,3f} which probably has a nonplanar equilibrium conformation in the seven-membered ring moiety. The fact that all of these species exhibit a comparable resolution of the vibrational fine structure (EPA, 77 K) is somewhat surprising, as one might expect considerable differences in the conformation of the exocyclic radical centers and in their flexibility.

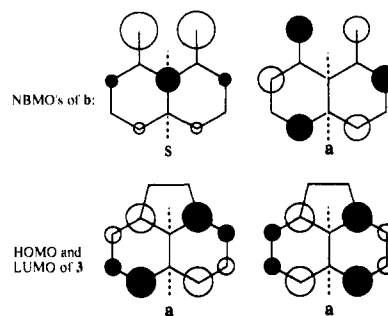


The photoinduced ring closure of the triplet biradical \mathbf{b} yields acenaphthene in the lowest triplet state, which was detected by its characteristic phosphorescence emission. Efficient photocyclization of $^3\mathbf{b}$ accounts for the absence of triplet-triplet fluorescence; the alkane-bridged derivatives $^3\mathbf{c}$ to $^3\mathbf{e}$ exhibit strong fluorescence and are less photoreactive.³ At ambient temperature, $^3\mathbf{b}$ decays to ground-state acenaphthene with a lifetime of ca. 100 μs in degassed solutions. A lifetime in the range of 0.4 to 10 μs would have been predicted by extrapolation with the Arrhenius parameters, $\log(A/s^{-1}) = 10.4 \pm 0.5$ and $E_a = 6.4 \pm 0.3 \text{ kcal mol}^{-1}$, which were determined for $^3\mathbf{b}$ in polycrystalline hexafluorobenzene over a temperature range of 110–125 K.^{2b} The mechanism of the thermally activated ring-enclosure reaction of $^3\mathbf{b}$ to acenaphthene ($\mathbf{3}$) has been discussed.^{2b} Phosphorescence of $\mathbf{3}$ was not observed when a sample of $^3\mathbf{b}$ in frozen hexafluorobenzene was annealed. Combined evidence from studies of the effects of temperature, solvent heavy atoms, and isotopic substitution led to the conclusion that the rate-determining step of the ring-closure reaction involves intersystem crossing to the singlet ground-state surface.

This is not obvious on thermochemical grounds. A thermochemical estimate of the reaction enthalpy for the cyclization reaction $\mathbf{b} \rightarrow \mathbf{3}$ may be obtained from the activation energy of 35 kcal mol^{-1} , which Roth and Enderer have determined for the ring inversion of naphthocyclopropane via $^1\mathbf{c}$.⁹ The latter reaction is facilitated relative to $\mathbf{3} \rightarrow \mathbf{b}$ by release of the cyclopropane ring strain of ca. 27.6 kcal mol^{-1} . This suggests that the reaction $^1\mathbf{b} \rightarrow \mathbf{3}$ is exothermic by ca. $35 + 27.6 \text{ kcal mol}^{-1} = 62.6 \text{ kcal mol}^{-1}$. The triplet energy of acenaphthene is 60 kcal mol^{-1} (the 0–0 band

of phosphorescence lies at 479 nm). Hence, thermal adiabatic cyclization of $^3\mathbf{b}$ to the lowest triplet state of acenaphthene ($^3\mathbf{3}$) is estimated to be approximately thermoneutral. Nevertheless, $^3\mathbf{3}$ is not formed by photolysis of $\mathbf{2}$ at ambient temperature.

The ring closure of the singlet biradical trimethylene to cyclopropane is not inhibited by a significant energy barrier.¹⁰ Also, ring closure of the singlet biradical \mathbf{c} to naphthocyclopropane was estimated to occur within less than 1 ps.^{3c} Why does cyclization of $^3\mathbf{b}$ to $^3\mathbf{3}$ not occur on the triplet surface? The answer is that adiabatic cyclization on the triplet surface is forbidden by *state symmetry* for both the disrotatory and conrotatory reaction paths, i.e., the triplet ground state of \mathbf{b} and the lowest triplet state of $\mathbf{3}$ belong to different symmetry species. This is most easily seen by inspection of the singly occupied π orbitals of $^3\mathbf{b}$ and $^3\mathbf{3}$, obtained by a simple Hückel calculation:



Thus, the electronic wavefunction describing the lowest triplet state of $\mathbf{3}$ is *symmetric* ($a \otimes a = s$) with respect to the plane of symmetry orthogonal to the molecular plane; i.e., it belongs to the representation A' under the C_2 point group (disrotatory path retaining a plane of symmetry) as is well known,¹¹ whereas that of the triplet ground state of \mathbf{b} is *antisymmetric* ($s \otimes a = a$, i.e., A'') with respect to the same symmetry element.¹² All orbital symmetry labels are reversed with respect to a 2-fold axis through the two bridgehead atoms of the naphthalene core, resulting in state symmetries A for the lowest triplet state of $\mathbf{3}$ and B for the triplet ground state of \mathbf{b} under C_2 (conrotatory path retaining a 2-fold axis). In fact, $^3\mathbf{b}$ cannot assume a fully planar structure due to the steric interaction of the hydrogen atoms on the exocyclic methylene groups. The relaxed geometry is likely to lie along the conrotatory reaction path considered above, with out-of-plane rotation and/or pyramidalization of the methylene groups that would favor the conrotatory pathway for ring closure. Nevertheless, adiabatic ring closure from $^3\mathbf{b}$ to $^3\mathbf{3}$ is forbidden by state symmetry for any reaction path retaining an element of symmetry. A substantial energy barrier is indeed predicted by simple model calculations (HMO or PPP) for this reaction. State-symmetry considerations are of no concern for thermal reactions in the electronic ground state, since closed-shell molecules generally have a totally symmetric ground-state wavefunction. However, state-symmetry rules have been discussed for pericyclic reactions of organic radical cations.¹³

In conclusion, the present work provides evidence that photolysis of the diazo compound $\mathbf{2}$ ($X = \text{N}_2$) yields (8-methyl-1-naphthyl)carbene (\mathbf{a}) as a primary reaction intermediate. In solution at ambient temperature, intra- and intermolecular reactions from both the singlet state and triplet ground state of \mathbf{a} compete for product formation. At low temperature, the formation of the biradical $^3\mathbf{b}$ by 1,5-H shift originating from $^3\mathbf{a}$ predominates. Thermal adiabatic cyclization of $^3\mathbf{b}$ to $^3\mathbf{3}$ is thermochemically feasible but is forbidden by state symmetry and does not occur.

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At ambient temperature, the product **3** is formed in the singlet ground state following rate-determining intersystem crossing of ³b to the singlet ground-state surface. At 77 K, ³b is persistent in the dark; photolysis of ³b yields **3** in the lowest excited triplet state by an adiabatic pathway.¹⁴

Experimental Section

Kinetic and Spectrographic Flash Photolysis. Pulses from a XeF excimer laser (351 nm, 25-ns pulse width, ≤150 mJ per pulse) or the frequency-tripled, Q-switched pulses from a Nd glass laser (353 nm, 20-ns pulse width, ≤50 mJ per pulse) were used for excitation. The detection system allowed for the capture of the transient kinetics (at a given wavelength) or of the transient spectrum (at a given time delay after excitation) in digital form with nanosecond time resolution. The kinetic and spectrographic data were processed and analyzed by computer. Details of the experimental setup have been described.¹⁶

Optical Spectra. Absorption spectra were recorded on a Beckman UV 5240, which was equipped with a thermostated quartz dewar for low-temperature spectra down to 77 K. Fluorescence spectra were obtained with a Spex Fluorolog 2 (Model 111 C), equipped with a red-sensitive R666 S photomultiplier tube, and were not corrected. For phosphorescence measurements, a pulsed lamp accessory (Model 1934 C) was available. The phosphorescence spectrum and lifetime were also monitored on the flash photolysis detection systems.

8-Methyl-1-naphthaldehyde (*p*-Tolylsulfonyl)hydrazone (2, X = N₂NaTs). 8-Methyl-1-naphthaldehyde¹⁷ (0.15 g, 0.882 mmol) and *p*-toluenesulfonohydrazide (0.17 g, 0.882 mmol) were heated with steam in 10 mL of absolute ethanol. The solution was boiled until the volume of ethanol was reduced to 3 mL. Upon cooling to room temperature, the product crystallized (0.20 g, 67% yield): mp 164–7 °C; ¹H NMR (TMS, CDCl₃, 250 MHz) 8.68 (1 H, s), 7.18–7.86 (6 H, m), 2.52 (3 H, s), 2.35 (3 H, s). Anal. (Calcd/Found) C (67.43/67.13); H (5.36/5.67); N (8.28/8.16); S (9.48/9.24) for C₁₉H₁₇N₂NaO₂S.

1-(Diazomethyl)-8-methylnaphthalene (2, X = N₂). 8-Methyl-1-naphthaldehyde (*p*-tolylsulfonyl)hydrazone (25 mg) was dissolved in 5 mL of ethanol and 50% aqueous sodium hydroxide, stirred vigorously, and heated to reflux in an oil bath. After 1 min, an orange color began to develop. The mixture was removed from the oil bath, stirred for another 2 min, dropped into 25 mL of cold hexane, and extracted with water. The organic layer, containing mainly **2**, was dried and kept in the refrigerator. Attempts to purify **2** by crystallization or chromatography on various solid phases failed. ¹H NMR: (TMS, CDCl₃, 250 MHz) 6.91–7.60 (6 H, m), 5.56 (1 H, s), 2.84 (3 H, s).

8-(Trideuteriomethyl)-1-naphthaldehyde (*p*-Tolylsulfonyl)hydrazone (2-d₃, X = N₂NaTs). In one preparation, 6.5 g of 1,8-naphthalic anhydride was suspended in 100 mL of dry THF in a three-necked flask equipped with a reflux condenser under a nitrogen atmosphere. To this was rapidly added 1 g of LiAlD₄ (Aldrich). The reaction mixture was allowed to warm spontaneously and was stirred for 30 min, during which time the anhydride dissolved completely and the reaction mixture turned a clear strawberry color. The reaction mixture was quenched first with water and then with 30% aqueous KOH. The side product 1,8-bis(hydroxymethyl)naphthalene was removed by repeated extractions with ether. Upon acidification with aqueous HCl, the desired dideuterio 1,8-naphthalic lactone precipitated (3 g, 49%). Dideuterio lactone (11 g) was dissolved with warming in 100 mL of D₂O plus 20 mL of 40% NaOD in D₂O (Aldrich). This solution was shaken over Pd/C with 60 psi of D₂ gas for 12 days. After removal of the catalyst by filtration, the solution was acidified with concentrated HCl, and the resulting precipitate was collected and air dried for 1 h. The precipitate was dissolved in 350 mL of CHCl₃ and extracted twice with 300 mL of 1% aqueous

KOH. The combined base washes were acidified with concentrated HCl to precipitate 8-(trideuteriomethyl)naphthalene-1-carboxylic acid. After the solid was washed with water, the carboxylic acid was dried at 70 °C under a 20-mm vacuum for 18 h to give 6.7 g of material (mp 147–151 °C). Evaporation of the CHCl₃ layer recovered 2 g of the lactone starting material.

A 1-L three-necked flask was equipped with a reflux condenser and was charged with 2.5 g of 8-(trideuteriomethyl)naphthalene-1-carboxylic acid and 100 mL of dry diethyl ether under a nitrogen atmosphere. To this was slowly added 1.1 g of LiAlH₄ (Aldrich). The solution was stirred for 12 h at room temperature, quenched successively with 2-propanol, H₂O, and 2 M H₂SO₄, and then poured into ether. The ether layer was separated, extracted twice with 75 mL of 5% aqueous KOH, and dried over MgSO₄; the solvent was removed to yield 1.5 g of 1-(hydroxymethyl)-8-(trideuteriomethyl)naphthalene (mp 93.5–94 °C). Acidification of the KOH extracts precipitated 1 g of unreacted 8-(trideuteriomethyl)naphthalene-1-carboxylic acid.

Activated MnO₂ (30 g) in 100 mL of benzene was connected to a Dean-Stark trap and refluxed for 90 min to remove water. At this point, 2.5 g of 1-(hydroxymethyl)-8-(trideuteriomethyl)naphthalene was added in 25 mL of benzene and refluxed for 14 h. The solution was then filtered hot with suction. The collected MnO₂ was washed with an additional 100 mL of benzene. The benzene washes were combined, the solvent was removed, and the residue was recrystallized from 95% ethanol to give 2.0 g of 8-(trideuteriomethyl)-1-naphthaldehyde (mp 65–66.5 °C).

8-(Trideuteriomethyl)-1-naphthaldehyde (50 mg) and *p*-toluenesulfonohydrazide (54 mg) were dissolved with heating in 10 mL of absolute ethanol. The solution was boiled until the volume of the solution was reduced to 3 mL. The product precipitated upon cooling to room temperature to yield 85 mg of **2-d₃**: mp 173–175 °C; ¹H NMR (250 MHz, δ, acetone-d₆) 10.30 (1 H, br s, NH), 8.92 (1 H, s), 7.3–8.0 (6 H, m), 2.36 (3 H, s); ¹³C NMR (250 MHz, δ, acetone-d₆) 151.718, 144.593, 137.733, 135.813, 132.945, 131.963, 130.743, 130.389, 128.534, 128.502, 128.385, 126.544, 12.392, 24.76 m (weak, CD₃); exact mass (measd/calcd) 341.1289/341.1275 for C₁₉H₁₅N₂O₂SD₃.

Photolysis of 8-(Trideuteriomethyl)-1-naphthaldehyde Tosylhydrazone Salt. 8-(Trideuteriomethyl)-1-naphthaldehyde tosylhydrazone (48 mg) was dissolved with heating in 4 mL of anhydrous methanol. To this was added 5 mg of metallic sodium cut under pentane. After the sodium was consumed, the solution was transferred to a 5-mm Pyrex tube and irradiated with three Rayonet RPR 350 bulbs for 20 h. The solution quickly took on the appearance of the orange color of the diazo compound, which faded to a very light yellow color by the end of the photolysis. The samples were analyzed by GC-MS, which revealed only two volatile products, **3-d₃** and **4-d₃**, which were identified by comparison with authentic samples. The solvent was removed and the residue analyzed by proton NMR spectroscopy to determine the ratio of **3** to **4**.

1-(Methoxymethyl)-8-methylnaphthalene (4). 1-(Hydroxymethyl)-8-methylnaphthalene¹⁸ (0.070 g, 0.40 mmol) was dissolved in 2 mL of dry THF and added to a solution of 0.5 mL of methyl iodide in 10 mL of THF at –77 °C. The solution was stirred for 20 min, another 0.5 mL of methyl iodide was added, and the dry ice bath was removed. The solution was refluxed for 1 h, and then the reaction mixture was extracted with ether (2 × 30 mL). The combined ether layers were dried with magnesium sulfate. Evaporation of the solvent gave an oil, which was purified by column chromatography to give **4** (0.026 g, 0.14 mmol, 34%): ¹H NMR (CDCl₃, TMS, 250 MHz) δ 2.889 (3 H, s), 3.363 (3 H, s), 4.867 (2 H, s), 7.212–7.842 (6 H, m); ¹³C NMR (TMS, CDCl₃, 250 MHz) 135.655, 134.858, 134.172, 132.047, 130.409, 130.106, 130.036, 127.794, 125.208, 124.567, 75.782, 57.568, 23.686; exact mass (measd/calcd) 186.2008/186.1004 for C₁₃H₁₄O.

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Registry No. **2** (X = N₂NaTs), 135733-96-9; **2** (X = N₂), 70840-50-5; **2-d₃** (X = N₂NaTs), 135733-97-0; **2-d₃**, 135734-02-0; **4**, 135734-04-2; **4-d₃**, 135734-03-1; MeOH, 67-56-1; 8-methyl-1-naphthaldehyde, 6549-57-1; 1,8-naphthalic anhydride, 81-84-5; 1,8-bis(hydroxymethyl)naphthalene, 2026-08-6; dideuterio 1,8-naphthalic lactone, 135733-98-1; 8-(trideuteriomethyl)naphthalene-1-carboxylic acid, 135733-99-2; 1-(hydroxymethyl)-8-(trideuteriomethyl)naphthalene, 135734-00-8; 8-(trideuteriomethyl)-1-naphthaldehyde, 135734-01-9; 1-(hydroxymethyl)-8-methylnaphthalene, 10336-29-5.

(14) A referee has raised the question whether the adiabatic reaction is one-way or two-way, i.e., whether the reaction ³a → ³b does occur. Indeed, the closely related reaction ³naphthocyclobutane → ³e has been shown to occur under pulsed laser photolysis of naphthocyclobutane, where ³e is readily detected by its characteristic fluorescence emission^{4f} and by the ultimate formation of 1,8-divinylnaphthalene.¹⁵ Hence, the reaction ³a → ³b is likely to occur also, but has escaped detection because ³b is nonluminescent and decays to the starting material **3**.

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