Photoequilibration of 2-Naphthylcarbene and 2,3-Benzobicyclo[4.1.0]hepta-2,4,6-triene

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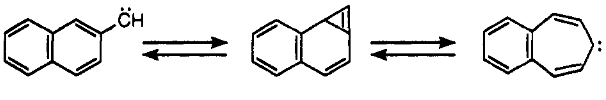
Abstract: Irradiation ($\lambda > 300$ nm or $\lambda = 480 \pm 6$ nm) of 2-naphthyldiazomethane (**4**), matrix-isolated in argon at 10 K, gives a mixture of 2-naphthylcarbene (**1**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**). 2-Naphthylcarbene (**1**) is characterized by infrared, UV/visible, and ESR spectroscopy and by chemical trapping with CO. 2,3-Benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) is characterized by infrared and UV/visible spectroscopy. A photoequilibrium exists between carbene **1** and bicyclic compound **2**. Photolysis ($\lambda = 290 \pm 6$ nm) of bicyclic compound **2** results exclusively in ring-opening to carbene **1**. Similarly, photolysis ($\lambda = 560 \pm 6$ nm, 360 ± 6 nm, >360 nm) of carbene **1** results exclusively in cyclization to bicyclic compound **2**. Thus, the photochemistry of 2-naphthylcarbene contrasts with that of phenylcarbene; 2-naphthylcarbene (**1**) cyclizes to bicyclic compound **2**, while phenylcarbene ring-expands to give 1,2,4,6-cycloheptatetraene.

Introduction

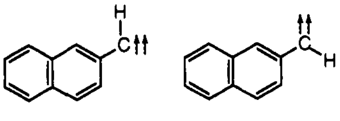
Despite long-standing interest in the rearrangement chemistry of arylcarbenes,[1] fundamental issues regarding rearrangement pathways and characterization of intermediates remain unanswered. Naphthylcarbene chemistry constitutes a central topic in the study of arylcarbene rearrangements, as many investigators have focused considerable effort on comparing the chemistry of naphthylcarbenes with phenylcarbene and its simple derivatives.[1] Various trapping studies demonstrate interconversions between 2-naphthylcarbene (**1**), 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**), and 4,5-benzocycloheptatrienylidene (**3**).[1-6] Remarkably, *none* of these individual, elementary transformations have been observed spectroscopically. This is due, in part, to the complete lack of information concerning the electronic absorption spectrum of bicyclic compound **2**. The absence of detailed absorption spectra for **1**-**3** also creates mechanistic ambiguities in distinguishing between thermal and photochemical rearrangement processes. Finally, the role of **1**-**3** as intermediates along the reaction coordinate for interconversion of the isomeric 1- and 2-naphthylcarbenes remains unclear.[1,4,5,7-9] In this article, we describe matrix isolation studies concerning the spectroscopic characterization and photochemical reactivity of both 2-naphthylcarbene (**1**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**). These studies permit the first detailed characterization of 2-naphthylcarbene (**1**) by infrared and UV/visible spectroscopy and bicyclic compound **2** by UV/visible spectroscopy. With the absorption spectra of **1** and **2** in hand, we are able to present the first unambiguous description of the photochemistry of **1** and **2**. We describe a clean, reversible photoequilibrium between carbene **1** and bicyclic compound **2**. We find no evidence for rearrangement of 2-naphthylcarbene (**1**) to 1-naphthylcarbene (**5**) under any of our photolysis conditions.



1 2 3

Background

Trozzolo et al. characterized triplet 2-naphthylcarbene (**1**) by low-temperature ESR spectroscopy.[10] Two rotational isomers of the carbene,[11] *s-Z* (**1a**) and *s-E* (**1b**), arise from restricted rotation about the aryl-CH bond.[12-14] Senthilnathan and Platz determined the barrier for *s-Z*-*s-E* interconversion to be greater than 4.5-6.3 kcal/mol.[13] Horn and Chateauneuf observed the transient absorption ($\lambda_{max} = 362$ nm) of triplet 2-naphthylcarbene (**1**) by laser flash photolysis.[15] Haider et al. observed the triplet-triplet fluorescence of carbene **1**.[16] The literature contains numerous reports describing the chemical trapping of 2-naphthylcarbene (**1**), as generated from various precursors,[3,4,6] with a variety of trapping agents.



1a 1b

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(1) (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (d) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, *41*, 1479-1507. (e) Platz, M. S.: Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 8. (f) Wentrup, C. In *Methoden der Organische Chemie* (*Houben-Weyl*); Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 824-976.

(2) (a) Krajca, K. E.; Mitsuhashi, T.; Jones, W. M. *J. Am. Chem. Soc.* **1972**, *94*, 3661-3662. (b) Krajca, K. E.; Jones, W. M. *Tetrahedron Lett.* **1975**, 3807-3810.

(3) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218-5227.

(4) (a) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026-4027. (b) Billups, W. E.; Reed, L. E.; Casserly, E. W.; Lin, L. P. *J. Org. Chem.* **1981**, *46*, 1326-1333. (c) Billups, W. E.; Haley, M. M.; Lee, G.-A. *Chem. Rev.* **1989**, *89*, 1147-1159.

(5) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316-1320.

(6) Chateauneuf, J. E.; Horn, K. A.; Savino, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 539-545.

(7) (a) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190-191. (b) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601-1612.

(8) (a) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456-2469. (b) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501-509.

(9) Miller, P. C.; Gaspar, P. P. *J. Org. Chem.* **1991**, *56*, 5101-5107.

(10) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129-130.

(11) Roth, H. D.; Hutton, R. S. *Tetrahedron* **1985**, *41*, 1567-1578.

(12) Various nomenclature schemes have been used to describe geometric isomerism in carbenes: cis and trans,[10,11] syn and anti,[13] and *s-Z* and *s-E*.[14] In many cases, cis ≡ syn ≡ *s-Z* and trans ≡ anti ≡ *s-E*, although this need not be true in general. We prefer the *s-Z*, *s-E* nomenclature, as it is the most systematic.

(13) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5503-5511.

(14) Torrres, M.; Safarik, I.; Murai, H.; Strausz, O. P. *Rev. Chem. Intermed.* **1986**, *7*, 243-270.

(15) Horn, K. A.; Chateauneuf, J. E. *Tetrahedron* **1985**, *41*, 1465-1470.

(16) Haider, K. W.; Platz, M. S.; Despres, A.; Migirdicyan, E. *Chem. Phys. Lett.* **1989**, *164*, 443-448.

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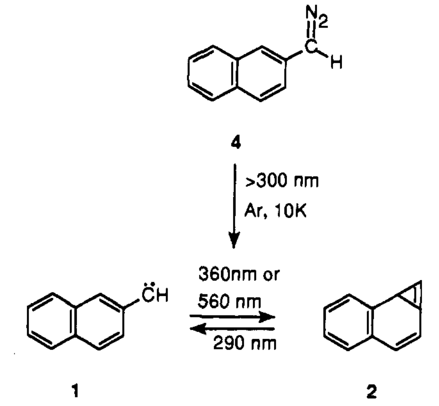
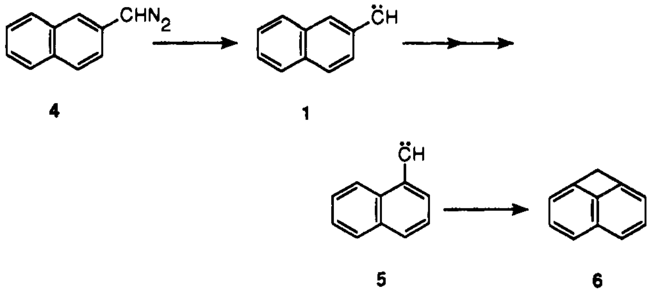
Scheme I



Evidence demonstrating the cyclization of 2-naphthylcarbene (**1**) to 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) comes from chemical trapping studies. Jones and Coburn trapped **2**, generated from 4,5-benzocycloheptatrienylidene (**3**), with cyclopentadiene or 1,3-butadiene to yield the Diels–Alder adducts.[3] Billups et al. described chemical trapping of related bicyclo[4.1.0]hepta-2,4,6-triene derivatives.[4] West et al. characterized **2** by infrared spectroscopy.[5] Bicyclic compound **2** presumably resulted from cyclization of 2-naphthylcarbene (**1**), but this conclusion could not be stated unequivocally because the carbene **1** was not observed.[17]

The solution studies described above provide evidence for cyclization of 2-naphthylcarbene (**1**) to **2**, but provide no evidence for isomerization of 2-naphthylcarbene (**1**) to 1-naphthylcarbene (**5**).[1] In contrast, gas-phase pyrolysis studies provide evidence for isomerization of 2-naphthylcarbene (**1**) to 1-naphthylcarbene (**5**), but no direct evidence for cyclization of 2-naphthylcarbene (**1**) to **2**.[5,7,18] Flash vacuum pyrolysis of 2-naphthyldiazomethane (**4**) (375 °C, 100% conversion), followed by cocondensation of the pyrolysate with argon, yields cyclobuta[*de*]naphthalene (**6**) as the major product. Bicyclic compound **2** was not observed.[5] There has been considerable speculation concerning the interconversion mechanism of 2-naphthylcarbene (**1**) and 1-naphthylcarbene (**5**), but most arguments rely on analogy with related systems.[1-9] Few mechanistic details are known with certainty.



Results and Discussion

Structural Characterization of Intermediates. Irradiation (λ > 300 nm) of 2-naphthyldiazomethane (**4**), matrix-isolated in argon at 10 K, results in complete disappearance of **4** and appearance of two products, triplet 2-naphthylcarbene (**1**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**), in a ratio of 3:7 (Scheme I) (Figures 1a and 2). We did not observe 2-naphthyldiazirine by IR or UV/visible spectroscopy. Presumably, carbene **1** is the sole primary photoproduct. Independent control experiments establish that carbene **1** photochemically cyclizes to bicyclic compound **2** under the conditions of the initial photolysis (>300 nm). Thus, **2** arises as a secondary photoproduct of diazo compound **4**.[19] This behavior does not, however, rule out the possibility that small amounts of **2** could also arise via cyclization of either excited-state diazo compound or vibrationally hot carbene.

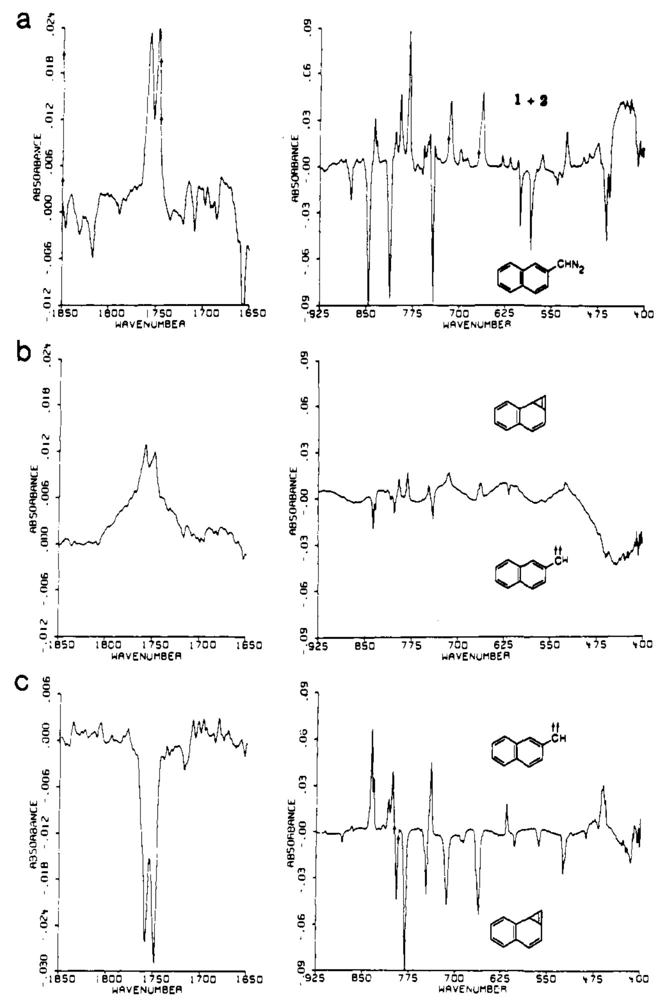


Figure 1. (a) IR difference spectrum showing spectral changes observed upon photolysis (λ > 300 nm, 17.25 h, 100% conversion) of 2-naphthyldiazomethane (**4**) (Ar, 10 K). The spectrum shows disappearance of **4** and appearance of a mixture of 2-naphthylcarbene (**1**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**). (b) IR difference spectrum showing spectral changes observed upon photolysis (λ = 360 ± 6 nm, 28 h, 100% conversion) of the mixture of carbene **1** and bicyclic compound **2** (Ar, 10 K). The spectrum shows disappearance of carbene **1** and growth of bicyclic compound **2**. (c) IR difference spectrum showing spectral changes observed upon photolysis (λ = 290 ± 6 nm, 24 h, 100% conversion) of bicyclic compound **2**. The spectrum shows disappearance of bicyclic compound **2** and appearance of carbene **1**.

We characterized triplet 2–naphthylcarbene (**1**) by IR, UV/visible, and ESR spectroscopy: IR (Ar, 10 K) 3076 w, 3053 w, 1492 w, 1272 w, 1185 m, 1122 m, 1022 m, 836 s, 809 m, 803 m, 741 s, 616 w, 463 s cm^{-1}; UV (Ar, 10 K) λ_{max} 561.4, 560.6, 558.8, 557.6, 554.6, 553.0, 550.6, 549.4, 546.2, 543.6, 542.2, 539.6, 536.8, 534.4, 523.6, 521.2, 518.8, 517.6, 515.4, 514.2, 510.6, 508.4, 500.0, 486.4, 360, 342, 279, 269, 240, 231, 220 nm; ESR (Ar, 15 K) *s*-*Z*-isomer (**1a**), $|D/hc| = 0.500$ cm^{-1}, $|E/hc| = 0.0242$ cm^{-1}, $Z_1 = 1880$ G, $X_2 = 5018$ G, $Y_2 = 6014$ G, $Z_2 = 8768$ *s*-*E*-isomer (**1b**), $|D/hc| = 0.480$ cm^{-1}, $|E/hc| = 0.0277$ cm^{-1}, $Z_1 = 1655$ G, $X_2 = 4886$ G, $Y_2 = 6014$ G, $Z_2 = 8536$ G, microwave frequency = 9.620 GHz. The zero-field splitting parameters show good agreement with those reported previously for 2-naphthylcarbene.[10] Our experiments allow us to obtain the first detailed UV/visible

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(17) An alternate possibility is that **2** resulted from an excited-state reaction of the diazo compound.

(18) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715–2718.

(19) Determining the primary photoproduct(s) of diazo compound **4** is not straightforward because the products exist in a wavelength-dependent photoequilibrium (vide infra). Despite considerable effort, we have been unable to find a suitable wavelength where **4** absorbs but neither **1** nor **2** absorbs. Thus, irradiation of **4** may produce exclusively carbene **1**, exclusively bicyclic compound **2**, or a mixture of **1** and **2**, depending on the photolysis conditions.

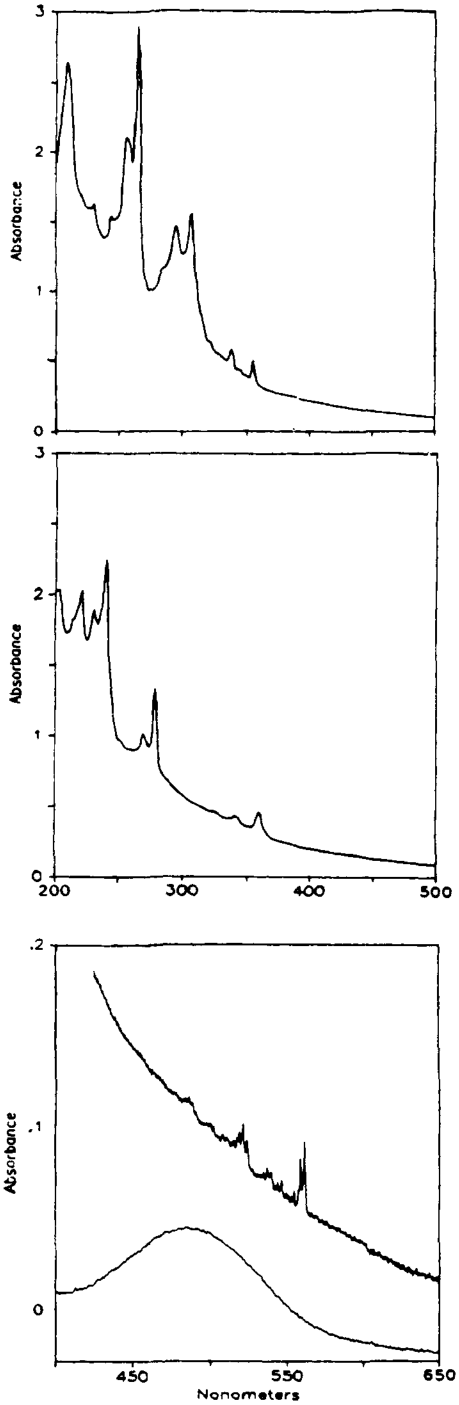

Figure 2. Top: UV/visible spectrum of 2-naphthyldiazomethane (4) (Ar, 10 K). Middle: UV/visible spectrum of resultant mixture of 2-naphthylcarbene (1) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (2) obtained upon photolysis ($\lambda > 300$ nm, 1 h, 100% conversion) of diazo compound 4. Bottom: Visible spectra of carbene 1 (Ar, 10 K) (upper curve) and diazo compound 4 (CH_3CN, 298 K) (lower curve).

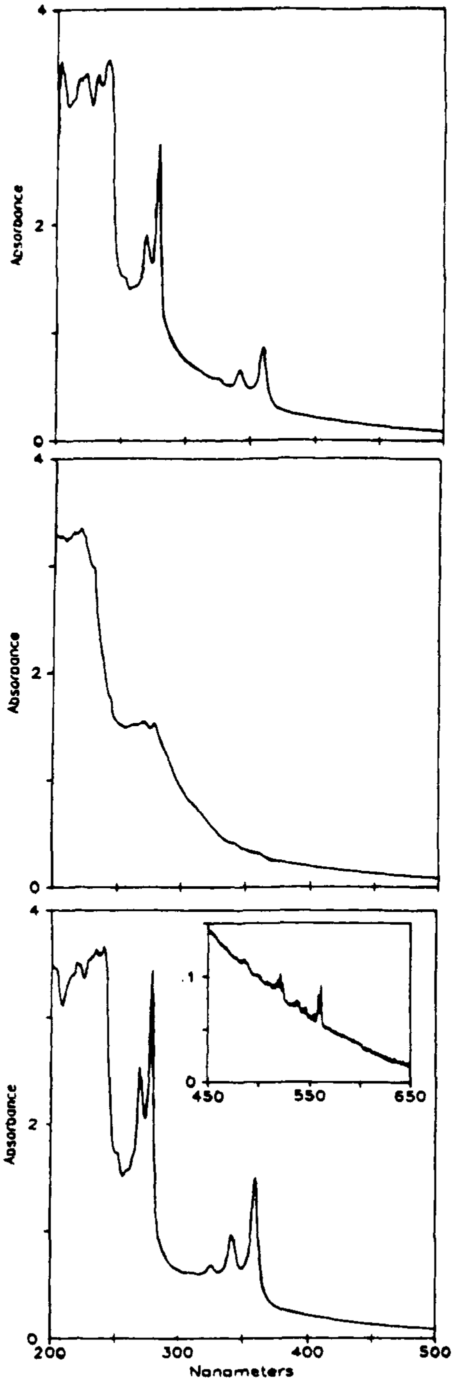

Figure 3. Top: UV/visible spectrum of a mixture of 2-naphthylcarbene (1) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (2) obtained upon photolysis ($\lambda > 300$ nm, 1 h, 100% conversion) of 2-naphthyldiazomethane (4). Middle: UV/visible spectrum of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (2) obtained upon photolysis ($\lambda = 360 \pm 6$ nm, 14.25 h, 100% conversion) of the mixture of carbene 1 and bicyclic compound 2. Bottom: UV/visible spectrum of 2-naphthylcarbene (1) obtained upon photolysis ($\lambda = 290 \pm 6$ nm, 3.33 h, 100% conversion) of bicyclic compound 2.

spectrum of 2-naphthylcarbene. The spectrum consists of a superposition of the absorptions of both rotational isomers. We observe the weak, highly-structured π–π^* transitions (λ_{max} 561–486 nm) (Figures 2 and 3) characteristic of triplet arylcarbenes[20] and doublet arylmethyl radicals.[21,22] This structure originates from vibronic coupling. It cannot be attributed to the presence of two rotational isomers of carbene 1, because other carbenes which cannot display geometric isomerism still show highly-structured electronic absorptions.[20] From the position of the (0,0) transition (561 nm), we calculate the energy of the T_0–T_1 excitation to be 51 kcal/mol. The structured emission spectrum of 1 previously observed by Haider et al.[16] probably arises as a consequence of the structured absorption spectrum. The IR

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(20) For leading references, see: (a) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597–7606. (b) Reference 1e, p 311.

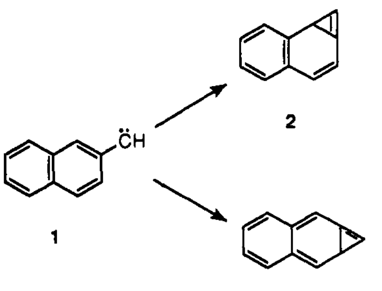
(21) We expect strong similarities between the absorption spectra of 2-naphthylcarbene (1) and 2-naphthylmethyl radical. Porter and Strachan reported the near-UV spectrum of 2-naphthylmethyl radical (λ_{max} 384.0, 368.7, 350.0, 342.2 nm) in an EPA glass at 77 K.[22] To our knowledge, the visible spectrum has not been reported.

(22) Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *54*, 1595–1604.

spectrum of 2-naphthylcarbene (**1**) shows deformation modes (836 s, 809 m, 803 m, 741 s cm^{-1}) similar to those of 2-naphthyldiazomethane (**4**) (847 s, 813 s, 744 s cm^{-1}) (Figure 1). These absorptions are characteristic of a 2-substituted naphthalene moiety.[23]

We note that the π–π^* absorptions of 2-naphthylcarbene (**1**) overlap the n–π^* transition of 2-naphthyldiazomethane (**4**) (Figure 2). This situation accounts for the inability of previous workers to build up high concentrations of carbene **1** using broad-band visible or UV/visible photolysis.[5] Under these conditions, photolysis of diazo compound **4** invariably leads to secondary photolysis of carbene **1**, thereby producing bicyclic compound **2** (vide infra). This inability to generate high concentrations of carbene **1** precluded characterization of **1** by infrared and visible spectroscopy in previous investigations.[5]

We characterized 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) by IR and UV/visible spectroscopy: IR (Ar, 10 K) 2985 w, 2968 w, 1755 m, 1749 m, 1475 m, 1446 m, 1216 w, 1117 w, 1008 m, 960 w, 883 w, 794 m, 781 s, 747 m, 714 m, 662 m, 603 w, 524 m, 497 w, 487 w, 474 m, 415 w, 408 w cm^{-1}; UV (Ar, 10 K) λ_{max} 270, 220 nm. The IR spectrum shows good agreement with that reported previously.[5] The absorptions at 1755 and 1749 cm^{-1} are characteristic of the cyclopropene moiety. The UV/visible spectrum displays two broad, featureless absorptions at 270 and 220 nm (Figure 3). In principle, the carbene could have cyclized in either of two directions to produce isomeric bicycloheptatrienes **2** and **7**. Each of these species would exhibit infrared absorptions near 1750 cm^{-1}. The earlier investigation[5] favored structure **2** on the basis of Wentrup's computational studies, which placed **2** 18 kcal/mol lower in energy than **7**.[7b] The UV/visible spectrum now provides experimental support for this structural assignment. The absence of absorptions between 350 and 400 nm is inconsistent with formulation as 3,4-benzobicyclo[4.1.0]hepta-2,4,6-triene (**7**). We expect the quinoid structure **7** to display absorptions similar to those of *o*-xylylene (**8**).[24] The observed spectrum is consistent with the assignment as 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**).



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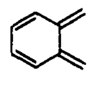

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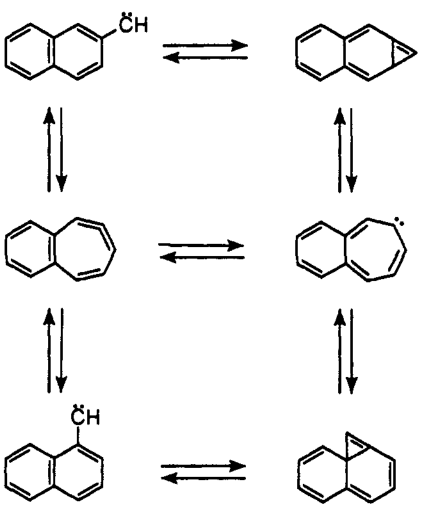
Chemical trapping is a useful method for confirming structures of intermediates assigned on the basis of spectroscopic data. This can be accomplished under matrix isolation conditions by doping the argon with a small amount of trapping agent. Carbon monoxide frequently reacts with carbenes to form ketenes.[8,20a] Photolysis ($\lambda > 300$ nm) of 2-naphthyldiazomethane (**4**) in an argon/carbon monoxide (99.67:0.33) matrix gives 2-naphthylketene as the major product (IR 2121 vs cm^{-1}), along with a small amount of bicyclic compound **2**. This result provides chemical evidence for the intermediacy of 2-naphthylcarbene (**1**). After diazo compound **4** has completely disappeared, continued photolysis ($\lambda > 300$ nm) results in disappearance of bicyclic compound **2** with concomitant growth of the ketene. This observation can be understood in terms of the photoequilibration mechanism described below.

Description of Photoequilibrium. A photoequilibrium between carbene **1** and bicyclic compound **2** can be directly observed by infrared and UV/visible spectroscopy (Scheme I).[25,26] Broad-band photolysis ($\lambda > 300$ nm) of 2-naphthyldiazomethane (**4**) matrix-isolated in argon at 10 K generates a mixture of both carbene **1** and bicyclic compound **2** (Figures 1a and 2). Photolysis of the mixture of **1** and **2** under various conditions (560 ± 6 nm, 360 ± 6 nm, >360 nm) results in disappearance of the IR, UV/visible, and ESR signals of carbene **1** with a concomitant increase in the IR and UV/visible signals assigned to bicyclic compound **2** (Figures 1b and 3). To reverse this reaction, we photolyze (λ = 290 ± 6 nm) bicyclic compound **2** at its absorption maximum (Figure 3). This photolysis results in a decrease of infrared and UV absorptions assigned to bicyclic compound **2** and an increase of infrared and UV absorptions assigned to carbene **1** (Figures 1c and 3). The complete reappearance of the UV/visible bands of carbene **1** demonstrates the high degree of reversibility of this reaction. Thermal equilibration of carbene **1** and bicyclic compound **2** does not occur under our reaction conditions; both are thermally stable at 10 K.[26]

Scheme II



Mechanistic Implications. Photoexcitation of ground-state triplet (T_0) 2-naphthylcarbene (**1**) produces the excited-state triplet (T_1). The T_1 state apparently partitions between fluorescence[16] and intersystem crossing to a singlet state (S_1 or higher). Cyclization[25] must occur prior to nonradiative decay of the singlet state to the triplet ground state.[26b] Quantum yields for these processes are not known. High-level ab initio calculations predict that singlet vinylcarbenes cyclize with low barriers. Computed activation barriers for cyclization of (*s-Z*)-vinylcarbene (S_1) and (*s-E*)-vinylcarbene (S_1) to cyclopropene are 1.1 and 4.5 kcal/mol, respectively.[27] We cannot distinguish the photochemical reactivity of the rotamers of 2-naphthylcarbene (**1**). Our ESR experiments show that the ratio of *s-Z*:*s-E* rotamers of carbene **1** does not change during photolysis. The cyclization reaction is highly

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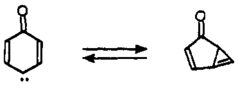
[23] Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley: Chichester, 1980; p 89.

[24] McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683–692.

[25] Vinylcarbenes and cyclopropenes interconvert both thermally and photochemically: (a) Misslitz, U.; de Meijere, A. In *Methoden der Organische Chemie* (*Houben–Weyl*); Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 664–755. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981; pp 21–27. (c) Berson, J. A. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. I, pp 315–322. (d) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310–317. (d) Reference 1a, pp 123–136.

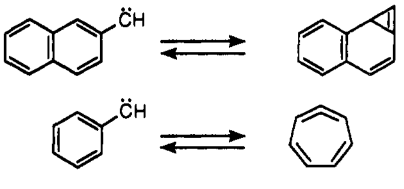
[26] Sander et al. recently observed photoequilibration of triplet 4-oxocyclohexadienylidene and 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one. Most importantly, they observed the *thermal* ring-opening of these cyclopropenes to vinylcarbenes at 10 K: (a) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311–5322; (b) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, 1346–1351.



[27] Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785–2798. Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 4198–4209.

regioselective, producing 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) as the only detectable product. Previous deuterium-labeling studies established that **2** does not photochemically equilibrate with 4,5-benzocycloheptatrienylidene (**3**) under matrix isolation conditions.[5] Our current work establishes that **2** undergoes photochemical ring-opening to yield 2-naphthylcarbene (**1**).[25]

Remarkably, we find no evidence for isomerization of 2-naphthylcarbene to 1-naphthylcarbene (Scheme II).[28] Thus, the photochemistry of 2-naphthylcarbene contrasts with that of phenylcarbene; 2-naphthylcarbene (**1**) cyclizes to bicyclic compound **2**, while phenylcarbene ring-expands to 1,2,4,6-cycloheptatetraene.[8]



Summary

2-Naphthylcarbene (**1**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) exist in a reversible photoequilibrium under conditions of low-temperature matrix isolation. These studies permit detailed spectroscopic characterization of both species by IR, UV/visible, and ESR spectroscopy. We could not observe isomerization of 2-naphthylcarbene (**1**) to 1-naphthylcarbene (**5**) under any of our experimental conditions.

Experimental Section

^{1}H NMR spectra were obtained with a Bruker WP-200 spectrometer. Chemical shifts are reported in parts per million downfield from internal Me_4Si. Uncorrected melting points were determined using a Thomas-Hoover Unimelt apparatus. Mass spectral data were obtained with a Kratos MS-80RFA spectrometer (DS55/DS90 detector).

Infrared spectra were obtained on a Nicolet 740 FT-IR instrument (MCT-B detector). Ultraviolet-visible spectra were obtained on a Hitachi U-3210 spectrometer. ESR experiments were performed on a Varian E-15 X-band spectrometer with a Varian E-101 microwave bridge or on a Bruker ESP 300 spectrometer with an ER 042 MRHE microwave bridge. An EIP microwave counter (Model 625A CW) provided the microwave frequency. Zero-field splitting parameters were determined from the best fit of the observed ESR spectra to the spin Hamiltonian[29] (assuming $g_x = g_y = g_z = g_e$).

Matrix Isolation Spectroscopy. The apparatus and experimental technique for low-temperature matrix isolation spectroscopy have been described elsewhere.[20a,30] Matrix:sample ratios are always maintained at ca. 500:1, but the absolute amount of sample deposited (i.e., the matrix thickness) depends on the intensity of the chromophore to be observed. Consequently, IR experiments typically require matrices of different thickness than do UV experiments. Differences in matrix thickness lead to corresponding differences in photolysis times. ESR experiments are normally performed using the same matrix thickness as that used in IR experiments.

2-Naphthaldehyde Tosylhydrazone. In a typical preparation, 1.0 equiv of 2-naphthaldehyde (Aldrich) is added to a magnetically stirred slurry of 1.0 equiv of (*p*-toluenesulfonyl)hydrazine (Aldrich) in absolute ethanol at room temperature. The tosylhydrazone precipitates upon stirring for 1.5 h, and the product is collected by suction filtration. The tosylhydrazone is then washed with hexane and recrystallized from absolute ethanol (80% yield): mp 173–174 °C (lit.[31] mp 174 °C); ^{1}H NMR ($CDCl_3/Me_2SO\text{-}d_6$) δ 2.38 (s, 3 H), 7.31–8.41 (m, 13 H); mass spectrum *m/z* (relative intensity) 324 (M^+, 2), 280 (25), 169 (22), 141 (100), 127 (14), 115 (20), 91 (35).

2-Naphthaldehyde Tosylhydrazone Sodium Salt. In a typical preparation, 0.15 g of tosylhydrazone is dissolved in 20 mL of freshly distilled CH_2Cl_2 (from CaH_2) and treated with 1.0 equiv of sodium hydride (60% NaH in mineral oil, Aldrich). After the mixture is stirred for 1–2 h, 20 mL of hexane is added, and the precipitated white tosylhydrazone sodium salt is collected by suction filtration. The salt is then dried in vacuo for 2 h (90–100% yield).

2-Naphthyldiazomethane (4). The freshly prepared salt is placed in a sublimation apparatus and crushed into a fine powder. The cold finger of the sublimator is inserted, and the apparatus is evacuated to 0.1 Torr. Dry ice is then placed into the cold finger, and the salt is heated with an oil bath. The temperature is slowly increased over 30–40 min to 90 °C. The deep red diazo compound deposits on the cold finger. After 1–1.5 h, the sublimation apparatus is vented to dry nitrogen. The diazo compound is rinsed into the deposition tube with dry CH_2Cl_2, which is then removed in vacuo at –41 °C. After the residual pressure drops below 10^{-5} Torr, the diazo compound is suitable for matrix isolation without requiring further purification: IR (Ar, 10 K) 3098 w, 3068 w, 2065 vs, 1604 s, 1635 m, 1512 m, 1477 m, 1471 sh, 1443 w, 1400 s, 1356 m, 1327 m, 1203 w, 1187 w, 1166 w, 1147 w, 1121 w, 877 w, 847 s, 813 s, 760 w, 744 s, 599 m, 583 m, 540 w, 532 w, 464 m cm^{-1}; UV/visible (MeCN, 298 K) λ_{max} (ϵ, M^{-1} cm^{-1}) 483 (23), 355 (1630), 338 (2090), 307 (15400), 296 (13900), 265 (29900), 256 (20300), 231 (23700) nm. The sample is sublimed at 25 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

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(28) We did not observe 1-naphthylcarbene (**5**) by ESR spectroscopy or cyclobuta[*de*]naphthalene (**6**) by IR spectroscopy under any of our photolysis conditions.

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