on alcohol basicity. (ii) If proton transfer is concerted with C–O bond breaking, electron-releasing substituents will be less effective than in spontaneous ionization of nonionic substrates, and this seems to be the situation here. In addition, the effects of electron donation should become less important with increasing solvent polarity and nucleophilicity.

An additional question is that of the timing of departure of the leaving group and attack of water. Nucleophilic solvent participation has been postulated in S_N1 solvolyses of *tert*-butyl compounds.[26b,44] Solvolyses of linalyl esters give linalool which is racemized or of retained configuration, so that water attack on C3 is not concerted with bond-breaking (Table VI and ref 8b and 13). However, attack upon C7, giving α-terpineol, from linalyl or neryl derivatives, does not necessarily have to follow loss of the leaving group.

Although participation of the remote, 6,7-double bond controls conversion of neryl into α-terpinyl derivatives, it is difficult to know whether it is always involved in formation of the transition state.[8,9,11-15,21,22] Overall rate effects are small, probably because of conformational effects on formation of a "folded", cisoid transition state.[14] In addition the kinetic role of π-participation may depend upon the structure of the substrate, for example, on the ease of departure of the leaving group, and it may be easier for a small neryl group than a large farnesyl group to take up a cisoid conformation.[14,21,22] However, the assumption that the initial ionization of neryl derivatives is not assisted by π-participation requires that conformational interconversion of the carbocation must be much faster than its capture by nucleophiles, despite the unfavorable conformational change.[14] The lifetime of the carbocation could be relatively long in apolar solvents, but not in solvents of high water content,[45] and it is hard to explain retention of configuration in oxygen exchange of linalool except in terms of π-participation.

Acknowledgment. This work was supported by the National Science Foundation (Chemical Dynamics Program and International Programs) and by the Departmento de Investigacion y Bibliotecas (Universidad de Chile), the Fondo Nacional de Ciencia y Technologia, and CONICYT.

Registry No. Linalyl chloride, 471-10-3; geranyl chloride, 5389-87-7; neryl chloride, 20536-36-1; α-terpinyl chloride, 39864-10-3; geraniol, 106-24-1; nerol, 106-25-2; linalool, 78-70-6; (−)-linalool, 126-91-0; neryl trifluoroacetate, 101010-61-1; α-terpinyl trifluoroacetate, 28664-18-8; 1,2-dihydrolinalyl trifluoroacetate, 101010-62-2; 6,7-dihydrogeranyl chloride, 101010-63-3; linalyl trifluoroacetate, 28673-26-9; geranyl trifluoroacetate, 74367-67-2; 6,7-dihydroneryl chloride, 101010-64-4; (*R*)-linalyl trifluoroacetate, 101010-65-5.

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(44) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

(45) Rappoport, Z. *Tetrahedron Lett.* **1979**, 2559. Richard, W. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1082**, *104*, 4689.

Benzobicyclo[4.1.0]hepta-2,4,6-trienes

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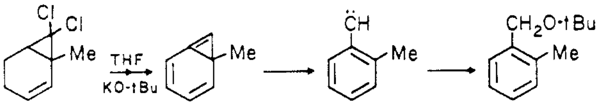
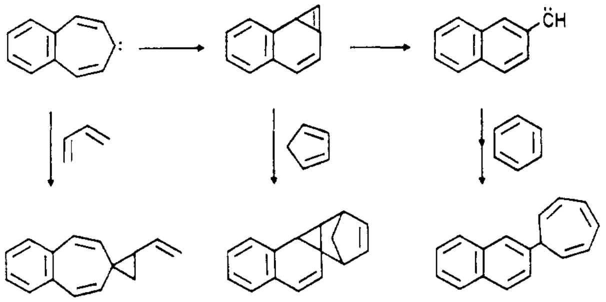
Irradiation of the naphthyldiazomethanes matrix isolated in argon at 15 K gives in each case the benzobicyclo[4.1.0]hepta-2,4,6-triene. The photochemistry of the naphthyldiazomethanes thus contrasts sharply with that of phenyldiazomethane, which gives 1,2,4,6-cycloheptatetraene. Flash vacuum thermolysis of the naphthyldiazomethanes followed by matrix isolation of the pyrolyzate produces a common product, tentatively identified as 4,5-benzocyclohepta-1,2,4,6-tetraene.

Vander Stouw and Shechter postulated a bicyclo[4.1.0]hepta-2,4,6-triene as the first intermediate in the rearrangement of arylmethylenes in 1964.[1,2] The firmly established cyclization of vinylmethylenes to cyclopropenes provided precedence for such a mechanism.[3] Billups generated 1-methylbicyclo[4.1.0]hepta-2,4,6-triene in solution.[4] The triene acts as a source of arylcarbene, but no role in the interconversion of arylcarbenes was demonstrated. Our thermal and photochemical studies of phenylmethylene failed to provide evidence for the triene intermediate and suggested that ring expansion is a direct process.[5]



Scheme I



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(1) Vander Stouw, G. G. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1964. Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655–1661.

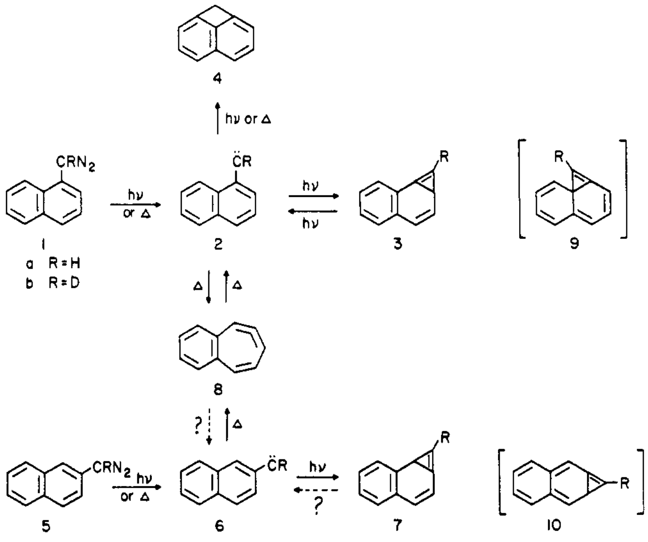
(2) (a) Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4.

(3) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 99–104 and references cited therein.

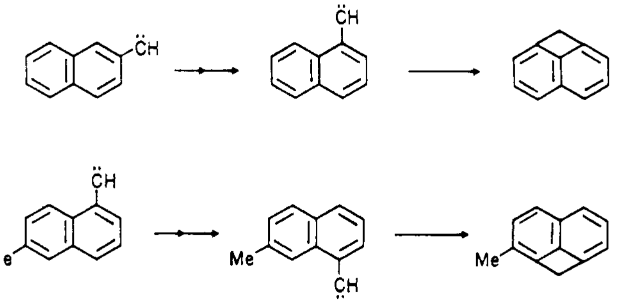
(4) Billups, W. E.; Reed, L. E.; Casserly, E. W.; Lin, L. P. *J. Org. Chem.* **1981**, *46*, 1326–1333.

0022-3263/86/1951-1316$01.50/0

Scheme II



In the benzo series, Billups obtained trapping evidence for derivatives of both 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene and 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene.[4,7] Jones trapped the parent 2,3-benzobicycloheptatriene, as well as 4,5-benzocycloheptatrienylidene and 2-naphthylcarbene (Scheme I).[6,7] Horn prepared 4,5-benzodiazocycloheptatriene and studied its chemistry by nanosecond laser-flash photolysis.[9] Becker and Wentrup demonstrated thermal rearrangement of 2-naphthylmethylene to 1-naphthylmethylene.[10] Engler and Shechter demonstrated thermal rearrangement of (6-methyl-1-naphthyl)methylene to the isomeric (7-methyl-1-naphthyl)methylene, presumably via the 2-naphthylmethylene.[11]



From the literature reports, we conclude that bicyclo[4.1.0]heptatrienes thermally open to arylcarbenes. It is not clear whether arylcarbenes thermally or photochemically cyclize to bicycloheptatrienes or whether bicycloheptatrienes are involved in the thermal interconversion of naphthylmethylenes. In this paper, we report evidence that the naphthylmethylenes photochemically cyclize to benzobicyclo[4.1.0]hepta-2,4,6-trienes. We also describe flash vacuum thermolysis studies of the naphthyldiazomethanes (Scheme II).

Results

Structural Assignments. The detailed arguments concerning the interpretation of infrared spectra and structural assignments of benzobicyclo[4.1.0]hepta-2,4,6-trienes **3a**, **3b**, **7a**, and **7b** are presented in the discussion section.

1-Naphthyldiazomethane (1a). Irradiation (>510 nm, 954 min) of argon matrix isolated 1-naphthyldiazomethane (**1a**) slowly produces 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3a**) (IR, Ar, 15 K, 3075 m, 3035 m, 2980 m, 1765 m, 1755 m, 1600 m, 1472 s, 1455 s, 1106 m, 1037 m, 1001 m, 947 m, 831 m, 806 m, 780 s, 757 s, 700 m, 671 s, 589 m, 570 m, 508 m, 492 m, 422 w cm^{-1}) and a small amount of 1*H*-cyclobuta[*de*]naphthalene[12] (**4**) (IR, Ar, 15 K, 792 cm^{-1}). More rapid conversion occurs with $\lambda > 336$ nm. Prolonged short-wavelength irradiation (>226 nm) of the bicyclo[4.1.0]hepta-2,4,6-triene (**3a**) results in a slight increase in cyclobuta[*de*]naphthalene concentration (792, 661 cm^{-1}). In contrast, flash vacuum thermolysis of **1a** (360 °C, 100% conversion) followed by cocondensation with argon produces cyclobuta[*de*]naphthalene[12] (**4**) as the major product and a small amount of a product also observed in the thermolysis of 2-naphthyldiazomethane (IR, Ar, 15 K, 1512 m, 1357 w, 1349 m, 1270 w, 832 m, 629 s, 500 m cm^{-1}). No 4,5-benzobicycloheptatriene (**3a**) was observed under thermal conditions.

(α-Deuterio-1-naphthyl)diazomethane (1b). Irradiation (>280 nm) of argon matrix isolated (α-deuterio-1-naphthyl)diazomethane (**1b**) produces 7-deuterio-4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3b**) (IR, Ar, 15 K, 1720 m, 1600 m, 1470 s, 1452 s, 1102 m, 1035 m, 999 m, 943 m, 823 m, 802 m, 795 s, 775 s, 747 s, 730 m, 668 m, 605 s, 580 s, 562 m, 465 m cm^{-1}).

2-Naphthyldiazomethane (5a). Irradiation (>364 nm) of argon matrix isolated 2-naphthyldiazomethane (**5a**) produces only 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**7a**) (IR, Ar, 15 K, 3060 m, 2968 m, 2860 w, 1755 m, 1750 m, 1475 m, 1448 m, 1131 m, 1006 m, 959 m, 879 m, 793 s, 780 s, 748 s, 713 s, 661 s, 523 m cm^{-1}). The infrared spectrum does not change upon shorter wavelength irradiation. Flash vacuum thermolysis of **5a** (375 °C, 100% conversion) followed by cocondensation with argon produces cyclobuta[*de*]naphthalene[12] (**4**) as the major product, a small amount of a product observed in the thermolysis of 1-naphthyldiazomethane (IR, Ar, 15 K, 1572 m, 1357 w, 1349 m, 1270 w, 832 m, 629 s, 500 m cm^{-1}) and a small amount of another, as yet unidentified, species. No 2,3-benzobicycloheptatriene (**7a**) was observed under thermal conditions.

(α-Deuterio-2-naphthyl)diazomethane (5b). Irradiation (>274 nm) of argon matrix isolated (α-deuterio-2-naphthyl)diazomethane (**2b**) produces 7-deuterio-2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**7b**) (IR, Ar, 15 K, 1715 m, 1449 m, 820 m, 792 m, 775 s, 746 s, 700 m, 677 m, 615 m, 551 m, 500 m, 490 m, 480 m, 410 m cm^{-1}).

Discussion

Irradiation (>336 nm) of 1-naphthyldiazomethane (**1a**) produces a small amount of 1*H*-cyclobuta[*de*]naphthalene

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[5] West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782. Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; McMahon, R. J.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.*, submitted for publication.

[6] Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218–5227.

[7] Dibenzobicyclo[4.1.0]hepta-2,4,6-triene has also been generated and trapped.[4,6,8]

[8] (a) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026–4027. (b) Mykytka, J. P.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 5933–5935. (c) Halton, B.; Officer, D. L. *Tetrahedron Lett.* **1981**, *22*, 3687–3688.

[9] Horn, K. A.; Chateauneuf, J.; Griffin, G. W. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Washington, DC, Aug, 1983; American Chemical Society: Washington, DC, 1983; ORGN 58. Horn, K. A., personal communication.

[10] Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190–191.

[11] Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715–2718.

[12] Identified by comparison of the infrared spectrum with that of the authentic material matrix isolated in argon (see Experimental Section).

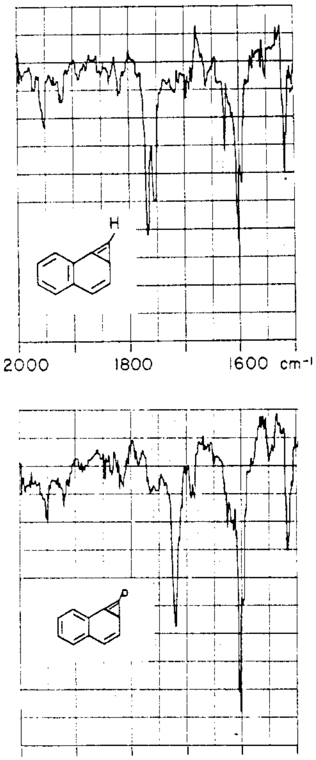


Figure 1. (Top) Infrared spectrum showing the cyclopropene vibrations of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3a**) formed upon irradiation (>336 nm, 985 min) of 1-naphthyldiazomethane (**1a**) matrix isolated in argon at 15 K. (Bottom) Infrared spectrum of 7-deuterio-4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3b**) formed upon irradiation (>280 nm, 1147 min) of (α-deuterio-1-naphthyl)diazomethane (**1b**) matrix isolated in argon at 15 K. Deuteration collapses the doublet absorption of **3a** and shifts the absorption to lower frequency.

(4)[12] and a species exhibiting infrared absorptions at 1765 and 1755 cm^{-1} (Figure 1). Similarly, irradiation (>364 nm) of 2-naphthyldiazomethane (**5a**) produces a species exhibiting infrared absorptions at 1755 and 1750 cm^{-1} (Figure 2). The position and intensity of the absorptions suggest cyclopropene formation (see the model compounds in Table I).[13] This hypothesis is easily tested, owing to the characteristic ~45-cm^{-1} shift of the cyclopropene ring vibration observed upon deuteration of one olefinic position (Table I).[16] Irradiation (>280 nm) of (α-deuterio-1-naphthyl)diazomethane (**1b**) gives rise to an infrared band at 1720 cm^{-1} (Figure 1), while irradiation (>274 nm) of α-deuterio-2-naphthyldiazomethane (**5b**) gives rise to an infrared band at 1715 cm^{-1} (Figure 2). We therefore assign the isomeric benzobicyclo[4.1.0]hepta-2,4,6-triene structures **3** and **7** to the photoproducts of the naphthyldiazomethanes. We consider the structures **9** and **10** unlikely, as aromaticity is destroyed in both rings of the naphthalene moiety.[17] The magnitude of the isotope shift allows us to rule out an allene structure (i.e., a benzocycloheptatetraene).[5] This result contrasts with the parent phenylmethylene system; phenylmethylene,[5] as well as other related carbenes,[18] ring expands directly to 1,2,4,6-

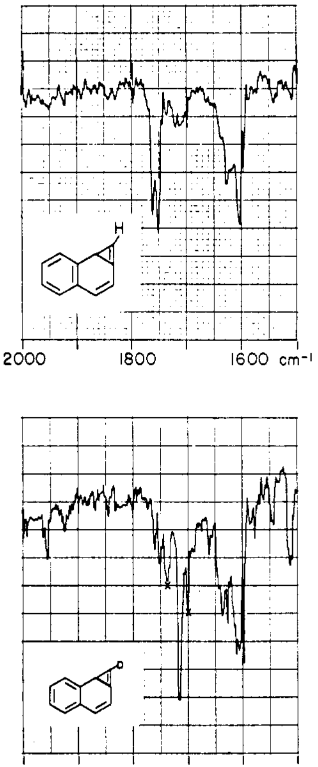
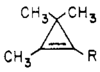
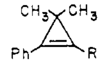
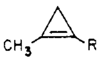
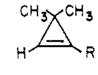
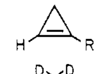
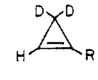
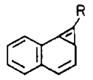
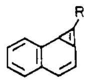


Figure 2. (Top) Infrared spectrum showing the cyclopropene vibrations of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**7a**) formed upon irradiation (>302 nm, 1139 min) of 2-naphthyldiazomethane (**5a**) matrix isolated in argon at 15 K. (Bottom) Infrared spectrum of 7-deuterio-2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**7b**) formed upon irradiation (>274 nm, 1361 min) of (α-deuterio-2-naphthyl)diazomethane (**5b**) matrix isolated in argon at 15 K. Deuteration collapses the doublet absorption of **7a** and shifts the absorption to lower frequency.

Table I. Cyclopropene Infrared Ring Vibrations

	R = H, cm^{-1}	R = D, cm^{-1}	ref
	1768	1718	*a*
	1740		*a*
	1790, 1787	1740	*b*
	1632	1578	*a*
	1653	1607	*c*
	1648	1593	*c*
	1765, 1755	1720	*d*
	1755, 1750	1715	*d*

[a] Reference 16. [b] Sheridan, R. S.; Chapman, O. L., unpublished results. [c] Reference 27. [d] This work.

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[13] We could not generate naphthylmethylenes **2a** or **6a** in high enough concentration to obtain their infrared spectra. The UV/visible absorption spectra of **2a** and **6a** are also unknown. However, model compounds (1- and 2-naphthylmethyl radicals[14] and 1-naphthylnitrene[15]) absorb at or beyond ca. 550 nm. Using cut-off filters, we are therefore unable to avoid irradiating the naphthylmethylenes under conditions required to irradiate the naphthyldiazomethanes.

[14] Watts, A. T.; Walker, S. *Trans. Faraday Soc.* **1964**, *60*, 484–487. Carsky, P.; Zahradnik, R. *J. Phys. Chem.* **1970**, *74*, 1249–1254.

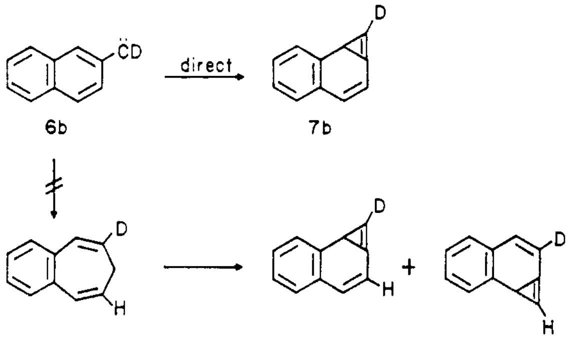
[15] Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162–3169.

[16] Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.

[17] Wentrup's force field–SCF calculations place **9** 27 kcal/mol above **3** and **10** 18 kcal/mol above **7**. Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601–1612.

cycloheptatetraene without proceeding through a bicyclo[4.1.0]hepta-2,4,6-triene intermediate.

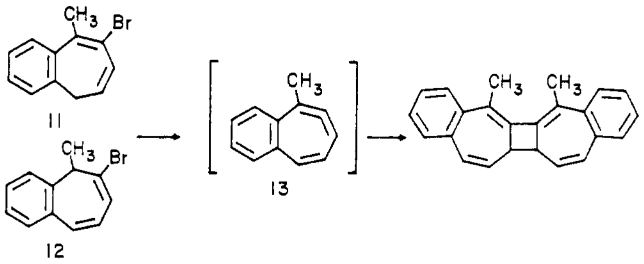
The deuterium labeling studies indicate that triene **7b** is the first-formed product and is not formed by an expansion–cyclization mechanism. The latter mechanism predicts that the cyclopropene formed will be half-labeled and half-unlabeled. If this were true, both would be easily detected by infrared spectroscopy.



Short-wavelength irradiation (>266 nm) of benzobicycloheptatriene **3a** results in a slight increase in the concentration of **4**. This establishes reversible photoequilibration of carbene **2a** and cyclopropene **3a**. Neither photochemical ring opening of **3** or **7** to benzocycloheptatrienylidenes or benzocycloheptatetraenes nor photochemical interconversion of 1-naphthylmethylene and 2-naphthylmethylene[19] was observed. The benzobicycloheptatrienes **3** and **7** are remarkably photostable. This contrasts with the matrix-isolation study of the naphthylnitrenes, which first cyclize to benzazirines but then expand to benzoazacycloheptatetraenes.[20]

Infrared spectroscopy shows that flash vacuum thermolysis (360–375 °C, 100% conversion) of either 1- or 2-naphthyldiazomethane followed by cocondensation with argon produces 1*H*-cyclobuta[*de*]naphthalene (**4**)[12] as the major product.[10] We also observe a minor product common to the thermolysis of both diazocompounds. It is not naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, or either of the benzobicyclo[4.1.0]heptatrienes, and it does not contain a carbonyl group. We suggest that it is 4,5-benzocycloheptatetraene (**8**). Formation of 4,5-benzocycloheptatetraene (**8**) accounts for the equilibration of 1-naphthylmethylene and 2-naphthylmethylene (Scheme II). In support of our assignment, we note that calculations place **8** as the lowest energy isomer of the six possible isomeric benzocycloheptatrienylidenes and benzocycloheptatetraenes.[21] In addition, dehydrohalogenation of a mixture of **11** and **12** produces 3-methyl-4,5-benzocycloheptatetraene (**13**), which yields an isolable [2 + 2] dimer.[22]

In summary, irradiation of 1- and 2-naphthyldiazomethane produces 4,5- and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene, respectively. The bicycloheptatrienes are remarkably photostable. Flash vacuum thermolysis of either 1- or 2-naphthyldiazomethane produces cyclobuta[*de*]naphthalene (**4**). In addition, we observe a common product, tentatively identified as 4,5-benzocyclohepta-1,2,4,6-tetraene (**8**). Our observations demonstrate the existence of the benzobicyclo[4.1.0]heptatrienes but do not address the question of whether they are involved in the flash vacuum thermolysis.



Experimental Section

^1H NMR spectra were recorded on a Varian T-60 instrument. Chemical shifts (δ) are reported as parts per million downfield from internal $SiMe_4$. Melting points were determined on a Thomas Hoover Unimelt apparatus in open capillaries and are uncorrected. Mass spectra were obtained on an AEI MS-9 spectrometer. Infrared spectroscopy was performed with a Beckman 4250 or a Perkin-Elmer 580B with a Model 3600 data station.

Matrix-Isolation Spectroscopy. The apparatus and experimental technique used for the study of matrix-isolated reactive species have been described elsewhere.[23]

Flash Vacuum Thermolysis/Matrix-Isolation Trapping. The sample is allowed to sublime through a 10-cm, unpacked, quartz tube wrapped with 18–22 gauge Nichrome wire. An iron vs. constantan thermocouple is secured with glass tape midway along the length of the tube, and the whole oven is wrapped with asbestos tape. Oven temperature is regulated by two Variac transformers connected in series. This simple setup proved quite reliable and could attain temperatures in excess of 900 °C. The pyrolysate cocondenses with argon onto a 15–25 K sample window using standard matrix-isolation sample deposition techniques.[23]

General Procedure for Tosylhydrazone Preparations. In a typical preparation, 1.0 equiv of naphthaldehyde is added to a magnetically stirred slurry of 1.0 equiv of *p*-toluenesulfonohydrazide (Aldrich; recrystallized from water) in absolute ethanol. The solution becomes homogeneous within minutes upon warming. The tosylhydrazone precipitates after stirring a few hours at room temperature. The product is collected by suction filtration, washed with petroleum ether, and recrystallized from absolute ethanol.

General Procedure for Tosylhydrazone Lithium Salt Preparation. In a typical preparation, 1.0 equiv of tosylhydrazone in dry THF is cooled to −78 °C and treated with 1.0 equiv of 2.4 M *n*-BuLi/hexane (Alfa). After being warmed to room temperature, the solution is evaporated to dryness. The tosylhydrazone lithium salt is dried in vacuo overnight and crushed to a fine powder with a spatula.

General Procedure for Diazo Compound Preparation. The freshly prepared tosylhydrazone salt is placed in the bottom of a small sublimator and heated to 70–90 °C (0.1 torr) with an oil bath. After 45 min, the deep red diazocompound collects on the cold finger and is transferred to a sample deposition tube.

General Procedure for Preparation of α-Deuterio Derivatives. The carboxylic acid corresponding to the desired deuterio aldehyde is treated with MeOH/HCl to produce the methyl ester. The ester is reduced to the (α,α-dideuterionaphthyl)methanol with $LiAlD_4$ in Et_2O. Oxidation of the naphthylmethanol with ceric ammonium nitrate in H_2O affords the α-deuterio aldehyde. The tosylhydrazone is prepared as described above. However, before the salt is prepared, the N-H proton must be exchanged for N-D. The deuteriotosylhydrazone is dissolved in CH_3CN and treated with D_2O. The solvent is evaporated, and the residual D_2O is azeotropically removed using several portions of CH_3CN. The lithium salt of the dideuteriotosylhydrazone is

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(19) If 2-naphthylcarbene photoequilibrated with 1-naphthylcarbene (by whatever mechanism), cyclobuta[*de*]naphthalene (**4**) should have been formed.

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then prepared in the usual manner. If the D_2O exchange step is omitted, the isotopic purity in the α-deuteriotosylhydrazone drops, due to scrambling in the salt-formation step.

1-Naphthaldehyde Tosylhydrazone. Prepared from 1-naphthaldehyde (Aldrich) in 91% yield: mp 132–133 °C (lit.[24] 144–146 °C); ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.33 (s, 3 H), 7.22–8.00 (m, 10 H), 8.42–8.65 (m, 1 H), 8.50 (s, 1 H), 11.33 (s, 1 H).

1-Naphthyldiazomethane (1a). IR (Ar, 15 K) 3078 m, 2065 s, 1594 m, 1582 s, 1523 m, 1515 m, 1471 s, 1453 m, 1418 s, 1386 w, 1370 w, 1338 s, 1267 w, 1252 m, 1220 w, 1173 w, 1148 w, 1093 w, 1012 m, 854 w, 807 w, 792 s, 773 s, 649 m, 632 w, 565 m, 411 m cm^{-1}. The deep red diazocompound was sublimed at 30 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuterio-1-naphthaldehyde Tosylhydrazone. Prepared from α-deuterio-1-naphthaldehyde in 70% yield: mp 128–129 °C dec; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.35 (s, 3 H), 7.17–8.00 (m, 10 H), 8.48–8.68 (m, 1 H); mass spectrum (16 eV), m/z (relative intensity) 325 (M^+, 4.3), 141 (100) (324 not detected).

(α-Deuterio-1-naphthyl)diazomethane (1b). IR (Ar, 15K) 3065 m, 2055 s, 1595 m, 1590 m, 1580 s, 1520 m, 1510 m, 1468 s, 1450 m, 1412 s, 1408 s, 1327 s, 1013 m, 851 m, 844 w, 802 m, 791 s, 787 s, 770 s, 649 m, 647 m, 562 m, 504 w, 453 w, 432 w, 419 w, 409 w cm^{-1}. The deep red diazocompound was sublimed at 40 °C (10^{-6} torr) and codeposited with argon to form a matrix.

2-Naphthaldehyde Tosylhydrazone. Prepared from 2-naphthaldehyde (Aldrich) in 85% yield: mp 169–170 °C dec (lit.[25] 174 °C); ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.37 (s, 3 H), 7.23–7.93 (m, 11 H), 8.03 (s, 1 H), 11.40 (s, 1 H).

2-Naphthyldiazomethane (5a). IR (Ar, 15 K) 3060 m, 2055 s, 1632 m, 1626 m, 1604 s, 1511 s, 1478 m, 1471 m, 1443 m, 1398 s, 1357 m, 1328 m, 1201 m, 1187 m, 1182 m, 1146 m, 872 m, 842 s, 809 s, 740 s, 600 m, 582 m, 460 s cm^{-1}; ^{1}H NMR (CCl_4) δ 5.03 (s, 1 H), 6.9–7.9 (m, 7 H). The deep red diazocompound was sublimed at 30 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuterio-2-naphthaldehyde Tosylhydrazone. Prepared from α-deuterio-2-naphthaldehyde in 66% yield: mp 164–165 °C dec; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.33 (s, 3 H), 7.20–7.97 (m, 11 H), 11.33 (s, 1 H); mass spectrum (16 eV), m/z (relative intensity) 325 (M^+, 1.2), 141 (100) (324 not detected).

(α-Deuterio-2-naphthyl)diazomethane (5b). IR (Ar, 15 K) 3059 m, 3020 w, 2060 s, 1633 s, 1603 s, 1511 s, 1506 m, 1475 m, 1390 s, 1368 m, 1331 m, 1313 m, 872 m, 844 s, 810 s, 741 s, 602 m, 580 m, 472 m, 411 w, 372 w cm^{-1}. The deep red diazocompound was sublimed at 36 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***1H*-Cyclobuta[*de*]naphthalene (4).** Prepared from 1,8-naphthalic anhydride by literature methods.[26] IR (Ar, 15 K) 3072 m, 3065 m, 3057 m, 3041 m, 2982 w, 2949 m, 2818 w, 1920 w, 1775 w, 1608 m, 1602 m, 1477 m, 1344 m, 1339 m, 1170 w, 1164 w, 1002 m, 966 w, 792 s, 761 s, 707 m, 478 m, 402 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 2 H), 7.05–7.83 (m, 6 H); mass spectrum (70 eV), m/z (relative intensity) 141 (13), 140 (M^+, 100), 139 (87), 113 (10), 89 (10), 87 (8), 74 (8), 70 (8). The compound was sublimed at −5 °C (10^{-6} torr) and codeposited with argon to form a matrix.

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Registry No. **1a**, 10378-55-9; **1b**, 78377-25-0; **3a**, 7078-38-8; **3b**, 100447-97-0; **4**, 24973-91-9; **5a**, 10378-56-0; **5b**, 78377-21-6; **7a**, 38617-06-0; **7b**, 100447-98-1; **8**, 52783-97-8; 1-naphthaldehyde tosylhydrazone, 19350-73-3; α-deuterio-1-naphthaldehyde, 42007-09-0; α-deuterio-2-naphthaldehyde tosyhydrazone, 100447-96-9; 2-naphthaldehyde tosylhydrazone, 19350-74-4; α-deuterio-2-naphthaldehyde, 42007-10-3; α-deuterio-2-naphthaldehyde tosylhydrazone, 78377-20-5; 1-naphthaldehyde tosylhydrazone lithium salt, 100447-99-2; α-deuterio-1-naphthaldehyde tosylhydrazone lithium salt, 100448-00-8; 2-naphthaldehyde tosylhydrazone lithium salt, 100448-01-9; α-deuterio-2-naphthaldehyde tosylhydrazone lithium salt, 100448-02-0; 1-naphthaldehyde, 66-77-3; 2-naphthaldehyde, 66-99-9.

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Reactions of *N*-Chlorobenzylmethylamines with Secondary Amines in Acetonitrile. Effect of Base Strength upon the Imine-Forming Transition State

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Reactions of *N*-chlorobenzylmethylamines 1 with R_2NH in MeCN have been investigated kinetically. Eliminations from 1 were quantitative and regiospecific, producing only benzylidenemethylamines. For the elimination reaction of 1 with Bu_2NH, $k_H/k_D = 8.8$, $\rho = 0.96$, $\Delta H^\ddagger = 7.6$ kcal/mol, and $\Delta S^\ddagger = -45.1$ eu were determined. The transition state structure is assessed as being highly symmetrical with similar extents of C_β–H and N_α–Cl bond cleavage, little carbanionic character, and significant π bond formation. The k_H/k_D and ρ values first increase and then decrease with enhancing amine base strength. Comparison of these results with those for related olefin-forming eliminations provides insight into the transition state differences between imine- and olefin-forming eliminations.

An understanding of the effect of changes in reactant structure and reaction conditions on the energies and structures of transition states is an important element for the detailed description of organic reaction pathways. Several studies of this type have been conducted for elimination reactions which form carbon–nitrogen double bonds.[2-11]

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