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Access to the Naphthylcarbene Rearrangement Manifold via Isomeric Benzodiazocycloheptatrienes

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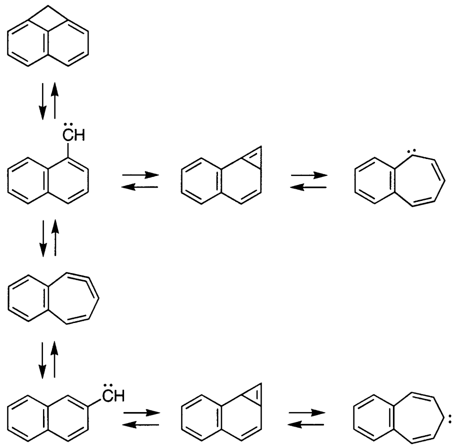
Irradiation ($\lambda = 670$ or >613 nm) of 4,5-benzodiazocycloheptatriene (**15**), matrix isolated in argon at 10 K, produces primarily 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**) accompanied by small amounts of triplet 4,5-benzocycloheptatrienylidene (**2**) and 2-naphthylcarbene (**10**). A reversible photoequilibrium is established in which **9** is converted to **10** at $\lambda = 290$ nm and then regenerated at $\lambda = 360$ nm. Similarly, matrix-isolated 2,3-benzodiazocycloheptatriene (**16**) produces 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**11**) at $\lambda = 670$ or >613 nm, but without detection of 2,3-benzocycloheptatrienylidene (**4**). Irradiation of **11** at $\lambda = 290$ nm induces ring opening to triplet 1-naphthylcarbene (**12**), which, in turn, cyclizes back to **11** at $\lambda = 342$ or >497 nm. The diazo compounds and photoproducts are characterized by IR, UV/visible, and ESR spectroscopy, where appropriate, and by comparison of the experimental and B3LYP/6-31G* calculated IR spectra for each species. Alternate rearrangement products such as allenes **6**, **7**, and **8** are not detected in the photolysis of either diazo compound.

Introduction

Investigations of the structure and reactivity of organic carbenes bear a long and vibrant history.[1] Arylcarbenes have attracted attention due to their complex thermal and photochemical transformations, as illustrated in Scheme 1 for the case of naphthylcarbenes.[2–16] The general features of arylcarbene rearrangements have long been established on the basis of inter- and intramolecular trapping studies, but a detailed understanding of the various reactive intermediates involved in these rearrangement mechanisms remains a challenge to both experimentalists and theorists. In a broader context, the chemistry of arylcarbenes, which are formed upon reaction of atomic carbon with aromatic compounds,[17] is relevant to an understanding of a variety of carbon-rich environments, including carbon arcs, discharges, inter-

SCHEME 1



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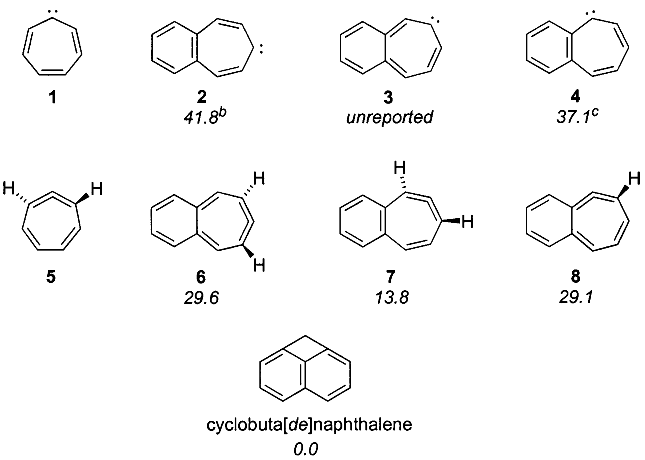
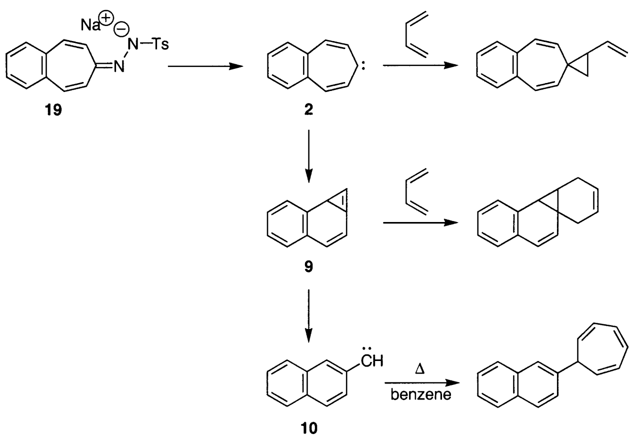
SCHEME 2[a]



[a] B3LYP energies (kcal/mol) given in italics (singlet state + ZPVE; reference 4) relative to cyclobuta[*de*]naphthalene. [b] Two imaginary frequencies. [c] One imaginary frequency.

SCHEME 3



stellar clouds, and circumstellar envelopes. Recent speculation concerning the build-up of polycyclic aromatic hydrocarbons in interstellar clouds has been discussed in the context of carbon atom chemistry and the intermediates involved in arylcarbene interconversions.[18]

In earlier studies of naphthylcarbene rearrangements, we investigated the chemistry and spectroscopy of naphthylcarbene, benzobicyclo[4.1.0]hepta-2,4,6-triene, and 4,5-benzocyclohepta-1,2,4,6-tetraene isomers.[11,13,15,16] In the current study, we describe experimental and computational studies of benzocycloheptatrienylidene and benzobicyclo[4.1.0]hepta-2,4-dien-7-ylidene isomers.

Background

The relationship between the benzocycloheptatrienylidenes **2**−**4** and the benzocyclohepta-1,2,4,6-tetraenes **6**−**8** is perhaps even more subtle and complex than the relationship between the parent species, cycloheptatrienylidene (**1**) and cycloheptatetraene (**5**) (Scheme 2). In the parent case, early qualitative arguments described cycloheptatrienylidene (**1**) as a planar aromatic singlet carbene. Experiment[19,20] and theory,[21−24] however, established that a nonplanar twisted allene structure, corresponding to cycloheptatetraene (**5**), lies ca. 25 kcal/mol lower in energy. The planar singlet cycloheptatrienylidene structure represents the transition state for enantiomerization of the C_2-symmetric allene, and the ground state of cycloheptatrienylidene (**1**) is, in fact, a triplet.[25−27] A precise description of the planar carbene is complex, in the sense that several electronic configurations lie close in energy (A_2 and B_2 for the triplet, A_2 and B_2 for the open shell singlet, and A_1 for the closed shell singlet).[24] In the benzo series, the position of benzannelation further modulates the relative stabilities of the various isomers.[14,28] At the B3LYP/6-311+G* level of theory, the planar singlet benzocycloheptatrienylidene structures **2** and **4** are found to be a second-order saddle point and a transition state, respectively.[14] Imaginary frequencies notwithstanding, singlets **2** and **4** ($^1A_1$ state) are calculated to be higher in energy than the corresponding planar triplet benzocycloheptatrienylidene and twisted singlet allene by approximately 5 and 10 kcal/mol, respectively.

Chemical trapping studies of the thermal or photochemical decomposition of the tosylhydrazone sodium salt of 4,5-benzotropone (**19**) suggest a sequence of rearrangements involving 4,5-benzocycloheptatrienylidene (**2**), 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**), and 2-naphthylcarbene (**10**) (Scheme 3).[8] Thermal decomposition of the tosylhydrazone salt of the 2,3-isomer (**23**) affords a trapping product of 1-naphthylcarbene (**12**)[29] (Scheme 4). Kirmse and Sluma interpret their trapping studies in terms of distinct carbenic vs allenic reactivity, supporting the concept of benzocycloheptatrienylidene and benzocycloheptatetraene as equilibrating intermediates.[30,31] Isolation of a formal [2+2] dimer of a simple derivative of 4,5-benzocyclohepta-1,2,4,6-tetraene supports the intermediacy of the strained allene during the dehydrohalogenation of benzo-chlorocycloheptatrienes.[9]

Of the three planar and three nonplanar $C_{11}H_8$ structures shown in Scheme 2, only two have been observed experimentally. Chateauneuf, Horn, and Savino reported the transient electronic absorption spectrum of triplet 4,5-benzocycloheptatrienylidene (**2**) in fluid solution, as

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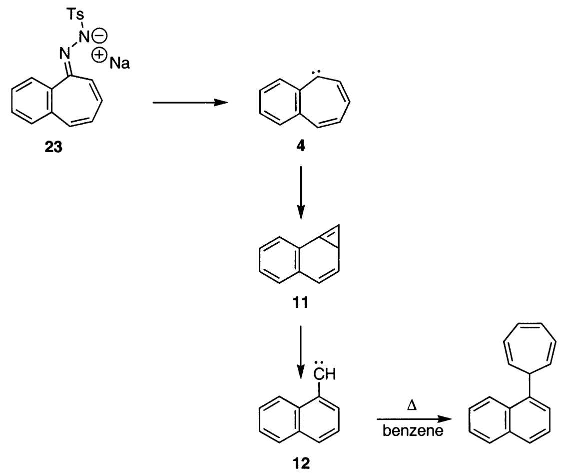
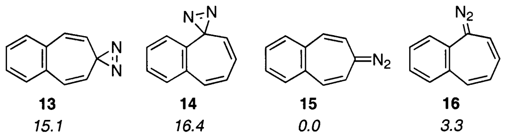
SCHEME 4



SCHEME 5[a]



[a] B3LYP/6-31G* energy (kcal/mol, ZPVE corrected) relative to **15** in italics.

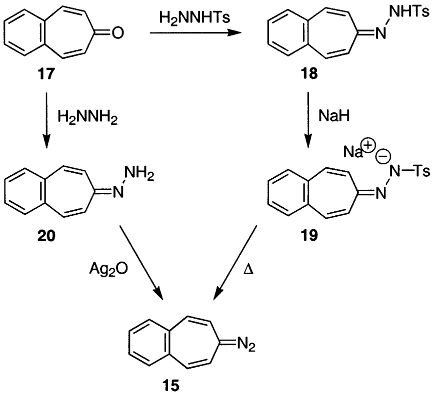
well as the triplet ESR spectrum of **2** in a frozen glass.[12] We recently reported the IR and UV/visible absorption spectra of the strained allene, 4,5-benzocycloheptatetraene (**7**), under matrix isolation conditions.[16]

Results and Discussion

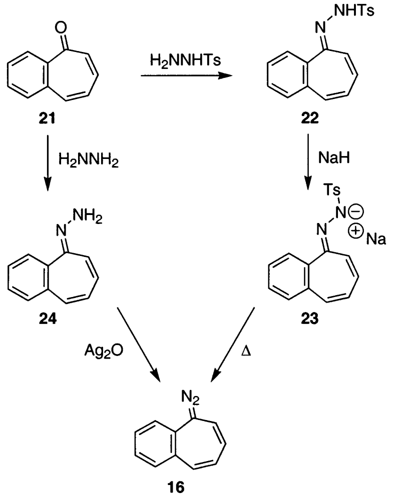
Preparation of Carbene Precursors. Diazirines generally serve as convenient and robust carbene precursors. A typical diazirine preparation involves oxidation of the corresponding diaziridine, which, in turn, is prepared by treatment of an activated imine derivative with ammonia.[32] Despite our considerable efforts, the attempted syntheses of diazirines **13** and **14** (Scheme 5) proved to be unfruitful, either because of the inability to prepare the activated imine derivative (due to the unusual electronic character of tropone derivatives[33]) or because the activated imine derivative reacts readily via the Beckmann rearrangement or other decomposition pathway.[34]

With simple routes toward the diazirines thwarted, we turned our attention to the preparation of diazo compounds **15** and **16**. One synthetic approach involves the oxidation of the corresponding benzotropone hydrazones **20** or **24** (Schemes 6 and 7). An earlier report[12] describes the rapid oxidation (5 min) of 4,5-benzotropone hydrazone at 0 °C with nickel peroxide.[35] In our hands, the hydrazone appears unreactive under these conditions, even upon extended reaction times. (The same batch of nickel peroxide readily converts benzyl alcohol to benzoic acid in a control experiment). In the presence of silver oxide at 0 °C, however, both benzotropone hydrazones are satisfactorily oxidized to afford the crude diazo compound as a dark red-orange solid. Although purified samples of diazo compounds **15** and **16** could not be isolated by laboratory-scale sublimation, small quantities of diazo compound could be volatilized from the crude mixture and co-deposited with argon at 30 K. The matrix-isolated sample of 4,5-benzodiazocycloheptatriene (**15**) generated by this method is substantially more pure than that obtained in the thermolysis of tosylhydrazone salt **19** (vide infra). The matrix-isolated sample of 2,3-benzodiazocycloheptatriene (**16**), on the other hand, is often impure and is obtained in extremely small amounts.

SCHEME 6



SCHEME 7



An alternate route to diazo compounds **15** and **16** involves the preparation of tosylhydrazones **18** and **22** (Schemes 6 and 7).[5,8] It has long been known that thermolysis of the corresponding tosylhydrazone salts **19** and **23** does not afford isolable quantities of diazo compound. Thermolysis of **19**, with direct co-deposition of the pyrolysate with argon at 30 K, however, affords a small amount of 4,5-benzodiazocycloheptatriene (**15**) accompanied by several unidentified impurities. Similarly, impure diazo compound **16** can be obtained upon pyrolysis of tosylhydrazone salt **23**. Although the direct oxidation of 4,5-benzotropone hydrazone (**20**) is the preferred method of preparing 4,5-benzodiazocyclohep-

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tatriene (**15**), pyrolysis of tosylhydrazone salt **23** is a more reliable method for the generation of 2,3-benzodiazocycloheptatriene (**16**). 2,3-Benzodiazocycloheptatriene (**16**), which has not been reported previously, appears to be more susceptible to decomposition than the isomeric diazo compound **15**.

Computational studies of diazirines **13** and **14** and diazo compounds **15** and **16** (Scheme 5) reveal that diazirines **13** and **14** are predictably higher in energy than the corresponding diazo compounds **15** and **16**. The energy difference between the two isomeric diazo compounds (3.3 kcal/mol), as well as the isomeric diazirines (1.3 kcal/mol), is relatively small. The experimental difficulty in preparing and handling 2,3-benzodiazocycloheptatriene (**16**) cannot be explained in terms of the compound possessing a significantly higher energy than the isomeric 4,5-benzodiazocycloheptatriene (**15**). The calculated geometry of diazo compound **16**, however, is noticeably distorted from planarity. This structural effect may play a role in the thermal instability of **16** in the laboratory.

Although the matrix-isolated samples of diazo compounds **15** and **16** inevitably contain (matrix-isolated) impurities, the combination of photochemical and spectroscopic data permits meaningful conclusions to be drawn from the experiments. IR difference spectra reliably reveal the major photochemical processes that occur in the matrix. UV/visible spectra, however, must be interpreted with caution, as minor impurities may have large extinction coefficients. ESR spectra of triplet carbenes are readily interpreted because of their unique characteristics.

Matrix Photochemistry of 4,5-Benzodiazocycloheptatriene (15). Irradiation ($\lambda = 670$ or >613 nm) of matrix-isolated 4,5-benzodiazocycloheptatriene (**15**), generated either from thermolysis of **19** or oxidation of **20**, causes complete disappearance of diazo compound accompanied by growth of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**) and trace amounts of triplet 2-naphthylcarbene (**10**) and 4,5-benzocycloheptatrienylidene (**2**) (Figures 1−3, Scheme 8). The detailed justification for the structural assignments is discussed below. Cyclopropene **9** is detected by IR and UV/visible spectroscopy, 2-naphthylcarbene (**10**) is detected by UV/visible and ESR spectroscopy, and 4,5-benzocycloheptatrienylidene (**2**) is detected only by ESR spectroscopy. As a result of its low concentration, **2** is not detected by other spectroscopic methods. Carbene **2** appears to exist in a low steady-state concentration under these photochemical conditions, as the intensity of the new ESR absorptions remains constant throughout the photolysis. Even after prolonged irradiation of the matrix ($\lambda = 670$ nm, 37 h), the ESR signal for **2** does not change, although 2-naphthylcarbene (**10**) gradually begins to appear (Figure 3). In a result reminiscent of an earlier study,[13] band-pass irradiation ($\lambda = 290$ nm) converts cyclopropene **9** to carbene **10** with a concomitant loss of carbene **2**. At this point, 2-naphthylcarbene (**10**) is observable by IR spectroscopy. Reversion of 2-naphthylcarbene (**10**) to cyclopropene **9** is achieved by band-pass irradiation ($\lambda = 360$ nm), thus establishing a clean, reversible photoequilibrium between **9** and **10**.

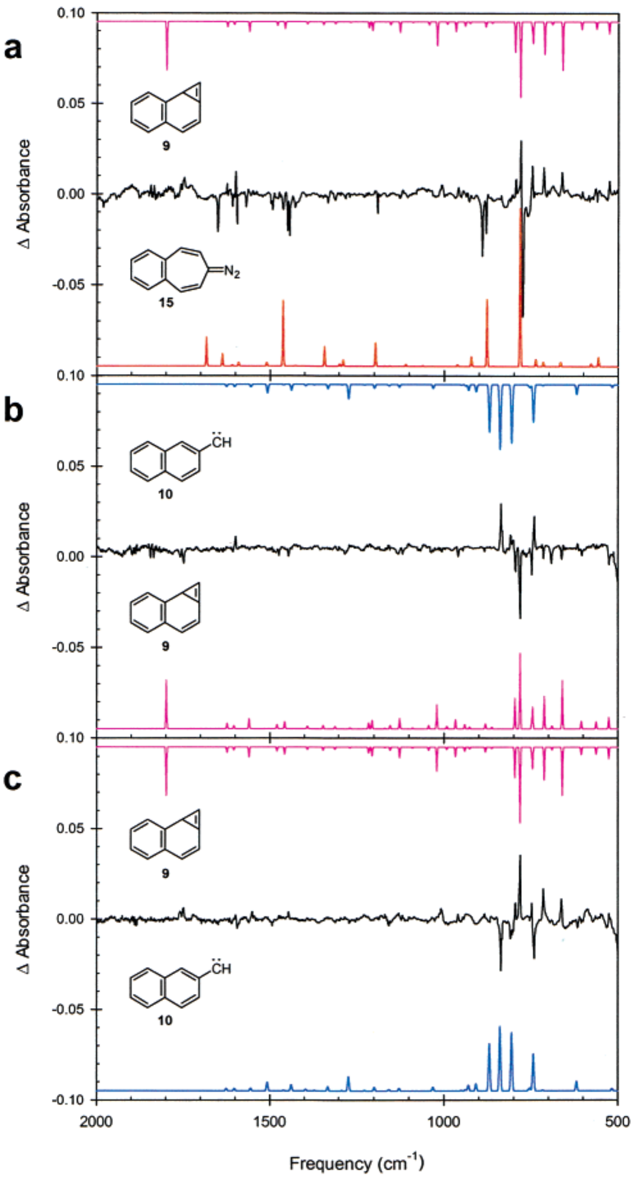

FIGURE 1. (a) Top: Calculated IR spectrum of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**). Middle: IR difference spectrum (Ar, 10 K) showing complete conversion of diazo compound **15** to cyclopropene **9** upon irradiation at $\lambda > 613$ nm, 18 h. Bottom: Calculated IR spectrum of 4,5-benzodiazocycloheptatriene (**15**). (b) Top: Calculated IR spectrum of triplet *s-E* 2-naphthylcarbene (**10**). Middle: IR difference spectrum showing disappearance of cyclopropene **9** and emergence of carbene **10** at $\lambda = 290$ nm, 4 h. Bottom: Calculated IR spectrum of **9**. (c) Top: Calculated IR spectrum of **9**. Middle: IR difference spectrum showing complete conversion of carbene **10** to cyclopropene **9** upon irradiation at $\lambda = 360$ nm, 4 h. Bottom: Calculated IR spectrum of **10**. All B3LYP/6-31G* calculated frequencies are scaled by 0.98.

Cyclopropene **9** is characterized by IR and UV/visible spectroscopy: IR (Ar, 10 K) 1758 w, 1747 w, 1474 w, 1118 w, 1009 w, 959 w, 885 m, 795 s, 781 s, 748 m, 715 m, 662 m, 604 w, 525 w cm^{-1}; UV/visible (Ar, 10 K) λ_{max} 217 nm. Triplet 2-naphthylcarbene (**10**) is characterized by IR, UV/visible, and ESR spectroscopy: IR (Ar, 10 K) 837 s, 809 m, 801 w, 741 s, 617 w cm^{-1}; UV/visible (Ar, 10 K)

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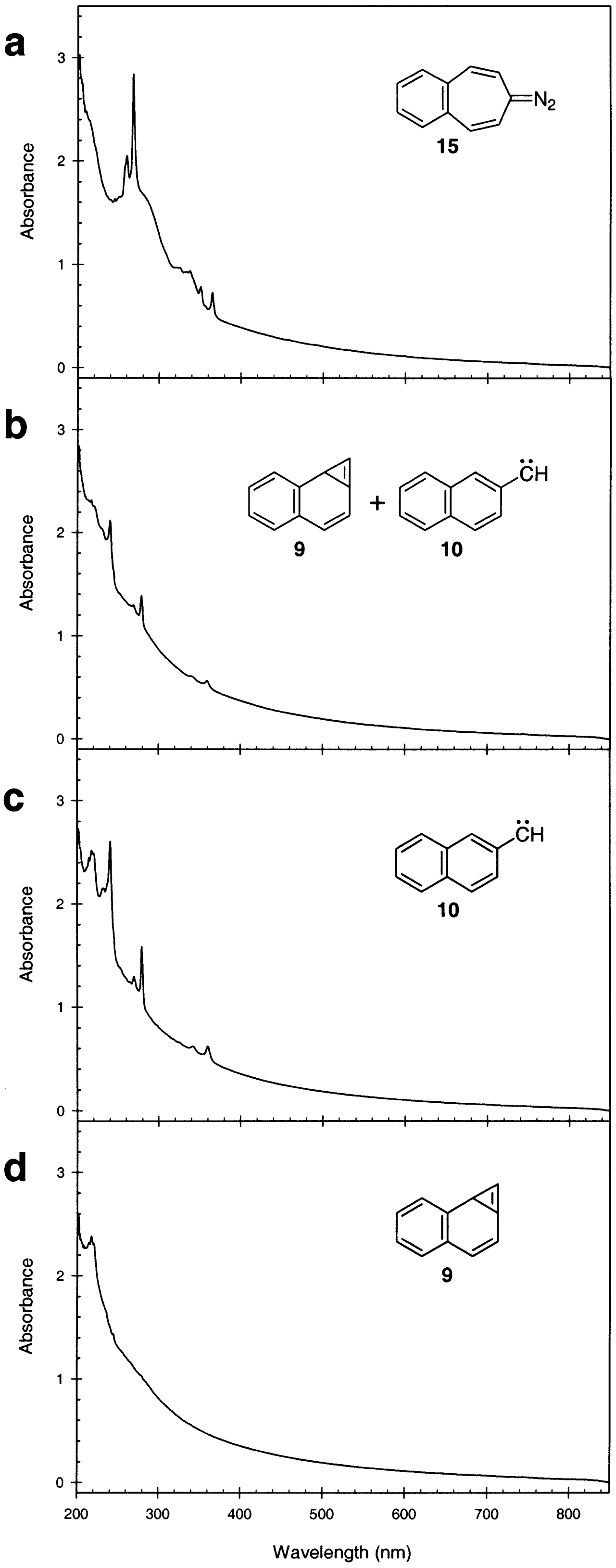


FIGURE 2. (a) UV/visible spectrum (Ar, 10 K) of 4,5-benzodiazocycloheptatriene (**15**). (b) Mixture of 2,3-benzobicyclo-[4.1.0]hepta-2,4,6-triene (**9**) and 2-naphthylcarbene (**10**) after irradiation at $\lambda > 613$ nm, 17 h. (c) Growth of carbene **10** at $\lambda = 290$ nm, 24 h. (d) Disappearance of **10** and emergence of **9** upon irradiation at $\lambda = 360$ nm, 23 h.

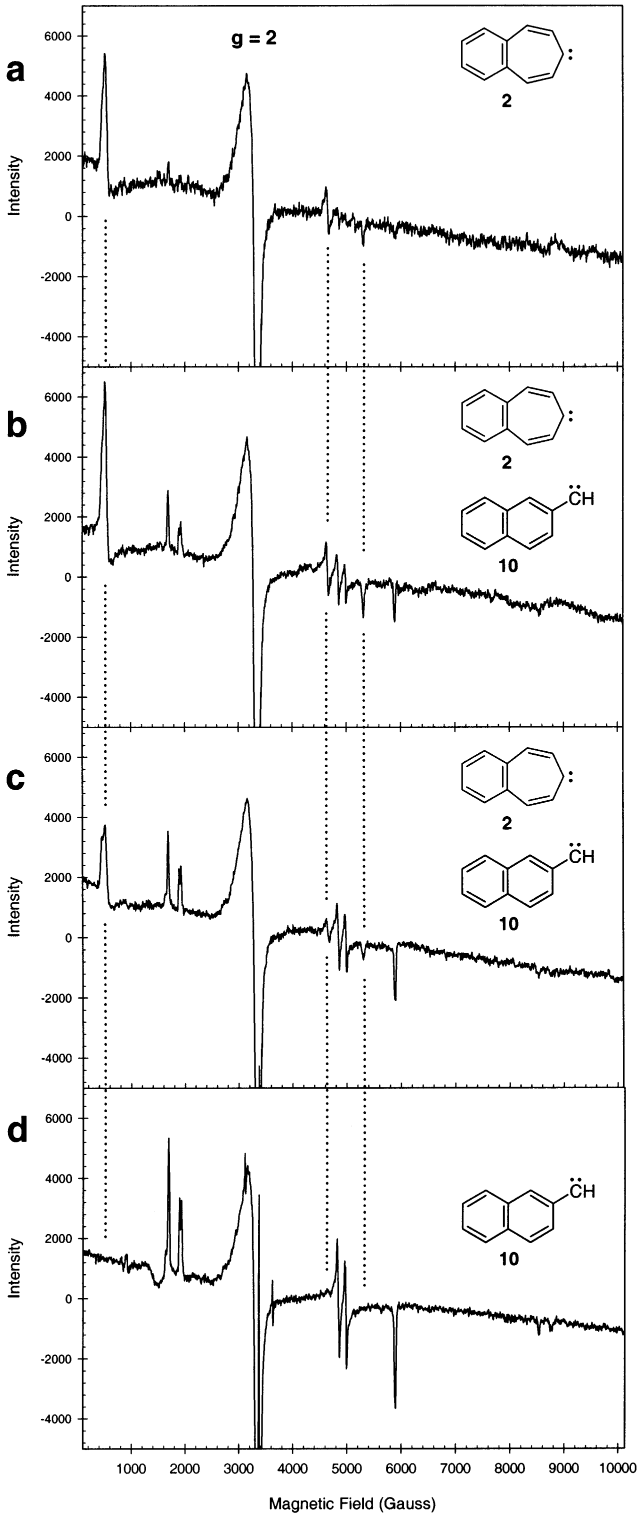
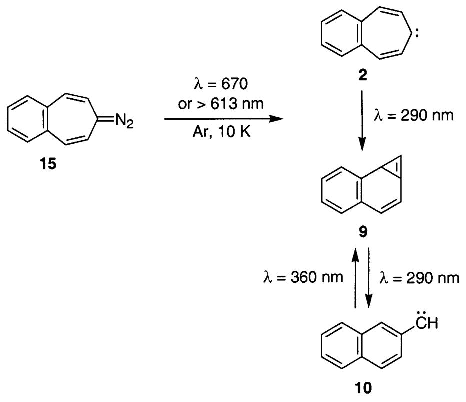


FIGURE 3. (a) ESR spectrum (Ar, 14 K) of 4,5-benzocycloheptatrienylidene (**2**) upon irradiation of diazo compound **15** at $\lambda = 670$ nm, 12 h. (b) Further growth of **2** and emergence of 2-naphthylcarbene (**10**) at $\lambda = 670$ nm, 37 h. (c) Rapid disappearance of **2** and growth of **10** upon irradiation at $\lambda > 261$ nm, 5 min. (d) Complete disappearance of **2** and continued growth of **10** at $\lambda > 261$ nm, 5 h. In each spectrum, the signal at ca. 3300 G is the $g = 2$ (radical) impurity.

SCHEME 8

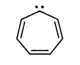
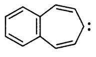
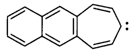
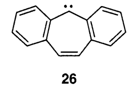
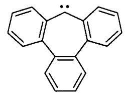
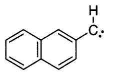
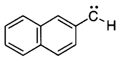


λ_{max} 360, 341, 326, 279, 270, 240, 232, 218 nm; ESR (Ar, 14 K) *s-E* isomer $Z_1 = 1692$ G, $X_2 = 4841$ G, $Y_2 = 5891$ G, $Z_2 = 8533$ G, $|D/hc| = 0.4785$ cm^{-1}, $|E/hc| = 0.0258$ cm^{-1}; *s-Z* isomer $Z_1 = 1909$ G, $X_2 = 4980$ G, $Y_2 = 5891$ G, $Z_2 = 8752$ G, $|D/hc| = 0.4985$ cm^{-1}, $|E/hc| = 0.0222$ cm^{-1}; microwave frequency = 9.530 GHz. Both of these structural assignments are confirmed by excellent agreement with previously reported spectroscopic data,[11,13,36,37] and by comparison with B3LYP/6-31G* calculated IR spectra (Figure 1). Other potential photoproducts, such as allenes **6**−**8**, can be ruled out on the basis of their calculated IR spectra.[34]

Three new ESR absorptions arising from the photolysis of **15** are ascribed to triplet 4,5-benzocycloheptatrienylidene (**2**): (Ar, 14 K) $Z_1 = 507$ G, $X_2 = 4651$ G, $Y_2 = 5317$ G, $|D/hc| = 0.368$ cm^{-1}, $|E/hc| = 0.0172$ cm^{-1}; microwave frequency = 9.529 GHz. On the basis of the zero-field splitting parameters and the microwave frequency,[38] a weak Z_2 transition is anticipated at ca. 7300 G. This absorption is likely unobserved due to the low concentration of **2**. The new species is thermally stable in the dark (14 K, 11 h). As would be expected for an endocyclic carbene, the signals are not mirrored by a second set of absorptions arising from rotational isomerism. The ESR transitions are consistent with a triplet carbene, yet they differ substantially from the transitions exhibited by the triplet naphthylcarbenes **10** and **12**.[11,13,15,37] Given that identical ESR signals are obtained regardless of the method of diazo compound preparation, the absorptions are unlikely to arise from a thermally rearranged diazo compound or impurity within the matrix.

In an earlier ESR study,[12] a triplet species assigned as 4,5-benzocycloheptatrienylidene (**2**) was obtained when a hydrocarbon glass containing diazo compound **15** was irradiated briefly with a 1000-W Xe−Hg arc lamp. In our experiments, irradiation of carbene **2** under comparable conditions ($\lambda > 261$ nm, 5 min, 300-W Xe arc lamp) produces a sudden decrease in the ESR signal of **2** and growth of the ESR signal of triplet 2-naphthylcarbene (**10**) (Figure 3). Further irradiation results in the complete disappearance of **2**, while triplet **10** persists. This control experiment suggests that triplet 4,5-benzocycloheptatrienylidene (**2**) would not survive under the irradiation conditions employed in the earlier study. Thus, the ESR signals previously attributed to triplet 4,5-benzocycloheptatrienylidene (**2**) may actually belong to triplet 2-naphthylcarbene (**10**).

TABLE 1. Zero-Field Splitting Parameters for Triplet Carbenes

Carbene	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})
 **1**	0.425 [a]	0.0222
 **2**	0.52 [b]	0.021
	0.489 [c]	0.020
	0.368 [d]	0.0179
 **25**	0.453 [a]	0.0193
 **26**	0.3787 [e]	0.0162
 **27**	0.4216 [e]	0.0195
 ***s-Z*-10**	0.500 [f]	0.0242
	0.4926 [g]	0.0209
 ***s-E*-10**	0.480 [f]	0.0277
	0.4711 [g]	0.0243

[a] Reference 25. See also refs 26 and 27. [b] Reference 12. [c] Reference 39. [d] This work. [e] Reference 41. [f] Reference 13. [g] Reference 37.

The zero-field splitting parameters that we assign to triplet 4,5-benzocycloheptatrienylidene (**2**) are in accord with those of structurally similar triplet carbenes **1** and **25**−**27** (Table 1), but they differ considerably from those reported earlier for **2**.[12,39] Actually, the previously reported zero-field splitting parameters of 4,5-benzocycloheptatrienylidene (**2**)[12,39] display better agreement with triplet 2-naphthylcarbene (**10**) than with triplet cycloheptatrienylidene derivatives (Table 1). In a simplistic analysis, benzannelation of cycloheptatrienylidene (**1**) might be expected to increase the average distance between the interacting π and σ electrons in triplet 4,5-benzocycloheptatrienylidene (**2**), thereby decreasing the value of D.[40] Although this relationship is borne out in the comparison of cycloheptatrienylidene (**1**) ($D = 0.425$ cm^{-1}) vs 4,5-benzocycloheptatrienylidene (**2**) ($D = 0.368$ cm^{-1}), Table 1 reveals that this relationship is not consistently manifested among a larger series of benzannelated cycloheptatrienylidenes. A simple structure−

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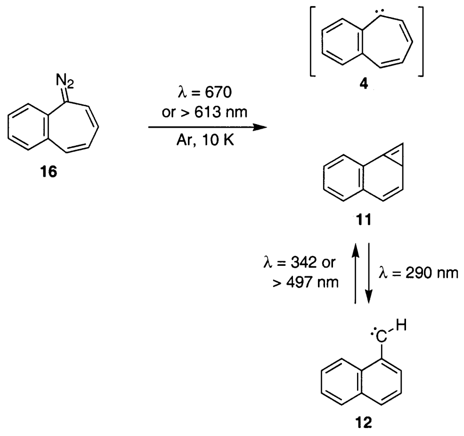
[37] Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129−130.

[38] Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763−1772.

[39] Using the original data of Horn and Platz, we recalculated the zero-field splitting parameters using an analytical mathematical solution, rather than a graphical solution. The analytical solution affords a somewhat smaller D value of 0.489 cm^{-1}.

[40] Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, 1967.

SCHEME 9



property relationship among the species depicted in Table 1 is not readily apparent. The anomalously large *D* value (0.52 cm^{-1}) reported previously for triplet 4,5-benzocycloheptatrienylidene (**2**) was rationalized in terms of a nonplanar "boat" conformation of **2**, conferred to the carbene by its diazo precursor **15** in a rigid matrix.[12,39] A similar argument regarding steric hindrance to planarity was invoked for carbene **27**.[41] In the case of 4,5-benzocycloheptatrienylidene (**2**), this explanation appears to be inconsistent with the computational predictions of planar geometries for both diazo compound **15**[34] and triplet carbene **2**.[14]

Matrix Photochemistry of 2,3-Benzodiazocycloheptatriene (16). Irradiation ($\lambda = 670$ or >613 nm) of matrix-isolated 2,3-benzodiazocycloheptatriene (**16**), generated from thermolysis of tosylhydrazone salt **23**,[42] results in the disappearance of diazo compound accompanied by the appearance of 4,5-benzobicyclo[4.1.0]-hepta-2,4,6-triene (**11**) as the sole product (Scheme 9) as determined by IR and UV/visible spectroscopy (Figures 4 and 5). The basis for structural assignments is discussed below. Neither triplet 1-naphthylcarbene (**12**) nor 2,3-benzocycloheptatrienylidene (**4**) is detected by ESR spectroscopy (Figure 6). Consistent with earlier work,[15] cyclopropene **11** can be completely converted to 1-naphthylcarbene (**12**) by irradiation at $\lambda = 290$ nm. Carbene **12** is characterized by IR, UV/visible, and ESR spectroscopy, although only the *s*-*E* rotational isomer is detected. As with the isomeric system (vide supra), a reversible photoequilibrium exists between the naphthylcarbene and its cyclopropene derivative. Band-pass or broadband irradiation ($\lambda = 342$ or >497 nm) induces complete disappearance of **12** and reappearance of **11**. Interestingly, conditions for the regeneration of 1-naphthylcarbene ($\lambda = 290$ nm) once again apparently produce only the *s*-*E* isomer of **12**.

Cyclopropene **11** is characterized by IR and UV/visible spectroscopy: IR (Ar, 10 K) 3020 m, 2981 m, 1763 m, 1751 m, 1468 s, 1450 s, 1102 w, 1033 w, 1003 w, 943 w, 930 w, 777 s, 752 m, 697 s, 669 s, 586 m, 568 m, 504 w, 489 w cm^{-1}; UV/visible (Ar, 10 K) λ_{max} 220 nm. Carbene **12** is characterized by IR, UV/visible, and ESR spectroscopy: IR (Ar, 10 K) 3062 m, 3046 m, 1494 w, 1213 w, 1095 m, 1020 m, 785 s, 764 s, 719 w, 540 m cm^{-1}; UV/visible (Ar, 10 K) λ_{max} 341, 328, 320, 307 nm; ESR (Ar, 14 K) *s*-*E* isomer $Z_1 = 1538$ G, $X_2 = 4895$ G, $Y_2 = 5740$ G, $Z_2 = 8376$ G, $|D/hc| = 0.4636$ cm^{-1}, $|E/hc| = 0.0209$ cm^{-1}; microwave frequency = 9.530 GHz. The structural assignment of each species is confirmed by excellent agreement with previously reported spectroscopic data[11,13,15,36,37] and by comparison with B3LYP/6-31G* calculated IR spectra (Figure 4). Other potential photoproducts, such as allenes **6**−**8**, are ruled out based on their calculated IR spectra.[34]

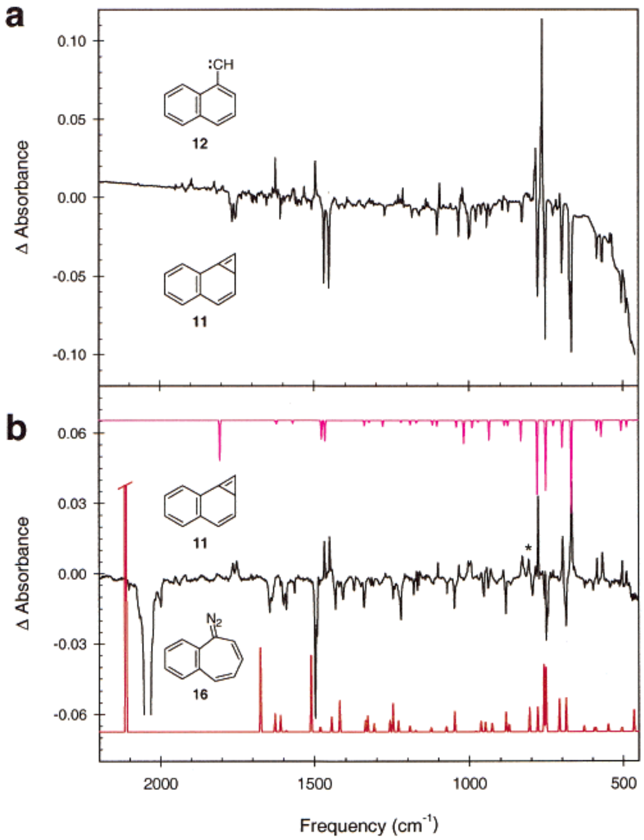


FIGURE 4. (a) IR difference spectrum (Ar, 10 K) showing independent IR spectra of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**11**) and triplet 1-naphthylcarbene (**12**), as generated upon irradiation of 1-naphthyldiazomethane (see ref 15). (b) Top: Calculated IR spectrum of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**11**). Middle: IR difference spectrum showing conversion of 2,3-benzodiazocycloheptatriene (**16**) to cyclopropene **11** after irradiation at $\lambda = 670$ nm, 21 h. Bottom: Calculated IR spectrum of 2,3-benzodiazocycloheptatriene (**16**). All B3LYP/6-31G* calculated frequencies are scaled by 0.98.

The failure to observe the minor (*s*-*Z*) rotational isomer of 1-naphthylcarbene (**12**) is a puzzling result. Given the reasonably intense ESR signals for **12** (Figure 6), it seems unlikely that the *s*-*Z* isomer is present below the threshold of instrumental detection. Previous investigations indicate that the ratio of the integrated Z_1 transitions for the *s*-*E* and *s*-*Z* isomers of 1-naphthylcarbene (generated from 1-naphthyldiazomethane or 1-naphthyldiazirine) is approximately 4:1.[15] The carbene precursor (generation of **12** indirectly from 2,3-benzodiazocycloheptatriene (**16**) versus directly from 1-naphthyldiazomethane) may impart a conformational bias through a

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(41) Moritani, I.; Murahashi, S.-I.; Nishino, M.; Yamamoto, Y.; Itoh, K.; Mataga, N. *J. Am. Chem. Soc.* **1967**, *89*, 1259−1260.

(42) Qualitatively identical results are obtained when **16** is prepared from the low-temperature oxidation of **24**, although the material is less pure and present in smaller amounts.

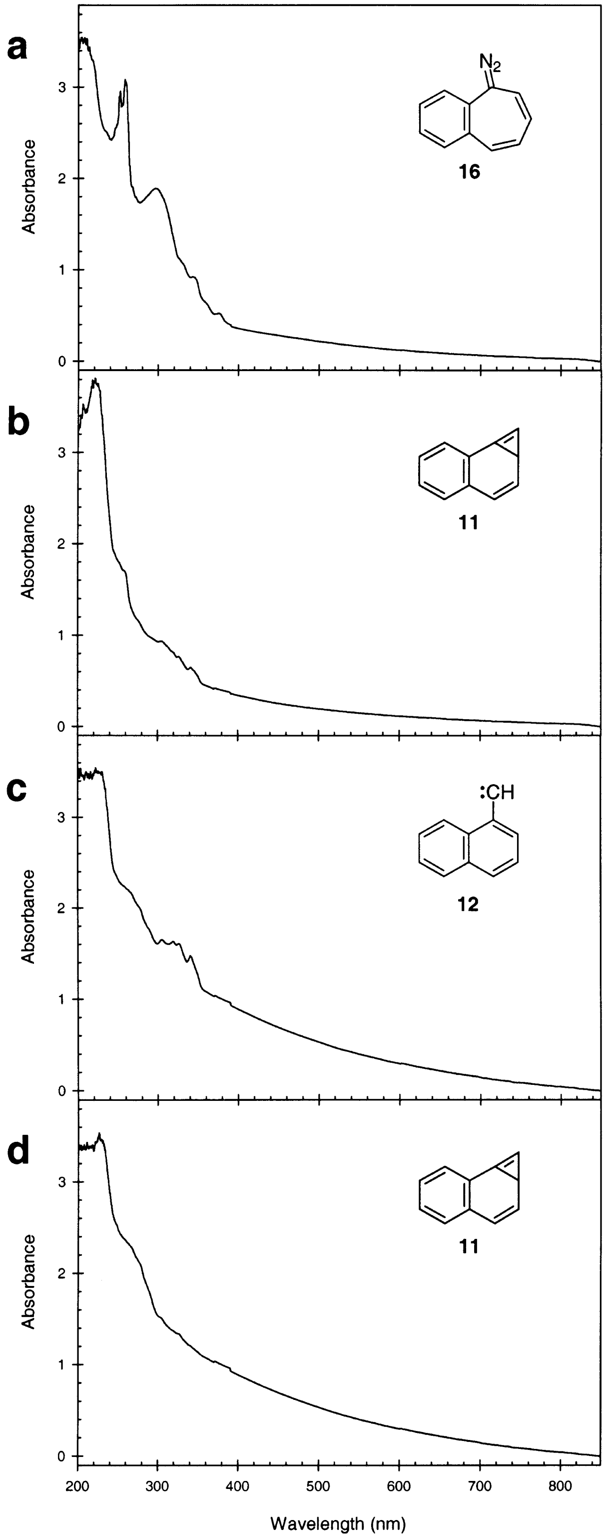


FIGURE 5. (a) UV/visible spectrum (Ar, 10 K) of 2,3-benzodiazocycloheptatriene (**16**). (b) Irradiation at $\lambda > 613$ nm for 7 h produces 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**11**). (c) Cyclopropene **11** is converted to 1-naphthylcarbene (**12**) at $\lambda = 290$ nm, 1 h. (d) Broadband irradiation ($\lambda > 497$ nm, 3 h) induces disappearance of **12** as **11** returns. Because the extinction coefficients of the absorptions for **12** are much smaller than that of the other species, spectra (a) and (b) were obtained from a thin matrix, while spectra (c) and (d) were obtained from a separate experiment employing a thicker matrix.

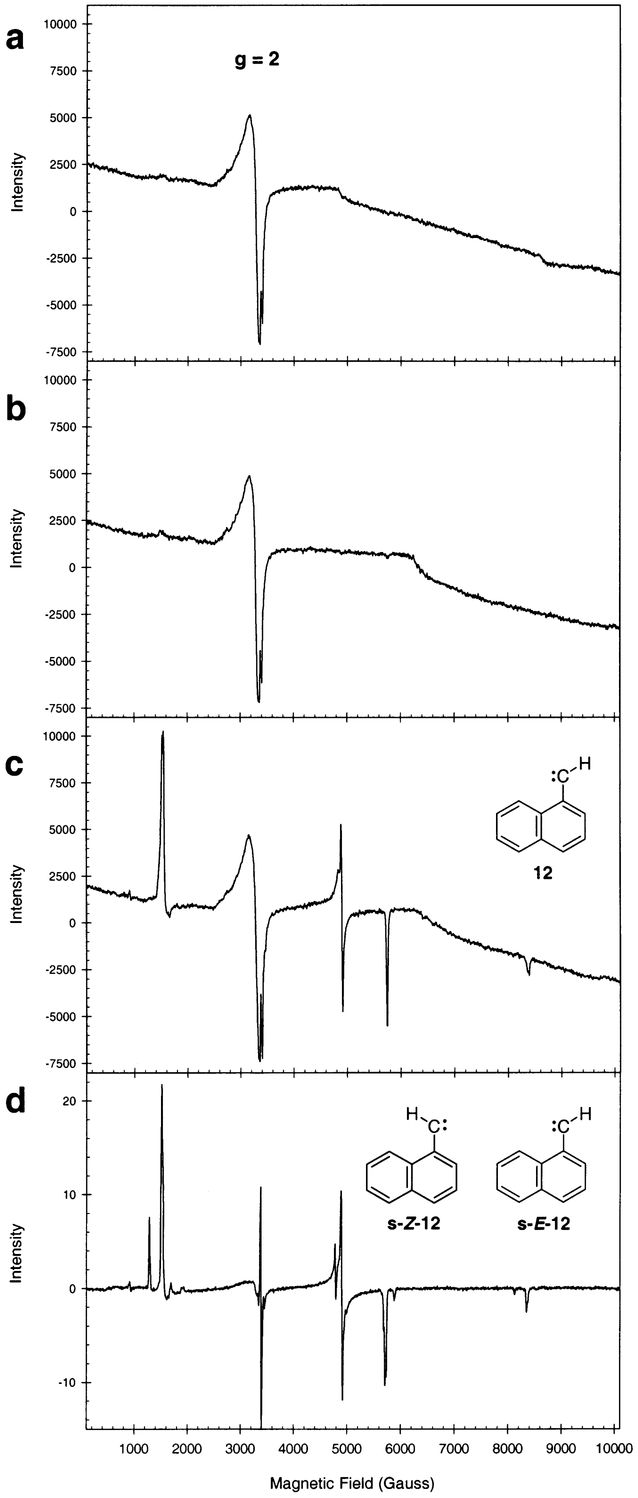
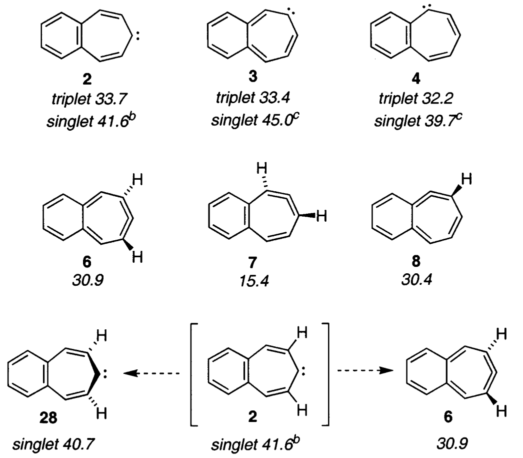


FIGURE 6. (a) ESR spectrum (Ar, 14 K) showing no detectable triplet signal upon irradiation of 2,3-benzodiazocycloheptatriene (**16**) at $\lambda = 670$ nm, 37 h. (b) Subsequent irradiation at $\lambda > 613$ nm for 13 h similarly fails to produce any triplet species. (c) Spectrum of triplet *s*-*E*-1-naphthylcarbene (**12**) after irradiation at $\lambda = 290$ nm, 14 h. (d) ESR spectrum (Ar, 14 K) displaying both rotational isomers of triplet 1-naphthylcarbene (**12**) generated upon irradiation ($\lambda > 300$ nm, 1 h) of 1-naphthyldiazomethane. (Shown for the purpose of comparison to spectrum (c).) In each spectrum, the signal at ca. 3300 G is the $g = 2$ (radical) impurity.

SCHEME 10[a]



[a] B3LYP/6-31G* energy (kcal/mol, ZPVE corrected), relative to cyclobuta[*de*]naphthalene, in italics. [b] Two imaginary frequencies. [c] One imaginary frequency.

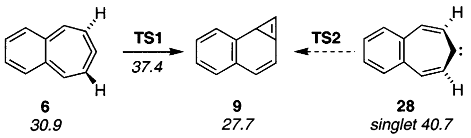
cavity effect in the solid matrix. This hypothesis must be considered with due caution, however, as the isomeric 2-naphthylcarbene system (vide supra) fails to display this effect and gives both rotational isomers of **12** in their “normal” proportion.

The ESR spectrum of carbene **12** obtained in this series of experiments differs slightly from those obtained previously.[15,37,43,44] The Z_1 and X_2 transitions are broad and display some fine structure, and the Z_2 transition is broad. These characteristics, which may arise from either matrix site effects or poor matrix isolation, could potentially obfuscate a weak signal corresponding to *s-Z* **12**. Surprisingly, even when photochemically converted to cyclopropene **11** and then regenerated, carbene **12** still exhibits a single rotational isomer.[34] This result differs from the photochemical ring opening of cyclopropene **11** in earlier experiments,[15] in which both rotational isomers of carbene **12** are clearly obtained. Professor Wentrup informed us of related observations regarding differences in ESR spectra of arylcarbenes and nitrenes depending on the precursor and method of generation (thermal or photochemical).[45,46] These intriguing phenomena are simply not understood at the current time.

Computational Results. Although significant portions of the $C_{11}H_8$ potential energy surface have already been explored computationally,[14] several issues regarding the benzocycloheptatrienylidenes remain to be described. The calculation of 3,4-benzocycloheptatrienylidene (**3**) completes the comparison drawn in Scheme 2.[47] Like its related isomers at the B3LYP level of theory,[14] planar triplet **3** is a minimum while planar singlet **3** is a transition structure for the enantiomerization of the twisted allene **7**. Singlet carbene **3** lies higher in energy than singlet allene **7** and triplet carbene **3** by 29.6 and 11.6 kcal/mol, respectively (Scheme 10).

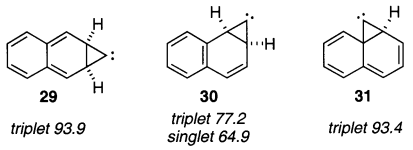
In singlet 4,5-benzocycloheptatrienylidene (**2**), calculated to be a second-order saddle point, both imaginary frequencies follow distinctly different modes of atomic motion. One of these (237*i* cm^{-1}), in which both hydrogens flanking the carbene twist in opposite directions, leads to either enantiomer of nonplanar allene **6**. The other imaginary frequency (297*i* cm^{-1}) corresponds to an upward out-of-plane deformation of the carbene carbon as the flanking hydrogens both stretch downward. The resulting structure converges to singlet C_s symmetric carbene **28**, which possesses zero imaginary frequencies (Scheme 11). This behavior has been independently discovered by Wentrup and co-workers.[48] Comparison of the calculated IR frequencies of “puckered” carbene **28** to the experimental data rule out its presence in the matrix-isolation studies.[34] Several unsuccessful attempts were made to discover a transition state (**TS2**) connecting singlet carbene **28** to cyclopropene **9** (Scheme 11). In each case a transition structure was found, but intrinsic reaction coordinate (IRC) calculations revealed that the species was actually **TS1**, which connects cyclopropene **9** to allene **6** rather than to carbene **28**. If **TS2** does exist, its structural similarity to **TS1** complicates characterization by computational study.

SCHEME 11[a]



[a] B3LYP/6-31G* energy (kcal/mol, ZPVE corrected), relative to cyclobuta[*de*]naphthalene, in italics.

SCHEME 12[a]



[a] B3LYP/6-31G* energy (kcal/mol, ZPVE corrected), relative to cyclobuta[*de*]naphthalene, in italics.

Elucidation of the structure of carbene **28** spurred us to explore the relationship of these “benzocycloheptatrienylidene” structures with the corresponding “benzonorcaradienylidene” structures (Scheme 12). The “benzonorcaradienylidene” (benzobicyclo[4.1.0]hepta-2,4-dien-7-ylidene) structures may be pertinent to the mechanism of addition of a carbon atom to naphthalene. Attempted geometry optimization of singlet **29**, whether the initial structure was C_s or C_1 symmetric, resulted in convergence to the puckered 4,5-benzocycloheptatrienylidene **28** reported above. Triplet **29**, on the other hand, is both a stationary point and a minimum. The isomeric singlet cyclopropylidene **30** is a minimum, in agreement with a previous report,[14] as is triplet **30**. Triplet **30** possesses an elongated carbon−carbon bond,[34] but is otherwise unremarkable. The third isomeric benzonorcaradienylidene **31** is also considered. Triplet **31** displays an abnormally long (1.94 Å)[34] and partially occupied[49] bond

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

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

(45) Kuzaj, M. Ph.D. Thesis, University of Marburg, Germany, 1985.

(46) Lüerssen, H. Ph.D. Thesis, University of Marburg, 1985.

(47) This species is also reported in the Supporting Information of ref 16.

(48) Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 9023−9030.

(49) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, 1996.

from the quaternary carbon to the carbene. Attempted geometry optimizations of singlet cyclopropylidene **31** generally converged to the ring-opened allene **8**. Employing the rather unusual optimized geometry of triplet **31** as a starting point in the search for singlet **31** resulted in convergence to the isomeric singlet benzonorcaradienylidene **30**. Due to their extremely high energy and failure to match with any experimentally observed IR absorptions,[34] none of the benzobicyclo[4.1.0]hepta-2,4-dien-7-ylidenes are likely to be involved in the photochemical interconversions of $C_{11}H_8$ isomers encountered in the current study.

Mechanistic Implications. The extensive rearrangements observed upon gentle visible irradiation ($\lambda = 670$ nm or >613 nm) of 4,5-benzodiazocycloheptatriene (**15**) raise interesting mechanistic questions. The "expected" triplet 4,5-benzocycloheptatrienylidene (**2**) is formed only in a small amount. Possible explanations for the formation of cyclopropene **9** include (i) photosensitivity of carbene **2** under the irradiation conditions, (ii) rearrangement of vibrationally hot carbene **2**, and (iii) rearrangement in an excited state of diazo compound **15**, bypassing carbene **2** altogether.[50] Control experiments rule out the thermal conversion of carbene **2** to cyclopropene **9** at 14 K. Explanations involving vibrationally hot carbene or excited-state diazo compound, while accounting for the partitioning of diazo compound between carbene and cyclopropene formation, do not rationalize the fact that the absolute amount of carbene cannot be increased by carrying the photolysis to higher conversion. Carbene concentration is independent of diazo compound conversion, which implies that carbene **2** is photosensitive under the irradiation conditions. (This circumstance, of course, does not preclude the involvement of vibrationally hot carbene or excited diazo compound.) The observation of triplet 2-naphthylcarbene (**10**) by ESR spectroscopy under these irradiation conditions is an intriguing result. Control experiments rule out the photochemical conversion of cyclopropene **9** to carbene **10** under the irradiation conditions ($\lambda = 670$ nm or >613 nm). Possible explanations for the formation of 2-naphthylcarbene (**10**) include (i) photochemical rearrangement of carbene **2** under the irradiation conditions, (ii) thermal rearrangement of vibrationally hot carbene **2** or cyclopropene **9**, and (iii) rearrangement via another undetected intermediate present in low, steady-state concentration.

The foregoing experiments establish the photosensitivity of carbene **2** at visible wavelengths. Other experiments establish the photosensitivity of carbene **2** in the UV. Irradiation ($\lambda = 290$ or >261 nm) of a matrix containing carbene **2** rapidly destroys **2** and causes triplet 2-naphthylcarbene (**10**) to appear (Figure 3), presumably via cyclopropene **9**.

Given our ability to prepare 2,3-benzodiazocycloheptatriene (**16**), for the first time, the inability to generate the corresponding triplet 2,3-benzocycloheptatrienylidene (**4**) is disappointing. We can only speculate that this circumstance reflects an even greater photosensitivity of carbene **4** to the irradiation conditions (compared to the case of the 4,5-isomer), or that it is a consequence of the nonplanar structure of diazo compound **16**, which leads to an enhanced participation by vibrationally hot carbene or excited-state diazo compound.

Summary

Matrix-isolated 4,5-benzodiazocycloheptatriene (**15**) is photochemically converted to a mixture of triplet 4,5-benzocycloheptatrienylidene (**2**), 2,3-benzobicyclo[4.1.0]-hepta-2,4,6-triene (**9**), and triplet 2-naphthylcarbene (**10**). Similarly, 2,3-benzodiazocycloheptatriene (**16**) produces 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**11**) and, eventually, the *s-E* rotational isomer of triplet 1-naphthylcarbene (**12**) without detection of triplet 2,3-benzocycloheptatrienylidene (**4**). Under the appropriate photoequilibrating conditions, each cyclopropene and its respective naphthylcarbene can be reversibly interconverted. Benzocycloheptatetraenes **6**−**8** are not detected under these experimental conditions.

Methods

Computational Methods. Calculations were performed with the Becke three-parameter gradient-corrected exchange functional[51] with the correlation functional of Lee, Yang, and Parr[52] (B3LYP) as implemented in the Gaussian 98 package.[53] Triplet states were computed using an unrestricted wave function (UB3LYP) and closed-shell singlet states were computed using a restricted wave function (RB3LYP). All singlet states reported in this study are closed-shell; open-shell singlet states were not investigated. The 6-31G* basis set was employed for geometry optimizations as well as for single-point energy and harmonic vibrational frequency calculations. Harmonic vibrational frequency calculations established the number of imaginary frequencies for each species, and afforded the zero-point vibrational energy correction and computed infrared spectrum. The location of bonds and lone electron pairs was verified with Natural Bond Orbital (NBO) calculations where appropriate.[49]

Matrix-Isolation Spectroscopy and Photochemistry. Techniques and apparatus for low-temperature matrix isolation spectroscopy are described elsewhere.[54,55] The deposition temperature and argon flow rate remained constant regardless of the particular instrumental technique employed, although the matrix thickness (i.e. the amount of sample) was generally greater for ESR and IR experiments than for a UV/visible experiment. Irradiation was carried out with a 300-W high-pressure xenon arc lamp, and wavelength selection was achieved with cutoff filters or a high-energy monochromator. Cutoff filters display <0.1% transmittance at the specified wavelength: Corning 2-58 (>613 nm), Corning 3-69 (>497

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[50] For a recent review and leading references, see: Platz, M. S. In *Advances in Carbene Chemistry II*; Brinker, U., Ed.; JAI Press: Boca Raton, FL, 1998; Vol. 2, p 133.

[51] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[52] Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B−Condens Matter* **1988**, *37*, 785−789.

[53] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

[54] McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597−7606.

[55] Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183−7189.

nm), Corning 0-53 (>261 nm). Wavelengths selected with the monochromator are ±10 nm. Photolysis times often varied depending on the instrumental technique employed. IR spectra were recorded on an FT-IR spectrometer equipped with a MCT-B detector. UV/visible spectra were acquired using a 2 nm slit width. ESR experiments were conducted at X-band. Zero-field splitting parameters were assigned by a best fit of the observed spectrum to the spin Hamiltonian (assuming $g_x = g_y = g_z = g_e$).[38]

General Experimental Methods. Carbon tetrachloride was dried over molecular sieves, and solvent grade dichloromethane and ether were distilled from CaH_2. All reactions are carried out under a nitrogen atmosphere. Compounds from commercial sources gave acceptable ^1H NMR spectra and were used without further purification. Uncorrected melting points were measured in open capillaries. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a 300-MHz spectrometer, with chemical shifts reported in parts per million downfield from Me_4Si. Mass spectra were obtained employing electron impact ionization unless otherwise specified.

Benzosuberene.[56] Sodium borohydride (6.03 g, 159 mmol) was added portionwise to a solution of 1-benzosuberone (20.05 g, 125 mmol) in 200 mL of methanol and 0.5 mL of water. After the vigorous reaction subsided, the solution was stirred for 16 h. The solution was then refluxed briefly (10 min), cooled, diluted with 200 mL of water, and extracted with 3 × 200 mL of ether. The combined organic extracts were dried with $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation to afford 1-hydroxybenzosuberane in quantitative yield as a white solid: ^1H NMR δ 1.75−2.09 (m, 6H), 2.71 (ddd, J =14, 10, 1 Hz, 1H), 2.91 (dd, $J = 14$, 8 Hz, 1H), 3.46 (d, $J = 4$ Hz, 1H), 4.92 (d, $J = 6$ Hz, 1H), 7.07−7.23 (m, 3H), 7.43 (d, $J = 7$ Hz, 1H); ^{13}C NMR δ 27.6, 27.8, 35.7, 36.5, 73.9, 124.5, 126.1, 126.9, 129.4, 140.8, 144.2; MS m/z (rel intensity) 162 (M^+, 13), 144 (100), 133 (61), 129 (64), 116 (24), 105 (31), 91 (60), 77 (17), 65 (11).

The white solid was dissolved in a solution of 600 mL of benzene and p-toluenesulfonic acid monohydrate (1.12 g, 6 mmol). Water was azeotropically removed (Dean−Stark trap) as the solution was refluxed for 4 h. The solution was cooled, washed with 400 mL of water, dried with $MgSO_4$, filtered, and concentrated to a pale yellow oil (16.79 g, 93% from 1-benzosuberone). The benzosuberene requires no further purification: ^1H NMR δ 1.92−2.00 (m, 2H), 2.39−2.45 (m, 2H), 2.83−2.86 (m, 2H), 5.90 (dt, $J = 12$, 4 Hz, 1H), 6.40 (dt, $J = 12$, 2 Hz, 1H), 7.08−7.16 (m, 4H); ^{13}C NMR δ 26.9, 32.5, 36.1, 125.9, 126.6, 129.0, 129.8, 130.8, 132.2, 136.3, 141.7; MS m/z (rel intensity) 144 (M^+, 56), 129 (100), 128 (37), 115 (20); HRMS calcd for $C_{11}H_{12}$ 144.0939, found 144.0937.

1,2-Benzo-1,3,5-cycloheptatriene.[57] A solution of benzosuberene (15.74 g, 109 mmol), NBS (19.44 g, 109 mmol), and benzoyl peroxide (72 mg, 0.3 mmol) in 110 mL of dry CCl_4 was refluxed for 2 h and irradiated with a 200-W tungsten lamp. The solution was cooled and the resulting solid succinimide was removed by vacuum filtration. The filtrate was washed with 40 mL of 5% $NaHCO_3$ followed by 80 mL of water, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to an orange oil. The product was isolated by vacuum distillation (64−68 °C, 0.2 mmHg) as a colorless oil (10.52 g, 68%): ^1H NMR δ 3.03 (d, $J = 7$ Hz, 2H), 5.77 (m, 1H), 6.07 (dd, $J =$ 10, 6 Hz, 1H), 6.46 (dd, $J = 12$, 6 Hz, 1H), 7.07 (d, $J = 11$ Hz, 1H), 7.18 (m, 2H), 7.31 (m, 2H); ^{13}C NMR δ 34.4, 125.4, 125.8, 127.0, 127.4, 127.8, 128.5, 128.6, 133.4, 136.0, 136.3; MS m/z (rel intensity) 142 (M^+, 73), 141 (100), 129 (17), 115 (33); HRMS calcd for $C_{11}H_{10}$ 142.0783, found 142.0768.

4,5-Benzotropone (17) and 2,3-Benzotropone (21).[57] 1,2-Benzo-1,3,5-cycloheptatriene (7.77 g, 54.6 mmol), SeO_2 (7.77 g, 70.0 mmol), and KH_2PO_4 (2.33 g, 17.1 mmol) in 70 mL of dioxane and 10 mL of water were refluxed for 16 h. The solution was cooled and filtered, and the filtrate was diluted with 300 mL of water. The solution was extracted with 3 × 250 mL of CH_2Cl_2 and the combined organic extracts were washed successively with 500 mL of water and 500 mL of brine. The extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to a dark brown oil. The products were isolated by column chromatography (silica gel, 30% ethyl acetate/hexane), 2,3-benzotropone (**21**) as a red-orange oil (534 mg, 6%, R_f 0.39) and 4,5-benzotropone (**17**) as a red-brown solid (1.03 g, 12%, R_f 0.21); 2,3-benzotropone (**21**) ^1H NMR δ 6.71 (ddd, $J = 12$, 8, 1 Hz, 1H), 6.96 (d, $J = 12$ Hz, 1H), 7.07 (ddd, $J = 12$, 8, 1 Hz, 1H), 7.33 (d, $J = 11$ Hz, 1H), 7.68 (m, 3H), 8.57 (dd, $J = 8$, 2 Hz, 1H); ^{13}C NMR δ 126.5, 130.3, 130.7, 132.2, 133.7, 135.3, 135.7, 136.1, 138.7, 139.3, 188.2; MS m/z (rel intensity) 156 (M^+, 85), 131 (13), 128 (100), 127 (27), 64 (21), 51 (26); HRMS calcd for $C_{11}H_8O$ 156.0575, found 156.0582; 4,5-benzotropone (**17**) mp 59−62 °C (lit.[57] mp 63−64 °C), ^1H NMR δ 6.82 (d, $J = 12$ Hz, 2H), 7.47 (d, $J = 12$ Hz, 2H), 7.60 (m, 2H), 7.68 (m, 2H); ^{13}C NMR δ 130.4, 134.0, 134.9, 136.0, 141.5, 188.3; MS m/z (rel intensity) 156 (M^+, 38), 133 (5), 128 (100), 64 (15), 51 (19); HRMS calcd for $C_{11}H_8O$ 156.0575, found 156.0577.

4,5-Benzotropone Tosylhydrazone (18).[5] A solution of 4,5-benzotropone **17** (625 mg, 4 mmol) and p-toluenesulfonylhydrazide (745 mg, 4 mmol) in 8 mL of absolute ethanol was stirred for 24 h. The resulting precipitate was isolated by vacuum filtration and washed with cold ethanol to afford the tosylhydrazone as a yellow solid (340 mg, 24%): mp 180−182 °C dec; ^1H NMR δ 2.41 (s, 3H), 6.43 (m, 2H), 6.64 (d, $J = 12$ Hz, 1H), 6.81 (d, $J = 12$ Hz, 1H), 7.30 (m, 6H), 7.69 (br s, 1H), 7.88 (d, $J = 8$ Hz, 2H); ^{13}C NMR δ 21.6, 119.1, 128.1, 128.9, 129.5, 130.2, 132.1, 132.4, 133.5, 134.4, 134.8, 135.3, 136.6, 138.8, 144.0, 152.6; MS m/z (rel intensity) 192 (7), 169 (74), 139 (100), 91 (99); electrospray ionization MS m/z 325 (MH^+); HRMS (electrospray ionization) calcd for $C_{18}H_{17}N_2O_2S$ 325.1011 (MH^+), found 325.1017.

2,3-Benzotropone Tosylhydrazone (22). A mixture of 2,3-benzotropone **21** (460 mg, 3.0 mmol) and p-toluenesulfonylhydrazide (490 mg, 2.6 mmol) in 5 mL of absolute ethanol was refluxed under nitrogen for 1 h and then stirred at room temperature for an additional 48 h. A light colored solid (91 mg), presumably a double tosylhydrazide adduct, was removed by vacuum filtration. The filtrate was concentrated and chromatographed (silica gel, 1:1 ether/hexanes) to afford unreacted 2,3-benzotropone (69 mg, 17%, R_f 0.29) and the tosylhydrazone as a bright yellow solid (263 mg, 31%, R_f 0.16): mp 132−134 °C (lit.[31] mp 134−135 °C); ^1H NMR δ 2.39 (s, 3H), 6.32 (m, 2H), 6.50 (ddd, $J = 12$, 7, 1 Hz, 1H), 6.92 (d, $J = 12$ Hz, 1H), 7.28 (d, $J = 8$ Hz, 2H), 7.33 (dd, $J = 8$, 2 Hz, 1H), 7.43 (td, $J = 7$, 2 Hz, 1H), 7.50 (td, $J = 7$, 2 Hz, 1H), 7.62 (br s, 1H), 7.80 (dd, $J = 8$, 2 Hz, 1H), 7.87 (d, $J = 8$ Hz, 2H); ^{13}C NMR δ 21.5, 121.1, 126.0, 128.1, 128.5, 129.0, 129.5, 130.2, 130.6, 131.8, 134.8, 135.4, 135.7, 136.5, 144.0, 152.6; MS m/z (rel intensity) 277 (11), 217 (100), 185 (53), 140 (100), 94 (44), 69 (62); HRMS (electrospray ionization) calcd for $C_{18}H_{17}N_2O_2S$ 325.1011 (MH^+), found 325.0994.

Benzotropone Tosylhydrazone Sodium Salts 19 and 23. Sodium hydride (60% dispersion in oil, 20 mg, 0.5 mmol) was slowly added to a solution of 4,5-benzotropone tosylhydrazone **18** or 2,3-benzotropone tosylhydrazone **22** (100 mg, 0.3 mmol) in 5 mL of dry CH_2Cl_2. The orange slurry was stirred under argon for 60 min and poured into 100 mL of hexane. The resulting bright orange precipitate was isolated by vacuum filtration and dried in vacuo (room temperature, $\leq 10^{-6}$ mmHg) before use. The salts were sensitive to moisture and thus were dried immediately.

4,5-Benzotropone hydrazone (20).[12] A solution of 4,5-benzotropone **17** (300 mg, 1.9 mmol) in 1.2 mL of absolute ethanol was added over 5 min to a solution of hydrazine monohydrate in 4.8 mL of ethanol at room temperature. The mixture was refluxed for 1 h and gradually darkened to a red-brown. After cooling and dilution with 35 mL of $CHCl_3$, the

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[57] Srivastava, K. C.; Dev, S. *Tetrahedron* **1972**, *28*, 1083−1091.

solution was washed with 3 × 15 mL of water. The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated to an orange solid. The hydrazone was purified by column chromatography (basic alumina, activity III, CHCl$_3$) as a bright red-orange solid (90 mg, 28%, R_f 0.09): ^{1}H NMR δ 5.26 (br s, 2H), 6.28−6.41 (m, 3H), 6.60 (d, J = 12.6 Hz, 1H), 7.14−7.26 (m, 4H); ^{13}C NMR δ 119.0, 128.2, 129.4, 130.8, 131.9, 132.9, 133.7, 135.2, 135.9, 137.0, 148.7.

2,3-Benzotropone Hydrazone (24). A solution of 2,3-benzotropone **21** (320 mg, 2.1 mmol) in 1.5 mL of absolute ethanol was added over 5 min to a solution of hydrazine monohydrate (290 mg, 6 mmol) in 5 mL of ethanol at room temperature. The mixture was refluxed for 20 h and gradually darkened to a red-brown. After cooling and dilution with 35 mL of CHCl$_3$, the solution was washed with 3 × 15 mL of water. The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated to an orange oil. The hydrazone was purified by column chromatography (basic alumina, activity III, CHCl$_3$) as a bright red-orange solid (90 mg, 28%, R_f 0.17): ^{1}H NMR δ 5.41 (br s, 2H), 6.17−6.23 (m, 1H), 6.28−6.31 (m, 2H), 6.79 (d, J = 12 Hz, 1H), 7.20−7.23 (m, 1H), 7.28 (td, J = 8, 1 Hz, 1H), 7.37 (td, J = 7, 1 Hz, 1H), 7.58 (d, J = 8 Hz, 1H); ^{13}C NMR δ 122.4, 126.3, 127.8, 128.0, 129.8, 103.0, 103.2, 134.5, 135.8, 137.5, 148.8.

Preparation and Matrix Isolation of Benzodiazocycloheptatrienes 15 and 16. (A) Pyrolytic method: benzotropone tosylhydrazone sodium salt **19** or **23** was transferred to a round-bottom flask that was affixed directly to the matrix isolation apparatus. The salt was heated in an oil bath (125 °C for **19**, 90 °C for **23**) at 10^{-7} mmHg and the pyrolysate co-deposited with argon onto a spectroscopic window at 30 K. **(B) Oxidative method:**[12] a suspension of silver oxide[58] (230 mg, 1 mmol) and benzotropone hydrazone **20** or **24** (90 mg, 0.5 mmol) in 25 mL of dry ether was stirred in the dark at 0 °C for 1 h. The solution was quickly filtered and transferred to a precooled round-bottom flask, and the solvent was removed by rotary evaporation in the dark at 0 °C. The dark orange solid was extracted with 5 × 2 mL of distilled hexane and the extracts were combined in a matrix-isolation deposition tube. Crude diazo compound was isolated as an orange solid after the hexane was removed by evaporation (0 °C at 0.02 mmHg). The diazo compound was matrix isolated by subliming the crude material (15 °C at 10^{-7} mmHg for both **15** and **16**) and co-depositing with argon at 30 K. 4,5-Benzodiazocycloheptatriene (**15**): IR (Ar, 10 K) 2045 vs, 1981 w, 1650 m, 1608 m, 1569 w, 1450 m, 1444 m, 1332 w, 1190 w, 1054 w, 891 m, 880 m, 775 s, 560 w cm^{-1}; UV/visible (Ar, 10 K) $\lambda_{\max}$ 365, 351, 338, 268, 260 nm. 2,3-Benzodiazocycloheptatriene (**16**): IR (Ar, 10 K) 3050 m, 3030 m, 2049 vs, 2040 vs, 1646 m, 1563 s, 1490 m, 1433 m, 1420 w, 1408 w, 1371 w, 1339 m, 1246 m, 1221 s, 1180 w, 1071 w, 1072 w, 1049 m, 953 m, 939 m, 882 s, 795 m, 750 s, 745 s, 686 s, 626 m, 598 w cm^{-1}; UV/visible (Ar, 10K) $\lambda_{\max}$ 376, 348, 332, 299, 259, 252 nm. In either method the matrix was cooled to 10 K prior to irradiation.

Thermolysis of 4,5-benzotropone tosylhydrazone sodium salt **19** (130 °C, 0.05 mmHg) in the dark in a sublimation apparatus afforded a dark orange solid (−78 °C coldfinger) that was nonvolatile and thus could not be co-deposited with argon to form a matrix. Proton NMR at room temperature indicated that the solid was a complex mixture of unknown composition.

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Supporting Information Available: Alternate synthesis of 2,3-benzotropone (**21**); attempted syntheses of diazirines **13** and **14**; additional spectra from matrix experiments; calculated energy, IR spectrum, and Cartesian coordinates of selected species. This material is available free of charge via the Internet at http://pubs.acs.org.

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