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Spectroscopic Characterization of Triplet 4,5-Benzocycloheptatrienylidene

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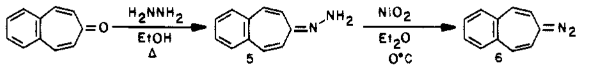
Abstract: 4,5-Benzodiazocycloheptatriene (**6**) has been prepared by the low temperature nickel peroxide oxidation of the hydrazone of 4,5-benzotropone. Thermolysis of **6** in benzene produces 4,5-benzocycloheptatrienylidene (**1**) which undergoes a facile carbene–carbene rearrangement to yield 2-naphthylcarbene (**2**) as evidenced by the formation of 7-(2-naphthyl)cycloheptatriene (**8**). Irradiation of **6** in a 2-methyltetrahydrofuran matrix at 4 K produces an ESR spectrum of triplet 4,5-benzocycloheptatrienylidene (**1**) with zero-field parameters of $|D|/hc = 0.52$ cm^{-1} and $|E|/hc = 0.021$ cm^{-1}. Excimer laser flash photolysis (308 nm) of **6** in benzene produces a transient spectrum of triplet 4,5-benzocycloheptatrienylidene (**1**) ($\lambda_{max} = 380$ and 395 nm). In hydrocarbon solvents (2,2,4-trimethylpentane and cyclohexane) the absorption spectrum of the 4,5-benzocycloheptatrienyl radical ($\lambda_{max} = 430$ nm) is also detected. Triplet 2-naphthylcarbene ($\lambda_{max} = 362$ nm) was not detected in any of the flash photolyses of 4,5-benzodiazocycloheptatriene (**6**). A competition between facile intersystem crossing from singlet to triplet **1** and intramolecular ring closure to **3** is consistent with the spectral data.

The rearrangement of 4,5-benzocycloheptatrienylidene (**1**) to 2-naphthylcarbene (**2**) has been investigated as a prototypical solution phase carbene–carbene rearrangement.[1] The experimental evidence is consistent with rearrangement of **1** to **2** in the singlet-state manifold[2] as shown in Scheme I, and the intermediacy of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3**) has been clearly demonstrated through Diels–Alder adduct formation.[3] However, the ground-state multiplicity of **1** and the role that the cycloheptatetraene **4**[4] plays in the rearrangement have not yet been determined. We now report the spectroscopic characterization of triplet **1** by ESR and laser flash photolysis techniques.

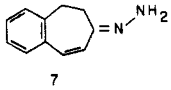
Results

Synthesis and Characterization of 4,5-Benzodiazocycloheptatrienylidene (6). 4,5-Benzodiazocycloheptatriene (**6**) was prepared from the hydrazone of 4,5-benzotropone (**5**) as shown in eq 1. Synthesis of the hydrazone **5** is readily accomplished



5 6 (1)

in 29% purified yield by the dropwise addition of a solution 4,5-benzotropone[5] to an excess of hydrazine hydrate in ethanol. Some reduction generally accompanies the formation of **5** as evidenced by the isolation of material whose spectral data are consistent with the half-saturated hydrazone structure **7**.[6]



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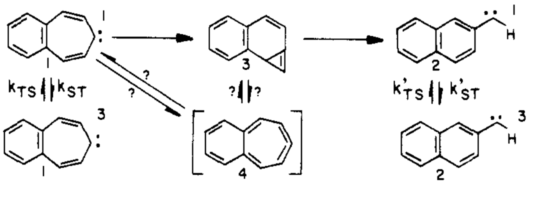
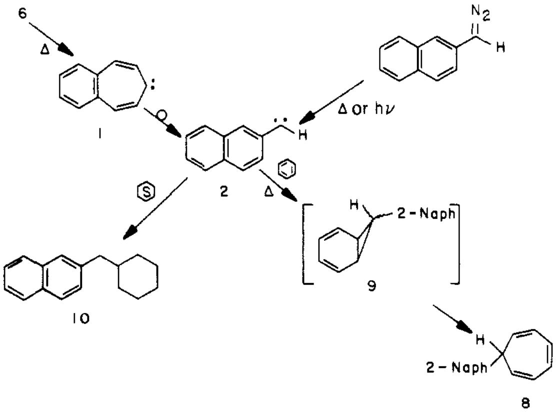
Oxidation of **5** to **6** proceeds efficiently with use of a slurry of nickel peroxide[7] in diethyl ether at 0 °C. The rapid, low temperature nickel peroxide oxidation is critical to the success of the synthesis because of the limited thermal stability of **6**. Initial separation of the diazo compound from unoxidized hydrazone can be accomplished by multiple extractions of the crude diazo compound by using ice-cold pentanes. Yields at this stage of purification can be as high as 50%. Since all attempts to crystallize **6** from pentanes or hexanes at low temperature failed, further purification was accomplished by sublimation or by chromatography on neutral alumina at −30 to −40 °C. The low temperature chromatographic technique provides isolated yields of **6** as high as 35%.

Scheme I



Scheme II



The red-brown diazo compound **6** exhibits a characteristic IR spectrum with a diazo group stretch at 2045 cm^{-1} in hexanes and a UV–vis spectrum with a strong, short wavelength absorption band (2,2,4-trimethylpentane, $\lambda_{max} = 230$ nm, log $\epsilon = 4.39$) and a long wavelength, low intensity absorption tail which extends to ca. 440 nm. The ^{1}H NMR in CDCl$_3$ shows only a sharp multiplet at 7.30 (4 H) and an AA′BB′ multiplet at δ 6.80–6.40 ($J \simeq 9$ Hz, 4 H) characteristic of symmetrically substituted 4,5-benzo-

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(6) ^{1}H NMR (CDCl$_3$) δ 7.30–7.00 (m, 4 H), 6.55, 6.30 (AA′BB′, quartet, $J = 12$ Hz, 2 H), 5.50–4.70 (s, br, 2 H), 3.05–2.45 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 152.10, 139.76, 136.03, 130.85, 129.70 (two carbons), 128.58, 127.17, 126.45, 31.32, 27.71; IR (neat film) 3368 (w), 3208 (w), 3015 (w), 2998 (w), 1611 (w), 1556 (w), 1489 (w), 1437 (w), 1104 (w), 801 (m), 749 (m); MS, *m/e* 70 (eV) 172 (M$^+$, base), 154, 141, 128, 115.

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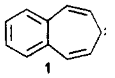
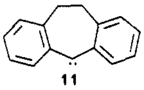
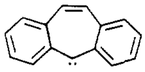
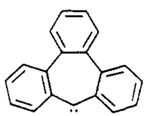
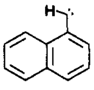
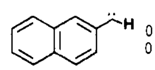
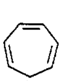
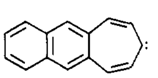
Table I. Zero-Field Parameters for 4,5-Benzocycloheptatrienylidene (**6**) and Some Related Carbenes

Carbene	$\lvert D\rvert/hc$, cm^{-1}	$\lvert E\rvert/hc$, cm^{-1}	$\lvert D\rvert/\lvert E\rvert$	Reference
 **1**	0.52	0.021	25	This Work
 **11**	0.3932	0.017	23	14
 **12**	0.3787	0.0162	23	14
 **13**	0.4216	0.0195	22	14
 **14**	0.741 (anti) 0.493 (cis)	0.0290 (anti)	23	15
 **2**	0.456 (anti) 0.443 (cis)	0.0202 (anti)	22	15
 **22**	0.317 0.425	0.0087 0.0222	36 19	41a 41b
 **26**	0.453	0.0193	23	41b

cycloheptatriene derivatives. Conspicuously absent in the ^{1}H NMR are any absorptions attributable to the NH_2 functionalty of the hydrazone **5**.

Thermolysis of **6** in benzene at reflux yields 7-(2-naphthyl)cycloheptratriene (**8**, 13%) the product also isolated from either the thermolysis or photolysis of the sodium salt of the tosylhydrazone of 4,5-benzotropone in benzene (Scheme II).[1a,8]

7-(2-Naphthyl)cycloheptatriene (**8**) is also formed by the thermolysis of 2-naphthyldiazomethane in benzene. The formation of **8** therefore requires a carbene–carbene rearrangement of 4,5-benzocycloheptatrienylidene (**1**) to 2-naphthylcarbene (**2**) as shown in Scheme II. The cycloheptatriene **8** presumably originates from the electrocyclic isomerization of 7-(2-naphthyl)norcaradiene (**9**)[9] which would be formed from the addition of **2**[10] to benzene. A similar mechanism has been postulated for the analogous addition reaction of 1-naphthylcarbene.[11]

Direct photolysis of **6** in cyclohexane gives a large number of products, the identification of most of which was precluded by their instability to either liquid or gas chromatography. A low yield (ca. 2–4%) of 2-(cyclohexylmethyl)naphthalene (**10**) was, however, isolated and identified through comparison with a sample prepared independently by the thermolysis of 2-naphthyldiazomethane in cyclohexane.[10] Thus, photolysis of 4,5-benzodiazocycloheptatriene (**6**) in cyclohexane or thermolysis in benzene yields products derived from 2-naphthylcarbene in analogy with

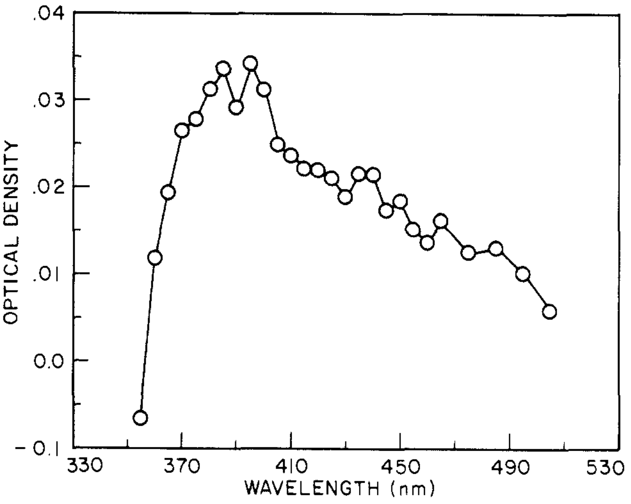
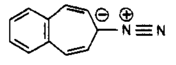


Figure 1. Transient absorption spectrum measured 100 ns after 308 nm pulsed irradiation of 4,5-benzodiazocycloheptatriene (**6**) in N_2-purged benzene.

the thermal and photochemical decomposition of the sodium salt of the tosylhydrazone of 4,5-benzotropone.[1a] The structural identity of **6** is therefore confirmed both by its spectral characteristics and its ability to act as a precursor for 4,5-benzocycloheptatrienylidene (**1**).

ESR Spectrum of Matrix Isolated Triplet 4,5-Benzocycloheptatrienylidene (1). Irradiation of **6** in either a methylcyclohexane or 2-methyltetrahydrofuran matrix between 4 and 12 K produces an ESR signal assigned to triplet **1**. The zero-field parameters $|D|/hc = 0.52$ cm^{-1} and $|E|/hc = 0.021$ cm^{-1} are similar to those of phenylcarbene[12] and larger than those of vinylcarbene.[13] Softening or melting the matrix results in loss of the ESR signal. Recooling and irradiation regenerates the original signal. Due to the low intensity of the ESR absorption and the instability of the carbene at higher temperatures, the temperature dependence of the signal intensity was not investigated. Summarized in Table I are the $|D|/hc$ and $|E|/hc$ values for **1**, several structurally related carbenes, and 1- and 2-naphthylcarbene. The $|D|/hc$ value for **1** is considerably larger than those observed for dibenzo[*a*,*d*]cycloheptadienylidene (**11**) or dibenzo[*a*,*e*]cycloheptatrienylidene (**12**)[14] thus indicating a smaller average distance between the interacting π and σ electrons at C-1. This may be a consequence of a nonplanar conformation of the seven-membered ring in matrix isolated **1** which would diminish the extent of delocalization of the π electron density compared to that in **11** and **12**. A similar argument has been advanced to explain the larger $|D|/hc$ value observed for **13** where there is substantial steric hindrance to planarity. A nonplanar conformation of the carbene precursor, 4,5-benzodiazocycloheptatriene (**6**), would in fact be expected by analogy with the favored "boat" conformation of 3,4-benzotropilidene.[16] In addition, the antiaromatic character of the planar resonance structure **15** of **6** should also favor adoption of a boat conformation in the glassy matrix. The conformational bias of the precursor **6** could possibly therefore accrue to the carbene.



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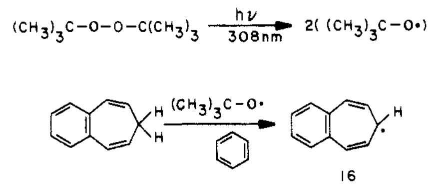
Scheme III



It has been previously noted[17] that the magnitude of the zero-field parameter $|E|/hc$ and the ratio $|D|/|E|$ both decrease as the carbene bond angle increases. These values thus provide an approximate measure of the decrease in 2s orbital character in the nonbonding σ orbital of the carbene with increased bond angle. While this analysis has been criticized,[18] there does seem to be a qualitative relationship between these parameters and carbene structure. The $|E|/hc$ value for **1** is similar to those measured for diphenylcarbene ($|E|/hc = 0.019$ cm^{-1})[19] and for tribenzo[*a*,*c*,*e*]cycloheptatrienylidene (**13**). On the basis of the correlation between ΔE_{ST} (singlet–triplet energy gap) and $|E|/hc$ recently suggested by Eisenthal[20] the ΔE_{ST} for **1** can be estimated at −3.5 to −4.0 Kcal/mol.

Transient Absorption Spectra of 4,5-Benzocycloheptatrienylidene (1). The excimer laser flash photolysis (308 nm, 15 mJ, 4 ns fwhm) of a 1.3×10^{-4} M, N_2-purged solution of diazo compound **6** in benzene produces the absorption spectrum shown in Figure 1. An identical spectrum is obtained regardless of whether **6** is purified by multiple pentane extractions, sublimation, or low-temperature chromatography. The observed transient appears within the duration of the excitation pulse and has two maxima at 380 and 395 nm. These maxima were reproduced in spectra obtained from independently prepared and purified samples. Other small features such as the apparent maximum at 430 nm were not. The transient has a long lifetime, decaying with an apparent pseudo-first-order rate of 2.0 (± 0.2) × 10^3 s^{-1}. The absorption spectrum is essentially identical with that observed for triplet **12** (λ_{max} = 380, 395, and 486 nm).[21] Irradiation of the sample with multiple laser pulses results in destruction of the diazo compound (monitored by FTIR at 2045 cm^{-1}) and elimination of the transient absorption. On the basis of the origin of the absorption spectrum, its strong kinetic and spectral resemblance to related carbenes,[22] and its characteristic carbene reactivity (vide infra), the 380- and 395-nm absorption bands are assigned to triplet carbene **1**. The appearance of triplet **1** within the 4 ns fwhm excitation pulse is consistent with the large singlet-to-triplet intersystem crossing rate observed for the related carbene, dibenzo[*a*,*d*]cycloheptatrienylidene (**11**) ($k_{ST} = 1.2 \times 10^{10}$ s^{-1}).[20]

Laser flash photolysis of **6** in 2,2,4-trimethylpentane produces a transient absorption spectrum similar to that observed in benzene (Figure 2a). However, a new transient (λ_{max} = 434 nm) is also present. This longer wavelength transient does not decay detectably within 1 μs and is the primary species observed in the flash photolysis of **6** in cyclohexane (Figure 2b). The observation of the 434-nm transient in aliphatic hydrocarbons but not in benzene implicates the 4,5-benzocycloheptatrienyl radical **16**. The origin of **16** would involve H-atom abstraction from solvent by triplet **1**, a process well documented for the dibenzannellated cycloheptadienylidenes[22] and cycloheptatrienylidenes.[21] The observed red shift of the absorption spectrum of the radical **16** compared to that of the triplet carbene **1** is also consistent with spectral data observed for the carbenes **11**, **12**, and **13** and their corresponding radicals.[21,22] Thus, the spectral characteristics of **1** and **16** are in accord with the general pattern observed for carbene systems having triplet ground states.[23]

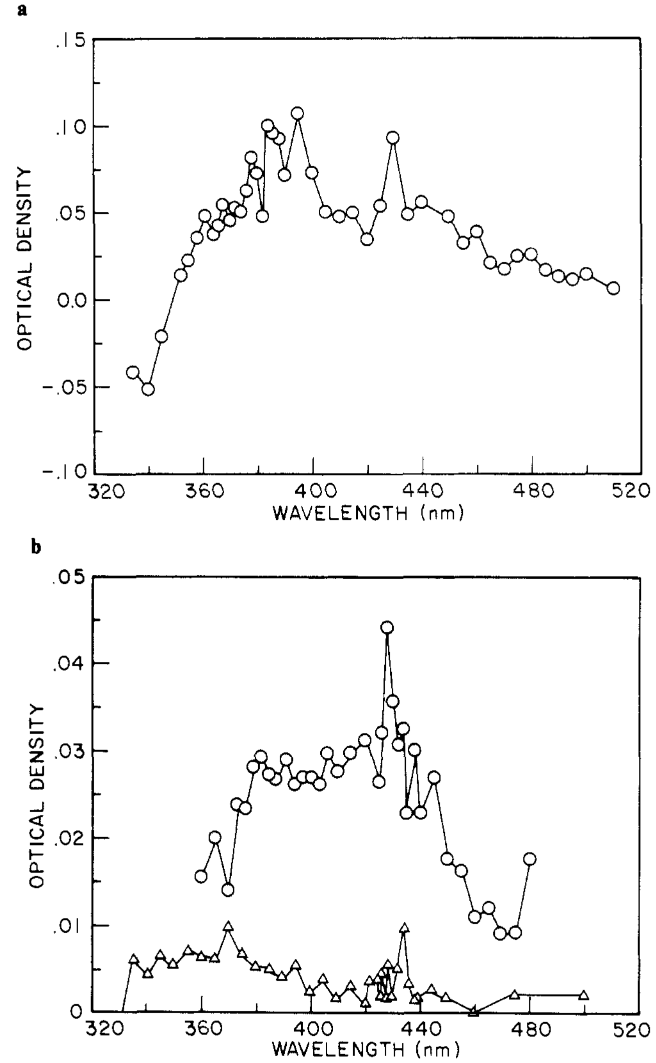


Figure 2. Transient absorption spectrum recorded 100 ns after the 308 nm excimer laser flash photolysis of 4,5-benzodiazocycloheptatriene (**6**) in (a) N_2-purged 2,2,4-trimethylpentane and (b) N_2-purged cyclohexane (○). Superimposed on this spectrum is the absorption spectrum from the 4,5-benzocycloheptatrienyl radical (**16**) recorded 200 ns after the 308 nm pulsed irradiation of a 1.02×10^{-2} M solution of 3,4-benzotropilidene in 4% V/V di-*tert*-butyl peroxide/benzene solution (△).

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[23] The triplet carbene absorption maxima for diphenylcarbene, fluorenylidene, 2,7-dichlorofluorenylidene, boranthrylidene, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptadienylidene, tribenzo[*a*,*c*,*e*]cycloheptatrienylidene, and 10,10-dimethyl-10-silaanthracen-9(10*H*)-ylidene are all blue shifted of those of the corresponding radicals. (a) Turro, N. J. *Tetrahedran* **1982**, *38*, 809. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198. (c) Hadel, L.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283. (d) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814. (e) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813. (f) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227. (g) Lapin, S. C.; Brauer, B. E.; Schuster, G. B. *Ibid.* **1984**, *106*, 2092. (h) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, N. T. H. *Chem. Lett.* **1983**, 1257.

In order to verify the assignment of the 434-nm transient as the 4,5-benzocycloheptatrienyl radical **16**, the radical was independently generated through H-atom abstraction from 3,4-benzotropilidene[24] by *tert*-butoxy radicals. Excimer laser decomposition of di-*tert*-butyl peroxide in benzene[22b] was used as a source of *tert*-butoxy radicals which subsequently react with 3,4-benzotropilidene to generate the radical **16** as shown in Scheme III. An absorption spectrum of **16** generated by the 308-nm flash photolysis of a 1.02×10^{-2} M solution of 3,4-benzotropilidene in 4% v/v di-*tert*-butyl peroxide/benzene is shown in Figure 2b. The control experiment of irradiation of 3,4-benzotropilidene alone at 308 nm showed no evidence of any transient between 370 and 450 nm. These spectra therefore show that the 4,5-benzocycloheptatrienyl radical **16** is characterized by a broad short wavelength absorption (λ_{max} = 370 nm) and a strong, sharp long wavelength band at 434 nm. Thus spectral agreement is found with the transient generated by the flash photolysis of **6** in 2,2,4-trimethylpentane or cyclohexane. A primary reaction pathway for triplet **1** in 2,2,4-trimethylpentane and cyclohexane is therefore H-atom abstraction. This pattern of reactivity is clearly analogous to that observed for the carbenes **11**, **12**, and **13**.[21,22]

Triplet 2-naphthylcarbene (**2**), the product of the carbene-carbene rearrangement of **1** followed by intersystem crossing (Scheme I) was not detected in any of the flash photolyses of **6**. Triplet **2** is, however, readily detectable under the experimental conditions used for the observation of triplet **1**[10] and can be shown to be spectrally and kinetically distinct from any of the transients observed in the flash photolysis of **6**. For example, the 308-nm laser flash photolysis of 2-naphthyldiazomethane in N_2-purged *n*-pentane or 2,2,4-trimethylpentane results in the formation of two transient absorptions between 300 and 800 nm. The shorter lived species shown in Figure 3a has a λ_{max} = 362 nm, appears simultaneously with the laser pulse, and decays with a pseudo-first-order rate constant of $3.33 \pm 0.4 \times 10^6$ in 2,2,4-trimethylpentane. The second intermediate (λ_{max} = 378 nm, 395 nm shoulder) exhibits a pseudo-first-order growth at the expense of the 362-nm transient (low intensity shoulder in Figure 3a, 60 ns) and is the only species 300 ns after excitation (Figure 3b). This long wavelength, long-lived species is significantly quenched by oxygen and can be observed in *n*-pentane, 2,2,4-trimethylpentane, and cyclohexane but is not observed in benzene. Thus, the 378-nm transient can readily be assigned as the 2-naphthylmethyl radical based on its characteristic lifetime, its reactivity, and the spectral agreement with the matrix isolation spectrum of the 2-naphthylmethyl radical measured by Porter and Strachan.[25] The short-lived, 362-nm transient shown in Figure 3a is observed in benzene as well as the aliphatic hydrocarbons. It is not observed, however, in cyclohexane where the 2-naphthylmethyl radical growth occurs simultaneously with the ca. 4 ns fwhm laser pulse. Oxygen, styrene, methanol, carbon tetrachloride, olefins, and a variety of other carbene-trapping reagents effectively quench this species. On the basis of its characteristic carbene reactivity, its kinetic correlation with the growth of the 2-naphthylmethyl radical in effective H-atom donating solvents, its formation within the excitation pulse, and the blue shift of its absorption maximum with respect to the radical[23] the 362-nm absorption can be assigned to triplet 2-naphthylcarbene (**2**).[10]

In the laser flash photolyses of **6** in 2,2,4-trimethylpentane, no 362-nm transient is observed. In addition, no transient with kinetic and spectral features consistent with triplet 2-naphthylcarbene (**2**) can be observed in the flash photolyses of **6** in benzene. The 308-nm irradiation of **6** in cyclohexane also clearly does not result in formation of detectable quantities of the 2-naphthylmethyl radical as evidenced by the lack of its characteristic absorption at 378 nm. Thus any mechanism postulated for the carbene-carbene rearrangement of 4,5-benzocycloheptatrienylidene (**1**) to 2-naphthylcarbene (**2**) must account for the absence of spectroscopically observable quantities of **2** under flash photolysis conditions. These results are most consistent with a mechanism in which the 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3**) has a substantial lifetime and isomerization to 2-naphthylcarbene is thermally activated (vide infra).

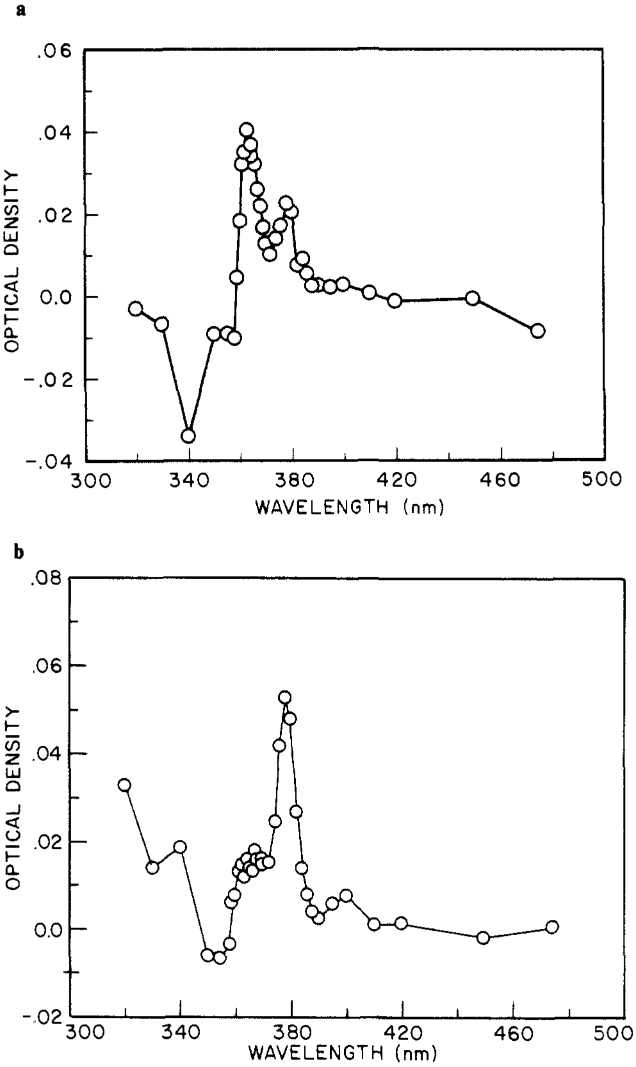

Figure 3. Transient absorption spectra obtained after the 308-nm excitation of 2-naphthyldiazomethane in N_2-purged *n*-pentane (a) 60 ns after excitation and (b) 300 ns after excitation.

Discussion

Many experimental investigations of carbene–carbene rearrangements have focused on the phenylcarbene rearrangements.[1-4] In particular, much of this work has involved the formation of phenyl- and tolyl-substituted carbenes under flash vacuum pyrolysis conditions.[26] The only examples of carbenes that have been observed to undergo solution phase carbene–carbene rearrangements are the benzannellated cycloheptatrienylidenes. Of these, 4,5-benzocycloheptatrienylidene (**1**) provided the first example of an ambient temperature carbene–carbene rearrangement.

The elegant experimental work of Jones[1] has provided valuable insight into the key mechanistic features of the rearrangement of **1** to 2-naphthylcarbene (**2**). The thermal or photochemical generation of 4,5-benzocycloheptatrienylidene (**1**) in benzene yields 7-(2-naphthyl)cycloheptatriene (**8**) and in cyclohexane gives 2-(cycylohexylmethyl)naphthalene (**10**), both products of the reactions of 2-naphthylcarbene. The rearrangement has been shown to not involve preliminary rearrangement of a nitrogen-containing precursor to 2-naphthyldiazomethane by the lack of formation

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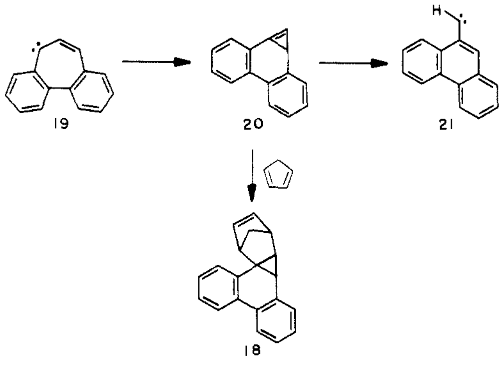
(24) Burdett, K. A.; Shenton, F. L.; Yates, D. H.; Swenton, J. S. *Tetrahedran* **1974**, *30*, 2057.

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

(26) Gaspar, P. O.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

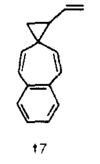
Scheme IV



of a pyrazoline with dimethyl fumarate.[1c] This result is corroborated by our investigations of **6**. Thermolysis of **6** in benzene at reflux yields no detectable 2-naphthyldiazomethane even though the complete decomposition of **6** occurs within minutes and 2-naphthyldiazomethane can be shown to have a half life of greater than $^1/_2$ h under identical conditions.

The rearrangement of **1** to **2** has also been shown to generate **2** specifically in its singlet state at its inception,[2] thus implicating rearrangement on the singlet energy surface. Evidence for this includes the fact that the stereospecificity of the cyclopropanation reaction of **2** (formed from **1**) with 2-butene increases in the presence of added triplet carbene quenchers such as 2,4-hexadiene and oxygen. In the absence of triplet quenchers, both singlet and triplet reactivity is observed for **2**. Recent evidence for a rapid singlet–triplet equilibrium and a large singlet-to-triplet intersystem crossing rate ($k_{ST} \geq 1 \times 10^8$ s^{-1})[10] for **2** are consistent with these observations.

The involvement of the valence satisfied intermediate 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**3**) in the rearrangement of **1** to **2** has also clearly been demonstrated by Diels–Alder adduct formation.[1,3] 1,3-Butadiene, tetracyclone, and cyclopentadiene have all been shown to give significant yields of the corresponding formal [4 + 2] adducts with **3**. For 1,3-butadiene as the trap, it can be shown that the formal Diels–Alder product does not arise from the thermal rearrangement of 1-vinyl-6,7-benzospiro[2.6]-nona-4,6,9-triene (**17**) even though this product is isolated in 3% yield.[3] While it could be mechanistically argued that **3** might not be on the rearrangement path, the benzannellated bicyclo-[4.1.0]hepta-2,4,6-trienes have been trapped only in those instances where carbene–carbene rearrangements are observed. In particular, the isolation of essentially quantitative yields of the Diels–Alder product **18** from the rearrangement of 2,3,4,5-dibenzocycloheptatrienylidene (**19**) strongly argues for its involvement in the rearrangement (Scheme IV).[3] More importantly, independent generation of **20** has yielded products resulting from solvent insertion by phenanthrylcarbene (**21**). Thus, the viability of benzannellated bicyclo[4.1.0]hepta-2,4,6-triene **20** as a precursor for **21** has been validated.[27]



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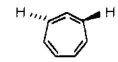
The bicyclo[4.1.0]hepta-2,4,6-triene **3** has also recently been spectroscopically characterized by matrix isolation IR techniques.[28] Irradiation of 2-naphthyldiazomethane (λ > 364 nm) in an argon matrix resulted in formation of a species exhibiting infrared absorptions at 1755 and 1750 cm^{-1}, the position and intensities of which are compatible with the cyclopropene structure. Deuteriation resulted in a characteristic 45-cm^{-1} shift of the cyclopropene ring vibration and ruled out the allene structure **4**. Importantly, the formation of **3** from **2** was shown to not involve an intermediate ring expansion to the allene **4**.

Two key mechanistic questions concerning the rearrangement of 4,5-benzocycloheptatrienylidene to 2-naphthylcarbene still remain: one, is **1** a discrete carbene with a finite lifetime and characteristic reactivity, and if so, what is its ground-state multiplicity? And two, is the allene **4** ever formed from **1** or **3**? If **4** is formed from either **1** or **3**, then it also remains to determine whether **4** is a key intermediate in the rearrangement of **1** to **2**. These questions are primarily raised as a result of the intriguing duality of reactivity observed for the parent cycloheptatrienylidene (**22**).[29]

While semiempirical INDO calculations[4a,30] place singlet cycloheptatrienylidene (**22**) lower in energy than singlet phenylcarbene, they also suggest that the nonplanar cyclohepta-1,2,4,6-tetraene (**23**), the valence isomer of **22**, is the lowest energy species on the singlet surface by ca. 48 kcal/mol. The MINDO/3 calculations of Dewar and Landman[31] place singlet cycloheptatrienylidene 26.8 kcal/mol below phenylcarbene and once again suggest a nonplanar allene valence isomer as the best structure for the lowest energy C_7H_6 singlet species. The ab initio calculations by Radom[32] are in qualitative agreement with these semiempirical calculations locating nonplanar cyclohepta-1,2,4,6-tetraene (**23**) 17.9 kcal/mol (15.8 kcal/mol when optimized at the 4-31G level) below singlet **22**. CNDO/2 and extended Huckel calculations,[33] however, place phenylcarbene below cycloheptatrienylidene. Interestingly, Waali[34] has suggested on the basis of MNDO calculations that the planar singlet carbene structure is the transition-state structure for the interconversion of the enantiomeric cyclohepta-1,2,4,6-tetraenes (**23**). If correct, this would imply that all observed bimolecular chemistry results from the allene structure **23**.

22



23

A series of experiments is consistent with the theoretical predictions of a lowest energy singlet cyclohepta-1,2,4,6-tetraene structure. Saito et al.[35] have shown that the reactive species generated by the thermolysis of the tropone tosylhydrazone sodium salt undergoes formal [4 + 2] cycloaddition reactions with anthracene and diphenylisobenzofuran. A concerted [4 + 2] cycloaddition reaction of allene **23** seems to be the most likely mechanistic explanation though alternate nonconcerted mechanisms involving a carbene can be postulated. Following the suggestion of Untch's[36] earlier work on the dehydrochlorination of the chlorocycloheptatrienes, Jones and Mayor[37] were also able to provide evidence for the intermediacy of the allene **23** in the dehydrochlorination of 2-chlorocycloheptatriene. Their initial report was followed by definitive evidence for the formation of cyclohepta-1,2,4,6-tetraene from the dehydrobromination of bromocycloheptatriene.[38] Both dehydrobromination of bromocycloheptatriene with potassium menthoxide and dehydrobromination of optically active monodeuteriobromocycloheptatriene produced optically active diphenyl–isobenzofuran adducts. Since the allene **23** is nonplanar and therefore chiral while planar **22** is not, these experiments strongly implicate the allene **23** as the species being trapped.

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[28] (a) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334. (b) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1985**, *51*, 1316.

[29] Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391.

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[31] Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179.

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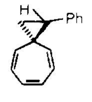
[36] Untch, K. International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan, August 1970.

[37] Mayor, C.; Jones, W. M. *Tetrahedron Lett.* **1977**, 3855.

[38] Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329.

Cyclohepta-1,2,4,6-tetraene (**23**) has also been detected by matrix isolation techniques.[39] Irradiation of phenylmethylene in an argon matrix at 10 K with light of $\lambda > 478$ nm gave a species exhibiting weak allene bands in the infrared spectrum. The same species was detected upon deposition of the pyrolysate of phenyldiazomethane in an argon matrix. Deuterium labelling studies were consistent with the assignment of an allene structure. The photochemical generation of **23** from phenylmethylene does not, of course, verify the involvement of **23** in the thermal rearrangement of **1** to **2**. It does, however, demonstrate that the allene can exist as a distinct, isolable chemical species.

However, in spite of evidence for the intermediacy of cyclohepta-1,2,4,6-tetraene (**23**), several experiments are consistent only with the carbene structure **22**. For example, in the dehydrobromination of bromocycloheptatriene with potassium menthoxide, studied by Jones, when styrene was used as a trap for cyclohepta-1,2,4,6-tetraene (**23**), the isolated spirononatriene **24** showed no optical rotation. This is the result one would expect for trapping the carbene **22** rather than a $\pi^2s + \pi^8s$ styrene plus allene cycloaddition. While this is negative evidence favoring participation by the carbene **22**, other experiments are more definitive. Kirmse has shown that either the photochemical decomposition of the tropone tosylhydrazone sodium salt in methanol or the dehydrochlorination of chlorocycloheptatriene with sodium ethoxide result in formation of the tropyl ether **25**.[40] This product is that expected from the reaction of the carbene **22**. The strained allene **23** is expected to give a vinyl ether rather than the observed allyl ether when trapped with RO^-/ROH. Thus, the carbene **22** is implicated in at least two types of bimolecular reactions.



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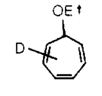
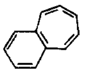


25

Within the last year two groups[41] have also provided direct evidence that the triplet state of **22** is generated upon photolysis of diazocycloheptatriene. Thermolysis of the tropone tosylhydrazone sodium salt and deposition of the product diazocycloheptatriene in argon at 12 K followed by irradiation produces a strong ESR signal assigned to triplet **22**. While the two groups have reported significantly different $|D|/hc$ and $|E|/hc$ values for triplet **22**,[41] there is no question that a triplet species with characteristic carbene reactivity is produced. Thus, the triplet state must either be the ground state of carbene **22** or lie within several calories per mol of the ground state. No photochemical or thermal conversion of triplet **22** to **23** has been detected. It thus appears that there is good evidence for the involvement of a discrete carbene **22** as well as an allene **23** in the reactions of the C_7H_6 species.

How is this situation then modified by benzannellation in the 4,5 position? While cycloheptatrienylidene **22** dimerizes to heptafulvalene in solution but does not rearrange to phenylcarbene, 4,5-benzocycloheptatriene (**1**) undergoes a facile rearrangement to 2-naphthylcarbene at temperatures as low as −78 °C.[42] Our EPR data now show that triplet 4,5-benzocycloheptatrienylidene (**1**) is the ground state of carbene **1** or lies within a few calories per mol of the ground state. In benzene solution it has a relatively long lifetime and a UV–vis spectrum similar to those of related triplet carbenes (vide supra). Thus, it shows similar energetic relationships to the parent cycloheptatrienylidene **22**. The triplet ground state of **1** is consistent with the MNDO calculation of Waali[34,43] but not the ab initio calculations of Radom.[32] Most interestingly, both through spectroscopic and product studies we have now established clear evidence for H-atom abstraction by triplet **1**. The naphthoannellated cycloheptatrienylidene **26** shows similar reactivity.[41b,44]

In contrast to the parent C_7H_6 system, to date there is no experimental evidence for the involvement of the allene valence isomer **4** in the solution phase reactions of **1**. Classical valence resonance energy arguments would suggest that the loss of aromatic resonance energy in **4** would make this an energetically, more difficultly accessible species than cyclohepta-1,2,4,6-tetraene (**23**). INDO calculations are consistent with these simple qualitative arguments, placing **4** only 7.3 kcal/mol below singlet **1**. Under gas-phase pyrolysis conditions the related allene, 4,5-benzocyclohepta-1,2,4,6-tetraene (**27**), is probably involved in the interconversion of 1- and 2-naphthylcarbene.[45] A recent investigation has tentatively assigned the 4,5-benzocyclohepta-1,2,4,6-tetraene structure to a minor product condensed at 15–25 K from the flash pyrolysate of either 1- or 2-naphthyldiazomethane.[28b] However, the involvement of **4** in these rearrangements even at high temperatures is not indicated.



27

Conclusion

We have definitively demonstrated that triplet 4,5-benzocycloheptatrienylidene (**1**) is a discrete chemical intermediate exhibiting bimolecular reactivity such as H-atom abstraction. The matrix isolation EPR data suggest either that the triplet state is the ground state of **1** or that the triplet state lies within a few calories per mol of the ground state. The observation of triplet **1** in fluid solution at ambient temperature upon direct photolysis of 4,5-benzodiazocycloheptatriene (**6**) shows that intersystem crossing from singlet **1** (or a singlet precursor to **1**) is competitive with ring closure to the bicyclo[4.1.0]hepta-2,4,6-triene (**3**). The lack of spectroscopically detectable 2-naphthylcarbene (**2**) from the flash photolysis of 4,5-benzodiazocycloheptatriene (**6**) is consistent with a significant lifetime for **3** ($\geq$several μs) and a thermally activated (endothermic) ring opening to 2-NC as suggested by recent SCF force-field thermochemical calculations.[46]

Experimental Section

General Methods. Melting points were obtained by using a Buchi circulating oil melting point apparatus and are uncorrected. NMR spectra were recorded either on a Bruker AM300 (300 MHz) or a Varian EM-360L (60 MHz) spectrometer. All ^1H chemical shifts are reported relative to TMS as an internal standard. Infrared (IR) spectra were recorded on a Perkin-Elmer 727-B scanning spectrophotometer. Low resolution mass spectra were taken with a Hewlett Packard Model 5985 mass spectrometer, and high resolution mass data were obtained on the Model CFC100B mass spectrometer of the NIH regional mass spectral laboratory at the Massachusetts Institute of Technology.

Materials. Cyclohexane and 2,2,4-trimethylpentane (Aldrich, Gold Label) were distilled from lithium aluminum hydride (LAH) prior to use. Benzene (Baker, reagent grade) was shaken with sulfuric acid, washed with water, dried over anhydrous magnesium sulfate, and distilled from calcium hydride. Acetonitrile (Aldrich, Gold Label) was distilled from calcium hydride. All other solvents were reagent grade and were used without additional purification unless otherwise noted.

4,5-Benzotropone was prepared by the method of Ewing and Paquette.[5] 2-Naphthyldiazomethane was prepared in the usual manner.[47] Samples of 2-naphthyldiazomethane for flash photolysis were purified

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(40) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935.

(41) (a) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713. $D/hc = 0.317$ cm^{-1}, $E/hc = 0.0087$ cm^{-1}. (b) Kuzaj, M.; Luerrsen, H.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 480. $D/hc = 0.425$ cm^{-1}; $E/hc = 0.0222$ cm^{-1}.

(42) The formation of heptafulvalene in solution may involve cyclohepta-1,2,4,6-tetraene (**23**)[1c] since 2,7-substitution of **22** does induce rearrangement to the corresponding phenylcarbene. Mayor C.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4498.

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by sublimation of the initially crystallized material at 0.2 Torr and temperatures between 30 and 45 °C. (**Caution!** While no explosions were encountered, all sublimations were carried out behind an explosion shield). The sublimed 2-naphthyldiazomethane had a mp of 44–45 °C (with gas evolution). Di-*tert*-butyl peroxide was purified by passage through alumina[22b] immediately before use.

Apparatus. The excitation source for the laser flash photolyses was a Quanta Ray EXC-1 excimer laser which produces 4 ns fwhm pulses of up to 20 mJ at 308 nm. The excitation energy can be varied by regulation of the high voltage discharge. The excitation beam is controlled by a 1.5 in. by 6 in. focal length cylindrical lens to give a ca. 3 mm by 11 mm irradiation area at the sample cuvette. The beam is not focused in the sample.

The probe source consists of a United States Scientific Instruments CP-3 Xenon flashlamp and model MCP-3 trigger module operated in pulsed mode with a controlled, high-voltage, capacitive discharge. The monitoring beam is approximately 2 × 3 mm and is arranged in a perpendicular orientation to the excitation source. The probe beam is monitored with a 1P28 photomultiplier tube (four dynodes used) mounted on an Oriel Model 7240 1/4 meter monochromator. Timing among the laser excitation pulse, the probe beam, and the detection system is achieved through a Model 113 DR digital delay generator (California Avionics Lab., Inc.). All transient pulses are digitized by a Tektronix 7912AD transient digitizer (7A19 vertical amplifier, 7B90P timebase) which is interfaced to a Hewlett Packard 9816 microcomputer. This allows for rapid processing and storage of the data and provides hard copy graphic capabilities. Each trace is also displayed on a NEC 11 in. TV monitor.

Laser pulse energies are monitored with a Laser Precision Corp. RKP314 energy head and are usually in the range of 15 mJ. Since the pulse-to-pulse energy reproducibility of the EXC-1 laser when operated in a single pulse mode is ±5%, a Hamamatsu S1226-5BQ silicon photodiode is used to monitor a reflection of the excitation beam in order to normalize the pulses for spectral purposes. The routine time resolution of the instrument is from 10 ns to 1 ms.

ESR Spectrum of Triplet 4,5-Benzocycloheptatrienylidene (6). ESR spectra were obtained with a Varian E-112 X-band ESR spectrometer equipped with a modified microwave cavity with a series of louvres on one side for sample irradiation. A solution (~0.1 M) of 4,5-benzodiazocycloheptatriene (purified as described below by low-temperature chromatography) was prepared in 2-methyltetrahydrofuran (Aldrich, Gold Label) in a 4-mm Suprasil quartz sample tube. The sample was sealed under vacuum after 3 freeze-pump-thaw cycles to remove oxygen. The sample was then placed in the ESR cavity and cooled to 4–12 K by using an Air Products helium transfer line and glass dewar. The sample was then irradiated with a Schoeffel 1000-W high pressure Hg–Xe lamp for 5 min, and the carbene spectrum was obtained at 10 mW of microwave power. The sample was then removed from the cavity, the matrix was thawed, and the sample was returned to the cavity and recooled to 4–12 K. Under these identical spectral conditions no triplet spectrum was observed. Further irradiation at 4 K did regenerate the initial spectrum.

4,5-Benzotropone Hydrazone (5). A solution of 4,5-benzotropone (250 mg, 1.6 mmol) in 1 mL of absolute ethanol was added dropwise over 10 min to a magnetically stirred solution of hydrazine hydrate (240 mg, 4.8 mmol) in 4 mL of absolute ethanol. The resulting orange-yellow solution was heated at reflux for 1 h, cooled to room temperature, and diluted with 35 mL of chloroform. The chloroform solution was washed 3 times with 10–15-mL portions of water and dried over sodium sulfate. Filtration and concentration in vacuo yielded 136.2 mg of a red-orange solid. Chromatography on basic alumina (eluant chloroform R_f 0.18 on neutral alumina plates) yielded orange-red plates of 4,5-benzotropone hydrazone (**5**) (80 mg, 29% mp 125–127 °C, crystallized from ether/hexane): ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.15 (s, 4 H), 6.55–6.13 (m, 4 H), 4.7 (broad s, 2 H, NH_2); IR ($CHCl_3$) 3400 (m), 3000 (m), 1640 (m), 1465 (m), 1075 (m), 820 (s) cm^{-1}; MS, *m/e* 170 (M^+), 141, 140, 139, 128 (base, $-CH_2N_2$), 115; HRMS $C_{11}H_{10}N_2$ *m/e* 170.0843 (calcd 170.0844).

4,5-Benzodiazocycloheptatriene (6). To a solution of 4,5-benzotropone hydrazone (136 mg, 0.8 mmol) in 25 mL of diethyl ether (distilled form LAH) which was maintained at 0 °C in the dark was added 400 mg of nickel peroxide.[7] This slurry was vigorously stirred at 0 °C for 5 min and then rapidly filtered through a sintered glass frit into a receiving flask precooled to 0 °C. The ether was then removed at low temperature (ca. 0–5 °C), and the resulting brown residue was extracted with 2–3 mL of hexanes (distilled over calcium hydride). The crude diazo compound was then transferred with use of hexanes to a 14 cm by 1.5 cm diameter jacketed column of neutral alumina (Fluka, Type 507 C) packed with hexanes which had been precooled to −35 °C by using a methanol–dry ice solution pumped through the circulating jacket. Methylene chloride was used to move the crude material onto the column. Rapid elution (flash chromatography) with hexanes with use of a positive pressure of nitrogen into a 0 °C receiving flask yielded a dilute solution of 4,5-benzodiazocycloheptatriene in hexanes. Concentration in vacuo at 0 °C yielded a brown solid (47 mg, 0.28 mmol, 35%). All attempts to crystallize **6** at low temperature failed: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.30 (m, 4 H), 6.80 and 6.40 (AA′BB′ m, $J = 9$ Hz, 4 H); IR ($CHCl_3$) 2045 cm^{-1}; UV (2,2,4-trimethylpentane $\lambda_{max} = 230$ nm, log $\epsilon = 4.39$, tail to 440 nm.

4,5-Benzodiazocycloheptatriene. Thermolysis in Benzene. A solution of 4,5-benzodiazocycloheptatriene (**6**) (148.7 mg, 0.99 mmol) in 15 mL of benzene was added dropwise to 400 mL of benzene at reflux under nitrogen. The resulting orange solution was heated at reflux for 20 h and cooled to room temperature, and the solvent was removed in vacuo to yield 137.7 mg of an orange solid. An initial purification of the residue was accomplished by chromatography on neutral alumina (Fluka type 507 C, eluant hexanes). The material with R_f 0.57–0.78 (TLC, silica gel, 20% ethyl acetate in hexanes, 54.7 mg) was rechromatographed on neutral alumina (eluant hexanes) to yield 7-(2-naphthylcycloheptatriene) (25.7 mg, 13%) which was spectrally identical with independently prepared material.[8]

Transient Absorption Spectra. 4,5-Benzocycloheptatrienylidene (1). A 1.28×10^{-4} M stock solution of 4,5-benzodiazocycloheptatriene (**6**) was prepared in 2,2,4-trimethylpentane which had been purified as described above. Aliquots (2–3 mL) were then placed in a 10 mm × 10 mm (3 mL) quartz fluorescence cuvette which was fitted with a Teflon stopcock used for introduction of the sample and N_2 purging. The sample was then degassed by bubbling oxygen-free nitrogen through the solution for 3 min by means of a 1-mm diameter Teflon tube. Single pulse (308 nm, ca. 15 mJ per pulse) wavelength-by-wavelength, time-resolved absorption data were then taken at ca. 2-nm intervals. The monochromator entrance and exit slits were adjusted to maintain ca. 2-nm spectral resolution over the entire region scanned. Spectral data points represent an average of two or three independent absorption measurements. The samples were mixed vigorously between excitation pulses and were changed before observation of a 5% decrease in optical density at a chosen wavelength. Thus, changes in absorbance due to sample depletion by laser excitation were minimized.

All stock solutions of 4,5-benzodiazocycloheptatriene were kept at ca. −20 °C and were prepared and used within ca. 6 h of their preparation due to the instability of the diazo compound. Stock solutions (1.14–3.2×10^{-4} M) in benzene, cyclohexane, and acetonitrile were prepared and used in an analogous manner to that described for 2,2,4-trimethylpentane. UV–vis absorption spectrum in 2,2,4-trimethylpentane: (100 ns after excitation) broad absorbance ca. 360–420 nm, $\lambda_{max} = 384$ and 395 nm, sharp absorbance, $\lambda_{max} = 434$ nm; cyclohexane (100 ns after excitation) UV sharp absorbance, $\lambda_{max} = 434$ nm.

4,5-Benzocycloheptatrienyl Radical. A 1.02×10^{-2} M solution of 3,4-benzotropilidene[16] in 4% V/V di-*tert*-butyl peroxide/benzene was placed in a 10 mm × 10 mm quartz fluorescence cuvette and degassed by bubbling oxygen-free nitrogen through the sample. Single pulse (308 nm, 8 mJ per pulse) wavelength-by-wavelength time-resolved absorption data were taken at 1–5-nm intervals. Spectral resolution of the monochromator was maintained at better than ca. 1 nm. The spectral data points represent an average of two separate absorption measurements. All samples were mixed between absorption measurements. Transient absorbance (200 ns after excitation): UV–vis broad absorbance 350–420 nm ($\lambda_{max} = 370$ nm); sharp absorbance $\lambda_{max} = 434$ nm.

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