

Generation, Characterization, and Rearrangements of 4,5-Benzocyclohepta-1,2,4,6-tetraene

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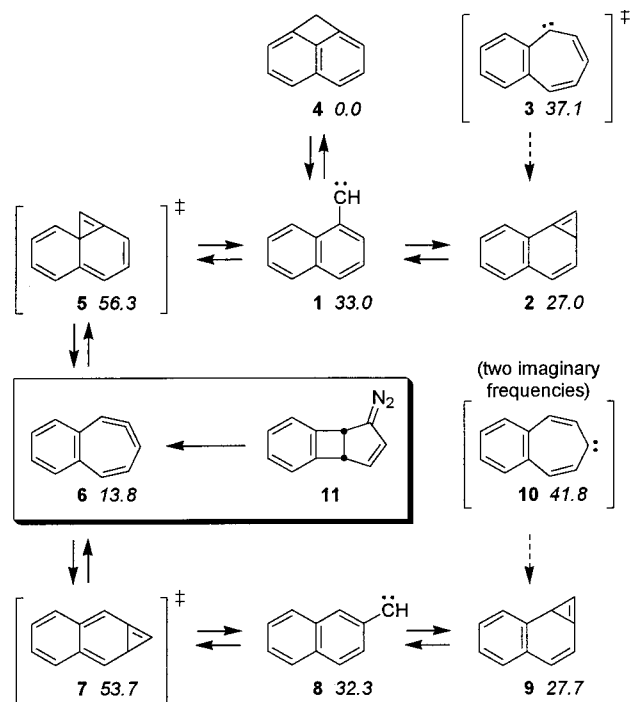
Received April 13, 2000

Revised Manuscript Received August 3, 2000

The complex chemistry of the $C_{11}H_8$ potential energy surface involves several fascinating skeletal rearrangements (Scheme 1).¹ 1-Naphthylcarbene (**1**), 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**), and 2,3-benzocycloheptatrienylidene (**3**) interconvert thermally in solution and photochemically in low-temperature matrices, as do the corresponding isomers in the 2-naphthylcarbene series (**8**, **9**, and **10**).^{2,3} Although the 1- and 2-naphthylcarbene rearrangement manifolds remain independent at moderate temperatures, a pathway connecting the two manifolds becomes accessible at higher temperatures. Flash vacuum pyrolysis of either 1- or 2-naphthylmethane^{4,5} or the highly exothermic reaction of naphthalene with atomic carbon⁶ affords cyclobuta[de]naphthalene (**4**), which arises from C–H insertion in 1-naphthylcarbene (**1**). 4,5-Benzocyclohepta-1,2,4,6-tetraene (**6**) has long been postulated as the key intermediate in the interconversion pathway connecting the isomeric 1- and 2-naphthylcarbenes (**1** and **8**), and recent density functional theory calculations support this interpretation.⁷ Yet, despite 20 years of study, direct experimental evidence for allene **6** remains confoundingly elusive,⁸ and the mechanism of the naphthylcarbene rearrangements remains the target of scrutiny.^{3–5,7}

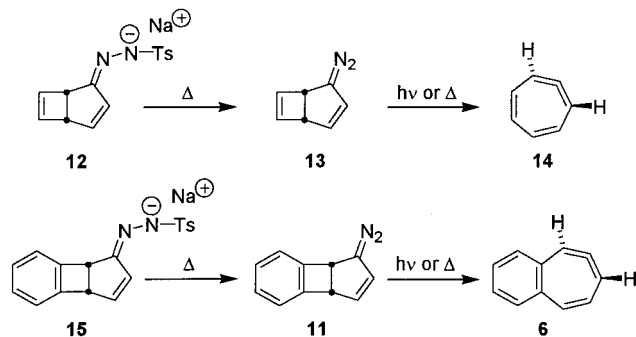
We report herein the generation, spectroscopic characterization, and photochemical and thermal reactivity of 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**). In devising a suitable route to **6**, we adapted the novel diazo precursor **13** that Chapman and Abelt utilized to generate the parent cyclohepta-1,2,4,6-tetraene (**14**) (Scheme 2).⁹ Synthesis of the α,β -unsaturated tosylhydrazone salt **15** proceeded from the corresponding saturated ketone, 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one,¹⁰ following the general protocol of Chapman and Abelt.⁹ Isolation of neat diazo compound **11** by the conventional thermolysis of tosylhydrazone salt **15** is problematic, as the deep purple diazo compound decomposes rapidly, even on a -78°C coldfinger. Matrix isolation of diazo compound **11** is achieved by pyrolysis of salt **15** and direct co-deposition of

Scheme 1^a



^a B3LYP/6-31G* relative energies (kcal mol⁻¹) given in italics (singlet state + ZPVE; ref 7).

Scheme 2



the pyrolysate with argon at cryogenic temperatures. The experimental and B3LYP/6-31G*^{11,12} calculated¹³ IR spectra for 2-diazo-6,7-benzobicyclo[3.2.0]hepta-3,6-diene (**11**) are in good accord (Figure 1).

Broadband irradiation ($\lambda > 571$, > 472 , or > 237 nm) of diazo compound **11**, matrix isolated in argon at 10 K, results in the complete disappearance of **11** accompanied by the appearance of 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**): IR (Ar, 10 K) 3060

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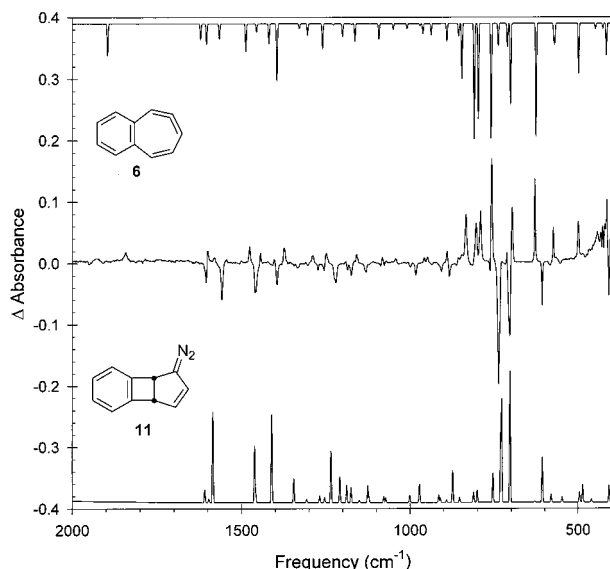
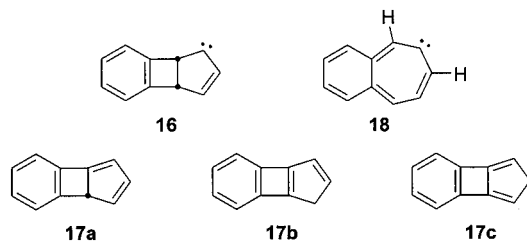


Figure 1. Top: Computed IR spectrum (B3LYP/6-31G*, scaled by 0.98) of 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**). Center: IR difference spectrum showing the appearance of **6** and disappearance of diazo compound **11** upon irradiation at $\lambda > 237$ nm, 40 min (Ar, 10 K). Bottom: Computed spectrum (B3LYP/6-31G*, scaled by 0.97) of diazo compound **11**.

m, 3030 m, 1842 w, 1600 w, 1476 w, 1445 w, 1374 w, 1290 w, 1248 w, 1159 w, 891 w, 834 m, 805 m, 792 m, 759 s, 735 w, 713 w, 697 m, 630 s, 574 m, 500 m cm^{-1} ; UV/visible (Ar, 10 K) λ_{max} 230 nm. The experimental and computed IR spectra for 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) display excellent agreement (Figure 1), and the absence of additional IR absorptions in the experimental spectrum establishes that **6** is the predominant photoproduct. The characteristic IR, UV/visible, and ESR spectra of benzobicyclo[4.1.0]heptatrienes **2** and **9** and triplet naphthylcarbenes **1** and **8** are not observed.³ Alternate structures 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-ylidene (**16**; either singlet or triplet), H-shift products **17a–c**, and planar 3,4-benzocycloheptatrienyliidene (**18**; triplet) can be ruled out on the basis of their



calculated IR spectra.¹⁴ B3LYP calculations suggest that singlet **18** is not a minimum on the potential energy surface.^{7,14} The computed barrier to ring opening of singlet **16** to **6** is 4.4 kcal/mol, while that for a 1,2 hydrogen shift to give **17a** is 24.5 kcal/mol.^{14,15} As in the case of the photochemical conversion of diazo compound **13** to cycloheptatetraene **14**,⁹ it is not clear whether the rearrangement of **11** to **6** occurs in the excited state of the

(14) Information available as Supporting Information.

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diazo compound, bypassing carbene **16**, or whether carbene **16** is formed with sufficient vibrational activation to undergo ring opening to allene **6**.

Benzocycloheptatetraene **6** does not display an efficient photochemical rearrangement, and the IR spectra display only very minor changes under a variety of irradiation conditions. Nevertheless, short wavelength irradiation ($\lambda > 237$ nm) of allene **6** affords weak signals for the characteristic UV/visible and ESR spectra of triplet 2-naphthylcarbene (**8**).^{3b,14,16} Triplet 1-naphthylcarbene (**1**) is not observed. From earlier studies,^{3b} we know that 2-naphthylcarbene (**8**) photoequilibrates with 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**) under these irradiation conditions. Although **9** could not be detected spectroscopically, its presence in low concentration was inferred from the fact that subsequent band-pass irradiation ($\lambda = 290 \pm 10$ nm) led to the expected increase in intensity of triplet 2-naphthylcarbene (**8**).

Thermolysis of tosylhydrazone sodium salt **15** (90–110 °C, 2×10^{-2} mmHg) followed directly by flash vacuum pyrolysis of the resulting diazo compound **11** (600 °C, 2×10^{-2} mmHg) produces an isolable mixture of cyclobuta[de]naphthalene (**4**, 51%), 1-methylnaphthalene (23%), 2-methylnaphthalene (9%), and naphthalene (17%) in low chemical yield. This result suggests that 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) is indeed a competent intermediate in the thermal equilibration of 1- and 2-naphthylcarbenes (**1** and **8**). Previously, West et al. reported a tentative assignment for 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) on the basis of several IR absorptions common to the pyrolysis/matrix isolation quenching of 1- and 2-naphthylidiazomethane.^{3a} Three bands reported in the fingerprint region (832, 629, 500 cm^{-1}) display excellent agreement with our spectrum of 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**), although weaker bands at higher energy (1200–1600 cm^{-1}) do not.

The methylnaphthalenes may be formed by trapping of carbenes **1** and **8** through a sequence of hydrogen abstraction reactions.^{5,6} The formation of naphthalene is mechanistically intriguing. Naphthalene is also a minor product in the gas-phase thermolysis of other 1-naphthylcarbene precursors,^{5b} and the pyrolytic loss of a one-carbon species to form naphthalene has been observed in the related benzocycloheptatriene system.¹⁷

In summary, the enigmatic allene 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**), predicted by theory to be a low-energy isomer on the C_{11}H_8 potential energy surface, is directly observed in an argon matrix at 10 K. A series of photochemical and thermal experiments establish the mechanistic pathways that connect allene **6** to naphthylcarbenes **1** and **8**.

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support of this project (CHE-9800716) as well as the departmental computational facilities (CHE-9522057) and ESR spectrometer (CHE-9013030).

Supporting Information Available: Experimental details on the preparation of diazo compound **11**; IR, UV/vis, and ESR spectra obtained upon photolysis of diazo compound **11**; computed geometry, energy, and IR spectrum of relevant species (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA001291E

(16) The disappearance of benzocycloheptatetraene **6** is highly sensitive to matrix thickness. The IR bands for **6** (thick matrix) decrease only slightly under these conditions, with no new absorptions appearing. In a UV/visible experiment (thin matrix), **6** disappears completely.

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