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The Elusive Benzocyclobutenylidene: A Combined Computational and Experimental Attempt

Athanassios Nicolaides,*,†,‡ Takeshi Matsushita,‡ Kohichi Yonezawa,‡ Shinji Sawai,‡ Hideo Tomioka,*,‡ Louise L. Stracener,§ Jonathan A. Hodges,§ and Robert J. McMahon*,§

Contribution from the Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507 Japan, and the Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396

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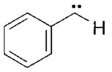
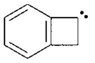
Abstract: Ab initio and density functional theory calculations predict that benzocyclobutenylidene (**1**) has a singlet ground state in contrast to the parent phenylcarbene and many other simply substituted arylcarbenes. Calculations also predict that **1** should lie in a relatively deep potential well, while its triplet state is 14.5 kcal mol^{-1} higher in energy. However, attempts to observe **1** directly by photolysis of two different nitrogenous precursors were not successful. Irradiation of diazobenzocyclobutene (**7**) (λ > 534 nm or λ > 300 nm) or azibenzocyclobutene (**10**) (λ > 328 nm) in Ar matrixes at 10 K leads to the formation of the strained cycloalkyne 7-methylenecyclohepta-3,5-dien-1-yne (**3**). ^{13}C-Labeled **3** was also prepared in a similar manner. There is very good agreement between experimental IR spectra and computationally derived harmonic vibrational frequencies for **3** and [^{13}C]-**3** and excellent agreement between observed and calculated isotopic shifts. Prolonged short-wavelength irradiation converts **3** into benzocyclobutadiene (**5**). Phenylacetylene (**6**) and benzocyclobutadiene dimer (**11**) were identified as products arising from flash vacuum pyrolysis of diazirine **10** at 500 °C.

Introduction

Phenylcarbene, the prototypical arylcarbene,[1] has a triplet ground state.[2] However, it is through its low-lying singlet state that phenylcarbene usually reacts.[3] Thus, factors that affect the S−T gap are important in understanding the reactivity of arylcarbenes.[1] In terms of geometric factors, a small bond angle at a carbenic center energetically favors the singlet state relative to the triplet. Thus, benzocyclobutenylidene (**1**) provides an attractive model for exploring the interdependence of carbene geometry, substitution, and multiplicity. The bond angle at the divalent carbon in **1** is significantly smaller than that of phenylcarbene (90° vs 135−155°),[2] although in other respects the electronic perturbation introduced by the small ring is minimal.





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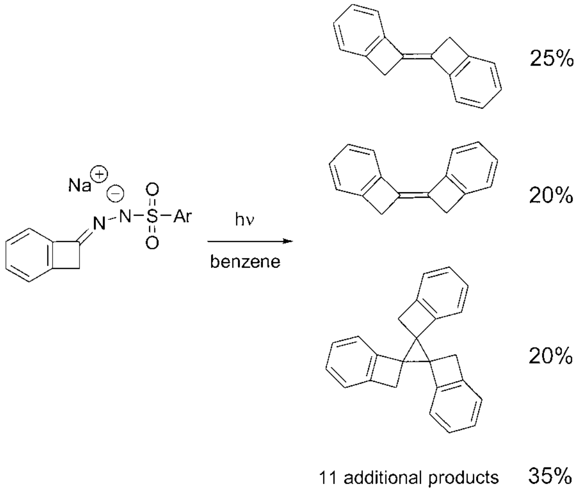
Several groups attempted to study carbene **1** or its simple derivatives by photolysis or thermolysis of various precursors.[4−6] Product analyses revealed a complex and intriguing reactivity for **1** but did not provide a clear conclusion as to the multiplicity of the ground state. Semiempirical calculations suggested a triplet ground state.[5] An equilibrium between singlet and triplet states was invoked to explain the experimental data. Photolysis of the sodium salt of benzocyclobutenone *p*-toluenesulfonylhydrazone in solution afforded the (formal) dimer and trimer of **1** as major products.[6] Although all of the earlier reactions gave products consistent with those expected from carbene **1**, the carbene has not been observed spectroscopically and its involvement in the aforementioned chemistry has not been



[†] Current address: Department of Chemistry, University of Cyprus, Nicosia, Cyprus.

[‡] Mie University.

[§] University of Wisconsin.

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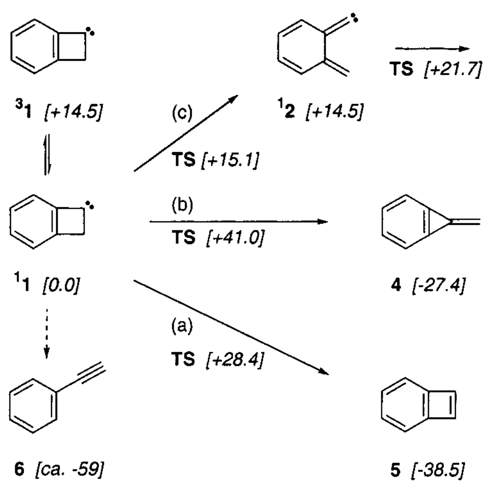
Scheme 1[a]



[a] G2(MP2,SVP) relative energies (kcal mol^{-1}).

Table 1. Relative Energies[a] of Various C_8H_6 Isomers (ΔH, kcal mol^{-1}) and Barriers of Reactions[a] ($\Delta H^{\ddagger}$, kcal mol^{-1})

	ΔH^b	ΔH^c		$\Delta H^{\ddagger,c}$
^{1}1	0.0	0.0	**TS(^{1}1−^{1}1)**[d]	6.8[b]−7.0[c]
^{3}1	7.8	14.5[e]		
2	13.3	14.5	**TS(1−2)**	15.1
3	−10.5	−9.2	**TS(1−3)**[f]	21.7
4	−27.8	−27.4	**TS(1−4)**	41.0
5	−37.5	−38.5	**TS(1−5)**	28.4
6	−59.2			

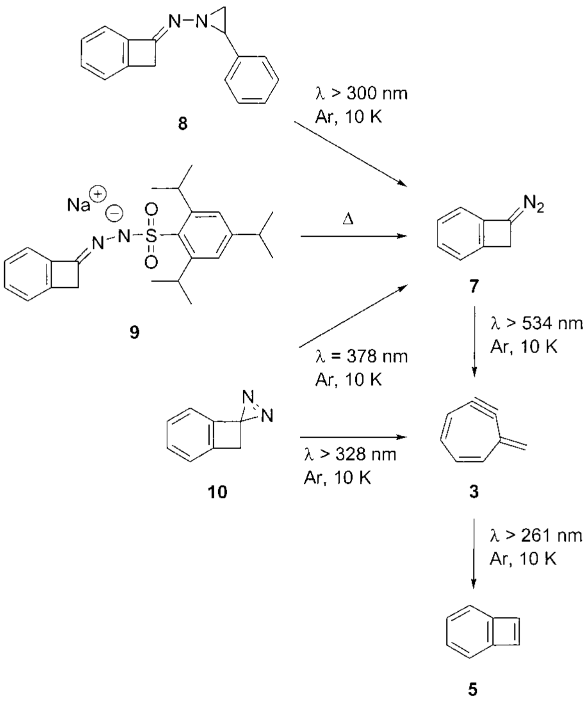
[a] At 0 K. [b] BLYP/6-31G(d) + ZPVE. [c] G2(MP2,SVP) relative energies using B3LYP/6-31G(d) optimized structures. [d] Transition state for conformational ring inversion in **^{1}1**. [e] Determined using isodesmic reaction (see text). [f] Via intermediacy of **2**.

unequivocally established. We therefore decided to investigate this interesting carbene by attempting to observe it directly in an inert matrix at low temperature and studying it at modern levels of theory.

Results and Discussion

The G2(MP2,SVP) relative energies for several C_8H_6 isomers (**1**−**6**), computed using B3LYP/6-31G(d) geometries, are given in Scheme 1 and Table 1. According to our calculations, the ground state of benzocyclobutenylidene **1** is a singlet and its geometry is nonplanar (Table S1). Singlet **1** undergoes conformational ring inversion through a planar transition state with a computed barrier of ca. 7 kcal mol^{-1}. Triplet **1** is found to be planar and to lie 8−15 kcal mol^{-1} higher in energy than the singlet ground state. This situation is similar to the simple analogue of **1**, cyclobutenylidene, which displays a pronounced deviation from planarity in its singlet state.[7−9] However, in the case of **1**, the presence of the rather rigid benzene ring does not allow for much out-of-plane deformation. The degree of stabilization afforded the singlet state by virtue of the geometric distortion is reflected in the planarization barrier, which is calculated to be 7 kcal mol^{-1} for benzocyclobutenylidene (**1**) but 21 kcal mol^{-1} for cyclobutenylidene.[8,9] The singlet−triplet energy gap (ΔE_{S-T}) of benzocyclobutenylidene (**1**) was estimated in two ways. The value of −7.8 kcal mol^{-1} was determined directly from the BLYP relative energies, while the value of −14.5 kcal mol^{-1} was determined using the experimental singlet−triplet gap of methylene (ΔE_{S-T} = +9.0 kcal mol^{-1})[10] and the G2(MP2,SVP) energy of the isodesmic reaction ^{3}**1** + $^1CH_2$ → ^{1}**1** + $^3CH_2$.

Scheme 2



The intramolecular rearrangement pathways of singlet benzocyclobutenylidene (^{1}**1**) were examined computationally (Scheme 1): (a) 1,2 hydrogen shift (the most common rearrangement path for carbenes bearing α-hydrogens),[11] (b) 1,2 carbon shift (this path can become dominant in sterically strained carbenes),[12] and (c) ring opening of the fused ring (forming vinylidene **2**) followed by a C−C insertion leading to strained cycloalkyne **3**. Path c may seem unusual, but it is likely to be the path followed in the isomerization of cyclobutenylidene.[7,8] From the calculated enthalpic barriers for the three processes (Table 1), it is found that while path c is preferred, its barrier of 21.7 kcal mol^{-1} is still large. Therefore, it appears that benzocyclobutenylidene **1** lies in a rather deep potential well and should be observable under suitable experimental conditions.

An obvious photochemical precursor for **1** is diazobenzocyclobutene (**7**), but this species was found to be too unstable for isolation and purification under normal preparative conditions. Therefore, we sought to generate **7** in the matrix by two different

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Table 2. Observed and Calculated[a] Frequencies (ν, cm^{-1}), Relative Intensities (%*I*) and ^{13}C Isotopic Shifts ($\Delta\nu$, cm^{-1}) for Cycloalkyne **3**

observed					calculated								
[^{12}C]-**3**		[^{13}C]-**3**			[^{12}C]-**3**		[1-^{13}C]-**3**			[2-^{13}C]-**3**			
ν	%I	ν	%I	$\Delta\nu$	ν	%I	ν	%I	$\Delta\nu$	ν	%I	$\Delta\nu$	
608	55.6	603	39.1	5	587	30.3	586	29.2	1	583	28.5	4	
616	59.3	616	48.4	0	614	19.0	613	18.6	1	613	20.0	1	
732	107.0	732	122.0	0	728	34.5	728	34.5	0	728	35.0	0	
848	66.7	848	57.8	0	813	61.5	813	61.4	0	813	62.7	0	
					1497[b]	34.1	1497[b]	34.2	0	1497[b]	34.6	0	
1564[b]	29.6	1564[b]	29.7	0	1569[b]	36.2	1569[b]	36.5	0	1569[b]	36.8	0	
1612	100.0	1606	100.0	6	1626	100.0	1626	100.0	0	1625	100.0	1	
2098	22.2	2062	18.8	36	2147	35.8	2106	32.5	41	2107	38.4	40	

[a] At the B3LYP/6-31G(d) level of theory. Only diagnostically useful frequencies are shown. For a complete list of the vibrational analysis data for **3** and its isomers, see Tables S2 and S3. [b] The observed peak is quite broad, suggesting that there are two absorptions very close to each other. Apparently this level of theory overestimates the relative distance of the two peaks.

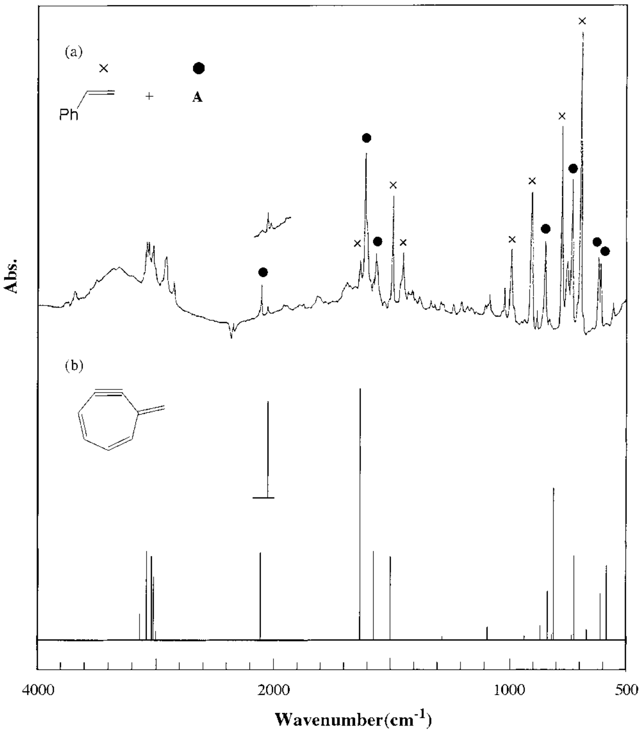
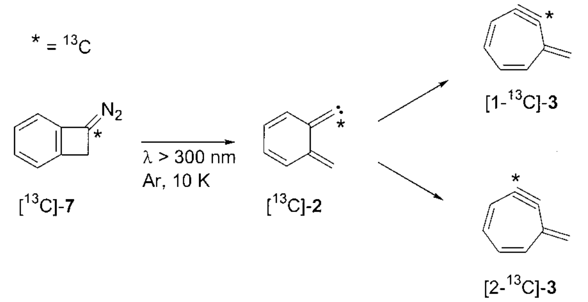


Figure 1. Comparison of experimental (Ar, 10 K) and theoretical IR spectra: (a) Experimental IR spectrum of the photoproducts formed by irradiation of unlabeled *N*-aziridinylimine **8**. Bands due to photoproduct **A** are marked with • and those due to styrene with ×. (b) Calculated IR spectrum (B3LYP/6-31G(d) scaled by 0.961) for unlabeled cycloalkyne **3**. The insets in both a and b show the major ^{13}C isotope effects on the spectrum (see Table 2).

methods (Scheme 2). In the first case, *N*-aziridinylimine **8** was prepared in a pure form and deposited into the Ar matrix. Irradiation of **8** (λ > 300 nm) gave rise to diazo compound **7** and styrene. In the second case, the trisopropylbenzenesulfonylhydrazone sodium salt **9** was thermolyzed and the volatile diazo compound **7** trapped in the Ar matrix. The structure of **7** was assigned on the basis of the strong, characteristic C=N=N absorption at 2042 cm^{-1} and the good agreement of the experimental and computed IR spectra.

Photolysis of diazo compound **7** (using either λ > 300 nm or λ > 534 nm) gave rise to new peaks assigned to **A** (•, Figure 1a). When the photolysis was carried out in an Ar matrix doped with 0.3% oxygen, the same final photoproduct was observed.[13] Furthermore, annealing the matrix containing the products at 30−35 K did not result in appreciable changes in the spectrum. An ESR study performed under similar experimental conditions failed to detect the presence of any triplet species. The agreement between the experimental IR spectrum of **A** and the computed spectrum for singlet benzocyclobutenylidene (^{1}**1**) is very poor (Table S2). These pieces of evidence are inconsistent with a benzocyclobutenylidene intermediate (^{1}**1** or ^{3}**1**), suggesting that intermediate **A** is perhaps a rearrangement product of **1**.

Scheme 3



Comparison between the experimental IR spectrum of **A** and the IR spectra computed for other C_8H_6 isomers (Scheme 1) enables the assignment of photoproduct **A** as 7-methylenecyclohepta-3,5-dien-1-yne (**3**) (Figure 1).[14] The main discriminating factor in the computed IR spectra of vinylidene **2** and cycloalkyne **3** is the presence of the C≡C bond absorption in the latter, which experimentally is observed at 2098 cm^{-1}.[15] While this absorption is weak, it is well separated from the rest of the absorptions and this suggests ^{13}C isotopic labeling as a means of differentiating between the two possible structures. Calculations predict an isotopic shift of approximately 10 cm^{-1} for the C=C of vinylidene **2**, and a much larger shift of approximately 40 cm^{-1} for either of the two ^{13}C isotopomers of the C≡C of cycloalkyne **3** (Tables 2 and S3). Labeled **7** (with the ^{13}C-label at the diazo carbon) was synthesized, and the photolysis was carried out under conditions identical to those described previously (Scheme 3). A small isotopic shift of 6 cm^{-1} (calculated: 4 cm^{-1}) was observed for the C=N=N stretch of the labeled diazo compound. The subsequent photoproduct (^{13}C-**A**, Figure 1a) showed an absorption at 2062 cm^{-1}

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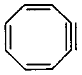
(13) In the presence of 24% oxygen, different products were obtained. The major product was benzocyclobutenone.

(14) Cycloocta-1,3,5-trien-7-yne can be excluded as the structure for intermediate **A** because the alkyne stretch (scaled frequency = 2083 cm^{-1}) is computed to have a vanishingly small intensity (0.026 km mol^{-1}).



Cycloocta-1,3,5-triene-7-yne is computed to be 15 kcal mol^{-1} higher in energy than cycloalkyne **3**.

(15) By comparison, the alkyne stretch in 3,3,7,7-tetramethylcycloheptyne is 2180 cm^{-1}. Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509−510.

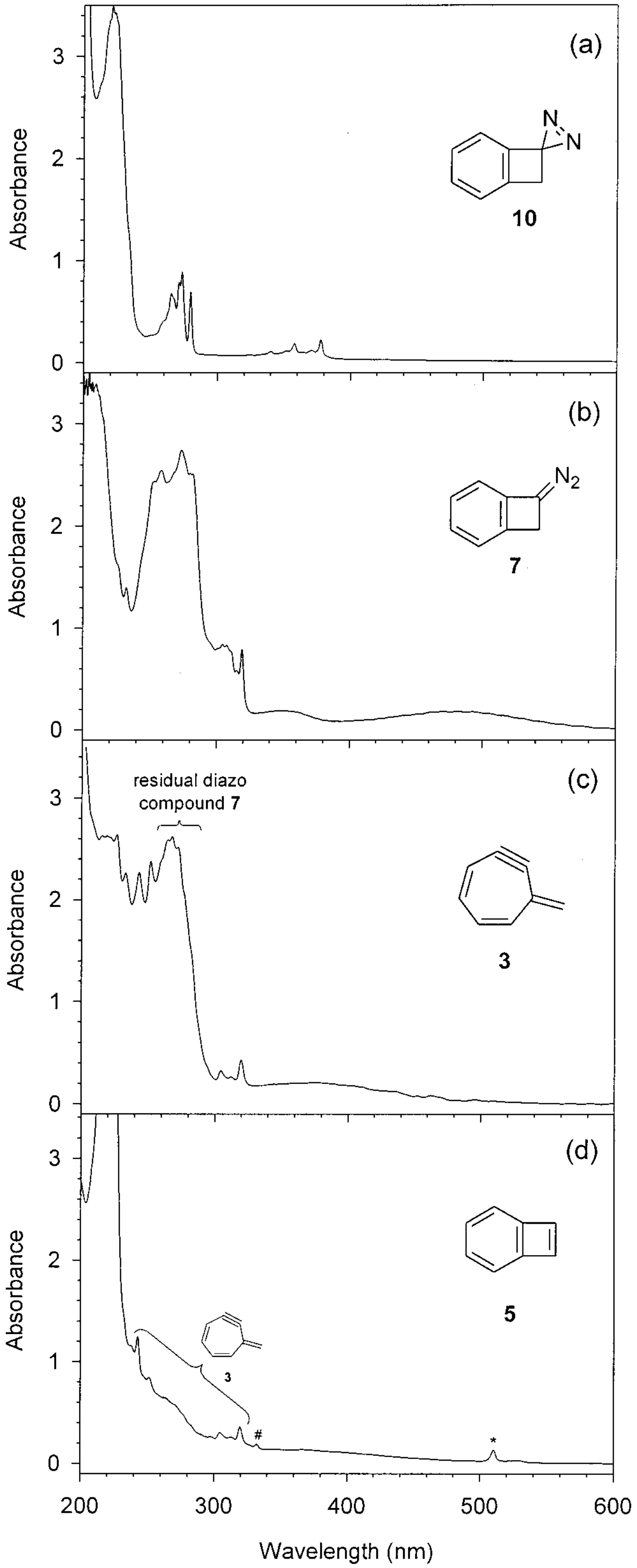


Figure 2. UV/vis spectra (Ar, 10 K): (a) azibenzocyclobutene (**10**) before photolysis; (b) diazobenzocyclobutene (**7**) formed upon irradiation ($\lambda = 378 \pm 10$ nm, 2.5 h) of diazirine **10**; (c) alkyne **3** formed upon subsequent irradiation ($\lambda > 534$ nm, 42.5 h) of diazo compound **7**; (d) benzocyclobutadiene (**5**) formed upon subsequent irradiation ($\lambda > 261$ nm, 82.9 h) of alkyne **3**. Peaks labeled # and * represent distinct, unidentified photoproducts.

corresponding to an isotopic shift of 36 cm^{-1} in excellent agreement with the predicted values (Table 2). Thus, there is little doubt that species **A** is the strained cycloalkyne **3**. The position of the ^{13}C label in cycloalkyne **3** is believed to be at C2, although this assignment is not established unambiguously. The small isotopic shift of 5 cm^{-1} observed experimentally at 608/603 cm^{-1} agrees better with the shift computed for [2-^{13}C]-**3** (4 cm^{-1}) than for [1-^{13}C]-**3** (1 cm^{-1}) (Table 2). The thermal barrier for the ring expansion of [^{13}C]-**2** to [2-^{13}C]-**3** (21.7 kcal/mol) is computed to be 2.1 kcal/mol lower than the barrier for the rearrangement of [^{13}C]-**2** to [1-^{13}C]-**3** (23.8 kcal/mol) (Scheme 3).

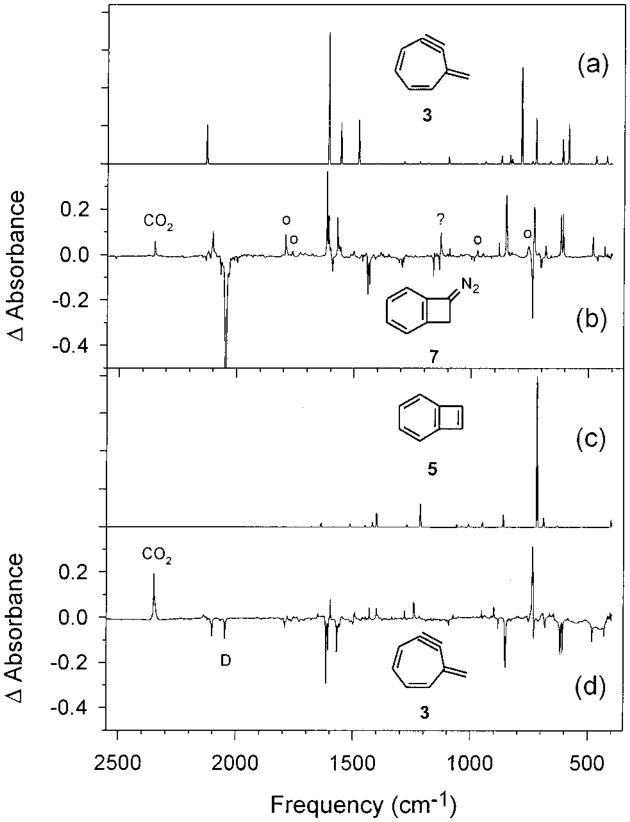


Figure 3. (a) Computed IR spectrum of 7-methylenecyclohepta-3,5-dien-1-yne (**3**) (BLYP/6-31G(d) scaled by 0.9945). (b) Difference IR spectrum (Ar, 10 K) showing formation of alkyne **3** and disappearance of diazobenzocyclobutene (**7**) upon irradiation ($\lambda > 534$ nm, 18 h). Small amounts of benzocyclobutenone (○), an unknown impurity (?), and CO_2 are also formed under these conditions. (c) Computed IR spectrum of benzocyclobutadiene (**5**) (BLYP/6-31G(d), scaled by 0.9945). (d) Difference IR spectrum (Ar, 10 K) showing formation of benzocyclobutadiene (**5**) and disappearance of alkyne **3** upon irradiation ($\lambda > 261$ nm, 48 h). The spectrum also shows the disappearance of residual diazo compound **7** (D) and the growth of CO_2.

A disadvantage of generating diazo compound **7** from **8** or **9** is that additional organic species are introduced into the matrix, in the form of either styrene or volatile impurities. Thus, we utilized azibenzocyclobutene (**10**),[16] which can be obtained in pure form, as an independent precursor to benzocyclobutenylidene (**1**). The "clean" diazirine enabled us to monitor the matrix photochemistry by UV/vis spectroscopy as well as IR spectroscopy. Broadband photolysis ($\lambda > 328$ nm) of matrix-isolated diazirine **10** produced diazo compound **7** and alkyne **3**. The diazo compound was photosensitive under the irradiation conditions and was converted to alkyne **3** upon continued irradiation. Band-pass photolysis ($\lambda = 378 \pm 10$ nm) of **10** displayed greater selectivity. At short irradiation times, diazirine **10** isomerized cleanly to diazo compound **7** (Scheme 2; Figure 2). Conversion of diazo compound **7** to alkyne **3** occurred only

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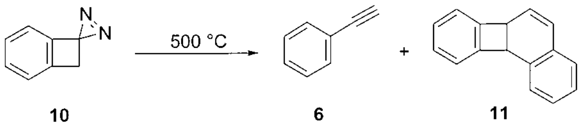
[16] Broadus, K. M.; Kass, S. R. *J. Org. Chem.* **2000**, *65*, 6566−6571.

Scheme 4

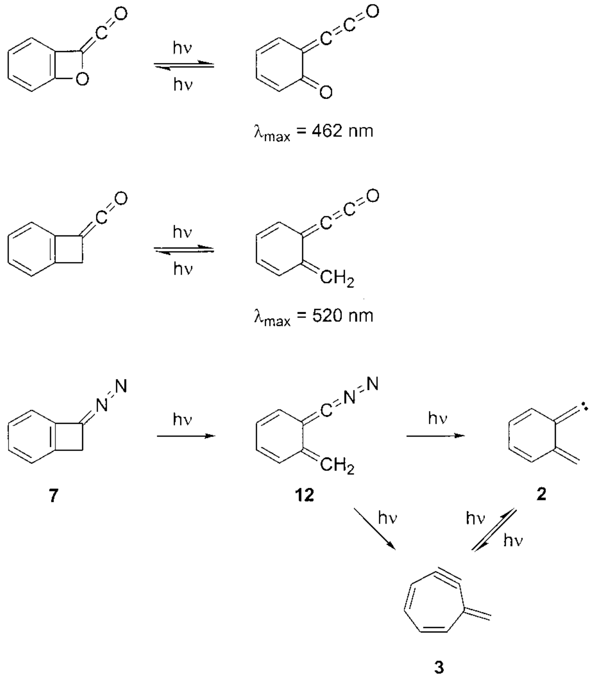


upon prolonged irradiation. Although it is clear that diazirine **10** serves merely as a source of diazo compound **7** under band-pass irradiation, we cannot exclude the possibility that **10** serves as a direct precursor to alkyne **3** (or carbene **1**) under other irradiation conditions. As in the earlier experiments, long-wavelength irradiation ($\lambda > 534$ nm) of diazo compound **7** afforded alkyne **3**. With the electronic absorption spectrum of alkyne **3** in hand, we investigated a variety of irradiation conditions in an attempt to photoisomerize alkyne **3** to the desired benzocyclobutenylidene (**1**). Although alkyne **3** did indeed exhibit photochemistry (see below), efforts to observe benzocyclobutenylidene (**1**) were unsuccessful.

Short-wavelength irradiation ($\lambda > 261$ nm) of alkyne **3** afforded benzocyclobutadiene (**5**) (Figure 3). Although the efficiency of this photochemical conversion varied from experiment to experiment,[17] there is little doubt about the identity of product **5**. The IR spectrum displayed good agreement with both the experimental spectrum previously reported by Chapman[18] and the computed IR spectrum (Table S3). To obtain independent evidence for the formation of **5**, diazirine **10** was subjected to flash vacuum pyrolysis (500 °C, unpacked quartz tube, 0.01 mmHg). A mixture containing phenylacetylene (**6**) and benzocyclobutadiene dimer (**11**; 7:1 ratio) was isolated in low overall yield (ca. 10%) and characterized by ^{1}H NMR spectroscopy (Scheme 4). This result is consistent with previously reported observations.[18,19] Chapman's experiments suggest that benzocyclobutadiene (**5**) is stable in the gas phase at 230 °C,[18] while Klärner's experiments suggest that benzomethylenecyclopropene (**4**), a higher-energy C_8H_6 isomer, rearranges to phenylacetylene (**6**) at 400 °C.[19]

Our results establish that cycloalkyne **3** is the photoproduct obtained upon irradiation of the precursors **7** and **10**. However, no evidence for the formation of carbene **1** was obtained. If carbene **1** is indeed formed as the photoproduct from diazo compound **7**, it must either be formed with sufficient vibrational energy during the decomposition of the excited-state precursor to overcome the barrier to isomerization to alkyne **3** or it must be photosensitive under the irradiation conditions ($\lambda > 534$ nm). Alternatively, there are several plausible pathways by which alkyne **3** could be formed from diazo compound **7** without intervention of carbene **1**.[20] By analogy to the known photochemical ring opening of benzocyclobutenes to *o*-quinodimethanes (Scheme 5),[21] photochemical ring opening of diazo compound **7**, with either concerted or stepwise loss of nitrogen, offers a route to alkyne **3** that circumvents carbene **1** (Scheme 5). The possible involvement of vinylidene **2** had not been postulated in earlier investigations of benzocyclobutenylidene (**1**), but this species may help explain data from both matrix and condensed phase experiments.[22] Under matrix isolation conditions, vinylidene **2** might be expected to undergo reversible photoequilibration with cycloalkyne **3**, a process analogous to the equilibration of cyclopentadienylidenecarbene and *o*-benzyne (Scheme 6).[23] The formation of benzocyclobutadiene (**5**) upon short-wavelength photolysis of cycloalkyne **3** may be considered to proceed by ring contraction to vinylidene **2**. Again, the intermediacy of carbene **1** remains uncertain. Vinylidene **2** may undergo direct insertion into a C−H bond to afford benzocyclobutadiene (**5**) or it may undergo electrocyclization to carbene **1** followed by 1,2-hydrogen migration (Scheme 6). It is clear that further experiments will be required in order to elucidate the intimate details of these photochemical transformations.

Scheme 5



In summary, photolysis of either diazo compound **7** or diazirine **10** provided the cycloalkyne 7-methylenecyclohepta-3,5-dien-1-yne (**3**). Alkyne **3** photochemically rearranged to benzocyclobutadiene (**5**). Benzocyclobutadiene (**5**), along with phenylacetylene (**6**), was formed upon flash vacuum pyrolysis of diazirine **10**. Vinylidene **2** is a possible intermediate that has

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[17] The variability in conversion efficiency of alkyne **3** to benzocyclobutadiene (**5**) may involve several interrelated factors, including (i) impurities in the matrix, (ii) internal filtering by strongly absorbing impurities and/or photoproducts, (iii) matrix thickness, and (iv) intensity of photolysis source.

[18] Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261−262.

[19] Klärner, F. G.; Dogan, B. M. J.; Weider, R.; Ginsburg, D.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 346−348.

[20] It has been amply demonstrated that the products of the photochemical decomposition of diazo compounds derive in substantial measure from rearrangements of the nitrogen-containing precursors themselves. Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072−3075. See also: Çelebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613−8620 and references therein.

[21] Chapman, O. L.; Chang, C. C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586−6588.

[22] One may ponder whether vinylidene **2** or cycloalkyne **3** play any role in the condensed phase experiments.[4−6] Vinylidene **2**, if formed, may be expected to undergo rapid thermal isomerization to benzocyclobutenylidene ^{1}**1**—the intermediate that has been presumed to be responsible for the solution phase chemistry. It is also intriguing to note that vinylidene **2** is computed to be isoenergetic with triplet benzocyclobutenylidene ^{3}**1**. The complex product mixture derived from solution chemistry does not appear to be derived from cycloalkyne **3**, and this result is perhaps not surprising, given the large thermal barrier of 21 kcal mol^{-1} separating **1** and **3** as well as the expected high reactivity of **1** and/or **2**. The matrix chemistry is dominated by photochemistry, while the solution chemistry, even if initiated photochemically, is likely to be dominated by thermal chemistry.

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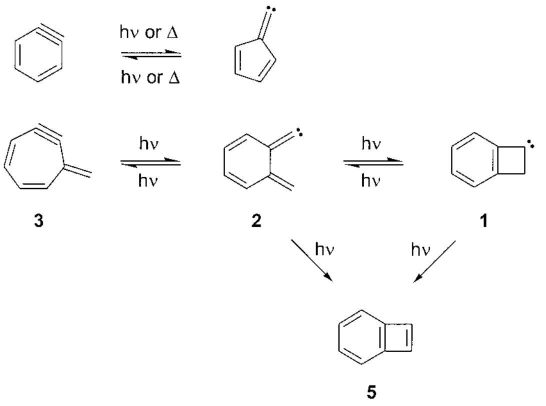
Scheme 6



not been previously considered in the thermal and photochemical transformations of nitrogenous precursors of benzocyclobutenylidene (**1**). The elusive benzocyclobutenylidene (**1**), which is computed to display a singlet ground state, was not observed in any of our experiments.

Methods Section

Computational Methods. Optimized geometries and harmonic vibrational frequencies were obtained at the BLYP/6-31G(d) and B3LYP/6-31G(d) levels of theory using the Gaussian 94 package of programs.[24] Vibrational frequencies were scaled by 0.9945 (BLYP) or 0.961 (B3LYP), and zero point vibrational energies were scaled by 1.0126 (BLYP) or 0.981 (B3LYP), as recommended by Scott and Radom.[25] Relative energies for the B3LYP/6-31G(d) structures are reported at the G2(MP2,SVP) level.[26] A full description of the geometries and vibrational frequencies computed for these species is provided in the Supporting Information.

Matrix Isolation Spectroscopy. Details of experimental procedures for matrix isolation spectroscopy have been described previously.[27] At Tsu, photolyses were carried out using a Wacom 500-W xenon high-pressure arc lamp. For broadband irradiation, Toshiba cutoff filters were used (50% transmittance at the wavelength specified.) At Wisconsin, photolyses were carried out using an ILC Technology 300 W xenon arc lamp. Wavelength selection was achieved with cutoff filters ($\lambda >$ 534 nm, Corning 3-67; $\lambda >$ 328 nm, Schott WG 345; $\lambda >$ 300 nm, Schott WG 320; $\lambda >$ 261 nm, Corning 0-53) or a Spectral Energy GM 252 monochromator (bandwidth 20 nm).

Preparation of *N*-(2-Phenylaziridyl)imine of Benzocyclobutenone (8). To a solution of 118 mg (1 mmol) of benzocyclobutenone[28] in 5 mL of benzene was added in one portion 132 mg (1 mmol) of 1-amino-2-phenylaziridine,[29] and the mixture was stirred at room temperature. The progress of the reaction was followed by TLC. After stirring overnight, the solvent was removed on a rotary evaporator with a bath at room temperature. The resulting crude hydrazone was purified with gel permeation chromatography with CHCl$_3$ to give a sticky liquid in 56% yield: ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.39−2.46 (m, 1 H), 2.56−2.60 (m, 1 H), 3.09−3.13 (m, 1 H), 3.85 (s, 2 H), 7.21−7.39 (m, 9 H); IR (Ar, 10 K) 3068 vw, 2932 w, 1687 m, 1608 w, 1586 w, 1496 m, 1461w, 1160 vw, 983 m, 935 m, 757 vs, 743 s, 703 m, 695 vs cm^{-1}.

Diazobenzocyclobutene (7). Sodium benzocyclobutenone 2,4,6-triisopropylbenzenesulfonhydrazonate (**9**; 0.5 g) was placed in a 100 mL flask, which was connected to the matrix isolation chamber by a glass tube. The entire system was evacuated to 10^{-6} mmHg; upon cooling the CsI window to 30 K, the flask was heated very slowly to 135 °C. Heating the salt too quickly resulted in rapid decomposition. Thermolysis of the salt afforded diazobenzocyclobutene (**7**), which was co-deposited with argon over a period of 45 min. The matrix was cooled to 10 K and photolysis was started: IR (Ar, 10 K) 3087 w, 3076 w, 3066 w, 2967 w, 2937 m, 2069 w, 2047 vs, 1599 m, 1593 m, 1464 m, 1443 s, 1434 s, 1410 w, 1309 w, 1296 w, 1289 w, 1163 m, 1137 m, 1000 w, 989 w, 740 s, 705 m, 701 m, 463 w cm^{-1} (Figure 3). A small amount of benzocyclobutenone was observed, indicated by the presence of IR absorptions at 1796, 1131, 954, and 764 cm^{-1}. UV/vis (Ar, 10 K): $\lambda_{\max}$ 225, 233, 248, 277, 283, 297, 302, 305, 309, 312, 316, 320 nm (Figure S2).

The UV/vis spectrum of diazo compound **7** in argon at 10 K displays subtle differences depending on whether the diazo compound is generated by thermolysis of salt **9** or by photoisomerization of diazirine **10**. These differences are attributed to impurities that co-deposit with diazo compound **7** during the thermolysis of **9**. Spectroscopic data for diazo compound **7**, as generated by photoisomerization of **10**: UV/vis (Ar, 10 K) $\lambda_{\max}$ 226, 233, 252, 258, 268, 274, 280, 282, 302, 305, 309, 311, 315, 319, 351 (broad), 482 (broad) nm (Figure S2).

Azibenzocyclobutene (10). Diazirine **10** was prepared by the method of Broadus and Kass.[16] Sublimation of the diazirine at −29 °C into argon provided matrix-isolated material: IR (Ar, 10 K) 3093 w, 3056 w, 2937 m, 2837 w, 1951 w, 1905 w, 1793 w, 1683 w, 1636 w, 1626 m, 1618 m, 1601 s, 1555 m, 1529 w, 1447 m, 1427 w, 1351 w, 1220 w, 1212 w, 1172 w, 1118 w, 1002 w, 783 w, 748 s, 712 m, 603 w, 505 w, 405 m cm^{-1} (Figure S1); UV/vis (Ar, 10 K) $\lambda_{\max}$ 221, 223, 249, 260, 265, 267, 271, 274, 280, 324, 334, 340, 352, 358, 365, 371, 378 nm (Figure 2).

Flash Vacuum Pyrolysis of Azibenzocyclobutene (10). To one end of an unpacked 60 cm quartz tube was affixed a 50 mL round-bottom flask containing 80 mg (0.6 mmol) of diazirine **10**. To the other end were affixed a vacuum adapter and a cold trap. Diazirine **10** was cooled to −78 °C, and the apparatus was evacuated to 0.01 mmHg while the quartz tube was heated to 500 °C in a furnace. After cooling the cold trap to 77 K, the temperature of diazirine **10** was raised to 0 °C. After 1 h, no **10** remained in the round-bottom flask and the system was vented to N$_2$. During the pyrolysis, the section of quartz tube near the entrance to the furnace became heavily coated with charred material. Approximately 5−10 mg of pyrolysate was recovered from the cold trap and analyzed by ^{1}H NMR spectroscopy (CDCl$_3$). An intense singlet at δ 3.07 revealed phenylacetylene (**6**)[30] as the primary pyrolysis product, and a series of alkenyl absorptions [δ 6.28 (d, $J = 9.9$ Hz, 1 H), 6.12 (dd, $J = 9.9$, 4.8 Hz, 1 H), 4.82 (d, $J = 6.9$ Hz, 1 H), 4.43 (m, 1 H)] were consistent with those reported for the benzocyclobutadiene dimer (**11**).[31] According to the NMR integrations, the ratio of phenylacetylene (**6**) to benzocyclobutadiene dimer (**11**) was about 7:1.

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[30] Phenylacetylene (**6**): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.07 (s, 1H), 7.28−7.42 (m, 3H), 7.46−7.62 (m, 2H), reported by Katritzky, A. R.; Wang, J.; Karodia, N.; Li, J. Q. *J. Org. Chem.* **1997**, *62*, 4142−4147. IR (argon, 10 K): 3339, 1606, 1490, 1445, 1218, 1071, 1028, 914, 758 cm^{-1}, reported by Jørgensen, T.; Pedersen, C. T.; Flammang, R.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 2* **1997**, 173−177.

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providing a sample of benzocyclobutenyl diaziridine and the procedure for converting it to azibenzocyclobutene (**10**). We thank Prof. Curt Wentrup (University of Queensland) and Prof. William L. Karney (University of San Francisco) for insightful discussions. We acknowledge the Computer Center of IMS for a generous allocation of time and JSPS and NSF for an award of a JSPS Fellowship (No. P96140) to A.N. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and by the U.S. National Science Foundation (CHE-9800716).

Supporting Information Available: Experimental details for the syntheses of ^{13}C-labeled hydrazone **8**, benzocyclobutenone triisopropylbenzenesulfonhydrazone **9**, and diazirine **10**. Various experimental IR and UV/vis spectra of the matrix isolation photochemistry; computed structures, energies, and IR spectra for various C_8H_6 and $C_8H_6N_2$ isomers. Archive entries for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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