Structures, Automerizations, and Isomerizations of C_3H_2 Isomers

Randal A. Seburg,† Eric V. Patterson,† John F. Stanton,*,‡ and Robert J. McMahon*,†

Contribution from the Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, and Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712

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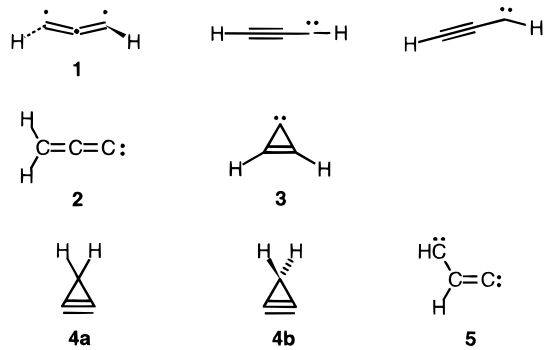
Abstract: A combination of experiment and theory provides insight into the structure and rearrangements of various C_3H_2 isomers. Photolysis of [^{13}C]diazopropynes **6a**−**c** under matrix isolation conditions affords C_3H_2 isomers containing a single ^{13}C-label. With the aid of computed vibrational frequencies and intensities (CCSD(T)/cc-pVTZ), the seven ^{13}C-isotopomers of triplet propynylidene **1a**,**b**, singlet propadienylidene **2a**−**c**, and singlet cyclopropenylidene **3a**,**b** are readily distinguished by IR spectroscopy. Monitoring the distribution of the ^{13}C-label during photolysis at either $\lambda = 313 \pm 10$ nm or $\lambda > 444$ nm reveals the involvement of two photochemical automerization processes. At $\lambda = 313 \pm 10$ nm, triplet propynylidene and singlet cyclopropenylidene photoequilibrate. The interconversion does not occur by a simple ring closure/ring opening mechanism, as hydrogen migration accompanies the interconversion. At $\lambda > 444$ nm, $H_2C{=}C{=}^{13}C$: (**2b**) and $H_2C{=}^{13}C{=}C$: (**2c**) rapidly equilibrate. Various lines of evidence suggest that the equilibration occurs through a cyclopropyne transition state. Computational results confirm that the *planar* isomer of singlet cyclopropyne (**4a**, C_{2v}) is the transition state for the interconversion of **2b** and **2c**. Unexpectedly, the calculations predict that the isomer of this compound containing a tetrahedral carbon atom (**4b**, C_{2v}) lies ca. 7 kcal/mol higher in energy than the planar form.

Introduction

The C_3H_2 potential energy surface contains fascinating isomers that challenge our understanding of structure and bonding (Scheme 1). Several C_3H_2 molecules represent the parent species of their class: propynylidene **1** is the simplest acetylenic carbene, propadienylidene **2** is the simplest vinylidene carbene, cyclopropenylidene **3** is the smallest aromatic carbene, and cyclopropyne **4** is the smallest cyclic alkyne. These highly-reactive molecules are fundamentally important not only within the context of organic chemistry,[1] but also within the context of the chemistry of the interstellar medium.[2−4]

In our previous investigation of triplet propynylidene **1**, differential ^{13}C-labeling of its photochemical precursors enabled us to conclude that **1** has a C_2-symmetric, allene diradical-like geometry (Scheme 1), rather than a C_s-symmetric, acetylene carbene-like structure.[5,6] Subsequent photolysis of the ^{13}C-isotopomers of propynylidene (**1a** and **1b**) revealed heretofore unknown automerizations in **1** and its isomers, propadienylidene **2** and cyclopropenylidene **3**.[6] In this paper, we present these photochemical rearrangements in full detail and discuss their mechanistic implications, focusing particular attention on the possible involvement of cyclopropyne **4** in the automerization of **2**.

Scheme 1



Background

Various chemical trapping studies have been reported for carbenes **1**,[7−9] **2**,[10,11] and **3**[12] and derivatives thereof. The first spectroscopic characterization of propynylidene **1** occurred in

† University of Wisconsin.
‡ University of Texas.
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(1) For reviews of the chemistry of acetylenic carbenes, see: (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (b) Jones, M., Moss, R. A., Eds. *Carbenes*; Wiley: New York, 1973; Vols. I and II. (c) Regitz, M., Ed. *Methoden der Organischen Chemie* (Houben Weyl); G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 769−774.

(2) (a) Winnewisser, G.; Herbst, E. *Rep. Prog. Phys.* **1993**, *56*, 1209−1273. (b) Herbst, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 595−608. (c) Herbst, E.; Leung, L. M. *Astrophys. J., Suppl. Ser.* **1989**, *69*, 271−300. (d) Winnewisser, G.; Herbst, E. *Top. Curr. Chem.* **1987**, *139*, 119−172. (e) Winnewisser, G. *Top. Curr. Chem.* **1981**, *99*, 39−71. (f) Hayatsu, R.; Anders, E. *Top. Curr. Chem.* **1981**, *99*, 1−37. (g) Winnewisser, G.; Mezger, P. G.; Breuer, H.-D. *Top. Curr. Chem.* **1974**, *44*, 1−81.

(3) Thaddeus, P.; Gottlieb, C. A.; Mollaaghababa, R.; Vrtilek, J. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2125−2129.

(4) Botschwina, P.; Horn, M.; Flügge, J.; Seeger, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2219−2230.

(5) Seburg, R. A.; DePinto, J. T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 835−836.

(6) Seburg, R. A.; McMahon, R. J. *Angew. Chem.* **1995**, *107*, 2198−2201; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2009−2012.

(7) (a) Skell, P. S.; Klebe, J. *J. Am. Chem. Soc.* **1960**, *82*, 247−248. (b) Skell, P. S.; Klebe, J. *Abstracts of Papers*, 141st National Meeting of the American Chemical Society, Washington, DC, March 20−29, 1962. (c) Gramas, J. V. Ph.D. Thesis, Pennsylvania State University, University Park, PA, 1965. (d) Closs, G. L. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Interscience: New York, 1968; Vol. 3, p 226.

(8) (a) Padwa, A.; Gareau, Y.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 983−986. (b) Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637−2647.

(9) Wierlacher, S.; Sander, W.; Marquardt, C.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1994**, *222*, 319−324.

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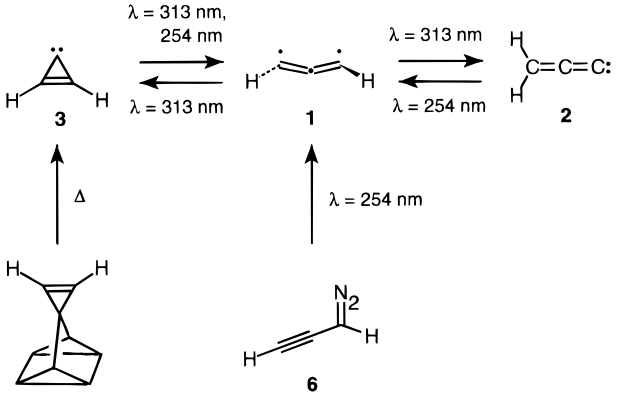
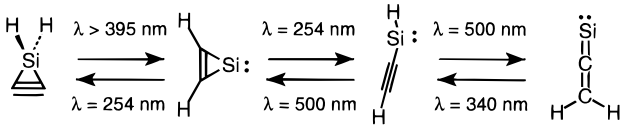
Scheme 2



1965. Bernheim and Skell photolyzed diazopropyne **6** in poly(chlorotrifluoroethylene) at 77 K and characterized the triplet ground state of **1** using ESR spectroscopy.[13] A linear geometry was assigned to **1** on the basis of the vanishingly small value of the zero-field splitting parameter, *E*. Photolysis of diazopropyne in the gas phase produces primarily C_3, although the transient absorption of a minor photoproduct was tentatively assigned to singlet propynylidene **1**.[14] Chi first reported the infrared spectrum of **1**, obtained upon photolysis of matrix-isolated diazopropyne, in 1972;[15] Jacox and Milligan later observed **1** upon photolysis of matrix-isolated propyne.[16] Flash vacuum pyrolysis of a quadricyclane derivative with trapping of the products in argon on a cold window led to the observation of matrix-isolated cyclopropenylidene **3** by IR spectroscopy.[17] Photolysis of **3** resulted in formation of **1** and ultimately **2**, a reversible photoprocess depicted in Scheme 2.[18] This was the first observation of propadienylidene **2**. A further investigation of the IR spectrum of **1** and its deuterated isotopomers followed.[19] Vacuum UV photolysis of propyne in the gas phase, followed by co-condensation of the products in argon at 10 K, produces IR absorptions of **1**−**3** as well as absorptions tentatively assigned to propene-1,3-diylidene (**5**).[20] Recent crossed molecular beam experiments implicate triplet **5** in the reaction of atomic carbon (^3P_j) with acetylene.[21a]

Observation of the rotational spectra of cyclopropenylidene **3**[22−25] and propadienylidene **2**[26,27] in the laboratory led immediately to the discovery of **3**[22] and **2**[28] in interstellar clouds. The dipole moments of **2** (4.1 D)[27] and **3** (3.43 D)[29] are unusually large for hydrocarbons, a feature which facilitates detection by radioastronomy. The electronic absorption spectrum of propadienylidene **2**[30] shows rich vibrational structure in the visible spectrum, inviting speculation concerning the $H_2C(=C:)_n$ family of carbenes as possible carriers for the "diffuse interstellar bands".[31] Photoelectron spectra, ionization potentials, electron affinities, proton affinities, and heats of formation have been reported for both **2** and **3**.[32−34]

Scheme 3



In an important series of recent investigations, Maier and coworkers spectroscopically observed several sila-analogs of C_3H_2 isomers, including a sila-analog of cyclopropyne—the first cyclopropyne derivative to be detected (Scheme 3).[35] Phenyl[36,37] and halo[38] derivatives of carbenes **1**−**3** have also been the subject of recent study.

The C_3H_2 potential energy surface has received extensive computational attention.[21,39] Singlet cyclopropenylidene **3**[39−41]

(10) For a review of the chemistry of substituted propadienylidenes, see: Stang, P. J. *Chem. Rev.* **1978**, *78*, 383−405.

(11) Al Dulayymi, J. R.; Baird, M. S. *Tetrahedron Lett.* **1995**, *36*, 3393−3396.

(12) Jones, W. M.; Stowe, M. E.; Wells, E. E., Jr.; Lester, E. W. *J. Am. Chem. Soc.* **1968**, *90*, 1849−1859.

(13) (a) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196−200. (b) Bernheim, R. A.; Kempf, R. J.; Reichenbecher, E. F. *J. Magn. Reson.* **1970**, *3*, 5−9.

(14) Merer, A. J. *Can. J. Phys.* **1967**, *45*, 4103−4111.

(15) Chi, F. K. Ph.D. Dissertation, Michigan State University, East Lansing, MI, 1972. See also: Chi, F. K.; Leroi, G. E. *Spectrochim. Acta* **1975**, *31A*, 1759−1771.

(16) Jacox, M. E.; Milligan, D. E. *Chem. Phys.* **1974**, *4*, 45−61.

(17) Reisenauer, H. P.; Maier, G.; Riemann, A.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 641.

(18) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 5183−5188.

(19) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Špirko, V. Hess, B. A., Jr.; Schaad, L. J. *J. Chem. Phys.* **1989**, *91*, 4763−4773.

(20) Huang, J. W.; Graham, W. R. M. *J. Chem. Phys.* **1990**, *93*, 1583−1596.

(21) (a) Kaiser, R. I.; Ochsenfeld, C.; Head-Gordon, M.; Lee, Y. T.; Suits, A. G. *Science* **1996**, *274*, 1508−1511. (b) Ochsenfeld, C.; Kaiser, R. I.; Lee, Y. T.; Suits, A. G.; Head-Gordon, M. *J. Chem. Phys.* **1997**, *106*, 4141−4151.

(22) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys. J.* **1985**, *299*, L63−L66.

(23) Bogey, M.; Demuynck, C.; Destombes, J. L.; Dubus, H. *J. Mol. Spectrosc.* **1987**, *122*, 313−324.

(24) Hirahara, Y.; Masuda, A.; Kawaguchi, K. *J. Chem. Phys.* **1991**, *95*, 3975−3979.

(25) Mollaaghababa, R.; Gottlieb, C. A.; Vrtilek, J. M.; Thaddeus, P. *J. Chem. Phys.* **1993**, *99*, 890−896.

(26) Vrtilek, J. M.; Gottlieb, C. A.; Gottlieb, E. W.; Killian, T. C.; Thaddeus, P. *Astrophys. J.* **1990**, *364*, L53−L56.

(27) Gottlieb, C. A.; Killian, T. C.; Thaddeus, P.; Botschwina, P.; Flügge, J.; Oswald, M. *J. Chem. Phys.* **1993**, *98*, 4478−4485.

(28) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1991**, *368*, L39-L41.

(29) Kanata, H.; Yamamoto, S.; Saito, S. *Chem. Phys. Lett.* **1987**, *140*, 221−224.

(30) Stanton, J. F.; DePinto, J. T.; Seburg, R. A.; Hodges, J. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 429−430.

(31) *The Diffuse Interstellar Bands*; Tielens, A. G. G. M.; Snow, T. P., Eds.; Kluwer: Dordrecht, The Netherlands, 1995.

(32) (a) Oakes, J. M.; Ellison, G. B. *Tetrahedron* **1986**, *42*, 6263−6267. (b) Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766−6778.

(33) Clauberg, H.; Minsek, D. W.; Chen, P. *J. Am. Chem. Soc.* **1992**, *114*, 99−107.

(34) (a) Chyall, L. J.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149/150*, 257−266. (b) Chyall, L. J.; Squires, R. R. Personal communication.

(35) (a) Maier, G.; Reisenauer, H. P.; Pacl, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1248−1250. (b) Maier, G.; Pacl, H.; Reisenauer, H. P.; Meudt, A.; Janoschek, R. *J. Am. Chem. Soc.* **1995**, *117*, 12712−12720.

(36) (a) DePinto, J. T.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 12573−12574. (b) DePinto, J. T., Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1993.

(37) Noro, M.; Masuda, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1994**, *116*, 6179−6190.

(38) (a) Maier, G.; Preiss, T.; Reisenauer, H. P. *Chem. Ber.* **1994**, *127*, 779−782. (b) Maier, G.; Preiss, T.; Reisenauer, H. P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 2014−2018.

(39) (a) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378−4383. (b) DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31-L35. (c) Cooper, D. L.; Murphy, S. C. *Astrophys. J.* **1988,** *333*, 482−490. (d) Jonas, V.; Böhme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640−1648. (e) Maclagan, R. G. A. R. *J. Mol. Struct.* **1992**, *258*, 175−178. (f) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 1507−1514. (g) Takahashi, J.; Yamashita, K. *J. Chem. Phys.* **1996**, *104*, 6613−6627.

(40) (a) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457−5460. (b) Lee, C. K.; Li, W. K. *J. Mol. Struct.* **1977**, *38*, 253−258. (c) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333−1338. (d) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2660−2664. (e) Shepard, R.; Banerjee, A.; Simons, J. *J. Am. Chem. Soc.* **1979**, *101*, 6174−6178. (f) Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137−142. (g) Bofill, J. M.; Farràs, J.; Olivella, S.; Solé, A.; Vilarrasa, J. *J. Am. Chem. Soc.* **1988**, *110*, 1694−1700. (h) Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900−5909.

Table 1. Experimental[a] and Calculated (CCSD(T)/cc-pVTZ)[b] Infrared Absorptions

1		**1a**			**1b**		
exptl	calcd	exptl	calcd	^{13}C shift exptl/calcd	exptl	calcd	^{13}C shift exptl/calcd
	3443 (3)	3273 (10)	3436 (3)			3443 (3)	
3265 (71)	3422 (86)	3257 (57)	3416 (86)	−8/−6	3265 (45)	3422 (86)	0/0
1621 (7)	1644 (10)	1612 (7)	1635 (10)	−9/−9	1581 (7)	1600 (9)	−40/−44
	1273 (0)		1250 (0)			1273 (0)	
550 (50)		547 (36)			550 (38)		
403 (25)	414 (15)	402 (23)	413 (16)	−1/−1	394 (30)	405 (17)	−9/−9
	412 (16)		410 (16)			402 (15)	
	334 (59)		333 (57)			333 (56)	
	242 (9)		241 (9)			241 (9)	
249 (100)	132 (77)	247 (100)	132 (76)	−2/0	247 (100)	132 (77)	−2/0

2		**2a**			**2b**			**2c**		
exptl	calcd	exptl	calcd	^{13}C shift exptl/calcd	exptl	calcd	^{13}C shift exptl/calcd	exptl	calcd	^{13}C shift exptl/calcd
	3210 (0.2)		3197 (0.2)			3210 (0.2)			3210 (0.2)	
	3146 (5)		3141 (5)			3147 (5)			3147 (5)	
1952 (100)	2019 (248)	1944 (81)	2010 (249)	−8/−9	1937 (74)	2003 (241)	−15/−16	1903 (100)	1967 (234)	−49/−52
1446 (16)	1503 (11)	1438 (4)	1495 (9)	−8/−8	1445 (15)[c]	1502 (11)	−1/−1	1445 (15)[c]	1503 (11)	−1/0
	1125 (2)		1108 (2)			1104 (3)			1124 (2)	
	1057 (3)		1049 (3)			1057 (3)			1052 (3)	
1002 (17)	1049 (19)	993 (3)	1039 (19)	−9/−10	1002 (7)[c]	1048 (19)	0/−1	1002 (7)[c]	1048 (19)	0/−1
	276 (1)		276 (1)			274 (2)			270 (1)	
	240 (3)		239 (3)			238 (3)			234 (3)	

3		**3a**			**3b**		
exptl	calcd	exptl	calcd	^{13}C shift exptl/calcd	exptl	calcd	^{13}C shift exptl/calcd
	3307 (0.6)		3300 (0.6)			3307 (0.6)	
	3259 (0.7)		3253 (0.7)			3259 (0.7)	
	1635 (0.4)		1608 (0.5)			1631 (0.1)	
1278 (100)	1316 (48)	1268 (100)	1306 (48)	−10/−10	1252 (100)	1290 (49)	−26/−26
	1089 (9)		1075 (9)			1083 (10)	
	998 (0)		992 (0)			998 (0)	
895 (14)	914 (4)		913 (18)			910 (18)	
883 (35)	914 (19)	888 (114)[d]	911 (5)		881 (114)[d]	906 (4)	
783 (54)	800 (20)	781 (77)[d]	798 (20)	−2/−2	781 (77)[d]	799 (20)	−2/−1

[a] Frequencies in cm^{-1}, relative intensities in parentheses; argon matrix, 8 K. [b] Frequencies in cm^{-1} (uncorrected), absolute intensities in parentheses in km/mol. [c] Intensity is the sum of both **2b** and **2c**. [d] Intensity is the sum of both **3a** and **3b**.

is the global minimum, singlet propadienylidene **2**[4,18,39,42] lies 10−14 kcal/mol above **3**, and triplet propynylidene **1**[19,39,43] lies 14−22 kcal/mol above **3**. A host of ab initio investigations has focused more narrowly on specific aspects of one or more C_3H_2 isomers. The geometry of triplet propynylidene **1** has proven to be especially challenging. Calculations based on electron correlation treatment by means of finite-order perturbation theory predict that **1** has an equilibrium geometry with C_s symmetry (Scheme 1).[19,39b,d,f,43b] However, methods based on a cluster expansion of the wave function (QCI and CC methods) predict that the equilibrium structure has C_2 symmetry.[43e] Vibrational frequencies predicted by QCISD with a 6-31G* basis display acceptable agreement with experiment.

Cyclopropyne **4** and silacyclopropyne are subjects of current experimental[6,35] and theoretical interest.[39a,d,41,44−47] The consensus is that singlet cyclopropyne (**4b**) is not a stable structure; whether it is a transition state or a higher-order saddle point depends on the level of theory used in the calculations. Remarkably, "planar" cyclopropyne (**4a**) lies lower in energy than "perpendicular" cyclopropyne (**4b**) at all levels of theory investigated thus far.[46,47]

Results

Generation and Characterization of Propynylidene. As described earlier,[5,6] photolysis (λ > 472 nm) of either [1-^{13}C]-diazopropyne (**6a**) or [3-^{13}C]diazopropyne (**6b**), matrix-isolated in argon at 8 K, produces exclusively [1-^{13}C]propynylidene (**1a**; IR (Ar, 8 K) Table 1; UV (Ar, 8 K) 231, 234, 240, 246, 251, 260, 275−350 (broad absorption exhibiting vibrational structure) nm; ESR (Ar, 14 K) $|D/hc| = 0.6412$ cm^{-1}, $|E/hc| = 0.001\,08$ cm^{-1}; $Z_1 = 3453$, $X_2 = 5873$, $Y_2 = 5922$, $Z_2 = 10\,243$ G, microwave frequency 9.5324 GHz; $A_X = A_Y = 38$ G, $A_Z = 7$ G) (Scheme 4). Similarly, new experiments establish that photolysis (λ > 472 nm) of [2-^{13}C]diazopropyne (**6c**), matrix-

(41) Lathan, W. A.; Radom, L.; Hariharan, P. C.; Hehre, W. J.; Pople, J. A. *Top. Curr. Chem.* **1973**, *40*, 1−45.
(42) (a) Kenney, J. W.; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6930−6936. (b) Dykstra, C. E.; Parsons, C. A.; Oates, C. L. *J. Am. Chem. Soc.* **1979**, *101*, 1962−1965.
(43) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc. London* **1957**, *A161*, 220−235. (b) Kühnel, W.; Gey, E.; Spangenberg, H.-J. *Z. Phys. Chem., Leipzig* **1982**, *263*, 641−645. (c) Fan, Q.; Pfeiffer, G. V. *Chem. Phys. Lett.* **1989**, *162*, 472−478. (d) Čársky, P.; Špirko, V.; Hess, B. A., Jr.; Schaad, L. J. *J. Phys. Chem.* **1990**, *94*, 5493−5496. (e) Herges, R.; Mebel, A. *J. Am. Chem. Soc.* **1994**, *116*, 8229−8237. (f) Walch, S. P. *J. Chem. Phys.* **1995**, *103*, 7064−7071.
(44) (a) Sherrill, C. D.; Brandow, C. G.; Allen, W. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1996**, *118*, 7158−7163. (b) Fitzgerald, G.; Schaefer, H. F. *Isr. J. Chem.* **1983**, *23*, 93−96. (c) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 3239−3240.
(45) Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362−367.
(46) Seburg, R. A. Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1995.
(47) Warner, P. Manuscript submitted.

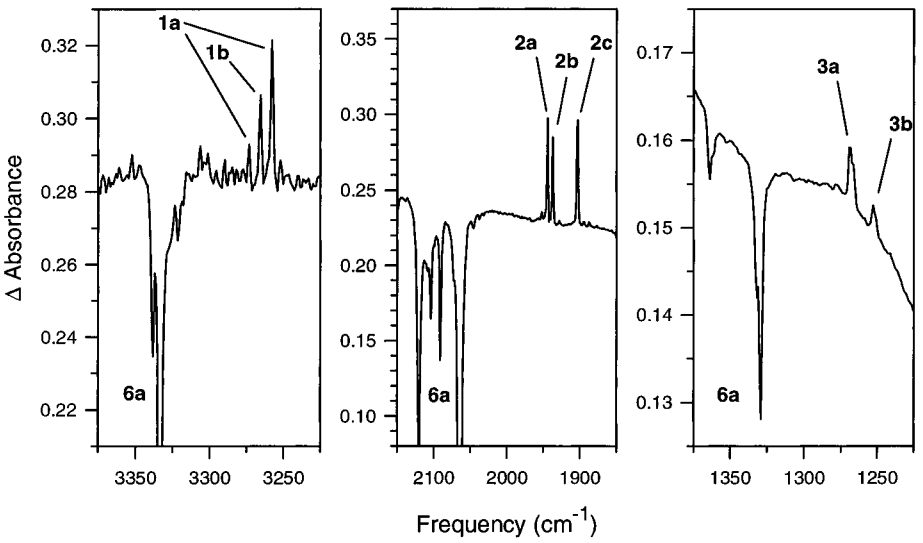
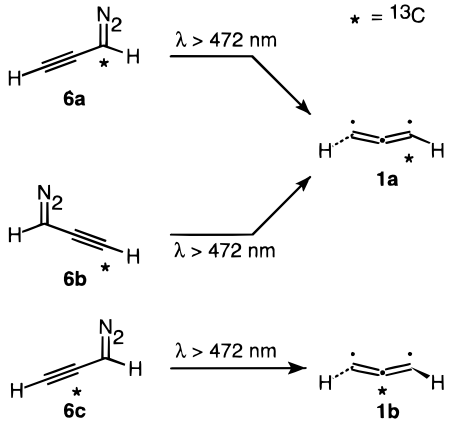


Figure 1. IR difference spectra obtained upon irradiation (λ > 472 nm, 6.75 h; λ > 237 nm, 15.5 h) of [1-^{13}C]diazopropyne (**6a**) in an argon matrix at 8 K, showing statistical scrambling of the ^{13}C-label in propynylidenes **1a** and **1b**, propadienylidenes **2a**, **2b**, and **2c**, and cyclopropenylidenes **3a** and **3b**.

Scheme 4



isolated in argon at 8 K, produces exclusively [2-^{13}C]propynylidene (**1b**; IR (Ar, 8 K) Table 1; ESR (Ar, 14 K) $|D/hc| = 0.6406$ cm^{-1}, $|E/hc| = 0.001\,08$ cm^{-1}; $Z_1 = 3458$, $X_2 = 5865$, $Y_2 = 5913$, $Z_2 = 10\,239$ G, microwave frequency 9.5126 GHz, $A_X = A_Y = 24$ G, $A_Z = 9$ G) (Scheme 4). We defer a detailed analysis and interpretation of the spectroscopic characterization of propynylidene to a subsequent publication.

Control experiments establish that no thermal rearrangements of **1** occur under the conditions of our matrix isolation experiments. Annealing an argon matrix containing only **1a** to 37 K reveals neither automerization to **1b** nor rearrangement to propadienylidene **2a**, **2b**, or **2c** or cyclopropenylidene **3a** or **3b**. Interestingly, annealing an argon matrix of **1** doped with 0.84% carbon monoxide to 37 K results in no reaction of **1** with CO to form ethynylketene.[48]

Broadband Irradiation (λ > 237 nm) of [1-^{13}C]Propynylidene (1a) and [2-^{13}C]Propynylidene (1b). Irradiation (λ > 237 nm, 15.5 h) of **1a** results in the decrease of **1a** and the appearance of IR signals due to [2-^{13}C]propynylidene (**1b**), three ^{13}C-isotopomers of propadienylidene (**2a**, **2b**, and **2c**), and two ^{13}C-isotopomers of cyclopropenylidene (**3a** and **3b**). The photoproducts exhibit complete scrambling of the ^{13}C-label (Figure 1). Assignment of the IR signals was made by comparison with the experimental IR bands of unlabeled **1**, **2**, and **3**,[18] with the known photochemical behavior of **1**, **2**, and **3**,[18] and with the computed IR spectra of the ^{13}C-isotopomers of **1**, **2**, and **3**.[6] These IR assignments are now further supported by studies of [2-^{13}C]propynylidene (**1b**). Irradiation (λ > 237 nm, 15.5 h) of **1b** produces **1a**, **2a**, **2b**, **2c**, **3a**, and **3b**, with relative IR intensities which equal those obtained from photolysis of **1a**. In particular, the agreement between the experimental and computed isotopic shifts in the IR spectra of **1**−**3** (Table 1) provides strong support for the proposed structural assignments.

ESR spectroscopy provides a complementary method for observing the photochemical automerization of ^{13}C-labeled propynylidene.[49] Irradiation (λ > 237 nm, 19 h; λ > 200 nm, 7 h) of a matrix containing only [1-^{13}C]propynylidene (**1a**) results in the appearance of the ESR signal of [2-^{13}C]propynylidene (**1b**). Separate irradiation (λ > 237 nm, 7 h; λ > 200 nm, 1 h) of a matrix containing only **1b** results in the appearance of the ESR signal of **1a**. In both cases, the experimental spectra obtained after the high-energy irradiations are satisfactorily reproduced by simulating[5,46] a 2:1 mixture of species (indicating a statistical distribution of the ^{13}C-label in **1a** and **1b**) with ^{13}C-hyperfine coupling constants of $A_X = A_Y = 38$ G for **1a** and $A_X = A_Y = 24$ G for **1b**.

The UV/vis spectrum of triplet [1-^{13}C]propynylidene (**1a**) is shown in Figure 2b; within the limits of our resolution, this spectrum does not differ from that of unlabeled **1**.[5] Bandpass irradiation (379 nm > λ > 273 nm, 13 h) of a matrix containing only **1a** produces the three isotopomers of propadienylidene (**2a**, **2b**, and **2c**; UV/vis (Ar, 8 K) 213, 218, 222, 227, 231, 235, 240, 246, 252, 258, 403, 421, 438, 461, 482, 510, 537, 604 nm). The UV/vis spectrum of the mixture of **2a**, **2b**, and **2c** is shown in Figure 2c; within the limits of our resolution, this spectrum does not differ from that of unlabeled **2**.[30] The extinction coefficient of **2** is qualitatively much larger than that of **1** (or **3**). IR spectra obtained after the corresponding photolysis of a separate matrix reveal only trace amounts of **1a**, **1b**, **3a**, and **3b**. Subsequent irradiation (λ > 399 nm, 57 h) of propadienylidenes **2a**, **2b**, and **2c** results in their decrease and in the appearance of cyclopropenylidenes **3a** and **3b** (Figure 2d). The only transitions we can confidently assign to **3a** and **3b** are those at 260 and 270 nm; nevertheless, the fact that **3a** and **3b** exhibit photochemistry upon long-wavelength irradiation

(48) Propynylidene **1** reacts photochemically in a CO-doped matrix (λ > 261 nm) to give ethynylketene: Seburg, R. A.; McMahon, R. J. Unpublished results.

(49) Data available as Supporting Information.

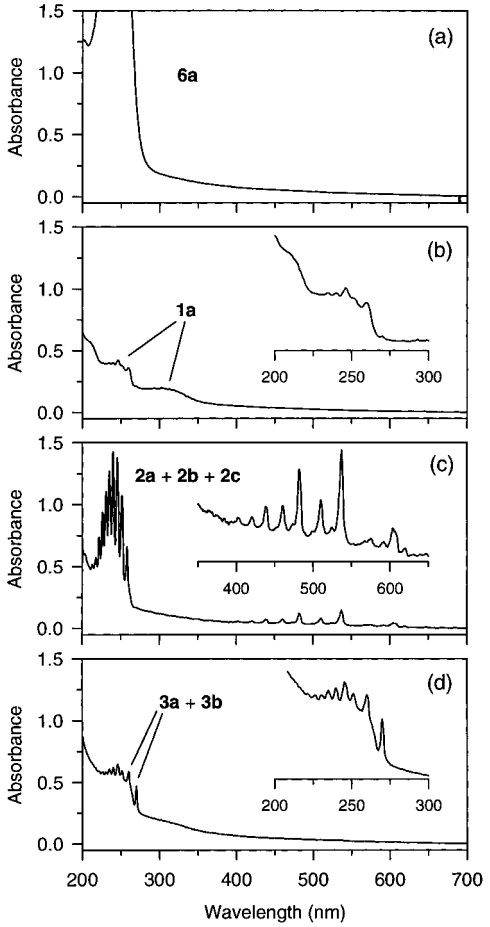
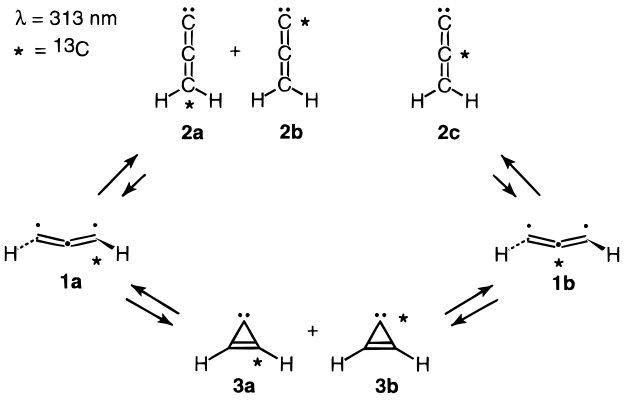


Figure 2. UV/vis absorption spectra (argon, 8 K): (a) [1-^{13}C]-diazopropyne (**6a**), (b) triplet [1-^{13}C]propynylidene (**1a**) obtained upon irradiation (λ > 472 nm, 18 h) of **6a**, (c) singlet [^{13}C]propadienylidenes **2a**, **2b**, and **2c** obtained by bandpass irradiation (379 nm > λ > 273 nm, 13 h) of **1a**, and (d) a mixture of predominantly singlet [^{13}C]cyclopropenylidenes **3a** and **3b** and traces of **1a**, **1b**, **2a**, **2b**, and **2c**, obtained by broadband irradiation (λ > 399 nm, 57 h) of the matrix in (c).

(λ > 444 nm, vide infra) implies that cyclopropenylidene (**3**) possesses weak, undetected visible absorptions. Monochromatic irradiation (λ = 271 ± 10 nm) causes the 260 and 270 nm absorptions to decrease and the absorptions of **1a**, **1b**, **2a**, **2b**, and **2c** to increase. The absorptions that occur at wavelengths shorter than 260 nm in Figure 2d are due to residual **2a**, **2b**, and **2c** and a trace of **1a** and **1b**. Again, the absorption spectra of **3a** and **3b** do not differ detectably from that of unlabeled **3**.

Monochromatic Irradiation (λ = 313 ± 10 nm) of [1-^{13}C]-Propynylidene (1a) or [2-^{13}C]Propynylidene (1b). Irradiation (λ = 313 ± 10 nm) of an argon matrix containing only [1-^{13}C]-propynylidene (**1a**) (as generated by λ > 472 nm photolysis of either [1-^{13}C]diazopropyne (**6a**) or [3-^{13}C]diazopropyne (**6b**)) scrambles the ^{13}C-label in the various photoproducts (Scheme 5).[6] The photolysis was monitored by IR spectroscopy at various time intervals. The following IR bands are well separated and thus convenient for observing this process and for determining relative integrated intensities of the species: 3265 (**1b**), 3257 (**1a**), 1944 (**2a**), 1937 (**2b**), 1903 (**2c**), 1268 (**3a**), and 1252 cm^{-1} (**3b**). Automerization of **1a** to **1b** is evident after only 0.4 h (Figure 3). Propynylidene **1b** reaches its maximum intensity at ca. 7 h of irradiation time, after which it decreases slowly.[49] A statistical scrambling of the label (2:1 intensity ratio) between **1a** and **1b** is achieved after roughly 10 h; the relative intensities of **1a** and **1b** remain constant through all subsequent photolyses. Cyclopropenylidenes **3a** and **3b** appear immediately upon photolysis, and statistical scrambling of the label (2:1 intensity ratio of **3a** to **3b**) is apparent even at the shortest irradiation times. This ratio remains constant throughout all subsequent photolyses. The growth of **3a** and **3b** gradually slows as the irradiation continues; prolonged irradiation (>40 h) eventually causes a slight decrease in intensity of **3a** and **3b**. Propadienylidenes **2a** and **2b** appear immediately in a 1:1 intensity ratio, and this ratio does not change significantly upon further photolysis at λ = 313 ± 10 nm. Appearance of center-labeled propadienylidene **2c**, however, lags well behind **2a** and **2b**; the intensity of the 1903 cm^{-1} band of **2c** still does not equal that of either **2a** or **2b** after 24 h of irradiation. The concentration of **1a** decreases to ca. 20% of its initial value upon extended irradiation (λ = 313 ± 10 nm, 67.6 h).[50]

Scheme 5



Irradiation (λ = 313 ± 10 nm) of a matrix containing only [2-^{13}C]propynylidene (**1b**) (as generated by λ > 472 nm photolysis of [2-^{13}C]diazopropyne (**6c**) in an argon matrix) provides additional and complementary evidence concerning the label-scrambling process (Scheme 5). Again, the photolysis was monitored by IR spectroscopy at various time intervals.[49] Upon photolysis of propynylidene **1b**, isotopomer **1a** appears immediately and grows to a maximum intensity at 6.7 h (Figure 3). Statistical scrambling of the ^{13}C-label (2:1 intensity ratio of **1a** to **1b**) occurs after roughly 10 h of photolysis. Cyclopropenylidenes **3a** and **3b** enter immediately. As their growth continues, the ratio of relative integrated intensities of the peaks at 1268 (**3a**) and 1252 cm^{-1} (**3b**) remains constant at ca. 2:1. Propadienylidene **2c** appears immediately, whereas production of **2a** and **2b** lags behind. Propadienylidenes **2a** and **2b** grow at the same rate, maintaining an intensity ratio of ca. 1:1. After 6.7 h, **2c** is still twice as prevalent as either **2a** or **2b**.

Broadband Photolysis (λ > 444 nm) of [^{13}C]Propadienylidenes 2a, 2b, and 2c. A matrix containing all seven ^{13}C-isotopomers was prepared by photolysis (λ = 313 ± 10 nm, 8 h) of an argon matrix containing only **1a**. The relatively short irradiation time was not sufficient to effect complete scrambling of the ^{13}C-label in the propadienylidenes **2a**, **2b**, and **2c** (cf. Figure 3). Subsequent broadband irradiation of this matrix at λ > 444 nm (up to 8 h) effects interconversion of **2b** and **2c**, as observed by IR spectroscopy (Figure 4 and Scheme 6). The slight decrease in **2a** indicates net disappearance of **2**.[51] In a similar manner, photolysis (λ = 313 ± 10 nm, 6.7 h) of a matrix containing only **1b** yields all seven ^{13}C-isotopomers with incomplete scrambling of the ^{13}C-label in **2a**, **2b**, and **2c** (cf.

(50) Maier et al. reported nearly complete conversion of **1** to **2** at 313 nm. We have been unable to achieve this high degree of conversion, which we attribute to minor differences in our irradiation source and monochromator.

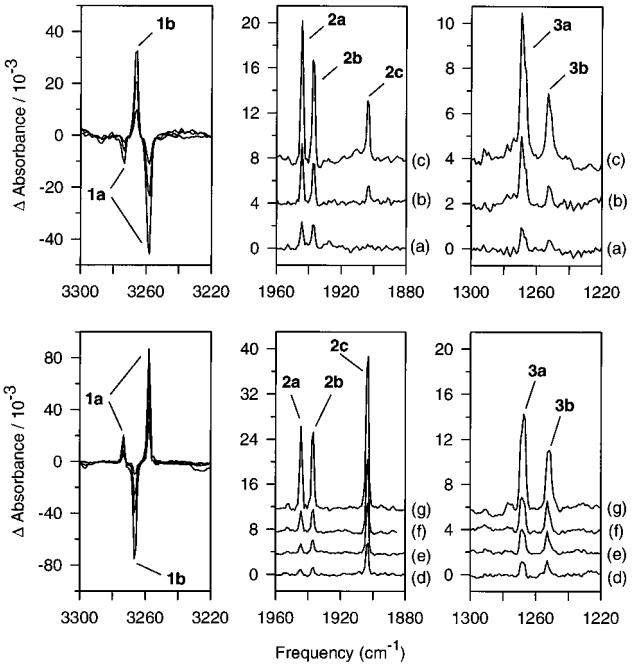


Figure 3. IR difference spectra obtained upon monochromatic irradiation ($\lambda = 313 \pm 10$ nm) of [^{13}C]propynylidene **1a** or **1b** in an argon matrix at 8 K, showing the time evolution of the ^{13}C-label scrambling in propynylidenes **1a** and **1b**, propadienylidenes **2a**, **2b**, and **2c**, and cyclopropenylidenes **3a** and **3b**. Top: Experiment begins with a matrix containing exclusively **1a**. The difference spectra result from subtraction of the spectrum of **1a** obtained before $\lambda = 313$ nm photolysis from those obtained after (a) 0.4, (b) 1.2, and (c) 3.0 h of irradiation. Bottom: Experiment begins with a matrix containing exclusively **1b**. The difference spectra result from subtraction of the spectrum of **1b** obtained before $\lambda = 313$ nm photolysis from those obtained after (d) 0.7, (e) 1.3, (f) 3.3, and (g) 6.7 h of irradiation.

Figure 3). Broadband irradiation ($\lambda > 444$ nm, up to 8 h) again yields interconversion of **2b** and **2c**, as observed by IR spectroscopy (Figure 4 and Scheme 6). Again, a slight decrease in **2a** occurs.

The following control experiments provide additional mechanistic evidence concerning the photoisomerizations of **2**. (i) Irradiation ($\lambda > 399$ nm) of a matrix containing only **1** results in no changes in the IR spectrum. Thus, **1** is not photosensitive under the conditions of the $\lambda > 444$ nm irradiation and is not a permissible ground-state intermediate in either the automerization of **2** or the conversion of **2** to **3**. (ii) Irradiation ($\lambda > 444$ nm, 2 h) of a matrix containing only **1** and **3** produces an extremely small quantity of **2** (0.0053*A* in the strong absorption band at 1953 cm^{-1}). Given the complete lack of photochemistry from **1** under these conditions, **3** must serve as the photochemical precursor of **2**. (The change in intensity of the IR absorptions of **3** is not detectable after only 2 h, presumably because of the significant differences in the extinction coefficients between **2** and **3**.) We thus conclude that **2** and **3** exist in a reversible photoequilibrium at $\lambda > 444$ nm. The very slow conversion of **3** to **2** under these conditions suggests that **3** is not a viable intermediate in the automerization of **2b** and **2c**.

(51) Prolonged irradiation ($\lambda > 444$ nm) of **2a**, **2b**, and **2c** results in the very slow conversion of propadienylidene **2** to cyclopropenylidene **3** and, eventually, propynylidene **1** (Scheme 6). IR difference spectra that illustrate this process are available as Supporting Information. After only 3 h, the decrease of the intense absorptions of **2a** and **2b** is evident, but growth of the weak absorptions of either **1** or **3** is not unambiguously apparent. After 7.5 h of irradiation, the growth of cyclopropenylidenes **3a** and **3b** becomes clear. Upon continued photolysis (21.5 h), **3a** and **3b** apparently achieve a photostationary concentration, and the growth of propynylidene **1** becomes evident. Prolonged irradiation (46.5 h total) leads to the net decrease of **2a**, **2b**, and **2c** and growth of **1a** and **1b**.

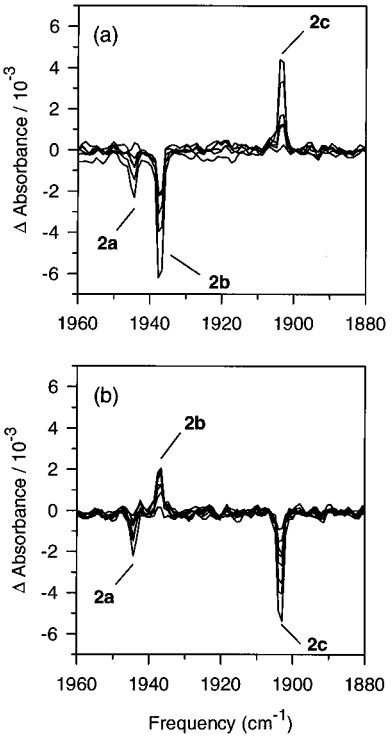
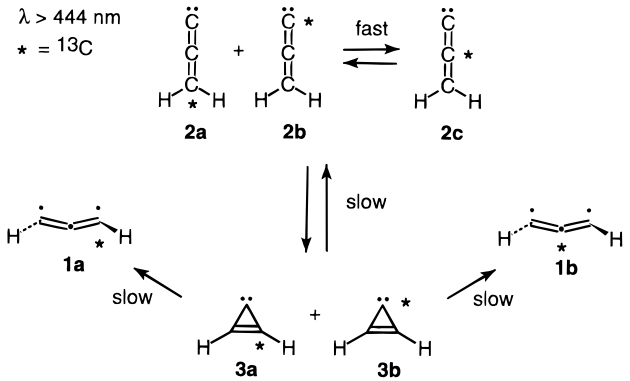


Figure 4. IR difference spectra obtained upon irradiation ($\lambda > 444$ nm) of a mixture of propynylidenes **1a** and **1b**, propadienylidenes **2a**, **2b**, and **2c**, and cyclopropenylidenes **3a** and **3b** containing a nonstatistical distribution of the ^{13}C-label. Spectra illustrate the photochemical automerization of **2b** and **2c**. Top: Experiment begins with a matrix containing a preponderance of **2a** and **2b** over **2c**. The difference spectra result from subtraction of the spectrum before 444 nm irradiation from those obtained after 20, 40, 50, 80, 180, and 240 min. Bottom: Experiment begins with a matrix containing a preponderance of **2c** over **2a** and **2b**. The difference spectra result from subtraction of the spectrum before 444 nm irradiation from those obtained after 10, 20, 30, 40, 60, 120, 180, 270, and 480 min.

Scheme 6



Computational Results. Propynylidene **1**, propadienylidene **2**, cyclopropenylidene **3**, cyclopropyne **4**, and propene-1,3-diylidene **5** were investigated at various levels of ab initio theory, including full geometry optimization at the CCSD(T)/cc-pVTZ level. Table 1 displays the uncorrected harmonic vibrational frequencies computed for the ^{13}C-isotopomers **1a**, **1b**, **2a**, **2b**, **2c**, **3a**, and **3b**. These frequencies provide the basis for assigning the experimental IR bands. The frequencies computed for triplet propynylidene **1** at the CCSD(T)/cc-pVTZ level actually display poorer agreement with the experimental frequencies than those computed at the QCISD/6-31G* level.[5,6,43e] The good agreement for the QCISD/6-31G* frequencies appears

Table 2. Computed Energies of C_3H_2 Isomers[a]

C_3H_2 isomer	total energy	imag freq	relative energy	ZPVE	ΔZPVE	relative energy + ΔZPVE
			CCSD(T)/cc-pVTZ			
HCCCH (**1**)	−115.157 218	0	14.0	16.18	−4.16	9.8
H_2CCC (**2**)	−115.157 026	0	14.1	19.48	−0.86	13.2
3	−115.179 519	0	0.0	20.34	0.00	0.0
4a (C_{2v}, planar)	−115.094 745	1	53.2	17.88	−2.46	50.7
4b (C_{2v}, perp)	−115.082 642	2	60.7			
			QCISD/6-31G*			
HCCCH (**1**)	−114.975 172	0	7.9	16.79	−3.69	4.2
H_2CCC (**2**)	−114.971 606	0	10.1	19.62	−0.86	9.2
3	−114.987 745	0	0.0	20.48	0.00	0.0
4a (C_{2v}, planar)	−114.906 199	1	51.2	18.1	−2.4	48.8
4b (C_{2v}, perp)	−114.891 962	2	60.1	18.8	−1.7	58.4
$C_2 + CH_2$[b]	−114.696 999	0	182.1			
			BLYP/6-31G*			
HCCCH (**1**)	−115.292 166	0	6.4	16.70	−2.81	3.6
H_2CCC (**2**)	−115.290 433	0	7.5	18.97	−0.54	7.0
3	−115.302 404	0	0.0	19.51	0.00	0.0
4a (C_{2v}, planar)	−115.224 510	1	48.8	17.3	−2.2	46.6
4b (C_{2v}, perp)	−115.208 998	2	58.6	18.1	−1.4	57.2
$C_2 + CH_2$[b]	−114.983 134	0	200.2			

[a] Total energy in hartrees; relative energy and zero-point vibrational energy (ZPVE) in kcal/mol. [b] Singlet C_2 + singlet CH_2.

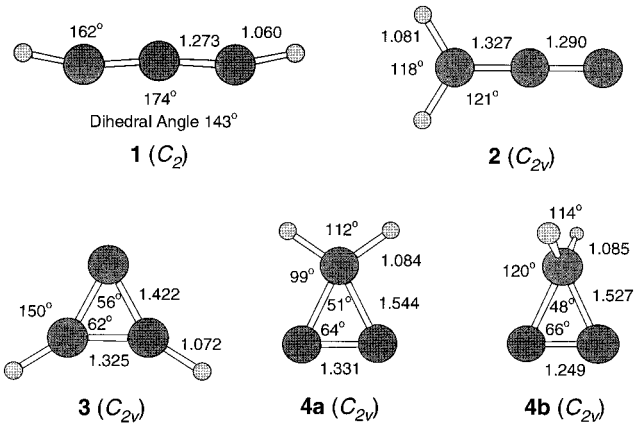


Figure 5. Computed structures of C_3H_2 isomers **1**−**4** (CCSD(T)/cc-pVTZ).

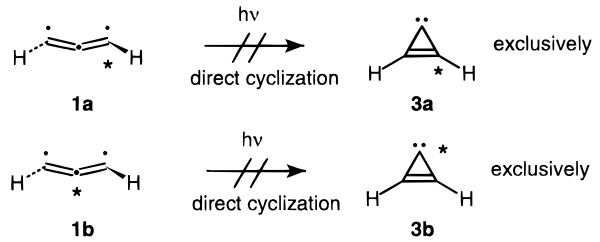
to be fortuitous; our current results suggest that the QCISD/6-31G* calculations are not converged with respect to either basis set or electron correlation (the basis set effect appears to be particularly significant).

Relative energies of the C_3H_2 isomers are presented in Table 2. Interestingly, our calculations predict triplet propynylidene **1** to lie 3−5 kcal/mol lower in energy than singlet propadienylidene **2**, in contrast to most previous studies.[39,43] The energy difference between propadienylidene **2** and cyclopropenylidene **3** (13.2 kcal/mol) computed at the CCSD(T) level is in good agreement with the experimental value (11.8 kcal/mol), determined from differences in heats of formation.[34]

Two structures of cyclopropyne **4** were considered, both having C_{2v} symmetry. In one of these (**4a**), the molecule is planar while the coordination of the central atom in the other isomer (**4b**) is approximately tetrahedral (Figure 5, Table 1). We designate these structures as planar C_{2v} and perpendicular C_{2v}, respectively.

At the CCSD(T)/cc-pVTZ, QCISD/6-31G*, and BLYP/6-31G* levels, the expected "perpendicular" geometry of singlet cyclopropyne **4b** displays two imaginary vibrational frequencies. One of the imaginary modes of **4b** corresponds to ring opening of **4b** to propadienylidene **2**. The other imaginary mode corresponds to torsional motion of the H_2C group.

Scheme 7



This latter mode led us to investigate planar cyclopropyne **4a**. Structures optimized for **4a** display a single imaginary frequency at the same levels of theory, thereby implicating this species as a transition state for the automerization of **2**. Remarkably, structure **4a**, which contains a planar, tetracoordinate carbon atom, lies 7−10 kcal/mol lower in energy than structure **4b**, which contains a tetrahedral carbon atom.

Discussion

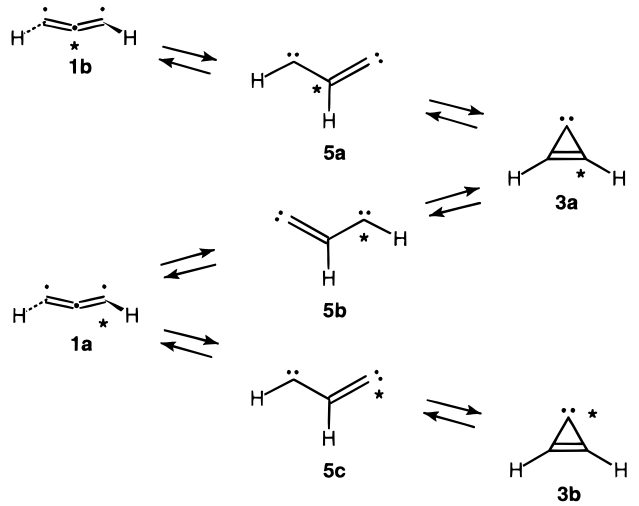
Our initial ^{13}C-labeling experiments revealed two distinct photochemical processes that scramble the ^{13}C-label in C_3H_2 isomers.[6] The current studies provide additional insight into these label-scrambling processes. New experimental studies of the scrambling in [2-^{13}C]propynylidene (**1b**) provide a critical test in support of our previously proposed mechanism. New computational studies provide important guidance in considering mechanistic alternatives.

1. Mechanism of the $\lambda = 313 \pm 10$ nm Photochemistry. A. Cyclopropenylidene Formation. Propynylidenes **1** partition between propadienylidenes **2** and cyclopropenylidenes **3** upon irradiation ($\lambda = 313 \pm 10$ nm). Cyclopropenylidenes **3a** and **3b** appear immediately upon photolysis of either **1a** or **1b** (Figure 3). The ratio of integrated intensities of **3a** and **3b** is ca. 2:1 at very early irradiation times and throughout the irradiation. The second propynylidene isotopomer **1b** or **1a**, respectively, also appears immediately. Statistical distribution of the label in **1a** and **1b** requires 10 h, but a quantitative interpretation of the rate of scrambling in **1a** and **1b** is very difficult.[52] Any mechanism that invokes either **1a** or **1b** to explain the scrambling of the label in **3** can be excluded, for the label is fully distributed in **3** long before in **1**. Formation of **3** by simple ring closure of **1** cannot account for the observed label scrambling in **3**: this mechanism predicts that **1a** would form exclusively **3a** and **1b** would form exclusively **3b** at early photolysis times (Scheme 7). A photochemical 1,2-hydrogen shift must accompany the formation of **3a** and **3b** from either **1a** or **1b**. Simple ring closure of **1** followed by rapid 1,2-hydrogen shifts in **3** accounts for the immediate statistical scrambling of the label in **3**, whereas hydrogen migration in concert with or preceding ring closure does not (Scheme 8).

Cyclization concomitant with hydrogen migration is inconsistent with the experimental data. This mechanism predicts that **1a** should initially produce **3a** and **3b** in a 1:1 ratio and that **1b** should initially produce only **3a**. Hydrogen migration prior to simple ring closure would produce transient propene-1,3-diylidene (**5**; Scheme 8). IR bands were attributed to this C_3H_2 species by Huang and Graham: (*Z*)-**5**, 3292 cm^{-1}; (*E*)-**5**, 1960 cm^{-1}.[20] We do not observe any IR bands which can be attributed to **5** during the $\lambda = 313$ nm irradiation, but this species may be too photolabile to build up an observable concentration.

(52) In all experiments, one isotopomer of propynylidene **1** is present in large excess at the beginning of the photolysis and throughout the early stages of photolysis. The rate of disappearance of **1** is influenced by the rate at which **1** is regenerated by photoequilibration with **3**, the extinction coefficient of **1** at the photolysis wavelength, and the quantum yield for rearrangement of **1** to **3**. None of these quantities are known.

Scheme 8

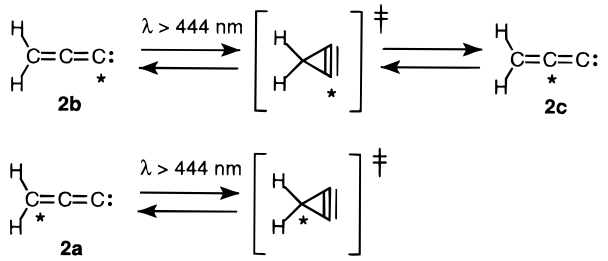


The mechanism depicted in Scheme 8 predicts that **1b** would afford solely **3a** at early photolysis times, for H-migration in **1b** can give only one isotopomer of **5**. To gain further insight into the structure and energetics of **5**, we carried out a preliminary theoretical investigation of the *Z* and *E* conformers of **5** at the MBPT(2)/DZP level of theory. It appears that both singlet isomers rearrange spontaneously to cyclopropenylidene **3**, while distinct but nearly degenerate minima are found for the triplets. The *Z* and *E* triplet isomers of **5** lie >50 kcal/mol above cyclopropenylidene **3**. We cannot unequivocally rule out the involvement of **5** in the photochemistry of propynylidene **1** and cyclopropenylidene **3**, but the simple involvement of **5** is not sufficient to explain the label scrambling process.

B. Propadienylidene Formation. The mechanism depicted in Scheme 5 for distribution of the ^{13}C-label in propadienylidenes **2a**, **2b**, and **2c** is consistent with the differential rates of formation of these species from either **1a** or **1b**. Conversion of **1** to **2** apparently occurs by a photochemical 1,3-hydrogen shift, since only **2a** and **2b** are formed initially from **1a**; in the complementary experiment, only **2c** is formed initially from **1b** (Figure 3).[53] In the former case, **2c** appears only after a significant amount of **1b** is present; in the latter case, **2a** and **2b** emerge only after **1a** is present. Conversion of **1** to **2** is slow relative to interconversion of **1** and **3**, for **1b** appears more rapidly than **2c** (from photolysis of a matrix of only **1a**) and **1a** appears more rapidly than **2a** and **2b** (from photolysis of a matrix of only **1b**). Also, **1a** and **1b** reach statistical distribution of the label after ca. 10 h, whereas the relative amounts of **2a**, **2b**, and **2c** have not yet converged after 50 h of separate photolyses of **1a** and **1b**. The conversion of **1** to **2** appears to be reversible upon photolysis at $\lambda = 313$ nm, although the conversion of **2** to **1** is very slow. Evidence for the photochemical conversion of **2** to **1** derives from the following experiment: starting from a matrix containing only **1b**, statistical scrambling in **1** precedes that in **2** by many hours. The eventual equilibration of **2c** with **2a** and **2b** is most plausibly interpreted in terms of reversion of **2c** to **1b**. As we will see below, there is a pathway to interconvert **2b** and **2c** using different photolysis conditions. But the requirement that these species must also equilibrate with **2a** seems to require reversion of **2** to **1**. The mechanistic scheme is consistent with that proposed by Maier et al. for the unlabeled C_3H_2 isomers.[18]

(53) Formally, the net 1,3-hydrogen migration in **1** to yield **2** might occur by consecutive 1,2-hydrogen shifts. This pathway requires biscarbene **5** as an intermediate. Calculations predict that singlet **5** will spontaneously cyclize to cyclopropenylidene **3**. Thus, the rearrangement of **1** to **2** by consecutive 1,2-hydrogen shifts appears implausible on the singlet surface. We cannot rigorously exclude the involvement of triplet **5**.

Scheme 9



2. Mechanism of the λ > 444 nm Photochemistry. Distinct photochemistry of the C_3H_2 species and evidence for a unique mechanism for scrambling of the ^{13}C-label in propadienylidenes **2a**, **2b**, and **2c** are observed upon irradiation with λ > 444 nm (Scheme 6). Figure 4 illustrates two important experimental observations. At short photolysis times, each of the individual propadienylidene isotopomers **2a**, **2b**, and **2c** displays unique photochemical behavior. Isomer **2a** slowly disappears, while isomers **2b** and **2c** rapidly photoequilibrate. The automerization of **2b** and **2c** occurs from both precursor propynylidenes **1a** and **1b** (Figure 4) but in opposite directions. At longer photolysis times, propadienylidenes **2** are converted directly to cyclopropenylidenes **3**, which subsequently suffer photochemical isomerization to propynylidenes **1**.

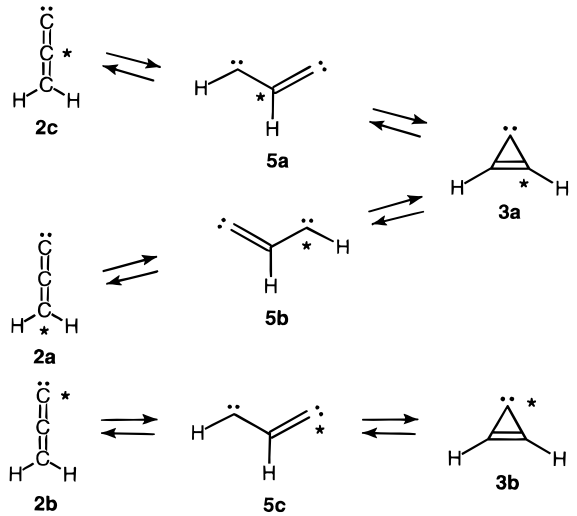
We consider three mechanistic possibilities for the automerization of **2b** and **2c**. First, **2b** and **2c** interconvert through a cyclopropyne **4** intermediate or transition state (Scheme 9). Second, **2b** and **2c** rapidly photoequilibrate with **3**, which provides the means for scrambling of the label (Schemes 6 and 10). Third, **2b** and **2c** fragment to CH_2 and ^{13}C═C, followed by recombination of CH_2 with either end of ^{13}C═C (Scheme 11). The automerization mechanism cannot involve triplet propynylidene **1**, for **1** is stable to irradiation at λ > 444 nm. The mechanism probably does not involve **2a**; after the effect of the overall conversion to **3a** and **3b** is removed from the intensity data, the relative amount of **2a** remains approximately constant.[49] Experimental and computational results favor the cyclopropyne mechanism.

The cyclopropyne mechanism (Scheme 9) predicts equilibration of **2b** and **2c**, with no change in **2a**. This is consistent with the experimental observations at short photolysis time. At longer irradiation time, the slow disappearance of **2a** serves as an "internal standard" to monitor the net conversion of **2a**, **2b**, and **2c** to **3a** and **3b**. Ab initio calculations predict planar singlet cyclopropyne **4a** to be the transition state for interconversion of **2b** and **2c**. Cyclopropyne **4a** is computed to lie 37.5 kcal/mol above **2**; **4a** is thus accessible under the photolysis conditions employed in the experiment (λ > 444 nm, <64 kcal/mol). In contrast to the sila-substituted analog,[35] we observed no IR bands that could be ascribed to **4** during the photolysis.

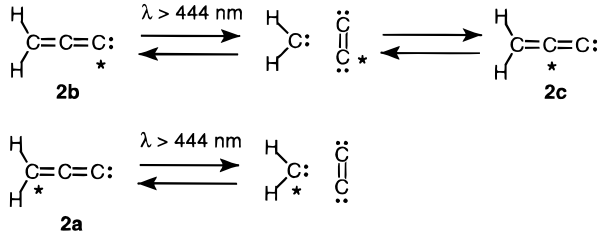
Two factors argue against the mechanism that invokes cyclopropenylidene **3** to explain the label scrambling in propadienylidene **2** (Scheme 6). Control studies establish that the conversion of **3** to **2** at λ > 444 nm is too slow to account for the rapid changes in **2b** and **2c**. Conversion of **3** to **2** (when no **2** is initially present) at λ > 444 nm is very slow; in 2 h, the 1953 cm^{-1} peak of unlabeled **2** increases by only 0.0053*A*. If this increase were spread among three isotopomers, each would increase by only 0.0018*A*. The magnitudes of the changes in intensity of the peaks of **2b** and **2c** after 2 h are 0.0053*A* and 0.0048*A* (Figure 4), too large to be accounted for by rearrangement of **3** to **2**.[54]

Although details concerning the interconversion of **2** → **3** remain incomplete, sufficient evidence exists to exclude the

Scheme 10



Scheme 11



equilibration of **2** and **3** as the basis for the observed label scrambling in **2**. The interconversion of **2** and **3** necessarily involves hydrogen migration. A photochemical 1,3-shift in **2** would produce propynylidene (**1**), which is known to be stable under the irradiation conditions. Thus, a 1,3-hydrogen migration in **2** is not consistent with the experimental observations. A 1,2-hydrogen migration in **2** can account for the slow overall conversion of **2** to **3**, but cannot account for the rapid label scrambling of **2b** and **2c**. As shown in Scheme 10, equilibration via 1,2-shifts would result in interconversion of **2a** and **2c**, not **2b** and **2c**. Finally, rapid 1,2-hydrogen migrations in cyclopropenylidene **3a** and **3b** (Scheme 6) are inconsistent with the experimental observations, as this process should equilibrate all three propadienylidenes, not just **2b** and **2c**.

Computational data argue against a fragmentation/recombination mechanism for interconversion of **2b** and **2c** (Scheme 11). The energies of the fragments CH_2 and C_2 in their lowest singlet states lie at least 170 kcal/mol higher in energy than **2** (Table 1).[55] This energy far exceeds the energy available from the λ > 444 nm irradiation (<64 kcal/mol).

3. Ab Initio Computations of Cyclopropyne 4: Mechanistic Implications. As in each of the previous theoretical studies,[39,41,44,46,47] we found that perpendicular C_{2v} cyclopropyne (**4b**) is not an energy minimum (Figure 5). The CCSD(T)/cc-pVTZ, QCISD/6-31G*, and BLYP/6-31G* levels of theory predict *two* imaginary frequencies at this geometry, in contrast to TCSCF/DZ+d computations[44a,b] and MP2/6-31G* computations,[39d,45] which each find one imaginary frequency. At the CCSD(T)/cc-pVTZ, QCISD/6-31G*, BLYP/6-31G*, and MP2/6-31G* levels of theory, true transition states were found for **4** with the planar C_{2v} structure **4a** (Figure 5), each about 7−10 kcal/mol below the corresponding **4b** (Table 2). Thus, the lower energy pathway for interconversion of propadienylidenes **2b** and **2c** involves bending the C−C−C angle in the plane of the molecule. Both **4a** and **4b** are accessible upon irradiation at λ > 444 nm, where the photon energy is <64 kcal/mol.

Summary

Two automerization processes occur among C_3H_2 isomers. UV photolysis ($\lambda = 313 \pm 10$ nm) leads to ^{13}C-label scrambling in propynylidenes **1a** and **1b** via reversible photoisomerization to cyclopropenylidenes **3a** and **3b**. The label scrambling appears to occur by rapid 1,2-hydrogen shifts in **3a** and **3b**. The appearance of propadienylidenes **2a**, **2b**, and **2c** at different rates indicates that conversion of **1** to **2** is much slower than interconversion of **1** and **3**. Broadband visible photolysis (λ > 444 nm) effects overall conversion of **2** to **1** through **3** and induces an automerization reaction of **2b** and **2c** that may access regions of the potential energy surface that correspond to the cyclopropyne **4** transition state. Calculations suggest that planar cyclopropyne (**4a**) lies approximately 7 kcal/mol below the perpendicular isomer (**4b**).

Methods Section

Computational Methods. Ab initio calculations were performed using the ACESII,[56] Gaussian 92,[57a] or Gaussian 94[57b] programs. Calculations employed cc-pVTZ[58] or 6-31G*[59] basis sets. Spin-unrestricted wave functions were used for triplets and spin-restricted wave functions for singlets. The computations utilized coupled cluster theory in the singles and doubles approximation[60] with a perturbative correction for the effects of triply excited determinants (CCSD(T)),[61] quadratic configuration interaction theory with single and double excitations (QCISD),[62] Møller−Plesset perturbation theory (MP2),[63] and density functional theory (DFT).[64] QCISD and MP2 calculations employed the frozen core approximation. DFT computations used the nonlocal exchange potential of Becke[65] and the nonlocal correlation

(54) Irradiation (λ > 444 nm, 3 h) of a matrix containing **2a**, **2b**, and **2c** (ca. 0.200*A* each) and no **3a** or **3b** results in an intensity increase in **2c** of 0.0113*A* and a decrease in **2a** and **2b** of 0.0130*A* and 0.0210*A*, respectively. These changes are at least 4 times too large to be accounted for by the minor conversion of **3** to **2**.

(55) A relatively large uncertainty in this energy difference exists because of the drastically different bonding environments of reactants and products, as well as the known difficulties of accounting for electron correlation effects in C_2. However, the associated error is certainly less than 100 kcal/mol.

(56) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.* **1991**, *S182*, 207.

(57) (a) *Gaussian 92* (Revisions A and G.3): Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian Inc., Pittsburgh, PA, 1992. (b) *Gaussian 94* (Revisions C.2 and D.3): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(58) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796−6806.

(59) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

(60) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(61) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

(62) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968−5975.

(63) (a) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244−4245. (b) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

(64) (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651−667 and reference therein. (b) Labanowski, J. K., Andzelm, J. W., Eds. *Density Functional Theory in Chemistry*; Springer-Verlag: New York, 1991. (c) Parr, R. G., Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(65) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

functional of Lee, Yang, and Parr (BLYP).[66] Geometries were optimized using analytic gradients. The nature of the stationary points (minima, transition states, or saddle points) was determined by calculating the harmonic vibrational frequencies. MP2 and BLYP vibrational frequencies were computed using analytic second derivatives, whereas numerical differentiation of analytic first derivatives provided CCSD(T) and QCISD vibrational frequencies.

Experimental Methods. Infrared spectroscopy employed a Nicolet 740 FTIR instrument. A liquid N_2 cooled MCT-B detector and a TGS detector were used for mid-IR (4000−400 cm^{-1}) and far-IR (600−200 cm^{-1}) spectroscopy, respectively. Ultraviolet−visible spectroscopy was performed with a Hitachi U-3210 spectrometer. ESR experiments employed a Bruker ESP 300 E spectrometer at X-band with a Bruker ER 042 MRHE microwave bridge. An EIP microwave counter (model 625A CW) provided the microwave frequency. An ILC Technology LX300UV 300-W high-pressure xenon arc lamp served as the irradiation source. Wavelength selection was carried out with glass cutoff filters (<0.1% transmittance of wavelengths shorter than the specified values): Corning 2-73 (>571 nm), Corning 3-71 (>472 nm), Corning 3-72 (>444 nm), Corning 3-73 (>399 nm), Hoya Optics U-340 (379 nm > λ > 273 nm), Corning 0-53 (>261 nm), Corning 0-56 (>237 nm). A Spectral Energy GM 252 monochromator effected narrow band photolysis (bandwidth ca. 20 nm).

Matrix Isolation Spectroscopy. The experimental technique and apparatus for low-temperature matrix-isolation spectroscopy have been described previously.[67] The research grade gases for the matrices were purchased from the following vendors: argon (99.9995%), Liquid Carbonic and Alphagaz; carbon monoxide (99.99%), Airco.

(66) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1993**, *37*, 785−789.
(67) (a) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183−7189. (b) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597−7606.

[1-^{13}C]Diazopropyne (6a), [3-^{13}C]Diazopropyne (6b), and [2-^{13}C]-Diazopropyne (6c). The diazo compounds were prepared by pyrolysis of the corresponding tosylhydrazone salts. The syntheses of the ^{13}C-labeled tosylhydrazones are reported elsewhere.[46]

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Supporting Information Available: Plots of the integrated IR intensities as a function of irradiation time for the spectra shown in Figures 3 and 4, ESR spectra illustrating photochemical automerization of triplet **1a** and **1b**, IR difference spectra obtained upon irradiation (λ > 444 nm) of **1** and **2**, MP2/6-31G* energies for various C_3H_2 isomers, plus structural data for unsymmetrical planar cyclopropyne, and cartesian coordinates for the computed structures of **1**−**4** (CCSD(T)/cc-pVTZ) (7 pages). See any current masthead page for ordering and Internet access instructions.

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