Evidence for the Non-Concerted Addition of Difluorovinylidene to Acetylenes**

Carsten Kötting, Wolfram Sander,* and Michael Senzlober

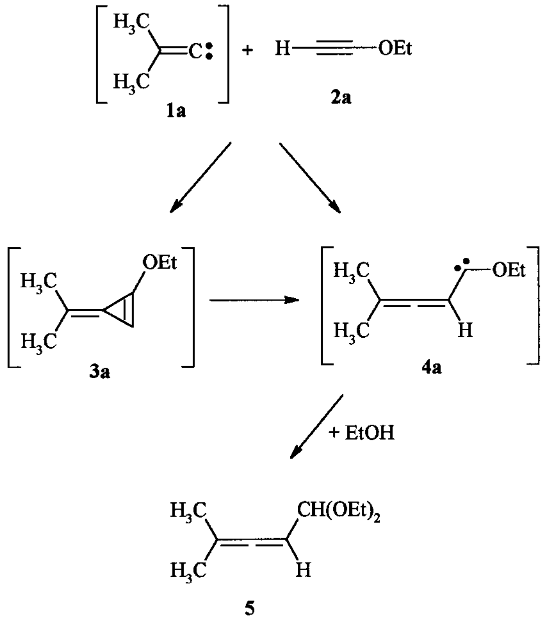
Abstract: Difluorovinylidene (**1b**) is an extremely electrophilic and reactive singlet carbene that can be generated in argon matrices in high yields. The thermal reaction of **1b** with difluoroacetylene (**2b**) at 35–40 K results in the formation of singlet allenylcarbene **4b** as the primary product, which on subsequent irradiation with visible light ($\lambda > 420$ nm) rearranges to methylenecyclopropene **3b**. The new compounds were identified by IR spectroscopy in combination with density functional theory (DFT) calculations at the B3LYP/6–311G(d,p) level of theory. These results clearly demonstrate the non-concerted formation of **3b**. Under similar conditions the thermal reaction of vinylidene **1b** with acetylene (**2c**) directly leads to methylenecyclopropene **3c** as the main product. Since—according to the DFT calcultations—allenylcarbene **4c** is not a minimum, the formation of **3c** most likely is a concerted, although highly asynchronous reaction. Visible irradiation ($\lambda > 420$ nm) of **3c** produces enyne **11**, which on UV irradiation gives 1,1-difluorobutatriene (**10**).

Keywords: alkynes • carbenes • matrix isolation • vinylidene

Introduction

The addition of carbenes or carbenoids to multiple bond systems is the most important synthetic route to three-membered ring systems.[1–3] Thus, a convenient way to synthesize methylenecyclopropanes is the cycloaddition of vinylidenes to olefins. Stang et al. investigated the stereochemistry of this reaction and concluded that the cycloaddition is a concerted reaction governed by the interaction of the virtual p orbital at the carbene center with the olefinic π system.[4] The reaction of triplet fluorenylidene with terminal alkynes at 77 K was shown by Lee and Jackson to produce vinylcarbenes.[5] The vinylcarbenes are indefinitely stable under these conditions, while in fluid solution only cyclopropenes are observed and the vinylcarbenes could not even be trapped. Since fluorenylidene has a very small singlet–triplet gap,[6, 7] one can speculate that the cyclopropenes are formed by reaction of the thermally populated singlet fluorenylidene.

Only a few reports on the cycloaddition of vinylidenes to acetylenes have appeared in literature. Newman and Beard investigated the reaction of dimethylvinylidene (**1a**), generated by α-elimination from the corresponding triflate, with ethoxyacetylene (**2a**) in ethanol as solvent (Scheme 1).[8] Allene **5**, the formal product of the insertion of allenylcarbene



Scheme 1. Reaction of dimethylvinylidene (**1a**) with ethoxyacetylene (**2a**) in ethanol.

---

[*] Prof. Dr. W. Sander, Dipl.-Chem. C. Kötting
Lehrstuhl für Organische Chemie II der Ruhr-Universität
D-44780 Bochum (Germany)
Fax: (+49) 234-709-4353
E-mail: sander@neon.orch.ruhr-uni-bochum.de

Dr. M. Senzlober
FB9 der Universität-GH, Anorganische Chemie
D-42097 Wuppertal (Germany)
Fax: (+49) 202-4392901
E-mail: buerger1@uni-wuppertal.de

[**] This work was financially supported by the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

4a into the OH bond of ethanol, was formed in 35% yield. From the experiments it could not be decided whether carbene **4a** was formed by ring-opening of cyclopropene **3a** or as the primary intermediate of the addition of **1a** and **2a**.

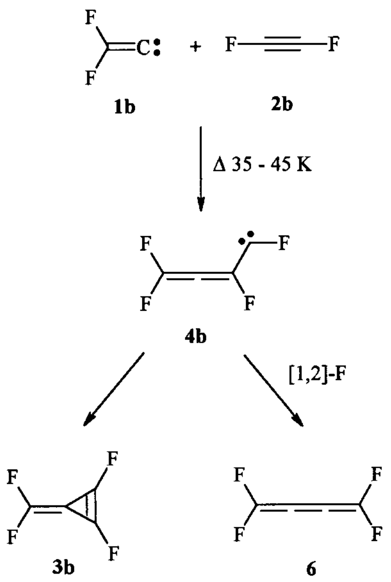
In gas-phase studies it was demonstrated that difluorovinylidene (**1b**) rapidly reacts with olefins and both inserts into CH bonds and adds to the double bonds.[9–11] Thus, the gas-phase reaction of **1b** and cyclopentene produces CH insertion products as well as difluoromethylenecyclopropane in low yields.[11] However, neither **1b** nor other reaction intermediates were directly observed in these studies, and the question whether or not this reaction is concerted was not addressed. In a theoretical study the addition of methylene, but not vinylidene, to acetylene was investigated by Jackson and O'Brien.[12] Based on semiempirical and ab initio methods they concluded that vinylcarbene is the primary product on the triplet surface, while on the singlet surface the formation of cyclopropene is concerted.

Recently we described the synthesis and spectroscopic characterization of **1b** in solid argon at 7 K. [13] Carbene **1b** is extremely electrophilic and even at cryogenic temperatures rapidly reacts with N_2, CO,[13] CO_2,[14] and Xe.[15] Here we report on the reaction of **1b** with both difluoroacetylene **2b** and acetylene **2c** and present evidence that at least in the former reaction a non-concerted pathway is followed.

Results and Discussion

Addition of difluorovinylidene (1b) to difluoroacetylene (2b): Irradiation of difluoroacetylene (**2b**), matrix-isolated in argon at 7 K, with an ArF excimer laser (193 nm) produces high yields (up to 90%) of difluorovinylidene (**1b**). Annealing of an argon matrix containing **1b** at 35–40 K—which allows the diffusion of small trapped species such as **1b** within several minutes—results in the dimerization of **1b** to give tetrafluorobutatriene (**6**) (Scheme 2). In addition, small amounts of diazo compound **7** are formed by the reaction of **1b** with traces of nitrogen (contamination of the argon matrix).

Abstract in German: *Difluorovinylidene (**1b**) ist ein extrem reaktives, electrophiles Singulett-Carben, das in hohen Ausbeuten in Argon-Matrizes erhalten werden kann. Die thermische Reaktion von **1b** mit Difluoracetylen (**2b**) bei 35–40 K führt zu Allenylcarben **4b** als dem primären Produkt, das sich bei anschließender Bestrahlung mit sichtbarem Licht (λ > 420 nm) zu Methylencyclopropen **3b** umlagert. Alle neuen Verbindungen wurden durch IR-Spektroskopie in Verbindung mit DFT-Rechnungen (B3LYP/6–311G(d,p)) charakterisiert. Diese Ergebnisse belegen eindeutig, daß **3b** in einer nicht-konzertierten Reaktion gebildet wird. Unter ähnlichen Bedingungen führt die Reaktion von Vinyliden **1b** mit Acetylen (**2c**) direkt zu Methylencyclopropen **3c** als dem primärem Produkt. Da nach den DFT-Rechnungen Allenylcarben **4c** kein Minimum auf der Hyperfläche darstellt, handelt es sich bei der Bildung von **3c** sehr wahrscheinlich um eine konzertierte, obgleich sehr asynchrone Reaktion. Bestrahlung von **3c** mit sichtbarem Licht (λ > 420 nm) führt zu Enin **11**, das sich wiederum bei UV-Bestrahlung in 1,1-Difluorbutatrien (**10**) umlagert.*



Scheme 2. Addition of difluorovinylidene (**1b**) to difluoroacetylene (**2b**).

If the matrix contains unconverted acetylene **2b** in addition to vinylidene **1b**, annealing of the matrix produces a further compound **A** with IR absorptions at 1996, 1444, 1187, and 1174 cm^{-1} (Table 1, Figure 1). Compound **A** is photolabile, and visible light irradiation (>420 nm, Figure 1) yields a second compound **B** with IR bands at 2000, 1318, 1253, 1242, and 875 cm^{-1} as major, and tetrafluorobutatriene (**6**, 938, 1271, 1735 cm^{-1})[15] as minor product. The IR spectrum of **B** nicely agrees with the calculated spectrum (all calculations are done at the B3LYP/6–311G(d) level of theory) of tetrafluoromethylenecyclopropene (**3b**). Compared to the parent methylenecyclopropene,[16, 17] the fluorine substitution in **3b** causes a substantial blue-shift of the characteristic high frequency C–C stretching vibration from 1770 to 2000 cm^{-1}.

Table 1. Computed harmonic and experimental vibrational wavenumbers [cm^{-1}] of **4b.**

Mode	Description	$\tilde{\nu}_{exp}$[a]	I_{exp}[a,b]	$\tilde{\nu}_{calcd}$[c,d]	I_{calcd}[b,d]
trans-14	$\tilde{\nu}(C_{allene}F)$	1174.2	100	1181.0	100
trans-15	$\tilde{\nu}(C_{carbene}F)$	1186.5	81	1199.4	53
16	$\tilde{\nu}_{as}(CF_2)$	1268.0	53	1266.5	66
17	$\tilde{\nu}_s(CCC)$	1444.4	32	1471.2	48
trans-18	$\tilde{\nu}_{as}(CCC)$	1995.6	59	2068.9	77
cis-15	$\tilde{\nu}(CF)$	1194.5		1203.5	
cis-18	$\tilde{\nu}_{as}(CCC)$	2006.8		2086.2	

[a] Argon at 10 K. [b] Relative intensities, based on the strongest absorption. [c] Other vibrations of **4b**, not observed in the experimental spectrum: $\tilde{\nu}_{calcd}(I_{rel})$: 47.1 (1), 64.7 (0), 112.9 (0), 127.3 (0), 273.5 (0), 397.1 (1), 449.5 (1), 507.8 (2), 577.6 (1), 606.7 (4), 627.4 (3), 711.9 (9), 980.0 (19). [d] B3LYP/6–311G(d).

Compound **A** is the precursor of both **6** and **3b** and thus a C_4F_4 isomer. The only known C_4F_4 isomer besides **6** is tetrafluorocyclobutadiene (**8**) which was readily excluded by comparison with the published matrix IR spectrum.[18] The calculated IR spectrum of tetrafluorobut-1-ene-3-yne (**9**) is

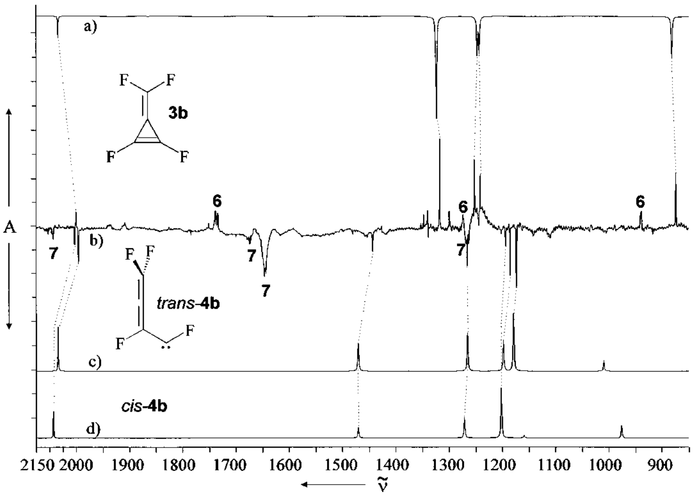
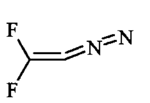
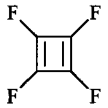


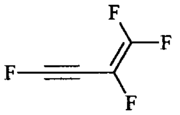
Figure 1. a) Calculated spectrum of **3b** (B3LYP/6-311G(d)). b) IR difference spectrum showing the photochemistry of carbene **4b** in argon at 7 K. Bottom part, bands disappearing; top part, bands appearing on irradiation with $\lambda > 420$ nm. c) Calculated spectrum of *trans*-**4b** (B3LYP/6-311G(d)). d) Calculated spectrum of *cis*-**4b** (B3LYP/6-311G(d)).



7



8



9

not in accordance with the spectrum of **A** and is thus also excluded. On the other hand, the calculated spectrum of *trans*-allenylcarbene (*trans*-**4b**) is in good agreement with the experimental spectrum of **A** (Table 1, Figure 1). Two additional minor IR absorptions at 1194.5 and 2006.8 cm^{-1} are assigned to *cis*-**4b**. The vibrations of the CCCF$_2$ group (modes 14, 15, 16) of the two isomers (Figure 2) are almost identical, but while the *trans* isomer shows two intense C–F stretching vibrations of the FCCF moiety at 1186.5 and 1174.2 cm^{-1}, respectively, the *cis* isomer shows only one intense band at 1194.5 cm^{-1} assigned to a motion revealing both C–F and C–C stretching character. The asymmetric C-C-C stretching mode could be identified at 2006.8 cm^{-1}. All other vibrations with significant IR intensities are either due to overlap *cis*-**4b** and *trans*-**4b** absorptions, or assigned to the *trans* isomer. By comparison of the experimental and theoretical band intensities a *trans*:*cis* ratio of 2.5:1 is estimated.

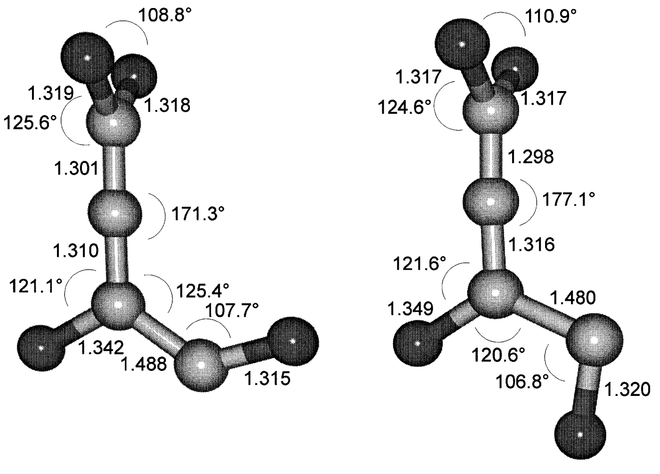


Figure 2. Calculated geometries of *trans*-**4b** and *cis*-**4b** (B3LYP/6-311G(d)).

The reaction of vinylidene **1b** with acetylene **2b** to give carbene **4b** is calculated (Figure 3) to be exothermic by 80.6 kcal mol^{-1} (B3LYP/6-311G(d) + zero-point energy). Since the formation of **4b** proceeds rapidly under the conditions of matrix isolation, one can conclude that the activation barrier must be very small or zero. A by-product of this reaction is methylenecyclopropene **3b** (Table 2), which could be formed via vibrationally hot **4b** generated in the strongly exothermic reaction. Secondary photolysis of **4b** rapidly produces **3b** by a vinylcarbene–cyclopropene rearrangement (18.1 kcal mol^{-1} exothermic) or, less efficiently, butatriene **6** by a [1,2]-fluorine shift (48.9 kcal mol^{-1} exothermic). The latter reaction is more exothermic but the fluorine shift is expected to proceed through a larger activation barrier.

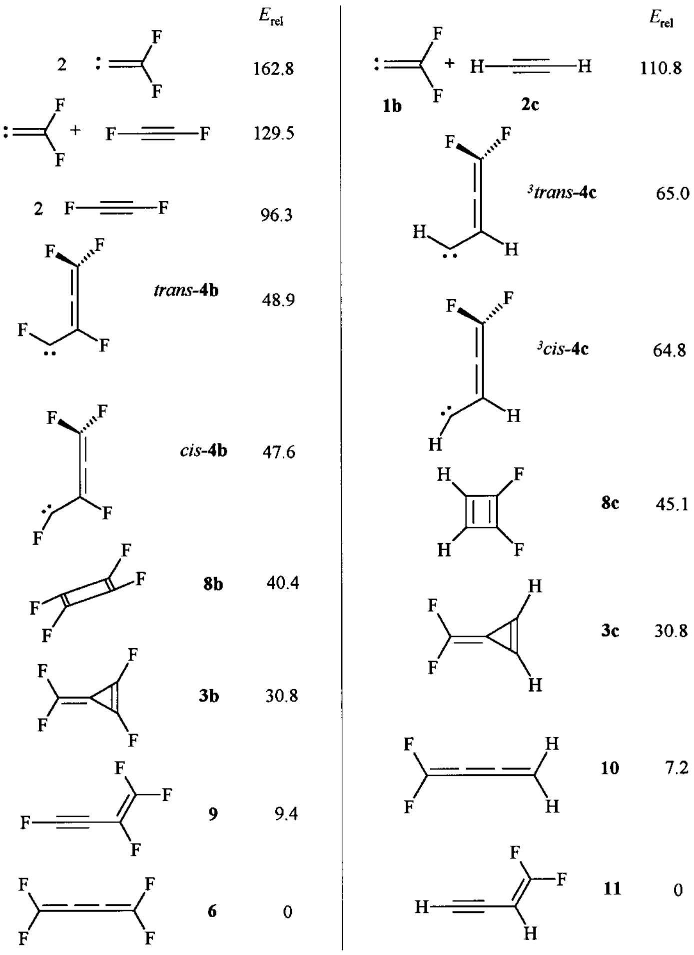
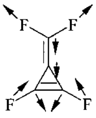
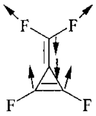
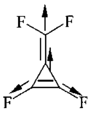


Figure 3. Calculated relative energies (B3LYP/6-311G(d)-ZPE) of some C_4F_4 species and some $C_4F_2H_2$ species. Additional calculations on the C_4F_4 hypersurface were performed by Wiberg and Marquez.[23]

In the *cis* and *trans* allenylcarbenes **4b** the fluorine substituent at the carbene center results in a singlet ground state which is, according to the B3LYP calculations, about 6 kcal mol^{-1} lower in energy than the triplets. The CF$_2$ moiety is orthogonal with respect to the FCCF group and the planar

Table 2. Computed harmonic and experimental vibrational wavenumbers [cm^{-1}] of **3b**.

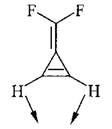
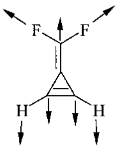
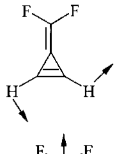
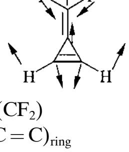
Mode	Sym.	Description	$\tilde{\nu}_{exp}$[a]	I_{exp}[a,b]	$\tilde{\nu}_{calcd}$[c,d]	I_{calcd}[b,d]
13	A_1		874.5	62	882.4	40
14	A_1		1241.9	40	1244.8	34
15	B_1	$\tilde{\nu}_{as}(CF_2)$	1252.8	56	1249.0	39
16	B_1	$\tilde{\nu}_{as}(FCCF)$	1317.8	100	1324.3	100
18	A1		2000.1	18	2068.6	21

[a] Argon at 10 K. [b] Relative intensities, based on the strongest absorption. [c] Other vibrations of **3b**, not observed in the experimental spectrum: $\tilde{\nu}_{calcd}(I_{rel})$: 99.5 (0), 146.5 (0), 157.3 (0), 235.5 (0), 336.9 (0), 358.9 (0), 429.1 (0), 440.3 (1), 544.5 (0), 654.3 (0), 711.9 (0), 818.8 (1), 1809.2 (0). [d] B3LYP/6–311G(d).

diradical structures with C_S symmetry do not correspond to minima on the C_4F_4 potential energy surface (singlet or triplet).

Addition of difluorovinylidene (1b) to acetylene (2c): Under similar conditions the thermal reaction of vinylidene **1b** and acetylene (**2c**) directly produces (difluoromethylene)cyclopropene (**3c**) as the main product, identified by comparison of experimental and calculated IR spectra (Table 3, Figure 4).

Table 3. Computed harmonic and experimental vibrational wavenumbers [cm^{-1}] of **3c**.

Mode	symmetry	description	$\tilde{\nu}_{exp}$[a]	I_{exp}[a,b]	$\tilde{\nu}_{calcd}$[c,d]	I_{calcd}[b,d]
7	B1	B1 	623.6	17	647.9	24
8	A1	A1 	705	8	711.2	6
12	B2	B2 	1038.3	5	1055.9	5
13	A1	A1 	1198.1	100	1221.4	100
14	B2	$\tilde{\nu}_{as}(CF_2)$	1215	79	1226.6	96
15	A1	$\tilde{\nu}(C=C)_{ring}$	1563.2	22	1628.7	14
16	A1	$\tilde{\nu}(C=C)$	1906.9	12	1953.1	13

[a] Argon at 10 K. [b] Relative intensities, based on the strongest absorption. [c] Other vibrations of **3c**, not observed in the experimental spectrum: $\tilde{\nu}_{calc}(I_{rel})$: 157 (0), 261 (0), 281 (3), 436 (3), 453 (1), 526 (2), 847 (0), 908 (1), 924 (4), 3164 (2), 3208 (1). [d] B3LYP/6–311G(d,p).

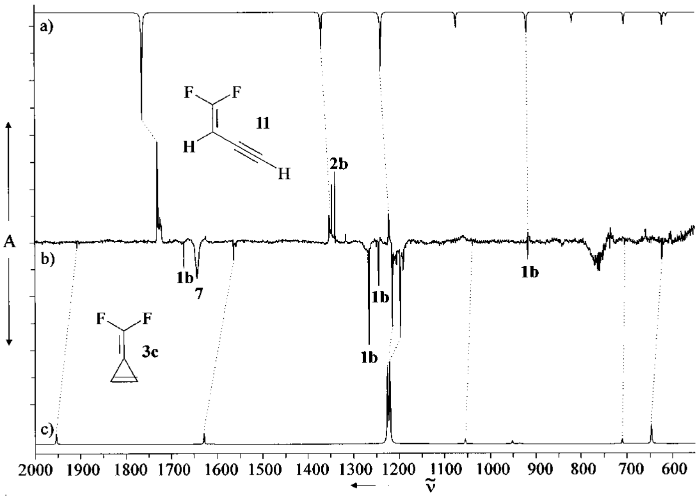


Figure 4. a) Calculated spectrum of **11** (B3LYP/6–311G(d,p)). b) IR difference spectrum showing the photochemistry of methylenecyclopropene **3c** in argon at 7 K. Bottom part, bands disappearing; top part, bands appearing on irradiation with $\lambda > 420$ nm. c) Calculated spectrum of **3c** (B3LYP/6–311G(d,p)).

B3LYP calculations predict triplet allenylcarbene **4c** to be 45.8 kcal mol^{-1} more stable than **1b** + **2c**, while singlet **4c** is not a minimum on the singlet surface. Since an intersystem crossing step is required to produce triplet **4c**, it is not expected to be formed efficiently in the thermal reaction. Small amounts of 1,1-difluorobutatriene (**10**) in the matrix might be the product of a rapid [1,2]-hydrogen shift of triplet **4c**. This indicates that the intersystem crossing can compete to some extent with the ring-closure to **3c**.

On irradiation with visible light ($\lambda > 420$ nm) methylenecyclopropene **3c** rearranges to 1,1-difluorobut-1-ene-3-yne (**11**) which in turn on UV irradiation ($\lambda = 193$ nm) produces butatriene **10** (Table 4, Table 5, Figure 5). Similar ring-opening of other methylenecyclopropenes to vinylacetylenes had been described before.[19–21]

Table 4. Computed harmonic and experimental vibrational wavenumbers [cm^{-1}] of **11**.

Mode	$\tilde{\nu}_{exp}$[a]	I_{exp}[a,b]	$\tilde{\nu}_{calcd}$[c,d]	I_{calcd}[b,d]
7	659.0	5	623.2	12
11	914.2	9	921.7	19
13	1223.3	30	1241.0	55
14	1348.1	46	1371.9	34
15	1731.1	100	1764.0	100

[a] Argon at 10 K. [b] Relative intensities, based on the strongest absorption. [c] Other vibrations of **11**, not observed in the experimental spectrum: $\tilde{\nu}_{calc}(I_{rel})$: 135 (0), 160 (0), 364 (2), 455 (1), 470 (1), 595 (3), 606 (1), 686 (11), 795 (10), 1043 (14), 2151 (1), 3091 (2), 3374 (24). [d] B3LYP/6–311G(d,p).

In summary, the addition of difluorovinylidene (**1b**) and difluoroacetylene (**2b**) to give methylenecyclopropene **3b** proceeds via allenylcarbene **4b**, and thus clearly is a non-concerted reaction. In the thermal reaction of **1b** with acetylene (**2c**) (Scheme 3) the carbene **4c** is calculated not to be a minimum on the singlet energy surface and therefore methylenecyclopropene **3c** most likely is formed in a con-

Table 5. Computed harmonic and experimental vibrational wavenumbers [cm^{-1}] of **10**.

Mode	$\tilde{\nu}_{\mathrm{exp}}$[a]	I_{exp}[a,b]	$\tilde{\nu}_{\mathrm{calcd}}$[c,d]	I_{calcd}[b,d]
12	1167.1	45	1187.1	66
13	1239.4	79	1242.4	65
14	1404.8	44	1436.5	19
15	1703.5	100	1762.5	45
16	2114.3	84	2222.9	100

[a] Argon at 10 K. [b] Relative intensities, based on the strongest absorption. [c] Other vibrations of **10**, not observed in the experimental spectrum: $\tilde{\nu}_{\mathrm{calcd}}(I_{\mathrm{rel}})$: 104 (0), 148 (0), 340 (0), 461 (3), 476 (0), 514 (0), 554 (1), 580 (1), 711 (6), 807 (13), 977 (0). [d] B3LYP/6–311G(d,p).

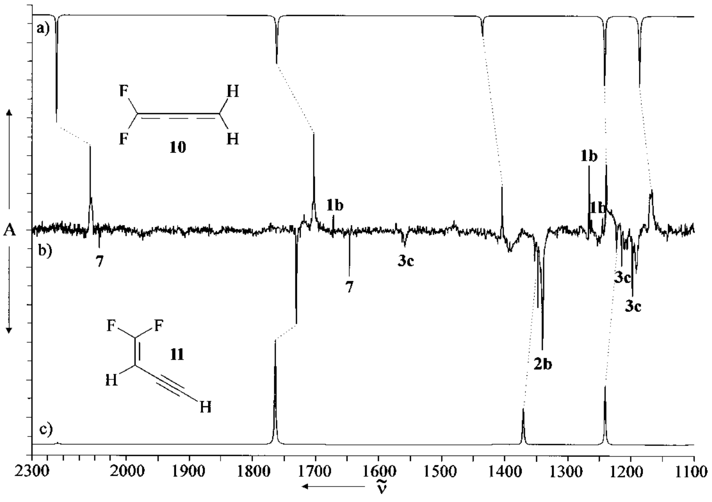
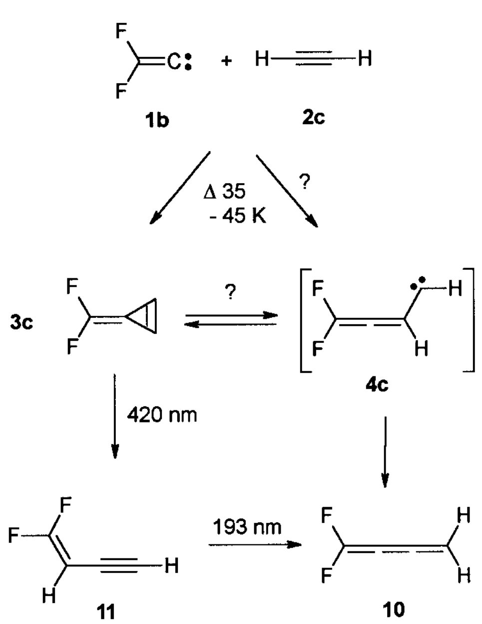


Figure 5. a) Calculated spectrum of **10** (B3LYP/6–311G(d,p)). b) IR difference spectrum showing the photochemistry of enyne **11** in argon at 7 K. Bottom part, bands disappearing; top part, bands appearing on irradiation with λ = 193 nm. c) Calculated spectrum of **11** (B3LYP/6–311G(d,p)).



Scheme 3. Addition of difluorovinylidene (**1b**) to acetylene (**2c**).

certed, although highly asynchronous reaction. Triplet carbene **4c** is expected to be short-lived with respect to the [1,2]-hydrogen migration and consequently is not found in our experiments. Indirect evidence for **4c** comes from the observation of traces of butatriene **10**. High-level ab initio or DFT calculations are required to elucidate at which point the singlet surface is leaking into the triplet manifold.

Experimental Section

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Messer-Griesheim, 99.9999%) on top of a CsI window with a rate of approximately 0.15 mmol min^{-1}. In order to prevent aggregation of difluoroacetylene (**2b**), depositions of the matrices were done at 7 K. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}.

Irradiations were carried out with use of an ArF excimer laser (λ = 193 nm; Lambda Physik COMPex 100) or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the arc lamps was absorbed by a 10 cm path of water. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Acetylene (Messer-Griesheim, 99.3%, stabilized with acetone) was purified by sublimation (three times).

Calculations were performed with the Gaussian 94 program package.[22] Geometries and vibrations were calculated at the B3LYP/6–311G(d,p) or the UB3LYP/6–311G(d,p) level of theory.

Acknowledgments: This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received: May 27, 1998 [F1173]

---

[1] P. J. Stang, M. G. Mangum, *J. Am. Chem. Soc.* **1975**, *97*, 3854–3856.
[2] W. Sander, A. Kirschfeld, *Matrix-Isolation of Strained Three-Membered Ring Systems, Vol. 4* (Ed.: B. Halton), JAI Press, London, **1995**, Ch. 2, pp. 1–80.
[3] G. L. Closs, *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.
[4] D. P. Fox, P. J. Stang, Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **1986**, *108*, 750–756.
[5] M. S. Lee, J. E. Jackson, *Res. Chem. Intermed.* **1994**, *20*(2), 223–247.
[6] D. Griller, L. Hadel, A. S. Nazran, M. S. Platz, P. C. Wong, J. C. Scaiano, *J. Am. Chem. Soc.* **1984**, *106*, 2227–2235.
[7] P. B. Grasse, B. E. Brauer, J. J. Zupancic, K. J. Kaufmann, G. B. Schuster, *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.
[8] M. S. Newman, C. D. Beard, *J. Org. Chem.* **1970**, *35*(7), 2412–2413.
[9] R. J. Norstrom, H. E. Gunning, O. P. Strausz, *J. Am. Chem. Soc.* **1976**, *98*, 1454–1461.
[10] R. A. Stachnik, G. C. Pimentel, *J. Phys. Chem.* **1984**, *88*, 2205–2210.
[11] J. C. Brahms, W. P. Dailey, *J. Am. Chem. Soc.* **1990**, *112*, 4046–4047.
[12] J. E. Jackson, T. A. J. O'Brien, *J. Phys. Chem.* **1988**, *92*, 2686–2696.
[13] J. Breidung, H. Bürger, C. Kötting, R. Kopitzky, W. Sander, M. Senzlober, W. Thiel, H. Willner, *Angew. Chem.* **1997**, *109*, 2072–2075; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1983–1985.
[14] C. Kötting, W. Sander, M. Senzlober, H. Bürger, *Chem. Eur. J.* **1998**, *4*, 1611–1615
[15] C. Kötting, W. Sander, J. Breidung, W. Thiel, M. Senzlober, H. Bürger, *J. Am. Chem. Soc.* **1998**, 120, 219–220.
[16] W. E. Billups, L.-J. Lin, E. W. Casserly, *J. Am. Chem. Soc.* **1984**, *106*, 3698–3699.
[17] B. A. Hess Jr, D. Michalska, L. J. Schaad, *J. Am. Chem. Soc.* **1985**, *107*, 1449–1450.

[18] E. J. Petersson, J. C. Fanuele, M. R. Nimlos, D. M. Lemal, G. B. Ellison, J. G. Radziszewski, *J. Am. Chem. Soc.* **1997**, *119*, 11122–11123.

[19] O. L. Chapman, *Pure Appl. Chem.* **1974**, *40*, 511–523.

[20] R. Albers, W. Sander, *J. Org. Chem.* **1997**, *62*, 761–764.

[21] R. Albers, W. Sander, *Liebigs Ann./Recl.* **1997**, 897–900.

[22] Gaussian 94 (Revision B.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[23] K. B. Wiberg, M. Marquez, *J. Am. Chem. Soc.* **1998**, 120, 2932–2938.

0947-6539/98/0411-2365 $ 17.50+.25/0