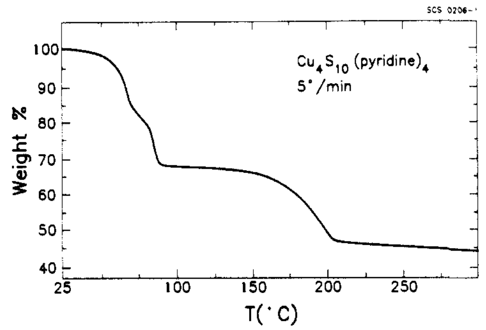

Figure 2. Thermal gravimetric analysis trace for $Cu_4(S_5)_2(py)_4$ (**1**) under an argon atmosphere. The heating rate was 5 °C/min. The theoretical values for weight changes are 82% for **1** - 2py, 64.5% for **1** - 4py. The theoretical residual weight fraction (CuS/**1**) is 43%.

proximate S_4 symmetry and can be viewed as the union of two norbornane-like Cu_2S_5 cages. The Cu-S distances indicate that each S_5 ligand is hexadentate. The copper centers achieve the inert gas configuration through bonding to three sulfur atoms as well as a nitrogen donor.

Compound **1** is an unusual example of a charge-neutral metal polysulfide and is the only polysulfide complex shown to undergo ligand substitution reactions. For example, dissolution of **1** in *N*-methylimidazole (*N*-MeIm) followed by diethyl ether precipitation gives $Cu_4S_{10}(N\text{-MeIm})_4$. This process is reversible, and the following experiment suggests that substitution occurs dissociatively (Scheme I). When suspended in toluene for 6 h at room temperature, **1** is transformed into a brown solid of the composition $Cu_4S_{10}(py)$.[7] This solid redissolves in pyridine (seconds, room temperature), and addition of hexane crystallizes **1** in 80% isolated yield.

Studies on the relationship of **1** to covellite were guided by thermogravimetric analysis (TGA).[8] The first two TGA events correspond reasonably well to the loss of 2py/**1**, and the final weight loss involves evaporation of sulfur, leaving a residue of covellite (Figure 2). Heating samples of **1** in vacuo at 70 °C cleanly gave microcrystalline covellite admixed with elemental (orthorhombic) sulfur. After a few hours at 70 °C, pyridine solutions of **1** deposited a microcrystalline powder of covellite, which was pure by powder X-ray diffraction. Given the stoichiometric simplicity of metal polysulfides, their conversion to technologically significant inorganic phases is an obvious area of application.[9,10]

The 4-Mepy and 4-*t*-Bupy analogues of **1** were prepared from suspensions of copper and sulfur in the substituted pyridines.[11] Our search for alternate solvents for this dissolving-metal synthesis uncovered the remarkable activity of *N*-methylimidazole. *A solution of sulfur in N-methylimidazole dissolves copper metal in seconds at room temperature, to give $Cu_4(S_5)_2(N\text{-MeIm})_4$ in 50% yield after diethyl ether precipitation.* Preliminary experiments show that this method works with several other metals.[12]

To summarize, we have isolated an intermediate in the reaction $M + S_8 \rightarrow MS$. Donor solvents promote this reaction, possibly by stripping polysulfide intermediates from the surface of the metal particles via complexation. Metal polysulfides have been shown to be the structural and mechanistic link between the sulfur homocycles, c-S_x,[13] and the binary metal sulfides, MS_n.

Acknowledgment. This research is supported by the National Science Foundation through Grants NSF CHE-87-11460 and NSF DMR-86-12860. We thank Professor John C. Bailar, Jr., for interesting discussions.

Supplementary Material Available: Powder X-ray diffraction patterns of covellite samples prepared under differing conditions and tables of selected bond distances and angles, positional parameters, and thermal parameters (7 pages); table of structure factors (15 pages). Ordering information is given on any current masthead page.

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[6] Other, *anionic* copper polysulfide clusters are known. $(Et_4N)_3[Cu_3(S_6)_3]$: Müller, A.; Schimanki, U. *Inorg. Chim. Acta* **1983**, *77*, L187. $(PPh_4)_2[Cu_4(S_5)_{3-x}(S_4)_x]$: Müller, A.; Römer, M.; Bögge, H.; Krickenmeyer, E.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *85*, L39. $(PPh_4)_2\{[Cu(S_6)]_2(\mu\text{-}S_8)\}$ and $(PPh_4)_2(NH_4)[Cu_4(S_4)_3]$: Müller, A.; Baumann, F.-W.; Bögge, H.; Römer, M.; Krickemeyer, E.; Schmitz, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *13*, 632; *Angew. Chem.* **1984**, *96*, 607. $(PPh_4)_2[Cu_6(S_4)_3(S_5)]$: Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Bergmann, D. *J. Chem. Soc., Chem. Commun.* **1984**, 384. Related copper 1,1-dithiolate clusters: Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.

[7] Anal. Calcd for $C_5H_5Cu_4NS_{10}$ (found, two samples for C, H, N): C, 9.18 (9.90, 8.51); H, 0.77 (0.81, 0.74); N, 2.14 (2.38, 2.05); S, 49.02 (47.63. -).

[8] Thermal gravimetric data were collected by using a Perkin Elmer TGA Series TAS instrument. X-ray powder diffraction data were collected on a Rigaku D/Max-B diffractometer using graphite-filtered Cu Kα radiation with a scan speed of 5 deg/min. The diffraction patterns were matched with CuS and orthorhombic S_8 (I/I_0 = 100 at d = 3.85 Å) in the JCPDS—International Centre for Diffraction Data 1989 powder diffraction files no. 6-464 (covellite) and 8-247 (orthorhombic S_8).

[9] A Chemical Abstracts Service search for "CuS" retrieved 24 patents for the three-year period 1987-1989. Subjects include secondary nonaqueous batteries, electrophotographic toners, fabrics, varistor materials, electrically conductive polymer composites, electrically conductive pastes, and synthesis gas catalysts.

[10] The advantages in the use of charge-neutral precursors are illustrated by recent low-temperature syntheses of iron and nickel tellurides: Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52. Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240.

[11] Analytical data for $Cu_4(S_5)_2(4\text{-}t\text{-Bupy})_4$: C, 39.13 (38.75); H, 4.83 (4.71); N, 4.92 (5.02); S, 28.92 (28.74). For $Cu_4(S_5)_2(4\text{-Mepy})_4$: C, 29.36 (30.43); H, 3.22 (2.99); N, 5.90 (5.92); S, 33.61 (33.84). For $Cu_4(S_5)_2(N\text{-MeIm})_4$: C, 21.52 (21.27); H, 2.80 (2.68); N, 12.60 (12.41); S, 35.24 (35.49).

[12] Dev, S.; Ramli, E.; Rauchfuss, T. B., to be published.

[13] Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 147.

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^{17}O Isotopic Tracer Evidence for the Formation of a Sulfurane Intermediate during Sulfide Photooxidation

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Received January 2, 1990

In 1983 Foote and co-workers[1] reported a detailed kinetic study of diethyl sulfide photooxidation which requires that sulfide photooxidation is more complicated than previously assumed.[2] Trapping experiments with diphenyl sulfide and sulfoxide in aprotic solvents demonstrated the need for at least two intermediates on the reaction surface. In contrast, in protic solvents only one intermediate was necessary to accommodate the kinetic results.

A variety of structures for these intermediates have been suggested and include a persulfoxide,[3] a thiadioxirane,[4] an ion pair,[5] a sulfurane,[6] and a hydrogen-bonded persulfoxide.[3] Direct experimental evidence, however, for the structures of these intermediates is limited. The scarce experimental evidence supporting one or more of these intermediates includes (1) Ando's report[7] that the intermediate is electrophilic in methanol, consistent with either a thiadioxirane or sulfurane; (2) Sawaki and Ogata's report[8] that the intermediate is nucleophilic in benzene, consistent

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[1] Liang, J.-J.; Gu, C-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

[2] Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

[3] For a diradical formulation of the persulfoxide, see: Takata, T.; Ando, W. In *Singlet Oxygen. Reaction Modes and Products. Part 2*; CRC Press, Inc.: Boca Raton, FL, 1985; Vol. III, p 1. For a zwitterionic formulation, see: Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

[4] For a critical discussion of the stability of a thiadioxirane, see: Foote, C. S.; Jensen, F. *J. Am. Chem. Soc.* **1988**, *110*, 2368.

[5] Inoue, K.; Matsuura, T.; Saito, I. *Tetrahedron* **1985**, *41*, 2177.

[6] Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1982**, *104*, 6060.

[7] Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191.

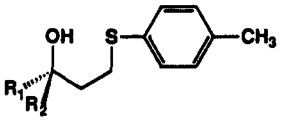
Table I. Product Compositions in the Photoxidations of **1**[a]

compd	T, °C	% yield[c] $\mathbf{2}^b$	**3**	**4**	**5E**	**5Z**
1a	−80	43	56			
1b	−80	45	55			
1c	−80	40	59			1
	−56	42	57			1
	−10	24	54			14
1d	−80	27	68			
1e	−80	30	48	15	6.5	0.5
1f	−80	39	17	21	19	

[a] Acetone-d_6 solutions presaturated with O_2 containing 2–4 × 10^{-2} M sulfide and 1–1.4 × 10^{-5} M Rose Bengal were irradiated with a WKO 120-V, 750-W lamp through a 5% $K_2Cr_2O_7$ filter solution. [b] Mixture of diastereomers. [c] The % yield reflects the fact that all reactions were not carried to 100% completion.

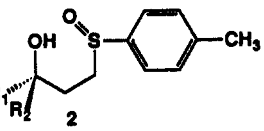
with a persulfoxide; and (3) Clennan and Chen's[9] contention that the diastereoselective oxidations of hydroperoxy sulfides can be attributed to the selective formation of cyclic sulfuranes.

We now report photooxidations of γ-hydroxy sulfides **1a–f** and an ^{17}O labeling experiment that provides compelling evidence for a sulfurane intermediate.



1a. $R_1 = R_2 = H$
1b, $R_1 = H$; $R_2 =$ Me-
1c. $R_1 = H$; $R_2 =$ tBu-
1d. $R_1 =$ Me-; $R_2 =$ Et-
1e. $R_1 =$ Me-; $R_2 =$ iPr
1f, $R_1 =$ Me-; $R_2 =$ tBu

Photooxidations of **1a**,**b**,**d** result in the formation of the expected sulfoxide diastereomers **2**[10] and sulfone **3**[11] (Table I). In contrast, photooxidations of **1c**,**e**,**f** produce, in addition to the anticipated sulfoxides and sulfones, the unexpected olefins **4**,[12] **5Z**,[13] and **5E**[14] (Table I).



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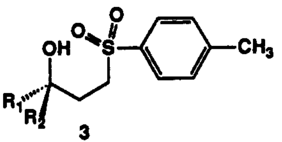

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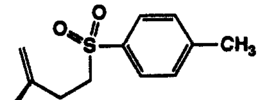

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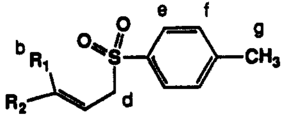
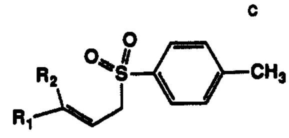


5E



5Z

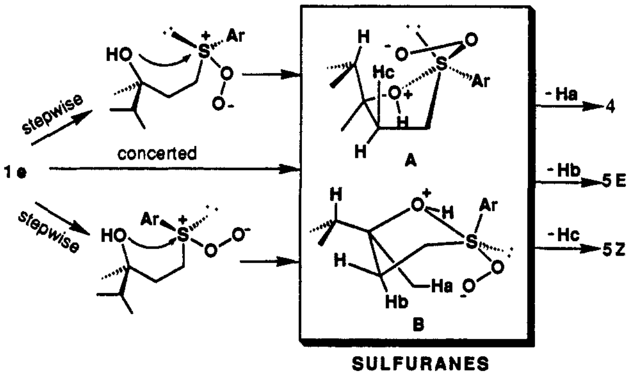


Figure 1. Mechanism of olefin formation.

The stereochemistry of the major trisubstituted olefin formed in the reaction of **1e** was conveniently assigned by a difference NOE experiment.[15] Low-power irradiation of the allylic methylene protons (d) adjacent to the sulfonyl group in the major isomer resulted in intensity enhancements at methyl (b), double-bond hydrogen (c), and aromatic protons ortho to the sulfonyl substituent (e), allowing assignment of the major isomer as **5E**. Verification of this assignment was provided by irradiation of the methyl protons (b), which resulted in intensity enhancements at the isopropyl methyl (a) and allylic methylene (d) protons.

Evidence for the origin of these unusual products was obtained by photooxidation of a sample of **1e** which was labeled with ^{17}O (δ ^{17}O, 46.5 ppm relative to H_2O).[16] Examination of the reaction mixture after complete disappearance of **1e** revealed both a hydroxyl peak at 46 ppm and a new peak at 141 ppm in the ^{17}O NMR spectrum in an 81/19 ratio, respectively. No ^{17}O NMR peaks were observed in unlabeled **2**, **3**, **4**, **5E**, or **5Z** with the same number of scans under identical experimental conditions. The ^{17}O chemical shift at 141 ppm is in the range (δ 120–183 ppm) expected for sulfonyl oxygen and substantially downfield of that anticipated for sulfinyl oxygen[17] (δ − 20 to +20 ppm). The ratio of the areas under the peaks at 46 and 141 ppm in the ^{17}O NMR spectrum of the photooxidized reaction mixture is very similar to the ratio [**2** + **3**]/[**4** + **5E** + **5Z**], obtained from analysis of the ^1H NMR spectrum of the crude reaction mixture. Indeed, chromatographic separation of the products followed by ^{17}O NMR revealed that only the hydroxyl oxygens in **2** and **3** and the sulfonyl oxygens in **4**, **5E**, and **5Z** were labeled.

These results are consistent with a mechanism of olefin formation (Figure 1) that proceeds by either stepwise, via persulfoxide, or concerted formation of peroxy sulfurane diastereomers.[18] Decomposition of the sulfuranes by hydrogen abstraction and

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(8) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947.

(9) (a) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787. (b) Clennan, E. L.; Chen, X. *Ibid.* **1989**, *111*, 8212.

(10) The ^1H NMR spectra of **2e** and **2e′** were nearly identical. Only twinning of the singlets at 1.06/1.07 and at 2.02/2.07 ppm revealed the presence of two compounds in the mixture. The remaining signals appeared at δ ($CDCl_3$) 0.83–0.93 (m, 6 H), 1.65–1.95 (m, 3 H), 2.42 (s, 3 H), 2.8–3.1 (m, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 7.51 (d, J = 8.2 Hz, 2 H); ^{13}C NMR **2e** ($CDCl_3$) δ 16.9, 17.0, 21.4, 22.7, 31.6, 37.2, 51.5, 73.6, 124.1, 129.9, 140.0, 141.0. The presence of the second diastereomer was revealed by peaks at 17.5, 17.6, 31.7, 37.8, 51.8, and 124.2.

(11) **3e**: ^1H NMR ($CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H), 1.05 (s, 3 H), 1.37 (br s, 1 H), 164 (hept, J = 6.8 Hz, 1 H), 1.8–1.9 (m, 2 H), 2.46 (s, 3 H), 3.1–3.3 (m, 2 H), 7.36 (d, J = 7.8 Hz, 2 H), 7.78 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0 (q, J = 126 Hz), 17.6 (q, J = 126 Hz), 21.8 (q, J = 127 Hz), 22.7 Hz (q, J = 126 Hz), 31.9 (t, J = 129 Hz), 37.7 (d, J = 127 Hz), 52.1 (t, J = 137 Hz), 73.7 (s), 128.2 (d, J = 165 Hz), 130.1 (d, J = 161 Hz), 136.3 (s), 144.5 (s).

(12) **4e**: ^1H NMR ($CDCl_3$) δ 0.98 (d, J = 7.0 Hz, 6 H), 2.18 (hept, J = 7.0 Hz, 1 H), 2.45 (m, 2 H), 2.46 (s, 3 H), 3.18 (m, 2 H), 4.65 (s, 1 H), 4.76 (s, 1 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.57, 21.64, 26.9, 34.0, 55.4, 108.2, 128.1, 129.9, 136.2, 144.7, 151.8.

(13) **5eE**: ^1H NMR ($CDCl_3$) δ 0.92 (d, J = 7.3 Hz, 6 H), 1.24 (s, 3 H), 2.24 (hept, J = 6.6 Hz, 1 H), 2.44 (s, 3 H), 3.78 (d, J = 7.9 Hz, 2 H), 5.20 (t, J = 7.9 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.5 (q, J = 126 Hz), 20.9 (q, J = 126 Hz), 21.6 (q, J = 127 Hz), 37.0 (d, J = 128 Hz), 56.0 (t, J = 137 Hz), 108.6 (d, J = 161 Hz), 128.7 (d, J = 166 Hz), 129.5 (d, J = 160 Hz), 136.0 (s), 144.4 (s), 151.7 (s).

(14) The small amount of **5eZ** formed in the reaction and the expected overlap with peaks from **5eE** only allowed the following ^1H NMR signals to be observed ($CDCl_3$): δ 0.74 (d, J = 6.8 Hz, 6 H) 3.90 (d, J = 8.3 Hz, 2 H), 5.08 (t, J = 8.1 Hz, 1 H).

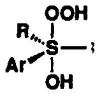
(15) Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Pergamon Books Ltd.; Pergamon Press: Oxford, England, 1987; Chapter 5, p 97.

(16) **1e** was synthesized from ^{17}O-labeled 3-oxobutyl *p*-methylphenyl sulfide. The label was introduced by stirring 201 mg (1.04 mmol) of unlabeled ketone in 5 mL of ether with 0.5 mL of labeled H_2O (21.72 atom % ^{17}O, 62.23 atom % ^{18}O) and 10 μL of 10% aqueous HCl for 24 h. ^{17}O NMR ($CDCl_3$): δ (relative to H_2O) 570 ± 2 ppm; line width 550 Hz. **1e** was synthesized from the ketone by addition of isopropyl Grignard: ^{17}O NMR ($CDCl_3$) δ (relative to H_2O) 46.5 ± 0.2 ppm; line width 370 Hz.

(17) Dyer, J. C.; Harris, D. L.; Evans, S. A. *J. Org. Chem.* **1982**, *47*, 3661.

(18) A pseudorotation mechanism interconverting diastereomers A and B requires passing through very unstable sulfuranes with apical lone pairs and is unlikely to occur. Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemisty*; Bernard, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, The Netherlands, 1985; p 436.

transfer of oxygen to sulfur to form hydrated sulfones **6a–c**, with subsequent loss of H_2O, produces olefins **4**, **5E**, and **5Z**, respectively.



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a, $R = -(CH_2)_2CR_2CH_2$
b. $R = -CH_2CHCR_1R_2$(E)
c. $R = -CH_2CHCR_1R_2$(Z)

The increase in the yield of abnormal products 4 and 5 with the increasing size of R_1 and/or R_2 is consistent with either (1) Thorpe–Ingold *gem*-dialkyl stabilization of the sulfurane, (2) steric enforcement of a conformation that places the peroxysulfurane anion close in space to the hydrogens undergoing abstraction, or (3) back strain[19] which facilitates transfer of oxygen to sulfur.

These reactions also produce large amounts of sulfones **3**, and unlike other sulfide photooxidations,[1] the sulfone yields do not decrease appreciably with increasing temperature (e.g., **1c**, Table I). Martin and Martin[20] suggested that the reaction of a dialkoxysulfurane with hydrogen peroxide gave a hydroperoxysulfurane, which also decomposed to give primarily a sulfone (80%), a small amount of sulfoxide (15%), and a trace of sulfide. It is tempting to suggest that sulfuranes A and B decompose to form sulfones **3** in competition with oxygen transfer to give **4**, **5E**, and **5Z**.

Additional work to clarify the mechanistic details of these reactions and to characterize sulfurane intermediates is currently in progress and will be reported in the near future.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Supplementary Material Available: Spectra depicting the NOE enhancement experiment (1 page). Ordering information is given on any current masthead page.

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[19] Brown, H. C.; Berneis, H. L. *J. Am. Chem. Soc.* **1953**, *75*, 10.
[20] Martin, L. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511.

Difluoropropadienone as a Source of Difluorovinylidene and Difluorodiazoethene

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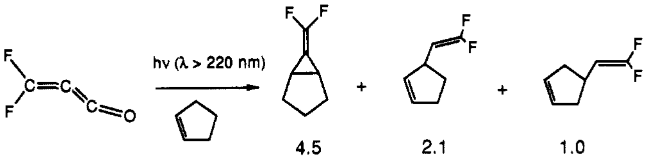
While there are several photochemical sources available for the generation of saturated carbenes,[1] the same is not true for alkylidenecarbenes (vinylidenes). This fact, combined with the propensity for vinylidenes to undergo extremely facile 1,2-migrations to form alkynes,[2] has greatly limited the spectroscopic study of these carbenes. It has been reported that difluorovinylidene (DFV), formed by mercury-sensitized photolysis[3] or multiphoton irradiation[4] of trifluoroethylene, undergoes intermolecular reactions rather than 1,2-fluorine atom migration. Herein we report that gas-phase irradiation of difluoropropadienone[5] (DFP) yields products consistent with the formation of difluorovinylidene. In addition, we report the first spectroscopic observation of a diazoethene, difluorodiazoethene.

Table I. Infrared Spectrum of the Intermediate Produced by Irradiation of Matrix-Isolated Difluoropropadienone in Nitrogen (cm^{-1})

normal,[a] $^{14}N_2$[b]	[1-^{13}C],[a] $^{14}N_2$[b]	normal,[a] $^{15}N_2$[b]
2104.7	2104.2	2033.8
2085.2	2084.4	
1672.7	1672.4	1668.8
1650.7	1650.7	1646.2
1262.8	1262.6	1261.4
1143.9	1143.9	1129.2
834.9	834.9	831.3

[a] Isotopomer. [b] Matrix.

Broad-band irradiation ($\lambda > 220$ nm)[6] of a gas-phase mixture of difluoropropadienone with a 10-fold excess of isopentane yields all four possible C–H insertion products. The selectivity of difluorovinylidene toward various C–H bonds is 3.0:1.8:1.0 (3°:2°:1°), which is only slightly better than that of singlet methylene.[7] When cyclopentene is used as the trapping agent, a mixture of the difluoromethylenecyclopropane and two C–H insertion products is produced in a 4.5:2.1:1.0 ratio, respectively. Neither addition of a large amount of inert buffer gas nor changing the wavelength of irradiation changed the product ratios.[8] The total chemical yield for both of these trapping reactions is only 10–15% after preparative GC, but we believe that the formation of these products offers strong evidence for the intermediacy of DFV.



While a variety of solution trapping studies have implicated alkylidenecarbenes as reactive intermediates,[9] direct spectroscopic evidence for their existence is scarce. In an attempt to observe DFV under matrix-isolation conditions, we irradiated ($\lambda > 185$ nm) an argon matrix of DFP (500:1) at 11 K, but surprisingly found that the molecule was inert under all photochemical conditions.[10] However, when a similar argon matrix containing CO and DFP isotopically labeled with ^{13}C in the carbonyl position[11] (500:5:1) was irradiated ($\lambda > 185$ nm) for 30 min, a 1:1 ratio of [1-^{13}C]DFP and the normal isotopomer of DFP was observed, in addition to a substantial amount of ^{13}CO. This result is consistent with the hypothesis that DFP does photochemically decarbonylate under the matrix-isolation conditions, but DFV efficiently recombines with the liberated CO. Remarkably, however, when a *nitrogen* matrix of DFP was irradiated under similar conditions, difluoroacetylene[12] and carbon monoxide were produced. Monochromatic irradiation ($\lambda = 240 \pm 10$ nm) of a similar matrix achieved the same end result, but now a small amount of an intermediate could be detected by IR spectroscopy[13] (Table I),

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[1] For a general review, see: Wentrup, C. *Reactive Molecules: The Neutral Reactive Intermediates in Organic Chemistry*; Wiley: New York, 1984.
[2] Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288.
[3] Norstrum, R. J.; Gunning, H. E.; Strausz, O. P. *J. Am. Chem. Soc.* **1976**, *98*, 1454.
[4] Stachnik, R. A.; Pimentel, G. C. *J. Phys. Chem.* **1984**, *88*, 2205.
[5] Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 3071.
[6] A much slower reaction occurs when longer wavelength light is used ($\lambda > 280$ nm).
[7] Carr, R. W., Jr. *J. Phys. Chem.* **1966**, *70*, 1970.
[8] Addition of 1% O_2 to the initial mixture also had no effect on the product ratios. These results are consistent with the fact that difluorovinylidene is calculated to have a singlet ground state.
[9] (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.
[10] In contrast, propadienone itself undergoes a facile reaction under similar conditions. See: Chapman, O. L.; Miller, M. D.; Pitzenberger, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 6867.
[11] Tam, H. S.; Harmony, M. D.; Brahms, J. C.; Dailey, W. P. *J. Mol. Struct.*, in press.
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[13] The IR spectra were recorded on an IBM IR/97 FT-IR spectrometer at 0.5-cm^{-1} resolution.

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