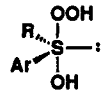
transfer of oxygen to sulfur to form hydrated sulfones **6a–c**, with subsequent loss of H_2O, produces olefins **4**, **5E**, and **5Z**, respectively.



6

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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Difluoropropadienone as a Source of Difluorovinylidene and Difluorodiazoethene

John C. Brahms and William P. Dailey*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

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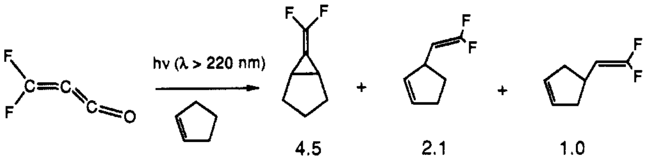
While there are several photochemical sources available for the generation of saturated carbenes,[1] the same is not true for alkylidenecarbenes (vinylidenes). This fact, combined with the propensity for vinylidenes to undergo extremely facile 1,2-migrations to form alkynes,[2] has greatly limited the 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]	[$1\text{-}^{13}C$],[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 [$1\text{-}^{13}C$]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.
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[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.
[12] Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8940.
[13] The IR spectra were recorded on an IBM IR/97 FT-IR spectrometer at 0.5-cm^{-1} resolution.

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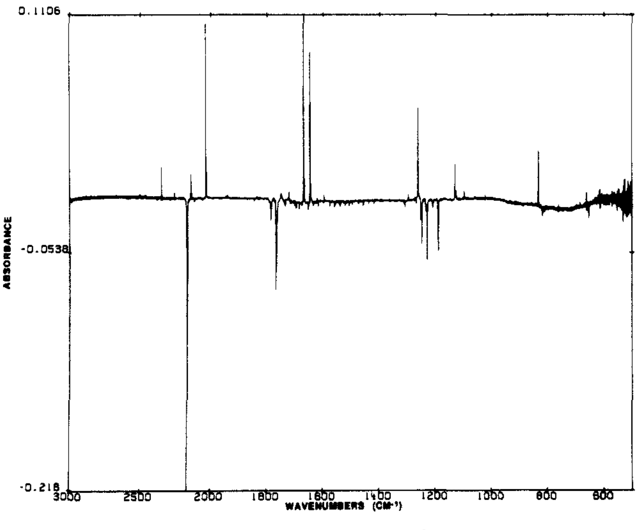


Figure 1. IR difference spectrum from the brief monochromatic photolysis (λ = 240 nm) of difluoropropadienone (DFP) in a $^{15}N_2$ matrix at 11 K. Bottom portion is DFP that has been lost and top is difluorodiazoethene that has been formed during the reaction.

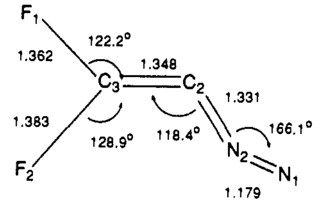
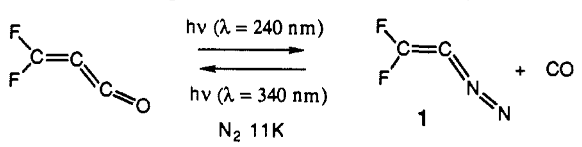


Figure 2. MP2/4-31G optimized structure for difluorodiazoethene. Bond lengths are in angstroms.

This intermediate quickly reached a photochemical steady state concentration of approximately 2% that of DFP. Similar monochromatic irradiation of isotopically labeled DFP containing ^{13}C in the carbonyl position[11] produced the same IR spectrum, implying the absence of CO in the intermediate. An analogous matrix experiment employing the normal isotopomer and $^{15}N_2$ as the matrix material caused a shift for all the IR bands, implying that nitrogen is present in the intermediate. A difference spectrum for the $^{15}N_2$/normal isotopomer experiment is shown in Figure 1. The new intermediate quantitatively reverts to DFP upon irradiation at longer wavelengths (λ = 340 ± 10 nm). On the basis of this fact and the IR data of the isotopic species, the intermediate is assigned as difluorodiazoethene (**1**).



As a further aid in the assignment of this structure, we have carried out ab initio calculations[14] on difluorodiazoethene.[15] The MP2/4-31G optimized structure is shown in Figure 2.[16] A frequency calculation at this level of theory predicted (unscaled) IR bands (with relative intensities) at: 2071 (0.56), 1647 (1.00), 1232 (0.17), 1101 (0.11), 812 (0.05), 614 (0.03), 603 (0.00), 558 (0.00), 476 (0.01), 436 (0.00), 170 (0.00), and 160 cm^{-1} (0.00). The agreement with Table I is very reasonable.[17] At the MP3/6-31G* level, the reaction of DFP plus nitrogen leading to **1** plus carbon monoxide is calculated to be endothermic by 50 kcal/mol. Fragmentation of **1** to DFV and nitrogen is calculated to be endothermic by 25 kcal/mol.

While diazoethenes have been postulated as reactive intermediates in solution,[18] they had not been detected spectroscopically. In contrast to other diazoethenes, **1** owes its existence and spectroscopic detection to the fact that DFV is kinetically much more stable to rearrangement than vinylidene.[19] This allows DFV to be generated reversibly from DFP under photochemical conditions without rearrangement to difluoroacetylene. In the absence of a suitable trapping agent (nitrogen), the thermal back-reaction to reform DFP is very facile under the matrix conditions and direct detection of DFV is not possible. Gas-phase flash photolytic conditions will eliminate this back-reaction, and direct spectroscopic observation of difluorovinylidene will be possible. Such experiments are underway and will be reported in due course.

Acknowledgment. We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8822674) for support of this work.

Supplementary Material Available: Ab initio HF/6-31G* optimized geometries and MP2 and MP3 single point energies for DFP, DFV, and **1** as well as general experimental procedures and spectroscopic properties of the DFV adducts with cyclopentene (7 pages). Ordering information is given on any current masthead page.

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[14] The calculations employed Gaussian 88: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Ragavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA.

[15] (a) A semiempirical study of difluorodiazoethene has been reported. See: Lahti, P. *Chem. Phys. Lett.* **1987**, *133*, 139. (b) A similar ab initio study on the parent diazoethene has recently appeared. See: Murcko, M. A.; Pollack, S. K.; Lahti, P. M. *J. Am. Chem. Soc.* **1988**, *110*, 364.

[16] Very similar structures were also obtained at the HF/6-31G* and MP2/6-31G* levels, but a frequency calculation at the latter level was prohibitively expensive.

[17] The IR bands at 2100 and 1650 cm^{-1} are assumed to be doubled due to matrix site defects. All the bands assigned to difluorodiazoethene grew in or disappeared at the same rate during its formation or destruction.

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Electrocatalytic Hydroxylation of Alkanes and Identification of a Fluoroiron(V) Porphyrin Intermediate

Alaganandan Nanthakumar and Harold M. Goff*

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

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High-valent iron porphyrin models for the active intermediate in the cytochrome P-450 cycle have been generated and used as catalysts for the selective epoxidation of alkenes and hydroxylation of alkanes.[1] In this regard, metallotetraarylporphyrins with electronegative substituents at the *o*-aryl position have been investigated due to their remarkable stability toward oxidative degradation and resistance to formation of dinuclear μ-oxo iron porphyrin complexes.[2,3] The horseradish peroxidase compound

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