Ligand substitution studies indicate that the trifluoromethyl-substituted Cp moiety of **7** is surprisingly resistant to nucleophilic displacement. No reaction was observed upon treating **7** with excess MeCN, CO, or PMe$_3$ at 80 °C. The apparent inertness of **7** may derive from kinetic effects associated with steric bulk around the Ru center, rather than inherent bond strengths. Heating the less hindered systems **8** (50 °C, 5 h) in the presence of PPh$_3$ (2 equiv) resulted in clean displacement of **5** rather than cod from the metal center, generating the stable adducts [(cod)M(PPh$_3$)$_2$]$^+$**5**$^-$ (**9a**, M = Rh; **9b**, M = Ir).

This work demonstrates that tetrakis(trifluoromethyl)cyclopentadienyl ligands are strongly electron withdrawing and can lead to relatively stable, fluorocarbon-soluble transition-metal complexes. Further studies on these and related systems are in progress.

Acknowledgment. We thank Dr. Michael D. Ward for performing the electrochemical experiments and Dr. Richard B. Flippen for the light scattering measurements. We are grateful to Dr. E. P. Janulis, Jr., whose work provided the initial sample of **1**. We also acknowledge John E. Feaster, William Marshall, and Patricia M. Trask for skilled technical assistance.

Supplementary Material Available: Full experimental details, including preparations and spectral and analytical data, for compounds **2** and **4**–**9**, X-ray diffraction data for **2** and **6**, including tables of crystal data, atomic coordinates, thermal parameters, bond distances, and bond angles, and ORTEP and packing diagrams of **2** (Figure 2) with full atom lables (17 pages). Ordering information is given on any current masthead page.

Difluoromaleic Anhydride as a Source of Matrix-Isolated Difluoropropadienone, Difluorocyclopropenone, and Difluoroacetylene

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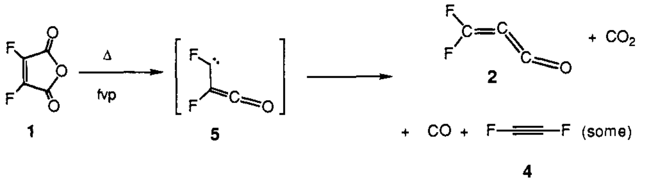
We wish to report some remarkably clean thermal and matrix-isolated photochemical transformations of difluoromaleic anhydride (**1**), which have led to a new synthesis of difluoropropadienone (**2**), the first synthesis and characterization of difluorocyclopropenone (**3**), and the first infrared characterization of difluoroacetylene (**4**).

Pyrolysis of difluoromaleic anhydride[1] is reported to yield fluoropropynoyl fluoride and small amounts of difluoroacetylene.[2] In our hands, flash vacuum pyrolysis (825 °C at 5 × 10^{-5} Torr) of a mixture of **1** in argon (1:500) and deposition of the pyrolysate on a cesium iodide window cooled to 22 K cleanly produced difluoropropadienone[3] and carbon dioxide along with a negligible amount of difluoroacetylene (1341 cm^{-1}). At much higher temperatures (975 °C), larger amounts of difluoroacetylene are produced, but **2** is still present. The reaction presumably proceeds via the ketene carbene **5**, which undergoes fluorine atom migration to yield **2**.



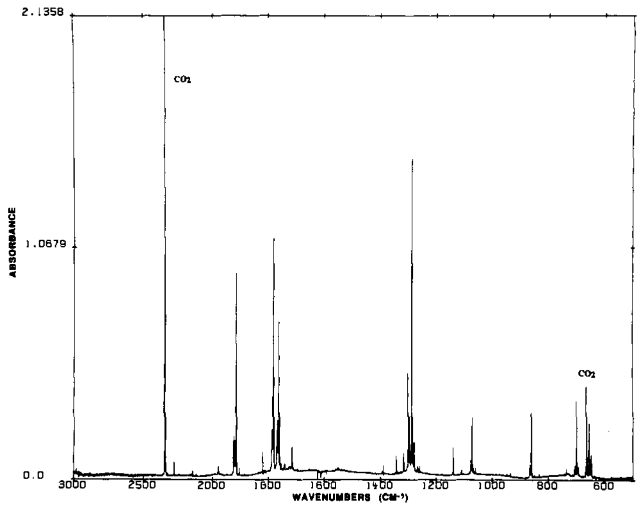
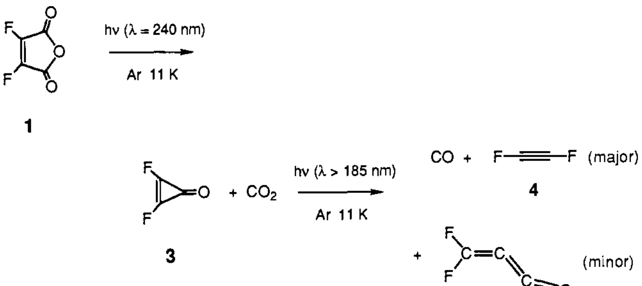


Figure 1. Infrared spectrum of matrix-isolated difluorocyclopropenone and carbon dioxide in argon at 12 K generated by photolysis of difluoromaleic anhydride.

When an argon matrix of **1**[4] is irradiated at 11 K with 240-nm light from a grating monochromator[5] for 1 h, the infrared bands for **1** completely disappear and in their stead arise bands corresponding to carbon dioxide (2344 and 665 cm^{-1}) and a species that we assign as difluorocyclopropenone[6] (**3**) (Figure 1). This compound is stable to prolonged irradiation at 240 nm, but irradiation with the full mercury arc through quartz (λ > 185 nm) leads to the rapid decomposition of **3** and the appearance of bands corresponding to carbon monoxide (2138 cm^{-1}), difluoroacetylene (1341 cm^{-1}), and difluoropropadienone.[7] The exact ratios of the photolysis products are difficult to quantify, but qualitatively the major photochemical process is decarbonylation.[8] Control experiments reveal that difluoropropadienone is photochemically inert under these conditions.



As an aid in understanding this system, we have carried out ab initio calculations[9] for several C$_3$F$_2$O potential energy minima using the 6-31G* basis set and complete geometry optimization.[10]

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(4) IR (Ar, 11 K): 1819 (s), 1809 (s), 1767 (m), 1757 (m), 1390 (s), 1140 (s), 1060 (s), 936 (s), 736 (m), 673 (w) cm^{-1}.

(5) An L-1 illumination system (Photon Technologies) with a 75-W mercury–xenon lamp and grating monochromator was used as the light source.

(6) For the preparation of another dihalocyclopropenone, dichlorocyclopropenone, see: West, R.; Chickos, J.; Osawa, E. *J. Am. Chem. Soc.* **1968**, *90*, 3885–3886.

(7) Similar photolysis of matrix-isolated maleic anhydride yields acetylene, carbon monoxide, and carbon dioxide; see: Dunkin, I. R.; MacDonald, J. G. *J. Chem. Soc., Chem. Commun.* **1979**, 772–773.

(8) Photolysis of matrix-isolated cyclopropenones is a general method for the preparation of strained acetylenes; see: Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033–7036.

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(10) The optimized geometries and total energies are available as supplementary material.

Table I. Calculated and Observed Matrix-Isolated Infrared Vibrational Spectral Data for Difluorocyclopropenone

frequencies, cm^{-1}			rel intensities[a]	
calcd	scaled	obsd	calcd	obsd
2169.5	1952	1914.5	11.9	18.2
2004.4	1803	1779.9	48.8	21.8
		1761.2		15.7
1518.3	1366	1285.5	27.7	28.3
1211.7	1090	1071.4	2.8	5.0
974.4	876	860.2	3.7	4.4
800.9	720	699.6	2.2	3.3
788.8	709	656.0	0.7	3.3
715.1	644	b	0.7	
694.3	624		0.0	
293	264		0.2	
287	258		0.6	
244	220		0.7	

[a] The intensities are normalized to 100. [b] Band assignment was not possible.

At the MP3/6-31G*//HF/6-31G* level of theory, the relative energies of **2**, **3**, **5**, and **4** plus carbon monoxide are calculated to be 0.0, 25.0, 47.6, and 44.3 kcal/mol, respectively. For the corresponding hydrocarbon derivatives, the relative energies are calculated to be 0.0, 2.1, 35.0, and −4.0 kcal/mol, respectively. It is obvious that fluorine substitution has had a major effect on the relative stabilities of these species. The great electronegativity of fluorine destabilizes difluoroacetylene by about 40 kcal/mol relative to acetylene.[11] A portion of this destabilization is apparently also present in difluorocyclopropenone, which is 20 kcal/mol more strained than the parent hydrocarbon. The relatively small energy change predicted for **3** opening to **5** (22.6 kcal/mol) forewarns of the potential lability of difluorocyclopropenone (see below).

The vibrational spectrum of difluorocyclopropenone was calculated analytically at the HF/6-31G* level of theory, and a comparison of the calculated, scaled (0.9),[12] and experimental values is shown in Table I. The agreement is quite reasonable.[13] In addition, we have calculated (HF/6-31G*) that the observed infrared-active mode for difluoroacetylene will occur at 1331 cm^{-1} (1479 cm^{-1} before scaling by 0.9). This value is consistent with our experimental value but is very different from the value reported in the literature (1149 cm^{-1}).[14] The agreement between our theoretical and experimental infrared spectra give us confidence that both of these structural assignments are correct. Unfortunately, we have so far been unable to remove either species intact from the matrix in order to characterize it more fully.

In conclusion, we have demonstrated that difluoromaleic anhydride is a useful source of matrix-isolated difluoropropadienone, difluorocyclopropenone, and difluoroacetylene.

Acknowledgment. We thank Professor D. M. Lemal for supplying a sample of difluoromaleic acid, and 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 compounds **2–5** as well as the corresponding hydrocarbon derivatives (2 pages). Ordering information is given on any current masthead page.

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Stereochemical Effects in Allylic Rearrangements of Cyclic Phosphates[†,1]

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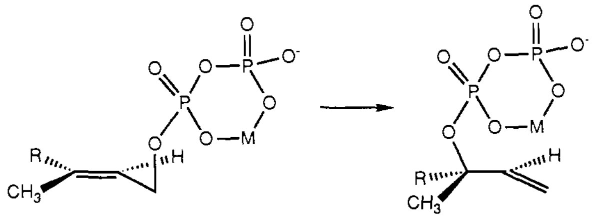
Allylic rearrangements (**1** → **2**) and nucleophilic displacements of prenyl pyrophosphates (prenyl PP) are important initiating steps in the biosynthesis of many mono-, sesqui- and diterpenes.[2,3]



1 **2** (1)

Although the participation of allylic carbocation/PP anion pairs in these processes[2,9] provides a simple means to rationalize the syn (suprafacial) stereochemistry established for several allylic rearrangements,[2a,4–6] the structure (or structures) of the enzyme-bound ion pairs remains uncertain in light of the variable oxygen-18 scrambling observed in two allylic PP rearrangements[10] and the absence of exchange in one PP displacement.[9b] In this communication, we report preliminary results on the allylic rearrangement of isomeric bridged phosphates **5a** and **5b** as chemical models for prenyl PP arrangements. The kinetic data demonstrate that the proximal *P*-oxide group in **5a** facilitates allylic rearrangement, evidently via symmetrical, bidentate ion pair **7A**.

The chemical reactions of various allylic phosphates,[11–13]

[†] Dedicated to the late Roger Adams on the occasion of the 100th anniversary of his birth in January 1889.

(1) Presented at the Great Lakes Regional American Chemical Society meeting in Duluth, MN, May 31, 1989.

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