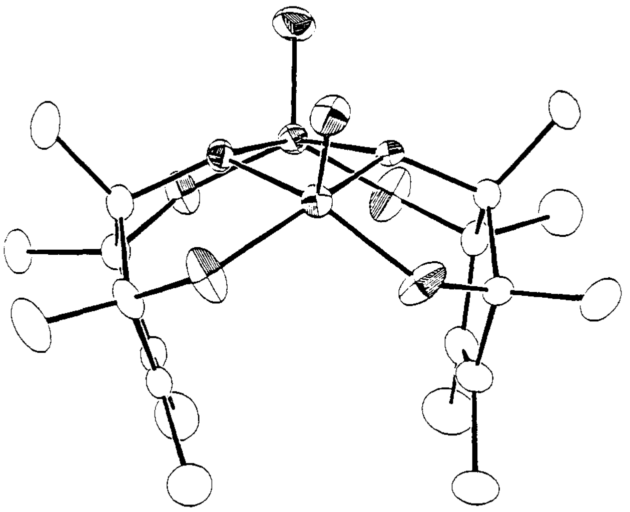
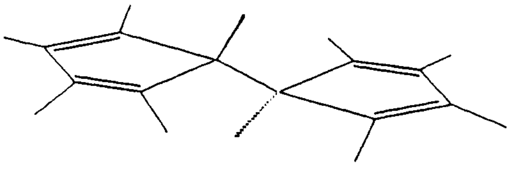


Figure 1. The molecular structure of $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ (**2**) as determined by X-ray diffraction.

red. Crystalline $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ (**2**) was obtained from this second eluate by slow removal of hexane in vacuum. The nature of **2** was proven by spectroscopy[12] and X-ray diffraction (Figure 1).[13]



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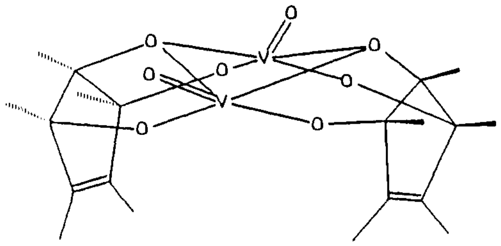

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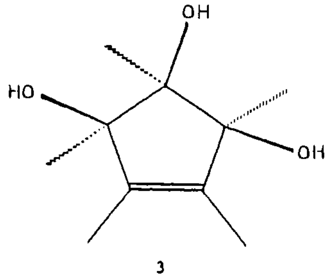

3

2 is a V^V derivative of the triol **3** and is produced by formal insertion of three oxygen atoms into adjacent V–C bonds of $(\eta\text{-}C_5Me_5)_2V$. It is very soluble in hexane and other nonpolar solvents and is stable to O_2. However, it is readily hydrolyzed, particularly in alkaline solution.

Almost as remarkable as **2** itself is that the reaction which produces it is quantitative according to eq 1. Since loss of C_5Me_5

$$2Cp_2^*V + 4O_2 \rightarrow \mathbf{2} + (C_5Me_5)_2 \qquad (1)$$

is not a feature of the chemistry of Cp_2^*V, an intermediate containing one intact Cp* ligand for each vanadium must be formed on oxidation. Preliminary work indicates that this intermediate is $[Cp^*V(O)(OC_5Me_5)]_2$, a vanadium(IV) derivative related to $Cp^*W(O)_2(OC_5Me_5)$ obtained on oxidation of $Cp_2^*W(O)$ with O_2.[14] We are presently attempting to confirm the intermediate and to extend the reaction, which has synthetic potential in carbohydrate chemistry, to other cyclopentadienyl derivatives.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Imperial Oil for support of this work and Professor Z. Valenta for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and the mass spectral fragmentation pattern for **2** (8 pages); table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(9) Characterization of $(C_5Me_5)_2$ (**1**): mp 53–58 °C dec; ^{1}H NMR 200 MHz ($C_6D_5CD_3$ solution) 1.10 (s, 6 H), 1.65 (s, 12 H), 1.72 (s, 12 H); ^{13}C NMR 50 MHz (C_6H_{14} solution) 10.5, 12.3, 19.4 ($C_5(CH_3)_5$), 60.1, 133.4, 141.8 ($C_5(CH_3)_5$); mass spectrum m/e = 270.2336 (4), calcd for $C_{20}H_{30}^+$, 270.2347; other major fragments were 180 ($C_{13}H_{24}^+$), 168 ($C_{12}H_{24}^+$), 151 ($C_{11}H_{19}^+$), 135 ($C_{10}H_{15}^+$). The results are in reasonable agreement with those in the literature.[10,11]

(10) Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

(11) Davies, A. G.; Lusztyk, J. *J. Chem. Soc. Perkin Trans II* **1981**, 692.

(12) Spectroscopic data for **2**: IR ν(V=O) 935 (m), 957 (sh) cm^{-1}; ^{1}H NMR 200 MHz ($C_6D_5CD_3$ solution) 2.12 (s, 12 H), 2.05 (s, 18 H); ^{13}C NMR 50 MHz (C_6H_{14} solution) 10.5 (CH_3C=), 27.2, 29.8 (CH_3C—O); 125.3 (C=C), 128.1 (C—O), 128.9 (C—O); ^{51}V NMR 52.5 MHz (C_6H_{14} solution) −672.5; mass spectrum m/e 500 ($\mathbf{2}^+$), 482 ($C_{20}H_{28}O_7V_2^+$), 350 ($C_{10}H_{16}O_7V_2^+$), 264 ($C_{10}H_{13}O_5V^+$), 249 ($C_{10}H_{14}O_4V^+$), 219 ($C_{10}H_{16}O_2V^+$), 167 ($C_{10}H_{15}O_2^+$), 151 ($C_{10}H_{15}O^+$); structural assignments for the fragments are given in the Supplementary Material.

(13) Crystal data for **2** ($C_{20}H_{30}O_8V_2$): monoclinic, $P2_1/n$; a = 11.309 (1) Å, b = 14.163 (1) Å, c = 14.212 (1) Å, β = 95.601 (9)°; Z = 4. Diffraction data: 2931 unique reflections with $2\theta < 45°$ (Mo Kα radiation), 1612 observed ($I > 2.5\sigma(I)$); no absorption correction (μ = 12·2 cm^{-1}). Refinement data: 272 parameters (all non-hydrogen atoms anisotropic, H riding on C with fixed B_{iso}); R = 0.066, R_w = 0.074, goodness of fit 1.553; highest final peak 0.75 e Å^{-3}, deepest hole −0.42 e Å^{-3}. Important molecular parameters (averaged over the two crystallographically inequivalent halves of **2**): V–O 1.581 (7), V–O(A) 1.770 (7), V–O(B) 1.957 (6), C–O 1.45 (1), C–C(ring) 1.52 (1), C–C 1.33 (1), C–CH_3 1.51 (1) Å (O(A) are bonded to a single V, O(B) to both V). Full details have been deposited.

(14) Bercaw, J. E.; Parkin, G. *Polyhedron* **1988**, *7*, 2053. Parkin, G.; Marsh, R. E.; Schaefer, W. P.; Bercaw, J. E. *Inorg. Chem.* **1988**, *27*, 3262.

Synthesis of Difluoropropadienone

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While both chemical intuition and ab initio calculations within the Hartree–Fock (HF) level of theory[1] predict that propadienone ($H_2C{=}C{=}C{=}O$)[2] should maintain a symmetric structure, both experiment[3] and ab initio calculations employing electron correlation[4] reveal that the actual structure is badly bent. A microwave spectrum[5] and matrix-isolated infrared spectrum[6] for

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(1) (a) Radom, L. *Aust. J. Chem.* **1978**, *31*, 1-9. (b) Komornicki, A.; Dykstra, C. E.; Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1652-1656.

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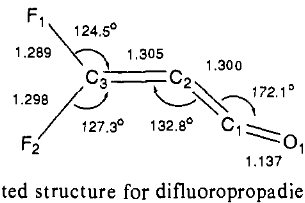


Figure 1. Predicted structure for difluoropropadienone (HF/6-31G*). Bond lengths in Å.

Table I. Calculated and Observed Gas Phase Vibrational Spectrum for Difluoropropadienone

	frequencies (cm^{-1})			intensities[a]	
sym	calcd	scaled	obsd	calcd	obsd
A′	2387.3	2149	2169.1	50.9	54.5
A′	1968.7	1772	1763.6	26.2	19.3
A′	1442.0	1298	1248.4	9.9	16.2
A′	1357.7	1222	1194.4	5.8	6.2
A′	901.2	811	821.9	2.5	2.3
A″	770.6	694	656.7	2.2	0.5
A″	712.2	641	*b*	0.6	
A′	682.1	614	611.2	1.1	0.8
A′	575.0	518	522.9	0.6	0.6
A′	531.8	479	486.3[c]	0.1	
A″	152.2	137	*b*	0.0	
A′	103.4	93	*b*	0.0	

[a] Intensities are normalized to 100. [b] Band assignment was not possible. [c] Band observed in an argon matrix at 10 K.

propadienone have been reported, but the molecule is extremely reactive, even in dilute gas phase, and quickly yields a polymer of unknown structure. On the other hand, the carbonyl derivative of propadienone, carbon suboxide (O=C=C=C=O),[7] is kinetically much more stable.[8] Experimentally carbon suboxide is also bent,[9] but again the heavy atom chain prefers a linear arrangement at the Hartree–Fock level of theory.[10] There are no reports of any halo-substituted propadienones. Organofluorine compounds, in general, have very different properties from their hydrocarbon relatives.[11] On the basis of other worker's observations, difluoropropadienone (**1**) might be expected to resemble carbon suboxide more closely in structure and stability than propadienone.[12] To address this point, we wish to report our theoretical and experimental results for **1**.

The structure of difluoropropadienone was determined using ab initio molecular orbital theory.[13] At the HF/3-21G level of theory, the molecule maintains C_{2v} symmetry. However at the HF/6-31G* level of theory, the main chain of the molecule is predicted to be badly bent, with the molecule adopting C_s symmetry (Figure 1). This is in contrast to the parent propadienone which continues to prefer C_{2v} symmetry, even with a very large basis set (HF/6-311(df,p)).[14] The vibrational spectrum for **1** was determined analytically at the HF/6-31G* level of theory. It is generally found that if the calculated harmonic frequencies are scaled by a factor of 0.9, they correspond well to the experimentally determined anharmonic frequencies.[15] The calculated and scaled results are shown in Table I.

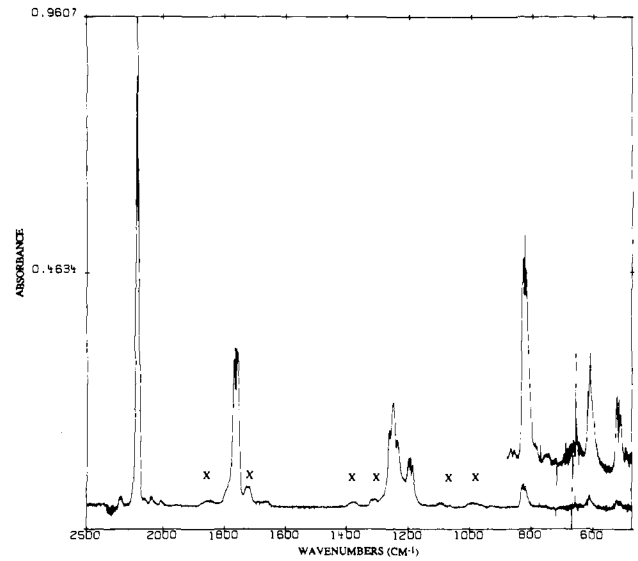
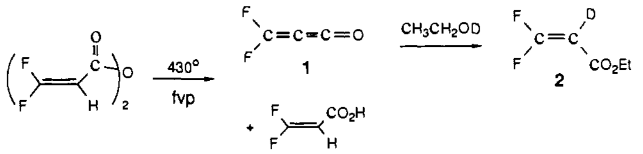


Figure 2. Vapor phase infrared spectrum of difluoropropadienone. Impurity peaks for 3,3-difluoroacryloyl fluoride are marked with an X.

Scheme I



One of the successful preparations of propadienone is the high vacuum pyrolysis of acrylic anhydride,[16] and we attempted to extend this method to the preparation of **1**. Thus, 3,3-difluoroacrylic anhydride[17] is sublimed (0.001 Torr) at room temperature through a 10 mm × 20 cm empty Pyrex tube heated to 430 °C, and the pyrolysate is passed through a series of two cold traps (−78 °C and −196 °C). The first trap contains almost pure 3,3-difluoroacrylic acid. The second trap contains a product which, if allowed to warm slowly, liquifies and then quickly polymerizes to a white solid well below room temperature. However, this reactive product can be successfully manipulated if the trap is warmed quickly and the volatile product is expanded into a large volume. A high resolution mass spectrum of this material yields a parent peak corresponding to $C_3F_2O^+$ (67%) and fragment ions of C_3FO^+ (100%), $C_2F_2^+$ (28%), C_2F^+ (33%), CF^+ (59%), and C_2^+ (14%); UV(vapor): λ_{max} = 375, 240 nm. A vapor phase infrared spectrum is shown in Figure 2 and corresponds well, both in position and relative intensity, with that calculated for difluoropropadienone (Table I). A small amount of 3,3-difluoroacryloyl fluoride (~5%) is also formed during the reaction, but its presence does not interfere with the characterization or stability of **1** ($\tau_{1/2}$ = 20 min at 25 °C).

If ethanol-*d* vapor is introduced into the pyrolysate stream after the first cold trap, ethyl 2-deuterio-3,3-difluoroacrylate (**2**) is obtained in 8% yield after preparative GLC. Deuterium incorporation was confirmed by high resolution mass spectral analysis and by ^{19}F NMR[18] which revealed signals at 64.7 ppm (dt, J_{FD}

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(7) For a general review of carbon suboxide, see: Kappe, T.; Ziegler, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 491–504.

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(17) 3,3-Difluoroacrylic acid: Gillet, J. P.; Sauvetre, R.; Normant, J. F. *Synthesis* **1982**, 297–301.

= 3.2, J_{FF} = 16.2 Hz) and 70.3 ppm (d, J_{FF} = 16.0 Hz). The ^{19}F NMR spectrum of ethyl 3,3-difluoroacrylate[19] has signals at 64.5 ppm (dd, J_{HF} = 21.5, J_{FF} = 15.7 Hz) and 70.3 ppm (dd, J_{HF} = 2.6, J_{FF} = 15.8 Hz).[20] We believe that this is convincing chemical evidence that difluoropropadienone is indeed formed.

Other reactions of difluoropropadienone, its microwave spectrum, and its use as a source of difluorovinylidene 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 for partial support of this work.

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(19) Eroy, J.; Moliiqes, N.; Wakseman, C. *J. Org. Chem.* **1987**, *52*, 290-291.

(20) The ratio J_{FH}/J_{FD} = 6.71 is close to that predicted from the H/D magnetogyric ratio of 6.51.

The Microwave Spectrum and Molecular Structure of the Ethylene-Ozone van der Waals Complex

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We have observed a weakly bound complex between ozone and ethylene in the gas phase by using a pulsed-beam Fourier transform microwave spectrometer. The rotational constants and electric dipole moment are consistent with a structure in which the planes containing ethylene and ozone are approximately parallel. As shown in Figure 1, the centers of mass for ozone and ethylene define a line perpendicular to the two planes of length R_{cm} = 3.30 Å. It is shown below that the complex represents a small minimum on the reaction coordinate prior to the transition state which leads to the product ethylene primary ozonide (PO) depicted in Figure 2.

Within the context of 1,3-dipolar cycloaddition theory and Woodward-Hoffman symmetry rules, the addition of ethylene to ozone produces ethylene PO.[1,2] Overlap of the π HOMO orbital of ethylene with the π^* LUMO orbital of ozone is shown in Figure 2.[2] This parallel plane approach maintains a symmetry plane along the reaction coordinate and leads to ethylene PO in the oxygen envelope configuration. Recently, we found that the lowest energy conformation of ethylene PO is the oxygen envelope (C_s symmetry) in the gas phase.[3,4]

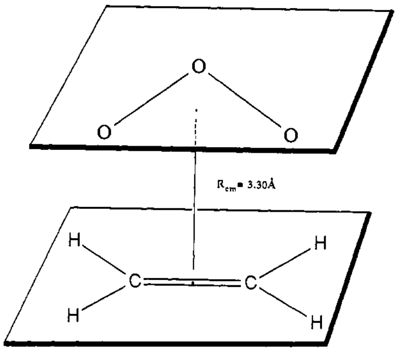

Figure 1. Approximate geometry of the ethylene-ozone complex showing the parallel planes of ethylene and ozone with a R_{cm} distance of 3.30 Å between the centers of mass of ozone and ethylene.

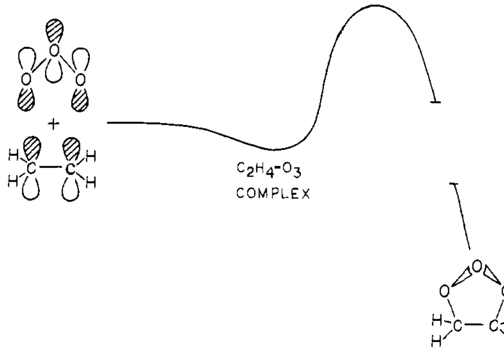

Figure 2. The reaction coordinate defined by a 1,3-dipolar cycloaddition of ozone plus ethylene producing ethylene primary ozonide through the complex observed in this work.

Table I. Rotational Transitions (MHz) of the Ethylene-Ozone Complex

transition	ground state		excited state	
$J'_{K_{-1},K_{+1}} - J''_{K_{-1},K_{+1}}$	ν_{obsd}[a]	$\Delta\nu$[b]	ν_{obsd}[a]	$\Delta\nu$[b]
$4_{04} - 3_{12}$	10 467.081	-1	10 471.375	0
$1_{10} - 0_{00}$	10 764.982	-3	10 760.404	0
$5_{05} - 4_{13}$	13 605.316	0	13 609.298	0
$5_{24} - 5_{14}$	14 450.736	0	14 441.138	-1
$4_{23} - 4_{13}$	15 569.090	0	15 559.478	2
$2_{11} - 1_{01}$	15 800.775	2	15 796.213	0
$3_{22} - 3_{12}$	16 484.367	1	16 474.752	-3
$2_{21} - 2_{11}$	17 181.317	0	17 171.717	1
$2_{20} - 2_{12}$	18 631.379	0	18 621.848	0
$3_{21} - 3_{13}$	19 466.737	-1		
$3_{12} - 2_{02}$	21 082.267	0	21 077.730	0

[a] The transition frequencies are estimated to be accurate to 4 kHz which is the resolution element. [b] $\Delta\nu$ is the observed minus calculated frequency (kHz) from the least-squares fit.

Two ab initio calculations find the transition-state geometry to be in accord with the parallel plane approach shown in Figure 2.[5,6] These studies indicate the transition state is more tightly bound than the complex reported here since the distance between the carbon and oxygen atoms varies from ~2.3 to ~2.0 Å in the two sets of calculations for the transition state.[5,6] One of the ab initio calculations identifies a π complex composed of ethylene bound to ozone prior to the transition state.[6] This species is weakly bound (6.2 kcal/mol more stable than ethylene plus ozone at the MP2 level dropping to only 0.9 kcal/mol in a SCF calculation).[6] While the structure is consistent with the geometry shown in

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