Received: August 29, 1986; accepted: January 11, 1988

#### SYNTHESIS OF PENTAFLUOROSELENIUMOXIDE FLUOROCARBONS

Carl J. SCHACK and Karl O. CHRISTE Rocketdyne, A Division of Rockwell International Canoga Park, CA 91304 (U.S.A.)

## SUMMARY

The reaction of xenon bis-pentafluoroseleniumoxide,  $Xe(OSeF_5)_2$ , with the haloolefins,  $CF_2=CF_2$ ,  $CF_3CF=CF_2$ ,  $CF_2=CFC1$ , and  $CF_2=CFH$ , results in the low to moderate yield addition of two  $SeF_5O$ - groups to the double bond. These are the first examples of this type of addition. From  $c-C_5F_8$  and the above olefins these same reactions also gave as products,  $C_2F_5OSeF_5$ ,  $n-C_3F_7OSeF_5$ ,  $c-C_5F_9OSeF_5$ , and  $SeF_5OCF_2COC1$  in higher yields than the bis  $SeF_5O$ - compounds. Surprisingly, those olefins capable of forming thermally stable epoxides, <u>i.e.</u>  $C_3F_6$  and  $c-C_5F_8$ , were found to produce significant yields of the corresponding epoxides as a by-product in these reactions, while the remaining olefins gave significant amounts of acid fluorides instead. Characterizing data are presented for all of these new  $R_f^{OSeF_5}$ compounds.

#### INTRODUCTION

Recently we reported on the high yield addition of  $\text{TeF}_5^{0-}$  groups to fluoroolefins using  $\text{Xe(OTeF}_5)_2$  and  $\text{TeF}_5^{OX(X=F,C1)}$  [1-4].



While a similar reaction of SeF<sub>5</sub>OF and c-C<sub>5</sub>F<sub>8</sub> has previously been reported [5], and the displacement of chlorine from chlorocarbons using Hg(OSeF<sub>5</sub>)<sub>2</sub> has yielded  $-C-OSeF_5$  compounds [6], we are not aware of any studies of the fluorocarbon—Xe(OSeF<sub>5</sub>)<sub>2</sub> reaction system. It was of interest therefore to

0022-1139/88/\$3.50

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examine the possibility of preparing  $R_f OSeF_5$  compounds using Xe(OSeF<sub>5</sub>)<sub>2</sub>. Furthermore, these derivatives would fill the gap between the newly discovered TeF<sub>5</sub>O- substituted materials and the well known SF<sub>5</sub>O- substituted analogues [7].

## EXPERIMENTAL

Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type gauge. The synthetic reactions employed here were usually conducted in stainless steel cylinders. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer using cells equipped with AgBr windows. Raman spectra were recorded at ambient temperature on a Cary Model 83 spectrophotometer with the use of the 488-nm exciting line of an Ar ion laser. Sealed quartz tubes, 3mm OD, or Pyrex mp capillaries were used as sample containers. <sup>19</sup>F nmr spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer with internal CFCl<sub>3</sub> as a standard with negative chemical shift being upfield from CFCl<sub>3</sub>. Literature methods were used to synthesize XeF<sub>2</sub> [8] which in turn was employed to convert SeOF<sub>2</sub> to Xe(OSeF<sub>5</sub>)<sub>2</sub> using a modification of a reported procedure [9]. Fluorocarbons used were commercial materials (SCM Specialty Chemicals).

For reactions with  $Xe(OSeF_5)_2$  a tared, prepassivated cylinder was loaded with the solid xenon compound in the dry box. After evacuation the cylinder was cooled to  $-196^{\circ}$  and a measured quantity of olefin was condensed in. The closed cylinder was allowed to warm to ambient temperature before placing it in an oven at a higher temperature. It was found that little reaction occurred below 50° while above 65° a drastic fall off in the yield of  $R_{f}OSeF_{5}$  compounds was experienced. The reactions were generally slow. Separation of the products was accomplished by fractional condensation. The  $R_{p}OSeF_{p}$  materials were of intermediate volatility compared to the other products. Where necessary a quick water wash was used to preferentially react some impurities thereby permitting isolation of a particular  $R_fOSeF_5$  product; eg., hydrolysis of SeF<sub>5</sub>OCFHCOF and SeF<sub>5</sub>OCF<sub>2</sub>COF to isolate SeF<sub>5</sub>OCF<sub>2</sub>CFH(OSeF<sub>5</sub>). However, contact with moisture must be minimized because even the saturated, non-functional  $R_fOSeF_5$  type materials seemed sensitive to moisture and underwent slow decomposition when stored in glass. All of the  $R_{f}OSeF_{5}$  compounds are colorless, mobile liquids of low volatility, although, as expected, slightly more volatile than their  $R_{f}OTeF_{5}$  analogues.

In addition to the synthetic and spectroscopic data listed in the Tables, further properties are given below for some of the compounds.  $\frac{C_2F_5OSeF_5}{C_2F_5}$ -vapor density; Found 311, calc. 309 g/mol. For the range -45 to 0° log P<sub>mm</sub> = 6.6198-1222/T°K with a calc. b.p. = 53.6° and  $\Delta H_v$  = 5.59 kcal/mol; m.p. <-80°.  $\underline{n-C_3F_7OSeF_5}$ -vapor density; Found 357, calc. 359 g/mol. For the range -32 to 11° log P<sub>mm</sub> = 6.6263-1271/T K with a calc. b.p. = 66.2° and  $\Delta H_v$  = 5.82 kcal/mol; m.p. <-80°.  $\underline{c-C_5F_8O}$ -vapor density; Found 231, calc. 228 g/mol. IR (gas) cm<sup>-1</sup> rel. intens., 1529s, 1370s, 1320s, 1293w, 1215vs, 1175w, 1088w, 1035w, 1000vs, 760vw, 615w, 560w, 455vw, and 419vw. Raman (liq.) cm<sup>-1</sup> (rel. intens.), 1528(0.4), 1385(0.9), 1362(0.3), 1320(0.2), 1295(0.4), 1190(0.3), 1175(0.2), 1032(0.8), 868(0.2), 795(0.1), 755(0.2), 730(0.3), 678(10), 640(0.5), 617(0.5), 598(1.1), 585(0.8), 565(0.2), 455(1.4), 418(1.0), 372(5.2), 343(1.6), 310(0.3), 297(0.4), 245(0.3), 235(0.4), 190(0.3), and 112(0.2). Perfluoropropylene oxide was identified by its IR and <sup>19</sup>F nmr spectra [10]. Other known products were similarly identified by their IR [11] and <sup>19</sup>F nmr [12] spectra.

## RESULTS AND DISCUSSION

The synthetic reactions are summarized in Table 1. It was found that the reactions of Xe(OSeF<sub>5</sub>), and simple olefins involve several paths. These include, 1) transfer of two SeF<sub>5</sub>O- groups to the olefin; 2) transfer of one SeF<sub>5</sub>Ogroup accompanied by fluorination; 3) transfer of two SeF<sub>s</sub>O- groups followed by elimination of SeF, and generation of an acyl halide; 4) oxygenation to give an epoxide; and 5) oxygenation and rearrangement to an acyl fluoride. The mechanisms of these various paths are unknown. From the observation that only a narrow temperature range was useful in generating significant amounts of R<sub>f</sub>OSeF<sub>5</sub> products and the fact that extensive oxygenation and fluorination also occurred, it seems likely that the activation energies for the formation and decomposition of  $SeF_50$  radicals are similar. This causes competing side reactions resulting in the fluorination and oxygenation of the available substrates. These findings are in marked contrast to the analogous TeF50chemistry where facile and efficient transfer of  $TeF_50$  radicals, generated from  $Xe(OTeF_5)_2$ , to substrates can be achieved [1,2]. Only when the reaction temperatures exceeded 100°, did breakdown of the thermally more stable TeF<sub>5</sub>0 radical become significant [4]. Extensive degradation of the  $SeF_{5}O$ - group was also encountered in reactions of fluoroolefins with SeF\_OF [5] while TeF\_OF gave good yields of the corresponding TeF\_O- adducts [3].

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TABL	

Fluoroolefin-Xe(OSeF<sub>5</sub>), reaction data

	.her b oducts <sup>b</sup>	(0	), c <sub>3</sub> <sup>F</sup> <sub>8</sub>	44) ) <sub>2</sub> (24)	(52), Xe(0SeF <sub>5</sub> ) <sub>2</sub>	cor, c <sub>2</sub> r <sub>5</sub> H cor,
	Ot Pr	CF <sub>3</sub> CFO(4	c <sub>3</sub> F <sub>6</sub> 0(36	c-C <sub>5</sub> F <sub>8</sub> 0( Xe(0SeF <sub>5</sub>	clcF <sub>2</sub> coF c <sub>2</sub> F <sub>5</sub> cl,	SeF <sub>5</sub> 0CFH SeF <sub>5</sub> 0CF <sub>2</sub>
	Vap. Pressure mm at 20°C	283 <sup>c</sup> 18	195 <sup>C</sup> 14	20 <sup>d</sup>	σ	10
	Rf <sup>OSeF</sup> 5 (% Yield) <sup>a</sup>	$c_{2}F_{5}OSeF_{5}(27)$ $c_{2}F_{4}(OSeF_{5})_{2}(10)$	$C_{3}F_{7}OSeF_{5}(51)$ $C_{3}F_{6}(OSeF_{5})_{2}(11)$	c-C <sub>5</sub> F <sub>9</sub> 0SeF <sub>5</sub> (39)	SeF <sub>5</sub> OCF <sub>2</sub> COC1(17) SeF <sub>5</sub> OCF <sub>2</sub> CFC1(OSeF <sub>5</sub> ) (10)	sef <sub>5</sub> ocfhcf <sub>2</sub> (osef <sub>5</sub> ) (37)
	Time	3d	3.5d	7đ	ld	3d
	т°с	50	65	55-64	62	55
7 0	Xe(OSeF <sub>5</sub> ) <sub>2</sub> mmo1	2.70	2.54	1.98	3.17	3.74
	R <sub>f</sub> Compound mnol	c <sub>2</sub> F <sub>4</sub> 3.20	C <sub>3</sub> F6 2.99	с-С <sub>5</sub> F <sub>8</sub> 2.00	c <sub>2</sub> F <sub>3</sub> c1 3.87	С <sub>2</sub> F <sub>3</sub> H 3.94

<sup>a</sup>Yields based on olefin taken.

<sup>b</sup>In all cases varying amounts of all or several of the following compounds were also observed: Xe, SeF<sub>6</sub>, SeF<sub>4</sub>, SeOF<sub>2</sub>, and SeF<sub>5</sub>OH.

<sup>c</sup>Extrapolated

d<sub>Reference 5</sub>

<sup>19</sup>F NMR data for  $R_{f}OSeF_{5}$  compounds<sup>a</sup> -CF<sub>2</sub>-----\_\_\_\_\_\_SeF40-\_\_\_CF2-\_\_\_COC1 -87.9t -86.4qi 61.4A 73.6B -63.5bs 71.3A 73.4tB -7.5--220--10.2 9.0 1.8 -CF3 — SeF<sub>4</sub>0---SeË,O-CF \62.1A -82.8t 78.6tB, 66.3A 77.8tB, -81.1cm -129.7t -221-F - SeF40. -125.6 -130.5 73.4B4 62.2A AB quadruplet From C<sub>3</sub> and C<sub>4</sub>,  $J_{AB}=254$ F -133.3 5 2 AB quadruplet From  $C_2$  and  $C_5$ ,  $J_{AB} = 254$ -136.6 cm From C, CF3-80.9cm -9.8 71 ---- F - SeF\_0-F CF -136.0gi 78.6tB, 65.7A -79.3cm 0 SeF4 80.9dB, 66.94 -9.5-4.7--226-- OSeF4 - сғн -SeF₄O CF, 63.1A 73.7tB -81.9b,st -137.9dqi 58.4dB4 65.6A

 $\delta = 5.98d(J_{HF} = 53)$  of  $t(J_{HF} = 1.9)$ 

$$\begin{array}{c} \hline 225 & 9.2 \\ \hline F & 5eF_40 & CF_2 \\ \hline 64.1A & 75.8tB_4 \\ \hline -81.4qi \\ -73.0qi \\ \hline 74.8A \\ \hline 63.3dB_4 \\ \hline \end{array}$$

<sup>a</sup>CFCl<sub>3</sub> reference, negative shift being upfield from the reference, \$\$\phi\$=chemical shift, ppm, J=Hz, where b=broad, \$\$\sigma\$ singlet, d=doublet, t=triplet, st=sextet, qi=quintet, cm=complex multiplet. The area ratios measured for these resonances agreed with the given assignments.

Table 2 lists the <sup>19</sup>F and <sup>1</sup>H nmr data for the new compounds. The magnetic inequivalence of the axial fluorine compared to the four basal fluorines in the SeF<sub>5</sub>O- group gives rise to  $AB_4$  type spectra. Chemical shifts and coupling

# TABLE 3

Vibrational spectra of R<sub>6</sub>OSeF<sub>5</sub> compounds and C<sub>2</sub>F<sub>5</sub>OTeF<sub>5</sub>

			Obsd. Freq	., cm <sup>-1</sup>	` ( r	el. intens.) <sup>a</sup>			
		C2F5 <sup>OSeF5</sup>		n	n-C3F7 <sup>OSeF5</sup>		C <sub>2</sub> F <sub>5</sub> OTeF <sub>5</sub>		
Assign. <sup>b</sup>	IR(g	as)	Raman(lig.)	IR(ga	is)	Raman(liq.)	IR(gas)	Raman(liq.)	
	,		1382(0.7)dp 1345(0.1) 1295(0.05)	1348 1314	mw m	1358(0.3)dp 1325(0.8)p		1392(0.8)dp	
VCF	1198 1180	vs m s	1245(0.1) 1200(0.1) 1175(0.3)p	1250 1210 1180	vs m m	1215(0.2)p 1175(0.1)	124/ VS 1190 VS	1240(0.1) 1185(0.1)p	
(				1164 1148	m s	1147(0.4)p			
νC0 νCC	) 1105	s	1102(0.4)p	1001	s	1010(0.5)p	1110 vs	1105(0.3)p	
<sup>δCF</sup> 2	860	w	857(0.4)p	835	w	840(0.4)p 825(0.4)p		868(0.5)p	
vas <sup>XF</sup> 4	768	S	770(0.2) 748(0.4)p	765	VŚ	753(1.1)p	745 vs	742(0.8)p	
VXF'	735	m	733(0.8)p 718(0.6)p	735	8	735(1.0)p	722 s	719(1.8)p	
vOX and v <sub>s</sub> XF <sub>4</sub> ip			698(10)p 670(4.2)p			700(8.1)p 675(10)p		690(9.2)p 678(10)p	
v <sub>s</sub> XF <sub>4</sub> op			652(4.2)dp 615(0.2)			652(1.7)dp 622(0.4)p 595(0.5)p		615(0.2)dp	
	540	vw	560(0.6)p	570	vw	565(0.3)p 535(0.6)p		525(0.2)p 367(0.7)p	
δ <sub>s</sub> XF <sub>4</sub> op1	432	s	423(0.4)dp	437	s	424(0.7)dp	328 s	320(1.2)ap	
<pre>SOXF4 and SFXF4</pre>			${398(0.8)dp}$			398(1.1)dp 380(0.4)p		311(1.3)dp	
4			(370(0.4)p			362(0.6)p 348(0.7)p		294(1.3)p 270(1.3)p	
<sup>8</sup> as <sup>XF</sup> 4 <sup>ipl</sup>			335(1.7)dp 304(0.7)p 222(1.4)p			340(1.5)dp 317(0.6) 220(1.2)p 188(0.9)p		262(1.3)dp	
			174(1.4)p 145(0.2)p			165(1.4)p 147(0.8)p		181(1.5)p 153(1.1)p	

<sup>a</sup>Uncorrected Raman intensities (peak heights)

 $b_X = Se$  or Te; ip = in phase; op = out of phase; op1 = out of plane; ip1 = in plane

constants are found in a narrow range: A = 61-66 and  $B_4 = 73-79$  ppm except for SeF<sub>5</sub>O- attached to CFH where the  $B_4$  resonance shifts markedly to 58.4 ppm. In unsymmetrical  $R_f(OSeF_5)_2$  type compounds the inequivalence of the two SeF<sub>5</sub>Ogroups is readily discernible. For the CF fluorines first order nmr spectra are observed except for c-C<sub>5</sub>F<sub>9</sub>OSeF<sub>5</sub> which shows a second order  $A_4B_4C$  type pattern similar to that of c-C<sub>5</sub>F<sub>9</sub>OCF<sub>2</sub> [13].

Vibrational spectra are given in Tables 3-5. For comparison the previously unreported Raman spectrum of  $C_2F_5$  OTEF<sub>5</sub> is included in Table 3. The strong infrared bands in the region 1300-900 cm<sup>-1</sup> are characteristic for C-F and C-0

## TABLE 4

		Obsd	. Freq., c	m <sup>-1</sup> (rel. inten	s.) <sup>a</sup>	
	SeF_OCI	F2 <sup>CF2<sup>OSeF5</sup></sup>	CF3CF(OS	F5)CF20SeF5	c-C5F9OSeF5	
Assign. <sup>b</sup>	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)
1	(	1345(1.7)p			1370 w	1370(0.1)
			1318 w	1338(0.6)	1323 s	1320(0.2)
VCF d	2		1274 m	1282(0.5)	1290 m	1290(0.2)
	1255 vw	1250(0.05)	1245 vs		1272 m	1270(0.2)
	1222 s	1205(0.2)	1180 sh		1230 vs	
,	1190 s	1178(0.5)p	1165 s	1173(0.5)p	1168 s	1160(0.2)p
	(1098 s	1095(0.05)	1115 s	1118(0.2)p	1087 w	1078(0.1)
	{				1040 w	1043(0.1)
	965 vw	945(0.1)p	986 s	995(0.3)p	990 vs	980(0.6)p
100	∮905 vw	885(0.3)p	850 vw	855(0.3)p		883(0.1)p
2	1845 vw	· · ·	832 vw	· · · •		
SeF,	777 s	770(0.3)p	768 vs	770(0.3)p	773 vs	775(sh)
as 4	∫740 s	737(0.7)p	732 s	724(5.0)p	740 sh	748(0.3)p
vser	1 I	715(5.2)0	724 mw		718 m	715(1.2)p
SeF <sub>4</sub> ip		680(10)p		675(10)p		678(10)p
SeO	675 vw	670(sh)p	675 ww		660 vw	
SeF.op		653(1.2)dp	650 vvw	652(1.5)dp	640 w	652(sh)
S 4 -		590(0.4)p	570 w	575(0.2)	610 w	600(0.3)p
				560(0.3)p	575 vw	582(0.4)p
				540(0.2)	525 w	525(0.2)p
		440(0.2)p	435 sh	445(0.2)p	438 vs	440(sh)
S_SeF4opl	431 s	425(0.4)dp	425 s	425(0.4)dp		420(0.4)dp
SOSeF, and		(398(0.8)dp		398(0.7)đp		396(0.6)dp
SESeF4		340(0.5)p		345(0.3)		355(1.0)p
S. SeF.inl		332(0.8)dn		330(0,7)do		330(0.6)dn
as 4		310(0.4)p		310(0.4)p		300)sh)
		240(0.1)p		227(0.7)		223(0,3)p
		223(1.0)		195(0.5)		180(1.2)n
		,, p		178(0.3)p		170(1,2)n
		140(2.5)		140(1.5)		106(0.1)

Vibrational spectra of R<sub>e</sub>OSeF<sub>5</sub> compounds

<sup>a</sup>Uncorrected Raman intensities (peak heights)

<sup>b</sup>ip = in phase; op = out of phase; opl = out of plane; ipl = in plane

stretching motions. For all the SeF<sub>5</sub>O- compounds intense infrared bands are found at about 770, 740, and 430 cm<sup>-1</sup> which are attributable to  $v_{as}$  SeF<sub>4</sub>, vSeF', and  $\delta_s$ SeF<sub>4</sub>, respectively, of the SeF<sub>5</sub>O- group. These assignments correspond closely to those given for other SeF<sub>5</sub>O- [14] and SeF<sub>5</sub>- [15] containing molecules.

Raman counterparts exist for many of these infrared bands, although they are, as expected, of relatively low intensity, especially for the C-F and C-O vibrations. The Raman spectra are generally dominated by a polarized band near  $675 \text{ cm}^{-1}$  which is assigned to the symmetric SeF<sub>4</sub> stretching mode, and which has no infrared counterpart. An analogous strong Raman feature was also observed for the vTeF<sub>4</sub> motion in R<sub>f</sub>OTeF<sub>5</sub> compounds [1-4]. Four Raman bands at about 425, 398, 370, and 330 cm<sup>-1</sup> are attributed to  $\delta_s$ SeF<sub>4</sub> out of plane,  $\delta$ OSeF<sub>4</sub>,  $\delta$ FSeF<sub>4</sub>, and  $\delta_{ae}$ SeF<sub>4</sub> in plane modes, respectively.

# TABLE 5

Obsd. Freq., cm <sup>-1</sup> (rel. intens.) <sup>a</sup>								
	sef <sub>5</sub> ocf <sub>2</sub> cfH(osef <sub>5</sub> )			SeF <sub>5</sub> OCF	2CFC1(OSeF5)	SeF50CF2C0C1		
Assign. <sup>b</sup>	IR(ga	as)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	
νCH νC≠O	3020	vw	3010(0.1)p			1843 s	1845(0.4)p	
<b>SCHwag</b>	1395	w	1395(0.9)p					
<b>&amp;CHrock</b>	1355	w	1360(0.2)					
VCF	$\begin{pmatrix} 1280\\ 1258 \end{pmatrix}$	m W	1275(0.5)p 1255(0.3)	1300 w 1272 vw 1248 ms	1303(1.3) 1272(0.2) 1243(0.2)	1300 √w 1246 m	1273(0.2) 1242(0.8)p	
	1188 1152	5 5	1180(0.2)p 1145(0.4)p	1207 ms 1178 s	1214(0.2) 1172(0.3)	1197 s	1190(0.2)	
νC0 νCC	1123	ms S M	1080(0.2)	1140 ms 1090 s 977 ms	1085(0.4) 976(0.2)	1093 s 970 s	1088(0.4)p 965(0.4)p	
SCF2	( 905 ( 830 802	ព ឃ ឃ	900(0.3)p 838(1.4)p	845 w 803 w	852(0.3)	822 m	825(0.6)p	
vas <sup>SeF</sup> 4 vSeF'	770 {740 {710	vs s m	760(0.4)p 732(1.9)p 709(8.6)p	770 vs 742 ms 728 ms	765(0.3) 735(sh) 723(2.0)	770 vs 740 s	760(0.4)p 725(sh)	
v <sub>s</sub> SeF <sub>4</sub> ip			688(6.6)p 675(10)p		672(10)		685(sh) 675(10)p	
vSeO v <sub>g</sub> SeF <sub>4</sub> op	655	w	665(8.8)p 645(sh)dp 628(1.6)p		651(1.7) 638(sh) 580(0.1)		650(sh) 618(2.1)p	
δ_Sef.opl	430	s	550(0.5)p 445(0.4)p 420(0.9)dp	428 s	560(0.2) 475(0.3) 442(0.4) 425(0.6)	432 s	480(0.3)p 440(1.8)p 425(sh)	
$\delta OSeF_4$ and $\delta FSeF_4$ $\delta as F_4$			f 395(1.2)dp { 352(0.9)p 330(0.7)dp 310(0.5)p		397(1.0) 328(0.6) 316(0.6)		399(1.1)dp 368(0.7)p 340(0.9)dp 310(0.3)	
			260(0.3)p 228(0.9)p 150(sh) 135(2.3)p		245(0.2) 230(0.4) 218(0.6) 184(0.5) 140(1.7)		239(2.6)p 200(1.2)p 160(1.6)p 100(0.3)dp	

Vibrational spectra of R<sub>f</sub>OSeF<sub>5</sub> compounds

<sup>a</sup>Uncorrected Raman intensities (peak heights)

b ip = in phase; op = out of phase; opl = out of plane; ipl = in plane

For SeF<sub>5</sub>OCF<sub>2</sub>CFH(OSeF<sub>5</sub>) both the infrared and Raman spectra contain bands at about 3015, 1395 and 1360 cm<sup>-1</sup> which are attributable to VCH,  $\delta$ CHwag, and  $\delta$ CHrock, respectively. A band typical for VC=0 is observed at 1845 cm<sup>-1</sup> for SeF<sub>5</sub>OCF<sub>2</sub>COCl in both the infrared and Raman spectra. All of the spectral data agree with the formulation of these compounds as R<sub>f</sub>OSeF<sub>5</sub> moieties.

The unexpected formation of epoxides in some of the Xe(OSeF<sub>5</sub>)<sub>2</sub> reactions was limited to  $C_3F_6^0$  and  $c-C_5F_8^0$ , probably because the remaining olefins studied do not form epoxides which are stable under these conditions. While  $C_3F_6^0$  is

well known, the cyclic epoxide  $c-c_5F_8^0$  is not and is mentioned only in the patent literature [16]. The infrared and Raman spectra of  $c-c_5F_8^0$  clearly show a strong band near 1530 cm<sup>-1</sup> which is attributable to a stretching motion of a fluorinated epoxide. In addition to strong infrared bands in the region 1370-1215 cm<sup>-1</sup> due to vCF, there is an intense band at 1000 cm<sup>-1</sup> assignable to a  $C_5$  ring stretching motion [11]. The <sup>19</sup>F nmr spectrum of  $c-c_5F_8^0$  is complex and its approximate analysis is given in Table 6.

## TABLE 6

<sup>19</sup>F NMR data for c-C<sub>5</sub>F<sub>8</sub>0

$F_{e}$ $F_{e$	
$F_e$	
e b 1 -125.2 d $J_{bc} = 247$	
$F_{Fd}$ $F$	e = 4.6
a a d 2 -141.0 dsp $J_{ad} = 259, J \approx 2.1$	
$f^{c}$ e 2 -187.4 sp $J_{c} = 4.6^{\dagger \dagger}$	

+ d=doublet, qi-quintet, sp-septet, m=multiplet

 $^{\dagger\dagger}$  Spectra need further computer analysis to extract J which is probably about 4.5 Hz.

The stability of this epoxide is exemplified by the fact that it was unaffected by long contact with CsF at  $50^{\circ}$ .

## CONCLUSION

Due to its lower thermal stability and greater oxidizing power, the SeF<sub>5</sub>O radical cannot be added as cleanly to olefinic double bonds as the TeF<sub>5</sub>O radical. The yields of the R<sub>f</sub>OSeF<sub>5</sub> adducts are decreased by competing side reactions involving fluorination, oxidation, and epoxidation of the substrates. All of the synthesized R<sub>f</sub>OSeF<sub>5</sub> compounds are similar to their R<sub>f</sub>OTeF<sub>5</sub> analogues.

#### ACKNOWLEDGEMENT

The authors are grateful for support of this work by the U.S. Air Force Office of Scientific Research under Contract F49620-81-C-0020 and to Dr. L. R. Grant for helpful discussions.

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