PENTAFLUOROTELLURIUMOXIDE DERIVATIVES OF FLUOROCARBONS

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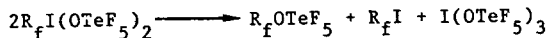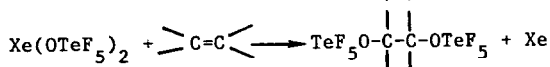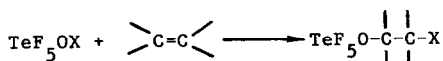
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SUMMARY

The reaction of xenon bis-pentafluorotelluriumoxide, $Xe(OTeF_5)_2$, with an excess of perfluorobutadiene gives almost exclusively $TeF_5OCF_2CF=CFCF_2OTeF_5$ and only very little $TeF_5OCF_2CF(OTeF_5)CF=CF_2$, the first examples of TeF_5O-substituted unsaturated fluorocarbons. A similar reaction of perfluorocyclo-hexene produces, depending on the reaction temperature, exclusively the addition product, $c\text{-}C_6F_{10}(OTeF_5)_2$, or predominantly $c\text{-}C_6F_{11}OTeF_5$, the mixed addition, fluorination product. In the case of TeF_5OF, an ambient temperature reaction with perfluorobenzene results, depending on the stoichiometry of the reaction, in the addition of either one TeF_5OF or two molecules of TeF_5OF accompanied by the oxygenation of the ring to a cyclohexanone derivative.

INTRODUCTION

Reactions of TeF_5OX (X=F,Cl) and $Xe(OTeF_5)_2$ with various fluoroolefins and fluorocarbon iodides have proven to be useful paths to a number of TeF_5O-substituted fluorocarbons [1-4].

$$TeF_5OX + \underset{}{>}C=C\underset{}{<} \longrightarrow TeF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$

$$Xe(OTeF_5)_2 + \underset{}{>}C=C\underset{}{<} \longrightarrow TeF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OTeF_5 + Xe$$

$$2TeF_5OCl + R_fI \longrightarrow R_fI(OTeF_5)_2 + Cl_2$$

$$2R_fI(OTeF_5)_2 \longrightarrow R_fOTeF_5 + R_fI + I(OTeF_5)_3$$

All of these TeF_5O- derivatives were saturated and it was of interest to determine whether similar moieties with residual unsaturation could be synthesized. These investigations involved perfluorobutadiene and perfluoro-benzene as the substrates. To facilitate the characterization of the benzene addition products, the reaction of $Xe(OTeF_5)_2$ with perfluorocyclohexene was also examined.
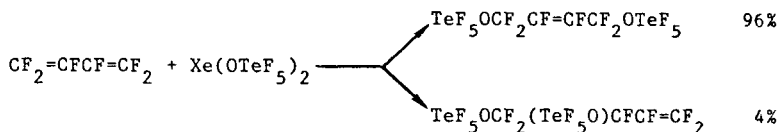

EXPERIMENTAL

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. ^{19}F nmr spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer with internal $CFCl_3$ as a standard with negative chemical shift being upfield from $CFCl_3$. Literature methods were used to prepare $Xe(OTeF_5)_2$ [5] and TeF_5OF [6]. Fluorocarbons used were commercial products (SCM Specialty Chemicals).

For reactions with $Xe(OTeF_5)_2$ a tared, prepassivated cylinder was loaded with the solid xenon compound in the dry box. The cylinder was evacuated, cooled to $-196°$, and a measured amount of olefin was condensed in. The closed cylinder was allowed to warm to ambient temperature before heating to a higher temperature if necessary. Monitoring the extent of reaction was accomplished, where desired, by recooling the cylinder to $-78°$ and measuring the amount of Xe evolved. The reactions of C_6F_6 and TeF_5OF were carried out by successively condensing the reactants into a cylinder cooled to $-196°$ and then allowing the cylinder to warm to ambient temperature. At the conclusion of the reactions the volatile products were separated by fractional condensation, with the R_fOTeF_5 being trapped at -45 to $0°$ depending on the particular product. A runaway reaction was experienced in one instance with C_6F_6 and TeF_5OF, as evidenced by the formation of COF_2, CF_4, and a grey powder as the products. All of the R_fOTeF_5 derivatives are colorless, mobile liquids of low volatility, and stable on storage.

RESULTS AND DISCUSSION

Data summarizing the synthetic reactions is presented in Table 1. Addition of only two TeF_5O- groups to the C=C system of perfluorobutadiene was accomplished in good yield, under moderate conditions, and with only slow consumption of the $Xe(OTeF_5)_2$ in the latter stages of the reaction. Based on spectroscopic properties, the TeF_5O- groups added overwhelmingly to the 1,4 carbons.

$$CF_2=CFCF=CF_2 + Xe(OTeF_5)_2 \Bigg\langle \begin{array}{l} TeF_5OCF_2CF=CFCF_2OTeF_5 \quad\quad 96\% \\[2em] TeF_5OCF_2(TeF_5O)CFCF=CF_2 \quad\quad 4\% \end{array}$$

This result is consistent with the transfer of TeF_5O radicals to the olefin and is comparable to the addition of NF_2 radicals from N_2F_4, which also forms the 1,4 adduct [7]. The ^{19}F nmr spectrum (Table 2) for the 1,4 TeF_5O- addition product is an A_2B_4 spin system for the CF resonances. Bonding of the TeF_5O- groups to the CF_2 carbons is confirmed by the observed coupling between the CF_2 fluorines and the four basal fluorines of the TeF_5O- group. The ^{19}F nmr spectrum showed, in addition to the main 1,4 substitution product, the presence of a small amount of the 1,2 addition compound. The chemical shifts and coupling constants characteristic of a perfluorovinyl group [8] effectively identify this component in the mixture. For the TeF_5O- groups in both compounds the nmr spectra exhibit AB_4 patterns typical of those previously noted for other R_fOTeF_5 species [1-3].

The 1,4 TeF_5O- addition compound of perfluorobutadiene exists as either a cis or a trans isomer. We prefer the trans-isomer for our product based on the observed nmr chemical shift of the CF=CF fluorines compared to those in the similar $(CF_3)_2CFCF=CFCF_3$ molecule [9]. Further support for the trans-isomer comes from the vibrational data (Table 3) which shows a very low intensity C=C stretching band. This is assignable to an internal $\nu C=C$ motion [10]. For the cis isomer this band would be expected to be more intense. The Raman data show a relatively strong band at 1740 cm^{-1} which is expected for both isomers.
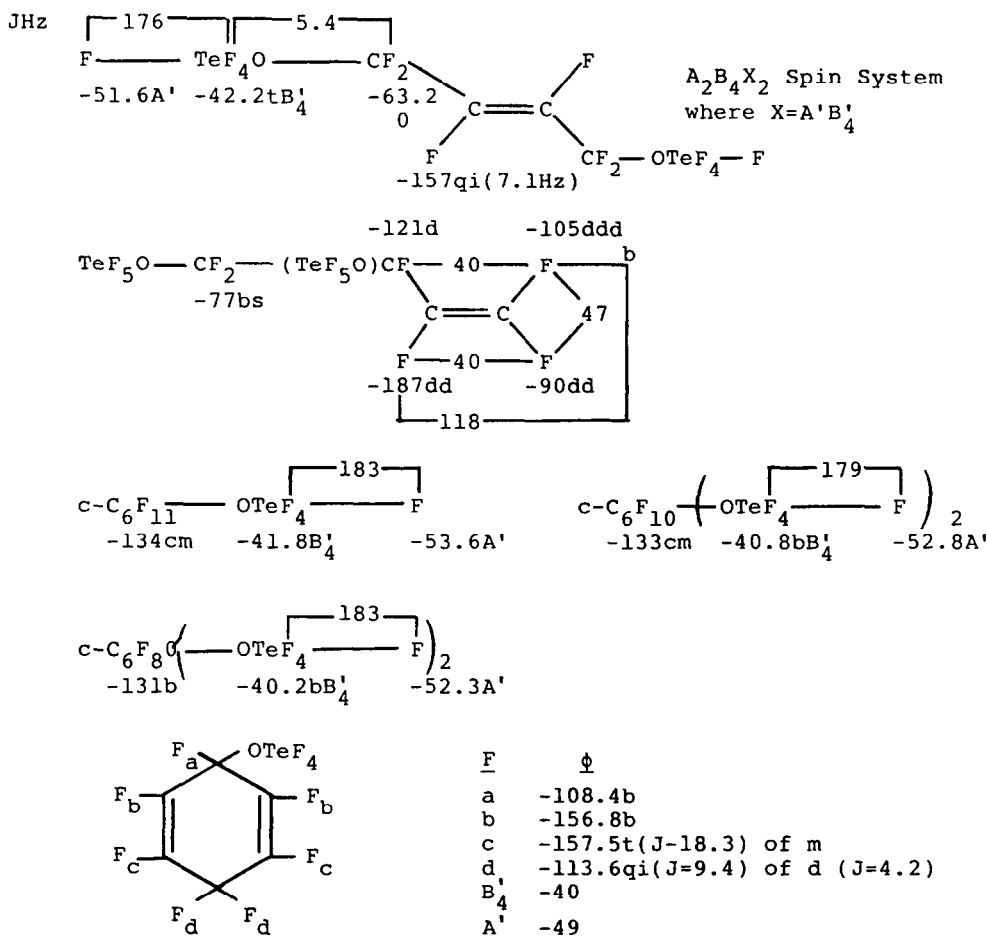
TABLE 1

Reaction parameters

R_f Compound mmol	TeF_5O- Compound mmol	T°C	Time	R_fOTeF_5 (% Yield)[a]	Pmm 20°C	Other Products
C_4F_6 2.73	$Xe(OTeF_5)_2$ 2.33	25 then 40	2d 5d	$C_4F_6(OTeF_5)_2$ 1,4(73); 1,2(3)	2	Xe(89) Xe, C_4F_6, $C_4F_6(OTeF_5)_4$
$c-C_6F_{10}$ 2.50	$Xe(OTeF_5)_2$ 2.14	95	5d	$c-C_6F_{10}(OTeF_5)_2$ (81)	<1	Xe, $c-C_6F_{10}$, TeF_5OH
$c-C_6F_{10}$ 3.16	$Xe(OTeF_5)_2$ 2.80	115	3d	$c-C_6F_{11}OTeF_5$ (69) $c-C_6F_{10}(OTeF_5)_2$ (6)	3	Xe, $c-C_6F_{10}$, TeF_6, TeF_5OH, $(TeF_4O)_n$
C_6F_6 1.0	TeF_5OF 0.73	25	4d	$C_6F_7OTeF_5$ (50)	2.5	C_6F_6, TeF_6
C_6F_6 0.80	TeF_5OF 2.90	25	14d	$C_6F_8O(OTeF_5)_2$ (6)	<1	TeF_5OF, $TeF\ OTeF_5$, TeF_5OH

[a]Yields based on limiting reagent.

TABLE 2

^{19}F NMR data for R_fOTeF_5 compounds[a]

JHz

┌─176─┐┌─5.4─┐
F────── TeF$_4$O ──────CF$_2$
-51.6A' -42.2tB$_4'$ -63.2
          0

$$\begin{array}{c} CF_2 \\ C=C \\ F \end{array}$$

F (top right)

$A_2B_4X_2$ Spin System
where $X=A'B_4'$

F
-157qi(7.1Hz)

CF$_2$— OTeF$_4$— F

        -121d   -105ddd

TeF$_5$O — CF$_2$──── (TeF$_5$O)CF── 40 ── F ──────[b]
        -77bs

C=C   47

F──40── F
-187dd   -90dd
└──118──┘

      ┌─183─┐
c-C$_6$F$_{11}$── OTeF$_4$──────F
  -134cm   -41.8B$_4'$ -53.6A'

          ┌─179─┐
c-C$_6$F$_{10}$(─OTeF$_4$────── F)$_2$
  -133cm   -40.8bB$_4'$ -52.8A'

        ┌─183─┐
c-C$_6$F$_8$(──OTeF$_4$────── F)$_2$
  -131b   -40.2bB$_4'$ -52.3A'

F	φ
a	-108.4b
b	-156.8b
c	-157.5t(J-18.3) of m
d	-113.6qi(J=9.4) of d (J=4.2)
B$_4'$	-40
A'	-49

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[a] CFCl$_3$ reference, negative shift being upfield from the reference. φ=chemical shift, ppm where b=broad, d=doublet, t=triplet, qi=quintet, c=complex, m=multiplet. The area ratios measured for these resonances agreed with the given assignments. $J125_{TE-F}$=3750-3790 Hz.

[b] AB$_4$ pattern of TeF$_5$O- groups obscured by those of the 1,4 adduct, the major component of the mixture.

The products from the reaction of $Xe(OTeF_5)_2$ with perfluorocyclohexene were found to be temperature dependent. At 95° a good yield of the expected adduct, $c-C_6F_{10}(OTeF_5)_2$, was obtained, but at 115° the primary product was the mono TeF_5O- substituted compound, $c-C_6F_{11}OTeF_5$. Thus, at the higher temperature, fluorination of one of the C=C carbons occurred. This fluorination could proceed either by a direct transfer of fluorine from a TeF_5O radical to the carbon or by an internal rearrangement and elimination after addition of the first TeF_5O- group.
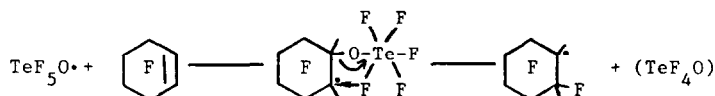
This type of reaction path had not been observed previously in similar TeF_5O- systems but none of those reactions involved temperatures over 100°. However in the case of the analogous selenium compounds, a more pronounced tendency towards fluorination, besides the expected XF_5O- addition, has been found [11].

The ^{19}F nmr spectra of the two cyclohexene derivatives are very much alike but the slight differences noted and the measured area ratios for total CF:TeF clearly reveal the formation of two products with one or two TeF_5O- substituents on the saturated ring. Slight differences in the volatility of the two compounds were also noted. However the vibrational spectra were virtually the same, a circumstance that was encountered also with the related $c-C_5F_9OTeF_5$ and $c-C_5F_8(OTeF_5)_2$ materials [2,3].

In the reaction of $Xe(OTeF_5)_2$ with perfluorobenzene the products proved to be complex mixtures involving oxygenation, fluorination, and addition of TeF_5O groups. This system will require more study and therefore will not be discussed further. An alternate mode of introducing TeF_5O- groups into the C_6F_6 ring was its reaction with TeF_5OF which has previously been shown to react readily with fluoroolefins [1]. At room temperature C_6F_6 was found to add one or two moles of TeF_5OF depending on the ratio of reactants. The listed yield (50%) of the mono adduct does not represent the maximum since the sample of TeF_5OF used was contaminated with an appreciable amount of TeF_6.

TABLE 3

Vibrational spectra of R_fOTeF_5 compounds

Assign.	$C_4F_6(OTeF_5)_2$[b] IR(gas)	Raman(liq.)	c-$C_6F_{10}(OTeF_5)_2$ IR(gas)	Raman(liq.)	c-$C_6F_7OTeF_5$ IR(gas)	c-$C_6F_8O(OTeF_5)_2$ IR(liq.)	Raman(liq.)
				Obsd. Freq., cm^{-1} (rel. intens.)[a]			
vC=O						1876 w	1885(0.2)p
vC=C	1785 w	1790(0.06)p			1745 m		
	1735 vw	1740(0.7)p					
		1415(0.1)dp					
	1370 w						
vCF	1318 w		1310 w	1315(0.2)	1366 w	1283 m	1288(0.2)dp
	1277 s	1275(0.1)p	1280 m	1275(0.3)p	1347 w	1238 ms	1240(sh)
	1230 ms		1245 s	1240(0.06)	1327 s	1223 ms	
					1290 mw		
					1233 m		
					1207 w		
	1185 ms		1195 s		1193 w	1184 s	1190(0.06)p
	1140 s	1135(0.2)p	1160 m	1160(0.1)p	1176 m	1162 ms	1160(0.1)p
	1085 w				1100 m		
vCO			1067 vw	1065(0.1)p	1055 m	1058 mw	1062(1.0)p
vCC	965 w	965(0.03)	995 s	995(0.15)p	1017 s	1000 sh	980(0.5)p
	925 w	925(0.08)p	975 s	980(0.05)	1000 w	980 s	
		835(0.2)dp			985 s	863 vw	850(0.03)p
δCF_2				827(0.1)p		848 w	
$v_{as} TeF_4$	748 vs	738(sh)	745 s	745(sh)	745 s	738 s	745(sh)
$vTeF'$	718 ms	713(3.4)p	715 m	731(0.6)p	718 m	712 m	717(3.0)p
$v_s TeF_4$		675(10)p		718(1.1)p			678(10)p
				678(10)p			
			640 vw	625(0.2)p		640 vw	630(0.5)p
				605(0.2)p		590 w	596(0.6)p
		540(0.5)p	530 vw	532(0.8)p		521 vw	528(0.2)p
						480 vw	475(0.1)p
							425(0.1)p
$\delta_s TeF_4$	320 s	315(0.6)dp	320 m	333(0.8)p	327 ms	320 ms	315(0.9)dp
$\delta F TeF_4$				315(0.6)dp			
$\delta_{as} TeF_4$		265(0.6)dp		265(0.3)dp			265(0.6)dp
		180(0.2)p		188(0.2)p			185(0.2)p
				160(1.1)p			165(0.2)p
		108(0.5)p		132(0.6)p			115(1.0)p

[a] Uncorrected Raman intensities (peak heights).

[b] 1,4 and 1,2 isomer mixture.

For $C_6F_7OTeF_5$ the ^{19}F nmr spectrum (Table 2) shows that the addition of F and TeF_5O- occurred in para positions to furnish the 1,3 cyclohexadiene derivative. For the ring fluorines the spectrum is quite similar to that of the corresponding $CF_3OF-C_6F_6$ adduct [12]. It is noteworthy that, in the CF_3OF case, both 1,2 and 1,4 addition occur and that the former predominates. Thus the observed exclusive 1,4 addition with TeF_5OF may be the result of steric hindrance by the bulkier TeF_5O- ligand. The infrared spectrum of $C_6F_7OTeF_5$ shows a medium intensity band at 1745 cm^{-1} attributable to $\nu C=C$.

When C_6F_6 was reacted with an excess of TeF_5OF, a vigorous reaction ensued which resulted in the formation of an addition compound containing two TeF_5O- groups as shown by the CF:TeF nmr area ratio of 8:10. This ratio agrees with that expected for a 2:1 adduct of the formula $C_6F_8(OTeF_5)_2$. The TeF_5O- groups were indistinguishable and the CF resonances consisted of a broad unresolved signal with a chemical shift similar to those of the above-mentioned cyclohexane examples. This was unexpected since a 2:1 adduct should still have one $^F{>}C=C{<}^F$ group whose fluorines should have a chemical shift of about -150 ppm, which is different from that of about -131 ppm expected for the CF_2 groups.

Furthermore, the vibrational spectra for this 2:1 adduct should have a moderate intensity band at about 1740 cm^{-1} due to the stretching mode of the $C=C$ bond. This was absent and instead a weak IR band was observed at 1876 cm^{-1}. This band is in a region typical for highly fluorinated carbonyl groups [10]. Therefore it appears that this 2:1 adduct is not a cyclohexene but most likely a cyclohexanone, $c-C_6F_8O(OTeF_5)_2$. One possible structure is shown.
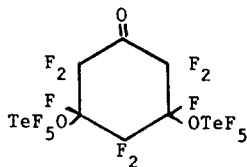
Observation of the by-product TeF_5OTeF_5 [13] in this system also indicates that an oxygenation reaction may have occurred.

All the R_fOTeF_5 compounds of this study exhibit characteristic AB_4 nmr spectra due to the TeF_5O- groups with A being in the range -49 to -54 ppm and B_4 being -40 to -42 ppm [1-3]. In the vibrational spectra strong infrared bands at about 745, 720, and 320 cm^{-1} are observed attributable to $\nu_{as}TeF_4$, $\nu TeF'$, and $\delta FTeF_4$, respectively, of the TeF_5O- group. The Raman spectra are dominated by a polarized band near 675 cm^{-1} which is assigned to the symmetric TeF_4 stretching mode, and which has no infrared counterpart. The $\nu TeF'$ IR band has a moderate intensity polarized Raman counterpart at about 715 cm^{-1}. In addition, two depolarized bands at about 265 and 315 cm^{-1} are assigned to $\delta_{as}TeF_4$ and a coincidence of $\delta_s TeF_4$, and $\delta FTeF_4$, respectively.

CONCLUSION

The synthesis of the first examples of unsaturated fluorocarbon TeF_5O- substituted compounds has been accomplished. For cyclic compounds, in addition to the transfer of TeF_5O- to the ring, a competitive fluorination and oxygenation reaction was observed.

ACKNOWLEDGEMENT

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