Journal of Fluorine Chemistry, *27* (1985) 53–60

Received: May 22, 1984; accepted: June 12, 1984

BIS-PENTAFLUOROTELLURIUMOXIDE FLUOROCARBONS

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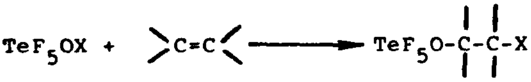
SUMMARY

The reaction of xenon bis-pentafluorotelluriumoxide, $Xe(OTeF_5)_2$, with the haloolefins; $CF_2{=}CFCl$, $CF_2{=}CCl_2$, and $CF_2{=}CFH$, results in the high yield addition of two TeF_5O-groups to the double bond. These compounds are the first examples of $R_f(OTeF_5)_2$ compounds in which R_f is not perfluorinated. For perfluorobutadiene, saturation of both double bonds occurs readily to give $1,2,3,4(TeF_5O)_4C_4F_6$ in 97% yield.

INTRODUCTION

Reactions of TeF_5OX (X=F,Cl) and $Xe(OTeF_5)_2$ with various fluoroolefins have proven to be an excellent route to TeF_5O-substituted fluorocarbons [1,2].



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

and

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

0022-1139/85/$3.30

However, all the bis TeF_5O derivatives previously prepared were perfluorinated. Since these TeF_5O- substituted fluorocarbons have good stability, it was of interest to prepare $X-\overset{|}{\underset{|}{C}}-OTeF_5$ derivatives in which X is not F. In addition the possibility of preparing fluorocarbons containing more than two TeF_5O groups was investigated.

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, 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 a negative chemical shift being upfield from $CFCl_3$. Literature methods were used to prepare XeF_2[3] and TeF_5OH[4] which were then reacted to form $Xe(OTeF_5)_2$[5]. Olefins used were commercial products (PCR Research Chemicals)

The synthetic procedure consisted of loading a tared and prepassivated cylinder with $Xe(OTeF_5)_2$ in the dry box. After evacuation the cylinder was cooled to -196°C 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 of the extent of reaction was accomplished where desired, by recooling the reactor to -78°C and removing and measuring the evolved Xe. At the end of the reaction the volatile products were separated by fractional condensation, trapping the $R_f(OTeF_5)_2$ compounds at -30 or -23°C. $(TeF_5O)_4C_4F_6$ was non-volatile at room temperature and remained in the cylinder after by-products were pumped away. An uncontrolled reaction occurred on one occasion with C_4F_6 when the reaction mixture was heated to 70°C after only a brief period at room temperature. This resulted in the formation of COF_2, CF_4, and a gray powder as the main products and no R_fOTeF_5 compounds. In one experiment with CF_2CFCl, a vigorous reaction was indicated by the formation of appreciable low molecular weight polymer, thereby lowering the yield of $R_f(OTeF_5)_2$ monomer to 43%.

RESULTS AND DISCUSSION

Using $Xe(OTeF_5)_2$ as a transfer reagent [2], two TeF_5O- groups per olefinic double bond were added in high yield to the following substrates; $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CF_2{=}CFH$, and $CF_2{=}CFCF{=}CF_2$ (see Table I). These results demonstrate that the TeF_5O- addition is not limited to perfluoroolefins but can be applied as well to chlorine or hydrogen containing olefins. Furthermore, it was demonstrated that more highly TeF_5O- substituted compounds can be prepared by adding four TeF_5O- groups to the conjugated double bonds in perfluorobutadiene.

These TeF_5O- substituted fluorocarbons are all colorless, mobile liquids of low volatility. They are stable for days at 70°C, the highest temperature tested, and have been stored unchanged for months at room temperature in glass or stainless steel vessels. Therefore the stability of the $X{-}\overset{|}{\underset{|}{C}}{-}OTeF_5$ group (X=Cl,H) appears to be comparable to that of the $F{-}\overset{|}{\underset{|}{C}}{-}OTeF_5$ group.

The good to excellent yields realized for the compounds of Table I are similar to those obtained with $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, and $c{-}C_5F_8$[2]. Based on the available data the order of reactivity of the olefins with $Xe(OTeF_5)_2$ is

$$CF_2{=}CF_2 \sim CF_2{=}CFCl > CF_2{=}CFH > C_4F_6 > C_3F_6 > c{-}C_5F_8$$

TABLE I.

REACTION PARAMETERS

$Xe(OTeF_5)_2$ mmol	Olefin mmol	Temp. °C	Time	Product (% Yield)[a]	Pmm at 20°C	m.p. °C
1.55	$CF_2=CFCl$ 2.08	25	16h	$TeF_5OCF_2CFCl(OTeF_5)$ (81)	6	-44
1.31	$CF_2=CCl_2$ 1.78	70	4wk	$TeF_5OCF_2CCl_2(OTeF_5)$ (60)	2	-62
2.84	$CF_2=CFH$ 3.92	25	3d	$TeF_5OCF_2CFH(OTeF_5)$ (71)	6	-43
6.26	C_4F_6 3.45	25 then 65	5d 5d	$(TeF_5O)_4C_4F_6$ (97)	<< 1	-17

[a] Yield based on the limiting reagent

Thus the less electron-withdrawing substituents, Cl and H, enhance the reactivity of these olefins relative to those of the perfluoro analogues ($CF_2=CF_2$ is anomalously reactive owing to its tendency to polymerize). These findings are in agreement with our expectations for a mechanism involving a free radical attack on the double bond [6].

Table II lists the ^{19}F and ^{1}H nmr data for the new compounds The AB_4 type spectra of TeF_5O- groups arise from the magnetic inequivalence of the axial fluorine compared to the four basal fluorines. Chemical shifts and coupling constants for the TeF_5O- groups are found in a narrow range here and in other R_fOTeF_5 compounds [1,2]. These are A = -49 to -54 and B_4 = -38 to -44 ppm except for TeF_5O- attached to CFH where the B_4 resonance is found at -53.4 ppm. The two TeF_5O- groups in each compound are nonequivalent owing to the different bonding environments. The nmr data for the CF fluorines are as expected and do not require special comment.

TABLE II

^{19}F NMR DATA[a]

		J_{TeF} = 3850[b]								J_{TeF} = 3860	
J(Hz)		191		5.6		2.1		7.4		182	
	F		TeF_4O		CF_2		CFCl		$OTeF_4$		F
Φ	-53.8A		$-43.7B_4$		-78.1(qi,d)		-69.4qi,t		$-41.2dB_4$		-52.1A
		J_{TeF} = 3850								J_{TeF} = 3870	
J(Hz)		187		5.7						180	
	F		TeF_4O		CF_2		CCl_2		$OTeF_4$		F
Φ	-51.5A		$-42.4tB_4$		-76.3qi				$-39.0B_4$		-49.7A
		J_{TeF} = 3770								J_{TeF} = 3720	
J(Hz)						5.1	54				
	F		TeF_4O		CF_2		FCH		$OTeF_4$		F
Φ	∿-53A		$-43.4B_4$		-78.5b		-136.8d		-53.4cm		∿-53A
							(δ6.47t,d)				
		J_{TeF} = 3880									
J(Hz)		184					-124b				
	(F		TeF_4O		CF_2		CF				
Φ	-53.1A		$-48.3bB_4$		-75b			182			
							$OTeF_4$		F		$)_2$
							$-41.5bB_4$		-52.3A		

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[a] $CFCl_3$ reference, negative shift being upfield from the reference. Φ = chemical shift, ppm (multiplicity); where b-broad, c-complex, d-doublet, t-triplet, qi-quintet, and m-multiplet. The area ratios measured for these resonances agreed with the given assignments. [b] $^{125}Te^{19}F$.

Vibrational spectra are given in Table III. The strong infrared bands in the region 1300-900 cm^{-1} are characteristic for C-F and C-O stretching motions. Furthermore intense infrared bands are found for all the compounds at about 740, 720, and 320 cm^{-1} which are attributable to $\nu_{as}TeF_4$, $\nu TeF'$, and $\delta FTeF_4$, respectively, of the TeF_5O- group. These assignments correspond closely to those given for other TeF_5- containing molecules [1,2,4,7].

Raman counterparts exist for many of these infrared bands, although they are, as expected, of relatively low intensity, especially the C-F and C-O vibrations. 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 [2,4,7]. Generally, the second strongest Raman band occurs at 695-715 cm^{-1} along with a somewhat weaker band at 720 cm^{-1}. Together these bands are assigned to $\nu TeF'$ and νTeO motions, but it is not certain which arises from which mode. Two depolarized bands at about 320 and 265 cm^{-1} are assigned to $\delta FTeF_4$ and $\delta_{as}TeF_4$ respectively [4,7].

For the chlorine containing compounds Raman bands of moderate intensity at 448 and 525 cm^{-1} are assigned respectively to $\nu C\text{-}Cl$ and νCCl_2. These C-Cl stretching frequencies are in the low frequency region for such bands [8]. In addition the assignment is supported by the fact that no other appropriately intense Raman bands remain unassigned in the expected C-Cl region. In the case of the hydrogen containing derivative both infrared and Raman bands are observed due to νCH (2995 cm^{-1}) and δCH wag and rock (1403 and 1355 cm^{-1}). All the spectral data agree with the formulation as $R_f(OTeF_5)_n$ moieties.

TABLE III. VIBRATIONAL SPECTRA OF $(TeF_5O)_nR_f$ COMPOUNDS

	Obsd. Freq., cm^{-1} (rel. intens.)[a]							
	$TeF_5OCF_2CFCl(OTeF_5)$		$TeF_5OCF_2CCl_2(OTeF_5)$		$TeF_5OCF_2CFH(OTeF_5)_2$		$1,2,3,4(TeF_5O)_4C_4F_6$	
Assign.	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(liq.)	Raman(liq.)
νCH					2995 vw	2998(0.1)p		
δCH wag					1403 w	1405(0.6)p		
δCH rock					1355 w	1358(0.1)		
	1286 mw	1285(0.8)p	1232 m	1230(1.0)p	1272 ms	1275(0.4)dp	1247 w	1295(0.3)
	1195 s		1195 ms		1175 s		1195 s	1220(0.1)
νCF	1184 s	1180(0.1)	1181 s	1160(0.1)p	1158 s		1173 s	
	1136 s	1135(0.1)	1172 s				1150 w	
			1100 w		1118 m		1126 w	
	1099 s	1100(0.1)	1077 s	1070(0.4)	1086 s		1045 mw	
	980 ms	980(0.1)	955 m	955(0.2)	939 m		950 mw	
νCO	965 ms	965(0.1)	878 m	877(0.2)	891 m	895(0.1)		
νCC	874 w							
$δCF_n$	849 w			840(0.2)	831 w	835(0.6)p		
	831 w				817 w	820(0.4)p		
	805 w		790 w	792(0.2)	787 w			790(0.1)
$ν_{as}TeF_4$	743 vs	745(0.3)	745 vs	740(0.2)	738 s	740(0.4)	734 s	740(0.2)
νTeF'	722 s	723 shp	722 s	720(1.2)p	719 s	720(1.8)p	716 s	715(1.6)p
νTeO	711 s	714(1.8)p	700 w	700(2.3)p	703 m	695(2.4)p		
$ν_sTeF_4$		676(10)p		673(10)p	665 w	675(10)p	675 vw	675(10)p
		615(0.5)p				618(0.6)p	630 vw	650(1.4)p
		525(0.1)		$ν_sCCl_2$ 525(2.1)p		520(0.2)		525(0.2)p
		νCCl 448(0.5)p		415(0.1)				440(1.5)p
				375(0.5)p				380(1.1)p
								350(0.9)p
$δFTeF_4$	323 s	320(0.7)dp	318 s	320(0.6)dp	317 s	315(0.6)dp	312 s	315(0.7)dp
$δOTeF_4$	315 sh	310 sh		310(0.8)				
$δ_{as}TeF_4$		262(0.7)dp		260(0.5)dp		265(0.5)dp		265(0.5)dp
				245(0.3)				235(1.1)p
		180(0.4)p		176(0.5)p		185(0.2)p		175(0.2)
		155(0.3)dp		158(0.8)dp				130(2.7)p
		115(1.2)p		115(1.2)p		115(0.7)p		105(1.0)p

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[a] Uncorrected Raman intensities (peak heights)

CONCLUSION

Hydrogen or chlorine containing bis-TeF_5O- substituted fluorocarbons can be synthesized in high yield from the corresponding olefins and $Xe(OTeF_5)_2$ as the transfer agent. Furthermore, flurocarbons containing one TeF_5O- group per carbon can be prepared in high yield by the reaction of $Xe(OTeF_5)_2$ with a conjugated fluoroolefin. All the resulting products are thermally stable fluids of low volatility.

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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