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# SYNTHESIS OF $SF_5O$- SUBSTITUTED FLUOROCARBONS

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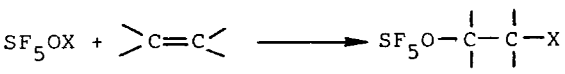
## SUMMARY

The reactions of $SF_5OCl$ and $SF_5OF$ with fluorinated ethylenes were used to prepare new $SF_5O$- substituted fluorocarbons in 44-77% yield. Compounds prepared were $SF_5OCF_2CFHCl$, $SF_5OCFClCF_2Cl$, and the isomeric mixture $SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$. Spectroscopic and other characterizing data for the adducts are presented. Numerous attempts to prepare $SF_5OCF{=}CF_2$ by dehalogenation of the dichloro or bromochloro materials were unsuccessful.

## INTRODUCTION

While $SF_5OX$ additions to olefins, where X=Cl or F, have been known for some time [1-4], these reactions have been limited to symmetrical fluoroolefins or non-fluorinated olefins. With care, all of these reactions produced acceptable yields of the corresponding 1:1 adducts through cleavage of the OX bond.



$$SF_5OX + \mathrm{>C{=}C<} \longrightarrow SF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$

However, no examples have been reported for unsymmetrical highly fluorinated olefins, in particular those that might furnish suitable products for subsequent conversion to the unknown perfluorovinyl derivative, $SF_5OCF{=}CF_2$. It was of interest therefore to examine such additions involving $SF_5OX$ compounds.

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## 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 conducted in stainless steel cylinders or a U-trap on the vacuum line. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer using cells equipped with AgCl or 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 3mm OD Quartz tubes 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 $SF_5OCl$ [5] and $SF_5OF$ [6]. Olefins used were commercial products (SCM Specialty Chemicals).

### Reaction of $SF_5OCl$ with $CF_2$=CFH

A prepassivated, evacuated cylinder was cooled to -196°C and loaded successively with $SF_5OCl$ (3.95 mmol) and $CF_2$=CFH (4.51 mmol) from the vacuum line. The cylinder was kept at -60°C for 20 hr. Fractional condensation of the products was carried out using a series of traps cooled at -64, -78, and -196°C. The olefin adduct was retained in the trap at -78°C (1.74 mmol, 44% yield). Identification of the adduct as $SF_5OCF_2CFHCl$ was based on its $^{19}$F and $^{1}$H nmr spectra together with infrared, and Raman spectra. Vapor density; Found 258, calc. 260 g/mol. Vapor pressure-temperature data recorded were (T°C; $P_{mm}$): -31.7, 11; -24.5, 16; 0.0, 47; 9.8, 70; 23.1, 108. For the range -32 to 23°C $\log P_{mm} = 6.4314 - 1300.4/T°K$ with a calc. b.p. = 93°C and $\Delta H_v$ = 5.95 kcal/mol.

## Reaction of $SF_5OCl$ with $CF_2{=}CFCl$

Sequential additions of $SF_5OCl$ (6.23 mmol) and $CF_2{=}CFCl$ (6.86 mmol) were made to a passivated, cold (-196°C) 30 ml stainless steel cylinder attached to the vacuum line. The closed cylinder was then left at -60°C overnight before warming to -20°C for 2 hrs. Fractional condensation of the products in a series of traps cooled to -56, -64 and -196°C resulted in retention of the $SF_5O$- adduct in the trap cooled to -64°C (3.09 mmol, 50% yield). This adduct was identified as $SF_5OCFClCF_2Cl$ on the basis of its $^{19}F$ nmr, infrared, and Raman spectra. Vapor density; Found, 292, calc. 295 g/mol. Vapor pressure-temperature data recorded were (T°C, $P_{mm}$): -31.9, 7; -23.4, 11; 0.0, 35; 19.5, 78. For the range -32 to 20°C log $P_{mm}$ = 6.8252-1443.4/T°K with a calc. b.p. 93°C and $\Delta H_v$ = 6.60 kcal/mol.

## Reaction of $SF_5OCl$ with $CF_2{=}CFBr$

A 10.5 mmol sample of $SF_5OCl$ was maintained at -78°C in a U-trap on the vacuum line and $CF_2{=}CFBr$ (11.0 mmol) was bled into the trap slowly over 3 hr before the contents were warmed toward room temperature. Separation of the products were carried out by fractional condensation in U-traps cooled, to -31, -78, and -196°C. The desired adduct was retained in the -78°C trap (6.16 mmol, 59% yield) and was identified as a mixture of the isomers $SF_5OCFBrCF_2Cl$ and $SF_5OCF_2CFBrCl$ based on $^{19}F$ nmr, infrared and Raman spectra. Vapor density; Found 334, calc. 339 g/mol. Vapor pressure-temperature data for this mixture were recorded (T°C, $P_{mm}$): -31.9, 3.5; -26.1, 5; 0.0, 21; 10.4, 34; 17.6, 46; 20.7, 54. For the range -32 to 20°C log $P_{mm}$ = 7.1578-1595.4/T°K with a calc. b.p. = 100°C and $\Delta H_v$ = 7.30 kcal/mol.

## Reaction of $SF_5OF$ with $ClCF{=}CFCl$

A prepassivated, evacuated, 30 ml cylinder was cooled to -196°C and loaded successively with $ClCF{=}CFCl$ (3.01 mmol) and $SF_5OF$ (2.14 mmol) from the vacuum line. The cylinder was allowed to warm slowly to -78°C using a liq. $N_2$-$CO_2$ slush and then to ambient temperature. After 2d the products were separated by fractional condensation in U-traps cooled to -45, -78, and -196°C. The adduct obtained, $SF_5OCFClCF_2Cl$, (1.65 mmol, 77% yield) was identical to that prepared using $SF_5OCl$ and $CF_2{=}CFCl$.

## RESULTS AND DISCUSSION

$SF_5OHal$ was successfully added to highly fluorinated olefins according to:

$$SF_5OCl + CF_2{=}CFH \longrightarrow SF_5OCF_2CFHCl \qquad 44\%\ \text{yield}$$

$$SF_5OCl + CF_2{=}CFCl \longrightarrow SF_5OCFClCF_2Cl \qquad 50\%$$

$$SF_5OF + ClCF{=}CFCl \longrightarrow SF_5OCFClCF_2Cl \qquad 77\%$$

$$SF_5OCl + CF_2{=}CFBr \longrightarrow \underset{77\% \;+\; 23\%\ \text{isomer mixture}}{SF_5OCFBrCF_2Cl + SF_5OCF_2CFBrCl} \qquad 59\%$$

These reactions required careful control. For example when $CF_2{=}CFBr$ was added fairly rapidly to $SF_5OCl$ at -78°C, the yield of $SF_5OR_f$ fell significantly. The principal by-products were $SF_4O$ and chloro-fluorinated adducts. All of the $SF_5O$- substituted fluorocarbons are thermally stable, storable, clear, colorless liquids of moderate volatility.

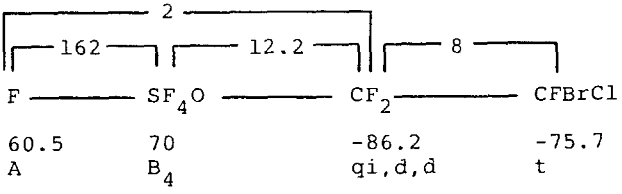
The observed modes of addition for $SF_5OCl$ are in general agreement with an electrophilic chlorine attacking the olefins as described for the analogous reactions of $CF_3OCl$ [7]. However the finding of one isomeric adduct only in the case of $CF_2=CFCl$ was surprising since both the above mentioned $CF_3OCl$ gave both isomers [3,4] as did $FO_2SOCl$ [8]. No simple explanation is apparent for this difference.

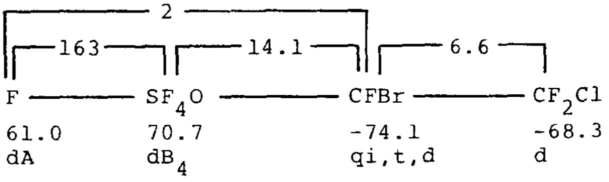
Table 1 lists the $^{19}F$ and $^{1}H$ nmr data for the new compounds. The magnetic inequivalence of the axial fluorine compared to the four basal fluorines in the $SF_5O$ group gives rise to $AB_4$ type spectra. Chemical shifts and coupling constants are typical of those for similar $SF_5O$- carbon compounds [2,9]. In highly halogenated derivatives the chemical shift of the apical F on sulfur is upfield from that of the basal $SF_4$ group whereas in the hydrogen containing compound it appears downfield. This is also observed for the chemical shifts of related $AB_4$ patterns from $SeF_5O$- [10] and $TeF_5O$- [11] substituted fluorocarbons. The first order CF and CH parts of the spectra allowed unambiguous determination of the isomer or isomers present and the measurement of the isomer ratio in the latter case.

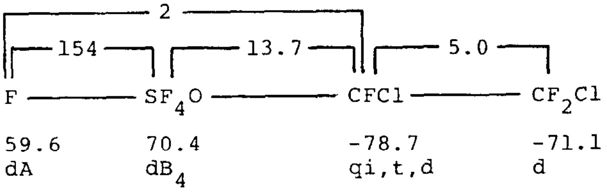
Vibrational spectral data are given in Table 2. The strong infrared bands in the region 1300-950 $cm^{-1}$ are characteristic for C-F and C-O stretching motions. For all the $SF_5O$- compounds intense infrared bands were found at about 930, 880, and 600 $cm^{-1}$ which are attributable to $\nu_{as}SF_4$, $\nu SF'$ and $\delta_s SF_4$, respectively, of the $SF_5O$- group. These assignments correspond closely to those given for other $SF_5$- containing molecules [12,13]. 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 730 $cm^{-1}$ which is assigned to the symmetric $SF_4$ stretching mode, and which has no infrared counterpart. Other tentative assignments appear in Table 2. All of the spectral data agree with the formulation of these compounds shown earlier.

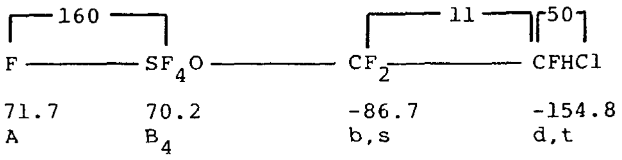
TABLE 1

$^{19}F$ NMR data for $R_fOSF_5$ compounds[a]









$\delta$ = 5.9d($J_{HF}$-49)

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[a] $CFCl_3$ reference, negative shift being upfield from the reference, $\phi$ = chemical shift, ppm. J=Hz, where b=broad, s=singlet, d=doublet, t=triplet, qi=quintet. The area ratios measured for these resonances agreed with the given assignments.

TABLE 2

Vibrational spectra of $R_fOSF_5$ compounds

| | Obsd. Freq., $cm^{-1}$ (rel. intens.)[a] | | | | | |
|---|---|---|---|---|---|---|
| | $SF_5OCF_2CFHCl$ | | $SF_5OCFClCF_2Cl$ | | $SF_5OCFBrCF_2Cl/SF_5OCF_2CFBrCl$ | |
| Assign.[b] | IR(gas) | Raman(liq.) | IR(gas) | Raman(liq.) | IR(gas) | Raman(liq.) |
| νCH | 2995 vw | 3005(0.5)dp | | | | |
| δCH | 1360 m | 1365(0.3) | | | | |
| | | 1290(0.3) | | | | |
| | 1270 m | 1275(0.3) | | | 1255 vw | |
| | 1252 m | 1255(0.4)dp | 1245 m | 1248(0.5)dp | 1235 w | 1240(0.3)dp |
| νCF | 1175 vs | 1175(0.2) | 1190 s | 1185(0.2) | 1185 s | 1180(0.1) |
| | | 1145(0.4) | 1145 sh | 1140(0.2) | 1150 sh | |
| | 1140 vs | | 1130 s | | 1130 s | 1135(0.1) |
| | 1105 s | 1105(0.4) | 1115 sh | 1110(0.2) | 1110 sh | 1105(0.3)p |
| νCO | 1035 w | | | 1045(0.9)p | 1030 ms | 1028(2.7)p |
| νCC | 945 vs | 930(0.4) | 950 vs | 955(0.2) | 948 vs | 950(0.2) |
| $\nu_{as}SF_4$ | 930 vs | 915(0.3) | 930 vs | 915(0.2) | 930 vs | 925(0.1) |
| νSF' | 863 s | 865(0.7)p | 885 s | | 890 vs | 890(0.3) |
| $\delta CF_2$ | 825 s | 825(3.2)p | 845 m | | 813 m | 870(0.3) |
| νCCl | | 775(3.3)p | 785 m | 782(0.7)p | | 775(1.3)p |
| νSO | 755 m | 760(4.2)p | 758 w | 745(1.8)p | 735 w | 745(4.2)p |
| $\nu_sSF_4ip$ | | 745(10)p | | 730(10)p | | 725(10)p |
| | 732 w | 730(6.6) | 722 m | | 718 w | |
| | | | | 685(0.4)p | | 690(0.4)p |
| | | | | 660(0.9)p | | 655(1.0) |
| $\nu_sSF_4op$ | | 640(1.2)p | 630 vw | 640(1.6) | | 635(2.2)p |
| | | 615(0.8)p | | 615(1.1)p | | 605(1.1)p |
| $\delta_sSF_4opl$ | 600 ms | 605(0.7)dp | 600 s | 605(0.4)dp | 605 s | 590(0.5) |
| | 575 w | 575(0.9)p | | | | |
| | 555 vw | 555(0.9)p | | 547(0.6)p | 535 vw | 535(0.5)p |
| | | 520(0.6)p | | 525(0.8)dp | 500 vw | 515(0.8)p |
| | | 485(1.3)p | | 490(1.2)p | | |
| | | 468(1.2) | | 470(0.8)p | | 475(1.5)p |
| | | 445(2.2)p | | 448(4.3)p | | 448(4.7)p |
| | | 430(2.8)p | | 420(1.5)p | | |
| | | 380(1.0) | | | | 372(2.3)p |
| | | 355(0.7)p | | 350(0.8) | | 350(1.0) |
| | | 315(0.7) | | 310(1.1) | | 318(3.7)p |
| | | | | 290(0.9) | | 295(2.9)p |
| | | 278(1.4)p | | 275(2.0)p | | 275(1.7)p |
| | | 235(1.9)p | | 230(1.0) | | 238(5.0)p |
| | | 210(1.7)p | | 215(1.5)p | | 215(5.4)p |
| | | 185(2.0)p | | 185(1.5)p | | 180(1.4)p |
| | | | | | | 165(0.8)p |
| | | | | | | 145(1.1)dp |

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[a] Uncorrected Raman intensities (peak heights)

[b] ip = in phase; op = out of phase; opl = out of plane

Numerous attempts were made to dehalogenate $SF_5OCFClCF_2Cl$, and also $SF_5OCFBrCF_2Cl$ in its isomer mixture, in order to obtain the unknown $SF_5OCF=CF_2$. Conditions similar to those employed for the analogous reaction of $CF_3OCFClCF_2Cl$ to give $CF_3OCF=CF_2$ [14] were used. Those authors noted that dimethyl sulfoxide was the only successful solvent for the dehalogenation. We were unsuccessful in our efforts using DMSO, diglyme, dioxane, or DMF solvents with Zn powder (activated) or Zn-Cu couple at temperatures up to 140°C. No olefinic material was obtained and increasing degradation of the starting material was noted at higher temperatures and longer reaction times. Ultrasound activation with DMSO/Zn at 45°C gave similar results. In the absence of a solvent these two $SF_5OR_f$ compounds could be heated with Zn to 195°C for 4 days and not be affected.

## ACKNOWLEDGEMENTS

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