DERIVATIVES OF TRIFLUOROVINYLSULFUR PENTAFLUORIDE ($SF_5CF=CF_2$) II

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SUMMARY

Trifluorovinylsulfur pentafluoride ($SF_5CF=CF_2$) and carbonyl fluoride will add, in the presence of cesium fluoride and acetonitrile, to form $SF_5CF(CF_3)C(O)F$. This new acid fluoride serves as a source for preparing derivatives containing the $SF_5CF(CF_3)$ - grouping. The following new compounds have been prepared and characterized: $SF_5CF(CF_3)X$ where X = $C(O)F$, $C(O)CH_3$, $C(O)OH$, $C(O)NH_2$, CN. The dimer, $(SF_5CFCF_2)_2$, has also been prepared. Infrared, mass, and nmr spectra are presented in order to support their proposed structure.

INTRODUCTION

In our continuing studies with trifluorovinylsulfur pentafluoride ($SF_5CF=CF_2$), we have found a productive method for preparing a number of compounds containing the $SF_5CF(CF_3)$-grouping. The number of compounds, by comparison to the corresponding perfluoroalkyl group $(CF_3)_2CF-$, containing this potentially useful grouping is limited [1,3]. The presence of the SF_5 group should increase the possible uses for these derivatives [4-8].

Previously it was suggested [1] that the electronegativity of the $SF_5CF(CF_3)$- group, comparable in value to that of the $SF_5CF(Cl)$-
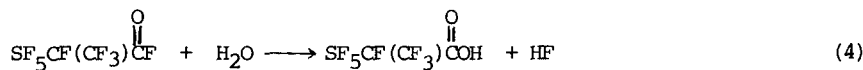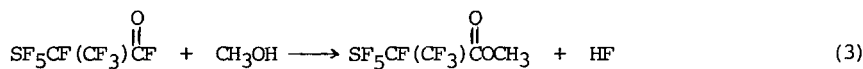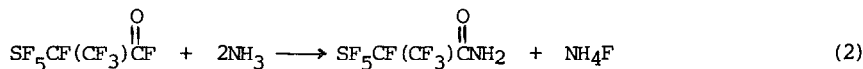
grouping, is less than that of the $(CF_3)_2CF-$ group. In addition, kinetic

acidity studies [8] have suggested that the SF_5 portion of the $SF_5CF(CF_3)-$

group was more effective than the CF_3 portion of the $(CF_3)_2CF-$ in stabi-

lizing a carbanionic site. Therefore, it is with considerable interest that

derivatives containing the $SF_5CF(CF_3)-$ grouping be prepared.


RESULTS AND DISCUSSION

We have found that carbonyl fluoride will add to trifluorovinylsulfur

pentafluoride in the presence of cesium fluoride and acetonitrile according

to the following equation:

$$SF_5CF{=}CF_2 + COF_2 \xrightarrow[CH_3CN]{CsF} SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}F \tag{1}$$
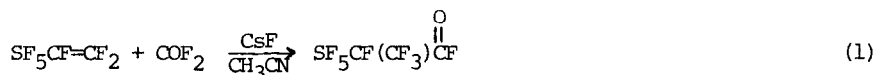
This new compound contains not only the $SF_5(CF_3)CF-$ grouping but a reactive

functional group as well. Reactions of $SF_5CF(CF_3)COF$ with NH_3, CH_3OH, and

H_2O gave the following results:

$$SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}F + 2NH_3 \longrightarrow SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + NH_4F \tag{2}$$

$$SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}F + CH_3OH \longrightarrow SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 + HF \tag{3}$$

$$SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}F + H_2O \longrightarrow SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}OH + HF \tag{4}$$

The amide produced in equation (2) reacts with P_4O_{10} according to the follow-

ing equation:

$$SF_5CF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + P_4O_{10} \longrightarrow SF_5CF(CF_3)CN + P_4O_{10}{\cdot}H_2O \tag{5}$$
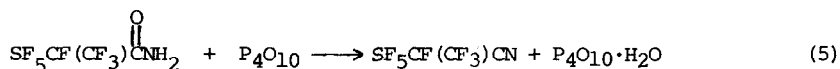
All of the above compounds except the amide are colorless stable liquids. The amide is a stable white solid.

In the addition of carbonyl fluoride to $SF_5CF=CF_2$, it is presumed that a fluoride ion adds to the SF_5-fluoroolefin to form an intermediate fluorocarbanion which reacts with COF_2:

$$F^- + SF_5CF=CF_2 \longrightarrow SF_5\bar{C}FCF_3 \qquad (6)$$

$$SF_5\bar{C}FCF_3 + COF_2 \longrightarrow SF_5CF(CF_3)COF + F^- \qquad (7)$$

This mechanism is similar to those proposed for the addition of COF_2 to other fluoroolefins [9], and is supported by the fact that Noftle and Fox [2] were able to isolate the $SF_5CF(CF_3)Ag \cdot CH_3CN$ solid from AgF and $SF_5CF=CF_2$ in acetonitrile. We also have obtained some evidence for a cesium fluoride $SF_5CF=CF_2$ complex. Interestingly, we have found that without the solvent and COF_2 the dimer of $SF_5CF=CF_2$ is found:

$$2SF_5CF=CF_2 \xrightarrow{\text{CsF}} (SF_5CFCF_2)_2 \qquad (8)$$

The infrared spectra for these derivatives has as a common feature the presence of the SF_5 group and its characteristic infrared absorptions. Cross and coworkers [10] reported that for compounds containing the SF_5 group the most intense bands should occur in the region 850-920 cm^{-1} (S-F stretching modes), and in the region of 600 cm^{-1} (S-F deformation modes). For the new compounds reported in this paper, absorption bands in the 840-900 cm^{-1} region are assigned to the S-F stretching vibrations. The S-F deformation modes are found near or at 600 cm^{-1}. For compounds containing a C-F group, and a CF_3 group, the C-F stretching vibration is usually located in the 1000-1100 cm^{-1} region [11] while marked absorption in the range 1360-1300 cm^{-1} can be correlated with the CF_3 group [12]. For our new compounds the stretch-

ing vibration for the CF group appears to be located in the 1006-1165 region while for the CF_3 group appears to be located in the 1240-1380 cm^{-1} region. The CF_3 deformation band is located in the 735-760 cm^{-1} region [13] . The other functional groups also exhibit characteristic infrared bands. The carbonyl containing compounds, $SF_5CF(CF)_3COX$, $(X = F, NH_2, OCH_3, OH)$ show the expected C=O absorption at 1880, 1720, 1790, and 1766 cm^{-1}, respectively. The spectrum of the nitrile contains a band at 2260 cm^{-1} which is assigned to the C≡N stretching vibration. In R_fCN this absorption is located in the 2276-2265 cm^{-1} region [14] . The absorptions in the 3192-3345 cm^{-1} region for $SF_5CF(CF_3)CONH_2$, is ascribed to N-H stretching vibration while the absorption at 1605 cm^{-1} is assigned to the N-H deformation frequency. The acid, $SF_5CF(CF_3)COOH$, in its liquid state contains the expected broad hydroxyl stretching absorption which is centered about 3100 cm^{-1}. The absorption at 2970 cm^{-1} for the methylester, $SF_5CF(CF_3)CO_2CH_3$, is assigned to the C-H stretching mode.

The major mass spectral peaks for these new compounds are listed in Table I. Parent peaks, although not strong, were found for $SF_5CF(CF_3)CONH_2$, and $SF_5CF(CF_3)CO_2CH_3$; the parent peaks minus a fluorine were present for $SF_5CF(CF_3)CO_2H$, and $(SF_5CFCF_2)_2$. Except for the dimer and amide, the mass spectra contained prominent peaks for CF_3^+, SF_3^+, and SF_5^+. The amide contained prominent peaks for $CONH_2^+$, CF_3^+, and CF^+ ions. The dimer contained intense peaks for $C_2F_5^+$ and $SF_5C_2^+$ ions.

The nmr spectra (see Table II for chemical shift values) generally consist of complex multiplets; however, with most compounds first-order coupling constants could be determined, and these are listed in Table III.

The SF_5 fluorine resonance consists of an AB_4 multiplet; the minimum between the B maxima is reported as the SF_4 (equatorial) chemical shift while the SF (axial) chemical shift is reported as the center (line #6) of its nine line pattern. The reported $J_{1,3}$ coupling is the observed doubling

of the nine line A pattern and is assumed to be due to SF (axial) to CF (vicinal) coupling. Because of the complexity of the CF resonance, unambiguous confirmation of the assignment cannot be documented. The single fluorine (C-F) attached to the carbon skeleton, labeled as F(3) in Table III, has the most complex pattern and depending upon the value of the SF_4-CF coupling ($J_{2,3}$) this resonance appears as a well resolved eight line pattern in the amide or a poorly resolved eleven or more line pattern for the acid and methyl ester. The acid fluoride shows the C-F resonance as two poorly resolved eight (or more) line multiplets where the doublet separation is given as $J_{3,5}$. In the nitrile spectrum however, the pattern is a quartet with each element a clearly resolved pentet.

The multiplet pattern of the CF_3 group is dependent on the magnitude of the $J_{2,4}$ coupling. When the value of the $J_{2,4}$ coupling is larger than $J_{3,4}$ coupling, the CF_3 resonance appears as a pentet with each of the pentet elements split into a doublet for all compounds except the nitrile. The CF_3 pattern in the nitrile appears as a well resolved six line pattern due to the equivalence of the $J_{3,4}$ and $J_{2,4}$ coupling values.

The -COF resonance of the acid fluoride is a ten line multiplet of two overlapping eight line patterns caused by the accidental degeneracy of J_{COF,SF_4} and J_{COF,CF_3}.

It is of interest to point out that the summation of the coupling constants for the $SF_5CF(CF_3)$- group ($J_{2,3} + J_{2,4} + J_{3,4}$) is essentially constant (20.6 ± 0.9) and implies a predominant through bond coupling mechanism.

The nmr spectrum of the dimer is more complicated than expected. The analysis of its resonances is in progress. Additional studies with $SF_5CF=CF_2$ and its derivatives are also underway.

TABLE I

MASS SPECTRA DATA

$SF_5CF(CF_3)\overset{\overset{O}{\|}}{C}F$ $CO^+(9)$, $CF^+(27)$, $C_2O^+(8)$, $COF^+(20)$, $CF_2^+(8)$,

$SF^+(7)$, $SFC^+(5)$, $CF_3^+(100)$, $SF_2^+(21)$, $C_2F_3^+(5)$,

$COF_3^+(98)$, $SF_3^+(99)$, $SFC_2O^+(8)$, $C_3F_3^+(5)$,

$C_2F_4^+(18)$, $SF_3C^+(7)$, $SF_4^+(3)$, $SF_3C_2^+(3)$,

$C_2F_5^+(97)$, $SF_5^+(96)$, $C_2F_4CO^+(3)$, $C_3F_5^+(15)$,

$C_2F_5CO^+(3)$, $C_3F_5^+(15)$.

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$SF_5CF(CF_3)\overset{\overset{O}{\|}}{C}NH_2$ $CO^+(3)$, $CF^+(\sim 25)$, $CONH^+,C_2F^+(3)$, $CONH_2^+(100)$,

$CF_2^+(2)$, $SF^+(3)$, $COF_2^+(4)$, $CF_3^+(\sim 25)$, $SF_2^+(3)$,

$C_2F_3^+(2)$, $SF_3^+(17)$, $SFC_2O^+(1)$, $C_3F_3^+(1)$,

$F_2CONH_2^+(3)$, $C_2F_4^+(9)$, $SF_3C^+(2)$, $C_2F_5^+(3)$,

$SF_5^+(5)$, $C_3F_4O^+(1)$, $C_3F_5^+(4)$, $C_2F_4CONH_2^+(5)$,

$SF_5CF(CF_3)CONH_2^+(0.1)$.

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$SF_5CF(CF_3)\overset{\overset{O}{\|}}{C}OCH_3$ CH_3CO^+, $C_2F^+(13)$, CS^+, $CO_2^+(20)$, $CF_2^+(7)$,

$SF^+(8)$, $CH_3CO_2^+(61)$, $CF_3^+(69)$, $SF_2^+(23)$,

$C_3F_2^+(16)$, $C_2F_3^+(21)$, $SF_3^+(86)$, $SFC_2O^+(8)$,

$C_2F_4^+(100)$, $SF_3C^+(7)$, $CF_2COOCH_3^+(17)$, $C_2F_5^+$,

$SFC_3O_2^+(56)$, $SF_5^+(48)$, $C_3F_4O^+(19)$, $C_3F_4^+(100)$,

$CF_3CFCO_2CH_3^+(8)$, $SF_5C_2F_3^+(3)$, $SF_5CFCO_2CH_3^+(3)$,

$SF_4CF(CF_3)COOCH_3^+(5)$, $SF_5CF(CF_3)CO_2CH_3^+(<1)$.

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$$SF_5 \overset{O}{\underset{||}{C}F(CF_3)\overset{||}{C}OH}$$ $CF_2^+(6)$, $SF^+(30)$, $SFC^+(2)$, CF_3^+, $C_3CO_2H^+(67)$,

$SF_2^+(5)$, $C_2F_3^+(10)$, $SF_2C^+(3)$, $SF_3^+(92)$, $C_2F_4^+(65)$,

$SF_3C^+(26)$, $SF_4^+(2)$, $C_2F_5^+$, $SFC_3O_2^+(5)$, $SF_3C_3^+$,

$C_3F_3O_2^+(5)$, $SF_5^+(34)$, $C_3F_5^+(5)$, $C_3F_4O_2H^+(5)$,

$SF_5C_2^+(3)$, $SF_5C_2F_3^+(16)$, $SF_4CF(CF_3)CO_2^+(2)$,

$SF_4CF(CF_3)CO_2H^+(1)$.

$SF_5CF(CF_3)CN$ $CF^+(6)$, $SC^+(2)$, $CF_2^+(2)$, $SF^+(2)$, $CFCN^+(3)$,

$SCN^+(4)$, $SCF^+(2)$, CF_3^+, $C_2FCN^+(47)$, SF_2^+,

$SC_2N^+(7)$, $CF_2CN^+(35)$, SF_3^+, $SFC_2N^+(65)$, $C_2F_4^+(3)$,

SF_3C^+, $SC_2FN^+(3)$, $C_2F_3CN^+(2)$, $SF_4^+(2)$, $C_2F_5^+(19)$,

$C_2F_5CN^+(75)$, SF_5^+, $SF_3C_2N^+(100)$, $C_3F_5^+(3)$, $SF_5C^+(3)$,

$SF_5C_2^+(10)$, $SF_5C_2N^+(1)$.

$(SF_5CFCF_2)_2$ $SCF^+(6)$, $CF_3^+(22)$, $SF_3^+(11)$, $SF_3C^+(21)$, $C_4F_3^+(4)$,

$SF_3C_2^+(7)$, $C_2F_5^+(100)$, $SF_5^+(10)$, $C_3F_5^+(11)$,

$SF_5C_2^+(71)$, $C_4F_6^+(10)$, $SF_5C_2F_2^+(3)$, $SF_5C_4F_4^+(8)$,

$SF_5C_4F_6^+(3)$, $S_2F_{10}C_4F_5^+(3)$.

TABLE II
NMR Chemical Shifts[a]

	$SF_{(ax)}$	$SF_{4(eg)}$	CF_3	CF	$C(O)F$	H
$SF_5CF(CF_3)C(O)F$	−64.6	−56.3	+75.6	+144.4	−30.1	
$SF_5CF(CF_3)C(O)NH_2$	−69.5	−54.3	+71.7	+137.5		$(7.0,7.4)$[b]
$SF_5CF(CF_3)CN$	−63.2	−53.3	+76.9	+137.3		
$SF_5CF(CF_3)C(O)OCH_3$	−67.6	−54.9	+74.8	+142		3.9
$SF_5CF(CF_3)C(O)OH$	−67.5	−55.7	+74.9	+141		5.1

[a] Fluorine chemical shifts in ppm from internal $CFCl_3$ and proton chemical shifts in ppm downfield from internal TMS

[b] Band centers for a broad doublet

TABLE III

NMR Data – Coupling Constants (Hz)

$$F(1) \quad (2) \quad F(3) \quad (4)$$
$$F - SF_4 - \overset{|}{\underset{|}{C}} - CF_3$$
$$X(5)$$

Compound	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$
X = C(O)F	135			3.0	12.0	8.0	6.0	~18	8.0
X = C(O)NH$_2$	144	4.2	~1	5.1	11.3		5.1		
X = CN	146	4.2		1.7	9.5		9.5		
X = C(O)OMe	144			2.8	11.4		5.5		
X = C(O)OH	144	2.8		2.8	12.0		5.6		

EXPERIMENTAL

$SF_5CF=CF_2$ was prepared and handled as previously reported [15]. Carbonyl fluoride and cesium fluoride were purchased from the PCR Research Chemicals. CH_3CN, CH_3OH and CCl_4 were spectral grade and obtained from Mallinckrodt. P_4O_{10} was reagent grade and obtained from J.T. Baker, Anhydrous ammonia was obtained from Matheson. All chemicals were used as received. The infrared (IR) spectra agreed with the published spectra (CsF and P_4O_{10} were not recorded).

The IR spectra were recorded on a Perkin-Elmer 476 spectrometer. Gas samples were contained in a Monel cell equipped with a Whitey brass valve. The cell windows were either NaCl or AgCl and the path length of the cell was 8.25 cm. The spectra were calibrated with a polystyrene film.

Gas chromotography analysis was carried out with an Aerograph Autoprep (Model A-700) gas chromotograph using a 10' x 3/8" column containing 20% carbowax adsorbed on "Chromosorb W".

Molecular weights were determined by the vapor density method.

The nmr spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.6 MHz for fluorine resonances. TMS and F-11 were used as internal standards. The mass spectra were taken on a CEC 21-110 B double focus mass spectrometer equipped with a 6 KV ion accelerator and operated at 70 volts. Perfluorokerosine (PFK) was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, West Germany.

Preparation of $SF_5CF(CF_3)COF$

$SF_5CF=CF_2$ (37.5 mmol), COF_2(54 mmol) and CH_3CN(574 mmol) were condensed into a 75 ml stainless steel vessel containing CsF(65 mmol).

The CH_3CN was dried over P_4O_{10} and distilled directly into the reaction vessel. CsF was dried under vacuum at 100° for 5 hrs. The reactants were heated at 50° (2 hr), 75° (2 hr), and 100° (5 hr). The product mixture was colorless and could not be separated by distillation because the product, $SF_5CF(CF_3)COF$ boils close to room temperature and appeared to azeotrope with COF_2. Purfication was achieved by a trap to trap transfer at -120°, -78°, and -50°. The -50° trap contents were further purified by pumping at -78° (3 mmol).

Calcd. for $SF_5CF(CF_3)COF$: C, 13.1: S, 11.7; F, 69.3. Found: C, 14.5: S (9.4): F (70.9). MW, calcd. 274, found, 269. The ^{19}F nmr spectrum gave the following relative peak areas: SF(1.1), SF(4.1), C(O)F(1.0), CF_3 (2.9), CF(1.0).

In a second run, $SF_5CF=CF_2$ (64.9mmol), COF_2 (133 mmol), and CH_3CN (375 mmol) were condensed into a 75 ml stainless steel vessel containing CsF (11 mmol). Heating at 50°(2 hr), 70°(2 hr) and 90°(5.5 hr) produced 29.6 mmol of $SF_5CF(CF_3)COF$ in 45% yield, (n.c.).

The gaseous infrared spectrum gave the following absorptions (cm^{-1}): 1880(s), 1312(m), 1240(s,b), 1180(m), 1148(s), 1000(w), 975(m), 890(s), 845(s), 815(w), 750(m), 635(w), 600(m), 570(w).

Preparation of $SF_5CF(CF_3)CONH_2$

In a 75 ml stainless steel vessel equipped with a Whitey brass valve, 24 mmol of $SF_5CF(CF_3)COF$ and 76 mmol of NH_3 were

condensed at −196°. After ∿15 hr at room temperature the
volatile materials were pumped away leaving behind a white
solid mixture of NH_4F and $SF_5CF(CF_3)CONH_2$. The amide was
isolated by dissolving it in CCl_4 leaving behind the NH_4F.
Removal of the CCl_4 left the white solid product $SF_5CF(CF_3)CONH_2$
in 50% yield; mp 32−34° (n.c.).

Calcd. for $SF_5CF(CF_3)CONH_2$: C,13.3; H,0.74; S,11.8;
N,5.17; F,63.1. Found: C,14.6; H,0.65; S,10.5; N,5.4;
F,63.6.

The solid infrared spectrum gave the following absorptions
(cm^{-1}): 3500(m,sh), 3445(m), 3340(m), 3250(m), 3192(m),
1720(s), 1605(m), 1380(m), 1275(ms), 1230(s), 1195(s), 1145(m),
1006(m), 875(s), 832(s), 740(m), 680(wm), 635(w), 600(m).

Preparation of $SF_5CF(CF_3)CN$

$SF_5CF(CF_3)CONH_2$ (12 mmol) and P_4O_{10} (16.5 mmol) were
placed together in a 100 ml round bottom flask and then attached
to a condenser which was connected to three traps cooled to
−19°, −78°, and −130°C respectively. The temperature was
slowly increased from 20° to 138° over a 3 hour period.
Additional P_4O_{10} (12 mmol) was added and the temperature was
increased to 152° over a 2 hour period. The product,
$SF_5CF(CF_3)CN$, collected mainly in the −78° trap and was formed
in a 74% yield; bp 39−41° (n.c.).

Calcd. for $SF_5CF(CF_3)CN$: C,14.24; S,12.67; N,5.53; F,67.56.
Found: C,14.34; S,12.19; N,5.43; F,68.1. MW, Calcd, 253,
found, 247. The ^{19}F nmr spectrum gave the following relative
peak areas: SF(1.0), SF_4(4.1), CF(1.1), CF_3(3.0).

The gaseous infrared spectrum of the distilled product
gave the following absorptions (cm^{-1}): 2260(m), 1600(vw),

1275(s), 1245(s), 1220(s), 1163(s), 1052(s), 955(w), 900(s), 850(s), 790(m), 735(s), 713(m), 687(m), 600(s).

$SF_5CF(CF_3)COOH$

In a 35 ml Kel-F vessel equipped with a Teflon top and Whitney Brass valve and containing 31 mmol of NaF, 15 mmol of $SF_5CF(CF_3)COF$ and 17 mmol of H_2O were condensed at -196°. After heating from room temperature to 55°C for 11 hours the volatile materials were pumped away leaving behind a white solid. Heating the white solid to 80°C over a 12 hour period, while pumping through a trap cooled to -196°, resulted in the transfer of the acid into the trap. The product, $SF_5CF(CF_3)COOH$ was formed in 52% yield; bp 86-88°/50.5 mm-Hg (n.c.).

Calcd. for $SF_5CF(CF_3)COOH$: C,13.24; H,0.37; S,11.78; F,62.84. Found: C,13.55; H,0.47; S,11.42; F,62.2. The ^{19}F nmr spectrum gave the following relative peak areas: SF(1.0), SF_4(4.0), CF(0.9), CF_3(3.0). Titration with 0.3701 M NaOH gave a molecular weight 274 g/mole. Calcd. 274.

The liquid infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 3100(b,m), 1766(s), 1415(m), 1318(m), 1280(s), 1240(s), 1200(s), 1160(s), 1125(s), 880(s), 843(s), 812(m), 760(w), 714(w), 680(m), 600(s).

$SF_5CF(CF_3)COOCH_3$

In a 75 ml stainless steel vessel equipped with a Whitey brass valve, 23 mmol of $SF_5CF(CF_3)COF$ and 22 mmol of CH_3OH were condensed at -196°. After heating at 68° for 2.2 hours the volatile materials were pumped away at -45°. The product $SF_5CF(CF_3)COOCH_3$ was formed in 54% yield; bp 43.5-44.5°/55 mm-Hg (n.c.).

Calcd. for $SF_5CF(CF_3)COOCH_3$: C,16.78; H,1.05; S,11.18; F,59.8. Found: C,17.56; H,1.17; S,10.76; F,57.4. The ^{19}F nmr spectrum gave the following relative peak areas: SF(1.0), SF_4(4.1), CF(1.0), CF_3(3.0).

The gaseous infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 2970(w), 1790(s), 1785(s), 1445(m), 1305(s), 1285(s), 1265(s), 1245(s), 1200(s, with sh, at 1190), 1160(s), 1130(m), 1040(m), 1020(m), 930(m), 880(s), 845(s), 795(s), 745(m), 665(m), 600(s).

Preparation of $(SF_5CFCF_2)_2$.

In a 75 ml stainless steel vessel containing 2 mmol of CsF (predried at 100° for 12 hours), 38 mmol of $SF_5CF=CF_2$ was condensed at -196°. The olefin was heated at 50°(2 hr), 80°(2 hr), 100°(2 hr) with frequent shaking (2 min. during every 15 min. heating stage). The dimer product was formed in 78% yield; bp 38.5±0.5°/24.6 mm-Hg (n.c.).

Calcd. for $(SF_5CFCF_2)_2$: C,11.67; S,15.26; F,73.1. Found C,11.54; S,15.38; F,73.08. MW, Calcd. 416, found, 413.

The gaseous infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 1325(s), 1300(w), 1270(s), 1240(s), 1200(s), 1165(ms), 1135(s), 1110(w,sh) 1050(w), 946(ms), 930(s), 890(s,b), 840(m), 800(s), 750(ms), 730(m), 690(w), 660(s), 650(w), 600(s).

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