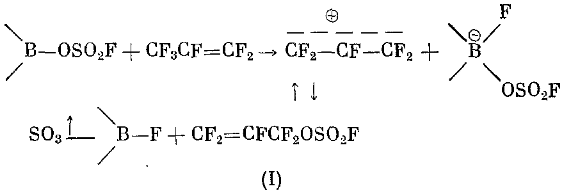
# SUBSTITUTIVE SULFOTRIOXIDATION OF UNSATURATED AND ARALIPHATIC ORGANOFLUORINE COMPOUNDS

V. F. Cherstkov, S. R. Sterlin,
L. S. German, and I. L. Knunyants

UDC 542.91:547.431.6:547.541.6:
546.16

It has previously been shown that perfluoropropylene reacts with $SO_3$ to give hexafluoropropane-$\beta$-sultone [1-3]. It has, however, recently been found that in the presence of $BF_3$, $B_2O_3$, or $B(OMe)_3$ this reaction follows a different course to give, in addition to hexafluoropropane-$\beta$-sultone, perfluoroallyl fluorosulfate (I) [4]. The mechanism of formation of (I) has been postulated [4] to involve the perfluoroallyl cation:



Similarly, the formation of perfluorocyclobutene-2-yl fluorosulfate (II) in the reaction of perfluorocyclobutene with $SO_3$ has been regarded as involving a mesomeric carbenium ion [5].

The decisive factor in the synthesis of the fluorosulfates (I) and (II) is clearly the allyl mobility of the F atoms, which determines the stability of the corresponding carbenium ions. Consequently, this reaction should be applicable to other perfluoro compounds which are capable of generating benzyl or allyl cations.

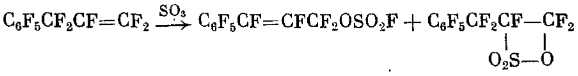
It has been found that perfluorotoluene (III) reacts with $SO_3$ on heating (100°C, 20 h) to give perfluorobenzyl fluorosulfate (IVa) [6]. Under similar conditions, 4-bromoperfluorotoluene (IIIb) and 1,1,2-trichloro-3,3,3-trifluoropropene (IIIc) also react with $SO_3$:

$$\underset{\text{(III a—c)}}{RCF_3} \xrightarrow{SO_3} \underset{\text{(IV a—c)}}{RCF_2OSO_2F}$$

$R = C_6F_5$ (IIIa), (IVa); $R = 4\text{-}BrC_6F_4$ (IIIb), (IVb); $R = CCl_2{=}CCl$ (IIIc), (IVc).

Perfluoroallylbenzene (V) reacts even more readily with $SO_3$, the exothermic reaction giving a mixture of cis- (VIa) and trans-fluorosulfates (VIb) together with perfluorophenylpropene-$\beta$-sultone (VII) in a ratio (VIa):(VIb):(VII) = 5:69:26:

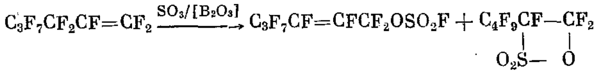
: (VI6) : (VII) = 5 : 69 : 26



$$\underset{\text{(V)}}{C_6F_5CF_2CF{=}CF_2} \xrightarrow{SO_3} \underset{\text{(VI a—b)}}{C_6F_5CF{=}CFCF_2OSO_2F} + \underset{\text{(VII)}}{\begin{array}{l} C_6F_5CF_2CF{—}CF_2 \\ \qquad\quad\;\; | \quad\;\; | \\ \qquad\quad O_2S{—}O \end{array}}$$

In the presence of catalytic amounts of $B_2O_3$ or $H_3BO_4$, the compositions and ratios of the reaction products undergo marked changes, the amount of the cis isomer (VIa) increasing substantially, and mixtures of cis- and trans-perfluoropropylbenzene (VIII) being formed. The ratio (VIa):(VIb):(VII):(VIII); =14:56:12:17.

In the reactions of 1-perfluorohexene (IX) and $\beta,\gamma$-dichloroperfluoropropylbenzene (XII) with $SO_3$, fluorosulfates are formed only in the presence of $B_2O_3$. In the first reaction, in addition to the fluorosulfate (X) (~95% trans isomer), the sultone (XI) is obtained:

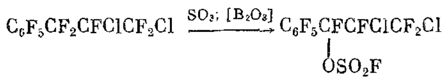


$$\underset{\text{(IX)}}{C_3F_7CF_2CF{=}CF_2} \xrightarrow{SO_3/[B_2O_3]} \underset{\text{(X a—b)}}{C_3F_7CF{=}CFCF_2OSO_2F} + \underset{\text{(XI)}}{\begin{array}{l} C_4F_9CF{—}CF_2 \\ \qquad\;\; | \quad\;\; | \\ \qquad O_2S{—}\;O \end{array}}$$

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2791-2795, December, 1982. Original article submitted April 6, 1982.

0568-5230/82/3112-2468$07.50

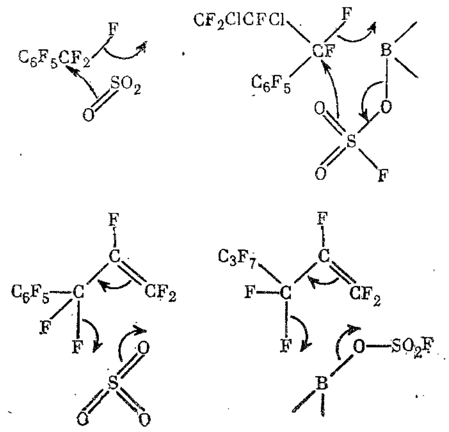


$$C_6F_5CF_2CFClCF_2Cl \xrightarrow{SO_3;\ [B_2O_3]} C_6F_5CF(OSO_2F)CFClCF_2Cl$$

(XII) (XIII)

Thus, the ease of formation of fluorosulfates decreases in the sequence ($C_6F_5CF_2CF=CF_2 \gg C_6F_5CF_3 \sim$ 4-$BrC_6F_5CF_3 \sim CCl_2=CClCF_3 \gg C_4F_9CF=CF_2 \sim C_6F_5CF_2CFClCF_2Cl$), in which the stability of the corresponding carbenium ions also decreases (benzyl-allyl > benzyl or allyl > substituted benzyl or allyl).

These findings give reason to suppose that in most instances the formation of fluorosulfates occurs via a cyclic transition state which may be either four- or six-membered. Fission of the C – F bond in the latter is dependent both on the mobility of the leaving F atom, which is determined by the same factors as the stability of the corresponding corresponding carbonium ion, and on the type of Lewis acid. In the case of compounds which can give rise to more stable carbenium ions, $SO_3$ can function directly as a Lewis acid. When the formation of the carbenium ion occurs less readily, however, reaction occurs only in the presence of boron compounds, the Lewis acid apparently being a mixed anhydride of the type $> B-OSO_2F$



The proposed reaction sequence is confirmed by the stereoisomeric composition of the sulfotrioxidation products of perfluoroallylbenzene and perfluoro-1-hexene. In both cases, the principal reaction products are the trans-fluorosulfates (VIb) and (Xa), the formation of which is readily explicable in terms of a cyclic transition state. The alternative mechanism involving carbenium ions [4] should give, in addition to the trans-fluorosulfates, comparable amounts of the cis isomers.

TABLE 1. Reaction of Fluoroolefins and Fluoroalkylbenzenes with $SO_3$

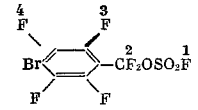
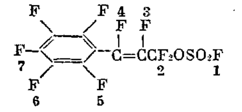
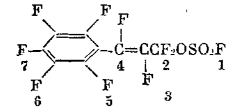
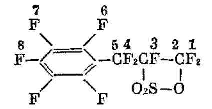
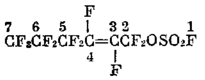
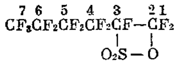
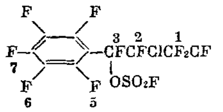
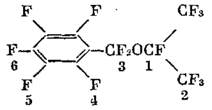
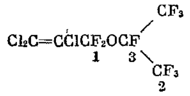
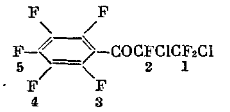
| Starting material/ method | Reaction products | Reaction conditions | bp, °C (p, mm Hg) | Yield, % | Found/Calculated, % | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | F | S | Br |
| (IIIb)/A | (IVb) | 100°, 3 days | 85 (6) | 27,6 | | 34,69/35,27 | 8.43/8,49 | 21,94/21,22 |
| (IIIc)/A | (IVc) | 100°, 7 days | 42 (8) | 94 | | 19,42/20,32 | 10,77/11,44 | |
| (V)/A | (VIa) *<br>(VIb)<br>(VII) * | Exothermic reaction | 75 (6) | 69 | 27.94/28,57 | 49,95/50,26 | | |
| (IX)/B | (X)† | 20°, 7 days | 115–118 | 37 | | | 8.25/8,42 | |
| | (XI)† | 100°, 3 h | | 42 | | | | |
| (XII)/B | (XIII) | 100°, 12 h | 70–80 (2) | 58 | 42,34/42,31 | 15,74/15,84 | 6,77/7,12 | |

---

* Structure proposed on the basis of $^{19}F$ NMR spectra.

† The mixture of (X) and (XI) was analyzed; structures confirmed by the $^{19}F$ NMR spectra and GC-MS. Mass spectrum of (X): 380 $(M)^+$, 361 $(M-F)^+$, 284 $(C_6F_{11})^+$, 231 $(C_5F_9)^+$, 131 $(C_3F_5)^+$, 83 $(SO_2F)$. Mass spectrum of (XI): 300 $(M-SO_3)^+$, 297 $(C_6F_{11}O)^+$, 131 $(C_3F_5)^+$, 83 $(SO_2F)^+$.

TABLE 2. $^{19}F$ NMR Spectra

| Structural formula | δ, ppm, J, Hz |
|---|---|
|  (IV) | $\delta_1=-126{,}7$ t.t., $\delta_2=-15{,}4$ d.t., $\delta_3=62{,}2$ м, $\delta_4=53{,}8$m, $J_{1-2}=8{,}1$, $J_{2-3}=28$, $J_{1-3}=2$ |
| $Cl_2C{=}\overset{2}{C}Cl\overset{1}{C}F_2OSO_2F$ (IVc) | $\delta_1=-126{,}8$ t, $\delta_2=15{,}8$ d, $J_{1-2}=9{,}5$ |
|  (VIa) | $\delta_1=-126{,}8$t (1F), $\delta_2=-4{,}4$m (2F), $\delta_3=68$ m (1F), $\delta_4=35$ m (1F), $\delta_5=60{,}5$ m (2F), $\delta_6=84$ m (2F), $\delta_7=70$ m (1F) |
|  (VIb) | $\delta_1=-126{,}2$ t., $\delta_2=-5{,}7$d.d.d, $\delta_3=81{,}1$ d.t.t, $\delta_4=55$ d.d.t.m, $\delta_5=58{,}5$ m, $\delta_6=83{,}6$ m, $\delta_7=69{,}6$ m, $J_{1-2}=9$, $J_{2-3}=12$, $J_{2-4}=27$, $J_{4-3}=140$, $J_{4-5}=8$, $J_{3-5}=12$ |
|  (VII) | $\delta_1=4{,}2$d.m (1F), $\delta_2=11{,}1$d.m (14 lines ) (1F) $\delta_3=60{,}0$ m (1F), $\delta_4=17{,}4$ m (1F), $\delta_5=20{,}6$ m (1F), $\delta_6=60{,}9$m (2F), $\delta_7=68{,}85$ m (1F), $\delta_8=86{,}9$ m (2F), $J_{1-2}=109$, $J_{4-5}=320$ (ABsystem in) |
|  $\overset{7}{C}F_3\overset{6}{C}F_2\overset{5}{C}F_2\underset{4}{C}F{=}\overset{3}{C}F\overset{2}{C}F_2OSO_2\overset{1}{F}$ (X) | $\delta_1=-126{,}2$ t, $\delta_2=-4{,}5$d.d.d, $\delta_3=75{,}5$d.d.t, $\delta_4=79{,}2$d.t.t, $\delta_5=42{,}7$d.d.t, $\delta_6=51{,}1$ t, $\delta_7=4{,}6$ br.s $J_{1-2}=9{,}4$, $J_{2-3}=9{,}8$, $J_{2-4}=26{,}5$; $J_{3-4}=132$, $J_{3-5}=27$; $J_{4-5}=10$, $J_{6-5}=10$ |
|  (XI) | $\delta_1=5{,}8$ d.m(1F), $\delta_2=9{,}8$d.m (1F), $\delta_3=74{,}6$ m (1 F), $\delta_4=49$ m (2F), $\delta_5=43{,}1$m (2F), $\delta_6=40$ m (2F), $\delta_7=4{,}8$ m (3F) |
|  (XIII) | $\delta_1=15{,}1$m (2F), $\delta_2=51{,}4$ m (1F), $\delta_3=31{,}2$ m (1F), $\delta_4=-129{,}3$ m (1F), $\delta_5=83{,}4$ m (2F), $\delta_6=58{,}7$ m (2F), $\delta_7=69{,}7$ m (1F) |
|  (XIVa) | $\delta_1=68{,}9$ m (1F), $\delta_2=4{,}3$ m (6F), $\delta_3=-18{,}7$ m (2F), $\delta_4=63{,}3$ m² (2F), $\delta_5=84{,}7$ m (2F), $\delta_6=79$ (1F) |
|  (XIVb) | $\delta_1=16{,}7$d.sep, $\delta_2=3$d.t, $\delta_3=68{,}7$ d.sep, $J_{1-2}=2{,}6$, $J_{1-3}=22{,}6$, $J_{2-3}=2$ |
|  (XVb) | $\delta_1=-12{,}8$m (1F), $\delta_2=53$ m (2F), $\delta_3=83{,}5$ m (2F), $\delta_4=61{,}2$ m (2F), $\delta_5=70{,}8$ m (1F) |

Thus, most of these reactions obviously do not involve carbenium ions. Only in one instance does the composition of the reaction products indicate the generation of a kinetically independent carbenium ion, viz., the reaction of perfluoroallylbenzene in the presence of $B_2O_3$, when the relative amount of the cis-fluorosulfate (VIa) rises to 25% (in the absence of the catalyst, 7%), and the formation of a mixture of cis- and trans-perfluoropropenzylbenzenes is observed. However, in view of the particularly high stability of the perfluorophenylallyl cation this reaction appears to be an exception to the general rule.

The fluorosulfates obtained, like perfluoroallyl fluorosulfate [4], undergo nucleophilic substitution. Thus, the fluorosulfates (IVa) and (IVc) react readily with potassium perfluoroisopropoxide to give high yields of the ethers (XIV):

$$RCF_2OSO_2F \xrightarrow[-FSO_2OK]{(CF_3)_2CFOK} \underset{(XIVa-b)}{RCF_2OCF(CF_3)_2}$$

$$R = C_6F_5 (XIVa);\ R = CCl_2{=}CCl\ (XIVb)$$

We have previously described [6] the formation of perfluorobenzyl chloride and iodide when the fluorosulfate (IVa) reacts with LiCl or KI.

It is necessary to point out that in the discussion of the mechanism of the reaction of the fluorosulfate (I) with nucleophilic reagents in [4], the possibility of nucleophilic substitution at the fluorinated $sp^3$-hybridized carbon atom is discounted, and an $S_N{}^{2'}$ reaction mechanism is proposed. While not denying such a possibility in the present case, it is not possible to agree with such a categorical assertion in all cases. The formation of the ethers (XIVa-b) unambiguously indicates the possibility of nucleophilic substitution at the fluorinated $sp^3$-hybridized C atom.

Despite the fact that fluorinated benzyl and allyl fluorosulfates are powerful alkylating agents, in their reactions with nucleophiles they may display dual reactivity, and react depending on the nature of the nucleophile at either C or S atoms. Thus, potassium perfluorosulfate reacts with the fluorosulfate (IVa) to give the ether (XIVa), whereas reaction of the latter with CsF gives pentafluorobenzyl fluoride (XVa). Similarly, the fluorosulfate (XIII) reacts with CsF at sulfur to give the ketone (XVb):

$$C_6F_5CRFOSO_2F \xrightarrow[-SO_2F_2]{[CsF]} \underset{(XVa-b)}{C_6F_5CR{=}O}$$

$$R = F(XVa);\ R = CF_2ClCFCl\ (XVb)$$

## EXPERIMENTAL

$^{19}F$ NMR spectra were obtained on a Perkin–Elmer R-32 NMR spectrometer (84.6 MHz, external standard $CF_3COOH$), and mass spectra of a Varian CH-5 mass spectrometer.

The reaction conditions, yields, boiling points, and elemental analyses of the fluorosulfates are given in Table 1, and the $^{19}F$ NMR spectra of (IVb)-(XVb) in Table 2.

Reaction of Fluoroolefins and Fluoroalkylbenzenes with $SO_3$. Typical Experiment. Method A. A mixture of equimolar amounts (50-100 mmole) of the starting material and $SO_3$ and freshly distilled $SO_3$ was kept and (or) heated in a sealed ampul, and the reaction products were separated by distillation. Method B. The reaction was carried out as in method A, but with the addition of 1.5-2.0% of $B_2O_3$ or $H_3BO_4$.

Perfluoroisopropyl Ethers (XIVa-b). To a solution of potassium heptafluoroisopropoxide (from 5 g (0.03 mole) of hexafluoroacetone and 1.75 g (0.03 mole) of KF) in 20 ml of diglyme was added at 0°C over 30 min 10 g (30 mmole) of (IVa). The mixture was stirred for 2.5 h, poured into water, the organic layer separated, and distilled over conc. sulfuric acid to give 8.8 g (73%) of (XIVa), bp 73-75°C/60 mm. Mass spectrum: Found 401.9747 $(M)^+$, 382.9732 $(M-F)^+$. Calculated: for $C_{10}F_{14}O$. 401,9725; for $C_{10}F_{13}O$ 382,9741. Similarly, from (IVc) there was obtained (XIVb), bp 134-136°C, yield 61%. Mass spectrum: Found: 363.8853 $(M)^+$, 365.8838 $(M)^+$, 367.8816 $(M)^+$. Calculated for $C_6F_9Cl_3{}^{35}O$ 363.8869; for $C_6F_9Cl_2{}^{35}Cl^{37}O$ 365.8840; for $C_6F_9Cl^{35}Cl_2{}^{37}O$ 367.8811.

Reaction of Fluorosulfates (XIII) and (IVa) with CsF. To 1 g (2.9 mmole) of (XIII) was added 0.1 g (0.6 mmole) of CsF. When the exothermic reaction was complete, slow distillation of the reaction mixture gave 0.74 g (98%) of (XVb), bp 185°C. Found: C 31.07; Cl 20.25%. $C_9F_8Cl_2O$. Calculated: C 31.12; Cl 20.46%. Similarly, fluorosulfate (I Va) afforded pentafluorobenzoyl fluoride (XVa), bp 141-143°C (cf. [7]), in quantative yields.

## CONCLUSIONS

Reaction of $SO_2$ or $SO_3/[B_2O_3]$ with terminal fluoroolefins or fluoroalkylbenzenes gives the corresponding fluoroalken-2-yl fluorosulfates and fluorobenzyl fluorosulfates.

## LITERATURE CITED

1. Yang Hsi Kwei, Acta Chim. Sinica, 26, 330 (1957); Chem. Abstr., 58, 15493 (1958).
2. M. A. Dmitriev, G. A. Sokol'skii, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 124, 581 (1959).
3. D. C. England, M. A. Dietrich, and R. V. Lindsey, J. Am. Chem. Soc., 82, 6181 (1960).
4. C. G. Krespan and D. C. England, J. Am. Chem. Soc., 103, 5598 (1981).
5. B. E. Smart, J. Org. Chem., 41, 2353 (1976).
6. L. S. German, I. L. Knunyants, S. R. Sterlin, and V. F. Cherstkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1933 (1981).

7. V. M. Vlasov, V. H. Odinokov, R. I. Rudakova, G. G. Yakobson, and N. N. Vorozhtsov, Jr., Zh. Obshch. Khim., 37, 171 (1967).

---

# SULFOTRIOXIDATION OF PERFLUOROISOPROPYL ALKENYL ETHERS

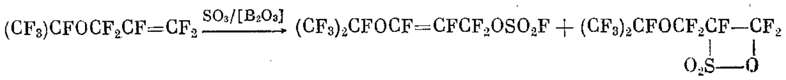
V. F. Cherstkov, S. R. Sterlin,
L. S. German, and I. L. Knunyants

UDC 542.91:547.431.6:546.16

Reaction of hexafluoropropylene with $SO_3$ in the presence of catalytic amounts of boron compounds affords a mixture of perfluoroallyl fluorosulfate (I) and hexafluoropropane-$\beta$-sultone [1, 2] (in the absence of the catalyst, no (I) is formed] [3, 4]).

We here report a study of the reaction of $SO_3$ with perfluoroisopropyl allyl ether (II) (prepared as in [1]) and the isomeric perfluoroisopropyl propenyl ether (III). The ether (II), like many of its homologs [1], is a substituted perfluoroallyl system, and hence fluorosulfates, obtained from perfluoroallyl ethers, represent a considerable extension of the range of electrophilic fluoroalkylating agents.

Reaction of (II) with $SO_3$ in the presence of 2-3 mole% of $B_2O_3$ results in the formation of isomers of the fluorosulfate (IV) (a mixture of cis and trans in the ratio 6:4), together with the sultone (V):



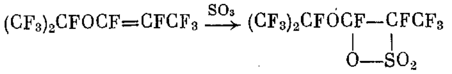
$$(CF_3)CFOCF_2CF{=}CF_2 \xrightarrow{SO_3/[B_2O_3]} (CF_3)_2CFOCF{=}CFCF_2OSO_2F + (CF_3)_2CFOCF_2\begin{array}{c} CF-CF_2 \\ |\quad\;\; | \\ O_2S-O \end{array}$$

(II) (IV) (V)

In the absence of $B_2O_3$, the sultone (V) is formed nearly exclusively.

The fluorosulfate (IV) appears to be formed by the reaction sequence proposed for the synthesis of perfluoroallyl fluorosulfate [2], If the alternative route, involving a six-membered transition state [5], were operative, much greater stereoselectivity would be expected.

The pathway involving preliminary electrophilic isomerization of (II) to (III) followed by insertion of $SO_3$ into the C–F bond of the $CF_3$ group can also be excluded; we have previously demonstrated the possibility of such a process in the case of 1,1,2-trichloro-3,3,3-trifluoropropene [6]. It was found that the ether (III) reacts readily with $SO_3$, but the sole reaction product is the sultone (VI):

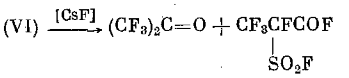


$$(CF_3)_2CFOCF{=}CFCF_3 \xrightarrow{SO_3} (CF_3)_2CFO\begin{array}{c} CF-CFCF_3 \\ |\quad\;\; | \quad\;\; \\ O-SO_2 \quad\;\; \end{array}$$

(III) (VI)

The ether (III) was obtained by isomerizing (II) with $SbF_5$. The stereoisomeric composition of (III) (cis:trans = 4:6) suggests that the reaction proceeds via the isomerization of perfluoroallylbenzene to cis- and trans-perfluoropropenylbenzenes [7].

The orientation of the addition of $SO_3$ to the ether (III) is confirmed by the reaction of the sultone (VI) with nucleophiles. Thus, the sultone (VI) reacts with CsF in diglyme, undergoing cleavage to form hexafluoroacetone and $\alpha$-fluorosulfonyltetrafluoropropionyl fluoride.



$$(VI) \xrightarrow{[CsF]} (CF_3)_2C{=}O + \begin{array}{c} CF_3CFCOF \\ | \\ SO_2F \end{array}$$

However, on reaction with a weaker nucleophile ($H_2O$), the C–O–C bond is retained, and the sultone (VI) merely rearranges to perfluoroisopropyl $\alpha$-fluorosulfonyltetrafluoropropionate (VII):

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimcheskaya, No. 12, pp. 2796-2798, December, 1982. Original article submitted April 6, 1982.

0568-5230/82/3112-2472$07.50