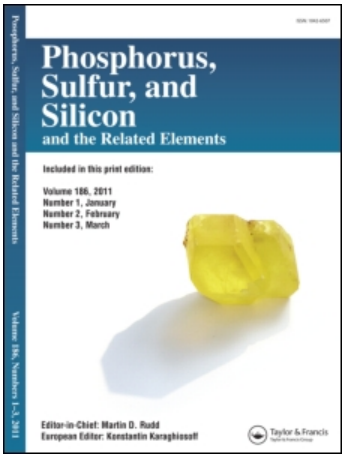

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Perfluoroalkyl Sulfur Compounds: An Unusual Reactivity Pattern of Perfluoroalkanesulfonic Esters

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ABSTRACT: Four kinds of perfluoro- or polyfluoroalkanesulfonic esters, namely $R_FSO_3CH_2R_F$, $R_FSO_3CF_2R_F$, $R_FSO_3C_6F_5$ and $C_6F_5SO_3C_6F_4$-X-*p* (X=F, Cl) and their nucleophilic substitutions were synthesized and investigated.

KEY WORDS: perfluoroalkanesulfonic esters, nucleophilic substitution, C-O bond cleavage, S-O bond cleavage

INTRODUCTION

The nucleophilic substitution of a sulfonic acid ester is an interesting subject, since the site of the ester attacked by the nucleophile can be sulfur (with S-O scission) or alcoholic carbon (with C-O scission), or both, depending on the type of ester, nucleophile and reaction conditions[1]. The C-O bond cleavage is well known in aliphatic compounds. However, for unsubstituted phenyl benzenesulfonate, such C-O bond cleavage is not important, and becomes significant only with p-nitrophenyl benzenesulfonate. In an extreme case, 2,4-dinitrophenyl benzenesulfonate is shown to undergo exclusive C-O bond cleavage when thiophenoxide is used as the nucleophile while S-O bond cleavage becomes dominant when phenoxide is used as the nucleophile[1a]. During our study on the synthesis and reactions of perfluoro- or polyfluoroalkanesulfonic acids and their derivatives, we found an unusual reactivity pattern of perfluoroalkanesulfonic esters as compared with those non-fluorinated analogues mentioned above[2]. We, herein, present the synthesis and nucleophilic substitutions of four kinds of perfluoro- or polyfluoroalkanesulfonic esters, namely: $R_FSO_3CH_2R_F$, $R_FSO_3CF_2R_F$, $R_FSO_3C_6F_5$ and

$C_6F_5SO_3C_6F_4$-X-*p*(X=F, Cl).

1, Synthesis and Nucleophilic Substitution of 1,1-Dihydro-perfluoroalkyl Perfluoroalkanesulfonates, $R_FSO_3CH_2R_F$

As a result of easy access to perfluoroalkanesulfonyl fluoride, by electrochemical fluorination in recent years, variety of esters have been synthesized by their reactions with fluorinated alcohols and phenols. The first example is the preparation of polyfluoroalkyl triflates in the presence of one equivalent of triethylamine in dichloromethane at -30°C[3].

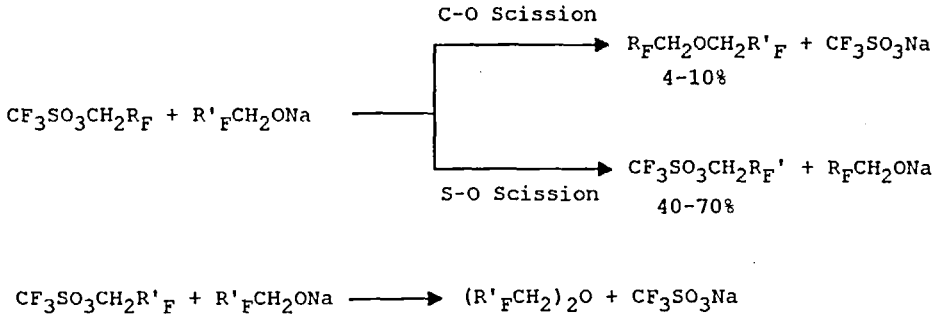
$$R_FCH_2OH + CF_3SO_2F \longrightarrow CF_3SO_2OCH_2R_F$$

Excessive base had to be avoided in the reaction, otherwise the nonvolatile quaternary ammonium salt, instead of the desired triflate, was obtained. Due to our discovery of a new synthetic method of polyfluoroalkanesufonyl fluoride(yield 30-70%)[4] from fluoroolefins, tetrafluoroethane-β-sultone, potassium fluoride and halogens (see Table1), a series of 1H,1H-perfluoroalkyl perfluoroalkanesulfonates from fluorinated alcohols have been synthesized[5]. In this reaction, both the reaction temperature and the amount of base are important in controlling the yield of the products, while the temperature is the most critical factor.

$$XCF_2OCF_2CF_2SO_2F + H(CF_2)_nCH_2OH \xrightarrow[-20\text{-}30^\circ C]{Et_3N} XCF_2OCF_2CF_2SO_3CH_2(CF_2)_nH$$

$X=Cl_2CF,\ ICF_2,\ ClCF_2 \quad n=2,4$

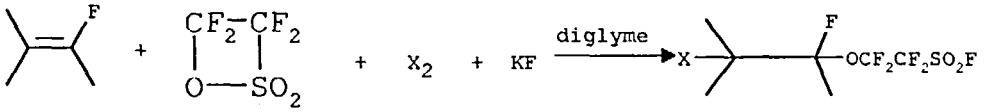
Early information about the modes cleavage of fluorinated sulfonates reported by Johncock[6] is that the ratios of sulfur-oxygen versus carbon-oxygen scission are 40-70%: 4-10% in 1H,1H-perfluoroalkyl triflates($CF_3SO_3CH_2R_F$, R_F=CF_3, n-C_3F_7) using fluoroalkoxide($R_FCH_2O^-$) or ethoxide as the nucleophiles.



$$CF_3SO_3CH_2R'_F + R'_FCH_2ONa \longrightarrow (R'_FCH_2)_2O + CF_3SO_3Na$$

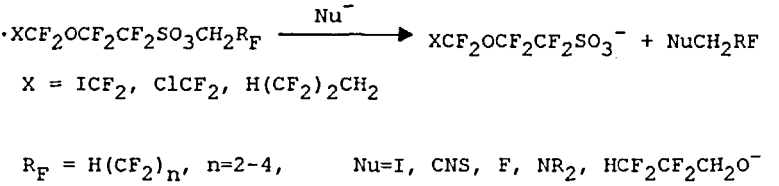
Table 1

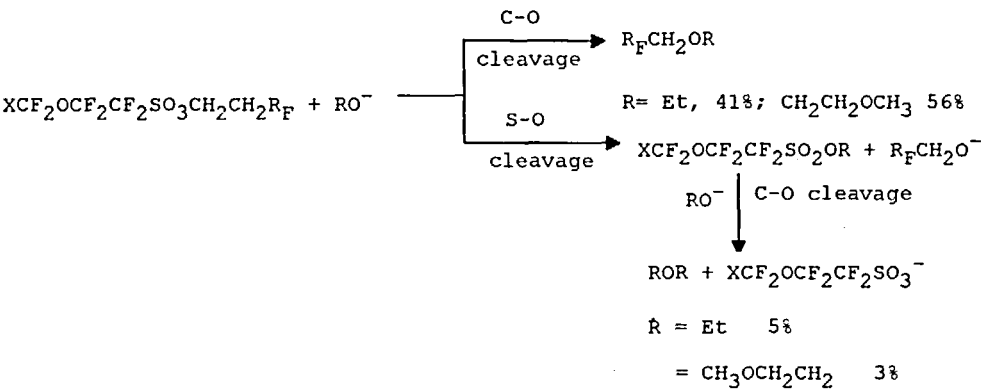
Reaction of fluoroethylene with sultone in the presence of KF and halogen



$CF_2=CF_2$	Cl_2	$ClCF_2CF_2OCF_2CF_2SO_2F$
	Br_2	$BrCF_2CF_2OCF_2CF_2SO_2F$
	$ICl(I_2)$	$ICF_2CF_2OCF_2CF_2SO_2F$
$CF_2=CFCl$	Cl_2	$Cl_2CFCF_2OCF_2CF_2SO_2F$
	Br_2	$BrClCFCF_2OCF_2CF_2SO_2F$
	ICl	$IClCFCF_2OCF_2CF_2SO_2F$
$CF_3CF=CF_2$	Cl_2	$CF_3CFClCF_2OCF_2CF_2SO_2F$
	Br_2	$CF_3CFBrCF_2OCF_2CF_2SO_2F$
$CF_2=CH_2$	Cl_2	$CH_2ClCF_2OCF_2CF_2SO_2F$
	Br_2	$CH_2BrCF_2OCF_2CF_2SO_2F$
$CFCl=CFCl$	Cl_2	$CFCl_2CFClOCF_2CF_2SO_2F$
$Cl(CF_2)_2CF=CF_2$	Cl_2	$Cl(CF_2)_2CFClCF_2OCF_2CF_2SO_2F$

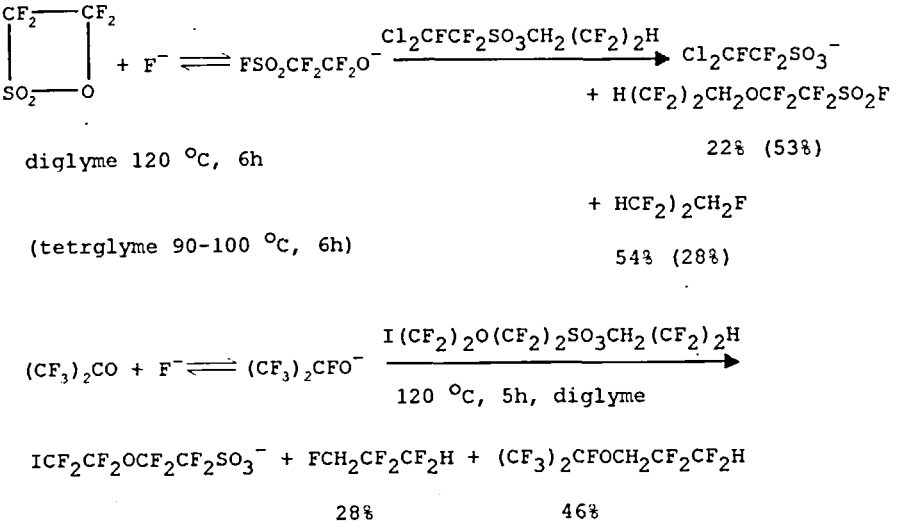
However, we found that the analogues triflates reacted with amines, halides, isocyanate and alkoxides ions to give only the products of C-O cleavage and even with ethoxide and $CH_3OCH_2CH_2O^-$, the C-O cleavage predominates and only a very minor proportion of S-O bond cleavage is observed[5].





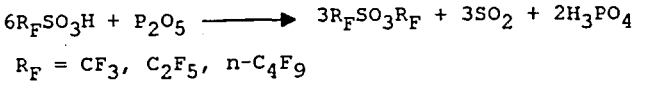
Perfluoroalkoxides, prepared *in situ* from the reaction of tetrafluoroethane β-sultone or hexafluoroacetone with fluoride ion in diglyme, underwent an attack onto the same sulfonic esters affording fluorinated ethers, as well as fluorinated alkanes. Both the products obviously resulted from the C-O bond cleavage of the esters by the nucleophilic attack of perfluoroalkoxide and fluoride ions on the alcoholic carbon, respectively.

In the more favorable conditions of the formation of perfluoroalkoxide ion, e.g. at lower temperature or using better solvent, the ether product may become the main product.

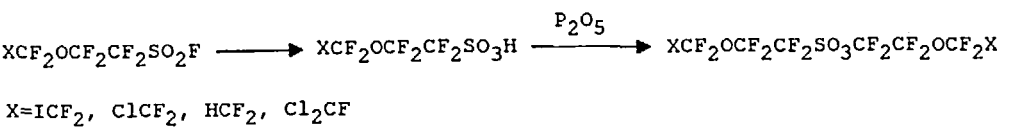


2. Synthesis and Nucleophilic Substitution of Perhaloalkyl Perfluoroalkanesulfonic Esters $R_FSO_3CF_2R_F$.

Although there are several approaches for the preparation of trifluoromethyl triflate($CF_3SO_3CF_3$)[7], the acid catalyzed decomposition of perfluoroalkanesulfonic anhydride seems to be the general and practical method developed by Commeyras and co-workers for the synthesis of fully fluorinated sulfonic esters[8]:

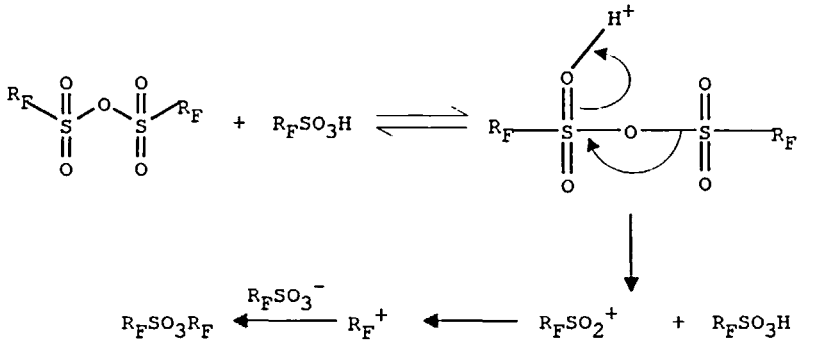


Using this method, long-chain polyfluoroalkyl perfluoroalkanesulfonates are obtained from the corresponding acids[9]:

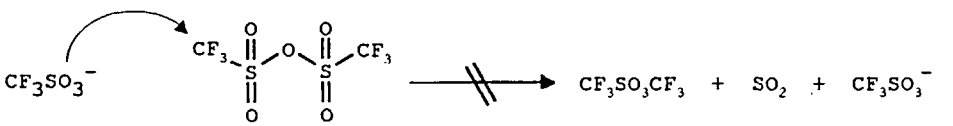


:r to obtain the esters rather than the anhydrides, the addition of a small amount of P_2O_5 and slower distillation are required.

The most probable mechanism of the formation of fully fluorinated sulfonic esters from the reaction of perfluoroalkanesulfonic anhydride with the parent or other acids is that the P_2O_5 or the acid promotes ionization of the acid anhydride to give the unstable cation $R_FSO_2^+$ and then R_F^+ reacts with the sulfonate anion to produce the desired ester[8b]:

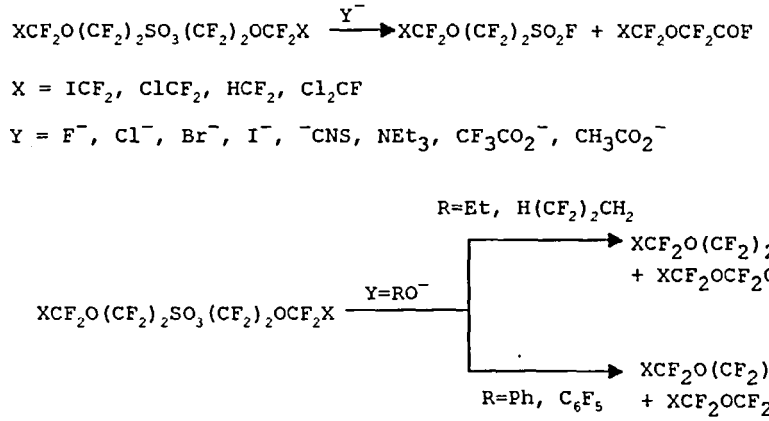


The previous postulated bimolecular mechanism for the formation of the esters involves the nucleophilic attack of the highly non-nucleophilic triflate anion on the CF_3 group of anhydride[8b] seems therefore unlikely[7]:

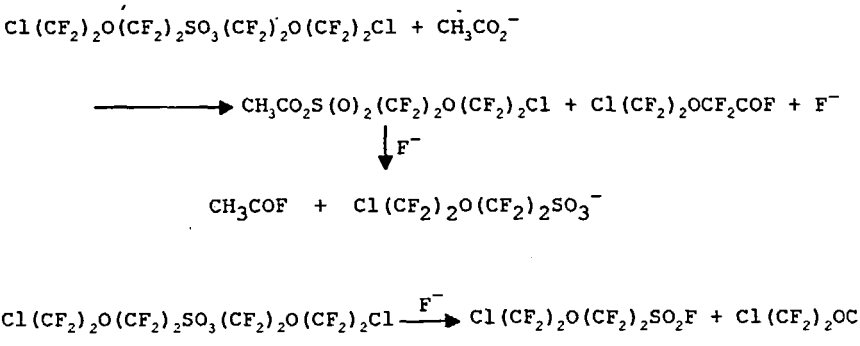


The only information existent before our work about nucleophilic substitution of fully fluorinated sulfonates was that trifluoromethyl triflate reacted with N-cyclohexenyl piperidine and dilute NaOH to give ketosulfone and salts, respectively. [8a, 10, 11].

We have systematically investigated the nucleophilic substitution of perfluoalkyl perfluoroalkanesulfonates and found that they behave quite differently from $R_FSO_3CH_2R_F$. The former react with nucleophiles to afford exclusively the S-O cleavage products, i.e. nucleophiles always attack the sulfur atom of the sulfonates[9].



Catalytic amounts of KF in diglyme cause a quantitative decomposition of the ester even at -50 °C to give the corresponding sulfonyl and acetyl fluorides(Y=Z=F), but KCl reacts similarly only at 100 °C and KBr only partially at 160 °C. These results indicate the following relative reactivity sequence: $F^- >> Cl^- > Br^-$. However, KI reacts anomalously, i.e. it readily induces a complete decomposition at room temperature to the same products which are accompanied by a small amount of iodine. The finding that addition of *p*-dinitrobenzene to the reaction system inhibits the formation of iodine but not of other products indicates that the iodide ion reacts with the ester through an ordinary S_N2 reaction on the sulfonyl sulfur and probably also by single electron-transfer pathway[9]. Since all the nucleophiles used attack the sulfur atom without exception to cause S-O bond cleavage with generation of F^-, the reaction products are derived from attack of the original nucleophile and of the F^- generated during the course of the reaction on the ester. The relative amounts of the various products depend upon the relative reactivities and the difference in concentration of the nucleophiles. For example:



Y. Kobayashi and co-workers[10] ascribed the S-O bond cleavage in these sulfonates to the effect of the strong electronegativity of R_F group, whereas Umemoto and Kuriu[12] ascribed it to the fact that R_FO^- is a better leaving group compared with $R_FSO_3^-$. However, as shown in the following equations, the sulfonates react readily with I^- whereas ethers do not. Therefore $R_FSO_3^-$ should be a better leaving group than R_FO^-. We explain the phenomenon by the shielding effect of the lone pairs of electron of two fluorine atoms and the perfluoroalkyl group even when the compound possesses a very good leaving group, such as $R_FSO_3^-$. This constitutes an additional example of the nonreactivity of highly fluorinated sp^3-hybridized carbon toward S_N2 attack[13].

$$R_FSO_3CH_2R_F + R_FO^- \rightleftharpoons R_FSO_3^- + R_FCH_2OR_F$$

$$R_FSO_3CH_2R_F + I^- \longrightarrow R_FSO_3^- + ICH_2R_F$$

$$R_FOCH_2R_F + I^- \not\longrightarrow R_FO^- + ICH_2R_F$$

In order to test this effect, difluoromethyl perfluoroalkanesulfonates have been synthesized and investigated. Difluoromethyl triflate was synthesized earlier from the insertion of difluorocarbene, generated by photolysis of difluorodiazirine into the O-H bond of triflic acid[14]. By using HCF_2SO_3H as a difluorocarbene precursor, difluoromethyl perfluoroalkanesulfonate can be obtained in 30-50% yields.[15]

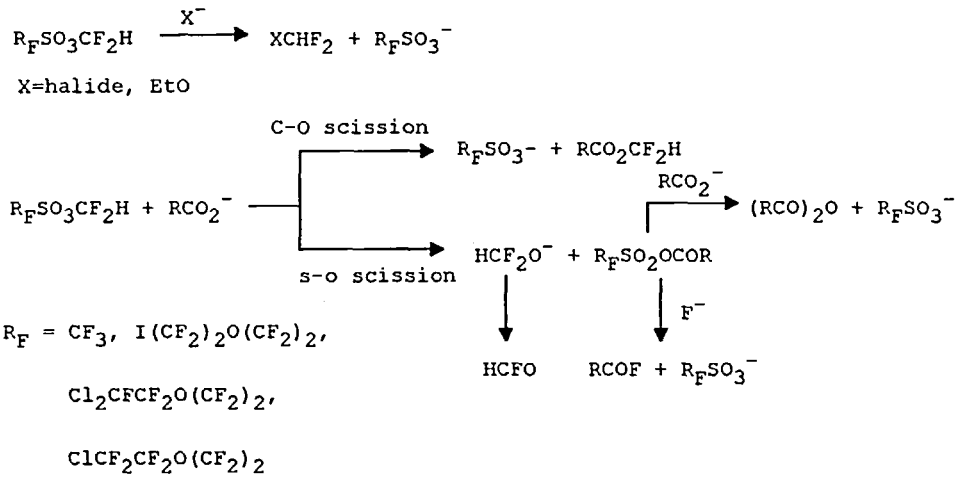
$$CF_3SO_3H + CF_2N_2 \xrightarrow{h\nu} CF_3SO_3CF_2H$$

$$R_FSO_3H + HCF_2SO_3H \xrightarrow[120\ ^oC]{P_2O_5} R_FSO_3CF_2H + HCF_2SO_3CF_2H$$

A more convenient method for preparing these esters involves utilizing readily available $FSO_2CF_2CO_2H$ as a difluorocarbene source in the presence of inorganic salt[16]

$$R_FSO_3H + FSO_2CF_2CO_2H \xrightarrow[70\text{-}100\ ^oC]{Na_2SO_4} \underset{40\text{-}50\%}{R_FSO_3CF_2H}$$

The difluoromethyl sulfonates react with halide X^- or ethoxide giving only HCF_2X and HCF_2OEt, respectively, resulting from C-O bond cleavage. Other reagents, such as RCO_2^- ($R=CF_3$, CH_3) or PhS^- can attack the carbon or sulfur of the ester to give the corresponding product of C-O and S-O cleavage, respectively[17].



The reaction of difluoromethyl sulfonate with KF is *ca* 40 times slower than that of methyl triflate. All these results indicate that the shielding effect caused by the two fluorine atoms in the difluoromethoxy carbon of difluoromethyl sulfonates to some extent prevents the nucleophilic attack on this carbon, although due to the presence of a hydrogen atom the shielding is not as complete as that in perfluoroalkyl perfluoroalkanesulfonates[17].

3. Synthesis and Nucleophilic Substitution of Phenyl, Polyfluorophenyl Perfluoroalkanesulfonates: R_FSO_3Ar (Ar=C_6H_5, C_6F_5, C_6F_4-Cl-*p*):

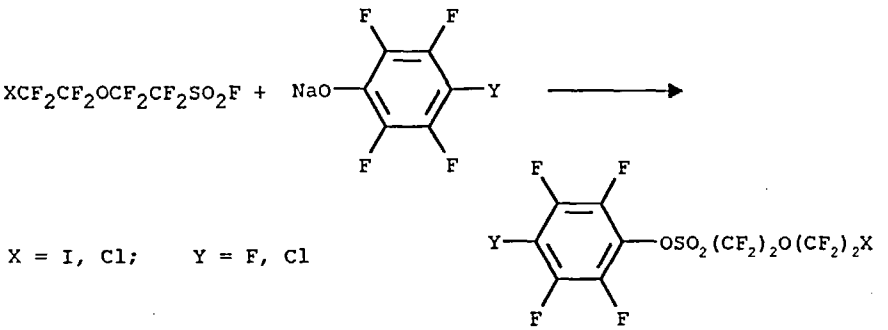
Phenols, like fluorinated alcohol, can react with perfluoroalkanesulfonyl fluoride to give the corresponding aryl perfluoroalkanesulfonates in 60-70% yields at room temperature in the presence of excess triethylamine. The amine is used both as a base and a solvent, which is unsuitable for the fluorinated alcohol as mentioned before[18].

$$R_FSO_2F + HOC_6H_4X \xrightarrow[r.t]{Et_3N} R_FSO_3C_6H_4X$$

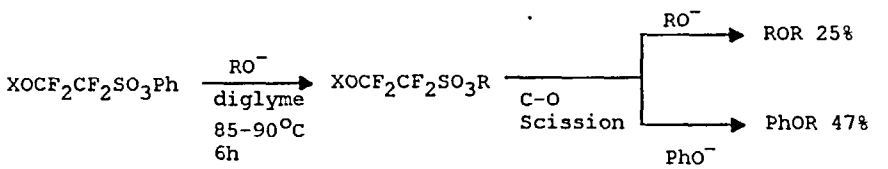
$R_F = H(CF_2)_2O(CF_2)_2$, $Br(CF_2)_2O(CF_2)_2$

X = o-Cl, m-OCH_3, H, 2,6-Me_2

The only perfluorophenyl perfluoroalkanesulfonate recorded in the literature before our work was $CF_3SO_3C_6F_5$, prepared from the reaction of CF_3SO_2Cl with C_6F_5OK in a sealed tube[19]. We found that polyfluoroalkanesulfonyl fluorides readily reacted with polyfluorophenoxide ion in diglyme, giving the corresponding sulfonates in high yields[20]:

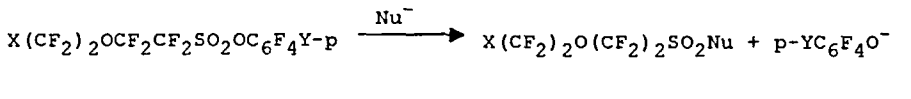


Judged from the products, symmetry and unsymmetry ethers, obtained in the reaction of phenyl perfluoroalkanesulfonate with fluorinated alkoxide in diglyme, the primary step must be the S-O bond cleavage due to the inability of attack on nonactivated sp^2-hybridized aromatic carbon[5].

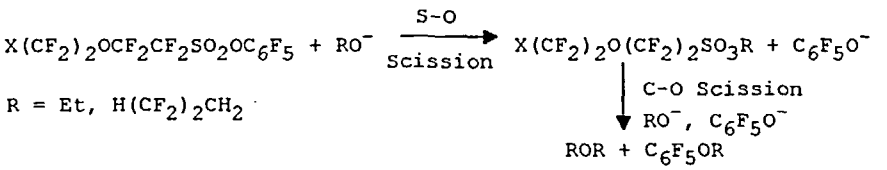


R = $H(CF_2)_2CH_2$

With regard to scission position of perfluoroaryl perfluoroalkanesulfonates, it was found that they reacted with nucleophiles such as halides, or alkoxides with lower rates to give S-O cleavage products[20]:

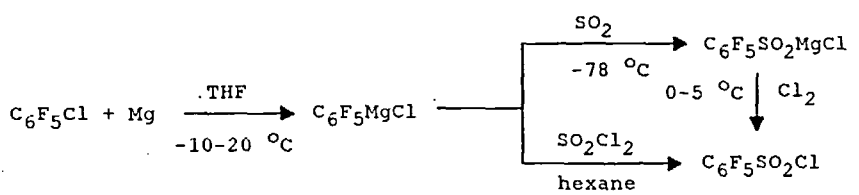


For example, pentafluorophenyl sulfonate reacted with KF only at 160 °C to give the corresponding aryl fluoride while with ethoxide both symmetric ether and aryl ether were obtained:

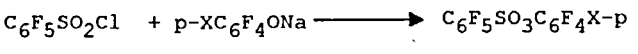


4. Synthesis and Nucleophilic Substitution of Polyfluorophenyl Perfluorobenzenesulfonates ($C_6F_5SO_3C_6F_4$-X-p, X = F, Cl)

In order to synthesize the target compound, we first modify the synthesis of pentafluorobenzenesulfonyl chloride by two methods: i.e. treatment of C_6F_5MgCl in THF at low temperature with SO_2 followed by chlorine gas or directly with SO_2Cl_2 in one pot[21] The yield of sulfonyl chloride achieved was 50-60% as compared with 35% given in the literature[22].

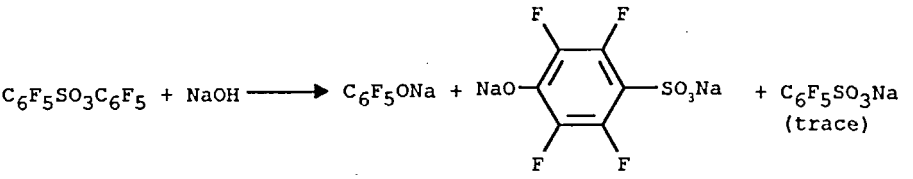


Treatment of sulfonyl chloride with sodium polyfluorophenoxide in diethyl ether gave the corresponding sulfonate in excellent yield:

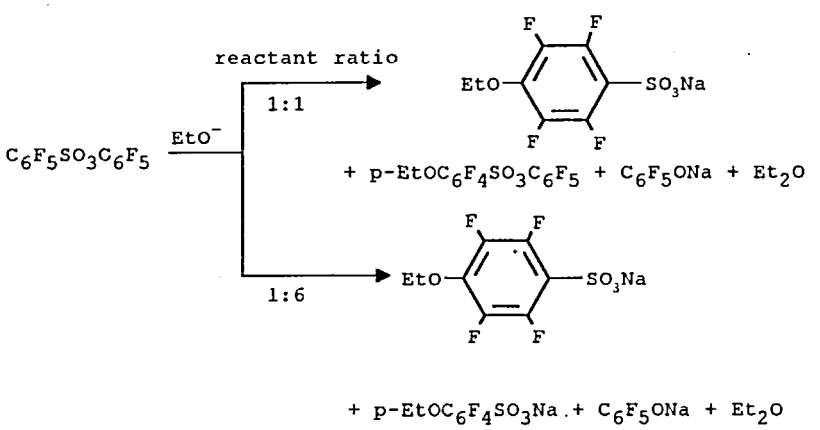


X = F, Cl, I

Complete alkaline hydrolysis of pentafluorophenyl perfluorobenzenesulfonate occurred only in the presence of excess NaOH at 100 °C for 10h giving the $C_6F_5O^-$ and disodium salt, p-$NaOC_6F_4SO_3Na$:



Nucleophilic attack of ethoxide on the same sulfonic ester gives, as usual, the ring substituted products in addition to hydrolysis products depending on the amounts of ethoxide used as shown in the following equation:



It was found that pentafluorophenyl perfluorobenzenesulfonate(**1**) reacts with NaI in diglyme at 80 °C for 8.5-12.5h giving biphenyl ethers **2** and **3**, pentafluorophenol **4** and sulfonate **5**:

$$\underset{1}{C_6F_5SO_3C_6F_5} + NaI \longrightarrow \underset{2}{p\text{-}IC_6F_4OC_6F_5} + \underset{3}{p\text{-}HC_6F_4OC_6F_5} + \underset{4}{C_6F_5OH}$$

$$(\underset{5}{p\text{-}C_6F_5OC_6F_4SO_3C_6F_5}) + SO_2$$

The relative amounts of the products were strongly dependent on the ratio of the reactants, **2** and **3** were the main products with a trace of **4** when the ratio was 1:3(**1**:NaI). Another compound **5** was isolated as the major product in addition to **2** and **3** when the ratio was 1:1 or 1:0.25(see Table 2). Interestingly, the same products **2** and **3** could be obtained from the reaction of **5** instead of **1** with NaI [reactant ratio 1:3(**5**:NaI)]:

$$p\text{-}C_6F_5OC_6F_4SO_3C_6F_5 + NaI \xrightarrow{\text{diglyme}} 2 + 3$$

Addition of a single electron-transfer scavenger, such as *p*-DNB or Bu^t_2NO or free radical inhibitors, such as *p*-hydroquinone(*p*-HQ) or oxygen to the reaction mixture in which reactant ratio was 1:3(1:NaI), caused a reduction in yield **2** and/or **3** to some extent (see Table 2). Among them, oxygen, hydroquinone and diallyl ether (DAE) (Entry 3, 6, 4, respectively) suppressed the yield of **2** significantly. In the case of reaction with reactant ratio 1:1(1:NaI), the suppression was not apparent except in the case of oxygen and hydroquinone, however, the yield of **5** increased dramatically when *p*-DNB and *p*-HQ were used as inhibitors. We have attempted to trap the $C_6F_5^{\cdot}$ with DAE (entry 4), however, no expected tetrahydrofuran derivative was detected, although the relative yields of **2** and **3** changed significantly.

All these results in addition to the known ability of iodide ion to act as an electron donor[23] seem to indicate the possibility of an electron transfer mechanism shown in the following equations:

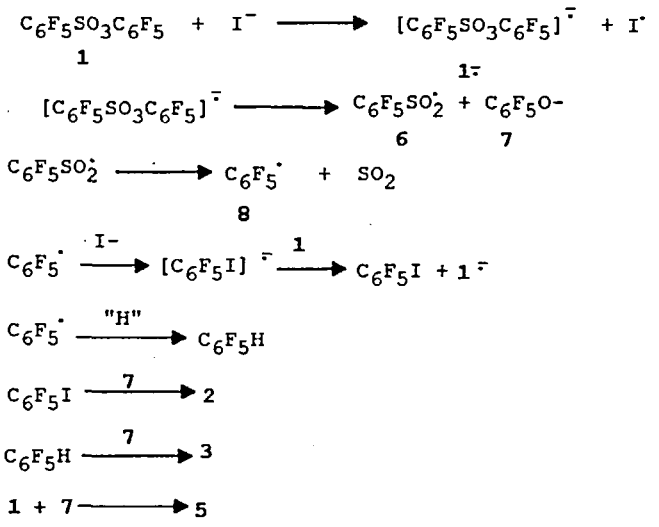


Table 2

Table Reaction of **1** and **5** with NaI at 80 °C[a]

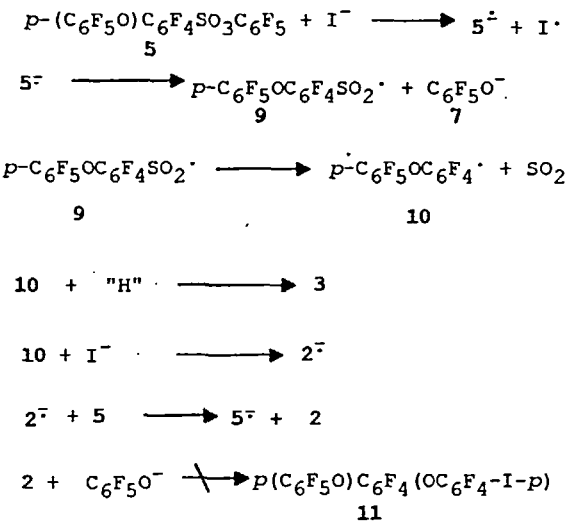
Entry	Reactants (molar ratio)	Additive (mol)	Reaction time(h)	2%[b]	3%[b]	5%[b]
1	**1**:NaI(1:3)	none	10	46.6	29.7	-
2		Bu^t_2NO(0.15)	11	47.5	15.8	-
3		O_2	10	10.3	31.2	-
4		DAE(2)	11	2.2	31.2	-
5		p-DNB(0.2)	10	48.3	17.6	-
6		p-HQ(0.2)	10	7.4	33.5	-
7	**5**:NaI(1:3)	none	12.5	13.9	23.6	-
8	**1**:NaI(1:1)	none	11	17.7	13.2	36.0
9		Bu^t_2NO(0.15)	10	12.0	9.0	34.8
10		O_2	10	2.0	12.0	41.5
11		p-HQ(0.2)	12.5	2.4	14.7	73.8
12		p-DNB(0.2)	11	21.5	7.2	62.2
13	1:NaI(1:0.25)	none	10	1.5	1.5	62.5

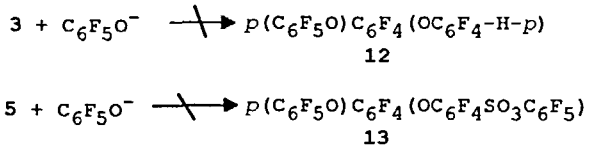
a: The conversion was complete, b: Isolated yield

The initiation step is a single electron-transfer process from the iodide to the sulfonate **1** with the formation of the radical anion $\mathbf{1}^{\dot{-}}$, which decomposes to give the pentafluorobenzenesulfonyl radical **6** and pentafluorophenoxide, **7**. The radical **6** is assumed to be a very unstable species which instantaneously fragments to afford the pentafluorophenyl radical, **8**. Radical **8** either reacts with iodide to give iodopentafluorobenzene or abstracts hydrogen from the solvent to give pentafluorobenzene. Nucleophilic attack of pentafluorophenoxide, (**7**) on iodopentafluorobenzene and pentafluorobenzene resulted in the formation of **2** and **3**, respectively. In the presence of a higher concentration of iodide ion(e.g. **1**:NaI=1:3), the decomposition of **1** goes to completion, thus **2** and **3** becoming the sole products. Whereas in the presence of a mole equivalent or catalytic amounts of NaI or of some inhibitors, radical **6** and consequently radical **8** were produced in a limited amount, most of the pentafluorophenoxide (**7**) produced underwent the nucleophilic substitution on **1** to yield **5**.

The formation of **3** from the direct nucleophilic attack of **7** on pentafluorobenzene has been reported in the literature[24]. That **2** from **7** and iodopentabenzene was clarified in a control experiment.

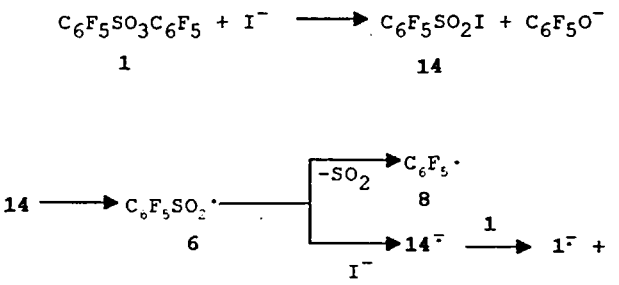
That **2** and **3**, as mentioned above, were also the products from the reaction of **5** can be explained by the following Scheme:





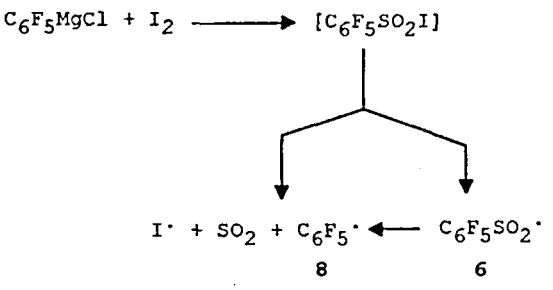
Compounds **2** and **3** are apparently obtained from the reactions of radical **10**, generated from the decomposition of **9**, with iodide or "hydrogen". Pentafluorophenoxide is unable to attack on **2** and **3** to give *p*-$(C_6F_5O)C_6F_4(OC_6F_4I$-*p*) (**11**) and *p*-$(C_6F_5O)C_6F_4(OC_6F_4H$-*p*) (**12**) respectively, because their para positions are occupied by an electron donating rather than electron accepting group. This also applies to the absence of **13**.

The initiation step can be accompanied by a mechanism other than SET, namely that pentafluorobenzenesulfonyl iodide(**14**) may be an intermediate(cf. the recent discovery of the existence and "pure" radical properties of analogues R_FSO_2I)[25]. This intermediate may be formed from the attack of iodide on the sulfur of **1**. The iodide **14** could then decompose to give **6** which either affords **8** after elimination SO_2 or captures iodide to form radical anion $\mathbf{14}^{\bullet-}$ in the presence of I^-. Pentafluorobenzenesulfonyl iodide (**14**) may generated from $\mathbf{14}^{\bullet-}$ and **1** by an electron transfer process:



In order to determine the role played by the intermediate **14** in the reaction, we attempted to synthesize this unknown compound. Treatment of a THF or ether solution of $C_6F_5SO_2MgCl$ with 1 mol equiv. of I_2 at 40 °C for 3h gave no desired sulfonyl iodide but $(C_6F_5)_2SO_2$ and C_6F_5I in a ratio of 1:5. Using CH_2Cl_2 as the solvent led to a product ratio

of 1:2. Attempt to detect or trap the radicals **6** and **8** met with failure. The products obtained may be resulted from the very fast radical decomposition of sulfonyl iodide which is even more unstable than its analogues R_FSO_2I[25]:



We believe that pentafluorobenzenesulfonyl iodide, generated by SET and/or S_N2 on sulfur in the initiation step followed by SET, plays an important role especially in the reaction of **1** and **5** with a higher concentration of iodide. The absence of $C_6F_5SO_2C_6F_5$ and C_6F_5I in the reaction of **1** with NaI may be ascribed to the fast consumption of C_6F_5· and easy nucleophilic substitution of C_6F_5I by $C_6F_5O^-$.

5. Summary

Due to the unique properties of C-F bond, most of the synthetical methods of fluorinated sulfonic esters are different from those of non-fluorinated analogues. For example, 1H,1H polyfluoroalkyl perfluoroalkanesulfonates, as mentioned above, can not be prepared in the presence of excessive base at room temperature. Ordinary aliphatic sulfonic anhydrides are usually obtained from the corresponding acids in the presence of P_2O_5 whereas fully perfluoroalkanesulfonic esters rather than anhydrides are formed conveniently in the presence of a small amount of P_2O_5. Four kinds of perfluoro- or polyfluoroalkanesulfonic esters, namely, $R_FSO_3CH_2R_F$, $R_FSO_3CF_2R_F$, $R_FSO_3C_6F_5$ and $C_6F_5SO_3C_6F_4X$-p(X=F, Cl) accordingly have been synthesized. Nucleophilic substitution of 1H,1H perfluoroalkyl perfluoroalkanesulfonic esters, $R_FSO_3CH_2R_F$, give predominant (if not sole) products of C-O cleavage, while of fully fluorinated sulfonic esters,

$R_FSO_3CF_2R_F$, afford exclusively the S-O cleavage products. Perfluoroaryl perfluoroalkane- or perfluorobenzenesulfonates react with nucleophiles leading also to S-O cleavage. It was found that the relative reactivity in nucleophilic substitution on the sulfur atom of the fluorinated ester decreases on decreasing the electron-withdrawing properties of the alkoxy or aryloxy group in the following order[20, 26]:

$R_FSO_3Ar<R_FSO_3Ar_F<R_FSO_3R_F$

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