Journal "Fluorine Notes", Volume # 3(28), May - June 2003

Perfluoroalkanesulfonic acids derivatives: synthesis and application

G.G. Furin

Novosibirsky Organic Chemistry Institute of N.N.Vorozhtsov , Siberian department of Russian Academy of sciences,

Ak. Lavrentiev avenue, 9, Novosibirsk, Russia, 630090

Fax: +7 3832 344752

E-mail : ***furin@nioch.nsc.ru***

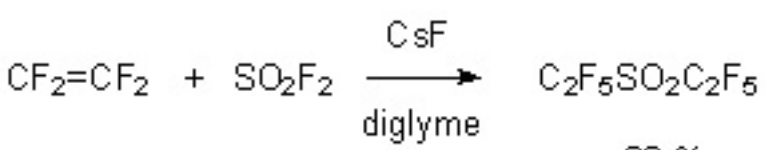
Abstracts

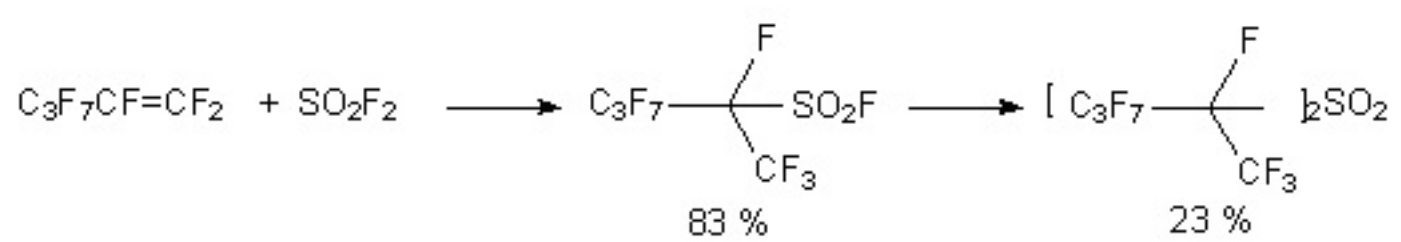
Information of the last 10 years regarding methods of synthesis and properties of perfluoroalkanesulfonic acids and some of its derivatives is listed and analyzed here. The opportunities of using the perfluoroalkane halides and syntons on the basis of perfluoroalkylsilicon derivatives for these purposes are uncovered. The main attention is paid to practical aspects of perfluoroalkanesulfonic acids salts and bis(perfluoroalkylsulfonyl)imides using as catalysts of different processes, electrolytes, ionic liquids and N-F bond containing compounds as mild fluorinating reagents. The ways of using of perfluoroalkanesulfonic acids derivatives in organic synthesis are discussed.

Table of contents

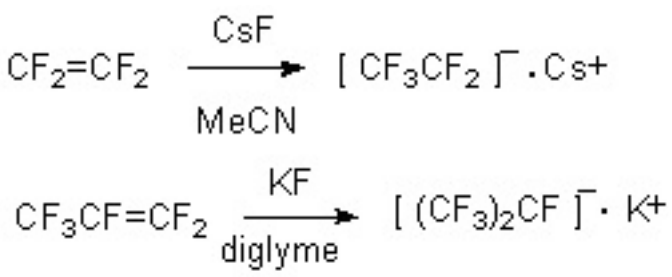
2.3. The reactions of fluorine-containing C-nucleophilic compounds with sulphur halogenderivatives .

Derivatives of quadrivalent and hexavalent sulphur, containing haloid atoms, exchange halogen groups for different functional ones when nucleophilic reagents are acting. As a result of this the main task is the generation of fluorine-contraining carbanions and their introduction into reactions with sulphur compounds. One of the approaches which are based on one of available and produced compounds is generation of carbanions out of perfluorolefines under the action of alkali metals fluorides. Thus sulfuryl fluoride joins to fluoroolefines in presence of alkali metals fluorides in polar aprotic solvent, producing respective sulfofluorides or sulfones [59].





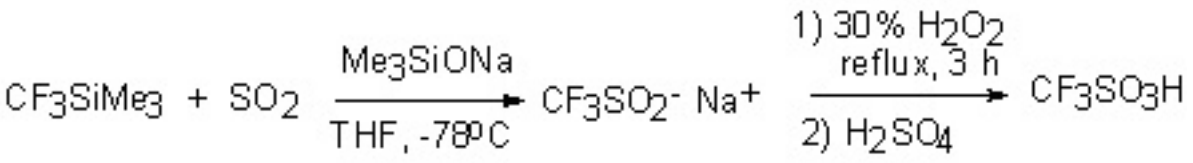
The mechanism of these changes is in initial addition of fluoride-ion with fluoroolefine and generation of carbanion, reacting with sulfuryl fluoride.



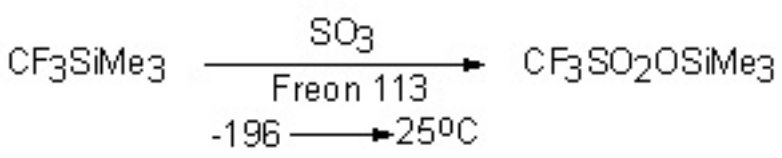
Similarly, perfluoro-isopropylsulfonyl fluoride with 72% yield was obtained from hexafluoropropylene and sulfuryl fluoride at the presence of KF [60].

2.4. The application of trimethyl(trifluoromethyl)silane in the synthesis of trifluoromethane-sulfo-acid and its derivatives.

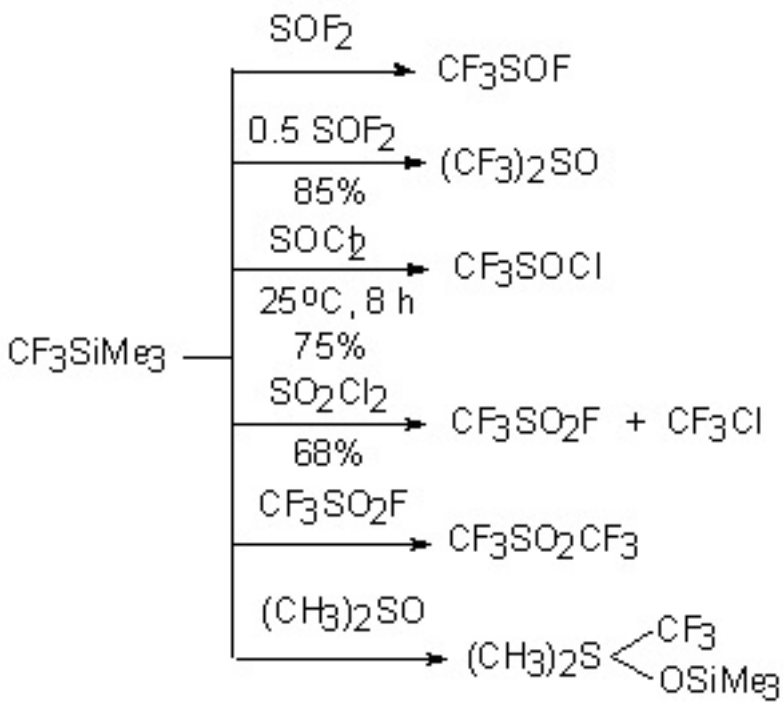
The other method is using of synthones on the base of IV group elements. Thus if interaction of trimethyl(trifluoromethyl)silane with SO_2 during absence of anionic initiators doesn't take place then in presence of fluoride-ion sources (for example, tetrabutylammonium fluoride (TBAF)), the formation of tetra(n-butyl)ammonium trifluoromethanesulphite [61] takes place. It was found that Me_3SiONa in tetrahydrofurane was able to employ instead TBAF. The further oxidization of this salt by 30% hydrogen peroxide results in formation of trifluoromethanesulfonate or free trifluoromethanesulfo-acid. Me_3SiONa is rather effective as initiator of this reaction. Though total yield of trifluoromethanesulfo-acid is not high (up to 30 %). At the same time this method can be competitive regarding electrochemical fluorination method.



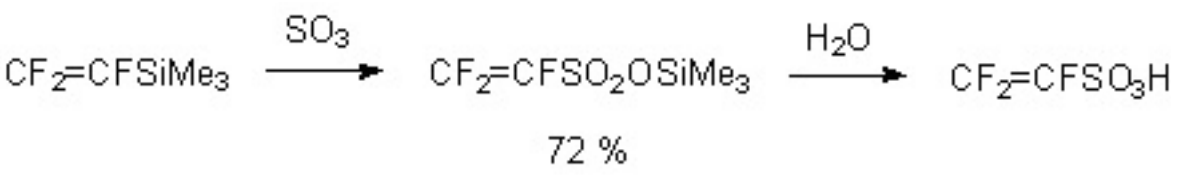
In the work [62] it was shown that reaction CF_3SiMe_3 with γ-SO_3 in freon 113 runs rather easy at temperature gradient from –196 to 25°C with formation of trimethylsilyl ester of trifluoromethanesulfo-acid.



It's natural that CF_3SiMe_3 at conditions of nucleophilic catalysis by fluoride-ion react with sulfo-compounds containing labile atom of halogen. Thus during reaction with SOF_2 (mole ratio of reagents 1:1 and 1:2) CF_3SOF and $(CF_3)_2SO$ was produced. Similarly this system reacts with SOCl and SO_2Cl_2 [63].



Analogously to this method trifluoroetylenesulfo-acid can be obtained [64].



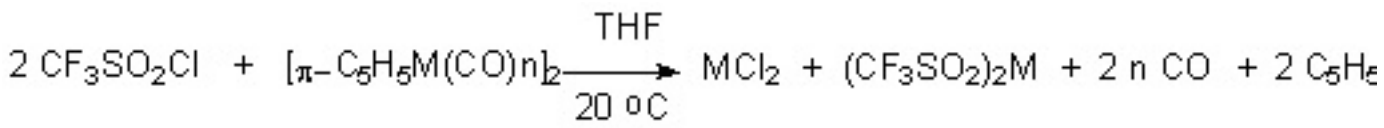
3. The synthesis and properties of perfluoroalkanesulfo-acids derivatives.

3.1. Haloidanhydrides of perfluoroalkanesulfo-acids

The main derivatives of perfluoroalkenesulfo-acids are its haloidanhydrides. Their chemistry is rather representative. That's why we give only such examples, that result in formation of strong acids and complexes.

Most reactive derivatives of perfluoroalkenesulfo-acids are their chloroanhydrides. The efforts for creating simple and convenient method of transforming corresponding perfluoroalkenesulfo-acids into their chloroanhydrides were undertaken. The most convenient method is interaction of for example trifluoromethanesulfo-acid with mixture of PCl_3 and Cl_2 (1:1) or PCl_3, $POCl_3$, Cl_2 (1:1,9:1,1) at 81 ^oC in 4 hours. The yield of CF_3SO_2Cl was 89,7 % [65]. Trifluoromethanesulfonyl fluoride was used for synthesis of C-H acids : $(CF_3SO_2)_2CH_2$ [66] (the review of synthesis methods

is listed in the work [67]), $(CF_3SO_2)_3CH$ [68] :

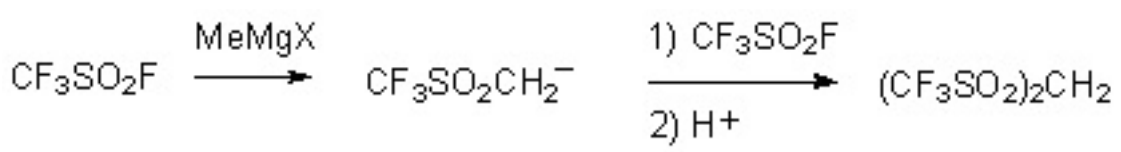


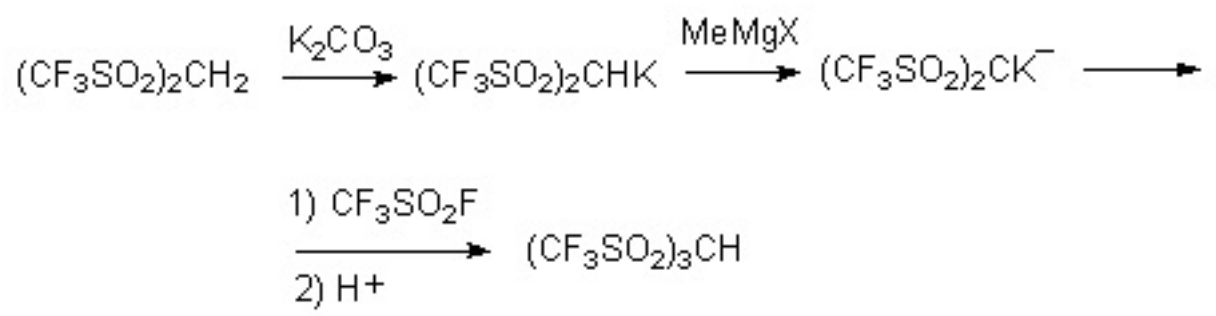
M = Mo, Fe, Ni

n = 1, 2, 3

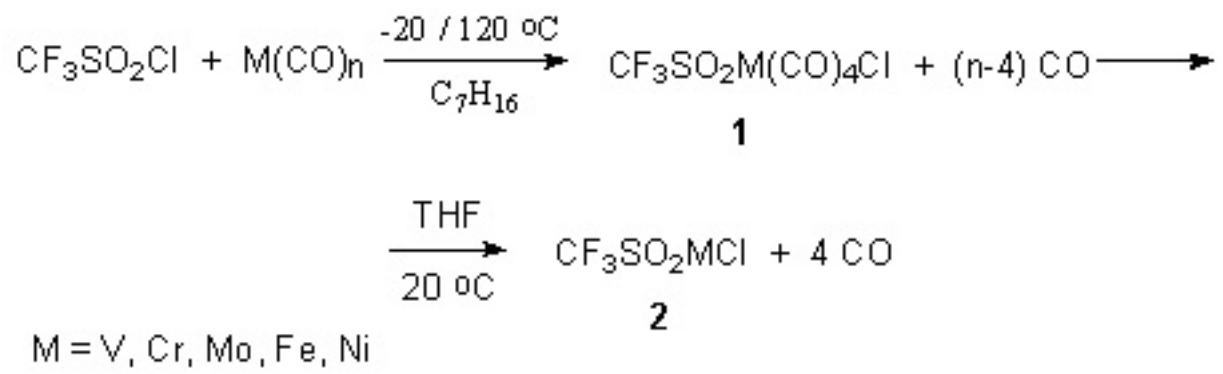
Tris(trifluoromethanesulfonyl)methane - is a strong acid in gaseous phase [69].
During action of methyllithium perfluoroalkylsulfonylchloride in diethyl ether the lithium salt of tris(trifluoromethanesulfonyl)methane is formed with the yield 31 % while interaction with anhydrous ammonia in isopropyl ether produces trifluoromethanesulfonamide [70]. During interaction of perfluoroalkanesulfonyl fluorides with dimethylamine or halogensulfonamides the fluorinated sulfonamides $X(CYZ)_mSO_2N(CRR^1R^2)_2$ (X = H, F, Cl; C_nF_{2n+1}; m = 1-9) with nearly quantitative yield are produced [71]. These compounds are used as difficult-to flame dissolvents in electrolytes of electrochemical elements, consisting of cathode, anode, separator and electrolyte. Particularly lithium batteries and super condensers are used as such elements.

Since the bond sulfur-chlorine in trifluoromethanesulfochloride is easily is exposed to nucleophilic agents action compare to sulfur-fluorine bond the main chemistry of this class is developed on perfluoroalkenesulfochlorides. It is shown [72-73], that trifluoromethanesulfochloride reacts with bis(cyclopentadienyl)metal carbonyles in polar medium like tetrahydrofurane and metal complexes are formed .

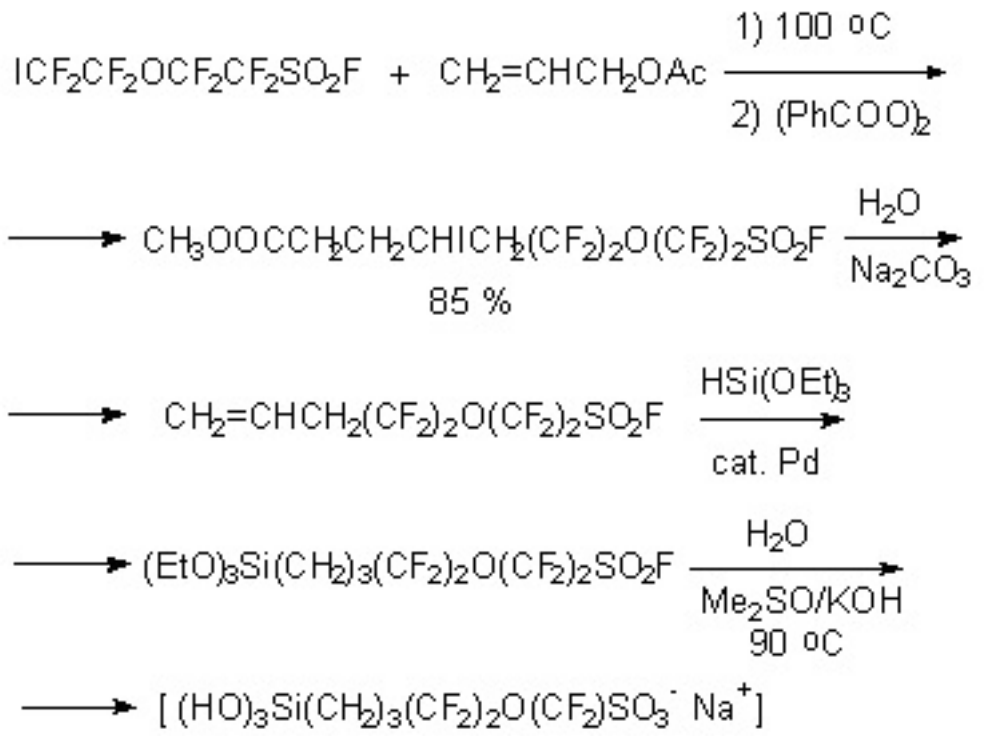




At the same time the interaction of perfluoroalkenesulfochlorides with carbonyls of V-, VI [74], VIII [74] groups metals results in formation via unstable compound **1** of sulfinate-O,O'-metalchlorides **2.**



Direct hydroxylation of olefine, obtained by reaction of perfluoroiodide and allyl-acetate, with further hydrolysis by $HSi(OEt)_3$ action in presence of palladium catalyst produces sulfofluoride.



The last one at hydrolysis allows to obtain new effective reagent (perfluorosulfonate/trisilanol) which effective as catalyst of alkenes isomerisation, alkylation and acylation reactions etc [75].

Reaction	Product yield, %		
	cat.	Nafion resin NR 50	Amberlyst 15
Alkylation of toluene by heptene (100°C, 2 hours)	99	5	13
Butene-1 isomerization (50°C)	95	14	47
Acylation of m-xylene (140°C, 6 hours)	89	90	-
Alkylation of benzene by dodecene-1 (80°C, 1 hour)	43	3	5
Constant ($[H^+]^{-1}hours^{-1}$) of α-methylstyrene dimerization (50°C)	1000	0,1	0,6

to be continued