

Perfluoroalkanesulfonic acids derivatives: synthesis and application

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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.

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1. Introduction. The role of organic compounds in the synthesis of semi-products and the creation of new materials on their basis

During last decades the organofluorine compounds chemistry had gained a rather high rating due to its wide range of practical use. For example we'll point out the problems of ozone-safe compounds and artificial blood substitutes. The modern conception of researches reaching the level of international cooperation is being formed. Today it is a question of working out the uniform approaches to studying of fundamental bases of organic framework perfluorination influence on its physical and chemical characteristics.

It's natural because at every stage of technical progress the role and direction of fundamental researches to a great extent is initiated by society's needs in new materials, which are impossible without creation of fundamentally new materials with advanced consumer characteristics, which are able to work in much more severe conditions. In this regard fluorine-containing materials have an exceptionally important role, they can't be found in nature but they are able to bring into molecules new fundamentally different from other elements characteristics. However the understanding of functional changes in the structure of organic molecule at introduction the fluorine atoms into it is not sensible and deep enough. How do the fluorine atoms influence the characteristics of molecule in whole? How do such compounds function in the organism of animal and man? How do they influence the vital functions of plants? Nevertheless the scientific approaches allowing to evaluate these questions and give a definite explanation has been already created. The production of fluorocontaining materials depends not only on the level of our knowledge but also on perspective of practical using, which is determined by the development of technical progress. The correct placing of priorities, the choice of key base compounds as a basis for production of materials, the perfection of technological decisions determines to great extent the tasks of production. Their solution allows to satisfy the needs of society on the base of basic materials fast.

The development of methods of obtaining of organic compounds with certain structure and specific characteristics is one of the central problems of organic chemistry. This is particularly important conformably to new classes of organic compounds, where nowadays the information regarding their characteristics which is available may be limited or inessential. Because of this the organic compounds, containing fluorine atoms, require rapt attention and conduction of wide researches owing to their specific influence that fluorine atoms have on characteristics of these compounds [1,2]. For the past years the understanding of fluorine compounds characteristics uniqueness has increased and many new tendencies of using appeared. The introduction of fluorine atoms into organic compounds is of big scientific and practical interest when creating new high-performance biologically active compounds and materials, possessing unique properties [3]. It is stated that these compounds possess many important aspects for practical application. The conduction of these researches has noticeably improved synthetic fluorine chemistry: plenty of new reagents and methods of synthesis were developed.

In the view of practice it is very important for synthesis methods of necessary fluorocontaining compounds with certain functional fragments to be noted for the simplicity of carrying out the process regarding reagents as well as conducting technique, for the good reproducibility, yields high enough and regio-selectivity. This is a guarantee of finding a way for study of chemical characteristics of new synthesized compounds as well as discovering of their application perspectives. In particular new materials, possessing the complex of unusual

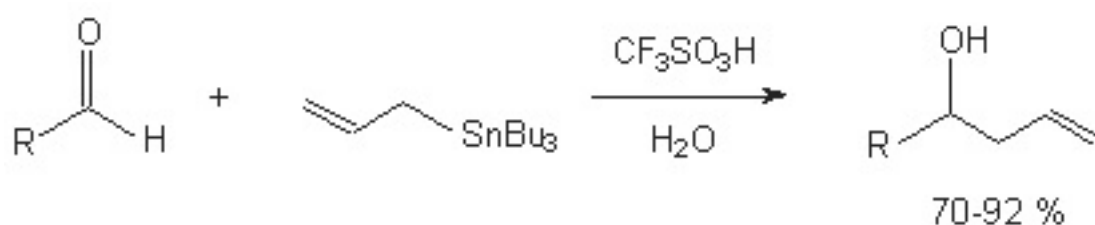
characteristics, enhancing the organic system itself are the most important task for synthetics chemists.

The author realizing that to cover all the tendencies of synthesis of fluorocontaining hexavalent sulfur derivatives is impossible concentrated his attention on systems, containing perfluoroalkylsulfonyl groups as substitutes.

Perfluoroalkanesulfonic acids are widely used in organic synthesis and their salts as intermediates in surface active compounds synthesis. Perfluorinated derivatives of alkanesulfonic acids are able to form stable foam even in the presence of strong oxidant like concentrated chrome and sulphuric acid [4]. Due to this characteristic they are efficiently used as additives for electrolytes at electrochemical refining of nickel and chrome. Surfactants on the basis of perfluoroalkanesulfonic acids are very efficient agents, lowering the surface tension (to 15 din/cm). Low concentrations necessary for such efficiency of these surfactant give big advantages in respect to environment. These compounds decrease the surface energy of plastics and add characteristics for unfriiction, inadhesiveness and antisoiling properties to the compounds. Such solutions are produced in commercial quantities and have found an application for practice. Perfluorinated bi-functional organic acids are rather strong ones and can be potentially used for creating of ingredients of electrolytes of fuel elements, particularly lithium batteries and accumulators.

The organization of surface active materials production on base of perfluoroalkanesulfonic acids will allow to obtain the characteristics noticeably higher than such ones for perfluorinated carboxylic acids which field of application is now huge and growing all the time. These surface active materials will find their application as new extracting materials and metal-dressing for non-ferrous metallurgy, for creation of fire-fighting compositions, they also can be used during electrofining of metals, creation of effective detergents, high-temperature lubricants, for natural materials treatment particularly cotton and cellulose for the purpose of their incombustibility, in the technology of semiconductor devices for the purpose of lowering the surface tension of liquids.

Perfluoroalkanesulfonic acid is one of the strongest acid and it is successfully used as catalyst of different chemical processes, at that in a number of cases and new reactions. For example, as catalyst for reactions of allyltributyltin with carbonyl compounds, giving homoallyl alcohols [5].



Trifluoromethanesulfonic acid is resistant to fluorine action, that is used for conducting of the direct fluorination process of aromatic compounds [6].

2. Perfluoroalkanesulfonic acids syntesis.

2.1. *Electrochemical fluorination of hexavalent sulfur derivatives.*

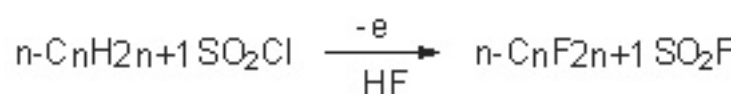
Electrochemical fluorination method of sulfur organic derivatives was the main one, used for obtaining of perfluorinated alkanesulfonic acids syntesis [3]. As a rule in this case the source material is sulfur hydrocarbon derivatives. Among important practical applications of electrochemical fluorination method there is working-off of obtaining method of perfluoroalkanesulfofluorides and perfluoroalkanesulfonic acids, starting from derivatives of alkanesulfonic acids, because the derivatives of perfluoroalkanesulfonic acids have special

$$\text{n-C}_7\text{H}_{15}\text{SO}_2\text{F} \xrightarrow[\text{HF}]{\text{e}} \text{n-C}_7\text{F}_{15}\text{SO}_2\text{F} \xrightarrow{\text{NaOH}} \text{n-C}_7\text{F}_{15}\text{SO}_3\text{Na}$$
$$\text{FSO}_2(\text{CH}_2)_4\text{SO}_2\text{F} \xrightarrow[\text{HF (0.25 molM)}]{5.5 \text{ A, } 0.25 \text{ A/dm}^2} \text{FSO}_2(\text{CF}_2)_4\text{SO}_2\text{F} + \text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{F} +$$

$$\text{CF}_3(\text{CF}_2)_2\text{SO}_2\text{F} + \text{FSO}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F} + \text{C}_2\text{F}_5\text{SO}_2\text{F} + \text{CF}_3\text{SO}_2\text{F} + \text{C}_4\text{F}_{10} + \text{SO}_2\text{F}_2$$

$$\begin{array}{ccccccc} & & 28 \% & & 1 \% & & \\ & & & & & & \\ & & 0.4 & & \text{traces} & & \\ & & 0.3 \% & & 0.3 \% & & 0.1 \% & & 7 \% \end{array}$$

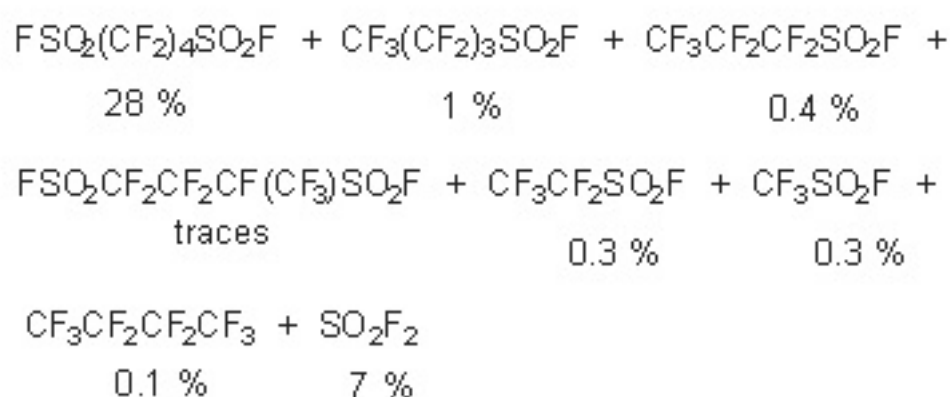
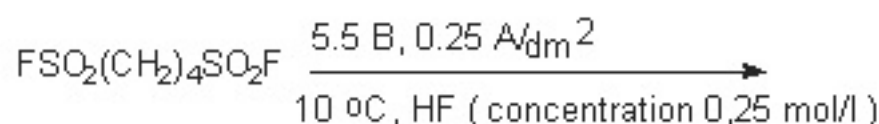
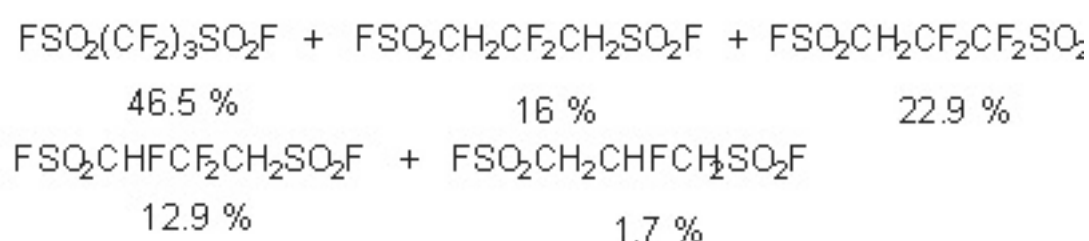
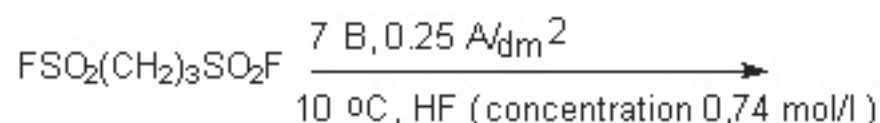
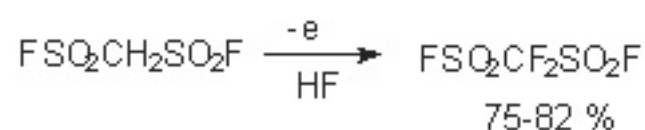
Chloronhydrides of alkanesulfonic acids can be used as start substartes too [10b].



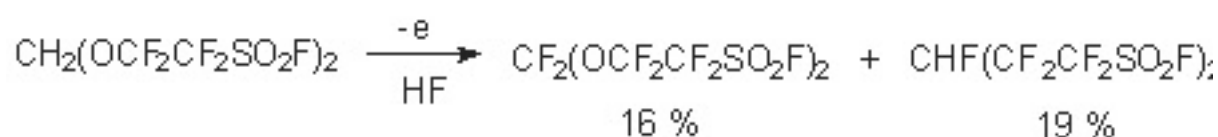
n	1	2	3	4	5	6	7	8
Yield, %	97	79	68	58	45	36	31	25

If there are two SO₂F groups in molecule, for example CH₂(SO₂F)₂ [11-16], 1,2- and 1,3-propanedisulfonylfluorides, electrochemical fluorination in anhydrous fluoride hydrogen (current density 0.2 A/m², voltage 3.75-6 V) results in formation of base products with yields high enough. Perfluoroalkanesulfonic acids fluoroanhydride is obtained by implication, subjecting the appropriate acid to electrochemical fluorination in electrolyzer with electrodes made from nickel in anhydrous HF. Thus fluoroanhydride of difluoromethanesulfonic acid is obtained with the yield 75-82% (effectiveness of using electric energy is 33%).

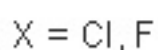
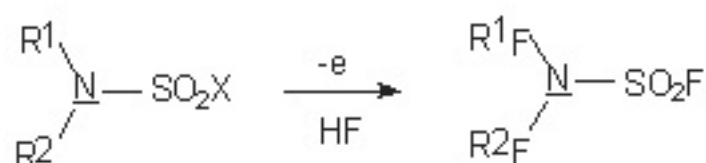
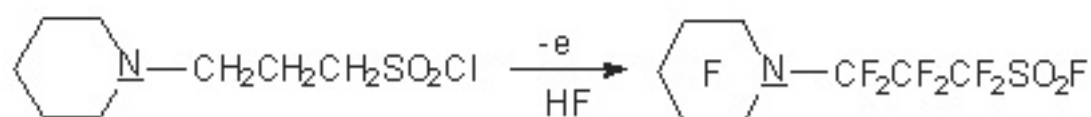
Fluoroanhydrides of 1,3-propane-, 1,3-butane- and 1,4-butanedisulfo-acids are obtained analogously to this [17,18]. It is determined that during the electrochemical fluorination process anode corrode 40 times faster than cathode, at that the corrosion is growing arcwise with the growth of anode tension. Because of this the development of convenient method of synthesis of dialkanesulfonic acids fluoroanhydrides is an important industrial task.



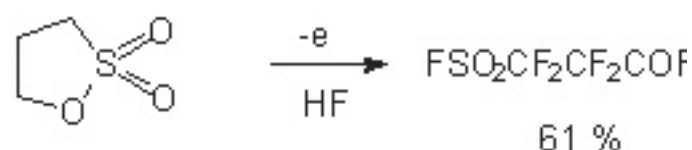
At that the character of alkyl row doesn't matter.



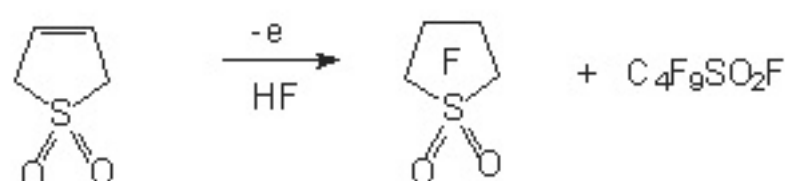
Nitrogen-containing functional group in linear part of alkanesulfonic acid doesn't influence in principle the passing of the electrochemical fluorination process [17-20].



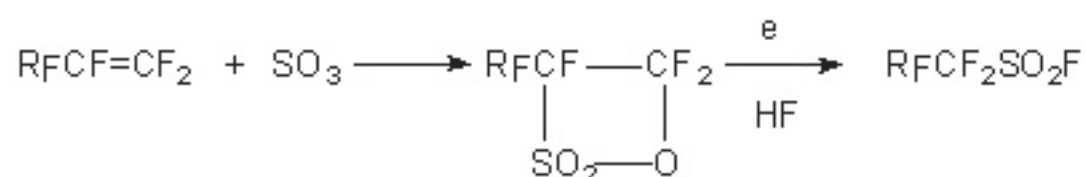
During the electrochemical fluorination of sultones the uncovering of cycle and fluoroanhydrides of sulfonic and carboxylic acids formation take place. Thus 1,3-propanesultone at electrochemical fluorination is turned into fluoroanhydride of β -fluorosulfonylbutanoic acid [21].



In the case of 2,5-dihydrothiophene-1,1-dioxide the uncovering of the cycle with the formation of perfluorobutansulfonic acid fluoroanhydride but with preserving of heterocyclic system takes place [22].



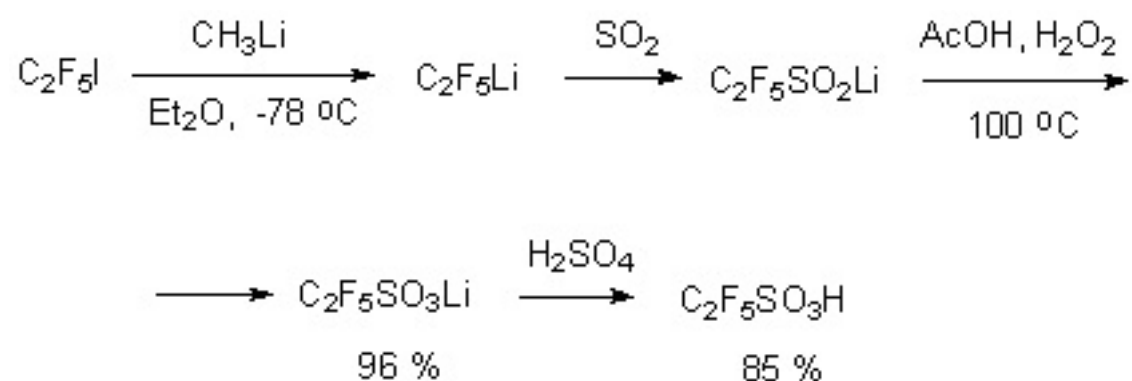
β,β -Difluoro β -sultones, which are obtained from commercial available perfluoroolefines, during electrochemical fluorination yield appropriate perfluoroalkanesulfonyl fluorides [23].



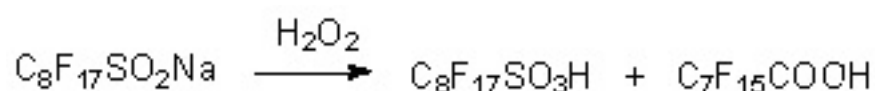
In the case of sultone on the basis of tetrafluoroethylene perfluoromethanesulfonyl fluoride, COF_2 , CH_4 and SO_2F_2 are obtained. This method is used for obtaining of perfluoroethanesulfonyl fluoride and perfluorobutansulfonyl fluoride.

2.2.. The use of perfluoroalkyl halides in the synthesis of perfluoroalkanesulfonic acids

One of the methods of perfluoroalkanesulfonic acids obtaining extensively used in the chemistry of organofluorine compounds is the transformation of perfluoroalkyliodides. As the iodine movability in these compounds is not high enough, at first lithium salts are obtained, which react with sulfur dioxide, producing lithium salts of perfluoroalkansulfinic acid. The last mentioned oxidize in acetic acid at temperature of 100 °C by forming lithium salt of perfluoroalkanesulfonic acid. Usually such acids is obtained by reaction of lithium salt with concentrated sulphuric acid [24].

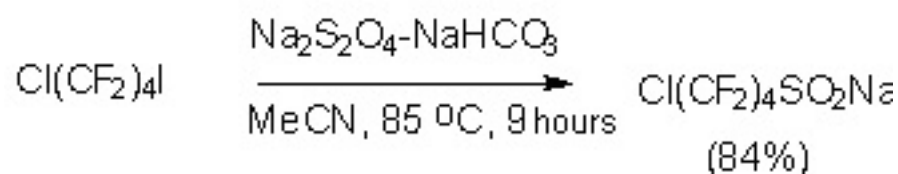


However this method is used only for lower acids, even perfluoropropyl iodide doesn't produce the base product. Here the limiting stage is the obtaining of trifluoromethyl-lithium and pentafluoroethyl-lithium. The oxidization of perfluoroalkansulfinic acid salts can be conducted by hydrogen peroxide. However in this case the formation of perfluoroalkancarboxylic acid is registered with limited for one unit carbon backbone chain [25].



The use of perfluoroalkyl iodides in the synthesis of sulfinic acids is inseparably linked with works of Chinese researchers on sulfinatehalogenation of halogen containing hydrocarbons. Thus they were the first to state, that perfluoroalkyl iodides are able to react with $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of Lewis' basis (NaHCO_3 , Na_2CO_3) in aprotic solvents (DMF, N-methylpyrrolidone, HMTPA) at 40-120 °C and at the reaction period 1-10 hours, the result of this was the synthesis of sulfinic acid derivatives. The review of perfluoroalkanesulfinate chemistry, including their obtaining, characteristics, reactions, and application is given in the works [33-35].

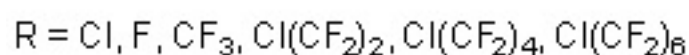
Using the cheap reducer (for example $\text{Na}_2\text{S}_2\text{O}_4$) one can obtain salts of perfluoroalkansulfinic acids from perfluoroalkyl halides ($\text{R}_\text{F}\text{X}$, where $\text{X}=\text{Br}, \text{I}$, $\text{R}_\text{F}\text{CCl}_3$) in mild conditions. The fact, that this method is extensively used for carrying out the reactions of mentioned salts with olefins, dienes, acetylene derivatives and aromatic compounds is more important. Along with that the present system is effective mainly for polyfluorinated alkyl halides [27]. Bromine and iodine situated in perfluorinated carbon backbone chain are easily replaced and base product is formed with high yield. In future such works were carried out by other researchers, who confirmed the effectiveness of this methodology [36-50].



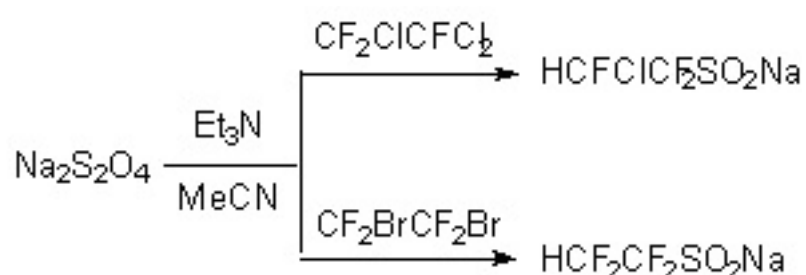
Later it was shown that another sulfur compounds, possessing nucleophilic properties, are able to react with perfluoroalkyl iodides forming salts of perfluoroalkansulfinic acid (table 1) [42,51-54]. Obviously, these reactions pass according to one-electron transfer mechanism (SET), the catching of perfluoroalkyl radical by olefins and nitroso compounds is the confirmation of this fact [26].

The process of sulfonylization by $\text{Na}_2\text{S}_2\text{O}_4$ appeared to be important, because it allows to obtain the corresponding perfluoroalkanesulfonic acids, which there are important intermediate components for surfactant synthesis, omitting the electrochemical fluorination stage and using available perfluoroalkyliodides [28,42,55,56]. For example, $\text{X}(\text{CF}_2)_{2n}\text{O}(\text{CF}_2)_2\text{SO}_3\text{Na}$ ($\text{X} = \text{Br}, \text{I}$, $n = 1, 2$), $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)\text{COONa}$, $\text{I}(\text{CF}_2)_n\text{O}(\text{CF}_2)_n\text{SO}_3\text{Na}$ can be obtained from corresponding perfluoroalkyl halides $\text{Cl}(\text{CF}_2)_n\text{I}$ ($n = 2, 4, 6$), $\text{H}(\text{CF}_2)_8\text{X}$ ($\text{X} = \text{Br}, \text{I}$); $\text{Br}(\text{CF}_2)_4\text{Cl}$ and $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$ in the presence of phase-transfer catalyst in polyethylene glycols 200 and -600 or in acetonitrile, ethanol, diglyme.

Also, this reaction can be carried out with perfluoroalkylbromides, for example CF_3Br , which produces sodium salt of trifluoromethansulfinic acid with 90% yield. 1,1,1-Trichloroperfluoroalkanes appeared adequate for these purposes (product yields 90% and more) [37-31, 57,58].



Triethylamine was used as a base [30].



The reactions α,ω -diiodoperfluoroalkanes [41] and α,ω -dibromoperfluoroalkanes with equivalent amount of $\text{Na}_2\text{S}_2\text{O}_4$ in the media $\text{MeCN-H}_2\text{O}$ in the presence of sodium bicarbonate result in mixtures of sodium salts of perfluoroalkanesulfinates (yields 66-90%)(see table 2).

$\text{I}(\text{CF}_2)_n\text{SO}_2\text{Na}$ and $\text{NaSO}_2(\text{CF}_2)_n\text{SO}_2\text{Na}$ at chlorine action at 0°C produce appropriate sulfochlorides $\text{I}(\text{CF}_2)_n\text{SO}_2\text{Cl}$ and $\text{ClSO}_2(\text{CF}_2)_n\text{SO}_2\text{Cl}$ [$n = 3,4,6$].

Table 1. Synthesis of perfluoroalkanesulfinic acid sodium salts

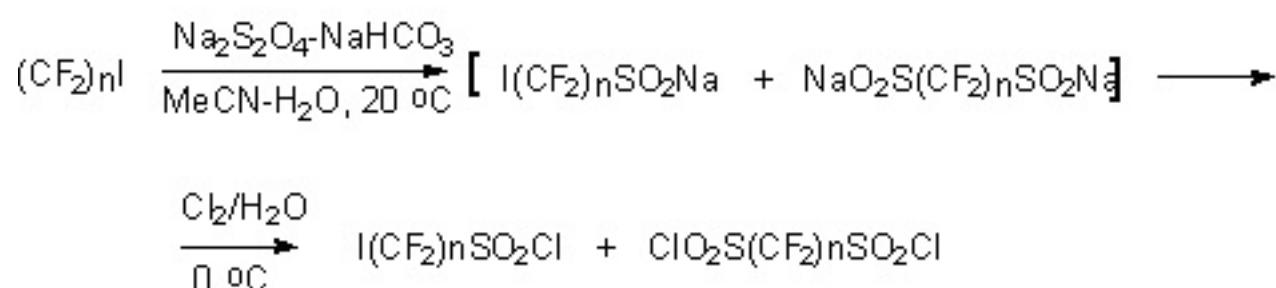
Nucleophiles	$\text{R}_\text{F}\text{X}$	Reaction conditions		Product	Yield, %
		Solvent	T, $^\circ\text{C}$		
$\text{Na}_2\text{S}_2\text{O}_4$	$\text{F}(\text{CH}_2)_8\text{I}$	$\text{MeCN-H}_2\text{O}$	80-85	$\text{F}(\text{CH}_2)_8\text{SO}_2\text{Na}$	95
	$\text{F}(\text{CH}_2)_8\text{Br}$	$\text{MeCN-H}_2\text{O}$	20	$\text{F}(\text{CH}_2)_8\text{SO}_2\text{Na}$	91
	CF_3CCl_3	$\text{MeCN-H}_2\text{O}$	25	$\text{CF}_3\text{CCl}_2\text{SO}_2\text{Na}$	73
	$\text{I}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{Na}$	H_2O	85	$\text{NaSO}_2(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{Na}$	96
$\text{HOCH}_2\text{SO}_2\text{Na}$	$\text{Cl}(\text{CF}_2)_6\text{I}$	$\text{MeCN-H}_2\text{O}$	85	$\text{Cl}(\text{CF}_2)_6\text{SO}_2\text{Na}$	65
	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{MeCN-H}_2\text{O}$	85	$\text{Cl}(\text{CF}_2)_8\text{SO}_2\text{Na}$	75
$\text{NaHSO}_3/$ $\text{K}_3\text{Fe}(\text{CN})_6$	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{DMF-H}_2\text{O}$	70-80	$\text{Cl}(\text{CF}_2)_6\text{SO}_2\text{Na}$	88
	$\text{Cl}(\text{CF}_2)_4\text{Br}$	$\text{DMF-H}_2\text{O}$	70-75	$\text{Cl}(\text{CF}_2)_4\text{SO}_2\text{Cl}$	
$\text{NaHSO}_3/$ FeCl_3	$\text{F}(\text{CF}_2)_6\text{I}$	$\text{DMF-H}_2\text{O}$	70	$\text{F}(\text{CF}_2)_6\text{SO}_2\text{Cl}$	63
$\text{Na}_2\text{S}_2\text{O}_5$	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{DMF-H}_2\text{O}$	80	$\text{Cl}(\text{CF}_2)_4\text{SO}_2\text{Na}$	85
	$\text{Cl}(\text{CF}_2)_6\text{Br}$	$\text{DMF-H}_2\text{O}$	80	$\text{Cl}(\text{CF}_2)_6\text{SO}_2\text{Na}$	79
NaHSO_3	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	$\text{DMF-H}_2\text{O}$	70-80	$\text{NaSO}_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{Na}$	95
	$\text{F}(\text{CF}_2)_6\text{Br}$	$\text{DMF-H}_2\text{O}$	70-80	$\text{F}(\text{CF}_2)_6\text{SO}_2\text{Na}$	90
K_2SO_3	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	$\text{dioxane-H}_2\text{O}$	70	$\text{KSO}_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	90

Table 2. Sulfinilizing and subsequent chlorination α,ω -diiodoperfluoroalkanes $\text{I}(\text{CF}_2)_n\text{I}$ [41,47].

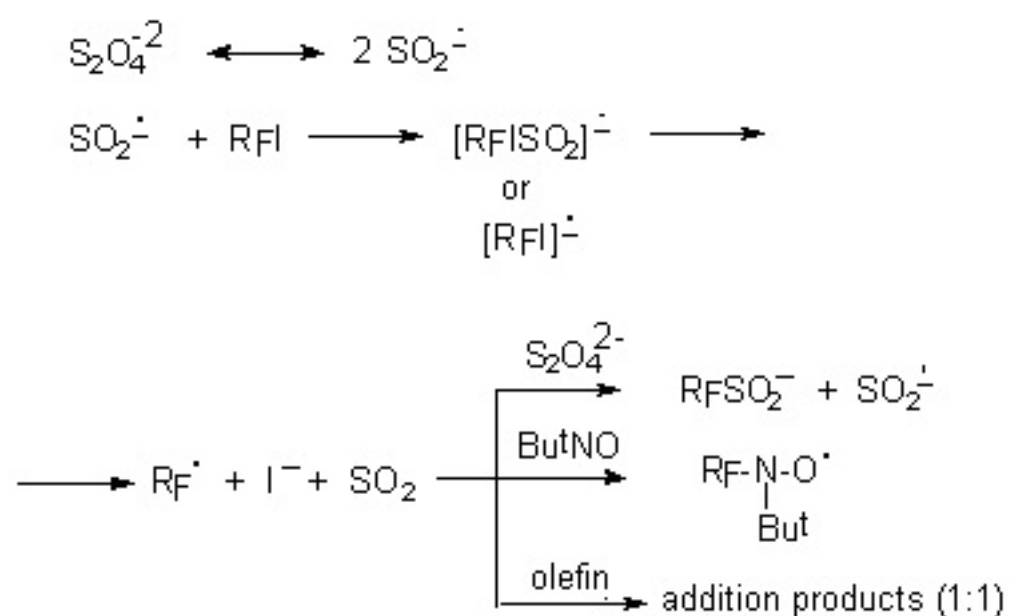
n	$\text{I}(\text{CF}_2)_2\text{I}:\text{Na}_2\text{S}_2\text{O}_4^{\text{a}}$	$\text{MeCN-H}_2\text{O}^{\text{a}}$	Product	Yield, % ^b
2	1:1	10:3	$\text{I}(\text{CF}_2)_3\text{SO}_2\text{Cl}$	28(80)
4	1:1	10:3	$\text{I}(\text{CF}_2)_4\text{SO}_2\text{Cl}$	25(90)
6	1:1	20:3	$\text{I}(\text{CF}_2)_6\text{SO}_2\text{Cl}$	39(84)
3	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_3\text{SO}_2\text{Cl}$	73(100)
4	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_4\text{SO}_2\text{Cl}$	83(100)
6	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_6\text{SO}_2\text{Cl}$	75(>95)

^amole ratio

^bin parentheses the yields from NMR ^{19}F information



The mechanism of this process can be presented as follows:



The sulfinatedehalogenation reaction had opened a new way to the synthesis of perfluoroalkane-sulfinic and -sulfonic acids and their derivatives. It is interesting, because perfluoroalkyl halides is transformed directly into perfluoroalkylsulfinate. In this case there is no need of intermediate section - the synthesis of organometallic derivative. This process is surely interesting for extensive application in the technology [27-30,36-39,58].

to be continued