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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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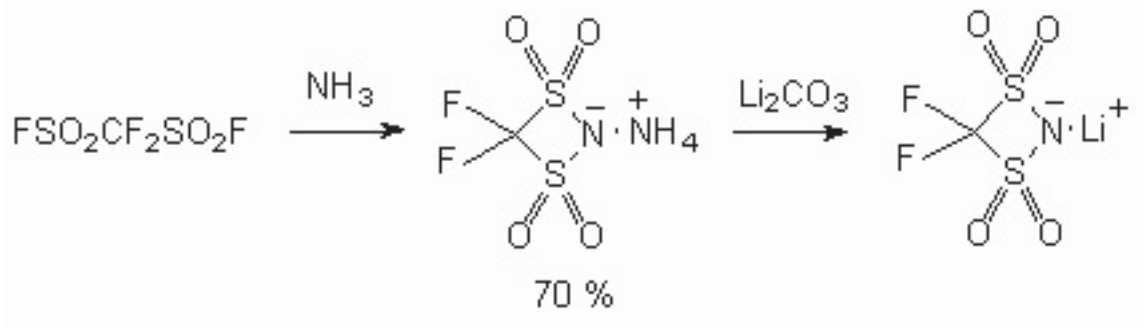
4. New in application of perfluoralkanesulfo-acides derivatives

4.1. Electrolytes and ionic liquids on the basis of bis-(perfluoroalkylsulfonyl) imide.

The search for new electrolytes for lithium batteries and new organic materials with high electroconductivity had stimulated the interest for synthesis of salts on the basis of bis-(trifluoromethanesulfonyl)amide. It was important that such salts should have had not only high electoconductivity but they also should have been stable at room temperature and well soluble in organic solvents and should have had low melting points and they should not have decayed in aqueous medium Besides this it was important to get quantity data regarding anion influence $(CF_3SO_2)_2N^-$ on salt elecroconductivity.

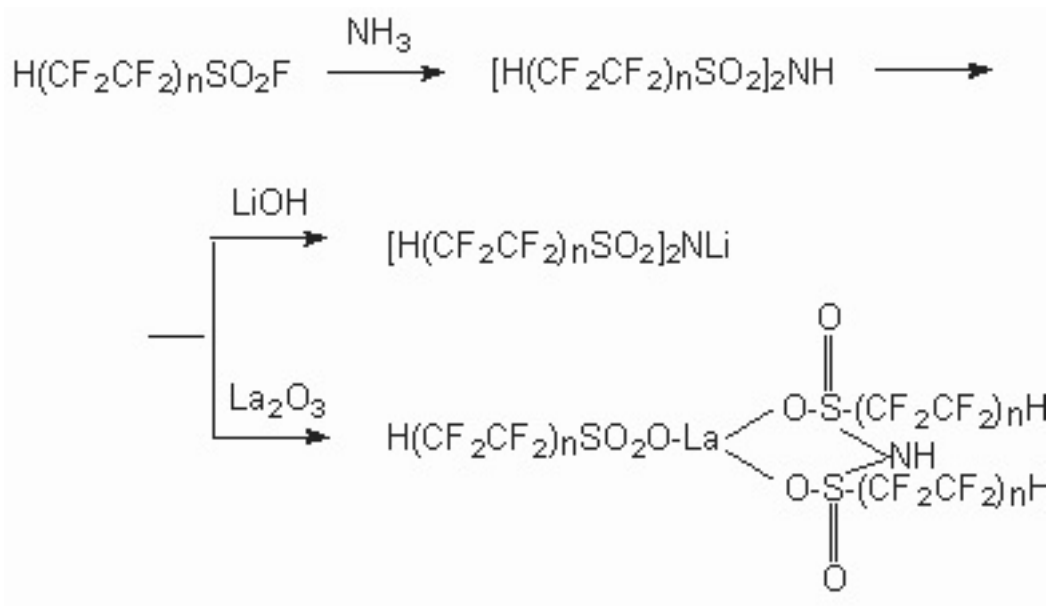
Lithium salt of bis-(trifluoromethanesulfonyl)imide may be used as solid electrolytes for batteries [167-179]. Moreover the other salts of bis-(trifluoromethanesulfonyl)imide (for example, aluminium salt [180-182], salts of Mg, Ca, Sr, Ba [183,184]) can be used for these purposes.

It was proposed the method of cyclic perfluoroalkane-bis-(sulfonyl)imides or it's salts producing via cyclization corresponding perfluoroalkane-bis-sulfonylfluorides during reaction with liquid ammonia [185]. Cyclo-difluoromethane-bis-(sulfonyl)imides of lithium use as conductive salts in non-aqueous solutions of electrolytes.



Lithium salts with different perfluoralkyl groups are also used as solid electrolytes in the material containing other elements, for example $Li_y(Mn_{2-x}M_x)O_4$ [M = Li, Ca, Fe, Ni, Cr, Co, In, Mg; x = 0-1] [186].

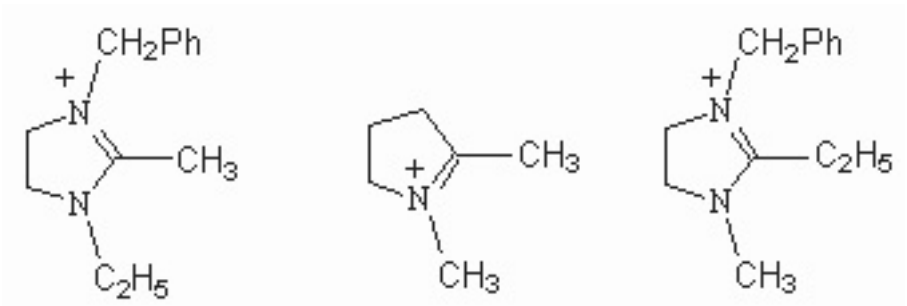
It can be supposed that the base for production of new electrolytes for lithium batteries and new complexing agent for rare-earth elements used as laser mediums will be created.



The following fields of application of perfluoralkanesulfo-acids derivatives can be supposed:

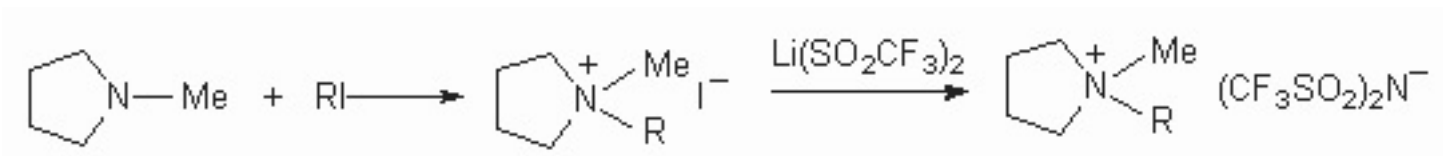
- the obtaining of polyfluoroalkanesulfo-acids and producing on their basis surface active materials and electrolytes for lithium batteries and rechargeable accumulators,
- new complexing agents for rare-earth elements salts
- creation of high-temperature liquid dielectric, heat-transfers and hydraulic liquids.

Along with lithium salts of perfluoralkanesulfo-acids the salts, which cationscontained different nitrogen-containing heterocycles and quaternary alkylamines, were obtained .



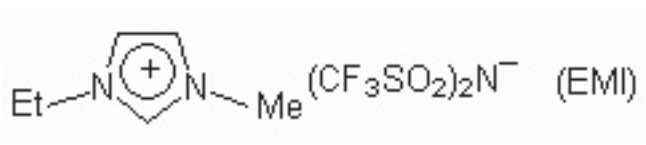
The structure of salts is confirmed by data of X-ray analysis [163,164].

In the work [162,163] was described the producing of salts with such anion, at that the cation was heterocyclic compound. The synthesis of salts was carried out according to the scheme :



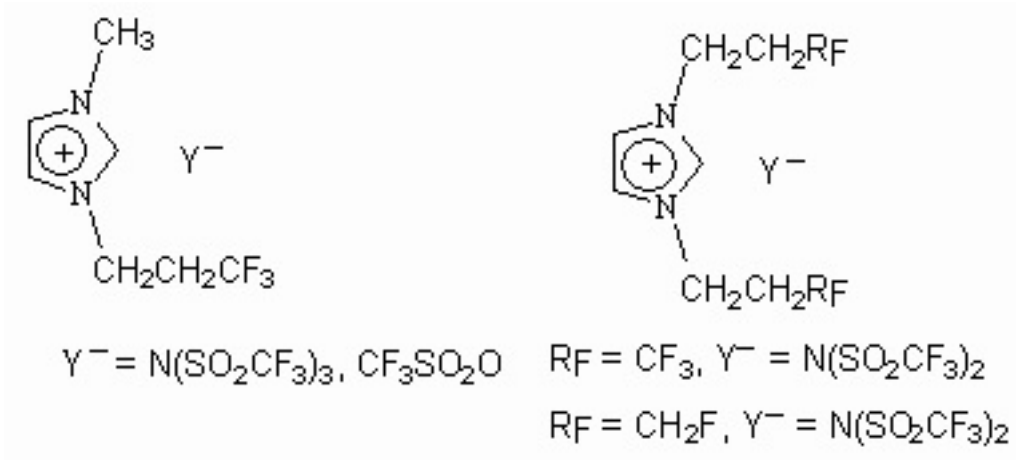
R = Me, Pr, Bu

It was found, that electroconductivity of methylbutyl derivatives of these salts is $2*10^{-3}$ S/cm at 20 ^{o}C, and the one of methylpropyl derivatives is $1*10^{-6}$ S/cm at 0 ^{o}C. It should be noted that at comparing to electroconductivity of sample system, containing **imidozonium** ion (EMI) [165] ($8*10^{-3}$ S/cm at 20 ^{o}C),



they are comparable.

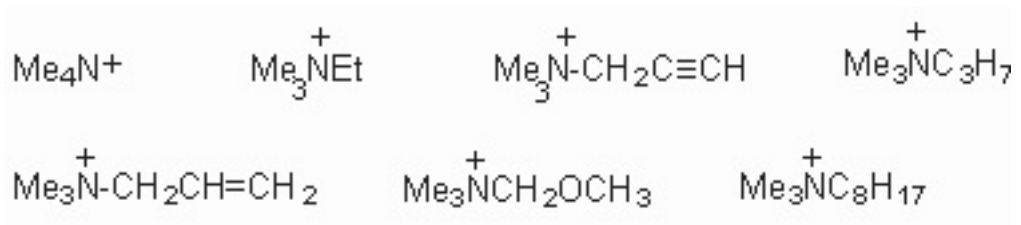
However, this sample salt can't be applied in realty at room temperature, because it decays at cathode voltage of a few hundred mv. Also other salts, containing **imidozonium** are obtained [166].



$Y^- = N(SO_2CF_3)_3, CF_3SO_2O$ $R_F = CF_3, Y^- = N(SO_2CF_3)_2$

$R_F = CH_2F, Y^- = N(SO_2CF_3)_2$

In the work [187] the similar salts are studied using aliphatic quaternary ammonium cations, which are stable in the open air and in water:



It was found that these salts are electrochemically stable and small sizes of trimethylalkylammonium cations create the conditions of high electroconductivity. It can be seen if you look at Fig. 1 and table 3.

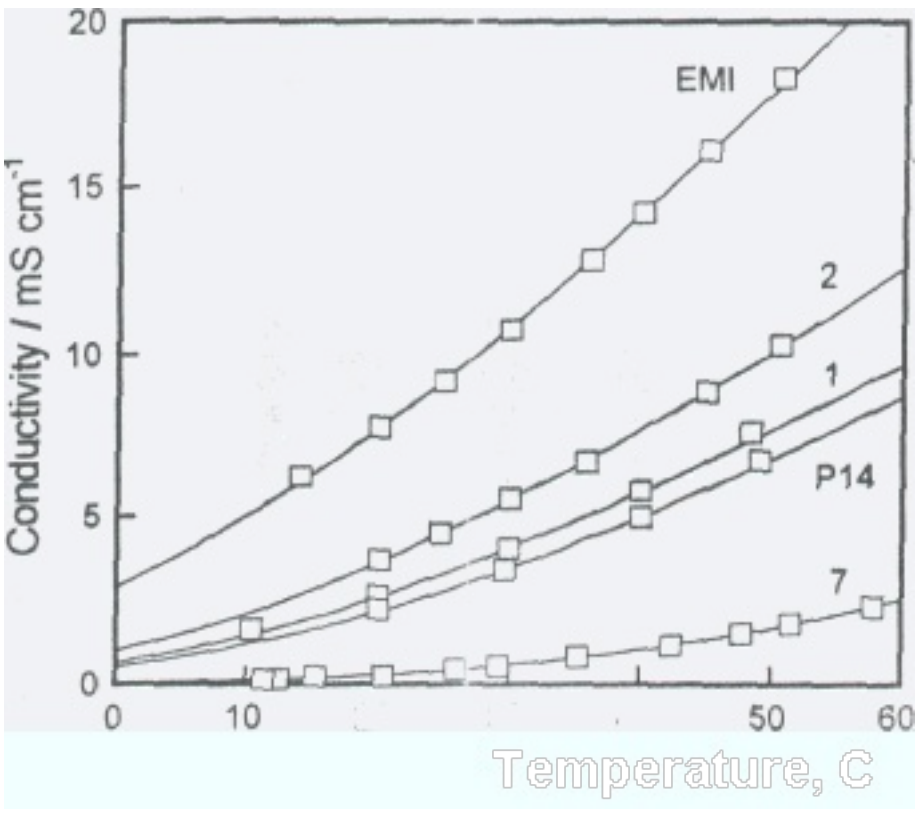
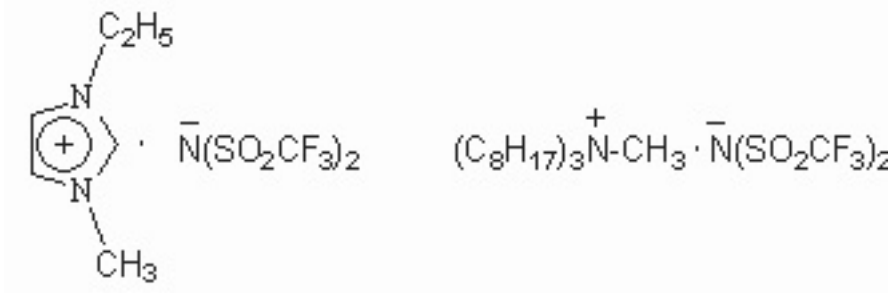


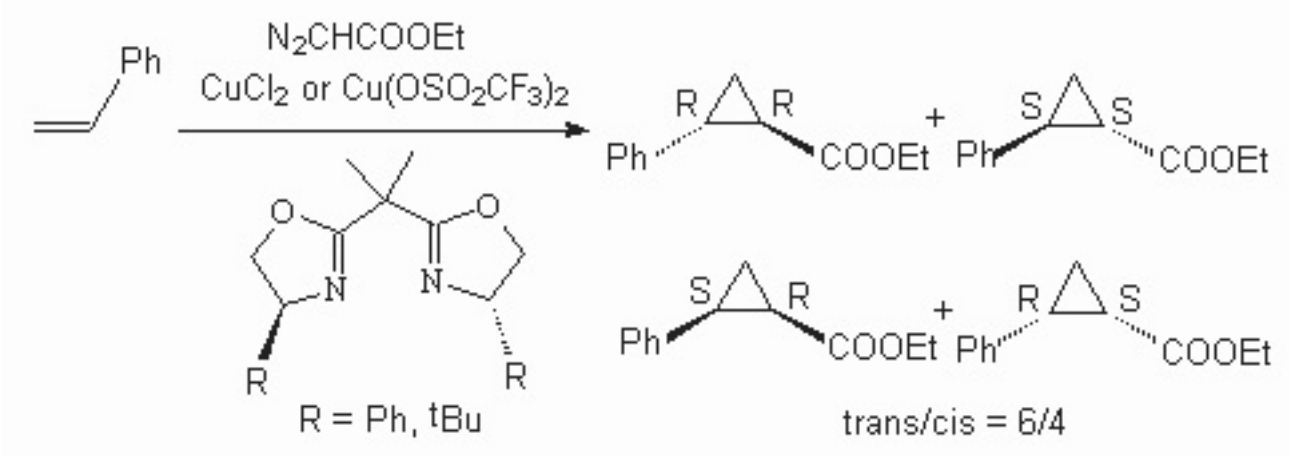
Fig. 1. Electroconductivity of salts on the base of anion $(CF_3SO_2)_2^-$.

Salt electroconductivity is not so great as the sample salt (EMI), nevertheless the opportunity of working at high temperature makes this salts more attractive from practical point of view, because it is not required to use cycle system for generation of cationoid part and use more available trimethylalkylammonium cations. The salts



which are ionic liquids are used as medium of some chemical processes. It was stated [188], that 1-ethyl-3-methyldiazolium bis-(trifluoromethylmethanesulfonyl)imide and 1-butyl-3-methyldiazolium bis-(trifluoromethylmethanesulfonyl)imide are active bicatalysts and ionic liquids for conducting of butyl-butyrate synthesis under the action of candida Antarctica lipase B **exime**. The process passes with high synthetic activity, selectively and stably in the medium of supercritical carbon dioxide.

The authors of the work [189] used this medium for the synthesis of asymmetric cyclopropanes by ethyl diazoacetate acting on styrene in presence of bis-(**oxozoline**)-copper complex.



Iodonium salt $(CF_3SO_2)_2NI(Ph)CH_2CF_3$ appeared to be excellent alkylating reagent (introducing of CH_2CF_3 group) into different amino acids [190]. The structure of reaction product is confirmed by X-ray analysis [190].

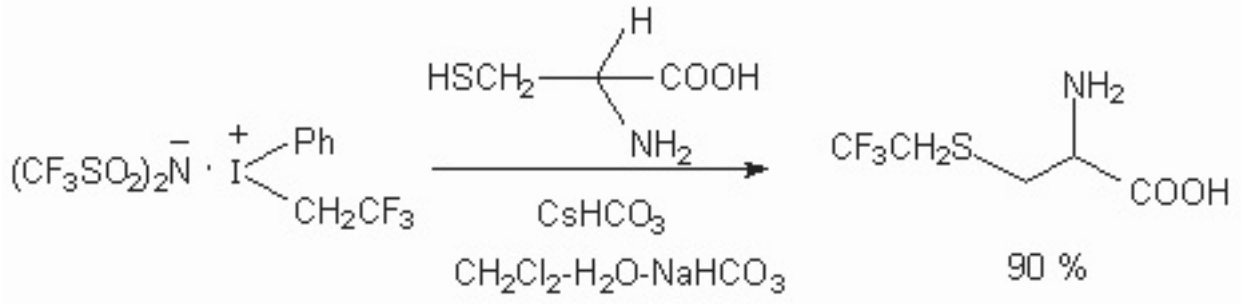
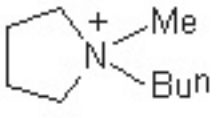
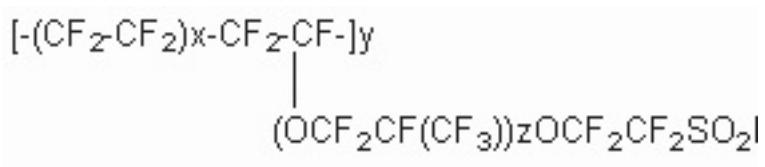


Table 3. *Salts characteristics of the basis of anion $(CF_3SO_2)_2N$- at 25 ^oC [187].*

Cation	MP °C	Density g cm^{-3}	Concentration mol dm^{-3}	Viscosity η мPa c	Electroconductivity σ mS cm^{-1}	Λ S cm^2 mol^{-1}
$Me_3\overset{+}{N}C_3H_7$ **1**	17	1.44	3.75	72	3.3	0.88
$Me_3\overset{+}{N}CH_2OCH_3$ **2**	4.5	1.51	3.93	50	4.7	1.2
 **EMI**	-12	1.51	3.88	34	9.2	2.4
 **P14**	-18	1.41	3.34	70	2.9	0.87

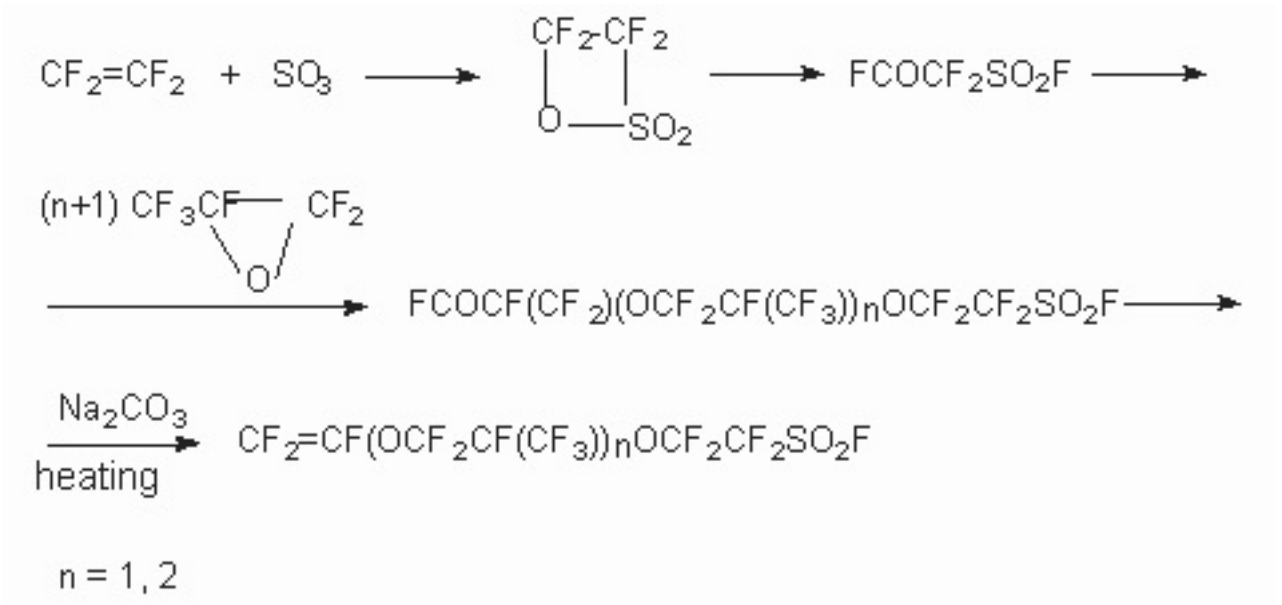
4.2. The membranes on the basis of perfluoralkansulfoacids.

Since 1960 the research regarding synthesis of fluorine containing ion-exchange membranes was started for the purpose of creating of diaphragms for fuel elements (electricity generation by interaction of hydrogen and oxygen on catalysts, applied on electrodes), used according to airspace programme. In 1972 "Du Pont" company created such corrosion and acid resistant membrane on the basis of perfluoralkanesulfo-acid under the trade mark Nafion. The structure of Nafion is the following:

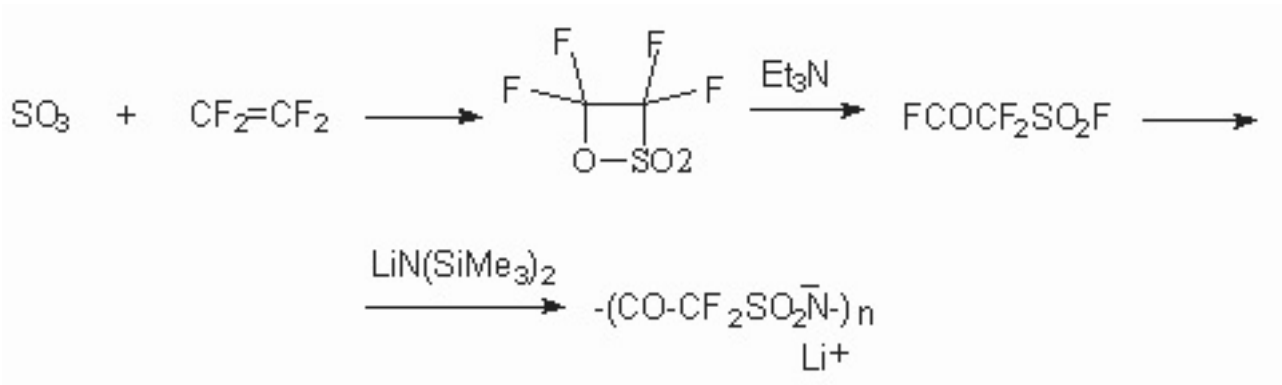


The last mentioned one allowed to increase operating temperature of the element and its capacity [191]. Later this acid had found an application in Olah works as solid strong acid in organic synthesis [192].

The synthesis of such membranes consists of several stages. In the beginning perfluorovinyl monomer with sulfofluoride group is obtained, which later is used for turning into ionogenic group. After that co-polymerization of this monomer with tetrafluorethylene is carried out. [193].



The using of sultones allowed authors of the work [194] to develop the new creating methodology of polymer electrolytes, which are successfully used for production of lithium batteries. The obtaining scheme of such materials is the following:

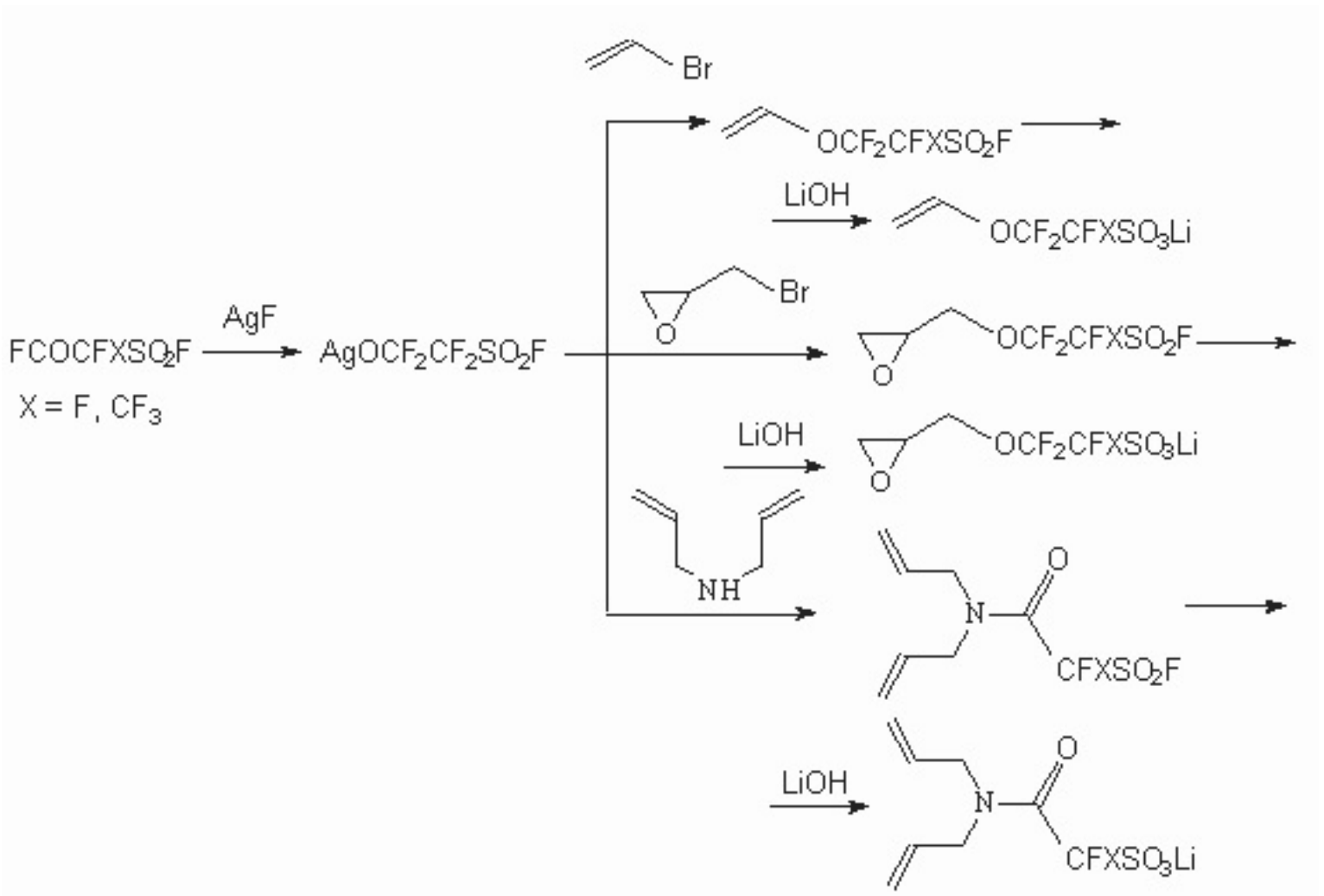


The electroconductivity of lithium salt of poly(2-oxo-diflluoroethylenesulfonyl)imide (LiPI) is high ($6*10^{-3}$ $S*cm^{-}1$) and this salt is a high dissocated poly-anion. This polymer is compatible with matrix made of polyesters.

The intermediate sulfofluoride is used for obtaining of different monomers, containing sulfo-groups, for example, SO_2F, SO_3H, which are used for obtaining of copolymers with such

monomers as ethylene oxide and its derivatives. [195].

Such polymers are applied as solid electrolytes (electroconductivity is about 10^{-5}-10^{-6} S * cm^{-1}. That makes them interesting materials, which properties are similar to Nafion-H.



The heating of tetrafluoroethane disulfofluoride with liquid ammonia in presence of sodium methylate give the salt $H(Na)NSO_2CF_2CF_2SO_2N(Na)H$, this salt together with $HN(SiMe_3)_2$ produces $Me_3Si(Na)SO_2CF_2CF_2SO_2N(Na)SiMe_3$. This compound polymerizes accompanied trimethylfluorosilane elimination with $FSO_2CF_2CF_2SO_2F$, producing new ionic polymer - $[CF_2CF_2SO_2N(Na)SO_2]$-n. The membranes on the basis of such polymers appeared to be rather effective.

The creation of such membranes allowed to proceed from mercury method of sodium chloride electrolysis to non-mercury one at obtaining of caustic alkali. Electrochemical and mechanic properties of membranes have a decisive influence on economy of the electrolysis process using ion-exchange membranes. From this point of view the membranes on the basis of sulfoacids have a number of drawbacks, which decrease, if you use membranes, which along with sulfogroups have carboxyl groups. High density of these groups usually exists on applied membranes, because the higher is the volume capacity, the easier is the transferring process of gegenions (sodium ions) and the higher is the electroconductivity of membranes. The fields of appliction of such membranes are described in [4].

Conclusion

The author of this review had paid attention to relatively new class of organic compounds - the compounds, containing perfluoralkylsulfonyl group, as long as along with theoretical questions, connected with reveal of fluorine atoms influence on organic molecule properties and their use as model objects for solving the fundamental questions of organic reactions theory, many of materials on the basis of this class compounds have found a wide application.

The author thinks, that the new information gathering together, reveal of problems, facing fluor-organic compounds chemistry and reveal of primary tasks, which can recall chemists attention to this interesting and fast developing field of chemistry and also help specialists, working in the field of synthesis of new materials for technical purposes.

At the same time the author didn't plan to give full and detailed review of perfluorinated sulphur-containing compounds chemistry, but made an attempt to analyze of main tendencies in development of synthesis methods of such compounds with the purpose of reveal of new approaches for their obtaining, showing the opportunity of using of perfluorolefines and …. As synthons for obtaining of this class compounds and prognosis of most new and advantageous ways of synthesis taking into account specific properties of fluorine-containing semi products.

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