α- FLUOROALKYLAMINES AS NEW SOURCES FOR UNHYDRATED FLUORIDE- ION

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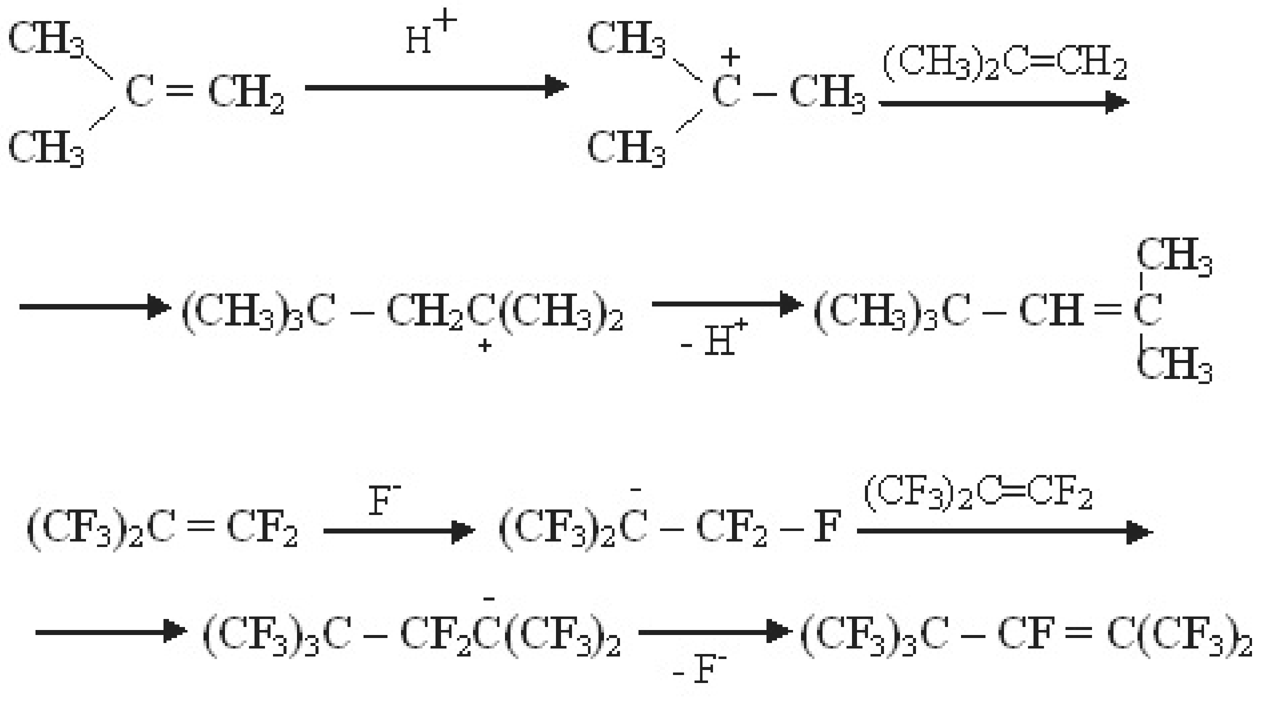
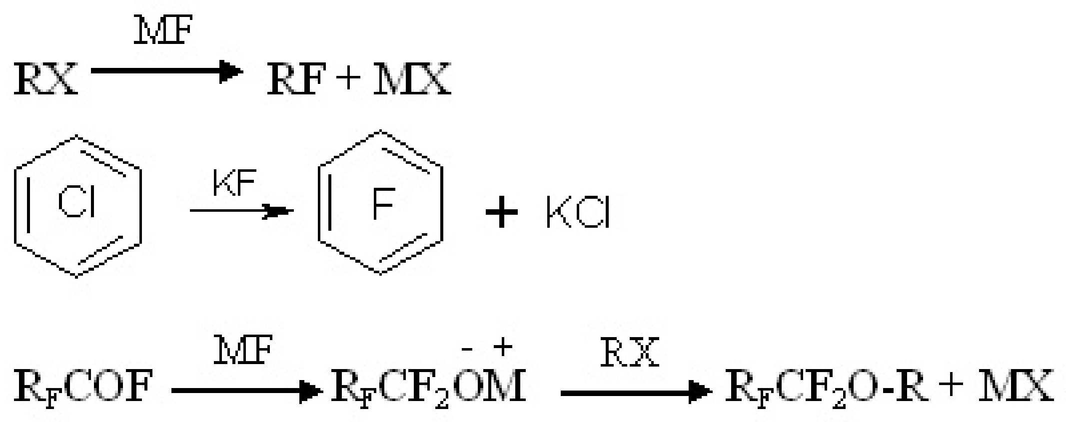
This article opens the subject of synthesis and application of fluoroalkylamines for the obta reactions of fluoroaliphatic and fluoroaromatic compounds.

I.L. Knuniantz was a staunch supporter to the fact, that anion fluorine would have the s enormous significance for the chemistry of fluororganic compounds as proton for the chemist organic compounds.

The analogy of fluorolefines' transformations in the presence of Bronsted's acids an perfluorolefines' transformations in the presence of fluorine anion [1] was cited as a proof.



In an enormous number of works by colleagues and followers of I.L. Knuniantz the prac importance of processes involving fluorine anion [2-5] was displayed and their theoretical asp were studied. For the present moment, these processes are among the main tendencie preparative and commercial synthesis of fluororganic compounds.



However, the picking up of sources of fluorine anion was limited by cesium fluorides, rubi and potassium fluorides. From the economical point of view, such choice for large-scale synthe: limited only by potassium fluoride. In its turn, the fluorides' low solubility in the mediums suitab carry out syntheses with anion fluoride had limited the opportunities of the method. In a vie that, I.L. Knuniantz had set a goal to find new sources of anion fluoride allowing extending the of application for such processes.

In 1979 the researches had begun. As a result of studies it was found, that in polar solve fluorotrimethylamine (covalent compound at ordinary conditions is liquid, which boiling point e $47^{o}C$, and it is easy to dissolve it in polar and non-polar solvents) easily adds accordin perfluorolefines' double bond forming stable products [6].

$$Me_2NCH_2F + CF_3CF=CF_2 \longrightarrow Me_2N-CH_2CF(CF_3)_2$$

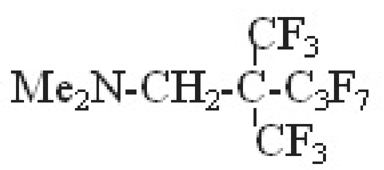
Besides that, it turned our that in NMR- spectra of α-fluorotrimethylamine's solutions in solvents H-F interaction doesn't take place. Taking these facts as a foundation we ma presumption, that dissociation of α-fluorotrimethylamine's molecule into ions occurred in solvents [7]:

$$\underset{\text{I}}{Me_2NCH_2F} \rightleftharpoons [Me_2N=CH_2]\ F^-$$

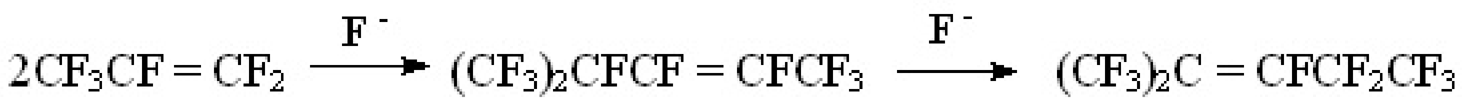
This assumption allows to realize the easiness of addition of α -fluorotrimethylamin fluorolefines. It's obvious, that here we encounter an anionic reaction scheme:

$$[Me_2N=CH_2]^+ F^- + CF_3CF=CF_2 \longrightarrow \left\{[Me_2N=CH_2]\ CF_3CFCF_3\right\} \longrightarrow$$
$$\longrightarrow Me_2NCH_2CF(CF_3)_2$$

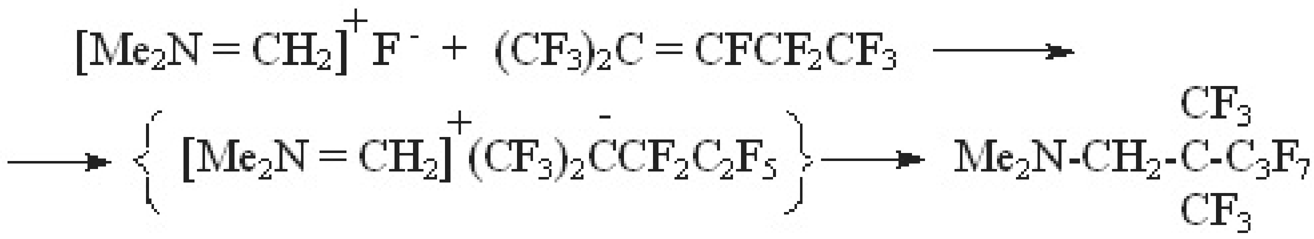
The suggested scheme is proved by forming of by-product that is (2-trifluoromethylperfluoro 2)trimethylamine



Perfluorinated radical is a derivative of perfluoropropylene dimer, formed out perfluoropropylene in the presence of anion fluoride [8]:

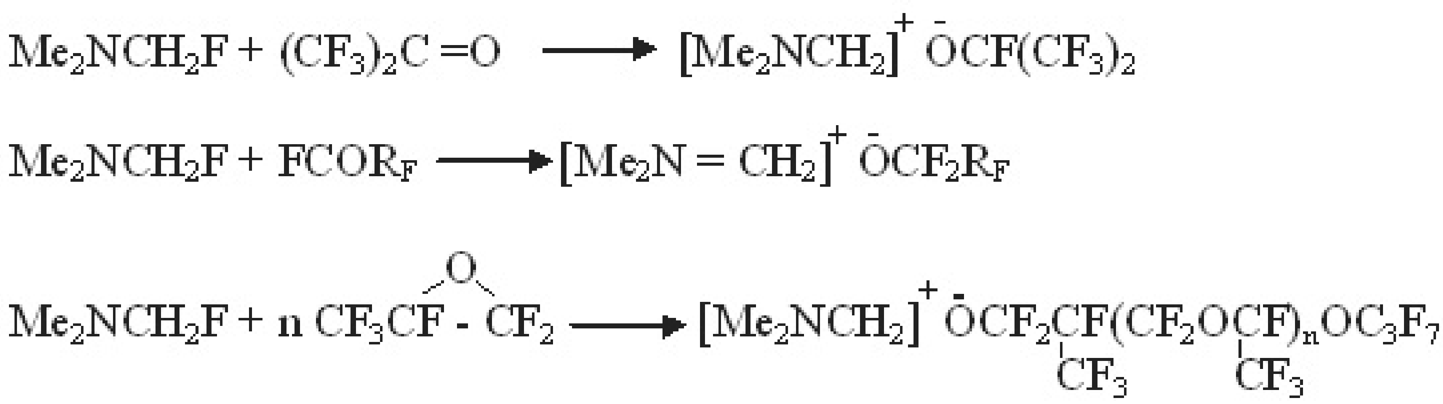


At the next stage α-fluorotrimethylamine adds perfluoropropylene dimer:

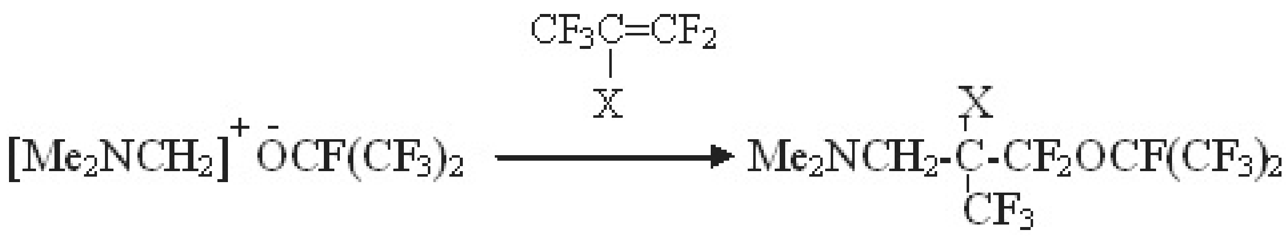


Thus, it became clear, that α-fluorotrimethylamine is a source for anion fluoride for h electrophilic fluorolefines.

After that the facts, that perfluorinated O-anions at interaction of fluorotrimethylamine perfluorinated carbonyl compounds were formed had been taken with no surprise [9-12].

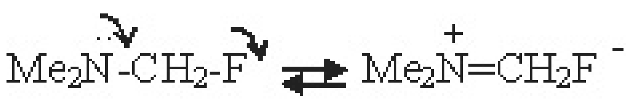


The formed ionic compounds add according to double bond of fluorolefines forming cova compounds



X=F, CF_3

The easy dissociation of stable C-F bond in α-fluorotrimethylamine must be determined by presence of nitrogen heminal atom:



It was natural that an interest for studying a number of such compounds and for comparing characteristics as sources for anion fluoride arose.

N,N,N',N'- tetramethylformamidinium fluoride (bisdimethylaminofluoromethane) (II) synthesized for this purpose, which is such a strong base, that eliminates HF from dimethyla fluorohydrate forming N,N,N',N'-tetramethylformamidinium bifluoride (III) [11]

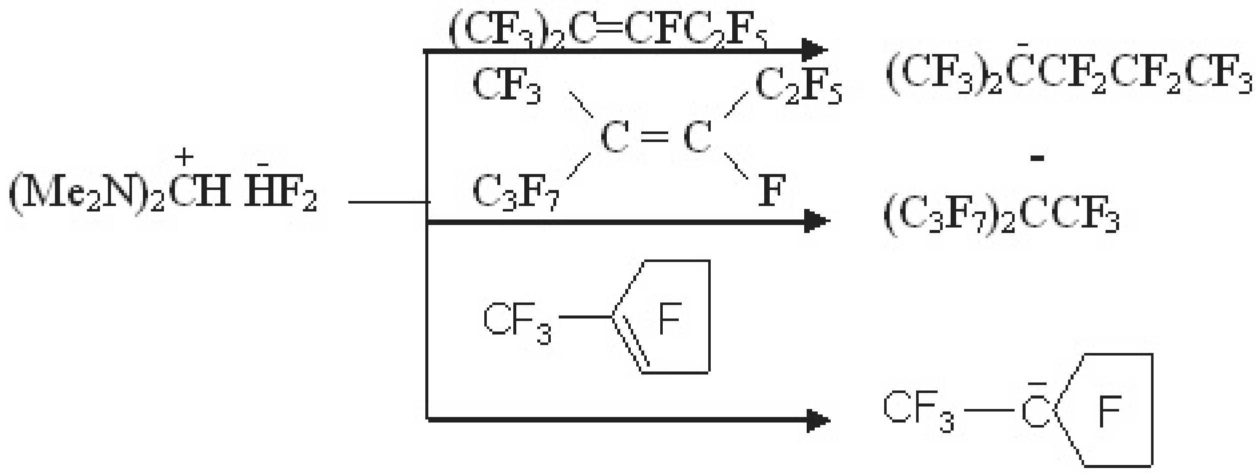
$$Me_2NCHF_2 + 2\,Me_2NH \longrightarrow [(Me_2N)_2\overset{+}{C}H\overset{-}{F} + Me_2NH\cdot HF] \longrightarrow$$

II

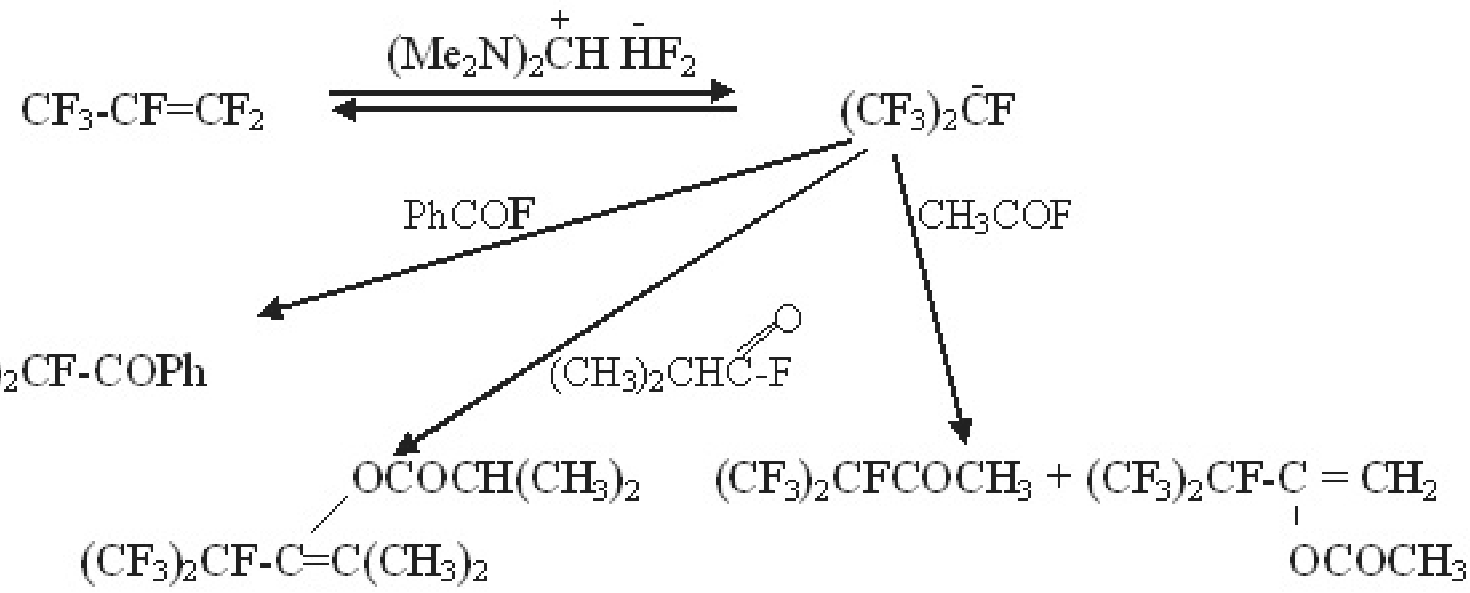
$$\longrightarrow (Me_2N)_2\overset{+}{C}H\ \overset{-}{HF_2} + Me_2NH$$

III

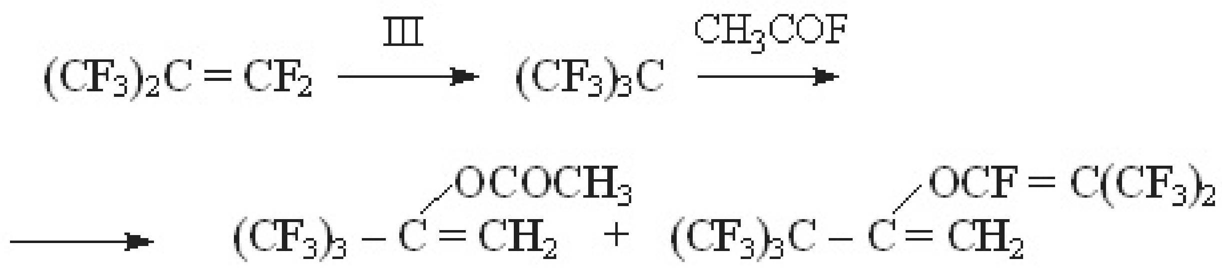
Obtained formamidinium bifluoride proved to be such a powerful source for fluorine anion having used it we for the first time managed to synthesize a number of perfluoroalkylcarbar and to study their NMR-spectra:



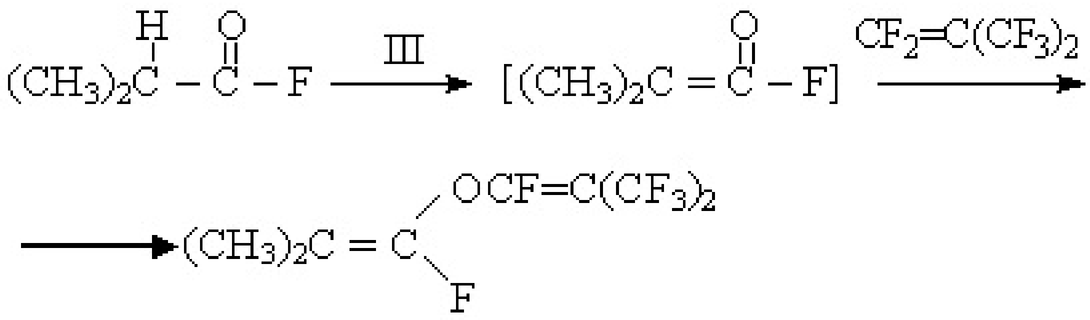
It was stated, that perfluoroalkylcarbanions generated this way enter typical for carbar reactions:



We also managed to generate and fully acylate perfluorotertbutylanion



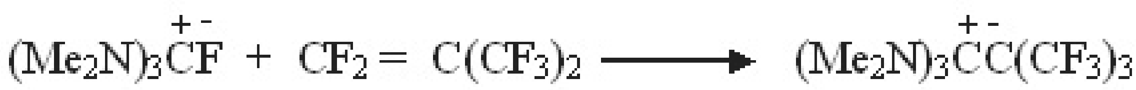
Fluorine-anion produced out of formamidinium bifluoride proved to be a foundation strong en to enable enolazation of isobutyryl fluoride:



A studying of tris-dimethylaminofluoromethane (IV) was a next logical step to take. It obtained by the reaction of hexamethylguanidinium pivaloate and dimethylaminotrifluorosulphu .

It was found, that (IV) as (III) exists only in ionic form of hexamethylguanidinium fluoride.

As it should have been expected (IV) is a great source for anion fluoride for genera perfluoroalkylcarbanions out of perfluorolefines. It practically irreversibly adds to perfluoroisobuty forming stable salt:



It for the first time allowed acylation of perfluorotertbutylanion form phenylperfluorotertbutylcetone [13]:

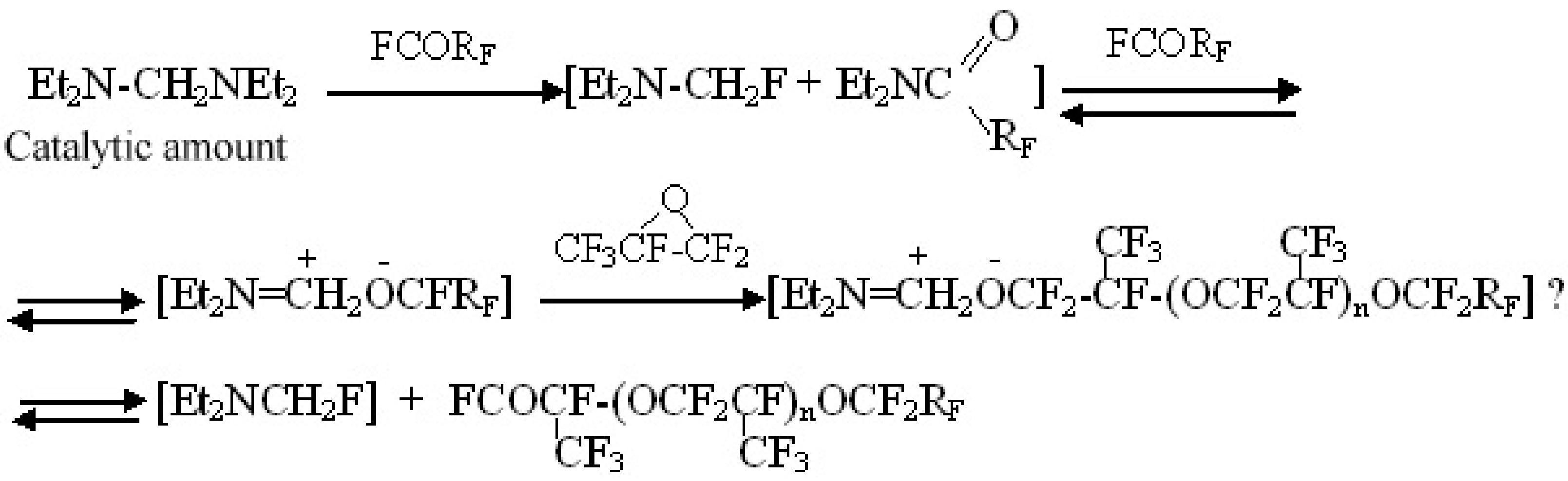
It is known, that the last compound mentioned easily decomposes in the presence of cata quantities of fluorine anion [14]:

The formation of phenylperfluorotertbutylcetone in the example listed above indicates absence of F^- in reaction mixture and the irreversibility of (IV) addition to perfluoroisobutylene.

Thus, in laboratory of I.L. Knuniantz under his direct supervision a theoretical foundatio obtaining and application of fundamentally new, well dissoluble in organic solvents, performance source of fluorine anion was laid.

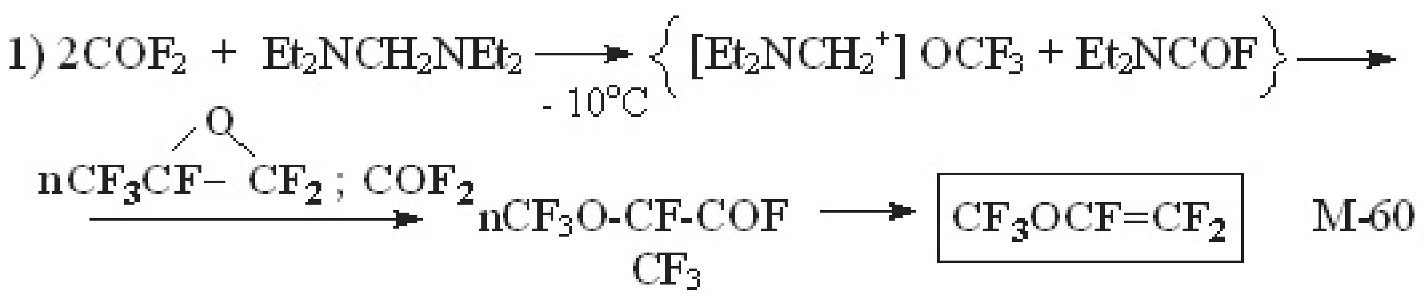
The knowledge obtained before found their practical realization.

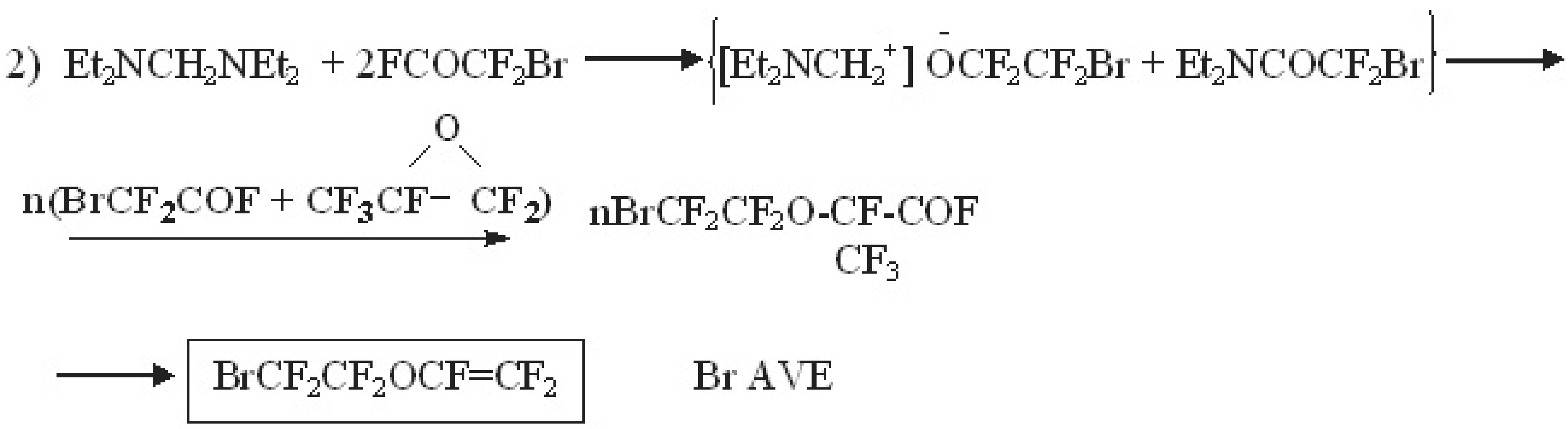
Thus, the ability of dialkylaminofluoromethanes to serve as a source of fluorine anion in reac with perfluorocarbonyl compounds was put into practice at a pilot plant of Russian Scientific Ce of Applied Chemistry Perm Branch for obtaining technologies of perfluorovinyl ethers and sur active materials [15]:

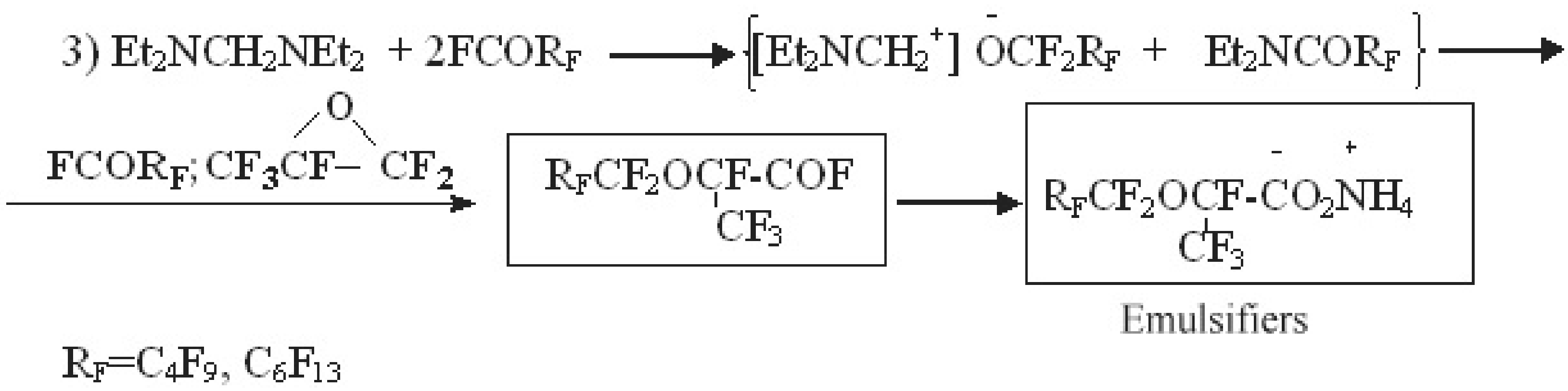


N,N,N',N' - tetraethylmethylenediamine is used in catalytic quantities for these processes. application of the catalysis method worked out allowed to put into practice many processes perfluorinated O-anions participating in at temperature ranging from - 10°C to room tempera and at atmospheric pressure.

Based on these foundations the following production processes are being carried out at F Branch of RSC of Applied Chemistry:

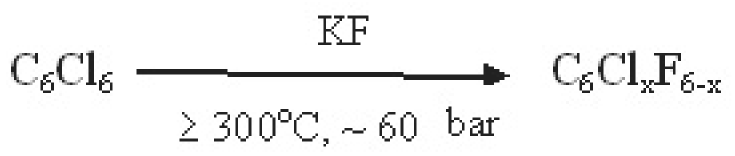






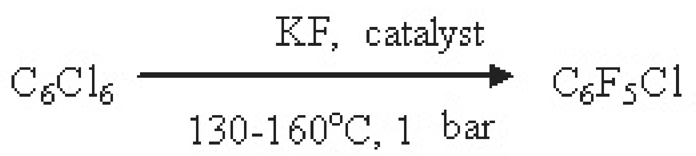
At the same time using of other sources of fluorine anion for many of analogous proce requires elevated temperatures (90- 150°C) and pressure (5 - 200 bar) [16].

The unique properties of new sources of fluorine anion found their application also for production of fluoroaromatic compounds. Thus, the fluorinating process of hexafluorobenzene u potassium fluoride, worked out by G.G. Jacobson [17] requires high temperatures and there high values of pressure:



It limits the volume of reactors (autoclaves) and makes it impossible to organize a large-s production.

Using hexaethylguanidium fluoride as a catalyst for this process allows decreasing temperature down to 130 - 150°C and carrying out the process with no pressure at condition uninterrupted isolation of target products [18]



The technology worked out allowed to set up commercial production of fluoroaron compounds at Perm Branch of RSC " Applied Chemistry".

Thus, theoretical works regarding search for new sources of fluorine anion carried out a Knuniantz laboratory under his direct supervision found and there is no doubt, that later w finding their wide practical application.

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