Translated from *Uspekhi Khimii*, **55**, 885-913 (1986) U.D.C. 547.471

Characteristic Features of the Chemical Properties of Fluorine-containing Unsaturated Compounds†

N.P.Gambaryan and E.M.Rokhlin

The review deals with the results obtained in the study of the chemical properties of organofluorine and saturated compounds containing the C = C, C = O, C = N, C = C = C, C = C = O, C = C = N, etc. groups. The characteristics of the reactions of fluoro-olefins and related compounds with nucleophiles as well as the methods of synthesis and the properties of fluorocarbanions (including mesomeric fluorocarbanions) are examined. The electronically amphoteric character of the C = C bond in fluorine-containing unsaturated compounds, ensuring the possibility of interaction with strong electrophiles, and the synthetic possibilities resulting from these reactions are demonstrated. The analogy between the chemical properties of polyfluoro-substituted carbonyl compounds, their derivatives, heterocumulenes, and nitro- and nitroso-compounds is discussed. The influence of fluorine atoms is manifested by the markedly electrophilic properties of these compounds and in many cases also by the singular stability of the unusual structures formed as a result of their reactions.
The bibliography includes 180 references.

CONTENTS

I. Introduction 480
II. Fluoro-olefins and related compounds 481
III. Polyfluorocarbonyl compounds and their analogues 486

I. INTRODUCTION

The establishment of the organic chemistry of fluorine as a separate branch of science dates back to the beginning and middle 1940's.[2] The development of this field was initially dictated by immediate practical needs (the necessity for the creation of materials resistant to the action of uranium hexafluoride). Since then organofluorine compounds are being increasingly used in a wide variety of fields, so that "it is at present difficult to name a branch of engineering which could do without materials containing fluorine".[2]

The possibilities in the application of fluorine compounds are determined by the characteristic features of this element. Fluorine is the most electronegative element in the Periodic System. The dissociation energy of its molecules is extremely low (the same as that for iodine) and the strength of its bonds with many elements is, on the other hand, high. As a result of this, the majority of substances, even the inert gases, can interact with fluorine.

Perfluorocarbon chains are exceptionally stable both thermally and chemically owing to the great strength of the carbon–fluorine bond (on average about 110 kcal mol^{-1}) and also the very favourable ratio of the carbon–carbon bond length to the size of the fluorine atom. The van der Waals radius of fluorine is smaller than the C–C bond length and for this reason the accumulation of fluorine atoms in perfluorocarbons does not lead to the extension and weakening of this bond (as in perchlorocarbons); on the contrary, fluorine atoms give rise to close packing, reliably protecting the carbon chain from external influences and in particular rendering it resistant to oxidation.

All these factors led to an abundance of compounds of a wide variety of classes in which all the hydrogen atoms have been replaced by fluorine. Organofluorine chemistry, which is, as it were, a copy of organic chemistry, has been created. However, this copy is so unusual and the results have so far been so unexpected that they have enriched organic chemistry and have greatly extended its theoretical ideas.

Since the creation of the Institute of Organoelemental Compounds of the USSR Academy of Sciences (INEOS) in 1954, the Laboratory of Organofluorine Compounds, headed by Ivan Lyudvigovich Knunyants, was organised in it. In the present review an attempt is made to survey some of the most interesting and important results obtained by the members of this laboratory during the one-third of a century of its existence. Many of these results have been described in a series of other reviews.[2–26] In describing the relevant data, we shall as a rule refer to these reviews and the original papers will be quoted only in the case of the latest investigations.

The principal direction taken by the studies in the above laboratory involves the investigation of the characteristic features of various multiple bonds in organofluorine compounds such as fluoro-olefins, including those with functional group substituents (the C=C bond), carbonyl compounds and their derivatives (the C=O, C=N, etc. bonds), nitro- and nitroso-compounds (the $N\overset{O}{\underset{O}{<}}$ and N=O groups), and cumulenes and heterocumulenes (the C=C=C, C=C=O, C=C=N, N=C=O, etc. groups). The present review is mainly devoted to these studies.

However, apart from the investigations of the multiple bonds, other branches of organofluorine chemistry also occupy an important place in the studies carried out in the Laboratory. Frequently these investigations are genetically related to the main field of study. Thus, numerous reactions of fluorine-containing unsaturated compounds, leading to the formation of carbocyclic and heterocyclic systems, including those with small rings, have been discovered. The study of the properties of these cyclic systems, which are frequently unusual, is of considerable interest.[2,3,13,16,27–31]

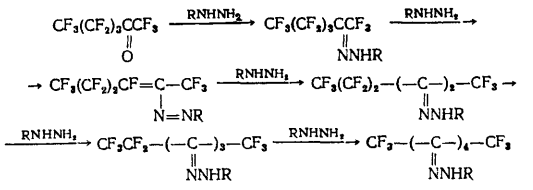
Fluorocarbanions, which are of very great synthetic importance# (see below), are formed as intermediates in various reactions of fluoro-olefins and related compounds in the presence of the F^- anion.

†The article has been written to commemorate the 80th birthday of the founder of the Soviet school of organofluorine chemists Academician I.L.Knunyants (cf.Rokhlin and Gambaryan[1]).

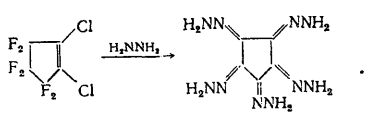
#Another important property of the F^- anion, namely its high basicity, was discovered by Knunyants and co-workers as early as the middle 1940's;[32] this property is nowadays used widely for synthetic purposes.[2,33–35]

The study of the reactivities of fluoroketones yielded functional-group derivatives of 2,2-diphenylhexafluoropropane and aryl- or alkyl-bis(fluoroalkyl) carbinols. Compounds of these types have been the objects of two major series of investigations associated with the development of methods of synthesis of monomers for polycondensation polymers with valuable properties,[36,37] and fluorine-containing epoxides—intermediates in many syntheses of organofluorine substances.[2]

Knunyants introduced the bold idea of an analogy between the CF_2 and C=O groups,[5] which proved fruitful as regards syntheses. In particular, a rearrangement of fluoroalkyl azides, resembling the Curtius rearrangement of acyl azides, was discovered.[5] Like keten, a terminal fluoro-olefin is capable of undergoing reactions of the Wittig–Staudinger type.[13] Perfluoromonocarbonyl compounds behave similarly to polycarbonyl compounds, forming osazones and polyhydrazones,[38,39] for example:

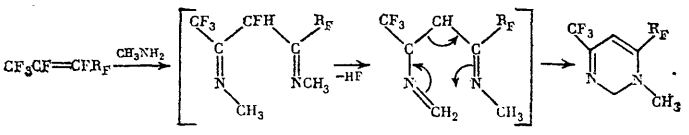


In the series of alicyclic compounds it has actually been possible to obtain "perhydrazones",[39,40] for example:

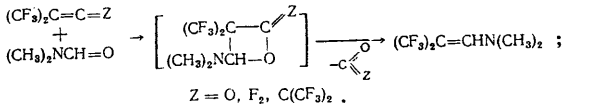


These interesting reactions demonstrate the possibility of "livening" the perfluorocarbon chain. They are based on the ability of hydrazones of α-fluoro-substituted carbonyl compounds to be dehydrofluorinated with formation of unsaturated azo-compounds which then react with the next mole of hydrazine.

Such dehydrofluorination is apparently possible also for α-fluoroketone methylimines. This explains the unexpected result of the interaction of certain internal perfluoro-olefins with methylamine, which leads to dihydropyrimidines.[41] The intermediate heptafluoroacetylacetone diimine (cf. Kurykin et al.[42]) is dehydrofluorinated to a 1,3,5-heterotriene, which is converted into a substituted dihydropyrimidine as a result of intramolecular [4 + 2]-cycloaddition:



An analogy has also been observed in the reactions of fluorine-containing unsaturated compounds with dimethylformamide, leading to the products of the cleavage of the unstable oxetans formed initially. Bis(trifluoromethyl)keten,[20] perfluoroisobutene,[22] and perfluorotetramethylallene[43] give rise to hexafluoroisobutenyldimethylamine under these conditions:



Z = O, F_2, $C(CF_3)_2$.

In the latter case the hexafluoroisobutenylidene group $C=C(CF_3)_2$ acts as an analogue of the carbonyl group.

Much attention has been devoted to the methods for the introduction of fluorine into an organic molecule. In particular, this applies to the discovery of the opening of the epoxide rings under the influence of HF, first discovered by Knunyants and co-workers,[32]§ and the coupled addition to olefins in hydrogen fluoride.[19] A number of studies have been devoted to the fluorination of organic compounds.[46–48] A convenient synthesis of the anticancer preparation 5-fluorouracil by the direct fluorination of the readily available uracil has been developed and introduced into practise.[46]

A method for the partial introduction of fluorine into organic molecules under mild conditions by means of anodic oxidation in the presence of the fluoride anion at low potentials is of special interest.[14,23] The method for the electrochemical trifluoromethylation of organic compounds (for example, of olefins, derivatives of αβ-unsaturated carboxylic acids, and aromatic compounds) with the aid of the CF_3 radical generated in the anodic oxidation of trifluoroacetic acid is also interesting.[49]

Studies on the synthesis and properties of chemically inert organic perfluoro-compounds, with an anomalously high capacity for dissolving various gases, in particular O_2 and CO_2, are very important. Such compounds are attracting increasing attention because various preparations for biomedical purposes, including artificial blood substitutes, can be obtained on their basis.[50]

However, as already stated, the principal research carried out at the Laboratory was devoted to the investigation of the reactions of multiple bonds in organofluorine compounds, particular emphasis being laid on the study of the C=C bond.

II. FLUORO-OLEFINS AND RELATED COMPOUNDS

The comparatively readily available fluoro-olefins can be regarded as "key" compounds in the organic chemistry of fluorine. An enormous range of the most varied organofluorine compounds can be obtained from them; in addition, the study of the reactivity of fluoro-olefins and related compounds made it possible to elucidate many important theoretical questions relevant to organofluorine chemistry (and organic chemistry in general).

The unusual chemical properties of perfluoro-olefins are caused by the high electronegativity of the fluorine atom and the ability of its electrons to effect various types of conjugation in the molecule. In contrast to the usual hydrogen-containing olefins, perfluoro-olefins react very readily with nucleophiles.[45,51]

Soon after the first communications on the addition of nucleophiles to fluoroethylenes,[52,53] the studies by Knunyants and co-workers, devoted to the interaction of various fluoro-olefins with nucleophiles, were published.[54–56] Perfluoroisobutene proved to be especially active in these reactions. Studies of its chemical properties, which have continued to this day, demonstrated the truly inexhaustible synthetic possibilities arising from the use of this fluoro-olefin.[22] Other branched perfluoro-olefins, in particular perfluoropropene dimers and trimers, for example, $(CF_3)_2C = CFC_2F_5$ and $CF_3CF = C[CF(CF_3)_2]_2$,[57–67] have attracted much attention recently. Their interaction with nucleophiles lead to ways of synthesising potential monomers, fluorine-containing surfactants, and other products of practical value.

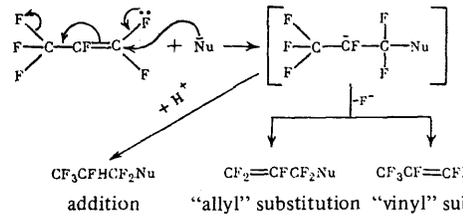
---

§ This reaction has found extensive applications, for example, in the synthesis of fluorine-containing steroids.[44,45]

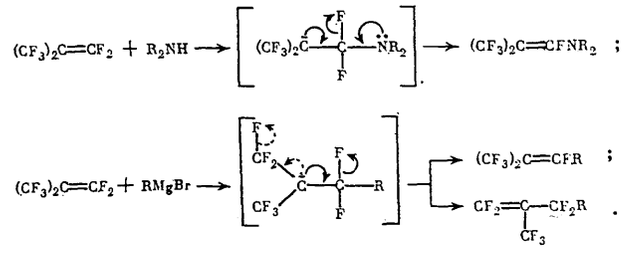
In the study of the reactivity of the C=C bond "depleted" in electrons owing to the influence of the fluorine atoms and the perfluoroalkyl groups, a wide range of other fluorine-containing compounds with a C=C bond were also investigated, namely, 1,3-dienes,[6,68–71] allenes,[2,43,72–74] derivatives of αβ-unsaturated carboxylic[5,11,24,75–79] and phosphonic[78,80] acids, and alkyl polyfluoroalkenyl ethers.[6,7,60,63,81–83] The most varied nucleophiles, including unusual ones, have been involved in reactions which yielded interesting and sometimes unexpected results.

The first investigations already revealed the occurrence of "vinyl" substitution in perfluoropropene and perfluoroisobutene.[56] This reaction was surprising from the standpoint of the "usual" organic chemistry, but it was found to be common in the chemistry of organofluorine compounds.

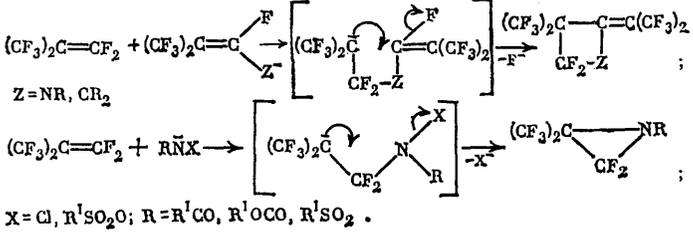
Subsequently it was shown (to a large extent as a result of the work of Knunyants and his school) that, in the reactions of fluoro-olefins with nucleophiles, the direction of attack depends on the conjugation in the fluoro-olefin molecule and the final result depends on the realisation of various possibilities for the stabilisation of the intermediate carbanions:[2,3,22,51]



These possibilities are determined both by the structure of the initial fluoro-olefin and by the nature of the nucleophile. In particular, the contribution of the "allyl" substitution increases in the absence of an unshared electron pair in the substituent obtained from the nucleophile:[22]

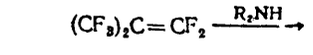


Instances of the stabilisation of the intermediate carbanions by intramolecular cyclisation are of special interest,[13,22,60,77,84–87] for example:

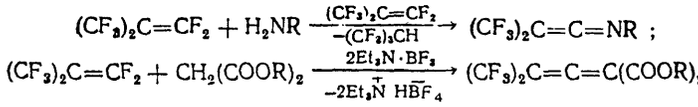


The anions $RCO\bar{N}X$, formed in the Hofmann and Lossen rearrangements, were "captured" with the aid of a reaction of this type for the first time.[22]

The intense electron-accepting effect of the trifluoromethyl groups in perfluoroisobutene and related compounds leads to the possibility of obtaining geminal compounds as a result of "double vinyl substitution",[22,56,88,89] for example:

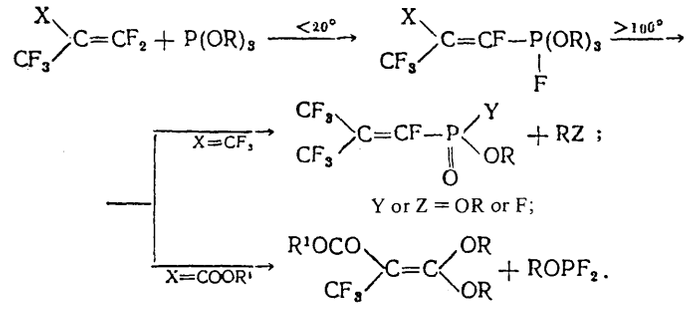


Novel methods of synthesising fluorine-containing cumulenes and heterocumulenes are also based on the substitution of both fluorine atoms in the $=CF_2$ group,[13,22,77,90] for example:



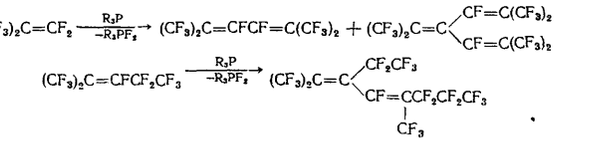
It is of interest that perfluoroisobutene itself plays the role of the dehydrofluorinating agent in the first of the above reactions; as in many other instances,[11,22,91–96] in the second reaction an unusual reagent, namely the triethylamine–boron trifluoride adduct,¶ has been used successfully for the smooth elimination of HF.

The reaction of the highly electrophilic fluoro-olefins with trialkyl phosphites yielded stable adducts—phosphoranes with a P–F bond, which are cleaved only on heating. Depending on the structure of the "fluoro-olefin" component of the phosphorane, its cleavage proceeds either in the direction of the Arbuzov reaction or follows an unusual pathway with formation of a compound of tervalent phosphorus and a fluorine-containing keten acetal:[11]



In the latter case the nucleophile (RO^-) attacks the highly electrophilic β-carbon atom of the "acrylic" system, which ultimately leads to the cleavage of the C–P bond.

When perfluoro-olefins were acted upon by tertiary phosphines, interesting reactions were observed, including the defluorodimerisation and defluorotrimerisation reactions,[15,22,98] for example:

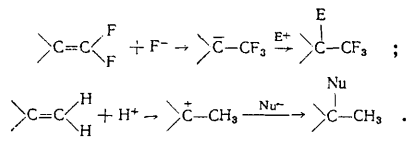


These reactions probably involve the intermediate formation of phosphorus ylides of the type $(CF_3)_2C=C=PR_3$ and $(CF_3)_2CFC(C_2F_5)=PR_3$ (cf. Stepanov and co-workers[65,67]).

¶ The dehydrofluorinating effect of the $Et_3N.BF_3$ adduct has been used to develop a new and apparently most convenient method of synthesis of derivatives of perfluoromethacrylic acid (potential monomers).[11] Other dehydrofluorinating agents are as a rule unsuitable in this case. The same adduct can sometimes be employed also to eliminate an alkyl fluoride, for example, in the conversion of trialkoxyhexafluoroisopropylidenephosphoranes $(CF_3)_2C=P(OR)_3$ into the "phosphorus analogues" of perfluoromethacrylates—the pentafluoroisopropenylphosphonates $CF_2=C(CF_3)PO(OR)_2$.[97]

Since the electron can play the role of a kind of "nucleophile", electrophilic fluoro-olefins undergo electrochemical reduction comparatively readily.[87,99-101] The study of the polarographic behaviour of fluoro-olefins† [87,100,101] showed that the reduction potential decreases with increase of the number of electron-accepting perfluoroalkyl groups at the C=C bond. A correlation was observed between the reduction potential of the fluoro-olefin and the energy of the lowest unoccupied molecular orbital (calculation by the MNDO method).[100,101]

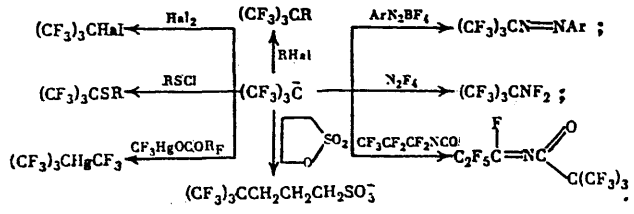
When the F^- anion is used as the nucleophile, the corresponding fluorocarbanions are obtained from perfluoro-olefins. Reactions involving the intermediate formation of fluorocarbanions occupy a notable place in the chemistry of fluoro-olefins.[33,35,102,103] As frequently happens in organofluorine chemistry, a "reverse analogy" obtains here between the reactions of the fluoro-olefins in the presence of the F^- anion and the reactions of non-fluorinated olefins in the presence of the H^+ cation (or a Lewis acid):[104]



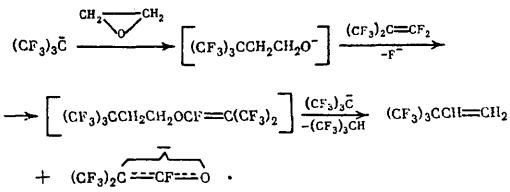
The main contribution made by the Laboratory of Organofluorine Compounds at the Institute of Organoelemental Compounds to this important field involved the study of the reactivity of highly branched fluorocarbanions (in particular the perfluoro-t-butyl anion[12,22] and the perfluoro-t-hexyl anion[57,105-107]), the development of the "nucleophilic mercuration" of fluoro-olefins,[12,22] the development of the chemistry of mesomeric fluorocarbanions,[7,24] the discovery of new sources of the weakly solvated F^- anion containing carbonium counterions,[108] the detection of fluorocarbanions by NMR,[12,109] and the involvement of fluorocarbanions in new types of reactions—azocoupling,[12,107] difluoroamination,[12] sulphenylation,[22] coupled addition to fluoro-olefins,[22,110] reactions with geminal and vicinal dihalogenopolyfluoroalkanes,[22,106,111] etc.

The reactions of branched fluorocarbanions are extremely varied—see, for example, Scheme 1.[12,112,113] Together with subsequent reactions of the products, these reactions lead to extensive possibilities for the synthesis of organofluorine compounds, including potential monomers and surfactants.

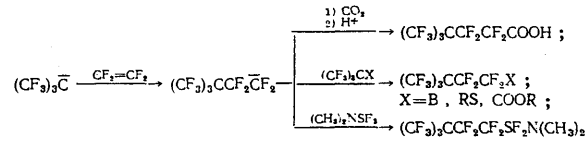
Scheme 1



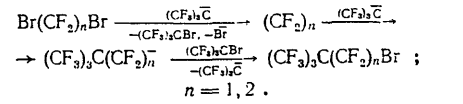
Interesting reactions take place between the carbanions $(CF_3)_2\bar{C}CF_2R_F$ (R_F = F or CF_3) and epoxides.[12,24,105] Under certain conditions, the fluoro-olefin can play in this case the role of not only the dehydrofluorinating agent but also of a kind of dehydrating agent, for example:



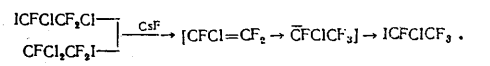
The reaction involving the coupled addition of the perfluoro-t-butyl anion and electrophiles to fluoro-olefins has been discovered recently.[22,110] It leads to ways of synthesising various functional-group substituted organofluorine compounds, for example:



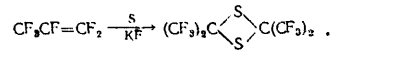
The coupled addition of the anion $(CF_3)_3C^-$ and bromine to tetrafluoroethylene also takes place in the intermediate stages of the reaction of the perfluoro-t-butyl anion with 1,2-dibromotetrafluoroethane, which leads to the substitution of one of the bromine atoms by the $(CF_3)_3C$ residue.[22] The reaction begins with the halogenophilic attack by the tertiary carbanion on the bromine atom of the vicinal dibromo-compound and is completed by a similar attack by the primary carbanion on the bromine atom in perfluoro-t-butyl bromide (or the initial vicinal dibromo-compound). Analogous reactions have been observed also in the reaction with a geminal dibromo-compound—dibromodifluoromethane.[22,106] Tetrafluoroethylene and difluorocarbene are formed respectively as intermediates in the reactions involving the vicinal and geminal dibromo-compounds:



Similar elimination–addition reactions have been observed also on treatment with other nucleophiles of organofluorine compounds containing halogen atoms other than fluorine in the vicinal positions. When the F^- anion is used, the formal result of such a reaction is the substitution of one of the halogen atoms by fluorine, which is accompanied in certain cases by a rearrangement,[111] for example



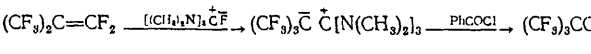
The reactions of fluorocarbanions with sulphur lead to fluorine-containing sulphides, disulphides, trisulphides, dithiacyclobutanes and trithiacyclopentanes.[12] In particular, a convenient method of synthesising the hexafluorothioacetone dimer has been discovered:#



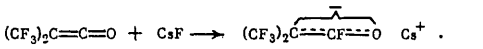
New effective sources of the fluoride anion, namely α-fluoroalkylamines, in which this anion is stabilised by organic cations, were found in subsequent years.[22,108,115] This extends the synthetic possibilities in the chemistry of fluorine-containing anions. Thus the benzoylation of the perfluoro-t-butyl anion has been achieved only when hexamethylguanidinium was used as the counterion:[22]

†The preparative reduction at the cathode via the intermediate formation of mesomeric fluorocarbanions is described below.

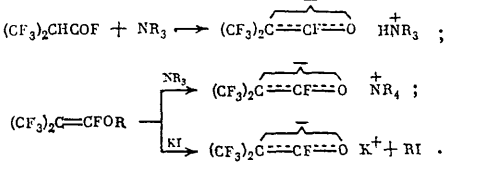
#Subsequently this method was improved.[114]



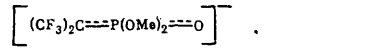
Other fluorine-containing unsaturated compounds react with the fluoride anion like fluoro-olefins (frequently even more readily). Perfluoromethylacryloyl fluoride,[11,24] bis-(trifluoromethyl)keten,[24,76,116] its *N*-benzenesulphonylimine,[91] fluorine-containing allenes,[72,74] and pentafluoroisopropenylphosphonate esters[80] give rise under these conditions to the corresponding stable mesomeric carbanions, for example:



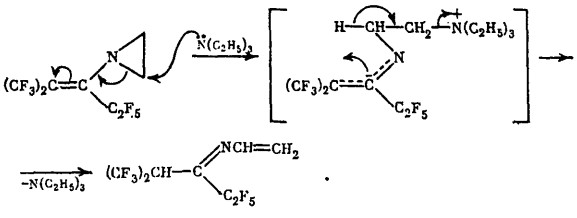
The chemistry of mesomeric fluorocarbanions of this type has been investigated on a fairly wide scale.[2,3,7,24,64] They can be generated not only by the method described above but also from the corresponding CH acids§ and sometimes by the dealkylation of alkyl polyfluoroalkenyl ethers,[2,3,7,24,64,118] for example:



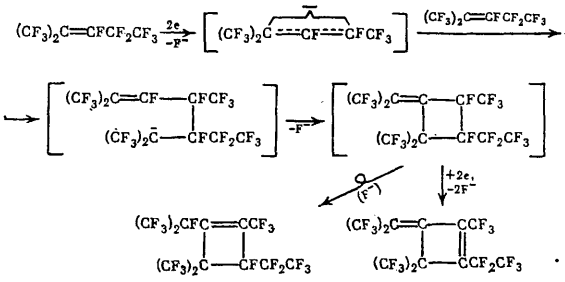
Hexafluoroisopropylidenetrimethoxyphosphorane is dealkylated similarly, forming the anion



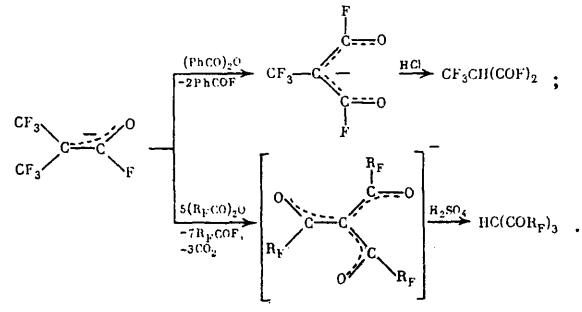
1-Perfluoroalkenylaziridines sometimes behave similarly to alkyl perfluoroalkenyl ethers, manifesting "alkylating" properties in relation to tertiary amines. This is in fact the explanation of the rearrangement of 3-(1-aziridinyl)-perfluoro-2-methylpent-2-ene to 2-hydroperfluoro-2-methyl-3-pentanone *N*-vinylimine:[62]



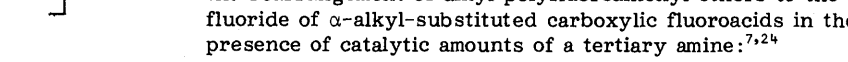
An unusual method of generating mesomeric fluorocarbanions involves the cathodic reduction of fluoro-olefins.[66,87,99] For example, in contrast to the effect of a tertiary phosphine (see above), the preparative electrochemical reduction of the perfluoropropene dimer leads to perfluorinated substituted cyclobutenes as a result of "cathodic dimerisation" involving defluorination and cyclisation. It has been suggested that a mesomeric fluorocarbanion is then formed as an intermediate as a result of the transfer of two electrons to the initial fluoro-olefin and the elimination of the F^- anion:



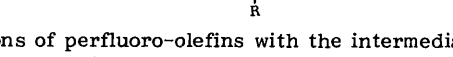
The stable salts formed by the mesomeric fluorocarbanions into a wide variety of reactions—halogenation, alkylation, and partial hydrolysis of the CF_3 groups.[2,7,24] On treatment with carboxylic acid anhydrides, the trifluoromethyl groups are converted into fluorocarbonyl or perfluoroacyl groups, which makes it possible to synthesise various di- and tricarbonyl compounds,[24,119] for example:



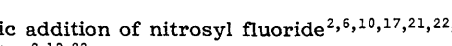
Fluorine-containing α-phosphonate anions enter into the Wittig–Horner reaction with carbonyl compounds:[80]



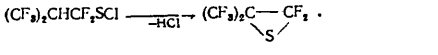
Mesomeric fluorocarbanions are formed as intermediates in the rearrangement of alkyl polyfluoroalkenyl ethers to the fluoride of α-alkyl-substituted carboxylic fluoroacids in the presence of catalytic amounts of a tertiary amine:[7,24]



Certain reactions of perfluoro-olefins with the intermediate formation of fluorocarbanions constitute characteristic examples of the inversion of the addition mechanism, where reagents usually regard it as electrophiles react via a nucleophilic mechanism. Thus, hydrogen fluoride readily adds to perfluoroisobutene in the presence of bases[6,10,12,22] (cf. Brice et al.[120]):

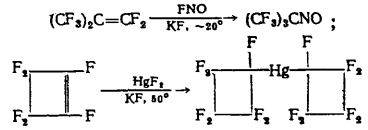


The nucleophilic addition of nitrosyl fluoride[2,6,10,17,21,22,121] or mercury fluoride[2,12,22] to electrophilic fluoro-olefins in the presence of the F^- anion belongs to reactions of the same type,¶ for example:

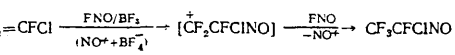


§Not only mesomeric but also perfluoroalkylcarbanions can be obtained by the heterolysis of the C–H bond. Thus it has been shown for the first time in relation to monohydroperfluoroisobutane $(CF_3)_3CH$ that the proton mobility of the hydrogen atom in monohydroperfluoroalkanes can find a synthetic application.[12,24,117] The intramolecular sulphenylation of β-hydroperfluoroisobutylsulphenyl chloride led to a perfluorinated thiiran:[31]

¶The inversion of the mechanisms takes place also in other cases. Thus, it has been found unexpectedly that highly electrophilic fluorine-containing unsaturated compounds very readily undergo the Prilezhaev epoxidation in ethereal solvents[11,24,122] and are halogenated in acetonitrile.[22,78] Evidently in this case even the use of weakly basic solvents is sufficient to shift the reaction from the usual electrophilic mechanism to a "nucleophilic track".

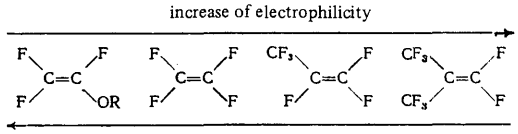


However, the interaction of nitrosyl fluoride with polyfluoroethylenes is catalysed by boron trifluoride in contrast to the analogous reactions of perfluoropropene and perfluoroisobutene:[6]

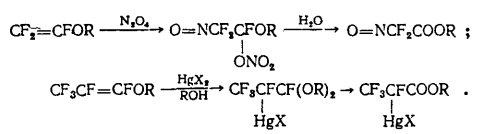


This example shows that reactions via the electrophilic mechanism usual for olefins are possible also in the case of fluoro-olefins.[2,10,21] Such reactions have been little investigated in the first stage of the study of the reactivity of fluoro-olefins, where attention was concentrated on the interaction with nucleophiles. At the same time, despite their low reactivity (or more correctly precisely because of it), fluoro-olefins have advantages in reactions with strong electrophiles over the usual non-fluorinated olefins because the replacement of hydrogen atoms by fluorine atoms as a rule prevents undesirable side processes—oxidation, polymerisation, etc.

The wide-scale study of the reactions of fluoro-olefins with nucleophiles and electrophiles made it possible to generalise the results obtained and to formulate the thesis of the electronically amphoteric character of the double bond in these compounds.[2,4,6] The order in which the electrophilic properties of fluoro-olefins are enhanced and the nucleophilic properties are correspondingly diminished can be accounted for by the electron-accepting effect of the fluorine atoms and the trifluoromethyl groups and also by the electron-donating mesomeric effect of fluorine atoms (and, in the case of alkyl polyfluoroalkenyl ethers, also the oxygen atoms) in the vinyl position acting in the opposite direction:

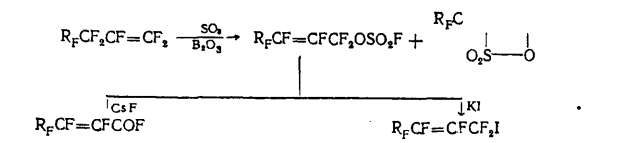


The reactions with electrophiles are more characteristic of the first members of this series than the last. Such reactions are achieved particularly readily for fluoro-olefins containing electron-donating substituents. The use of alkyl polyfluoroalkenyl ethers for the synthesis of a wide variety of derivatives of fluorine-containing carboxylic acids is based on this fact,[6,81-83] for example:



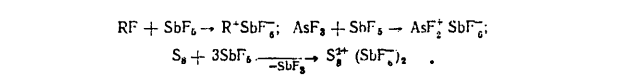
Under fairly severe conditions, strong electrophiles also react with very weak nucleophilic perfluoro-olefins. A typical example is provided by the interaction with sulphur dioxide, which leads to the corresponding cyclic adducts—β-sultones and pyrosultones; these compounds exhibit a varied reactivity and their reactions lead to a wide variety of sulphur-containing organofluorine compounds.[2,123]

It has been shown recently[124-126] that another reaction, substitutional sulphotrioxidation, takes place together with cycloaddition in the presence of Lewis acids. The perfluoroallyl fluorosulphates formed have been used successfully in the synthesis of various fluorine-containing unsaturated compounds—iodides, derivatives of carboxylic acids, dienes, organomercury compounds, etc.[79,127-129], for example:

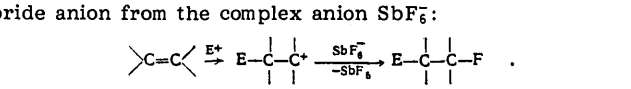


The use of antimony pentafluoride as the Lewis acid makes it possible to obtain fluorosulphates not only from terminal but also from internal fluoro-olefins.[130]

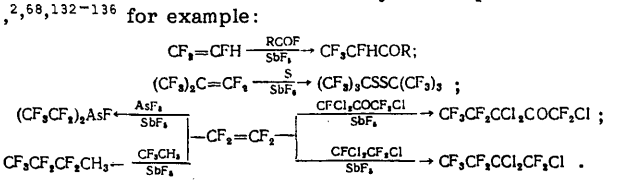
In general the reactions of fluoro-olefins in the presence of antimony pentafluoride are of great interest. Antimony pentafluoride is a very strong Lewis acid, exhibiting in addition oxidative properties, which is capable of generating cationoid species from various reagents,[2,131] for example:



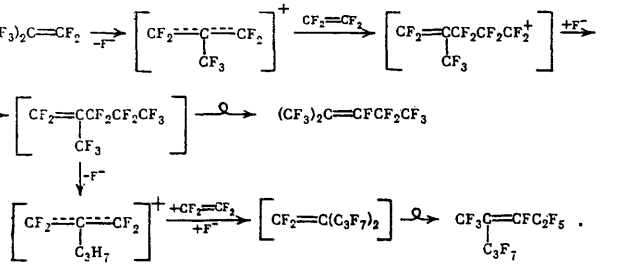
Highly electrophilic cationoid species attack the molecule of a fluoro-olefin and the resulting carbonium ions abstract a fluoride anion from the complex anion SbF_6^-:



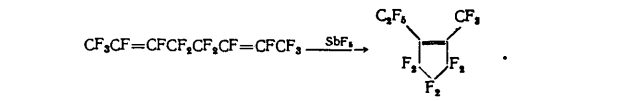
Such reactions have led to extensive synthetic possibilities,[2,68,132-136] for example:



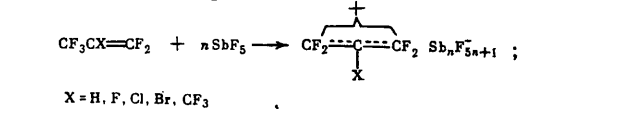
Reactive cationoid species (carbonium ions) can be formed not only from an acyl halide, a halogenoalkane, or a halogenoketone but also from a fluoro-olefin on treatment with SbF_5 as a result of the elimination of the fluoride anion from the allyl position. The resulting fluorine-substituted allyl cations can react with another molecule of the fluoro-olefin, which entails dimerisation and, in the case of different olefins, mixed dimerisation or trimerisation,[68,136] for example:



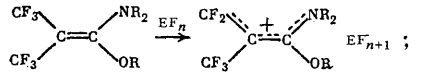
Intramolecular cyclisation has been observed similarly in the case of a perfluorodiene:[137]



Fluorine-containing polyhalogenoallyl cations proved to be so stable in a number of instances that they could be detected by NMR,[138-141] for example:

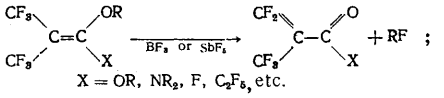


The mesomeric carbonium ion intermediate can be isolated in the form of a salt in the reaction of a Lewis acid with a fluoro-olefin having electron-donating substituents:[11]



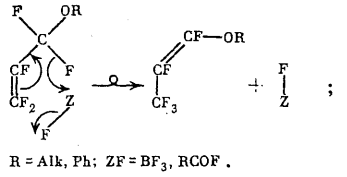
$EF_n = BF_3, SbF_5$.

Such cations are evidently formed as intermediates in the electrophilic elimination of alkyl fluorides from alkyl polyfluoroalkenyl ethers on treatment with Lewis acids. This reaction is used to synthesise αβ-unsaturated fluorocarbonyl compounds,[2,11,142] for example:



X = OR, NR_2, F, C_2F_5, etc.

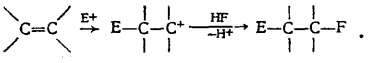
The rearrangement of perfluoroallyl ethers to perfluoropropenyl ethers is also catalysed by fluorine-containing Lewis acids.[143] A synchronous cyclic mechanism has been proposed for this reaction:



R = Alk, Ph; ZF = BF_3, RCOF .

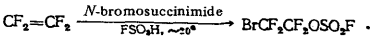
The driving force in this and similar rearrangements is the energy gain resulting from the formation of compounds with a more conjugated bond system.

Apart from Lewis acids, hydrogen fluoride can also be used as the catalyst for the generation of the cationoid species and as a source of F^- anions. The coupled addition of various reagents in HF to olefins, including fluoro-olefins, is of considerable synthetic value:[19]



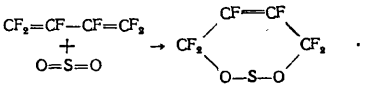
Fluoronitration, fluorohydroxymethylation, fluoroaminomethylation, fluorohydroxylation, etc. products have been obtained in this way.

The coupled electrophilic addition of a halogen and the fluorosulphonic acid residue to fluoro-olefins proved to be a convenient method of synthesis of halogenopolyfluoroalkyl fluorosulphates,[144] for example:

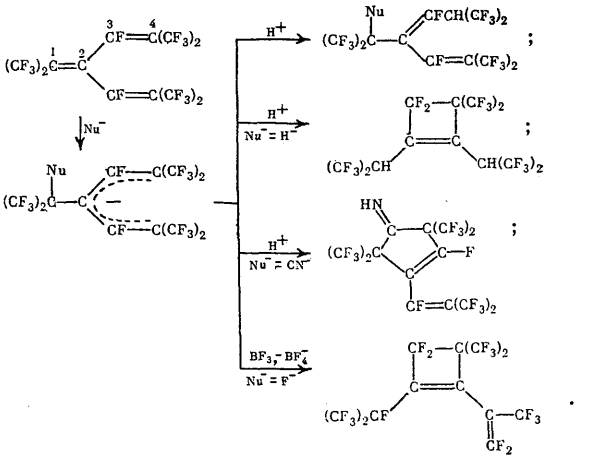


The compounds obtained are of interest as intermediates in the synthesis of derivatives of carboxylic chloro- and bromoperfluoroacids.

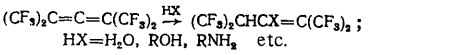
Interesting data have been obtained in the study of the reactivity of fluorine-containing dienes. In the reactions of perfluorobuta-1,3-diene with nucleophiles, π,π-conjugation is usually not observed in the diene molecule.[6]† However, the photochemical or thermal reactions of perfluorobuta-1,3-diene with substituted styrenes or phenylacetylene afford mixtures of cyclic [2 + 2]- and [4 + 2]-adducts apparently as a result of a stepwise biradical reaction.[69,70] The 1,2- and 1,4-cycloaddition products are also formed as a result of the photochemical reaction with sulphur dioxide;[71] however, in the latter case sulphur dioxide reacts in a completely unusual manner, serving as the source of the –O–S–O fragment and not –O–S(=O)–; a new type of heterocyclic compound was thereby obtained—a seven-membered cyclic ester of sulphoxylic acid:



The interaction of the cross-conjugated perfluorotriene with nucleophiles involves 1,4-addition, the attack by the nucleophilic species being directed to the C(1) atom.[146] In certain cases the carbanionic intermediate is stabilised by cyclisation:[147,148]

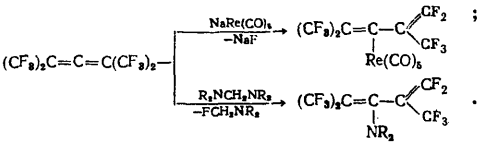


The cumulated perfluorodiene (perfluorotetramethylallene) proved to be extremely reactive. It readily combines with nucleophiles:[2]



HX=H_2O, ROH, RNH_2 etc.

It is of interest that the 1,2-diene system of this compound cannot as a rule be converted into the conjugated 1,3-diene system.[2] The reactions with trialkyl phosphites, the anions of metal carbonyls, and tetraalkylmethylenediamines are exceptions,[149,150] for example:



III. POLYFLUOROCARBONYL COMPOUNDS AND THEIR ANALOGUES

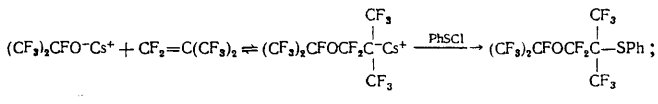
An extensive cycle of studies carried out at the Laboratory of Organofluorine Compounds of the Institute of Organoelemental Compounds has been devoted to the investigation of the influence of fluorine-containing groups on the reactivity of heteroatomic multiple bonds. These studies have made a decisive contribution to the investigation of the chemical properties of fluorine-containing ketones, ketens, and their derivatives, as well as analogues of carbonyl compounds such as aliphatic fluoronitroso- and fluoronitro-compounds.

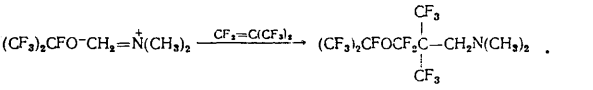
† Perfluorodimethylbuta-2,3-diene behaves analogously.[145]

The introduction of perfluoroalkyl groups enhances the electrophilic properties and diminishes the nucleophilic properties of the multiple bonds. Furthermore, perfluoroalkyl groups increase the stability of the corresponding compounds and a wide variety of derivatives obtained on their basis, so that structures which are unstable or do not exist at all in the "usual" organic chemistry become entirely stable. The most striking example is provided by the stable enol of pentafluoroacetone[25,151] (see below). Geminal diols, hydroxyamines, and diamines are all compounds whose existence conflicts with the El'tekov–Erlenmeyer rule, being stable in the series of organofluorine compounds.[18] Furthermore, unusual structures such as those of the "enols" of *N*-fluoroamides,[152] *N*-fluoroazoxy-compounds,[17] and many others are entirely stable.

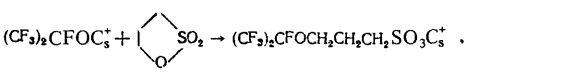
All these findings impart a considerable variety of fluorocarbonyl compounds and their analogues, which entails not only a radical change in their reactivity in the usual reactions but also the appearance of the possibility of reactions which are completely atypical of non-fluorinated compounds. In this Section we shall consider mainly reactions of the latter type.

In contrast to the non-fluorinated ketones, perfluoroketones and their derivatives yield relatively stable adducts with alkali metal fluorides[16,33,35,153] or with α-fluoroalkylamines.[108] The α-fluoroalkoxides formed can in principle add to fluoro-olefins, but this reaction is reversible and the equilibrium is displaced towards the initial reactants. Nevertheless, the formation of the adduct, a perfluoroalkoxycarbanion, has been detected by reactions with electrophiles such as halogens, sulphenyl halides, or the methyleneimmonium cation:[22,108]

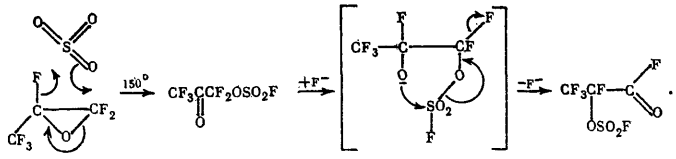




On reaction with propane sultone (1,2-oxathiolan 2,2-dioxide), α-fluoroalkoxides give rise to perfluoroalkoxy-substituted sulphonates, which are of interest for the synthesis of surfactants:[113]

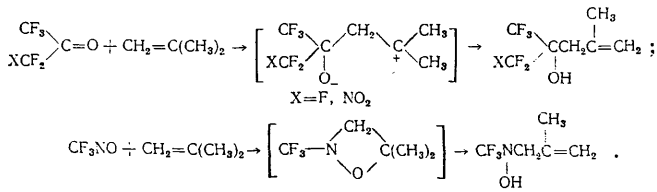


The rearrangement of the fluorosulphate derived from hydroxypentafluoroacetone into α-formylperfluoroethyl fluorosulphate under the influence of the F^- anion has been accounted for by the intermediate formation of a α-fluoroalkoxide and its intramolecular acylation:[2,154]

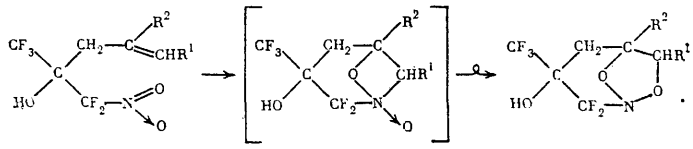


A certain analogy in the reactivities of ketones, ketens, and nitroso- and nitro-compounds is most conveniently traced in relation to stable polyfluoro-compounds, because aliphatic ketens and nitroso-compounds without fluorine are unstable.

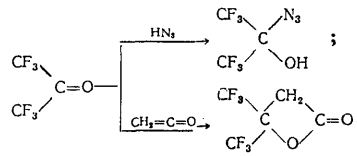
Perfluoroketones,[18,155] bis(trifluoromethyl)keten,[20] and perfluoronitrosoalkanes[17] react with a weak nucleophile such as isobutene in the cold and, in contrast to the non-fluorinated analogues, without catalysts:



The nitro-group reacts similarly with an olefinic double bond but the cyclic adduct formed initially isomerises in this case to a derivative of 1,3,2-dioxazolidine:[156]

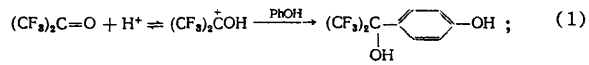


Hydrazoic acid and a keten readily interact with perfluoroketones in the absence of a catalyst[18] whereas their reactions with non-fluorinated ketones take place only in the presence of acids (protic or aprotic):[18]

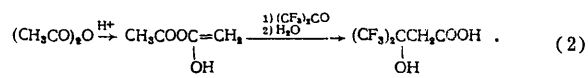


Thus it has been found that increase of electrophilic reactivity and a decrease of nucleophilic reactivity entail the "inversion" of the reaction mechanism: electrophilic addition (for non-fluorinated ketones) is transformed into nucleophilic addition (for perfluoroketones). It is of interest to note that trifluoroacetone reacts with keten only in the presence of BF_3 and the reaction proceeds with difficulty compared with the reaction involving acetone. Evidently the presence of one trifluoromethyl group is insufficient to convert the ketone from a nucleophile into an electrophile.[18]

Despite the highly electrophilic properties of perfluorocarbonyl compounds, they are frequently incapable of reacting with very weak nucleophiles. In such cases success has been achieved with the aid of acid catalysis; the catalyst then activates either the fluoroketone [Eqn.(1)] or the attacking agent [Eqn.(2)], for example:[18]



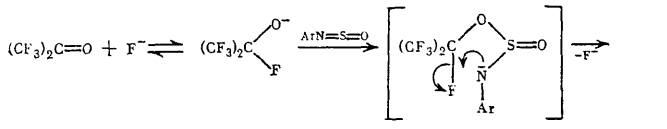
(1)



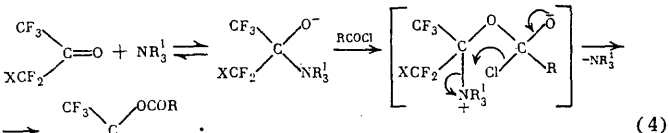
(2)

In view of the reduced basicity of fluoroketones and their derivatives, electrophilic addition of type (1) is difficult.[18]

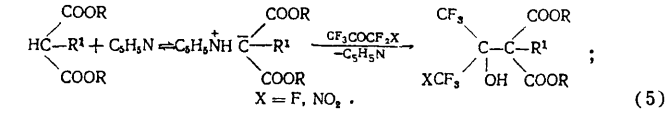
The use of basic catalysts in reactions with electrophiles proved to be no less successful. As in acid catalysis, the basic catalyst can activate either the fluorocarbonyl compound, by converting it into a nucleophilic α-substituted alkoxide [Eqns.(3) and (4)] [157–159] (cf. Zeifman et al.[160]), or the attacking agent, by converting it into a nucleophilic conjugate base [Eqn.(5)]:[18]



(3)

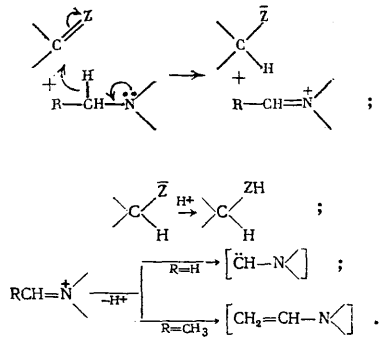


(4)



(5)

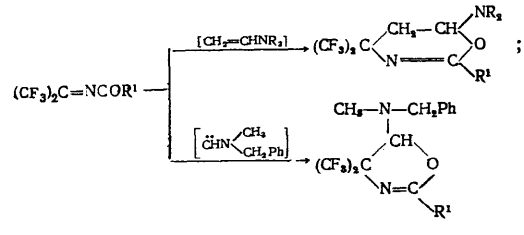
The very high electrophilicity of the C=O groups in fluoroketones[18] and in derivatives of carboxylic fluoroacids,[2,161] of C=N groups in hexafluoroacetone acylimines,[162,163] and of the C=C bond in perfluorotetramethylallene[2] is manifested in oxidation-reduction reactions with tertiary amines. The first stage of these reactions yields an immonium cation, which can be subsequently transformed into an aminocarbene or a vinylamine:



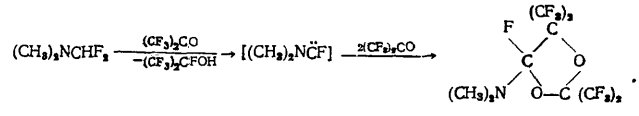
The intermediate formed reacts subsequently with the initial electrophilic fluorine-containing unsaturated compound, for example:

$$[CH_2{=}CHNR_2] + R_FCOX \rightarrow R_FCOCH{=}CHNR_2 .$$

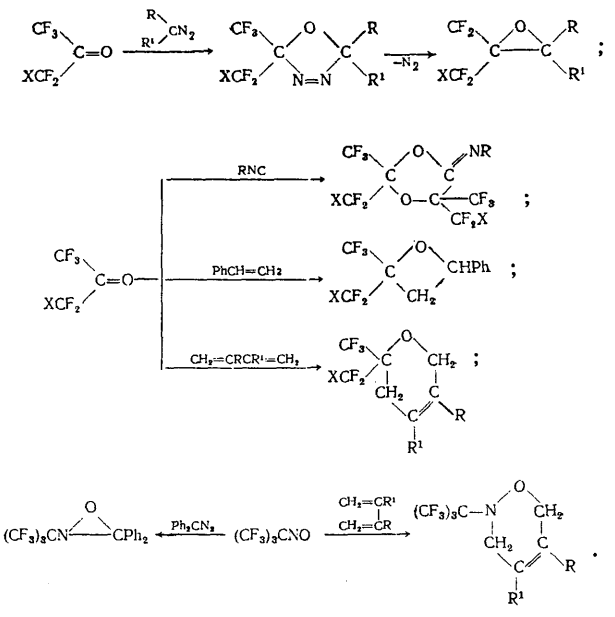
Hexafluoroacetone acylimines give rise to cyclic adducts under these conditions:



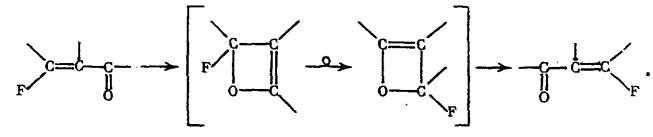
The aminocarbene obtained as a result of the dehydrofluorination of the αα-difluoroalkylamine by the perfluoroketone also undergoes cycloaddition to the initial ketone to form a 1:2 adduct:[115]



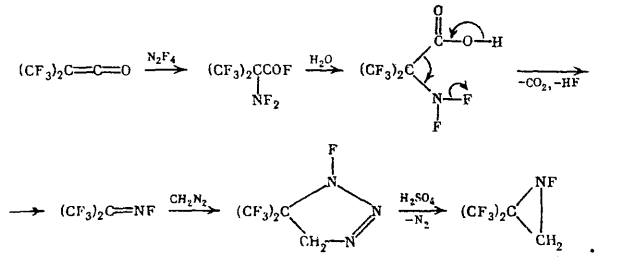
Cycloaddition reactions are in general very characteristic of fluorine-containing ketones[18,164] and ketens,[20] trifluoropyruvate esters,[165] and fluoronitrosoalkanes,[17] for example:



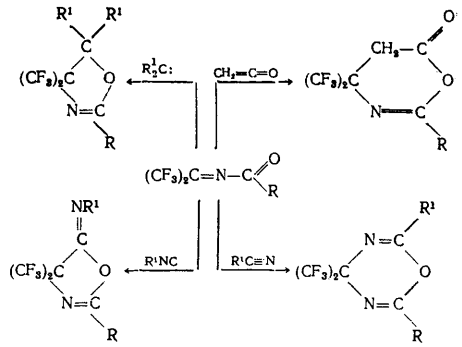
The carbonyl group can also add intramolecularly to the C=C double bond in certain fluorine-containing αβ-unsaturated carbonyl compounds. This entails a kind of rearrangement as a result of which the oxygen and fluorine atoms change places:[11,166]



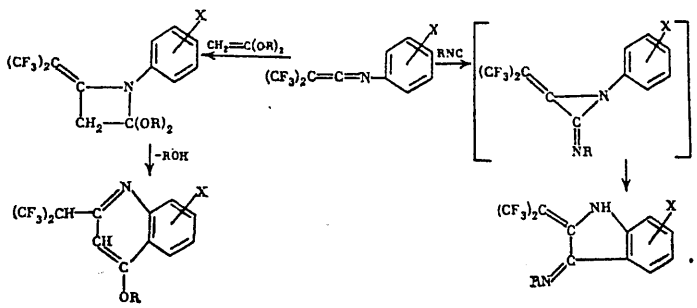
Fluoroketone imines also enter into cycloaddition reactions with dienes and diazo-compounds.[16,167] Imines with electron-accepting substituents both at the carbon atom and at the nitrogen atom are particularly active. For example, hexafluoroacetone *N*-fluoroimine, which is readily obtained from bis(trifluoromethyl)keten, reacts with diazomethane at −50 °C:[152]



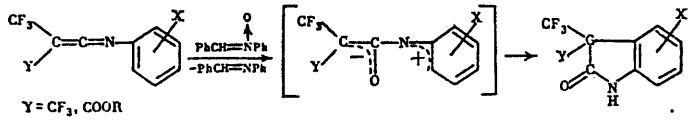
Fluoroketone *N*-acylimines are very reactive, typically undergoing 1,4-dipolar cycloaddition reactions with diazomethane, carbenes, isonitriles, and compounds containing the C=C, C≡C, C=O, and C≡N multiple bonds:[16,168]



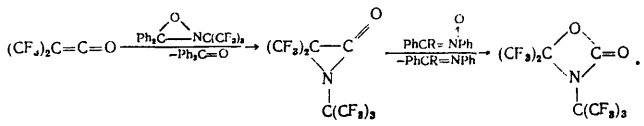
Cycloaddition reactions involving the aromatic ring have been discovered for bis(trifluoromethyl)keten *N*-arylimines. These reactions resemble structurally the Diels–Alder reactions, i.e. keten *N*-arylimines formally behave in this instance like 1,4-dipolar compounds. However, a two-stage mechanism rather than a synchronous mechanism is more likely for reactions of this type, where one of the double bonds of the 1,3-diene forms part of an aromatic ring: betaines or small rings are formed initially, being subsequently stabilised as a result of the reaction with the aromatic ring,[13,169] for example:



The unusual reaction of keten *N*-arylimines with nitrones, which in this instance play the role of oxygen sources, belongs to the class of reactions of this type:[13,169,170]

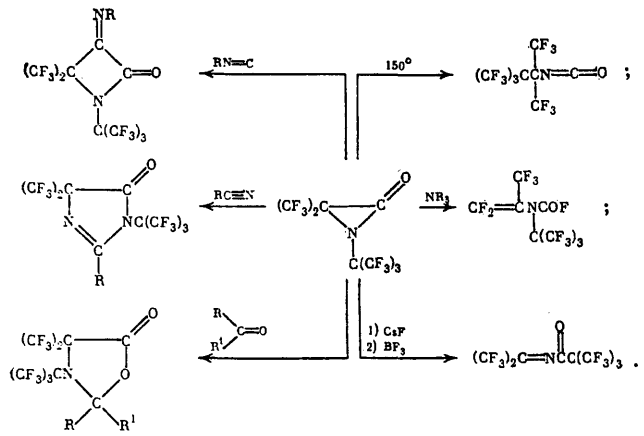


Nitrones react as oxidants also with the uniquely stable perfluoro-α-lactam, which is obtained by the epimination of bis(trifluoromethyl)keten:[27]



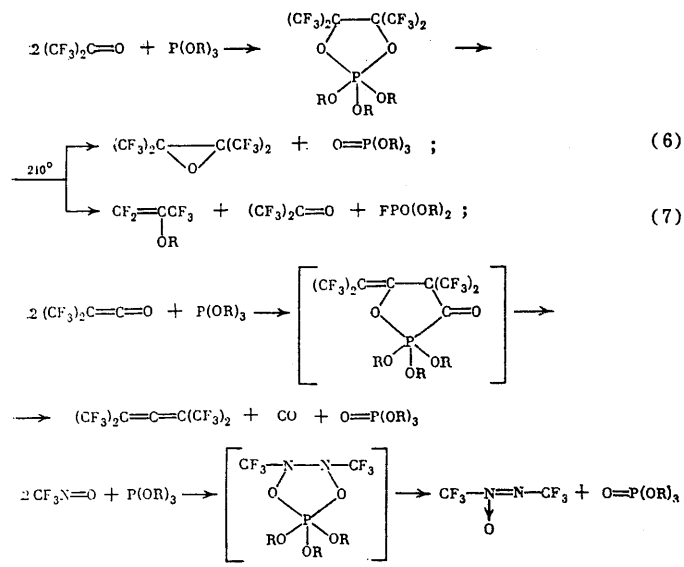
Any of the bonds of the three-membered ring can be ruptured in the cycloaddition reactions with perfluoro-α-lactam, four- or five-membered heterocycles with two heteroatoms being formed. On treatment with nucleophiles (NR_3, CsF) or after prolonged heating, perfluoro-α-lactam rearranges to linear isomers: a perfluoroalkyl isocyanate, an unsaturated carbamoyl fluoride, and a ketone acylimine; similar rearrangements of non-fluorinated α-lactams are unknown[28,29] (Scheme 2).

Scheme 2



The analogy between the properties of fluorine-containing ketones, ketens, and nitroso-compounds is manifested particularly strikingly in the isotypical nature of the reactions with phosphite esters. Thus it has been shown that triethyl phosphite reacts in the cold with perfluoroketones,[18] bis(trifluoromethyl)keten,[20] and trifluoronitrosomethane,[17] forming "pinacolisation" products, which decompose in the last two cases already under the conditions of the synthesis (Scheme 3).

Scheme 3



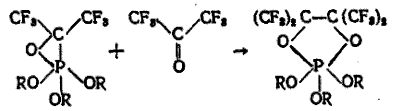
The cyclic phosphorane formed from hexafluoroacetone decomposes only on heating and the reaction proceeds via two pathways [Eqns.(6) and (7)]; the second decomposition pathway [Eqn.(7)] is analogous to the formation of oxime ethers from secondary perfluoronitrosoalkanes:[17]

$$(CF_3)_2CFNO + P(OR)_3 \rightarrow (CF_3)_2C{=}NOR + FPO(OR)_2 .$$

A complete analogy has been observed between the Allen reactions of α-chloroperfluoronitrosoalkanes and the Perkow reactions of α-chlorofluoroketones.[17]

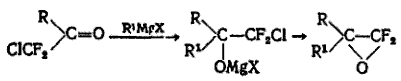
The first step in all these reactions involves the attack by the phosphite on the electrophilic carbon or nitrogen atom.[17,18] The strained three-membered cyclic phosphorane formed then either isomerises or combines with the next molecule of the unsaturated electrophile with rupture of the

C–P and not the P–O bond[18] (as in the decomposition of the four-membered cyclic intermediates in the Wittig reaction), for example:

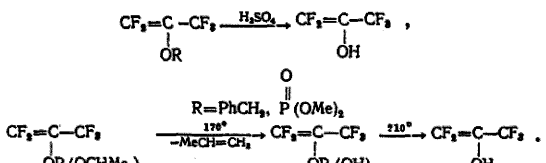


In the reaction with phosphites, two molecules of the fluorine-containing ketone or keten therefore combine with one another via the formation of a C–C bond, in contrast to the reaction with isonitriles, in which a C–O bond is formed.[8,18]

The trifluoromethyl groups in hexafluoroacetone and its derivatives are inert and do not react.# Although this restricts the synthetic possibilities of perfluoroketones, it is nevertheless convenient in the sense that the reactions of carbonyl groups are not complicated by the involvement of the other reaction centres of the molecule.[18] However, the replacement of one or several fluorine atoms by chlorine appreciably "activates" the fluoroalkyl groups, so that chlorofluoroketones are able to enter into the Perkow reaction.[25] It has been found that the chlorine atoms also readily undergo intramolecular nucleophilic substitution in the alkoxides of tertiary polyfluorocarbinols.§ This resulted in the formation of a wide range of polyfluorinated epoxides:[2]

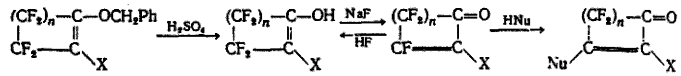


An outstanding investigation by Knunyants, Dyatkin, and Bekker and co-workers was devoted to metastable enols. It is known[25] that pentafluoroacetone HCF_2COCF_3 does not enolise because of its low acidity (the greater thermodynamic stability of the keto-form of pentafluoroacetone compared with the enolic form has been confirmed by a non-empirical calculation by the SCF method[172]). However, it has been found that the corresponding enol (pentafluoro-2-propenol) is entirely stable and can be obtained by the acid hydrolysis of benzyl pentafluoroisopropenyl ether or dimethyl pentafluoroisopropenyl phosphate or by the thermolysis of diisopropyl pentafluoroisopropenyl phosphate:[25,151,173]



The first representative of the sterically unhindered metastable enols was synthesised in this way. The exceptionally high kinetic stability of this compound can be accounted for by the optimum combination of its properties. Pentafluoro-2-propenol manifests, on the one hand, a relatively low kinetic acidity as a consequence of the destabilisation of the corresponding anion due to the mesomeric electron-donating effect of the vinyl fluorine atoms and, on the other hand, it exhibits a low proton affinity owing to the electron-accepting effect of the fluorine-containing group.[25,174] Certain other aliphatic polyfluoroenols, for example, 3-chlorotetrafluoro-2-propenol $CF_2 = C(OH)CF_2Cl$ or nonafluoropent-2-en-3-ol $CF_3CF = C(OH)C_2F_5$ also proved to be entirely stable.[25,174]

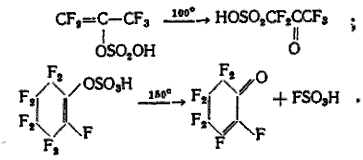
Alicyclic fluorine-containing enols have been likewise synthesised.[25,175] Their most characteristic feature is their ready dehydrofluorination by weak bases and subsequent "vinyl" substitution of the β-fluorine atom:[25,173,175,176]



X = H, F; $n = 1-3$; Nu = RO, R_2N.

It is of interest that the dehydrofluorination is reversible, thus confirming experimentally the hypothesis of the 1,4-addition of hydrogen halides to αβ-unsaturated carbonyl compounds.[173,177]

A general property of the aliphatic and alicyclic enols obtained is their ability to give rise to *O*-derivatives as a result of the substitution of the mobile hydrogen atom by an alkyl, acyl, or sulpho-group. Pentafluoropropenyl sulphate isomerises to a sulphoketone on heating, while an alicyclic sulphate eliminates fluorosulphonic acid:[25,176]



Pentafluoro-2-propenol gives rise also to other O-derivatives, namely $CF_2 = C(CF_3)OX$ (X = Li, R_3Si, R_3Ge, R_3Sn, or R_2P) or the *C*-derivatives XCF_2COCF_3 (X = halogen, NO, ArN = N, or RHg).[25,178] When mercuripentafluoroacetone is treated with acids, the initial enol is regenerated; the transfer of the reaction centre in the protodemercuration of α-mercuricarbonyl compounds, suggested previously, has thus been confirmed.[25,178]

The metastable pentafluoro-2-propenol isomerises wholly to pentafluoroacetone on prolonged heating at 180 °C and also in the presence of weak bases.[25,173]¶ In contrast to this, α-hydrohexafluoroisobutyraldehyde $(CF_3)_2CHCHO$ is involved in a tautomeric equilibrium with the corresponding enol, whose content increases (up to 100%) with increase of the basicity of the solvent.[7] The presence of the electron-accepting trifluoromethyl groups greatly increases, as was to be expected, the tendency towards enolisation in this instance.

However, it has been found that in the case of bis-(perfluoroacyl)methanes, the introduction of perfluoroalkyl or perfluoroacyl groups has the opposite effect, causing a sharp suppression of the enolisation, so that the compounds $(R_FCO)_2CHCF_3$ exists wholly in the diketone form, while the compound $(C_3F_7CO)_3CH$ exists to the extent of 90% in the triketone form.[119] Evidently the bulky groups prevent the formation of the planar chelate ring of the cis-enol.

#On the other hand, the mobility of the allyl fluorine atoms in bis(trifluoromethyl)keten and in *N*-perfluoropropyldiphenylketen imine are responsible for the ready isomerisation of these heterocumulenes to 1,3-heterodienes.[13]

§Analogous intermolecular reactions are also known.[171]

¶The metastable enethiol $(CF_3)_2C = C(SH)C_2F_5$ isomerises analogously to the thioketone $(CF_3)_2CHC(=S)C_2F_5$.[179] However, the isomerisation of the corresponding sulphenyl chloride $(CF_3)_2C = C(SCl)C_2F_5$ to the α-chlorothioketone $(CF_3)_2CClC(=S)C_2F_5$ is reversible;[180] a new type of cationotropic tautomerism (chlorotropism) was observed in this instance.

It is of interest that a fairly considerable energy barrier to the enolisation of the metastable diketone form has been observed for heptafluoroacetylacetone $(CF_3CO)_2CHF$. At equilibrium, this β-diketone is 90% enolised[42] in contrast to the wholly enolised hexafluoroacetylacetone $(CF_3CO)_2CH_2$.

--o0o--

We believe that the foregoing data provide an idea about the extent to which the presence of perfluoroalkyl groups alters the chemical properties of organic compounds. "When one views the path traversed by fluorine chemistry, one sees that many features which previously outraged the chemist's imagination have become commonplace; however, the unusual characteristics of this field of chemistry are so pronounced that it still yields new phenomena and facts, which, on the one hand, expand theoretical ideas in chemistry and, on the other, lead to important practical results. Both these aspects are a source of enormous satisfaction to the investigator".[2]

REFERENCES

1. E.M.Rokhlin and N.P.Gambaryan, Arm.Khim.Zhur., 1980, 33, 551.
2. I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1098.
3. I.L.Knunyants and V.R.Polishchuk, Uspekhi Khim., 1976, 45, 1139 [Russ.Chem.Rev., 1976(7)].
4. V.R.Polishchuk and I.L.Knunyants, Uspekhi Khim., 1975, 44, 685 [Russ.Chem.Rev., 1975(4)].
5. I.L.Knunyants, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1962, 7, 276.
6. B.L.Dyatkin and I.L.Knunyants, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1970, 15, 5.
7. I.L.Knunyants, E.M.Rokhlin, and Yu.A.Cheburkov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1970, 15, 15.
8. N.P.Gambaryan, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1967, 12, 65.
9. I.L.Knunyants and G.G.Yakobson (Editors), "Sintezy Ftororganicheskikh Soedinenii" (The Syntheses of Organofluorine Compounds), Izd. Khimiya, Moscow, 1973.
10. B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants, Uspekhi Khim., 1966, 35, 979 [Russ.Chem.Rev., 1966(6)].
11. E.M.Rokhlin, E.G.Abduganiev, and U.Utebaev, Uspekhi Khim., 1976, 45, 1177 [Russ.Chem.Rev., 1976(7)].
12. B.L.Dyatkin, N.I.Delyagina, and S.R.Sterlin, Uspekhi Khim., 1976, 45, 1205 [Russ.Chem.Rev., 1976(7)].
13. N.P.Gambaryan, Uspekhi Khim., 1976, 45, 1251 [Russ.Chem.Rev., 1976(7)].
14. I.N.Roshkov, Uspekhi Khim., 1976, 45, 1222 [Russ.Chem.Rev., 1976(7)].
15. V.V.Tyuleneva, E.M.Rokhlin, and I.L.Knunyants, Uspekhi Khim., 1982, 51, 3 [Russ.Chem.Rev., 1982(1)].
16. A.V.Fokin, A.F.Kolomiets, and N.V.Vasil'ev, Uspekhi Khim., 1984, 53, 398 [Russ.Chem.Rev., 1984(3)].
17. I.L.Knunyants, Yu.A.Sizov, and O.V.Ukharov, Uspekhi Khim., 1983, 52, 976 [Russ.Chem.Rev., 1983(6)].
18. N.P.Gambaryan, E.M.Rokhlin, Yu.V.Zeifman, Ching-yun Chen, and I.L.Knunyants, Angew.Chem., 1966, 78, 1008.
19. L.S.German and I.L.Knunuantz, Angew.Chem., 1969, 81, 321.
20. Yu.A.Cheburkov and I.L.Knunyants, Fluor.Chem. Rev., 1967, 1, 107.
21. B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants, Fluor.Chem.Rev., 1969, 3, 45.
22. Yu.V.Zeifman, E.G.Ter-Gabrielyan, N.P.Gambaryan, and I.L.Knunyants, Uspekhi Khim., 1984, 53, 431 [Russ.Chem.Rev., 1984(3)].
23. I.N.Rozhkov, in "Organic Electrochemistry. An Introduction and a Guide" (Edited by M.M.Baizer and H.Lund), Marcel Dekker, Inc., New York–Basel, 1983, p.805.
24. I.L.Knunyants and E.M.Rokhlin, "Soviet Scientific Reviews, B, Chemical Reviews", Vol.5 (Edited by M.E.Vol'pin), OPA, Amsterdam, 1984, p.97.
25. R.A.Bekker and I.L.Knunyants, "Soviet Scientific Reviews, B, Chemical Reviews", Vol.5 (Edited by M.E.Vol'pin), OPA, Amsterdam, 1984, p.145.
26. G.G.Belen'kii and L.S.German, "Soviet Scientific Reviews, B, Chemical Reviews", Vol.5 (Edited by M.E.Vol'pin), OPA, Amsterdam, 1984, p.183.
27. D.P.Del'tsova, N.P.Gambaryan, E.I.Mysov, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1980, 253, 886.
28. D.P.Del'tsova, N.P.Gambaryan, and E.I.Mysov, Izv. Akad.Nauk SSSR, Ser.Khim., 1981, 2343.
29. D.P.Del'tseva and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 1367.
30. R.A.Bekker, V.Ya.Popkova, L.A.Rozov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2558.
31. R.A.Bekker, L.A.Rozov, and V.Ya.Popkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 2575.
32. I.L.Knunyants, O.V.Kil'disheva, and E.G.Bykhovskaya, Dokl.Akad.Nauk SSSR, 1947, 57, 49.
33. G.G.Yakobson and N.E.Akhmetova, Synthesis, 1983, 169.
34. J.H.Clark, Chem.Rev., 1980, 80, 429.
35. J.Svoboda, Chem.Listy, 1980, 74, 469.
36. B.R.Livshits, T.Kh.Dymshits, S.V.Vinogradova, and I.L.Knunyants, French P.2212361 (1974); Chem.Abs., 1975, 82, 157007.
37. B.R.Livshits, S.N.Vinogradova, I.L.Knunyants, G.L.Berestneva, and T.Kh.Dymshits, Vysokomol. Soed., 1973, 15A, 961.
38. S.I.Pletnev, M.D.Bargamova, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1092.
39. I.L.Knunyants, M.D.Bargamova, and S.J.Pletnev, J.Fluor.Chem., 1985, 29, 161.
40. I.L.Knunyants, Yu.T.Struchkov, M.D.Bargamova, and A.A.Espenbetov, Izv.Akad.Nauk SSSR, Ser. Khim., 1985, 1097.
41. L.S.German and M.A.Kurykin, "The IInd Regular Meeting of Soviet–Japanese Fluorine Chemists", Moscow, 1981, p.100.
42. M.A.Kurykin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2827.
43. M.D.Bargamova, N.S.Mirzabekyants, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1326.
44. N.F.Taylor and P.W.Kent, Symposium, "Uspekhi Khimii Ftora" (Advances in Fluorine Chemistry), Izd.Khimiya, Leningrad, 1970, Vols.3 and 4, p.374.
45. M.Hudlicky, "Chemistry of Organic Fluorine Compounds", Ellis Horwood Ltd., Chichester, 1976.
46. I.L.Knunyants, L.S.German, and N.B.Kaz'mina, BRD P.2014216 (1971); Chem.Abs., 1972, 76, 25310.

47. V.R.Polishchuk and L.S.German, Tetrahedron Letters, 1972, 5169.
48. N.B.Kaz'mina, L.S.German, I.D.Rubin, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1970, **194**, 1329.
49. V.A.Grinberg, V.R.Polishchuk, L.S.Kanevskii, L.S.German, and Yu.B.Vasil'ev, Izd.Akad.Nauk SSSR, Ser.Khim., 1979, 2356.
50. G.Ya.Rozenberg and K.N.Makarov, Zhur.Vses. Khim.Obshch.im.Mendeleeva, 1985, **30**, 387.
51. R.D.Chambers and R.G.Mobbs, Symposium, "Uspekhi Khimii Ftora" (Advances in Fluorine Chemistry), Izd.Khimiya, Leningrad, 1970, Vols.3 and 4, p.255.
52. US P.2409274 (1946); Chem.Abs., 1947, **41**, 982.
53. US P.2409315 [1946); Chem.Abs., 1947, **41**, 987.
54. I.L.Knunyants and A.V.Fokin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1952, 261.
55. I.L.Knunyants, A.I.Shchekotikhin, and A.V.Fokin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1953, 282.
56. I.L.Knunynats, L.S.German, and B.L.Dyatkin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk,, 1956, 1353.
57. K.N.Makarov, L.L.Gervits, and I.L.Knunyants, J.Fluor.Chem., 1977, **10**, 157.
58. K.N.Makarov, L.L.Gervits, Yu.A.Cheburkov, I.L.Knunyants, and V.P.Sass, J.Fluor.Chem., 1977, **10**, 323.
59. Yu.A.Yuzhelevskii, N.N.Fedoseeva, K.N.Makarov, and L.L.Gervits, Vysokomol.Soed., 1977, **19B**, 874.
60. V.D.Snegirev, L.L.Gervits, K.N.Makarov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2641.
61. V.F.Snegirev, K.N.Makarov, V.F.Zabolotskikh, M.T.Sorokina, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 2775.
62. V.F.Snegirev, E.V.Zakharova, and K.N.Makarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 1352.
63. V.F.Snegirev and K.N.Makarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 2066.
64. V.F.Snegirev and K.N.Makarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 106.
65. A.A.Stepanov and I.N.Rozhkov, Dokl.Akad.Nauk SSSR, 1982, **267**, 106.
66. I.L.Knunyants, I.N.Rozhkov, and A.A.Stepanoff, J.Fluor.Chem., 1980, **16**, 403.
67. I.N.Rozhkov and A.A.Stepanoff, "The IIIrd Regular Meeting of Soviet–Japanese Fluorine Chemists", Tokyo, 1983, p.12-1.
68. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv. Akad.Nauk SSSR, Ser.Khim., 1980, 1920.
69. N.B.Kaz'mina, E.I.Mysov, B.A.Kvasov, M.Yu.Antipin, and Yu.E.Struchkov, Izv.Akad. Nauk SSSR, Ser.Khim., 1984, 2743.
70. N.B.Kaz'mina, A.P.Kurbakova, L.A.Leites, B.A.Kvasov, and E.I.Mysov, Zhur.Org.Khim., 1986 (in the press).
71. N.B.Kaz'mina, I.L.Knunyants, E.I.Mysov, and G.M.Kuz'yants, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 163.
72. L.L.Gervits, L.A.Rozov, N.S.Mirzabekyants, K.N.Makarov, Yu.V.Zeifman, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 1976, 1676.
73. N.S.Mirzabekyants, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2517.
74. N.S.Mirzabekyants, L.L.Gervits, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 1977, 2772.
75. Yu.V.Zeifman, L.T.Lantseva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2640.
76. E.P.Lur'e, E.G.Gal'pern, Nina P.Gambaryan, E.M.Rokhlin, and E.I.Mysov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 619.
77. I.L.Knunyants, L.A.Rozov, Yu.V.Zeifman, and Yu.A.Cheburkov, J.Fluor.Chem., 1977, **10**, 351.
78. Yu.V.Zeifman, L.T.Lantseva, A.A.Kadyrov, and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 1116.
79. V.F.Cherstkov, M.V.Galakhov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 1208.
80. A.A.Kadyrov and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1353.
81. B.L.Dyatkin, R.A.Bekker, Yu.S.Konstantinov, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1965, **165**, 1305.
82. B.L.Dyatkin, R.A.Bekker, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1966, **166**, 106.
83. V.R.Polishchuk, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 2024.
84. E.G.Ter-Gabrielyan, N.P.Gambaryan, and Yu.V.Zeifman, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1888.
85. L.A.Simonyan, Z.V.Safronova, N.P.Gambaryan, M.Yu.Antipin, and Yu.T.Struchkov, Izv.Akad. Nauk SSSR, Ser.Khim., 1980, 358.
86. Yu.V.Zeifman, E.M.Rokhlin, U.Utebaev, and I.L.Knunynats, Dokl.Akad.Nauk SSSR, 1976, **226**, 1337.
87. I.L.Knunyants, I.N.Rozhkov, A.A.Stepanov, M.Yu.Antipin, M.A.Kravers, and Yu.T.Struchkov, Dokl.Akad.Nauk SSSR, 1979, **248**, 1128.
88. M.V.Urushadze, E.G.Abdugantsev, Z.E.Samoilova, Kh.Khafizov, E.M.Rokhlin, and R.G.Kostyanovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 176.
89. S.O.Koshtoyan, Yu.V.Zeifman, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1969, **185**, 837.
90. E.G.Ter-Gabrielyan, E.P.Lur'e, Yu.V.Zeifman, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser. Khim., 1975, 1380.
91. Yu.V.Zeifman, D.P.Del'tsova, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 591.
92. R.A.Bekker, G.G.Melikyan, B.L.Dyatkin, and I.L.Knunyants, Zhur.Org.Khim., 1975, 11, 1600.
93. A.F.Benda, N.V.Vasil'ev, A.F.Eleev, and G.A.Sokol'skii, Zhur.Org.Khim., 1983, **19**, 1181.
94. A.F.Ermolov and A.M.Eleev, Zhur.Org.Khim., 1983, **19**, 1343.
95. N.V.Vasil'ev, O.V.Verenikin, A.F.Kolomiets, and G.A.Sokol'skii, Zhur.Org.Khim., 1984, **20**, 1498.
96. N.V.Vasil'ev, S.A.Khokhlova, A.F.Molomiets, and G.A.Sokol'skii, Zhur.Org.Khim., 1984, **20**, 1983.
97. A.A.Kadyrov and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2583.
98. A.A.Stepanov, G.Ya.Bekker, A.P.Kurbakova, L.A.Leites, and I.N.Rozhkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2746.
99. A.A.Stepanov and I.N.Rozhkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 890.
100. I.Rozhkov, A.Stepanoff, Yu.Borisov, and M.Kurykin, J.Fluor.Chem., 1985, **29**, 227.
101. I.N.Rozhkov, A.A.Stepanoff, and Y.A.Borisov, "The IVth Regular Meeting of Soviet–Japanese Fluorine Chemists", Kiev, 1985.
102. J.A.Young, Fluor.Chem.Rev., 1967, **1**, 359.

103. W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.236.
104. R.D.Chambers, R.A.Storey, and W.K.R.Musgrave, Chem.Comm., 1966, 384.
105. L.L.Gervits, K.N.Makarov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1085.
106. S.A.Postovoi, L.T.Lantseva, and Yu.V.Zeifman, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 210.
107. Yu.V.Zeifman, L.T.Lantseva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 401.
108. S.M.Igumnov, N.I.Delyagina, Yu.V.Zeifman, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 827.
109. N.I.Delyagina, S.M.Igumnov, V.F.Snegirev, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2238.
110. Yu.V.Zeifman, S.A.Postovoi, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1982, **265**, 347.
111. V.D.Cherstkov, S.A.Postovoi, L.T.Lantseva, S.R.Sterlin, Yu.V.Zeifman, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2740.
112. L.P.Del'tsova, Yu.V.Zeifman, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 2533.
113. I.L.Knunyants, L.S.German, and N.I.Delyagina, J.Fluor.Chem., 1985, **29**, 188.
114. L.G.Anello and M.Van Den Puy, J.Org.Chem., 1982, **47**, 377.
115. I.L.Knunyants, N.I.Delyagina, and S.M.Igumnov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 861.
116. L.L.Gervits, K.N.Makarov, Yu.A.Cheburkov, and I.L.Knunyants, J.Fluor.Chem., 1977, **9**, 45.
117. Yu.V.Zeifman and L.T.Lantseva, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1102.
118. V.F.Snegirev, K.N.Makarov, and I.L.Knunyants, J.Fluor.Chem., 1981, **17**, 441.
119. A.Yu.Volkonsky and E.J.Rokhlin, J.Fluor.Chem., 1984, **26**, 183.
120. T.J.Brice, J.D.LaZerte, L.J.Hals, and W.H.Pearlson, J.Amer.Chem.Soc., 1953, 75, 2698.
121. S.Andreades, J.Org.Chem., 1962, 27, 4163.
122. A.A.Kadyrov, E.M.Rokhlin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2344.
123. I.L.Knunyants and G.A.Sokolski, Angew.Chem. Internt.Ed., 1972, 11, 583.
124. C.G.Krespan and D.C.England, J.Amer.Chem. Soc., 1981, **103**, 5598.
125. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2791.
126. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2796.
127. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1872.
128. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2152.
129. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 220.
130. V.F.Cherstkov, S.R.Sterlin, L.S.German, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1917.
131. G.A.Olah and Y.K.Mo, Adv.in Fluor.Chem., 1973, **7**, 69.
132. G.G.Belen'kii, G.I.Savicheva, E.P.Lur'e, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1430.
133. G.G.Belen'kii, G.I.Savicheva, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1433.
134. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2117.
135. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2821.
136. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1591.
137. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2411.
138. V.A.Petrov, G.G.Belen'kii, and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 438.
139. V.A.Petrov, G.G.Belen'kii, M.V.Galakhov, V.I.Bakhmutov, L.S.German, and E.I.Fedin, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2811.
140. M.V.Galakhov, V.A.Petrov, V.I.Bakhmutov, G.G.Belen'kii, B.A.Kvasov, L.S.German, and E.I.Fedin, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 306.
141. M.V.Galakhov, V.F.Snegirev, K.N.Makarov, and V.I.Bakhmutov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 2302.
142. V.M.Izmailov, R.N.Sterlin, V.L.Isaev, A.A.Listov, I.V.Topnikov, and I.L.Knunyants, Zhur.Vses. Khim.Obshch.im.Mendeleeva, 1974, **19**, 354.
143. B.L.Dyatkin, L.T.Lantseva, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1967, **176**, 1306.
144. L.S.German and G.I.Savicheva, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 478.
145. N.B.Kaz'mina, G.S.Krasnikova, E.P.Lur'e, E.I.Mysov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 2525.
146. M.Yu.Antipin, Yu.T.Struchkov, E.G.Ter-Gabrielyan, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 588.
147. E.G.Ter-Gabrielyan and N.P.Gambaryan, Izv.Akad. Nauk SSSR, Ser.Khim., 1980, 1214.
148. E.G.Ter-Gabrielyan, Z.N.Parnes, N.P.Gambaryan, and L.A.Simonyan, Izv.Akad.Nauk SSSR. Ser. Khim., 1983, 1656.
149. A.N.Nesmeyanov, N.E.Kolobova, I.B.Zlotina, B.V.Lokshin, I.F.Leshcheva, G.K.Znobina, and K.N.Anisimov, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1124.
150. N.P.Gambaryan, D.P.Del'tsova, V.A.Livshits, and E.G.Ter-Gabrielyan, Izv.Akad.Nauk SSSR, Ser.Khim., 1986 (in the press).
151. R.A.Bekker, G.G.Melikyan, E.P.Lur'e, B.L.Dyatkin, and I.L.Knunyants, Dokl.Akad. Nauk SSSR, 1974, 217, 1320.
152. B.L.Dyatkin, K.N.Makarov, and I.L.Knunyants, Tetrahedron, 1971, **27**, 51.
153. M.E.Redwood and C.J.Willis, Canad.J.Chem., 1967, **45**, 389.
154. I.P.Kolenko, T.I.Filyakova, A.Ya.Zapevalov, E.P.Mochalina, L.S.German, and V.R.Polishchuk, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 667.
155. R.L.Adelman, J.Org.Chem., 1968, **33**, 1400.
156. A.A.Espenbetov, A.I.Yanovskii, Yu.T.Struchkov, L.A.Simonyan, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 607.
157. Yu.V.Zeifman, E.G.Ter-Gabrielyan, D.P.Del'tsova, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser. Khim., 1979, 396.

158. Z.Zubovics and N.Ishikawa, J.Fluor.Chem., 1976, **8**, 43.
159. U.Utebaev, E.G.Abduganiev, E.M.Rokhlin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 386.
160. Yu.V.Zeifman, L.A.Simonyan, Z.V.Safronova, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1367.
161. A.M.Krzhizhevskii, N.S.Mirzabekyants, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad. Nauk SSSR, Ser.Khim., 1974, 2513.
162. Z.V.Safronova, L.A.Simonyan, and N.P.Gambaryan, Arm.Khim.Zhur., 1979, **32**, 315.
163. N.P.Gambaryan, G.S.Kaitmazova, E.M.Kagramanova, L.A.Simonyan, and Z.V.Safronova, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 1102.
164. R.A.Bekker, G.G.Melikyan, B.L.Dyatkin, and I.L.Knunyants, Zhur.Org.Khim., 1976, **12**, 1377.
165. I.L.Knunyants, N.P.Gambaryan, and V.V.Tyuleneva, Izv.Akad.Nauk SSSR, Ser.Khim., 1967, 2662.
166. I.L.Knunyants, M.D.Bargamova, and E.I.Mysov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2822.
167. R.G.Kostyanovsky, I.I.Tchervin, A.A.Fomichov, Z.E.Samojlova, C.N.Makarov, Yu.V.Zeifman, and B.L.Dyatkin, Tetrahedron Letters, 1969, 4021.
168. D.P.Del'tsova, Z.V.Safronova, and N.P.Gambaryan, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2736.
169. N.P.Gambaryan, E.A.Avetisyan, D.P.Del'tsova, and Z.V.Safronova, Arm.Khim.Zhur., 1981, **34**, 380.
170. D.P.Del'tsova, Z.V.Safronova, N.P.Gambaryan, M.Yu.Antipin, and Yu.T.Struchkov, Izv.Akad. Nauk SSSR, Ser.Khim., 1978, 1881.
171. C.G.Krespan, J.Org.Chem., 1978, **43**, 637.
172. J.Murto, Finn.Chem.Letters, 1980, 48.
173. H.Hart, Chem.Rev., 1979, **79**, 520.
174. R.A.Bekker, V.Ya.Popkova, V.F.Snegirev, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 621.
175. R.A.Bekker, V.Ya.Popkova, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1193.
176. R.A.Bekker and V.Ya.Popkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2775.
177. R.A.Bekker, V.Ya.Popkova, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1976, **231**, 864.
178. R.A.Bekker, G.G.Melikyan, B.L.Dyatkin, and I.L.Knunyants, Zhur.Org.Khim., 1976, 12, 1379.
179. R.A.Bekker, V.Ya.Popkova, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2347.
180. R.A.Bekker, V.Ya.Popkova, V.F.Snegirev, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2167.

Nesmeyanov Institute of Organoelemental Compounds, Moscow