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# New Data on Reactions of Organofluorine Compounds

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The review surveys data obtained in recent years for chemical reactions of organofluorine compounds. Data for new reactions of these compounds are considered in combination with new concepts concerning the mechanisms of processes known previously separated ionic and radical reactions.
The bibliography includes 280 references.

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Methods for the introduction of fluorine into organic molecules as well as data obtained by physical methods for organofluorine compounds have been considered in an earlier review[1]. The present review surveys the available information about their chemical reactions.

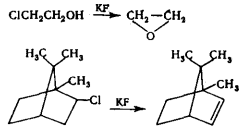
## I. ANIONOID REACTIONS

Reactions of this type are most common in the chemistry of organofluorine compounds. A number of reviews have been devoted to their detailed discussion[2-6].

### 1. Fluorocarbanions Generated with the Aid of Fluoride Ions

The fluoride ion plays an exceptionally important role in the chemistry of organofluorine compounds. Historically the first compound containing the C–F bond (benzoyl fluoride) was obtained by Borodin in 1862 by treating benzoyl chloride with potassium hydrogen fluoride[7].

The high basicity of potassium fluoride, which was already known to Berzelius (quoted after Borodin[7]), began to be used from 1947, when the dehydrochlorination of β-chloroethanol and bornyl chloride was achieved[8]:



Subsequent studies showed that anhydrous salts of hydrofluoric acid are very strong bases. Thus tetraethylammonium fluoride splits off HCl from β-phenylethyl chloride 800 times faster than sodium ethoxide[9]. Strong CH acids (nitro-compounds with $pK_a < 7$) form salts upon reaction with alkali metal fluorides in an alcoholic medium[10]. On the other hand, in an aprotic medium, the anion is generated even from a CH acid with $pK_a = 25$ (acetonitrile[11]). Triphenylmethane ($pK_a = 28.8$)virtually does not form an anion[12].

The extremely high energy of the hydrogen bonds formed by the fluoride ion is the cause of certain experimental difficulties associated with the use of thermally unstable tetra-alkylammonium fluorides, from which it is impossible to eliminate completely the water of crystallisation (two $H_2O$ molecules remain[12,13]).

The highest degree of charge delocalisation is acheved when $F^-$ is incorporated in an octahedral cage containing 4 or 6 water molecules. The hydration energies calculated by the CNDO method (128 and 117 kcal mole$^{-1}$ respectively) agree well with the experimental value of 120 kcal mole$^{-1}$.[14] The high energy of the H–F hydrogen bond is also the cause of acid catalysis in the hydrolysis of, for example, benzyl fluoride[15] (the mechanisms of fluorine-substitution reactions have been reviewed[16]). In the absence of solvation (in the gas phase), the nucleophilic properties of $F^-$ (determined from the kinetics of its reaction with $CH_3Cl$) are close to those of $OH^-$ and $NH_2^-$ (determined mass-spectrometrically[17]).

Alkali metal fluorides form compounds with hydrogen peroxide[18] just as readily as with water and, like alkalis, with carbon dioxide[19] ($F_2CO_2^{2-}$ is analogous to $CO_3^{2-}$) and isocyanates[20]:

$$FSO_2NCO + MF \rightarrow FSO_2\bar{N}COF\overset{+}{M};$$
$$M = Na, K, Cs.$$

The ability of the fluoride ion to add to the electrophilic double bonds of fluorine-containing olefins[21] and carbonyl compounds[22] is extremely important for organofluorine chemistry. The anions formed are capable of a series of transformations analogous to those of carbonium ions in the chemistry of hydrocarbons. Thus the dimerisation of octafluoroisobutene under the influence of caesium fluoride[23],

$$(CF_3)_2C{=}CF_2 \xrightarrow[(C_2H_5)_2O]{CsF} [(CF_3)_3\bar{C}] \xrightarrow{(CF_3)_2C=CF_2} \rightarrow (CF_3)_3C{-}CF{=}C(CF_3)_2 + (CF_3)_2C{-}CF_2{-}\underset{\displaystyle CF_3}{\underset{|}{C}}{=}CF_2,$$

constitutes, as it were, a mirror image of the classical dimerisation of isobutene by sulphuric acid, which Butlerov discovered[24]:

$$(CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} [(CH_3)_3\overset{+}{C}] \xrightarrow{(CH_3)_2C=CH_2} \rightarrow (CH_3)_3C{-}CH{=}C(CH_3)_2 + (CH_3)_3C{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2.$$

This example clearly illustrates the role of the fluoride ion as "the proton of organofluorine chemistry". Oligomerisation catalysed by the fluoride ion is also characteristic of other polyfluorinated olefins or carbonyl compounds. It has been shown for hexafluoropropene that this reaction is reversible (when the trimer $C_3F_6$ is heated with CsF, it is partly converted into the dimer and the monomer[25]). The reversibility of the dimerisation of trifluoroacetyl fluoride is much more marked: in the

presence of KF, its dimer ("perfluoroethyl perfluoroacetate") decomposes at −78°C [26]:

$$CF_3C(=O)OC_2F_5 \xrightarrow[-78^\circ]{KF} 2\,CF_3\overset{O}{\overset{\|}{C}}F \quad .$$

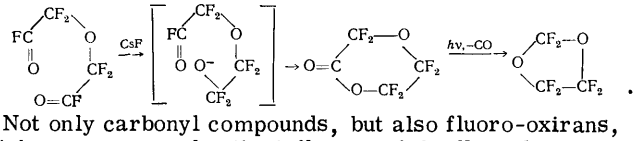
In the absence of fluorine atoms in the *gem*-position relative to the oxygen atom, fully fluorinated esters, for example dodecafluoro-t-butyl acetate, are resistant to the action of CsF even on heating [27].

The dimers of fully fluorinated thioketones also dissociate in the presence of fluoride ions, which makes it possible to generate their monomeric form directly in the reaction medium [28]:

$$(CF_3)_2C\underset{S}{\overset{S}{\diagup\diagdown}}C(CF_3)_2 \xrightarrow{KF} (CF_3)_2C{=}S \xrightarrow{ROH} (CF_3)_2C\underset{OR}{\overset{SR}{\diagup\diagdown}} + (CF_3)_2C(OR)-S-S-C(OR)(CF_3)_2;$$

$R=CH_3,\ C_2H_5,\ C_3H_7.$

In contrast to fluoro-olefins, the oligomerisation of which usually stops at the stage involving the formation of trimers or tetramers, hexafluorobut-2-yne forms a polymer on treatment with KF under analogous conditions [29]. An elegant application of "internal dimerisation" in combination with ultraviolet irradiation made it possible to synthesise hexafluoro-1,3-dioxacylopentane [30]:



Not only carbonyl compounds, but also fluoro-oxirans, which rearrange under the influence of the fluoride ion into acyl fluorides, can serve as sources of "perfluoroalkoxides" [31]:

$$\underset{\diagdown O \diagup}{CF_2{-}CF_2} \xrightarrow{KF} [CF_3CF_2O^-] \rightarrow CF_3CF{=}O.$$

The method of synthesising hexafluoromethyloxiran is based on this reaction:

$$CF_3CF\underset{\diagdown O \diagup}{-CF_2} \xrightarrow{KF} [CF_3CF_3CF_2O^-] \xrightarrow{(n-1)\ C_3F_6O} CF_3CF_2CF_2O(CF(CF_3)-CF_2O)_nCF(CF_3)COF;$$

$n=0-35.$

Oligomers in which the terminal acyl fluoride group is replaced by another more inert group are used as lubricating materials and hydraulic liquids [32].

Unusual reactions occur when hexafluorobenzene is treated with potassium fluoride under severe conditions. Together with the formation of fully fluorinated toluene and xylenes, which evidently occurs with participation of difluorocarbene [33],

$$C_6F_6 \xrightarrow[470-590^\circ]{KF} [C_6F_7^-] \rightarrow \ddot{C}F_2 + [C_5F_5^-],$$
$$\downarrow C_6F_6$$
$$C_6F_5CF_3$$

decafluoromethylcyclopentene is also formed in this reaction [34].

The oligomerisation of a fluoro-olefin or a carbonyl compound can be suppressed when the anion is generated in the presence of electrophilic agents capable of reacting with it†. Thus, when octafluoroisobutene is treated with caesium fluoride in the presence of $CH_3I$, alkylation and not the dimerisation of the olefin takes place [35]:

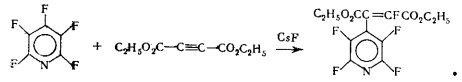
$$(CF_3)_2C{=}CF_2 + CsF + CH_3I \rightarrow (CF_3)_3C{-}CH_3.$$

In the presence of acrylic acid derivatives, products resulting from the formal addition of $(CF_3)_3CH$ to them are formed after treatment with water [35]:

$$(CF_3)_2C{=}CF_2 \xrightarrow{CsF} [(CF_3)_3\bar{C}] \xrightarrow{CH_2=CHX} \rightarrow [(CF_3)_3C{-}CH_2{-}\bar{C}HX] \xrightarrow{H_2O} (CF_3)_3C{-}CH_2{-}CH_2{-}CH_2X;$$
$$X=CN,\ COOCH_3.$$

The nonafluoro-t-butyl anion substitutes halogen atoms just as readily in unsaturated and aromatic compounds — pentafluoropyridine, cyanuryl chloride, 1-fluoro-2,4-dinitrobenzene, *p*-fluoronitrobenzene [36], and chlorophenylacetylene. [37] From the standpoint of synthetic possibilities in the series of aromatic fluoro-compounds such as octafluorotoluene, pentafluoropyridine, and others, this reaction may be compared with Friedel-Crafts alkylation. The carbanions generated from hexafluoropropene, tetrafluoroethylene, and other fluoro-olefins can also be involved in this reaction [4,5,38].

An anion capable of similar reactions is generated as a result of the addition of $F^-$ to the electrophilic triple bond of the acetylene dicarboxylate ester [39]:



The reaction involving hexafluorobut-2-yne is complicated by polymerisation.

The fluorinated carbanions are capable of adding to cationoid species, forming stable covalent compounds. It has been possible to synthesise in this way mixed azo-compounds [40]:

$$R_f^- + C_6H_5N_2^+Cl^- \rightarrow R_fN{=}NC_6H_5;$$

or metal fluoroalkyl derivatives [41-43]:

$$R_f^- + M^+ \rightarrow R_f - M;$$
$$M=Ag,\ {}^1/_2\,Hg \quad .$$

When fluorocarbanions are treated with elemental sulphur, the products are mercaptide anions capable of both eliminating the fluoride ion (which leads to thiocarbonyl compounds) and of being oxidised by the excess sulphur with formation of di- and poly-sulphides [44]:

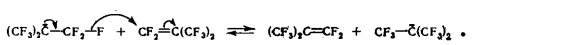
$$CF_3CF{=}CF_2 \xrightarrow{KF} \left[\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>\bar{C}F\right] \xrightarrow{S} \left[\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>CF{-}S^-\right] \longrightarrow$$
$$\xrightarrow{S} \left[\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>CF{-}S^\cdot\right] \rightarrow (CF_3)_2CF{-}S_n{-}CF(CF_3)_2$$
$$\xrightarrow{-F^-} \begin{matrix}CF_3\\CF_3\end{matrix}\!\!>C{=}S \rightarrow \text{dimer}.$$

One may say that, in terms of the ease of their formation and the scope of their synthetic applications, "perfluorocarbanions" (actually ionised fluoroalkyl derivatives of alkali metals) can replace to some extent Grignard reagents in fluorine chemistry. In view of the instability of Grignard reagents associated with the ease of elimination of magnesium fluoride, evidently only those fluorine-containing Grignard reagents which contain unsaturated or primary fluoroalkyl residues can be of some preparative value [45].

The attempts at direct detection of fluorocarbanions with with the aid of $^{19}F$ NMR showed that these species are in a state of rapid exchange. Thus the exchange between the nonafluoro-t-butyl anion and octafluoroisobutene in

†See the review of B. L. Dyatkin (deceased), N. I. Delyagina, and S. R. Sterlin "The Perfluoro-t-butyl Anion in the Synthesis of Organofluorine Compounds" in this issue.

1,2-dimethoxyethane cannot be made slow in terms of the NMR time scale even at −100°C [46]:

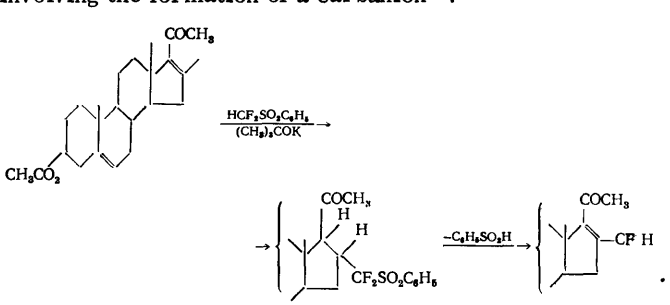


Comparison of fluoro-olefins and carbonyl compounds in their reactions with the fluoride ion showed that the latter are more reactive: trifluoroacetyl fluoride exchanges with $Cs^{18}F$ seven times faster than hexafluoropropene [47]. Hexafluoroacetone, taken in a minimal excess, causes the complete dissolution of ceasium fluoride in acetonitrile, while one of the most electrophilic fluoro-olefins (octafluoroisobutene) causes only a slight increase of the solubility of CsF in aprotic solvents. By virtue of this feature, hexafluoroacetone is used for the preparation of extremely reactive highly dispersed CsF (by the vacuum evaporation of a solution of "perfluoroalkoxide" [48]).

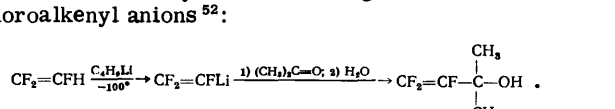
## 2. Fluorocarbanions Generated by Other Methods

Apart from the methods specific to fluorocarbanions—the addition of the fluoride ion to electrophilic multiple bonds—they can be generated by the general methods of carbanion chemistry. As a result of the high proton mobility of the hydrogen atom at a tertiary carbon atom in polyfluoroalkanes, fluorocarbanions are generated when the alkanes are treated with comparatively weak bases. Thus the reaction of the nonafluoro-t-butylanion with acrylic systems, discussed above, can be achieved also by treating acrylic systems with a mixture of $(CF_3)_3CH$ and triethylamine [49]. Kinetically independent carbanions can probably be in fact involved in processes of this kind. The study of the kinetics of the dehydrohalogenation of compounds having the general formula $C_6H_6CHClCF_3X$, where X = F or Cl, showed that the presence of a chlorine atom in the β-position greatly accelerates the process, probably in consequence of synchronous elimination. If, on the other hand, X = F, a kinetically independent carbanion is evidently formed [50].

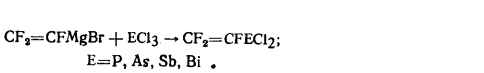
Base-catalysed reactions, which ultimately reduce to the insertion of a carbene, can also include a stage involving the formation of a carbanion [51]:



The hydrogen atom at the double bond of a fluoro-olefin can also be sufficiently acidic for the generation of perfluoroalkenyl anions [52]:

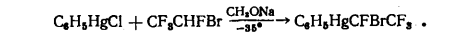


A wide range of organic derivatives of the elements can be synthesised with the aid of fluoroalkenyl derivatives of lithium or magnesium (see the review by Knuyants et al. [53]):



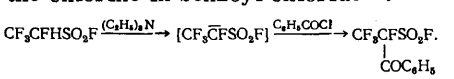
Trifluorovinyl derivatives of sulphur, silicon, germanium, tin, mercury, platinum, and palladium have been obtained similarly.

CH acids are also widely used for synthesising organomercury compounds—the sources of halogenocarbenes. For example [54]:

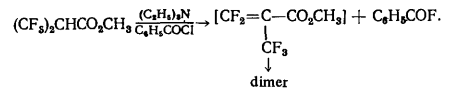


When the product is heated, trifluoromethylfluorocarbene is formed.

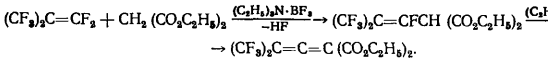
The anion generated when 1,2,2,2-tetrafluoroethanesulphonyl fluoride is treated with triethylamine can substitute the chlorine in benzoyl chloride [55]:



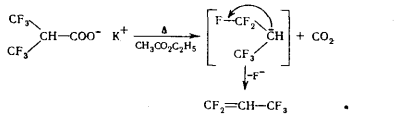
The analogous acylation of polyfluoro-α-hydrocarboxylic acids cannot be achieved; the main reaction pathway involved dehydrofluorination [56]:



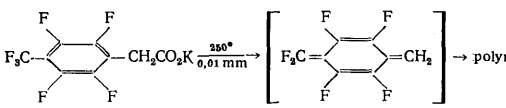
Benzoyl chloride has an electrophilic cooperative effect on dehydrofluorination, making it irreversible in consequence of the binding of the fluoride ion in the form of a covalent compound—benzoyl fluoride. Lewis acids, introduced in the form of complexes with tertiary amines, have a similar effect. The use of these complexes makes it possible to synthesise many interesting unsaturated compounds in preparative yields, for example [57]:



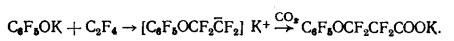
The leaving group in the generation of fluorocarbanions may be not only a proton but also $CO_2$, which makes it possible to use fluorocarboxylate salts in reactions of this kind. Decarboxylation can be used for the synthesis of fluoro-olefins [58]:



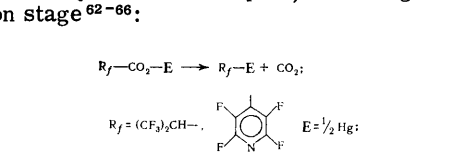
The synthesis of fluorine-containing quinonemethides, which form polymers on vacuum condensation on a cold surface, is carried out similarly [59]:

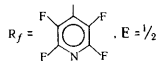


The elimination of $CO_2$ by fluorocarboxylate salts can be reversible (fluorocarbanions are capable of combining with carbon dioxide [60]). A method for the synthesis of nonafluoro-β-phenoxypropionic acid is based on this fact [61]:



The decarboxylation of heavy metal salts has been used successfully in the synthesis of a wide variety of fluorine-containing organometallic compounds. The mechanism of this process may be more complex, involving a radical generation stage [62-66]:

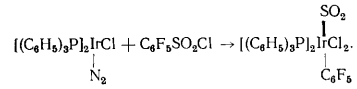




$R_f$ = , E = ½ Zn, ½ Cd;

$R_f = C_6F_5$, E = Cu, Au, ½Ni

$SO_2$ or $SO_3$ can also be the leaving groups in reactions of this kind—for example in the synthesis of polyfluoroaryl derivatives of mercury[67,68] or iron[69]. In the synthesis of σ-pentafluorophenyliridium, $SO_2$ is combined as the ligand, displacing molecular nitrogen[70]:



$$[(C_6H_5)_3P]_2IrCl + C_6F_5SO_2Cl \rightarrow [(C_6H_5)_3P]_2\overset{SO_2}{\underset{C_6F_5}{Ir}}Cl_2.$$

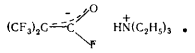
The decarboxylation of silver hexafluoroisobutyrate leads to the formation of hexafluoroisopropylsilver[71]:

$$(CF_3)_2CH{-}CO_2{-}Ag \rightarrow (CF_3)_2CH{-}Ag + CO_2.$$

The basicity of the solvent has a significant influence on the ease of reaction: $CO_2$ is not evolved in boiling tetrahydrofuran (THF); in acetonitrile, the reaction takes place at 40–50°C and, in pyridine, at room temperature. This demonstrates the important role played in such reactions by the nucleophilic cooperation of solvent molecules. Such cooperation affects just as strongly the reactions of fluoroalkyl derivatives of heavy metals, which can be particularly readily coordinated to bases by virtue of the electron-accepting properties of the fluoroalkyl groups and can also serve as sources of fluorocarbanions. Thus the decomposition of bis(nonafluoro-t-butyl)mercury, which takes place readily in the presence of iodide salts in aprotic solvents, leads to the formation of octafluoroisobutene. The action of KF does not lead to the decomposition of the organomercury compound, but in the presence of KF it reacts much more readily with agents such as sulphur or iodine[72]:

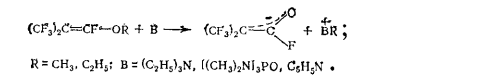
$$[(CF_3)_3C]_2Hg \overset{F^-}{\rightleftarrows} [(CF_3)_3C]_2\overline{H}gF \xrightarrow{I_2} (CF_3)_3CI.$$

On treatment with triethylamine, hexafluoroisobutyryl fluoride (in contrast to the chloride) does not eliminate the hydrogen halide. The reaction stops at the stage involving the formation of a solid salt-like complex containing a mesomerically stabilised carbanion [73] (see the review of Knunyants et al.[74]):



$$(CF_3)_2C{=}\overset{-}{C}{-}\overset{O}{\overset{\|}{C}}{-}F \quad \overset{+}{H}N(C_2H_5)_3 .$$

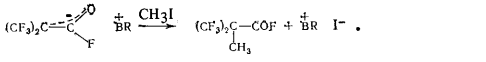
The extremely high stability of such fluorocarbanions makes it possible to obtain them by a novel method—by treating with bases alkyl polyfluorovinyl ethers, which have been found to be capable of acting as alkylating agents[75–77]:



$$(CF_3)_2C{=}CF{-}OR + B \rightarrow (CF_3)_2C{=}\overset{-}{C}{-}\overset{O}{\overset{\|}{C}}{-}F + \overset{+}{B}R; \qquad (1)$$

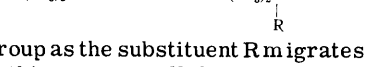
$R = CH_3, C_2H_5$; $B = (C_2H_5)_3N, [(CH_3)_2N]_3PO, C_5H_5N$ .

In its turn, the mesomeric anion can be also alkylated—for example with methyl iodide[78]:



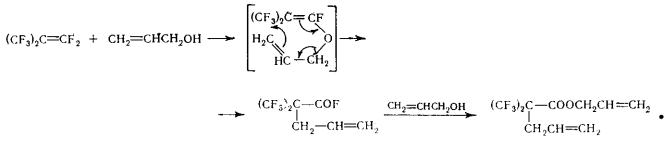
$$(CF_3)_2C{=}\overset{-}{C}{-}\overset{O}{\overset{\|}{C}}{-}F \quad \overset{+}{B}R \xrightarrow{CH_3I} (CF_3)_2\underset{CH_3}{C}{-}COF + \overset{+}{B}R\ I^- .$$

An excess of the initial vinyl ether can also serve as an alkylating agent, so that its heat treatment in the presence of bases leads to a rearrangement[79]:



$$(CF_3)_2C{=}CF{-}OR \xrightarrow{(C_2H_5)_3N} (CF_3)_2\underset{R}{C}{-}CF{=}O.$$

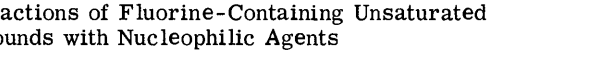
The allyl group as the substituent R migrates particularly readily. For this reason, allyl heptafluoroisobutenyl ether cannot be synthesised at all: under the conditions of the reaction of octafluoroisobutene with an alcohol usually employed for this purpose, a rearrangement takes place immediately, so that the final product is allyl α-allylhexafluoroisobutyrate[80]:



$$(CF_3)_2C{=}CF_2 + CH_2{=}CHCH_2OH \rightarrow \left[\begin{array}{l}(CF_3)_2C{=}CF\\ H_2C\\ HC\\ CH_2\end{array}\right] \rightarrow$$

$$\rightarrow (CF_3)_2\underset{CH_2{-}CH{=}CH_2}{C}{-}COF \xrightarrow{CH_2{=}CHCH_2OH} (CF_3)_2\underset{CH_2CH{=}CH_2}{C}{-}COOCH_2CH{=}CH_2 .$$

Evidently yet another rearrangement is of a related type—the conversion of 2,2-bis(trifluoromethyl)-3-methoxyazirine, obtained by treating heptafluoroisobutenyl methyl ether with sodium azide, into the corresponding isocyanate[81]:

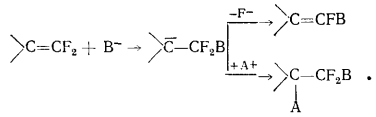


$$(CF_3)_2C{=}CFOCH_3 + NaN_3 \overset{}{\underset{-N_a}{\rightleftarrows}} (CF_3)_2\underset{N}{C}{-}C{-}OCH_3 \xrightarrow{\Delta} (CF_3)_2\underset{CH_3}{C}{-}N{=}C{=}O.$$

## 3. Reactions of Fluorine-Containing Unsaturated Compounds with Nucleophilic Agents

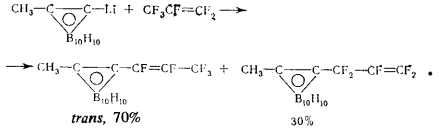
It has been shown[82] that the fluorine atom in the vinyl position of a fluoro-olefin is more mobile than the atom in the allyl position. This property is specific to organofluorine compounds and distinguishes them from the majority of substances for which the traditional concept of a greater mobility of the halogen atom in the allyl position is valid.

When a fluoro-olefin is attacked by an anion $B^-$, the intermediate carbanion may be stabilised either by eliminating the fluoride ion (substitution) or by combining with a cation $A^+$ (addition):



$$>C{=}CF_2 + B^- \rightarrow >\overset{-}{C}{-}CF_2B \begin{array}{l}\xrightarrow{-F^-} >C{=}CFB\\ \xrightarrow{+A^+} >\underset{A}{C}{-}CF_2B\end{array} . \qquad (2)$$

When a fluoro-olefin is attacked by an uncharged nucleophilic species B′ with a lone electron pair, the product is a dipolar species $>\overset{-}{C}{-}CF_2{-}\overset{+}{B}'$, which can be stabilised not only by the two pathways indicated above, but also by a third pathway, leading to the formation of cycloaddition products. Studies in recent years make it possible to refine somewhat this general mechanism. Substitution in fluoro-olefins, initially studied in relation to nucleophilic agents ultimately forming in this reaction a substituent with a lone electron pair ($HNR_2, RO^-$) [82], can be directed to some extent also to the allyl position, provided that it results in the introduction of an electron-accepting substituent[83]:



$$CH_3{-}C{\equiv}C{-}Li + CF_3CF{=}CF_2 \rightarrow$$

$$\rightarrow \underset{B_{10}H_{10}}{CH_3{-}C{\equiv}C{-}CF{=}CF{-}CF_3} + \underset{B_{10}H_{10}}{CH_3{-}C{\equiv}C{-}CF_2{-}CF{=}CF_2} .$$

*trans*, 70% 30%

However, the *meta*-carborane analogue, which has a smaller *–I* effect, forms exclusively the vinyl isomer[84].

The interaction of octafluoroisobutene with Grignard reagents also leads to the partial formation of allyl

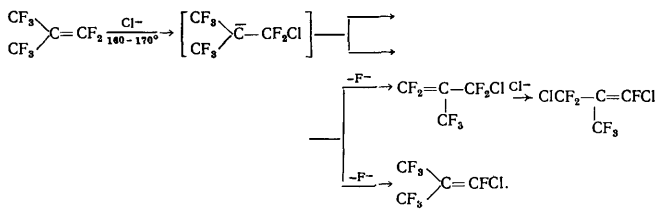
isomers. The ratio of the reaction products depends on the nature of the group introduced[85]:

$$(CF_3)_2C{=}CF_2 + RMgBr \rightarrow (CF_3)_2C{=}CFR + CF_2{=}\underset{\underset{CF_3}{|}}{C}{-}CF_2R;$$

(I) (II)

R=$(CH_3)_2CH$, (I) : (II)=68 : 32; R=n-$C_4H_9$, (I) : (II) = 82 : 18; R=$C_6H_5CH_2$, (I): (II)=60:40.

The reaction of octafluoroisobutene with the chloride ion occurring in the presence of phosphoryl chloride, which binds $F^-$, leads to a mixture of compounds which includes products of both vinyl and allyl substitution[86]:

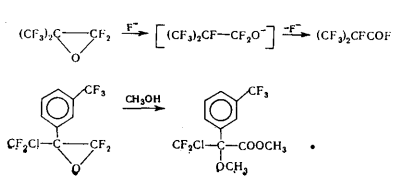


Fluoro-olefins with a non-terminal double bond were previously regarded as relatively unreactive. However, it has been shown recently that they are capable of reversible isomerisation to olefins with a terminal C=C bond on treatment with an attacking nucleophilic agent. As a result of this, it has been possible to introduce into the reaction with amines hexafluoropropene dimers, which constitute a mixture of $(CF_3)_2CFCF{=}CFCF_3$ and $(CF_3)_2C{=}CFCF_2CF_3$.[25] The reaction leads to the formation of $R_2NCF{=}CFCF_2CF_3$, which may indicate a preliminary
$\underset{CF_3}{|}$
isomerisation of the dimers to $CF_2{=}\underset{\underset{CF_3}{|}}{C}(CF_2)_2CF_3$.[87] This result makes possible the extensive application in synthesis of the very readily available fluoro-olefin oligomers. Dialkylaminoheptafluoroisobutenes are also capable of reacting with secondary amines[88]:

$$(CF_3)_2C{=}CFNR_2 + HNR'_2 \rightarrow (CF_3)_2C{=}C\begin{matrix}NR_2\\NR'_2\end{matrix}.$$

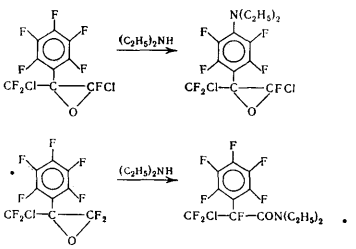
The reaction proceeds readily when R or R′ is a methyl group. When both substituents are a piperidine residue, the reaction proceeds slowly and, when R = R′ = $C_2H_5$, it is altogether impossible to achieve selective substitution. Evidently steric hindrance plays a decisive role in this instance.

Steric hindrance plays an important role in the reactions of fluoro-oxirans with nucleophilic agents. In the absence of steric hindrance, the attack is directed to the central carbon atom[89,90]:

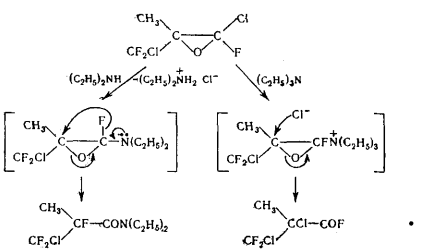


The second reaction takes place fairly readily when the $CF_3$ group is present in the *meta*- or *para*-position, but does not occur when it occupies the *ortho*-position[90].

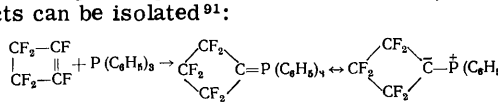
The *ortho*-fluorine atoms of the pentafluorophenyl group are evidently also capable of shielding the central carbon atom sufficiently for the attack by the nucleophilic agent to be directed to another centre[90]:



In the second case the reaction is accompanied by a rearrangement, which is of a general type. With its aid, it is possible to synthesise the derivatives of a wide variety of fluorocarboxylic acids. Evidently the driving force of the reaction is the small volume of the halide ions formed in the first stage of the interaction with bulky nucleophilic agents, which are bound to attack the terminal carbon atom[90]:



According to mechanism (2), the primary products of the reactions of fluoro-olefins with uncharged nucleophilic agents are dipolar species. In certain cases, these products can be isolated[91]:



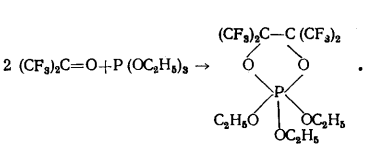
Heptafluoroisobutenylphosphonic acid esters have been obtained by the reaction between octafluoroisobutene and trialkyl phosphites (in which a betaine is an intermediate)[92]:

$$(CF_3)_2C{=}CF_2 + P(OR)_3 \rightarrow [(CF_3)_2\bar{C}{-}CF_2{-}\overset{+}{P}(OR)_3] \rightarrow (CF_3)_2C{=}CF{-}\underset{\underset{O}{\|}}{P}(OR)_2;$$

R=$CH_3$, $C_2H_5$.

The analogous reaction involving allyl heptafluoroisobutenyl ethers takes place with simultaneous alkylation of the trialkyl phosphite via mechanism (1).[93] The influence of steric hindrance, preventing the attack on the carbon atom of the =CF- group, probably has an effect in this case.

The reaction of triethyl phosphite with hexafluoroacetone is unusual. The addition of two ketone molecules results in the formation of a cyclic phosphorane in which there is a linkage between two carbon atoms previously forming part of the carbonyl groups, i.e. hexafluoroacetone is converted into a "pinacol" derivative[94]:



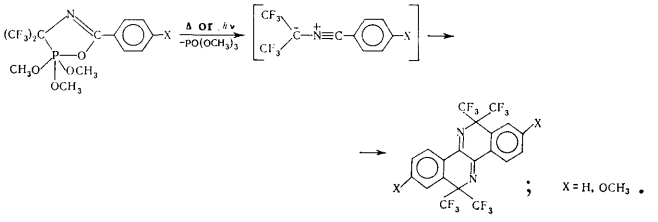
(3)

The study of the interaction of Wittig reagents with unsaturated organofluorine compounds, which was begun in relation to hexafluorobenzene [95], is extremely promising:

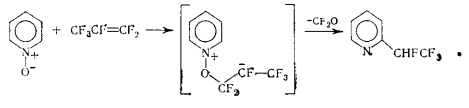
$$(C_6H_5)_3\overset{+}{P}{-}\bar{C}H_2 + C_6F_6 \rightarrow [(C_6H_5)_3\overset{+}{P}{-}CH_2C_6F_5][F^- \xrightarrow{-H^+} (C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6F_5.$$

The reaction leads to the formation of a new ylid, which is likewise capable of typical reactions of such compounds.

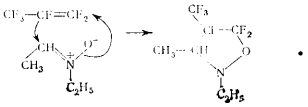
Nitrogen-containing ylids usually cannot be isolated, but the products of their reactions are frequently extremely interesting[96]:



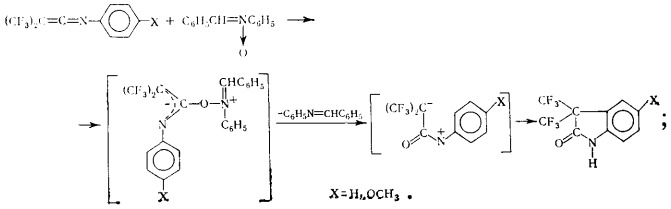
The reaction of the *N*-oxides of pyridine (and its homologues) with hexafluoropropene makes it possible to introduce the polyfluoroalkyl group under mild conditions into the $\alpha$-position of the pyridine ring[97]:



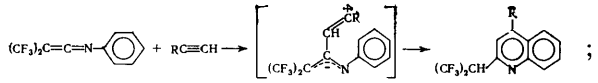
Nitrones also react steadily with hexafluoropropene, but there is no elimination of the $COF_2$ group[98]:



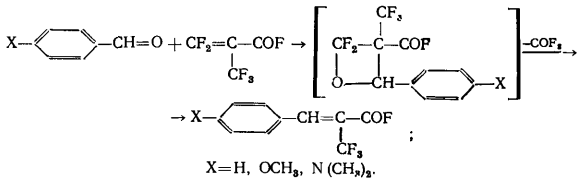
$\alpha$,*N*-Diphenyl nitrone behaving as an oxygen donor reacts in an unexpected manner with *N*-arylbis(trifluoromethyl)ketenimines [99]:



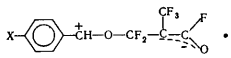
The reaction of a ketenimine with acetylenes probably also includes a stage involving the formation of a dipolar ion, which is stabilised by cyclisation[100]:



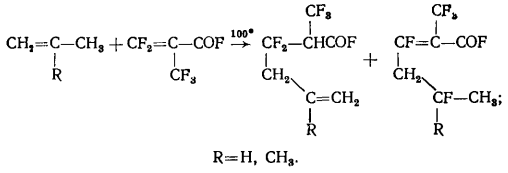
Another pathway to the stabilisation of the dipolar ion, involving the elimination of carbonyl fluoride, which has already been mentioned, occurs in the interaction of aromatic aldehydes with pentafluoromethacryloyl fluoride. The intermediate oxetans are unstable[101]:



The extreme ease of this reaction, which is formally similar to the Wittig reaction, is not surprising if one bears in mind that both charges in the intermediate dipolar ions are highly delocalised, so that it constitutes a combination of the benzoyl cation with a mesomeric anion:

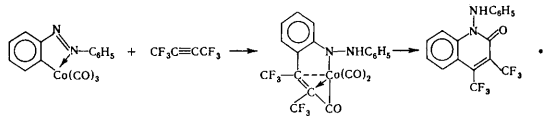


The C=C bond in pentafluoromethacryloyl fluoride is so electrophilic that it reacts with olefins[101] (i.e., as regards its electrophilic properties, it approaches the C=O bond of fluorinated ketones—see a previous review[1]):



R=H, $CH_3$.

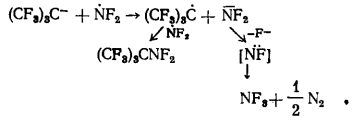
An example illustrating the extremely great promise of the use of transition metal complexes for the synthesis of organofluorine compounds is provided by the incorporation of hexafluorobut-2-yne in the cobalt complex of azobenzene accompanied by carbonylation[102]:



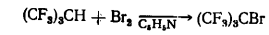
The intermediate complex has been isolated and its structure has been confirmed by X-ray diffraction.

## 4. New Ideas About the Mechanisms of Anionoid Processes

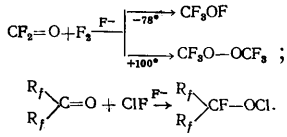
The reactions involving fluorocarbanions cannot always be accounted for within the framework of purely ionic concepts. For example, the interaction of octafluoroisobutene with tetrafluorohydrazine, resulting in the formation of $(CF_3)_3CNF_2$, is catalysed by KF. Since $N_2F_4$ decomposes on heating with formation of $\dot{N}F_2$ radicals, the decisive stage in the process is probably the oxidation of the carbanion $(CF_3)C^-$ by this radical[103]:



The "ionic" bromination of polyfluoroalkanes[104]:

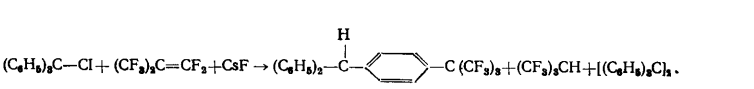


and the reactions of "perfluoroalkoxides" with halogens or interhalogen compounds[105,106]:



are just as likely to have oxidative mechanisms.

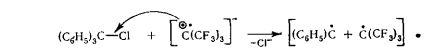
The ability of the fluorocarbanion to behave under mild conditions as an electron donor was confirmed directly in an ESR study of an unusual reaction between the nonafluoro-t-butyl anion and chlorotriphenylmethane involving the transfer of the reaction centre[107]:



At the beginning of the reaction, the concentration of the triphenylmethyl radical increases sharply, and then falls only gradually to the level corresponding to the equilibrium

$$2\,(C_6H_5)_3C^{\cdot} \rightleftarrows [(C_6H_5)_3C]_2 \ .$$

Thus the main reaction product is obtained as a result of the recombination within a cage of the radical pair formed via electron transfer:

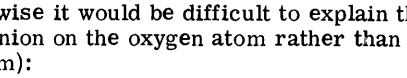


On the other hand, the side products are obtained as a result of the liberation of the radicals from the "cage".

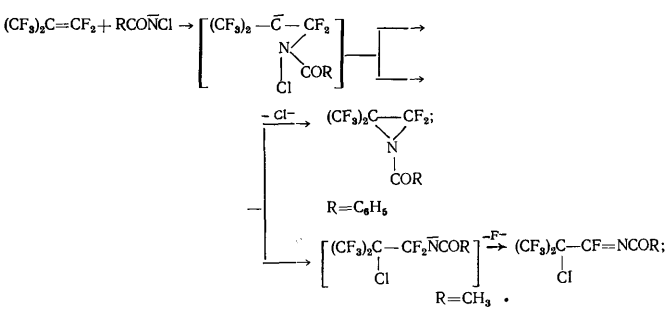
Yet another interesting reaction of carbanions, namely their reaction with nitroso-compounds, takes place with transfer of the reaction centre [108]:

$$(CF_3)_2CF{-}NO + (CF_3)_2C{=}CF_2 \xrightarrow{CsF} (CF_3)_2C{=}NOC(CF_3)_3 \ .$$

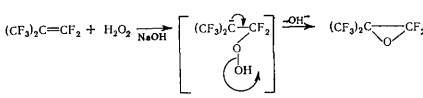
Since it is known that in an aprotic medium fluoroalkylnitroso-compounds behave as one-electron oxidants (demonstrated by polarography in dimethylformamide [109]), this reaction presumably includes an electron transfer stage (otherwise it would be difficult to explain the attack by the carbanion on the oxygen atom rather than on the nitrogen atom):



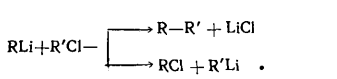
The reaction between octafluoroisobutene and *N*-chloramide anions can take place in two ways, depending on the nature of the acyl residue [110]:



The first, which is an example of the fixation of the intermediate of the Hofmann–Lossen rearrangements, is in essence related to the familiar alkaline epoxidation of fluoro-olefins [111] (see Bluterio's review) [112]:

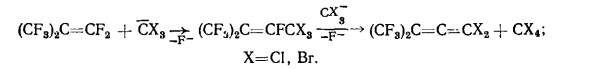


The relation between the two pathways of the reaction with *N*-chloramides is the same as that between the Wurtz reaction and the metal halide exchange:

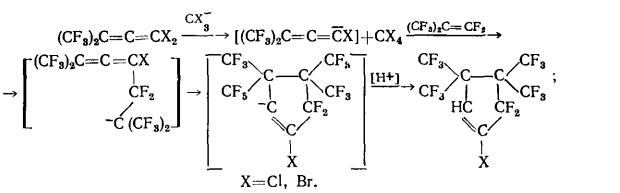


In both cases the key stage involves one-electron transfer [113].

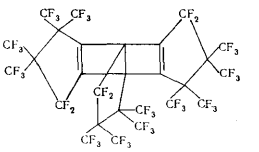
The one-electron transfer stages evidently include also multistep transformations occurring when haloforms are added to a solution of the nonafluoro-t-butyl anion. The initial step is the generation of the trihalogenomethyl anion by virtue of the greater acidity of $CX_3H$ (X = Cl or Br) compared with $(CF_3)_3CH$. The anion formed substitutes the vinyl fluorine atom in octafluoroisobutene:



The dehalogenation of the resulting olefin takes place immediately afterwards, evidently under the influence of the trihalogenomethyl anion, which thus behaves as an electron donor. This leads to the formation of the carbon tetrahalide and an extremely electrophilic allene, which can be detected as an adduct with furan. In the absence of furan, the allene reacts with octafluoroisobutene via the following probable mechanism:



Thus an unusual conversion of octafluoroisobutene into a pinacol derivative takes place [cf. reaction (3)]. When X = Br, the cyclopentene formed is the final product. On the other hand, when X = Cl, the reaction proceeds further and a trimer is formed via an HCl elimination stage:



It was difficult to predict the formation of such final products on the basis of the structure of the initial reactants [114].

The reaction of bis(trifluoromethyl)thioketen with *NN*-dimethylaniline is accompanied by the formation of red intermediates, while the final product is $C_6H_5NCH_2SCH{=}C(CF_3)_2$. [115] Presumably an electron transfer



takes place in this case too, since the products of the substitution of the $CH_3$ group in *NN*-dimethylaniline are in fact usually formed as a result of one-electron oxidation of this amine, which readily gives rise to a radical-cation [116]. It is remarkable that other bases (alcohols, mercaptans, secondary amines) combine with bis(trifluoromethyl)thioketen via the C=C bond and not the C=S bond, i.e. the thioketen behaves as a normal acylating agent [115].

Yet another example of the "nucleophilic" reaction, the result of which is difficult to explain fully on the basis of purely ionic ideas, involves the dimerisation of bis(pentafluorophenyl)methyl bromide on treatment with cyanide ions or triphenylphosphine [117]:

$$2\,(C_6F_5)_2CHBr + CN^- \rightarrow (C_6F_5)_2CH{-}CH(C_6F_5)_2 + BrCN + Br^- \ .$$

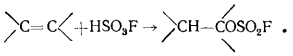
The product of this reaction is probably formed as a result of the recombination of the bis(pentafluorophenyl)methyl radicals.

A similar process is a side reaction in the substitution of pentafluorobenzyl chloride by butyl-lithium; it has been shown by physical methods that the reaction has a one-electron mechanism [118].

## II. CATIONOID REACTIONS

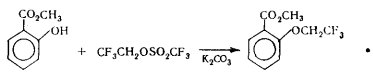
Owing to the presence of electron-accepting substituents in organofluorine compounds, their electrophilic reactions are more difficult than those of the non-fluorinated analogues. For this reason, either severe conditions or the use of very strong acids as the reaction medium are usually required in order to carry out such reactions successfully (see the review of Mochalina et al.[119]). On the other hand, the resistance of organofluorine compounds to severe conditions and strong acids, which cause charring of compounds, such, as for example, non-fluorinated olefins, makes their electrophilic reactions extremely valuable from the synthetic standpoint.

The simplest reaction occurring in strong protic acids is the formation of carbonium ions as a result of the protonation of organic molecules. The interaction of fluoro-olefins with fluorosulphonic acid has proved a convenient method for the synthesis of alkyl fluorosulphonates:



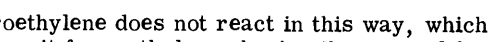
Fluoroethylenes react under extremely mild conditions[120] and tetrafluoroethylene and hexafluoropropene react under severe conditions, the products of their reactions being formed in low yields. $\alpha$-Chloroperfluoroalkyl sulphonates are readily obtained by the addition of $ClOSO_2F$ to fluoro-olefins[121].

Alkyl fluorosulphonates are the strongest alkylating agents for $O$- and $N$-bases[122]. The reactivity of fluoroalkyl trifluoromethanesulphonates is just as high[123]:



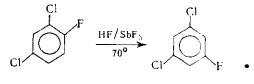
Remarkable prospects arise from the previously unknown ability of fluorosulphonates (other than methyl and ethyl fluorosulphonates) to function as $C$-alkylating agents for aromatic systems[120].

When fluoroethylenes are treated with the $HF-SbF_5$ mixture, they are hydrofluorinated. The reaction is reversible: the intermediate carbonium ion can be regenerated from the final products[124]:

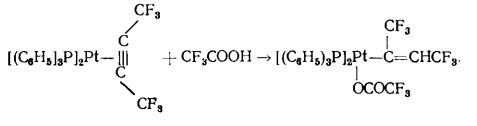


Tetrafluoroethylene does not react in this way, which distinguishes it from ethylenes having the general formula $CF_2=CFX$, where X = Cl, Br, or I.

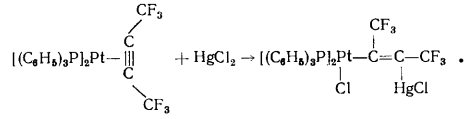
The benzenium ions formed on protonation of fluorobenzenes can be involved in rearrangements associated with the migration of both the proton[125] and the fluorine atom[126]:



The ability of fluorine-containing unsaturated compounds, coordinated to transition metals, to be protonated much more readily than in a free state is an extremely promising property. Thus, hexafluorobut-2-yne forming part of a platinum complex is readily protonated by trifluoroacetic acid[127]:

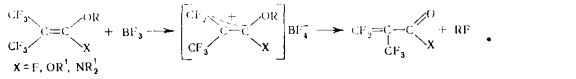


Evidently the range of electrophilic reactions of this kind can be greatly extended. Only the mercuration of this complex by mercury(II) chloride, an extremely mild mercurating agent, has been described so far[127]:



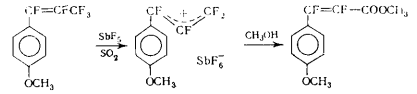
For comparison, one should note that the mercuration of perfluoro-olefins takes place only when the latter are heated with the much more active $HgF_2$ in HF or $AsF_3$ (see the review of Mochalina et al.[119]), while fluoro-olefins containing a hydrogen atom or an alkoxy-group at the C=C bond are mercurated by $Hg(NO_3)_2$.[128]

Carbonium ions are also formed when organofluorine compounds are treated with strong Lewis acids. It has been found that the fluorine atoms forming part of the $CF_3$ group of alkoxypolyfluoroisobutenes are sufficiently mobile for this purpose[129]:



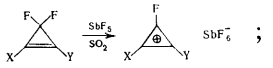
Salt-like intermediate products, containing a mesomerically stabilised cation, can be isolated after the reaction of the aminoacetals of bis(trifluoromethyl)keten (X = $NR_2'$). The final outcome of the reaction is the formation of derivatives of pentafluoromethacrylic acid and an alkyl fluoride.

On treatment with $SbF_5$, 4-pentafluoropropenylanisole also gives rise to a stable cation[130]:



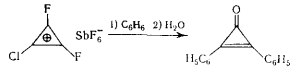
When the cation is treated with methanol, an ester of difluoro-$p$-methoxycinnamic acid is produced.

The salts containing fluorocycloprenyl cations do not decompose until a temperature near 80°C [131]:

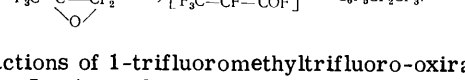


X, Y = F, Cl.

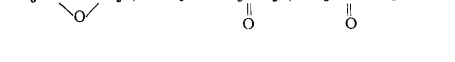
They are capable of alkylating benzene:



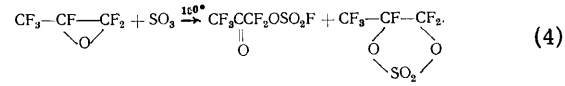
Owing to the ability of the acylium cations generated from carboxylic acid fluorides to eliminate CO, fluoroalkanes can be synthesised from the acids[132]. Oxirans, which are capable of being converted into acid fluorides under the influence of $SbF_5$, react similarly[90]:



The reactions of 1-trifluoromethyltrifluoro-oxiran catalysed by Lewis acids take place differently: antimony pentachloride converts it into a mixture of hexafluoro- and chloropentafluoro-acetones[133]:

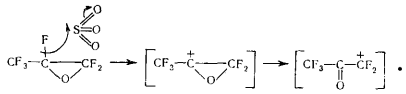


Treatment with sulphur trioxide leads to the formation of two main products [133]:

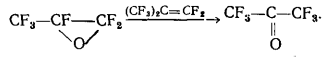


(4)

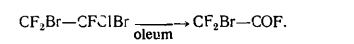
The hypothesis that Lewis acids can not only attack the oxiran at the oxygen atom, which results in the formation of the second product of reaction (4), but can be also coordinated to the fluorine atom of the CF group constitutes a very attractive explanation of these results:



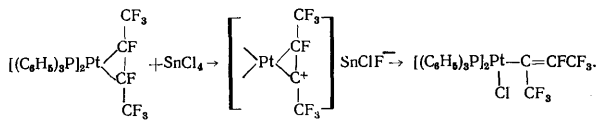
The rearrangement of the carbonium ion with subsequent attack by the anion on the $CF_2$ group can lead to substituted pentafluoroacetones. The validity of this hypothesis has been confirmed by the isolation of a certain amount of chloropentafluoroacetone in the reaction between 1-trifluoromethyltrifluoro-oxiran with $SO_3$ in the presence of NaCl. Furthermore, the oxiran is capable of an unexpected rearrangement in the presence of octafluoroisobutene, which is a very weak acid but exhibits a powerful affinity for the fluoride ion [133]:



The conversion of halogenofluoroalkanes into acid halides, catalysed by oleum, is based on the ability of $SO_3$ to be coordinated to a covalently linked halogen [134]:

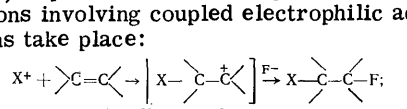


The stage involving the formation of cations probably occurs also in the reaction of tin(IV) chloride with platinum complexes of fluoro-olefins [135]:



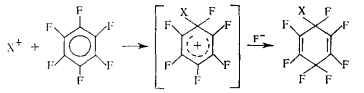
Reaction with the hexafluoropropene complex is accompanied by the exchange of the vinylfluorine atom for chlorine, as a result of which the final product is $[(C_6H_5)_3P]_2Pt(Cl)-CCl=CFCF_3$.

Carbonium ions are generated when a fluoro-olefin is attacked by cationoid species. When the medium contains fluoride ions, capable of recombining with the carbonium ions, reactions involving coupled electrophilic addition to fluoro-olefins take place:

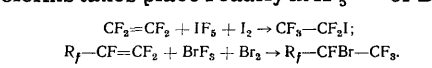


These processes, involving anhydrous hydrogen fluoride as a solvent and a source of $F^-$ ions, have been reviewed in detail [136].

Aromatic fluoro-compounds are capable of similar reactions [137]:

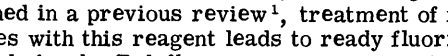


Studies of such processes in other strong acids have developed in recent years. Thus, coupled fluorohalogenation of fluoro-olefins takes place readily in $IF_5$ [138] or $BrF_3$: [139]

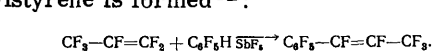


It is noteworthy that the last reaction is also undergone readily by hexafluoropropene dimers, which cannot be introduced into any other electrophilic addition reaction. The reaction involving the addition of chlorofluoroalkanes to fluoro-olefins, catalysed by the $AlCl_3$ (see the relevant reviews [119,140]), is related to these processes.

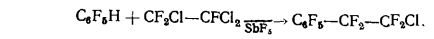
The results obtained using antimony pentafluoride as the reaction medium are particularly interesting. As already mentioned in a previous review [1], treatment of fluoroethylenes with this reagent leads to ready fluorination of the double bond. Polyfluoropropenes unexpectedly undergo electrophilic dimerisation [141]:



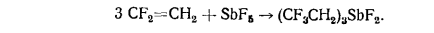
On the other hand, when hexafluoropropene reacts with $SbF_3$ in the presence of pentafluorobenzene, decafluoro-$\beta$-methylstyrene is formed [142]:



Pentafluorobenzene is alkylated also on treatment with 1,1,2-trichloro-1,2,2-trifluoroethane in $SbF_5$. The reaction is accompanied by the partial substitution of chlorine by fluorine, so that its main product is $\beta$-chlorononafluoroethylbenzene, from which octafluorostyrene can be readily obtained [143]:

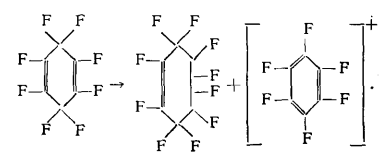


When vinylidene fluoride was allowed to react with $SbF_5$, it was possible to isolate an addition product [144]:



The behaviour of fluoro-olefins in $SbF_5$ is at present difficult to account for unambiguously: possibly the fluorination of the double bond involves a stage where fluoroalkyl derivatives of antimony(V) are formed with subsequent elimination of $SbF_5$. Presumably the dimerisation of fluoropropenes also includes a stage in which organoantimony compounds are produced. However, the analogous dimerisation of 3,3,3-trifluoropropene occurs when it is acted upon by fluorosulphonic acid and not $SbF_5$. The intermediate formation of the difluoroallyl cation in this reaction with its subsequent rearrangement to the final dimer has been suggested [145].

However, the dimerisation of hexafluoropropene or its reaction with $C_6F_5H$ can be satisfactorily accounted for by assuming the formation of the vinyl cation $CF_3CF=CF^+$. Moreover, one must not fail to take into account the oxidising properties of $SbF_5$. Thus hexafluorobenzene forms a stable radical-cation in antimony pentafluoride. [146] The same radical-cation has been detected when $SbF_5$ was allowed to react with octafluorocyclohexa-1,4-diene, which also leads to the formation of decafluorocyclohexene—the disproportionation product [147]:



In principle, one cannot rule out the involvement of one-electron transfer processes also from the above reactions of fluoro-olefins, the study of which is being continued.

The oxidising properties of $SbF_5$ play a decisive role in the recently developed method for the synthesis of organofluorine derivatives of Group VI elements (sulphur,

selenium, and tellurium). The method is based on the ability of these elements to form in $SbF_5$ the double charged cations $E_n^{2+}$ ($n$ = 4, 8, or 16).[148] When these solutions are allowed to react with fluoro-olefins, disulphides or diselenides are formed[149,150]:

$$CF_3{-}CF{=}CF_2 + E_n^{2+} \cdot 2SbF_6^- \xrightarrow[SbF_5]{} (CF_3)_2CF{-}E{-}E{-}CF(CF_3)_2;$$
$$E = S, Se.$$

When sulphur reacts with pentafluorobenzene in $SbF_5$, substitution takes place[151]:

$$C_6F_5H \xrightarrow[SbF_5]{S} (C_6F_5)_2S.$$

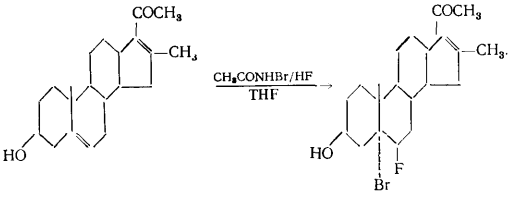
Similar results have been obtained when the pure salts $S_8(AsF_6)_2$,[152] $Se_8(AsF_6)_2$,[153] and $Te_4(AsF_6)_2$[154] were used instead of the solutions. The products of the reactions with tetrafluoroethylene are the corresponding organic derivatives of the elements, hexafluoroethane being formed as a side product.

Antimony pentafluoride in catalytic amounts effectively promotes the addition of arsenic trifluoride to fluoro-olefins[155]:

$$AsF_3 + \text{>C=C<} \xrightarrow[SbF_5]{} As\left(\text{—C—C<}F\right)_3.$$

Sulphur trioxide reacts with fluoro-olefins just as readily as $SbF_5$, with formation of $\beta$-sultones, the chemistry of which has been reviewed[156].

Together with studies on new synthetic possibilities, arising from the application of highly reactive reagents, the development of mild synthetic methods suitable, for example, for physiologically active substances, is important. Thus the use of hydrogen fluoride diluted with tetrahydrofuran as the medium for coupled fluorobromination makes it possible to involve in the reaction only one (more reactive) double bond of 16-methylpregnadiene[157]:



The use of hydrogen fluoride in pyridine as the medium constitutes a significant improvement, permitting reactions involving coupled addition to systems which are unstable in anhydrous hydrogen fluoride[158]. A mild version of fluorohalogenation involves treatment of unsaturated compounds with iodine or bromine in the presence of AgF.[159]

The addition of $(CF_3)_2N{-}X$ (X = Cl, Br, or I)[160] or $SF_5Br$[161] to fluoro-olefins, the direction of which corresponds to electrophilic addition, should be nevertheless probably classified as a radical process, the direction of which is associated with the pronounced electrophilic properties of the attacking radicals[1]. The stereospecificity of the addition of $(CF_3)_2N{-}X$ (X = Cl or Br) to *cis*- and *trans*-butenes (*trans*-addition[162]) does not constitute exhaustive proof of an ionic process mechanism, since the addition of fluoroalkyl iodides to cyclopentene under the conditions of a radical reaction also leads exclusively to the *trans*-adduct[163].

## III. RADICAL REACTIONS

Both free-radical processes and reactions to which a latent radical mechanism can be attributed will be considered in this section. Since the latter reactions frequently include thos which have been treated previously as purely "ionic", the assignment of a process to the series of "ionic" or "radical" reactions is in many cases based merely on a traditional classification.

The radical reactions of organofluorine compounds are frequently distinguished by high selectivity, which makes them valuable in syntheses. Thus, using a radical process, it has proved possible to ("liven") activate fluoroalkanes containing the $CF_2H$ group, which were regarded as inert with respect to any influences under mild conditions[164]:

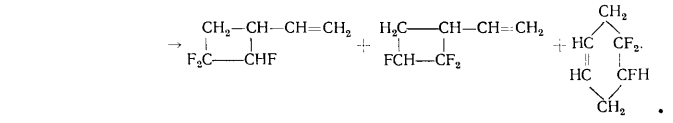
$$n\text{-}C_3F_7H + FSO_2O{-}OSO_2F \xrightarrow{60-70^\circ} n\text{-}C_3F_7OSO_2F.$$

Cycloaddition processes belong to radical reactions of unsaturated organofluorine compounds which are of preparative value. The cyclodimerisation of fluoro-olefins, occurring readily on heating, proceeds very specifically: two molecules of an asymmetrically substituted olefin always combine "head to head":

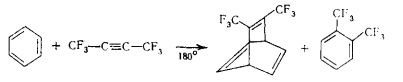
$$2\,CF_2{=}CFX \rightarrow \begin{matrix} F_2C{-}CFX \\ | \quad\quad | \\ F_2C{-}CFX \end{matrix};$$

$$X = Cl^{165},\ C_6H_5^{166}.$$

The direction of cycloaddition indicates its "non-concerted mechanism", i.e. the involvement in the reaction of a stage where biradicals are formed, the formation of biradicals of the type $XCFCF_2CF_2CFX$, with a higher degree of delocalisation of electrons, being preferable[165,167]. The addition of tetrafluoroethylene to ethylene and to *cis*- and *trans*-butenes is also a non-concerted process[168]. However, when trifluoroethylene adds to 1,3-dienes, there is evidence of competition between two process mechanisms—a non-concerted mechanism leading to "2 + 2" addition and a concerted mechanism, which results in "2 + 4" addition[169,170]:

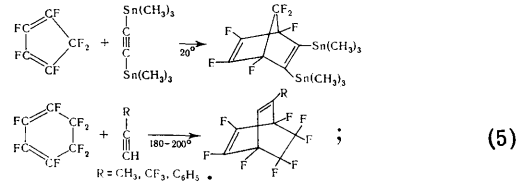


Hexafluorobut-2-yne, which has an extremely electrophilic triple bond, reacts as a dienophile even with aromatic hydrocarbons[171]:



At a higher temperature, bicyclic adducts can not be isolated and poly(fluoroalkyl)benzenes become the main reaction products. The process thus reduces to the substitution of acetylene by hexafluorobut-2-yne. When the same starting materials are irradiated with ultraviolet light in the gas phase, the main reaction product is 1,2-bis(trifluoromethyl)cyclo-octatetraene.[171]

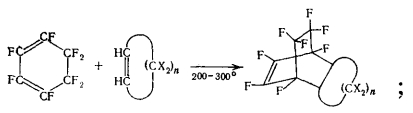
Fully fluorinated cyclic 1,3-dienes are also capable of involvement in diene synthesis[172,173]:



(5)

Pyrolysis of the products of reaction (5) leads to the elimination of $C_2F_5$ and the formation of substituted 1,2,3,4-tetrafluorobenzenes.[173]

Octafluorocyclohexadiene adds also to cyclo-olefins [174]:



X = H, F; $n$ = 2-4.

Reactions using fluoroalkyl radicals generated by electrochemical methods are of preparative interest, since readily available carboxylic acids can then be used as the starting compounds. The simplest process occurring in the electrolysis of acids is the Kolbe reaction, for example [175]:

$$2\,(CF_3)_2CH{-}CO_2H \xrightarrow[\text{Pt anode}]{} (CF_3)_2CH{-}CH(CF_3)_2 + 2CO_2.$$

The resulting product is a convenient starting compound for the synthesis of decafluoro-2,3-dimethylbutadiene.

In the presence of agents capable of reacting with a radical, the Kolbe synthesis is suppressed, which leads to many interesting possibilities [176,177]:

$$CF_3COOH + Br_2 \xrightarrow[\text{anode}]{} CF_3Br + CO_2; \qquad (6)$$

$$CF_3COOH + H_2O \xrightarrow[\text{anode}]{} CF_3{-}O{-}O{-}CF_3 + CO_2.$$

It is noteworthy that, under certain electrolysis conditions, an unexpected product of reaction (6) (a peroxide) is obtained in yields up to 80%. Its formation is caused by the fact that the oxidation potential of water is somewhat lower than that of trifluoroacetic acid. Hexafluoroethane, the "normal" reaction product, becomes an impurity (together with trifluoromethyl ether).[177]

Interesting possibilities arise from the "mixed" version of the Kolbe reaction. Thus joint electrolysis of propionic and trifluoroacetic acids gave 3,3,3-trifluoropropene in 23% yield (in a mixture with other products). The authors[178] suggest that the formation of an unsaturated product is caused by the preliminary dehydrogenation of propionic acid, leading ultimately to ethylene, which actually reacts with the $\dot{C}F_3$ radical.

The condensation of acetone with chlorotrifluoroethylene, a cathodic process, is likewise of interest [179]:

$$(CH_3)_2C{=}O + CF_2{=}CFCl \xrightarrow[H_2SO_4,\ 45V]{} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CF_2CFClH.$$

Evidently the species attacking the $C_2F_3Cl$ molecule is the fairly stable radical $(CH_3)_2\dot{C}OH$, formed as a result of the protonation of the acetone ketyl.

Electrochemical reduction of the $CF_3$ group linked to an aromatic ring cannot be stopped at the stage involving the formation of the $CHF_2$ or $CH_3F$ group when there is a methoxycarbonyl group in the *meta*- or *para*-position. Two different mechanisms then operate—a one-electron reversible mechanism for the *meta*-isomer and a two-electron irreversible mechanism for the *para*-isomer (cyclic voltammetry [180]).

The reduction of fluorine atoms linked to the benzene ring is facilitated as they accumulate. Each fluorine atom in pentafluorobenzene is reduced in a one-electron irreversible process via the following mechanism [181]:

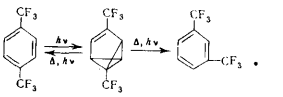
$$ArF \xrightarrow{e} [ArF]^{\cdot} \xrightarrow{H^+} [ArFH]^{\cdot} \xrightarrow{e} [ArFH]^- \xrightarrow{-F^-} ArH.$$

The first reduction product of pentafluorobenzene is 1,3,4,5-tetrafluorobenzene, i.e. the hydrogen atom is introduced in the *meta*-position relative to that already present and the direction of substitution is similar to that observed in nucleophilic reactions [181]. The reduction of fluorobenzene is difficult, but potassium in liquid ammonia causes it to react with potassium acetonate [182]:

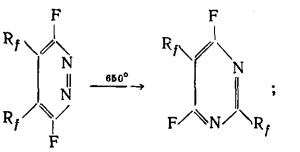
$$C_6H_5F \xrightarrow[K/NH_3,\ -78^\circ]{} [C_6H_5^-] \xrightarrow{[CH_3COCH_2]K^+} C_6H_5CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3.$$

Even a Grignard reagent can be synthesised from fluorobenzene with the aid of specially prepared highly reactive magnesium (admittedly in a low yield) [183].

As already mentioned [1], when aromatic fluoro-compounds are irradiated with ultraviolet light, their valence isomers are readily formed. When the aromatic ring contains fluoroalkyl groups, irradiation leads to rearrangements including a benzvalene formation stage [184]:

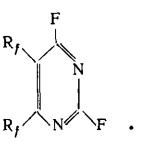


The reaction has a low quantum yield. Similar rearrangements occur also in the series of heterocycles at high temperatures [185]:

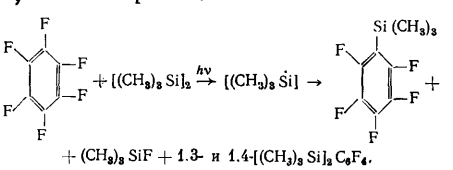


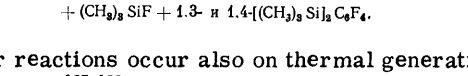
$R_f = (CF_3)_2CF{-}$.

When $R_f = C_2F_5$, there is no migration of the fluoroalkyl group and the following compound is formed:

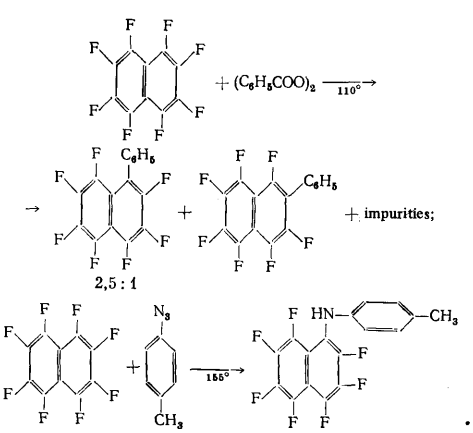


A new type of photochemical reaction of aromatic fluoro-compounds is substitution or addition involving C–F bonds, for example [186]:

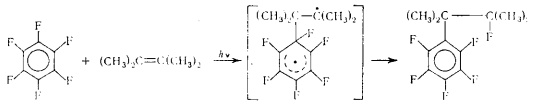




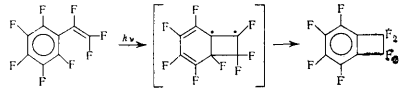
Similar reactions occur also on thermal generation of radical species [187,188]:



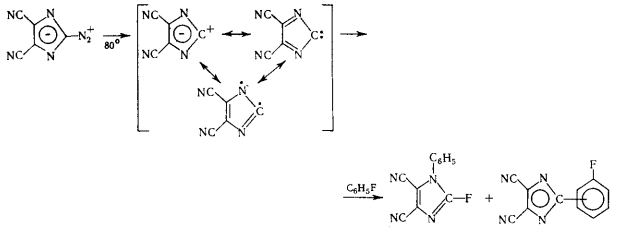
On ultraviolet irradiation, olefins are capable of being "inserted" in the C–F bond[189]:



An intramolecular version of this reaction is the cyclisation of polyfluorostyrenes to benzocyclobutenes[190]:



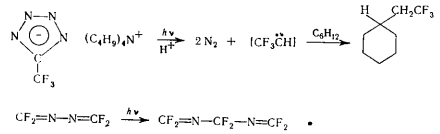
The reaction of fluorobenzene with an extremely interesting carbene having the overall formula $C_5N_4$ constitutes an unexpected insertion in the C–F bond[191]:



The search for new convenient sources of carbenes is a characteristic feature of research in the chemistry of these species (see Hoffmann's review[192]). Organosilicon ($CHF_2CF_2SiF_3$)[193] or organomercury ($CF_3HgOCOCF_3 + NaI$)[194] compounds are accessible sources of fluorine-containing carbenes. The ready decomposition, promited by iridium complexes, of $CF_2ClCOONa$, which is a traditional source of difluorocarbene, holds out some promise. The only reaction products isolated were iridium compounds, in particular $ClCF_3COOIr(CO)[P(C_6H_5)_3]_2$. Research on its

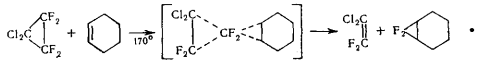
$$\mathrm{CF_2H}$$

synthetic applications is being continued[195]. Fluorine-containing carbenes are readily generated also with the aid of photochemical reactions[196,197]:

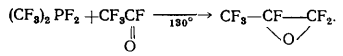


In the latter case the source of the carbene itself plays the role of a carbene trap[197].

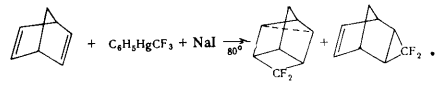
Another source of difluorocarbene employed is 1,1-difluorocyclopropanes—the products of the addition of difluorocarbene to olefins. It is remarkable that the transfer of carbene takes place under milder conditions than the decomposition of the cyclopropane in the absence of the other reactant. This suggests that the transfer proceeds without the formation of a kinetically independent carbene and constitutes "nucleophilic substitution" at the $CF_2$ group. The reaction takes place with a quantitative yield[198]:



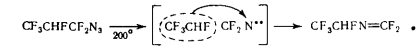
1-Trifluoromethyltrifluoro-oxiran, a widely used source of $CF_2$, can also be obtained from trifluoroacetyl fluoride—its usual decomposition product[199]:



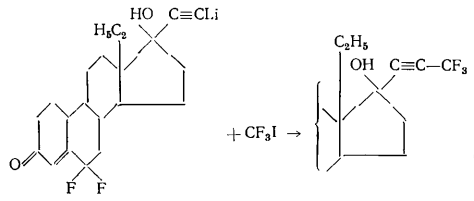
Owing to the weak electrophilic properties of difluorocarbene, it has been possible to cause its addition to norbornadiene in an unusual manner[200]:



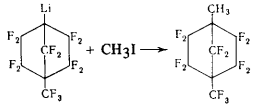
Fluoroalkylnitrenes, formed in the thermolysis of the corresponding azides, undergo a rearrangement analogous to the Curtius rearrangement. This finding illustrates the similarity between the $CF_2$ and C=O groups[201]:



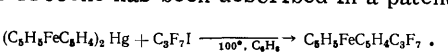
Reactions involving the single-stage introduction of a polyfluoroalkyl group into an organic molecule are extremely important from the preparative point of view. Certain examples of such reactions have been examined in previous sections, but they were not general. The simplest method for combining hydrocarbon and fluorocarbon residues, namely the Wurtz reaction, does not occur in many cases: when organomagnesium compounds, for example, interact with fluoroalkyl iodides, there is only metal halide exchange[45], caused by the large difference between the electronegativities of the fluoroalkyl and alkyl groups[113]. However, acetylides are probably capable of substituting iodine in fluoroalkyl iodides[203]:



The reason for this mode of reaction may be the high electronegativity of carbon in the *sp*-hybridised state. Other examples of this reaction are not quoted in the literature. The "opposite" case—the Wurtz reaction between fluoroalkyl derivatives of lithium and methyl iodide—is apparently specific to the bicyclic system involved in it[203]:

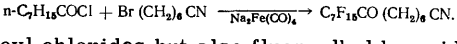


An unusual method for the introduction of a fluoroalkyl group into ferrocene has been described in a patent[204]:



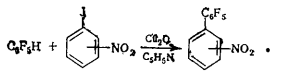
Since the reaction is unknown for other organomercury compounds, presumably the reducing properties of the iron atom forming part of ferrocene play an important role in this case. This hypothesis is supported by the finding that reactions of the type of the Wurtz reaction ($RMgBr + R'Br$) are effectively promoted by transition metal salts (silver or copper salts) and also (for R = alkenyl) by metallic iron[205].

The recently described synthesis of fluorine-containing ketones is a related process. The reaction is catalysed by a carbonylate anion:



Not only acyl chlorides but also fluoroalkyl bromides can be used as the starting compounds. In this case the carbonylate serves as a source of CO.[206]

However, univalent copper is a particularly effective and widely used catalyst. Thus, in the presence of copper(I) oxide, pentafluorobenzene is readily arylated[207]:



Fluoroalkyl halides add to olefins under mild conditions when the reaction is catalysed by a CuCl complex with ethanolamine. The reaction takes place with a high yield and is not accompanied by telomerisation[208]:

$$n\text{-}C_3F_7X + n\text{-}C_6H_{13}CH{=}CH_2 \xrightarrow[(CH_3)_3COH]{CuCl\cdot H_2NCH_2CH_2OH} C_3F_7CH_2\underset{\displaystyle X}{\underset{|}{C}}HC_6H_{13}\text{-}n;$$

X=Br, I.

Copper can be involved in electrophilic cooperation in the substitution of a halogen other than fluorine in the compounds $C_6F_5X$ (X = Br or I). In the absence of copper, only fluorine undergoes nucleophilic substitution by alcohols, amines, or mercaptans, but in its presence the mode of reaction changes completely. Thiourea, which binds copper, restores the usual mode of reaction[209]:

$$C_6F_5Br + C_4H_9SCu \xrightarrow[(CH_3)_2NCHO]{} \begin{cases} \longrightarrow C_6F_5SC_4H_9 \\ \xrightarrow[4(NH_2)_2C=S]{} n\text{-}C_4H_9SC_6F_4Br. \end{cases} \quad (7)$$

The reaction with secondary amines in the presence of CuBr involves the reduction of the C–Br bond together with the substitution of fluorine[209].

Evidently the catalytic activity of univalent copper is due to its ability to be oxidised by transferring an electron to the C–Br or C–I bond. Copper forming part of fluoroalkyl derivatives, which are fairly resistant to heat and hydrolysis, probably retains this ability (see Normant's review[210]). These compounds are readily obtained by the general method for the synthesis of many organometallic derivatives—the reaction between the metal and the halide. In the series of organofluorine derivatives, the reaction is used for a particularly wide range of elements[211-213]:

$$R_fI + M \rightarrow R_fM + MI;$$
$$R_f = n\text{-}C_3F_7,\ n\text{-}C_7F_{15},\ M = Cu;$$
$$R_f = C_6F_5,\ M = \frac{1}{2}\,Zn,\ Cd.$$

Other examples are quoted in a previous review[1].

Fluoroalkyl derivatives of copper are capable of adding to olefins, which results in the formation of a mixture of alkanes and alkenes[214]:

$$C_7F_{15}Cu + CH_2{=}CHC_5H_{11} \xrightarrow[(CH_3)_2SO,\ 110^\circ]{-Cu^0} [C_7F_{15}CH_2\dot{C}HC_5H_{11}] \rightarrow$$
$$\rightarrow C_7F_{15}CH_2CH_2C_5H_{11} + \underset{1:2}{C_7F_{15}CH{=}CHC_5H_{11}}.$$

This reaction probably includes a "*cis*-insertion" stage, which is common to many reactions of σ-derivatives of transition metals. When a fluoro-olefin is inserted, new σ-derivatives sufficiently stable to be isolated are formed[215]:

$$(C_6H_5)_3PAu{-}CH_3 + C_2F_4 \xrightarrow{h\nu} \left[(C_6H_5)_2PAu\begin{array}{l}CF_2\\|\\CF_2\\|\\CH_3\end{array}\right] \rightarrow (C_6H_5)_3PAu{-}CF_2CF_2{-}CH_3.$$

A similar stage may be involved also in the fluoroalkylation of halogeno-olefins by copper compounds[214]:

$$R_fCu + \underset{}{\overset{Br}{}}C{=}C \rightarrow \left[R_f{-}\overset{Br}{C}{-}C{-}Cu\right] \xrightarrow{-CuBr} R_f\!\!>\!\!C{=}C\!\!<\!\!;$$

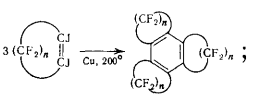
$R_f = C_3F_7,\ C_7F_{15}$.

Another explanation is that copper is merely involved in electrophilic cooperation in the substitution of a halogen by the $R_f$ anion, as in reaction (7).[216]

All these processes closely resemble the classical Ullmann reaction, whose "mixed" version can be very successfully achieved using fluoroalkyl derivatives of copper:

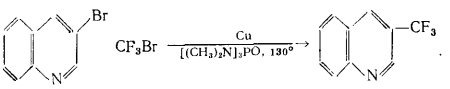
$$R_fHal + RHal \rightarrow R_f{-}R.$$

Since RHal is added to a previously prepared solution of $R_fCu$, the formation of $R_f{-}R_f$ or R–R is ruled out[217,218]. A novel method for the synthesis of an aromatic system has been described in a patent[219]:



$n = 2, 3$.

A particularly valuable feature is that the Ullmann reaction makes it possible to introduce a fluoroalkyl group into heterocyclic compounds and it has been found that fluoroalkyl bromides, which are much cheaper than the iodides, can be used as a source of such groups[220]:



Under more severe conditions, a fluoroalkyl group can be introduced into the benzene ring, substituting a hydrogen atom, with the aid of fluoroalkyl derivatives of copper. The reaction evidently has a free-radical mechanism[221].

## ADDENDUM

During the preparation of the review for the press, a number of new publications of significant interest appeared. Among these, mention should be made of a two-volume edition[222], which is a valuable compilation of studies in organofluorine chemistry published during 1969–1972. Another publication is a book entitled "Ftorpolimery" (Fluoro-Polymers)[223], which includes, among others, an extensive chapter devoted to the synthesis and properties of fluorine-containing monomers. In addition, data concerning the thermal stabilities[224] of fluoro-polymers and their resistance to benzene and oils[225] have also been reviewed. Among other new reviews, mention should be made of a paper[226] devoted to fluorine-containing medicinal preparations, a compilation of data[227] concerning the applications of fluorocarbon emulsions as blood substitutes, a review[228] of the valence isomers of aromatic poly-(fluoroalkyl) compounds, and a paper[229] containing data on the silylation reactions of certain organofluorine compounds. A paper by Liebman[230], containing an extensive compilation of data on nucleophilic substitution reactions directed to the fluorine atom, is also of interest.

New data concerning the influence of the $CF_3$ group on the benzene ring to which it is linked have been obtained[231] by photoelectronic spectroscopy. The wide scope of this research technique in the study of organofluorine compounds has been demonstrated by an investigation[232] in which the structure of the hexafluorocyclobutene trimer has been proved with its aid and also in a study[233] where the method has been used to investigate thin layers of fluoro-polymers obtained photochemically on supports.

A number of new studies of the properties of the fluoride ion have been published. Thus a new version of the synthesis of alkyl fluorides has been proposed: by treating alkyl trifluoromethylsulphinates with caesium fluoride[234]. A method suggested[235] for increasing the reactivity of KF and also its solubility in aprotic solvents (acetonitrile,

benzene) with the aid of a macrocyclic complex-forming agent (18-crown-6) also apparently gives rise to important possibilities. The geometry of the hydrogen fluoride ion has been studied[236]. A paper[237] is devoted to the anodic oxidation of *para*-disubstituted benzenes in the presence of the fluoride ion.

Reactions involving the elimination of the fluoride ion from organic molecules have been investigated[238,239]. The first study is devoted to the unusual reaction of polyfluorinated aldehydes with hydrazines, leading to the formation of alkazones. In the second study, an extremely convenient agent is proposed for the dehydrofluorination of polyfluorinated hydrocarbons—the complex $(C_2H_5)_3N.BF_3$. Derivatives of pentafluoromethacrylic acid can be readily synthesised with its aid[239]. The reactions of these derivatives with amines[240], isonitriles[241], and trialkyl phosphites[242] have also been investigated. The last reaction constitutes an unusual version of the substitution of vinyl fluorine atoms by alkoxy-groups. Among other studies in the chemistry of highly electrophilic organofluorine compounds, mention should be made of an investigation[243] of the synthesis and properties of 6,6-bis(trifluoromethyl)fulvene. A paper[244] deals in detail with the reaction of octafluoroisobutene with haloforms in the presence of CsF. New electrophilic olefins (perfluoromethylenecyclopropane[245]) and also ethylenes containing the $CF_3SO_2$ group[246] have been investigated.

A study has been made of the synthesis and properties of acetylene containing the same substituent[247].

The reactions of fluoro-olefins with nucleophilic agents have been the subject of a study[248] in which the erroneous results of studies by earlier workers, who investigated the reactions of fluoro-olefins with sodiomalonic ester have been revised, a study dealing with the addition-elimination mechanism in nucleophilic reactions[249], and also a study[250] where the radical and ionic pathways in the reactions between fluoro-olefins and phosphines are considered. The characteristics of nucleophilic substitution in perfluoromesitylene are discussed by Markov et al.[251]

A number of studies have been devoted to fluorine-containing organometallic compounds: that of Nefedov et al.[252], who investigated the mechanism of the elimination of LiF by the *o*-fluorophenyl-lithium ether adduct, a study by Fedorov et al.[253] of the stoichiometry of the solvation of fluoroalkyl derivatives of mercury (by NMR), and a study[254] where an unusual type of thermal decomposition of 1,6-di(bromomagnesio)dodecafluorohexane, leading to high yields of decafluorocyclohexene, has been demonstrated. The syntheses of a number of fluorine-containing $\beta$-diketones—analogues of thenoyltrifluoroacetone which are promising complex-forming agents—have been described[255].

New reactions of fluorine-containing oxirans have been investigated—their synthesis form $\alpha$-substituted difluoroacrylic acids[256] and the interaction of oxirans with azides[257] and lithium aluminium hydride[258]. In addition the mode of the opening of the oxiran ring has been studied as a function of the catalyst employed and the reaction conditions[259].

Among investigations devoted to electrophilic reactions of fluoro-olefins, mention should be made of those concerned with the reactions of metastable enols of polyfluoroacetones[260] (see Bekker et al. for the synthesis of the enols[261]). The behaviour of polyfluorinated 1,3-dienes under the conditions of ionic halogenation has been studied[262]. It is remarkable that the authors demonstrated the tendency of these compounds towards 1,4-addition. The alkenylation of aromatic polyfluoro-compounds by hexafluoropropene[263] and by polyfluorinated arenonium ions[264] (the generation of these ions has been described[265]) has been studied in detail. The remarkable ability of the $SO_2$–$SbF_5$ mixture (usually employed merely as a catalyst of electrophilic processes) to serve as an agent for introducing the $SO_2$ group into organic molecules has been discovered[266].

New radical reactions involving the addition of $CF_3$–O–O–Cl [267] and $CF_3$–S–S–Cl [268] to fluoro-olefins under mild conditions have been described[268]. The directions and rates of reaction have been studied in relation to the addition of $CBr_4$ and $CHBr_3$.[269] The high-temperature reaction between trifluoroiodoethylene and sulphur leads to a dimeric product: tetrafluorodithiosuccinyl fluoride[270]. It has been established that the free radicals $C_2F_5$ react with hexafluorobenzene, forming a mixture of isomers of 4,4′-diethylperfluorotetrahydrobiphenyl.[271] A novel method for the generation of $CF_3$ radicals by the action of a glow discharge on hexafluoroethane enabled Lagow et al.[272] to synthesise in high yields derivatives of mercury, tellurium, tin, and germanium fully substituted by $CF_3$ groups. The photochemical generation of the $CF_3$ group from $CF_3I$ permitted the synthesis of $\alpha$-fluoroalkyl ketones from enamines[273]. The photolysis of $CF_3I$ in the presence of benzene derivatives leads to substituted trifluoromethylbenzenes; the direction of substitution has been studied[274]. Among other photochemical reactions, mention should be made of an elegant synthesis of tetrakis(trifluoromethyl)cyclobutadiene dimer from the ozonide of hexakis(trifluoromethyl)benzvalene[275]. The selectivity and kinetics of the addition of difluorocarbene to substituted styrenes have been investigated[276].

The research on a very promising method for the introduction of fluoroalkyl groups into organic molecules with the aid of organocopper compounds by a reaction of the Ullmann type (a new review of this reaction has been published[277]) is being continued. Methods for the synthesis of acids and alcohols[278] and alkynes[279] containing fluoroalkyl groups have been developed on the basis of products obtained by the substitution of bromine in bromoalkenes. Interesting results have been obtained in a study of the reactions of fluoroalkylcopper compounds with 1-bromo-1-fluoroalkylethylenes[280]. Unexpectedly, this results in the formation of 1,2-bis(fluoroalkyl)ethylenes, i.e. the substitution of bromine takes place with transfer of the reaction centre, which suggests the involvement of the copper *d* electrons in the intermediate stages of the process.

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