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Halogen Fluorides in Organic Synthesis

L.S. Boguslavskaya

The reactions of halogen fluorides with organic compounds are considered and the possibilities for their employment as selective fluorinating agents for the synthesis of organic mono- and poly-fluoro-compounds are discussed. The reactivities of halogen monofluorides are compared with those of their stoichiometric equivalents. The mechanisms of the reactions of halogen fluorides and their inorganic complexes are discussed.
The bibliography includes 160 references.

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I. INTRODUCTION

The unusual practical value of organofluorine compounds for modern technology, medicine, and agriculture has stimulated chemists to seek continuously new and selective methods for the introduction of fluorine into an organic molecule. The endeavour to "tame" molecular fluorine, to bind it in a milder fluorinating agent, has for many years occupied the minds of chemists specialising in organofluorine chemistry. From this standpoint, halogen fluorides have attracted the attention of investigators for a long time.[1] Until recently, despite the well-developed technical methods for their synthesis and the commercial availability of some of them, these reagents have been hardly used in organic synthesis.[1-5] The idea arose that halogen fluorides are almost as corrosive as molecular fluorine[4] and therefore their applications are restricted to reactions with polyfluorinated compounds. It was difficult to expect that, being so corrosive, halogen fluorides would find applications in the controlled fluorination of polyhydro-compounds. In reactions with unsaturated polyhydro-compounds, only the stoichiometric equivalents of halogen monofluorides, namely "HalF *in situ*", obtained mainly from *N*-halogenoamides in anhydrous hydrogen fluoride, have been investigated.[4-6]

Nevertheless in recent years, preparative possibilities of halogen fluorides have been discovered and experimental data have accumulated which make it possible to regard certain halogen fluorides, particularly chlorine monofluoride, as promising selective fluorinating agents.

Chlorine monofluoride is of special interest also from the standpoint that it can be obtained and used in synthesis in two ways: gaseous ClF can be obtained from the elements and introduced into the reaction with the substrate in both non-polar and polar media; the "stoichiometric equivalents of ClF", obtained from *N*-chloroamides (or *N*-chloroamines) in HF, always react in a polar medium. Comparison of the results of these reactions permits well-founded conclusions about the mechanism of fluorination by halogen fluorides.

This review deals with the synthetic aspects of reactions involving fluorination by halogen fluorides and provides a critical survey of studies on the mechanism of these and related reactions.

II. THE SYNTHESIS AND PROPERTIES OF HALOGEN FLUORIDES

Halogen fluorides have been obtained and widely used by inorganic chemists because at one time they found applications in the atomic industry for the synthesis of uranium and other metal fluorides and also as powerful oxidants in rocket engineering.[2,3,5] Virtually all halogen fluorides have been synthesised directly from the elements. Gaseous chlorine monofluoride is obtained by passing stoichiometric amounts of chlorine and fluorine through heated copper or nickel tubes:[7-10]

$$Cl_2 + F_2 \xrightarrow{200-250^\circ} 2ClF\ .$$

The design and materials of the apparatus, the conditions of the synthesis, and the kinetics of the process have been described in detail in a monograph[2] and in recent communications.[8,10] In the laboratory, chlorine monofluoride can also be obtained by mixing theoretical amounts of chlorine trifluoride and chlorine at 350 °C [11] or by passing chlorine into a melt of alkali metal fluorides at 800–1000 °C:[12]

$$Cl_2 + MF \rightleftarrows MCl + ClF\ ;\quad M=K,\ Na,\ Li\ .$$

A method of synthesis of ClF by passing chlorine into a solution of SbF_5 in anhydrous HF at 35 °C has been patented.[13] Chlorine trifluoride is a low-boiling liquid and is an industrial product. The methods of its synthesis and apparatus have been described in detail.[1,2] ClF_3 is usually synthesised from chlorine monofluoride and fluorine or directly from chlorine and fluorine:

$$ClF + F_2 \xrightarrow{250-280^\circ} ClF_3\ .$$

Chlorine trifluoride is condensed, purified by fractionation, and stored in cylinders.

Chlorine pentafluoride (a low boiling liquid; at abient temperature—a gas) is difficult to obtain. It can be synthesised from chlorine trifluoride and fluorine by heating under

high pressure[14] or in quartz apparatus under ultraviolet irradiation:[15]

$$ClF_3 + F_2 \xrightarrow[250\ atm]{350^\circ} ClF_5 ;$$

$$ClF_3 + F_2 \xrightarrow[30^\circ]{h\nu} ClF_5 .$$

Bromine monofluoride is a low-boiling unstable liquid, which has been obtained from the elements at +10 °C and purified by successive condensation of the impurities.[16,17] BrF is usually contaminated with bromine and bromine polyfluorides owing to its tendency to disproportionate:[18,19]

$$Br_2 + F_2 \xrightarrow{10^\circ} 2BrF ;$$

$$3BrF \rightarrow Br_2 + BrF_3 .$$

Bromine trifluoride is a stable liquid and is manufactured industrially by passing purified fluorine into liquid bromine in copper apparatus with subsequent vacuum distillation of the product. The design of the apparatus and the technique of the synthesis have been described in detail:[1,2]

$$Br_2 + 3F_2 \xrightarrow{80^\circ} 2BrF_3 .$$

Bromine pentafluoride is an entirely stable product; it is produced industrially directly from bromine and fluorine:[1,2]

$$Br_2 + 5F_2 \xrightarrow{200^\circ} 2BrF_5 .$$

Among iodine fluorides, only IF_5 and IF_7 are stable. The methods of their synthesis from the elements have been described in detail.[1-3] Iodine pentafluoride can be obtained also from chlorine trifluoride and iodine, their interaction occurring with spontaneous combustion in accordance with the equation[2]

$$10\,ClF_3 + 3I_2 \rightarrow 6IF_5 + 5Cl_2 .$$

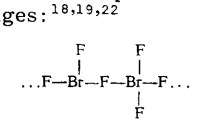
Iodine pentafluoride is a colourless liquid which can be stored in quartz or steel vessels.

Iodine heptafluoride is a colourless gas and has been obtained from the elements in platinum apparatus at high temperatures.[2] Iodine pentafluoride is formed initially and then absorbs fluorine under more severe conditions and is converted into IF_7:

$$I_2 + 5F_2 \rightarrow 2IF_5 ;$$

$$IF_5 + F_2 \xrightarrow{250-280^\circ} IF_7 .$$

Table 1 presents the physical properties of halogen fluorides and, for comparison, those of the molecular halogens. Halogen fluorides are polar compounds and have significant dipole moments. Chlorine and bromine monofluorides have comparatively high dissociation energies $E_d \cong 60$ kcal mol^{-1}. Hence the tendency of these interhalogen compounds to undergo heterolysis rather than homolysis is understandable. The dissociation energies of halogen polyfluorides (ClF_3, IF_7) are actually lower than that of molecular fluorine and hence one may expect their ready decomposition into free radicals. It is striking that the boiling points of halogen fluoride are significantly higher than might have been expected from their molecular weights. Their low volatility can be accounted for by the ability of these compounds to associate with formation of fluorine bridges:[18,19,22]



An important property of halogen fluoride is their amphoteric behaviour. Thus bromine trifluoride is capable of self-ionisation:[23]

$$BrF_3 \rightleftarrows BrF_2^+BrF_4^- .$$

Halogen fluorides react with Lewis acids and bases forming complex fluorine-containing cations and anions:[2,23,24]

$$XF_n + YF_m \rightarrow XF_{n-1}^+YF_{m+1}^- ;$$

$$XF_n + MF \rightarrow M^+XF_{n+1}^- .$$

Compounds of this type are interesting because they can be used as fluorinating agents, which are frequently more convenient to handle than the halogen fluorides themselves.

Table 1. The physical properties of the halogens and halogen fluorides.[2,5,20,21]

Compound	B.p., °C	M.p., °C	Dipole moment, D	Interatomic distances, Å	E_d, kcal mol^{-1}
F_2	−188	−219	—	1.418	38
Cl_2	−35	−101	—	1.988	58
ClF	−100	−155	0.89	1.63	61
ClF_3*	+12	−76	0.65	1.598; 1.698	25
ClF_5**	−13	−93	—	—	—
Br_2	+59	−7	—	2.284	46
BrF	+20	−33	1.29	—	60
BrF_3*	+126	+9	1.19	1.72; 1.81	—
BrF_5**	+41	−30	1.51	1.68; 1.78	—
I_2	+184	+113	—	2.666	36
IF	+1 (decomp.)	—	—	—	58
IF_3*	−35 (decomp.)	—	—	—	—
IF_5**	+100	+9	2.18	—	66
IF_7	+5 (sublimes)	+6	—	—	29

*Planar T-shaped structure.
**Tetragonal pyramid.

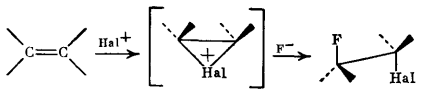
III. THE REACTIONS OF BROMINE AND IODINE MONOFLUORIDES

Bromine and iodine monofluorides are unstable compounds and have therefore been little studied as such in organic synthesis, although the reactions of their stoichiometric equivalents "BrF" and "IF" have been studied quite widely.

1. The Reactions of the Stoichiometric Equivalents "BrF" and "IF"

The *N*-bromoamide or *N*-iodoamide–anhydrous hydrogen fluoride systems[4,6] and more rarely the molecular halogens Br_2 or I_2 in anhydrous hydrogen fluoride[25-27] as well as Br_2--AgF [28,29] constitute the stoichiometric equivalents of BrF and IF. As will be shown below, this does not by any means imply that bromine and iodine monofluorides are actually formed in such systems. *N*-Halogenoamides of molecular halogens are sources of the electrophilic halogen, while HF or AgF provide the nucleophile—the fluoride anion.

In essence, the only application of these systems involves the addition of BrF and IF to a multiple bond. As a rule, halogenofluorination proceeds under mild conditions—at temperatures ranging from −80 °C to room temperature.[4,30] Electron-donating substituents at the multiple bond accelerate while electron-accepting substituents retard their reaction.[31] The halogenofluorination by such systems is a typical electrophilic addition reaction:



A multiplicity of preparative modifications of halogenofluorination depending on the type of unsaturated compound and the source of the electrophilic halogen are known. Oxygen-containing solvents, namely ether and tetrahydrofuran,[4,30] 70 : 30 HF-pyridine,[25,26,32] or anhydrous HF without a solvent[31] are used. The application of oxygen-containing solvents is not always desirable, since they can participate in the addition reaction as nucleophiles.[33,34] Halogenofluorination in a hydrogen fluoride–pyridine mixture gives fairly satisfactory yields in the case of phenylolefins.[25,26,32,35,36] Electrophilic halogenation of the aromatic ring does not then occur. The influence of substituents at the multiple bond on the regiospecificity and stereochemistry of the bromofluorination has been thoroughly investigated (Table 2).

Table 2. The regiospecificity and stereochemistry of the bromofluorination of substituted olefins by *N*-bromoamides in anhydrous hydrogen fluoride.

No.	Initial olefin	Regiospecificity, %		Stereospecificity,* %	Refs.
		$>C^1(Br)-C^2(F)<$	$>C^1(F)-C^2(Br)<$		
1	$C^1H_2=C^2Cl_2$	100	0	—	[37]
2	*Z*-$CHCl=CHCl$	—	—	100	[37]
3	*E*-$CHCl=CHCl$	—	—	85	[37]
4	$CH_2=C^2HCH_2Cl$	40	60	—	[38]
5	*Z*-$C^1HCl=C^2HCH_2Cl$	0	100	100**	[39]
6	*E*-$C^1HCl=C^2HCH_2Cl$	0	100	100	[39]
7	*Z*-$C^1HCl=C^2(Me)CH_2Cl$	100	0	100	[27]
8	*E*-$C^1HCl=C^2(Me)CH_2Cl$	100	0	100	[27]
9	*Z*-$C^1HCl=C^2ClCH_2Cl$	100	0	100	[27]
10	*E*-$C^1HCl=C^2ClCH_2Cl$	100	0	60	[27]
11	*Z*-$C^1HCl=C^2FCH_2Cl$	100	0	—	[27]
12	*E*-$C^1HCl=C^2FCH_2Cl$	100	0	—	[27]
13	$C^1H_2=C^2HCOOMe$	—	>90	—	[33]
14	$C^1H_2=C^2(Me)COOMe$	100		—	[40]
15	*E*-$C^1HCl=C^2(Me)COMe$	0	100	100	[31,41]
16	*Z*-$C^1HCl=C^2ClCOOMe$	30	70	100	[31,41]
17	*Z*-$C^1HCl=C^2FCOOMe$	22	78	100	31,41]
18	*Z*-$CH_3C^1Cl=C^2HCOOEt$	0	100	65	[41]
19	*E*-$CH_3C^1Cl=C^2HCOOEt$	0	100	70	[41]
20	*Z*-$CH(COOMe)=CHCOOMe$	—	—	100	[33]
21	*E*-$CH(COOMe)=CHCOOMe$	—	—	100	[33]
22	$C^1H_2=C^2HPh$	100	0	—	[35]
23	$C^1H_2=C^2Ph_2$	100	0	—	[35]
24	$C^1HF=C^2Ph_2$	100	0	—	[35]
25	$C^1HCl=C^2Ph_2$	100	0	—	[35]
26	$C^1HBr=C^2Ph_2$	100	0	—	[35]
27	$C^1H_2=C^2(Me)Ph$	100	0	—	[35]
28	$C^1H(CH_3)=C^2Ph_2$	100	0	—	[35]
29	*Z*-$C^1HBr=C^2HPh$	100	0	—	[35]
30	*E*-$C^1HBr=C^2HPh$	100	0	—	[35]
31	*Z*-$C^1H(Me)=C^2HPh$	100	0	65**	[35]
32	*E*-$C^1H(Me)=C^2HPh$	100	0	100	[35]
33	*Z*-$CHPh=CHPh$	—	—	70**	[35]
34	*E*-$CHPh=CHPh$	—	—	100	[35]
35	*Z*-$(Me)_3CC^1H=C^2HPh$	100	0	0**	[35]
36	*E*-$(Me)_3CC^1H=C^2HPh$	100	0	100	[35]
37	*Z*-$C^1H(COOEt)=C^2HPh$	100	—	100	[32]
38	*E*-$C^1H(COOEt)=C^2HPh$	100	—	100	[32]
39	*Z*-$C^1F(COOEt)=C^2HPh$	100	—	100	[32]
40	*E*-$C^1F(COOEt)=C^2HPh$	100	—	100	[32]
41	*Z*-$C^1Cl(COOEt)=C^2HPh$	100	—	100	[32]
42	*E*-$C^1Cl(COOEt)=C^2HPh$	100	—	100	[32]
43	*Z*-$C^1H(COOEt)=C^2ClPh$	100	—	50	[32]
44	*E*-$C^1H(COOEt)=C^2ClPh$	100	—	50	[32]

*The content of the *anti*-adduct.
**The *Z*-isomer is partly converted into the *E*-isomer during synthesis.

On the whole, the mode of addition of the electrophile and nucleophile expected for an electrophilic mechanism is observed. Since unsaturated compounds with electron-deficient multiple bonds, which usually react with the halogens via a free-radical mechanism, can be introduced into the bromofluorination reaction, it is of interest to compare the competing influences of the substituents on the mode of addition and the stereochemical characteristics of the bromofluorination.

The bromofluorination of 1,3-dichloroprop-1-enes (Table 2, Nos.5 and 6) proceeds regiospecifically in such a way that the electrophilic bromine is directed to the central carbon atom, while the nucleophile F^- ion is directed to the terminal carbon atom:

$$CHCl=CHCH_2Cl \xrightarrow[HF]{>NBr} CHClFCHBrCH_2Cl .$$

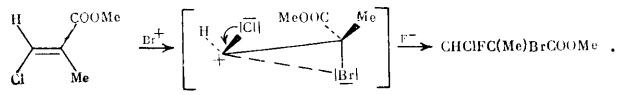
The chlorine atom attached to the multiple bond behaves as a *p*-donor and fully controls the mode of addition. The introduction into the 2-position of 1,3-dichloropropene of substituents delocalising the positive charge of the carbonium ion completely alters the mode of addition—the electrophile is directed to the terminal carbon atom, while the nucleophile goes to the central carbon atom (Table 2, Nos.7–12):

$$CHCl=CRCH_2Cl \xrightarrow[HF]{>NBr} CHClBrCRFCH_2Cl ;$$

$$R=CH_3,\ Cl,\ F .$$

Overall, the CH_2Cl and CH_3, F, or Cl substituents exhibit a more powerful directing effect than the chlorine atom.

An analogous effect has been observed in the bromofluorination of acrylates. Methyl acrylate is brominated almost entirely contrary to the Markovnikov rule (Table 2, No.13), while methyl methacrylate is brominated in accordance with the Markovnikov rule (Table 2, No.14). *p*-Donor substituents have a significantly greater stabilising influence on the intermediate carbonium ion than the CH_3 group. This is readily seen in relation to the bromofluorination of the methyl esters of α-R-β-chloroacrylic acids (Table 2, Nos.15–17):



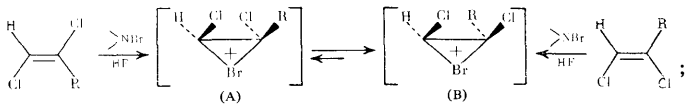
$\rightarrow CHClFC(Me)BrCOOMe$.

In the methyl ester of *E*-α-chloro-β-methylacrylic acid (Table 2, No.15) the chlorine substituent fully controls the mode of addition—the reaction is regiospecific. The bromofluorination of the double bond in the methyl esters of αβ-dihalogenoacrylic acids is non-regiospecific (Table 2, Nos.16 and 17). The phenyl group as the π-donor is a significantly more effective directing group than the halogen as the *p*-donor (Table 2, Nos.29 and 30): the phenyl group controls the addition of BrF to 1-bromo-2-phenylethylenes:

$$CHBr=CHPh \xrightarrow[HF]{>NBr} CHBr_2CHFPh .$$

The bromofluorination of multiple bonds takes place mainly stereospecifically as an *anti*-addition reaction. In a number of instances (Table 2, Nos.2, 3, 32, 34, and 36) this has been demonstrated reliably by the stereospecific dehydrobromination of the diastereoisomers obtained to the corresponding fluoro-olefins. The observed discrepancies, namely incomplete *anti*-stereospecificity (Table 2, Nos.3, 10, 18, 19, 31, and 33) or *syn*-addition (Table 2, No.36), can be convincingly accounted for by taking into account the known conditions governing the stability of bridged bromonium and open-chain carbenium ions, which are evidently intermediates in bromofluorination in hydrogen fluoride. The complete *anti*-stereospecificity of the addition of BrF to *E*-1,2-dichloroethylene and *E*-1,2,3-trichloropropene (Table 2, Nos. 3 and 10) can be explained by the fact that the bromonium ions (A) with transoid chlorine atoms are less stable than

the ions (B) with cisoid chlorine atoms, just as *trans*-dihalogenoethylenes are less stable than *cis*-dihalogenoethylenes:[42,43]

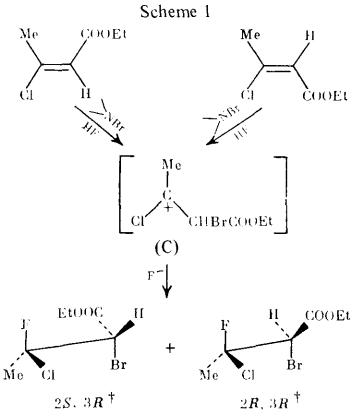


(A) (B)

R = H, CH_2Cl.

Because of this factor, the partial rearrangement of the ion (A) to the ion (B) takes place. For this reason, the bromofluorination of *Z*-olefins is fully *anti*-stereospecific (Table 2, Nos.2 and 9), while the bromofluorination of *E*-olefins (Table 2, Nos.3 and 10) is only stereoselective (85 and 60% of the *anti*-adducts respectively). The non-stereospecific addition of BrF to the ethyl esters of *E*- and *Z*-β-chlorocrotonic acids (Table 2, Nos.17 and 18) can be accounted for by other causes[41] (Scheme 1). The addition of electrophilic bromine to the double bond in β-chlorocrotonates results in the formation of an intermediate which is in essence not a bromonium ion but an open-chain carbenium ion (C). This is promoted by the two geminal substituents (the methyl group and the chlorine atom) at the carbonium ion centre, which stabilise carbonium ions, and by the electron-accepting alkoxycarbonyl group at the vicinal carbon atom. As a result, the reaction is regiospecific and non-stereospecific.

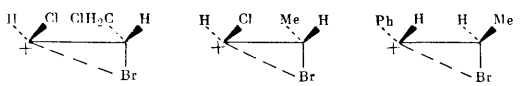
Scheme 1



(C)

2*S*, 3*R*† 2*R*, 3*R*†

However, the examples in Table 2 (compounds Nos.5, 6, 14, 32, and 37–42) show that even a weak *p*-bridge bond in the asymmetric bromonium ions (D), (E), and (F) is sufficient for the fully regiospecific reaction to proceed as an *anti*-stereospecific process.



(D) (E) (F)

The deviations of the bromofluorination of phenylethylenes from *anti*-stereospecificity (Table 2, Nos.31, 33, and 35) are associated with the fact that during the reaction *cis*-olefins isomerise to the more stable *trans*-olefins.[35] In the case of the sterically very greatly hindered *cis*-1-t-butyl-2-phenylethylene, *syn*-addition is observed exclusively.

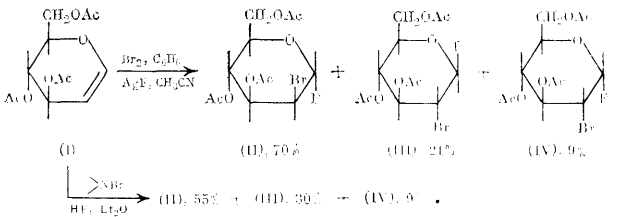
† One enantiomer is shown in Scheme 1 for each diastereoisomer. Owing to the incorrect designation of the sequence of substituents in terms of priority, in the original communications[31,41] incorrect names in terms of the *R*,*S*-system are given under the corresponding perspective formulae.

It has been reported[44–47] that cyclic unsaturated sugars, namely acetylated glucals, are iodofluorinated and bromofluorinated by *N*-iodo- and *N*-bromo-succinimide in hydrogen fluoride with formation of *syn*-adducts. In a later study[28] it was shown with the aid of ^1H and ^{19}F NMR that these reactions proceed predominantly as *anti*-addition and that the assignment of the configurations of the halogenated sugars in earlier studies[44–47] was incorrect.

A system containing a molecular halogen (Br_2, I_2), finely ground silver fluoride, and benzene or its mixture with acetonitrile as the solvent has been recommended[28,29,48] for the successful halogenofluorination of unsaturated sugars and other compounds which readily polymerise or rearrange in hydrogen fluoride.

On treatment with both Br_2–AgF and *N*-bromosuccinimide in hydrogen fluoride, *anti*-adducts are formed from the glucal triacetate (I) (Scheme 2)—2-bromo-2-deoxy-α-D-mannosyl fluoride triacetate (II) and 2-bromo-2-deoxy-α-D-glucopyranosyl fluoride triacetate (III), together with a small amount of the *syn*-adduct, namely the β-anomer (IV).[28,29]

Scheme 2

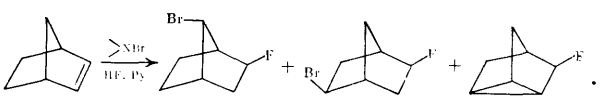


(I) (II), 70% (III), 21% (IV), 9%

(II), 55% + (III), 30% + (IV), 9%

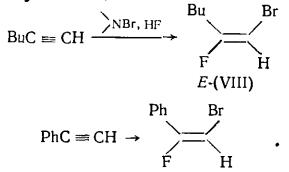
The bromofluorination of norbornene and related compounds by *N*-bromosuccinimide and hydrogen fluoride in ether or pyridine is accompanied by the Wagner–Meerwein rearrangement.[25,49–51] Norbornene gives rise to three main products (Scheme 3): 7-*anti*-bromo-2-*exo*-fluoronorbornane (V), 5-*exo*-bromo-2-*exo*-fluoronorbornane (VI), and 3-fluoronortricyclene (VII).

Scheme 3



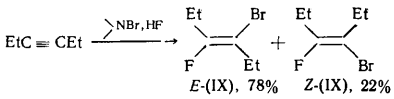
(V), 37% (VI), 35% (VII), 20%

The regiospecificity and stereochemistry of the bromofluorination of substituted acetylenes by *N*-bromoacetamide in anhydrous hydrogen fluoride has been investigated.[52] Vicinally substituted bromofluoroalkenes can be obtained with the aid of this reaction in satisfactory yields, but treatment of substituted acetylenes with the Br_2–AgF system resulted in the formation of bromination products only. The bromofluorination of terminal acetylenes takes place regiospecifically in conformity with the Markovnikov rule and *anti*-stereoselectively (>95%):



E-(VIII)

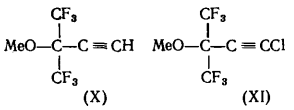
The product of the bromofluorination of hex-1-yne, namely *E*-1-bromo-2-fluorohex-1-ene (VIII), gradually isomerises on storage to the thermodynamically more favourable *Z*-isomer; a 60 : 40 mixture of the *E*- and *Z*-isomers of compound (VIII) is formed after one month, which indicates the kinetic control of the bromofluorination of hex-1-yne. Hex-3-yne is bromofluorinated non-stereospecifically with formation of 78% of the *anti*-adduct and 22% of the *syn*-adduct (IX):



E-(IX), 78% *Z*-(IX), 22%

The mixture of the bromofluoroadducts (IX) does not undergo a change in composition on storage for 15 months.

1,4-Dichlorobut-2-yne gives rise to only one bromofluoroadduct, probably as a result of the *anti*-addition, but the configuration of the resulting 2-bromo-1,4-dichloro-3-fluorobut-2-ene has not been demonstrated.[52] The influence of the structure of acetylenes on the ease of their bromofluorination has been noted: the halogenoacetylenes (X) and (XI) are not bromofluorinated at all under these conditions:



(X) (XI)

The observed facts show that the intermediates in the bromofluorination of acetylenes have the character of oriented π-complexes which differ from the classical carbonium ions; otherwise a lower stereospecificity would have been expected.

It has been reported that the iodofluorination of 1-phenylalk-1-ynes by methyl iodide difluoride (CH_3IF_2) takes place as *syn*-addition.[53]

2. Fluorination by Bromine and Iodine Monofluorides

Mixtures of stoichiometric amounts of bromine trifluoride and molecular bromine or of iodine pentafluoride and molecular iodine have been used as sources of bromine and iodine fluorides in reactions involving addition to perfluoro- and chlorofluoro-olefins[54–58] and also to alkyl perfluoroalkenyl ethers:[57]

$$BrF_3 + Br_2 \rightleftarrows 3BrF \ ;$$
$$IF_5 + 2I_2 \rightleftarrows 5IF \ .$$

Evidence has been obtained that BrF is indeed formed in a mixture of bromine trifluoride and bromine.[59] The reactions of these systems with olefins have been achieved in steel apparatus in the temperature range from 20° to 150–170 °C. The corresponding adducts have been obtained in most cases in exceptionally high yields. The mode of addition of IF and BrF to certain olefins indicates an electrophilic mechanism of the reaction:[54–57]

$$CF_2{=}CH_2 \xrightarrow[100°]{IF_5-I_2} \underset{86\%}{CF_3CH_2} \ ;$$
$$CF_2{=}CFCF_3 \xrightarrow[20°]{BrF_3-Br_2} \underset{46\%}{(CF_3)_2CFBr} \ ;$$
$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[40-50°]{BrF_3-Br_2} \underset{29\%}{(CF_3)_2CFCF_2CFBrCF_3} + \underset{29\%}{(CF_3)_2CFCFBrCF_2CF_3} \ ;$$
$$(CF_3)_2C{=}CFOMe \xrightarrow[0°]{BrF_3-Br_2} \underset{43\%}{(CF_3)_2CBrCF_2OMe} \ .$$

The interaction of ethyl perfluoroalkenyl ethers with the BrF_3–Br_2 system involves the substitution of the α-hydrogen atom in the ethyl group by fluorine together with the addition of BrF to the double bond:[57]

$$(CF_3)_2C{=}CFOEt \xrightarrow[60°]{BrF_3-Br_2} \underset{28\%}{(CF_3)_2CBrCF_2OCHFMe} \ .$$

The BrF_3–Br_2 system has been used for the substitutional fluorination of bromopolyfluoroalkanes.[60] The gradual addition of a solution of the bromofluoroalkane in molecular bromine to a mixture of BrF_3 with bromine at 0–50 °C leads to substitution products in a high yield:

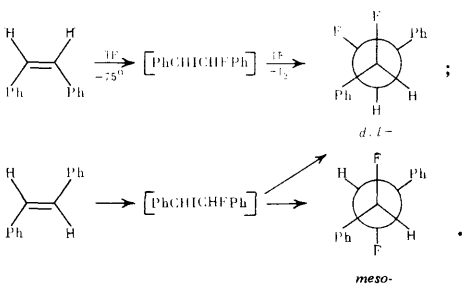
$$CF_3CHBr_2 \xrightarrow[25-35°]{BrF_3-Br_2} \underset{92\%}{CF_3CHBrF} + \underset{5\%}{CF_3CHF_2} \ ;$$
$$CF_2BrCHBr_2 \rightarrow \underset{77\%}{CF_3CHBrF} \ ;$$
$$CF_2BrCBr_3 \rightarrow \underset{79\%}{CF_2BrCFBr_2} + \underset{4\%}{CF_2BrCF_2Br} \ .$$

A possible mechanism has been proposed for the substitutional fluorination taking into account the tendency of bromine to undergo self-ionisation:

$$2BrF_3 \rightarrow BrF_2^+BrF_4^- \ ;$$
$$-\overset{|}{\underset{|}{C}}-Br + BrF_2^+ \rightarrow \left[-\overset{|}{\underset{|}{C}}^{\delta+} \cdots Br^{\delta-} \cdots Br^{\delta+}\begin{matrix}F\\F\end{matrix}\right] \rightarrow -\overset{|}{\underset{|}{C}}^{+} + Br_2F_2 \ ;$$
$$-\overset{|}{\underset{|}{C}}^{+} + BrF_4^- \rightarrow -\overset{|}{\underset{|}{C}}-F + BrF_3 \ .$$

Since chlorine monofluoride readily enters into an analogous fluorination reaction in a non-polar medium (see below), it is extremely likely that a molecule of bromine monofluoride participates in the electrophilic debromofluorination.

In a recently published study[61] iodine monofluoride was obtained by passing molecular fluorine diluted with nitrogen into a solution of iodine in trichlorofluoromethane (Freon) at −75 °C. By adding olefins to the resulting cold IF solution in Freon, fluoroiodoalkanes were synthesised in satisfactory yields. 2-Fluoro-1-iodo-octane (70%), *trans*-1-fluoro-2-iodocyclohexane (64%), etc. have been obtained by this method. The iodofluorination of *cis*- and *trans*-stilbenes by this procedure is accompanied by further substitution of the iodine in the fluoroiodoadducts by fluorine. The unusual stereochemistry of these reactions has been noted: only *dl*-1,2-difluoro-1,2-diphenylethane has been obtained from *cis*-stilbene, while *trans*-stilbene gave rise to a mixture of the *meso*- and *dl*-diastereoisomers in proportions of 1 : 1:



d,l-

meso-

IV. THE REACTIONS OF CHLORINE MONOFLUORIDE

Chlorine monofluoride is the only gaseous reagent among all the halogen fluorides which is stable under the usual conditions and is therefore the most convenient. ClF can be readily obtained from the molecular halogens (see Section II) and can be immediately brought into contact with the organic substrate in rigorously controlled amounts, which makes it possible to regulate the process. In recent years this reagent has attracted the continuous attention of chemists concerned with organofluorine chemistry, as shown by a recently published review.[62] The data obtained after the publication of this review illustrate the new possibilities for chlorine monofluoride in the fluorination of organic compounds and make it possible to consider certain general theoretical aspects of the reactions of electrophiles.

1. The Reactions of the Stoichiometric Equivalents "ClF"

The *N*-chloroamide–HF,[25] the hexachloromelamine–HF,[63] or the molecular chlorine–HF [63,64] systems serve as sources of "ClF". It has been reported that, in the presence of boron trifluoride, methyl hypochlorite is also capable of chlorofluorinating unsaturated compounds.[65] The conditions under which the reactions involving the chlorofluorination of unsaturated compounds take place differ little from the bromofluorination conditions; depending on the type of substrate, the reactant ratio, and the solvent, the yields attained (with respect to the initial alkene) are 30–80%.[25–27, 31,37,41,66–75] The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by the hexachloromelamine–HF system have been studied in greatest detail (Table 3).

Table 3. The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by hexachloromelamine in anhydrous hydrogen fluoride.

No.	Initial olefin	Regiospecificity, %		Stereospecificity, %	Refs.
		>C¹(Cl)–C²(F)<	>C¹(F)–C²(Cl)<		
1	$C^1H_2{=}C^2Cl_2$	100	0	—	[37]
2	$C^1H_2{=}C^2HCH_2OH$	90	10	—	[66]
3	$C^1H_2{=}C^2HCH_2OCOCF_3$	67	33	—	[67]
4	$C^1H_2{=}C^2HCH_2Cl$	68	32	—	[68]
5	$C^1H_2{=}C^2HCH_2Br$	60	40	—	[68]
6	$C^1H_2{=}C^2ClCH_2OH$	100	0	—	[69]
7	$C^1H_2{=}C^2FCH_2OH$	100	0	—	[69]
8	$C^1H_2{=}C^2ClCH_2Cl$	100	0	—	[70]
9	$C^1H_2{=}C^2FCH_2Cl$	100	0	—	[70]
10	Z-$C^1HCl{=}C^2HCH_2Cl$	0	100	93	[39, 71]
11	E-$C^1HCl{=}C^2HCH_2Cl$	0	100	87.5**	[39, 71]
12	$C^1HCl{=}C^2(Me)CH_2Cl$	100	0	—	[27]
13	$C^1HCl{=}C^2ClCH_2Cl$	100	0	—	[27]
14	$C^1HCl{=}C^2FCH_2Cl$	100	0	—	[27]
15	$C^1H_2{=}C^2HCOOMe$	19	81	—	[63, 72]
16	$C^1H_2{=}C^2(Me)COOMe$	95	5	—	[72, 73]
17	$C^1H_2{=}C^2(OMe)COOMe$	100	0	—	[74]
18	$C^1H_2{=}C^2(OAc)COOMe$	100	0	—	[74]
19	E-$C^1HCl{=}C^2(Me)COOMe$	0	100	100	[31, 41]
20	Z-$C^1HCl{=}C^2ClCOOMe$	35	65	—	[31]
21	Z-$C^1HCl{=}C^2FCOOMe$	8	92	100	[31, 41]
22	Z-$C^1Cl(Me){=}C^2HCOOEt$	0	100	50	[41]
23	E-$C^1Cl(Me){=}C^2HCOOEt$	0	100	50	[41]

*The content of the *anti*-adduct.
**The *E*-isomer is partly converted into the *Z*-isomer during synthesis.

As in the bromofluorination reactions, the expected regiospecificity and stereospecificity of the electrophilic addition of ClF to multiple bonds has been observed (cf. Table 2). Thus allyl alcohol and its derivatives are chlorofluorinated non-regiospecifically (Table 3, Nos.2–5). Derivatives of allyl alcohol give rise to 60–70% of adducts in conformity with the Markovnikov rule and to 30–40% of adducts contrary to the Markovnikov rule. The extensive migration of bromine from the allyl position to the central carbon atom [adduct (XIV), Scheme 4] has been demonstrated in relation to allyl bromide:

Scheme 4

$$CH_2{=}CHCH_2Br \xrightarrow[HF]{>NCl} \left[CH_2{-}\overset{+}{C}H{-}CH_2 \;\; (Br,\ Cl) \right] \xrightarrow{F^-} \begin{cases} \rightarrow CH_2ClCHFCH_2Br\ (XII),\ 60\%; \\ \rightarrow CH_2FCHClCH_2Br\ (XIII),\ 15\%; \\ \rightarrow CH_2FCHBrCH_2Cl\ (XIV),\ 25\%. \end{cases}$$

The introduction of carbonium ion-stabilising substituents in the 2-position in the propene system (Table 3, Nos.6–9) makes the chlorofluorination reaction regiospecific and makes it conform to the Markovnikov rule:

$$CH_2{=}CHalCH_2X \xrightarrow[HF]{>NCl} CH_2ClCHalFCH_2X;$$

Hal=Cl, F, X=OH, Cl.

An analogous influence of the substituents is manifested in the chlorofluorination of methyl acrylate and its α-substituted derivatives (Table 3, Nos.15–18). The chlorofluorination of *E*- and *Z*-1,3-dichloropropenes is regiospecific and to a high degree *anti*-stereoselective (93–100%) (Table 2, Nos.10 and 11). As in the bromofluorination of these alkenes, the chlorine atom at the double bond controls the mode of addition: electrophilic chlorine is directed to the central carbon atom, while the fluoride anion is directed to the terminal carbon atom. Compound Nos.19 and 21 (Table 3) show that other regioselective chlorofluorination reactions can also be *anti*-stereospecific. The electrophilic chlorofluorination of the methyl esters of *E*- and *Z*-β-chlorocrotonic acids (Table 3, Nos.22 and 23) takes place non-stereospecifically due to the cause already considered (Scheme 1).

The substitution fluorination of certain organic bromo-derivatives can be achieved with the aid of systems consisting of compounds with an active chlorine atom and anhydrous hydrogen fluoride at temperatures between −10° and +10 °C.[76] Compounds with both N–Cl and O–Cl bonds are suitable as sources of electrophilic chlorine, for example, hexachloromelamine, trichloroisocyanuric acid, and trifluoroacetyl hypochlorite:

$$-\underset{|}{\overset{|}{C}}Br + \underset{(-OCl)}{>NCl} + HF \rightarrow -\underset{|}{\overset{|}{C}}F + \underset{(-OH)}{>NH} + BrCl.$$

N-Bromosuccinimide does not enter into this reaction. For successful fluorination, it is essential that either the reagent or the substrate should dissolve readily in anhydrous hydrogen fluoride. The best results (yield of fluoro-derivatives 50–70%) have been obtained with polyhalogenoalkanes containing bromine atoms at a secondary or tertiary carbon atom. The substitutional fluorination of 1,2-dibromo-3-chloroisobutane by the hexachloromelamine–hydrogen fluoride system, in which one equivalent of >NCl acts on one mole of the alkane, yields exclusively 1-bromo-3-chloro-2-fluoroisobutane (XV):

$$BrCH_2\underset{Me}{\overset{|}{C}}BrCH_2Cl \xrightarrow[HF]{>NCl} \left[BrCH_2\underset{Me}{\overset{|}{\overset{+}{C}}}CH_2Cl \right] \xrightarrow{F^-} \underset{Me}{\overset{|}{BrCH_2CFCH_2Cl}} \quad (XV).$$

On treatment with an excess of the electrophile, the primary bromine atom in the alkane (XV) is not substituted by fluorine. Evidently, the rate-determining stage in the substitution reaction is the electrophilic debromination of the substrate with formation of an intermediate carbonium ion, which is stabilised by capturing a fluoride ion. The substitutional fluorination by these systems does not always proceed regioselectively. Vicinal dibromides can give rise to both isomeric fluoro-derivatives, probably as a consequence of the formation of bridges bromonium intermediates (Scheme 5):

Scheme 5

$$\underset{(XVI)}{CH_2BrCHBrCH_2Cl} \xrightarrow[-ClBr]{>NCl,HF} \left[CH_2{-}\overset{+}{C}HCH_2Cl \;\; (Br) \right] \xrightarrow{F^-} \begin{cases} \rightarrow CH_2BrCHFCH_2Cl\ (XVII) \xrightarrow{>NCl,HF} \\ \rightarrow CH_2FCHBrCH_2Cl\ (XVIII) \xrightarrow{>NCl,HF} CH_2FCHFCH_2Cl\ (XIX). \end{cases}$$

On treatment of 1,2-dibromo-3-chloropropane (XVI) with one equivalent of hexachloromelamine in hydrogen fluoride, a mixture of the isomeric monofluorides (XVII) and (XVIII) was obtained in proportions of 3 : 1 in an overall yield of 60%. On treatment with an excess of the electrophile, the secondary bromide (XVIII) is converted preferentially into the chlorodifluoropropane (XIX). It is evident from the examples of the substitutional fluorination reactions presented here that the chlorine atoms in the molecule are not involved.

This fact shows unambiguously that chlorine monofluoride is not formed as such in the $\rangle$NCl–HF systems. As will be shown below, ClF readily substitutes bromine in primary bromides of the type of compounds (XV) and (XVII), while in anhydrous hydrogen fluoride it substitutes chlorine in primary chloro-derivatives.

2. Chlorination with Chlorine Monofluoride

Chlorine monofluoride readily reacts with both organic and inorganic hydroxy-compounds and some of their derivatives, forming the corresponding hypochlorites in accordance with the general mechanism[77–86]

$$ROH + ClF \rightarrow ROCl + HF .$$

Such processes usually proceed extremely vigorously with evolution of much heat; the final products (hypochlorites) are explosive. Caution must therefore be exercised in carrying out these reactions: the reagent must be introduced gradually, inert solvents must be employed, and the temperature must be rigorously controlled. Chlorine nitrate,[77,78] perfluoroalkyl hypochlorites,[79–81] CF_3OOCl,[82,83] acyl hypochlorites,[84,85] and chlorine trifluoromethanesulphonate[81,86] have been synthesised in this way in high yields. The above compounds have been used in subsequent syntheses as effective electrophiles.[62] ClF reacts with water in a more complex manner, forming $ClFO_2$, Cl_2, O_2, and HF.[87]

Chlorine monofluoride chlorinates aromatic compounds—benzene, chlorobenzene, and even nitrobenzene.[88] The *o*- and *p*-derivatives have been obtained from chlorobenzene and toluene in proportions of 2 : 1, while *m*-chloronitrobenzene has been synthesised from nitrobenzene.

3. The Addition of Chlorine Monofluoride to Multiple Bonds

Chlorine monofluoride adds to the heteroatomic multiple bonds C≡N,[89] N≡S,[90] S=O,[91,92] S=N,[93] C=N,[94–97] and C=O.[79,98–100] In certain cases such addition proceeds in the absence of catalysts. For example, sulphur trioxide readily interacts with ClF, forming chlorine fluorosulphate:

$$SO_3 + ClF \rightarrow ClOSO_2F .$$

Carbonyl fluoride reacts with ClF only in the presence of catalysts—Lewis acids or bases, forming trifluoromethyl hypochlorite:

$$COF_2 + ClF \xrightarrow{CsF} CF_3OCl .$$

The fluorides of carboxylic perfluoro-acids react with ClF in the presence of CsF. It has been suggested that caesium perfluoroalkoxide is formed initially and is then converted into the corresponding hypochlorite with regeneration of CsF:

$$R_FC(=O)F + CsF \rightarrow R_FCF_2OCs ;$$
$$R_FCF_2OCs + ClF \rightarrow R_FCF_2OCl + CsF .$$

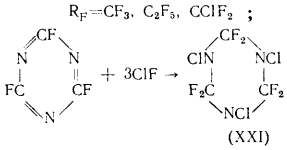
Chlorine monofluoride activated by hydrogen fluoride adds to the carbonyl group of perfluoroketones. In this case the action of the catalyst is apparently directed to ClF and not the substrate:

$$ClF + HF \rightarrow Cl^+ \rightarrow Cl^+HF_2^- ;$$
$$R_F{}_2C{=}O + Cl^+HF_2^- \rightarrow \left[R_F{}_2C^+{-}OCl\right]HF_2^- \rightarrow R_F{}_2CFOCl + HF .$$

The nitriles of carboxylic perfluoroacids and cyanuric fluoride combine with ClF via their $-C\equiv N$ and $C=N$ bonds, the corresponding adducts being formed in high yields (70 to 90%):[101,102]

$$R_FC\equiv N + 2ClF \xrightarrow{-78-0^\circ} R_FCF_2NCl_2 ;$$
(XX)

R_F = CF_3, C_2F_5, $CClF_2$;



(XXI)

The chlorofluoroadducts, namely the *N*-chloroamines (XX) and (XXI), are themselves mild fluorinating agents.[102] Chlorocyanogen also combines with two moles of ClF and the resulting chloroamine is dechlorinated during the reaction to give the corresponding *N*-chloroimines:[103]

$$ClCN + 2ClF \rightarrow CF_2ClNCl_2 \rightarrow CF_2{=}NCl + Cl_2 .$$

Fluorinated isocyanates readily combine with ClF at room temperature:[95]

$$R_FN{=}C{=}O + ClF \rightarrow R_FNClC(=O)F ;$$
(XXII)

R_F = CF_3, CF_3CO, FCO, Cl .

Derivatives of *N*-chlorocarbamic acid (XXII) are formed in yields of 75–90%. The fluoroketone *N*-perfluoroacylimines,[104] *N*-halogenoimines,[96] and *N*-perfluoroalkylimines[70,89,97] react analogously with ClF. Chlorine monofluoride diluted with nitrogen, under conditions where the substrate is highly diluted with an inert solvent (CCl_4, 15–20 : 1 by volume), readily adds even to butadiene and styrene.[105,106] The addition of ClF to halogeno-olefins and certain derivatives of αβ-unsaturated carboxylic acids (esters and acid chlorides) takes place in solvents (CCl_4, CCl_2FCF_2Cl, $CHCl_3$) at room temperature without preliminary dilution of the reagent with an inert gas. The chlorofluoroadducts have been obtained in satisfactory yields and in a number of instances in very high yields (50–90%).[107,108]

The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by chlorine monofluoride in a non-polar medium and in anhydrous hydrogen fluoride have been investigated (Table 4).

The mode of addition of ClF to the double bonds of substituted alkenes depends on the substituents and the medium. Vinyl chloride and trichloroethylene are chlorofluorinated in Freon-113 in conformity with the Markovnikov rule (Table 4, Nos.1 and 4). The chlorofluorination of vinylidene chloride under the same conditions gives rise to 12% of the adduct formed contrary to the Markovnikov rule (Table 4, No.3) and is to a large extent accompanied by the elimination of a proton and the formation of trichloroethylene:

$$CH_2{=}CCl_2 \xrightarrow[\text{Freon, } 20-30^\circ]{ClF} \left[CH_2{-}\overset{+}{C}Cl_2 \leftrightarrow CH_2{=}CCl_2{}^+\right] \xrightarrow{F^-} CH_2ClCCl_2F + CH_2FCCl_3 ;$$
$$\xrightarrow{-H^+} CHCl{=}CCl_2 .$$

The chlorofluorination of allyl derivatives both in a non-polar medium and in hydrogen fluoride takes place non-regiospecifically (Table 4, Nos.6–10): adducts formed in conformity with the Markovnikov rule predominate in the mixture of isomers (60–70%) regardless of the type of allyl substituent.

Table 4. The regiospecificity and stereochemistry of the chlorofluorination of substituted alkenes by an equimolar amount of chlorine monofluoride (reaction carried out in $CHCl_3$ or $CF_2ClCFCl_2$*; the data for the reaction in HF are given in brackets**).

No.	Initial alkene	Regiospecificity, %		Stereospecificity, %	Refs.
		$C^1(Cl)-C^2(F)$	$C^1(F)-C^2(Cl)$		
1	$C^1H_2=C^2HCl$ ***	100	0	—	[105]
2	$CHCl=CHCl$ ***	—	—	—	[105, 108]
3	$C^1H_2=C^2Cl_2$ ***	88	12	—	[108]
4	$C^1HCl=C^2Cl_2$ ***	100	0	—	[88, 108]
5	$CCl_2=CCl_2$ ***	—	—	—	[108]
6	$C^1H_2=C^2HCH_2Cl$ ***	57	43	—	[88, 108]
7	$C^1H_2=C^2HCH_2Br$ ***	55	45	—	[108]
8	$C^1H_2=C^2HCH_2OCHO$	64 (75)	36 (25)	—	[107]
9	$C^1H_2=C^2HCH_2OCOOMe$	60 (68)	40 (32)	—	[107]
10	$C^1H_2=C^2HCH_2OCOCCl_3$	60	40	—	[107]
11	Z-$C^1HCl=C^2HCH_2Cl$ ***	2	98	90	[107, 108]
12	E-$C^1HCl=C^2HCH_2Cl$ ***	20	80	90	[107, 108]
13	$C^1H_2=C^2HCCl_3$ ***	0	100	—	[108]
14	$CF_2=CFCF_3$ ***	0	100	—	[108, 109]
15	E-$CF_3CF=CFCF(CF_3)_2$	Does not react		—	[108]
16	$C^1H_2=C^2HCOOMe$	30 (9)	70 (91)	—	[107]
17	$C^1H_2=C^2(Me)COOMe$	53 (95)	47 (5)	—	[107]
18	$C^1H_2=C^2(Me)COCl$	35	65	—	[107]
19	Z-$C^1HCl=C^2FCOOMe$	22 (0)	78 (100)	50 (100)	[107, 108]
20	Z-$C^1HF=C^2FCOOMe$	—	—	—	[108]
21	$C^1F_2=C^2(CF_3)COOMe$	0 (0)	100 (100)	—	[108]
22	Z-$C^1Cl(Me)=C^2HCOOEt$	(0)	(100)	—	[107]
23	E-$C^1Cl(Me)=C^2HCOOEt$	(0)	(100)	—	[107]
24	Z-$CH(COOMe)=CHCOOMe$	—	—	100 (100)	[107]
25	E-$CH(COOMe)=CHCOOMe$	—	—	100 (100)	[107]
26	Z-$C^1H(COOMe)=C^2ClCOOMe$ ****	100 (100)	0	2:1 (1:4)*****	[108]
27	E-$CH(COOMe)=CClCOOMe$ ****	100 (100)	0	1:4 (1:1)*****	[108]
28	$C^1Cl(COOMe)=C^2FCOOMe$ ****	40 (10)	60 (90)	15:1 (1:8)*****	[108]

*15% (by volume) of alkene in chloroform or Freon.

**50% (by volume) of alkene in anhydrous HF.

***The halogenoalkenes are insoluble in liquid HF and their chlorofluorination in this medium was not therefore investigated.

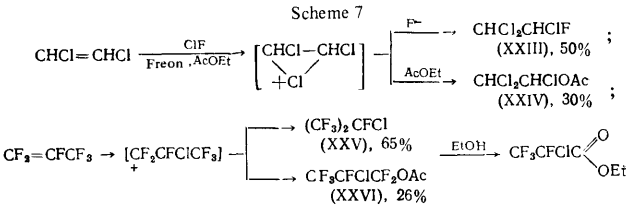
****A 2–10-fold excess of ClF was passed into a solution of the alkene in Freon.

*****The reaction is non-stereospecific and the configuration of the diastereoisomeric adducts was not determined. The ratio of the diastereoisomers is given; it is seen from the figures quoted that one diastereoisomer predominates in a non-polar medium and the other in hydrogen fluoride.

The chlorofluorination of allyl bromide involves the migration of bromine from the allyl position to the central carbon atom; the ratio of the regioisomers (XII)–(XIV) is the same as in the coupled chlorofluorination by the hexachloromelamine–hydrogen fluoride system (see Scheme 4). The addition of ClF to Z- and E-1,3-dichloropropenes (Table 4, Nos.11 and 12) takes place regioselectively (98% of the Z-isomer and 80% of the E-isomer, in contrast to the complete regiospecificity in the coupled chlorofluorination of these olefins—cf. Nos.10 and 11 in Table 3) and *anti*-stereoselectively.

The electrophilic mechanism of the chlorofluorination of polyhalogenoalkenes, including tetrachloroethylene and perfluoropropene, by chlorine monofluoride in non-polar media has been confirmed by the involvement of an external nucleophile—ethyl acetate:[10] the chlorofluorination of dichloroethylene and perfluoropropene in Freon in the presence of ethyl acetate afforded up to 30% of the acetates (XXIV) and (XXVI) together with the chlorofluoroadducts (XXIII) and (XXV) (Scheme 7):

Scheme 7



The regio- and stereo-specificities are markedly different in the reactions of the esters of αβ-unsaturated carboxylic acids with ClF in a non-polar medium and in liquid hydrogen fluoride (Table 4, Nos.16–28). Methyl acrylate (Table 4, No.16) gives rise to regioisomers in proportions of 1 : 2.5 in $CHCl_3$ and 1 : 10 in HF, while for methyl methacrylate (Table 4, No.19) the corresponding ratios are 1 : 1 and 19 : 1. Nevertheless, these unsaturated compounds react with ClF via an electrophilic mechanism in both media: the reactions are extremely fast and, together with chlorofluoroadducts, give rise to products resulting from the involvement of the external nucleophile—acyloxychloroadducts.[107]

Dimethyl maleate and dimethyl fumarate readily combine with ClF in both $CHCl_3$ and HF. The addition takes place *anti*-stereospecifically in both media, which also indicates an electrophilic mechanism.

The esters of αβ-unsaturated acids containing more than two electron-accepting substituents at the multiple bond are smoothly chlorofluorinated only by the ClF–HF system (Table 4, Nos.20–23 and 26–28). The reactions in the instances investigated have been non-stereospecific. In order to complete the reactions of unsaturated esters containing electron-deficient multiple bonds, an excess of the reagent is required in a non-polar medium and the stereochemical result is completely different from that in HF (Table 4, Nos.26–28).

Chlorine monofluoride activated by hydrogen fluoride is an extremely effective electrophilic addend. No multiple bonds incapable of homophase chlorofluorination by this system for electronic or steric reasons have been found. Methyl perfluoromethacrylate, for which no electrophilic addition reactions had been known,[110] interacts smoothly with the stoichiometric amount of ClF in hydrogen fluoride.

4. Substitution of the Halogens in Organic Halogenoderivatives by Fluorine

Chlorine monofluoride is an active agent for the selective substitutional fluorination of bromoalkanes and bromoesters. The reaction takes place when a stoichiometric amount of gaseous ClF is passed through a liquid bromoalkane or a solution of a bromoalkane in a suitable inert solvent (CCl_4, $CFCl_2$, $CFCl_2$) at temperatures between −50° and 50 °C.[111,112] Under these conditions, the chlorine atoms and alkoxycarbonyl groups in the substrate molecule are not involved. The yields are exceptionally high in most cases. Chlorine monofluoride abstracts a bromide anion from the organic substrate with formation of bromine monochloride and the

corresponding carbonium ion, which is stabilised by capturing a fluoride anion:

$$RBr + ClF \rightarrow ClBr + [R^+] \xrightarrow{F^-} RF .$$

The bromine monochloride evolved makes the reaction conditions milder, diminishing the risk of combustion of the polyhydro-substrate on contact with ClF. Naturally, for this mechanism of the substitution of bromine by fluorine, the usual bromide reactivity series is observed: tertiary > secondary > primary.

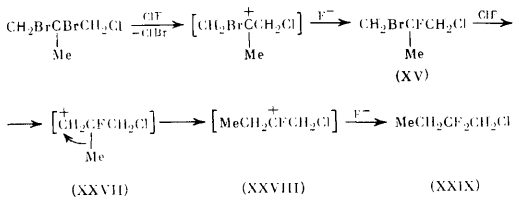
The most favourable conditions for the substitutional fluorination of bromo-derivatives obtain at temperatures in excess of 0–10 °C. At these temperatures, chlorine monofluoride debrominates almost any bromo-derivative with the exception of compounds of the type of R_FCF_2Br and RCHBrCOOR'.

At low temperatures (between −20° and −50 °C) in the case of unreactive substrates, the bromine monochloride evolved enters into a competing reaction with ClF, forming bromine trifluoride (T_m = 9 °C), which is frozen out from the reaction mixture. On fusion, BrF_3 reacts vigorously with the substrate. The reaction becomes uncontrollably explosive even with CCl_4. At temperatures in the range 20–40 °C almost the entire bromo-derivative reacts with ClF smoothly and selectively, giving rise to the corresponding fluorides.[112]

The high selectivity of the substitutional fluorination can be seen from the following example (Scheme 8).

When 1,2-dibromo-3-chloroisobutane is acted upon by one mole of ClF, the tertiary fluoride (XV) is formed regioselectively; the abstraction of the primary bromine atom on treatment with a second mole of ClF also takes place readily and is accompanied by the migration of the methyl group in the carbonium ion (XXVII). This results in the formation of the more stable α-fluorocarbonium ion (XXVIII), which captures a fluoride anion and gives rise to the geminal difluoride (XXIX):

Scheme 8

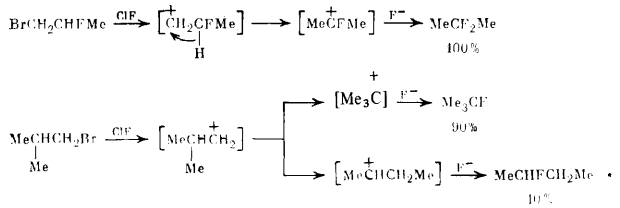


(XXVII) (XXVIII) (XXIX)

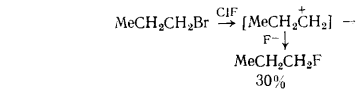
It is seen from this example to what extent gaseous ClF in a non-polar medium is a stronger electrophile than hexachloromelamine in hydrogen fluoride. The latter is incapable of abstracting a primary bromine atom from the halogenoalkane (XV) (see above). The debromination of the primary bromides is accompanied in most cases by the migration of the vicinal substituents—methyl groups and chlorine atoms. 1-Bromo-2-chloropropane (XXX) is readily fluorinated with migration of a chlorine atom. The primary bromoalkanes (XXX) and the isomeric secondary bromoalkane (XXXI) therefore give rise to the same fluorination product—1-chloro-2-fluoropropane (XXXII):

$$\underset{\text{(XXX)}}{MeCHClCH_2Br} \xrightarrow{ClF} \underset{\text{(XXXII)}}{MeCHFCH_2Cl} \xleftarrow{ClF} \underset{\text{(XXXI)}}{MeCHBrCH_2Cl} .$$

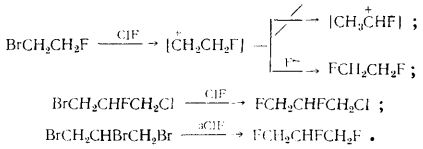
The driving force of all the migrations observed in substitutional fluorination is the formation of a stable carbonium ion. If migration can produce a stable tertiary carbonium ion, then a hydride shift takes place even in a non-polar medium:



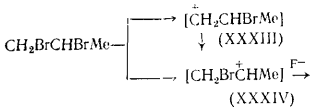
In the fluorination of n-propyl bromide in Freon-113 at 0–10 °C the debromination of the substrate is also accompanied by a hydride shift, but 1-fluoropropane is formed together with 2-fluoropropane:



Primary fluorides can be obtained in non-polar media in all cases where the alternative hydride shift would have led to an insufficiently stable carbonium ion:[111,112]



Comparison of the relative rates of fluorination of n-propyl and isopropyl bromides showed that the difference between their reactivities is small (1 : 2).[112] Nevertheless 1,2-dibromopropane reacts selectively with one mole of ClF to form 1-bromo-2-fluoropropane:



Bearing in mind the tendency of the halogens (Br, Cl) to migrate, it is understandable why the primary cation (XXIII) formed on debromination rearranges to the more stable secondary cation (XXXIV), which in fact accounts for the high selectivity of the substitution.

A study of the relative rates of the substitutional fluorination of bromoalkanes in non-polar media by the method of competing reactions[112] established that the vicinal halogens very greatly retard the fluorination reaction. The following sequence of reactivities has been observed for secondary bromides:

$$MeCHBrMe \gg MeCHBrCH_2Cl \gg ClCH_2CHBrCH_2Cl .$$

Analogously for primary bromides, we have

$$EtCH_2Br \gg MeCHClCH_2Br .$$

The geminal halogen atoms retard the fluorination reaction only very slightly. Thus ethyl bromide and 1-bromo-1-chloroethane are fluorinated at approximately equal rates, while in the series of dibromoethanes the following ratios of the rates of fluorination have been observed:

$$BrCH_2CH_2Br : BrCH_2CHClBr : BrCH_2CCl_2Br = 10 : 3 : 1 .$$

α-Halogenofluorides are formed exclusively under these conditions on reaction with a stoichiometric amount of ClF:

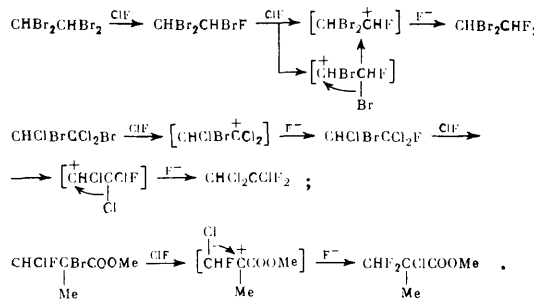
$$\underset{\text{(XXXV)}}{BrCH_2CHClBr} \xrightarrow{ClF} [BrCH_2\overset{+}{C}HCl] \xrightarrow{F^-} BrCH_2CHClF .$$

Such high selectivity is associated with the fact that, for example, in compound (XXXV) the bromine atom in the CH_2Br group is deactivated by the two vicinal halogens to

a much greater extent than the bromine atom of the CHClBr group is deactivated by one geminal and one vicinal halogen atom.

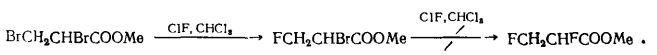
For the same reason, MeCHClBr is fluorinated incomparably faster than $ClCH_2CH_2Br$. Since the halogen atoms are distinguished by dual electronic properties, i.e. exhibit negative inductive and positive resonance effects, the resonance delocalisation of the positive charge of the α-halogenocarbonium ion is in all probability manifested already in the transition state of the debromination reaction, while the vicinal halogens do not show an anchimeric cooperation with the electrophilic dehalogenation.

The fluorine atoms exhibit a high resonance effect and do not tend to migrate, so that the substitutional fluorination of vicinal dibromoalkanes and polybromoalkanes leads to geminal difluorides:

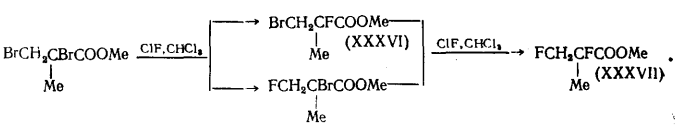


A high selectivity is probably not to be expected in the fluorination of bromoalkanes where the CH_2Br and CHHalBr (or $CHal_2Br$) groups are located in positions more remote than the vicinal position.

The ester group deactivates the bromine atom in the α-position. Methyl αβ-dibromopropionate reacts with ClF in a non-polar medium to form the product of the substitution mainly of the β-bromine atom:[111]



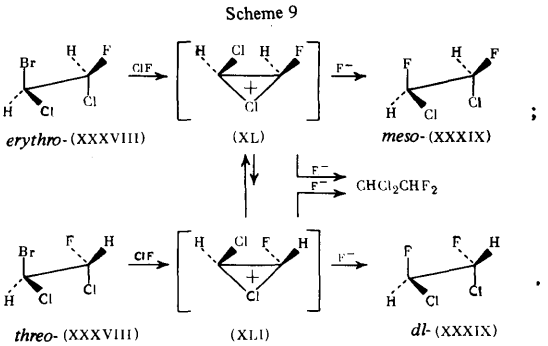
The introduction in the α-position of a substituent stabilising carbonium ions activates the α-halogen. For this reason, methyl αβ-dibromoisobutyrate reacts with one mole of ClF to form a mixture of the α-fluoro- and β-fluoro-regioisomers in proportions of 3 : 1, while treatment of the same mixture with a further mole of ClF results in the formation of the same mixture with a further mole of ClF results in the formation of methyl αβ-difluoroisobutyrate (XXXVII):



It is striking that in a non-polar medium the methyl group does not migrate on debromination of the primary bromide (XXXVI), while the debromination of the same compound in hydrogen fluoride entails the migration of the methyl group and the formation of the geminal difluoride, namely methyl αα-difluorobutyrate, and not the vicinal difluoride (XXXVII).[76] It is to be expected that the substitutional fluorination reactions proceeding via the dehalogenation stage will exhibit a low selectivity.

The fluorination of *erythro*- and *threo*-1-bromo-1,2-dichloro-2-fluoroethanes (XXXVIII) by chlorine monofluoride in the absence of a solvent proceeds non-stereospecifically[111] (Scheme 9). Mainly *meso*-1,2-dichloro-1,2-difluoroethane (XXXIX) (85% in a mixture of diastereoisomers) is formed from the *erythro*-isomer of compound (XXXVIII), while the *threo*-isomer gives rise to a mixture of equal amounts of the *meso*- and *dl*-isomers of compound (XXXIX).

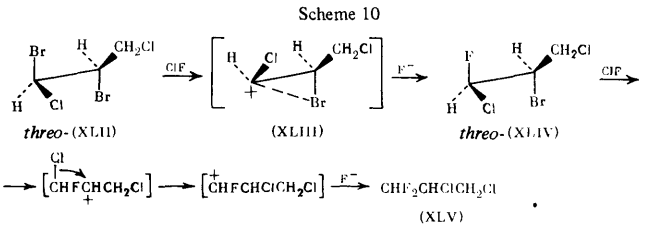
Scheme 9



The preferential retention of the configuration in the case of the *erythro*-isomer of compound (XXXVIII) is probably to be accounted for by the stabilisation of the intermediate carbonium ion (XL) by the interaction of the cisoid chlorine and fluorine atoms (cf. Section III above); in the case of the *threo*-isomer of compound (XXXVIII) there is no such stabilisation in the carbonium ion (XLI) and the reaction is non-stereoselective.

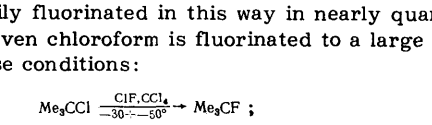
The substitutional fluorination of *erythro*- and *threo*-1,2-dibromo-1,3-dichloropropanes (XLII) takes place regiospecifically at the terminal bromine atom and mainly (85–90%) with retention of the configuration, which can probably be accounted for by the formation of the bromonium ion (XLIII) as a result of the involvement of the neighbouring bromine atom maintaining the configuration of the carbonium ion (Scheme 10):

Scheme 10



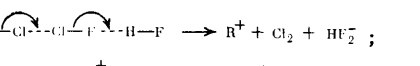
On treatment of 2-bromo-1,3-dichloro-1-fluoropropane (XLIV) with a second mole of ClF, the debromination is accompanied by the migration of a chlorine atom and the only fluorination product is therefore the geminal difluoride (XLV).

In the absence of special catalysts, chlorine monofluoride can substitute the chlorine atoms by fluorine in compounds which give rise to fairly stable carbonium ions following the elimination of Cl^-.[113] Reactions of this kind occur when ClF is passed into the corresponding substrate or its solution in an inert solvent at temperatures between −50° and −10 °C. t-Butyl chloride, 1,2-dichloropropane, and 1,2,3-trichloropropane are readily fluorinated in this way in nearly quantitative yields. Even chloroform is fluorinated to a large extent under these conditions:



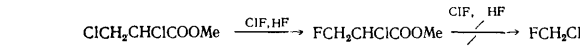
The examples quoted demonstrate the high selectivity of the fluorination reaction: the primary chlorine atoms are not involved. For a more far-reaching fluorination, ClF must be activated by hydrogen fluoride or Lewis acids.[113]

In anhydrous hydrogen fluoride, chlorine monofluoride readily substitutes the chlorine in organic chloro-derivatives by fluorine at temperatures between −60° and 10 °C. The reaction proceeds readily when gaseous ClF is passed into a solution or a stirred emulsion of the chloro-derivative in hydrogen fluoride:

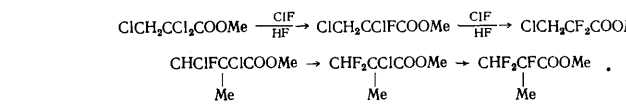


$$R^+ + HF_2^- \longrightarrow RF + HF \ .$$

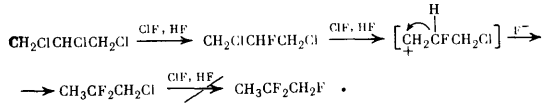
The reaction suffers from the same limitation as the substitution of bromine by fluorine: the chlorine atom of the CHCl group in the α-position relative to the alkoxycarbonyl group is not substituted. When one mole of methyl dichloropropanoate is treated with one mole of ClF, only the β-chlorine atom is substituted:



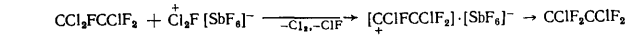
When a second mole of ClF is passed in, the chlorine atom in the α-position is not involved and the electrophilic attack by ClF is directed to the oxygen atom of the carbonyl group (see below). The introduction in the α-position of substituents stabilising carbonium ions promotes the substitution of the α-chlorine atom by fluorine:



Hydrogen fluoride used as a medium in substitutional fluorination promotes hydride shifts with formation of more stable carbonium ions. When 1,2,3-trichloropropane interacts with one mole of ClF, the central chlorine atom is substituted selectively and subsequent attack on the primary chlorine atom in 1,3-dichloro-2-fluoropropane is accompanied by a hydride shift, which results in the formation of a single product—1-chloro-2,2-difluoropropane, whose chlorine atom is not subsequently substituted under these conditions:

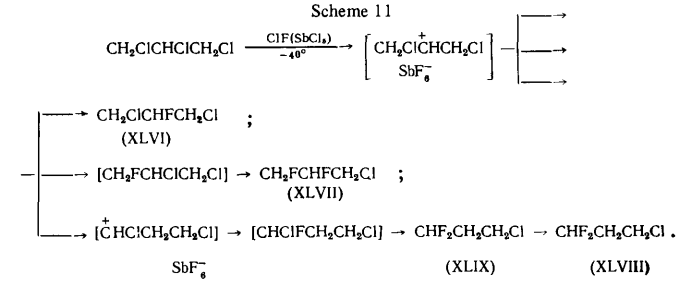


Catalytic amounts of antimony(V) halides (3–5%) enhance the fluorinating activity of chlorine monofluoride in a non-polar medium,[113] which can probably be accounted for by the formation of dichlorofluoronium hexafluoroantimonate,[114] in which the electrophilic activity of the chlorine is so high that the complex is capable of fluorinating Freon-113 to Freon-114 at temperatures between −40° and −60 °C.



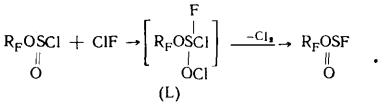
The substitutional fluorination by chlorine monofluoride catalysed by antimony salts is less selective than the fluorination in the absence of a catalyst or using the ClF–HF system. Thus considerable amounts of 3-chloro-1,2-difluoropropane (XLVII), 3-chloro-1,1-difluoropropane (XLVIII), 3-chloro-1,1-difluoropropane (XLIX), and 1,1,3-trifluoropropane (XLIX) have been obtained together with the main product, namely 1,3-dichloro-2-fluoropropane (XLVI), from 1,2,3-trichloropropane by its reaction with an equimolar amount of ClF in the presence of 5% $SbCl_5$ (Scheme 11):

Scheme 11



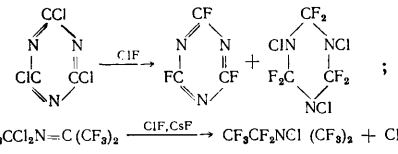
Fluorination by chlorine monofluoride thus has extensive preparative possibilities for the specific synthesis of various mono- and poly-fluorides by varying the temperature of the reaction and the catalytic additives.

Chlorine monofluoride is capable of substituting also the chlorine of acid chlorides in perfluoroalkyl chlorosulphites:[115]



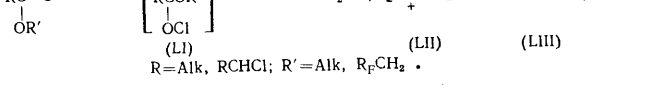
Since such substitution does not occur on treatment with alkali metal fluorides at high temperatures, presumably the reaction proceeds via the electrophilic addition of ClF to the S=O group and subsequent dechlorination of the hypochlorite (L).

It has been suggested that the analogous chlorofluorination with subsequent dechlorination takes place on fluorination of cyanuric chloride, hexachloromelamine,[116] hexachlorobutadiene,[117] and certain chlorine-containing polyfluoroalkylimines[89] by chlorine monofluoride:



5. The Conversion of the Carbonyl Group into the Difluoromethylene Group

When chlorine monofluoride is allowed to react with a solution of an ester in anhydrous hydrogen fluoride at temperatures from −70° to −20 °C, the oxygen of the carbonyl group is smoothly substituted with formation of the difluoromethylene group.[118] The familiar reaction involving the addition to ClF to the carbonyl group probably takes place initially with formation of the hypochlorite (LI) (see above). On further interaction with ClF, the electrophilic elimination of the ClO group probably takes place and the stable carbonium ion (LII) is formed. The latter captures a fluoride anion and is converted into the αα-difluoroether (LIII):



R=Alk, RCHCl; R′=Alk, R_FCH_2 .

The requirements for the stability of the intermediate ion (LII) are so stringent that the introduction of two electron-accepting substituents in the α-position relative to the carbonyl group prevents the reaction. For example, the RCF_2COO group cannot be converted under these conditions into RCF_2CF_2O. Since many examples of compounds of type (LIII), such as, for example, $MeCF_2OCH_2CF_2CF_2H$ are

hydrolytically unstable, in their isolation from the reaction system it is necessary to avoid contact with water. Fluoroethers, for example, $ClCH_2CF_2OCH_2CF_2CF_2H$, which are potential anaesthetics and are fairly resistant to hydrolysis can be synthesised in this way.[119]

When the ethyl esters of acids are used as substrates, more far-reaching fluorination is observed. On treatment with three moles of ClF, ethyl chloroacetate gives rise to a high yield of 1-chloro-2,2,4-trifluoro-3-oxapentane:

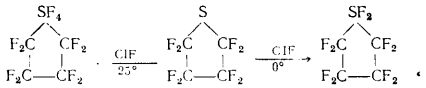
$$ClCH_2COOCH_2Me \xrightarrow[HF]{3ClF} ClCH_2CF_2OCHFMe\ .$$

6. Oxidative Fluorination of Sulphur-containing Compounds

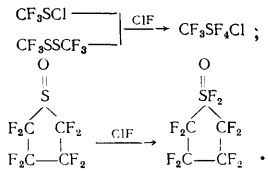
Chlorine monofluoride readily effects the successive oxidation of sulphur(II) to sulphur(IV) and sulphur(VI). Reactions of this kind have been thoroughly investigated in relation to perfluorinated sulphur-containing compounds and have been discussed in reviews.[62,120] We shall therefore quote only certain examples of such reactions achieved with high yields of the products. Perfluoroalkyl sulphides react smoothly with ClF at −78 °C, forming *SS*-difluorides, while at a higher temperature further oxidation of sulphur(IV) to sulphur(VI), accompanied by the partial dissociation of the C–S bonds, takes place:

$$R_FSR'_F \xrightarrow[-78°]{ClF} R_FSF_2R'_F\ ;$$

$$CF_3SCF_3 \xrightarrow[20°]{ClF} CF_3SF_4CF_3 + CF_3SF_4Cl\ ;$$



Perfluoroalkanesulphenyl chlorides, disulphides, and sulphoxides are also readily oxidised and fluorinated under mild conditions:



7. Chlorine Monofluoride as a Member of the Series of Fluorine-containing Reagents with Electrophilic Halogens

The reactions considered show that chlorine monofluoride is a typical electrophile, the majority of the reactions of which with organic substrates proceed via polar mechanisms, thoroughly investigated in organic chemistry, with formation of carbonium ion intermediates. On the whole, the observed facts (the mode of addition to multiple bonds as a function of the electronic nature of the substituents and the medium, the stereochemistry of the addition and substitution, and the skeletal rearrangements and migrations accompanying these reactions in non-polar and polar media or in the presence of antimony salts) are consistent with the predictions based on the extensive experience gained in the chemistry of carbonium ions. The observed specific features in individual reactions are not of fundamental importance, reflecting merely the influence of the medium, the counterion, and the neighbouring groups on the stability of the carbonium ions.

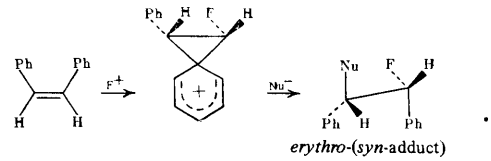
In contrast to other halogens, ClF does not tend to undergo homolytic reactions at the usual temperatures and, as a consequence of the considerable polarity of its bond (μ = 0.89 D), it adds via an electrophilic mechanism even to polyhalogenoalkenes in non-polar solvents, which implies that its reactivity is close to that of a powerful electrophile such as chlorine fluorosulphate.[121–125]

The high selectivity of ClF as a reagent and as a consequence the great preparative scope of its application in the synthesis of a wide variety of mono- and poly-fluorides proved to be somewhat unexpected. The majority of the related reagents containing an electrophilic halogen, namely chlorine and bromine fluorosulphates $FSO_2OCl(Br)$,[121–125] chlorine and bromine trifluoromethanesulphonates CF_3SO_2OCl. .(Br),[127–130] chlorine perchlorate ClO_3OCl,[131,132] perfluoroalkyl hypochlorites and hypofluorites $R_FOCl(F)$,[133–135] and perfluoroacyl hypochlorites and hypofluorites,[136–138] have been used for preparative purposes mainly in reactions with polyhalogeno- and perfluoro-compounds. Reactions involving electrophilic addition to multiple bonds and electrophilic debromination and dechlorination of organic halogeno-derivatives with formation of carbonium ions, which are stabilised by capturing the corresponding nucleophilic residue, are characteristic of these reagents as well as chlorine monofluoride. Polyfluoroalkyl fluorosulphates, trifluoromethanesulphonates, perchlorates, perfluoroalkyl ethers, and perfluoroacylates have been obtained with the aid of these reactions. It has been shown that even molecular fluorine is capable of adding at −78 °C to certain alkenes in Freons 11 and 12 via an electrophilic mechanism.[139]

The electrophiles enumerated have been investigated in reactions with a limited number of substrates and under different conditions, so that it is difficult to set up an electrophile reactivity series which includes also ClF. Nevertheless, presumably chlorine fluorosulphate, chlorine trifluoromethanesulphone, and chlorine perchlorate are stronger electrophiles than ClF. Thus chlorine fluorosulphate is capable of abstracting a chloride anion, in the absence of special catalysts at temperatures below 0 °C, from dichloroethane[123] and methyl chloroacetate;[140] chlorine perchlorate and trifluoromethanesulphonate debrominate compounds of the type R_FCF_2Br,[129,132] while chlorine monofluoride does not react with compounds of this kind under the conditions indicated.

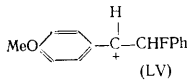
Comparison of the stereochemistries of the addition of electrophiles containing the O–Cl and O–F bonds and of chlorine monofluoride to unsaturated compounds merits attention. The *cis*- and *trans*-isomers of stilbene give rise preferentially to *syn*-adducts on reaction with reagents containing electrophilic fluorine: CF_3OF (70–80%),[136] CF_3CF_2OF (83),[134] CF_3COOF (100%).[137] The configurations of *erythro*- and *threo*-PhCHXCHFPh (X = CF_3O, CF_3CF_2O, or CF_3COO) in the studies quoted have been demonstrated reliably by NMR and do not give rise to any doubts.

The most convincing explanation of the causes of the *syn*-addition of these reagents to stilbenes is that the carbonium ion formed as a result of the electrophilic attack by fluorine is in essence a phenonium ion (LIV) as a result of the involvement of the neighbouring phenyl group, and the subsequent nucleophilic attack by this ion can lead only to the *syn*-adduct:[134,136,137]



erythro-(*syn*-adduct)

The entering fluorine atom, which behaves as a relatively ineffective neighbouring group, cannot compete with the phenyl substituent as regards its capacity to form a bridged cation. The introduction of electron-donating substituents in one of the aromatic rings of stilbene decreases the *syn*-stereospecificity of the electrophilic fluorination. since the intermediate under these conditions is the open-chain carbonium ion (LV), the attack on which by the nucleophile



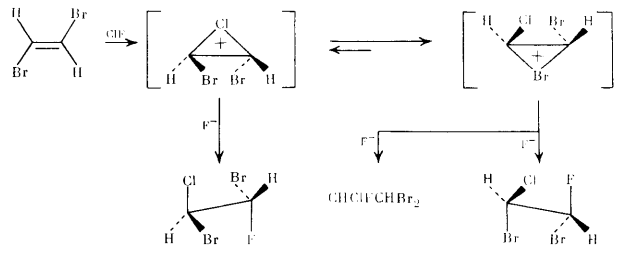
(LV)

is equally probable on either side. The stereochemistry of the addition of these electrophiles to aliphatic olefins has not been investigated but a study has been made of the addition of chlorine and bromine trifluoromethanesulphonates to *cis*- and *trans*-difluoroethylenes and also to *trans*-dichloroethylene.[128] The complete stereospecificity of the addition reaction has been demonstrated: only one diastereoisomer has been obtained from each olefin. The NMR spectroscopic parameters have been calculated for the adducts obtained [*erythro*- and *threo*-$CF_3SO_2OCHFCHFCL$ (LVI) and also for the single diastereoisomer $CF_3SO_2OCHClCHClBr$]. It has been shown that the diastereoisomeric 2-chloro-1,2-difluoroethyl trifluoromethanesulphonates (LVI) have significantly different vicinal spin–spin coupling constants $^3J_{FF} = 19.5$ and 25.5 Hz. Tentative examination of the conformations of each diastereoisomer led to the assignment of their configurations: J_{FF} = 25.5 Hz and 19.5 Hz have been assigned to the *threo*- and *erythro*-isomers of compound (LVI). The assignment of the configurations of the esters (LVI) as *syn*-adducts and also the proposed mechanism involving a concerted *syn*-addition of chlorine and bromine trifluoromethanesulphonates to 1,2-dihalogeno-ethylenes[128] appear to be extremly doubtful.

Indeed it has been established[107] that ClF, which is a less effective electrophile, adds to similar unsaturated compounds via a two-stage electrophilic mechanism with the preferential formation of *anti*-adducts (cf. Table 4). Furthermore, it has been shown[111,141] that the constants $^3J_{FF}$ for the diastereoisomeric alkanes *dl*- and *meso*-CHClFCHClF are respectively 20.8 and 26.2 Hz, while those for *dl*- and *meso*-$(CHFCOOMe)_2$ are 9.1 and 13.9 Hz. Thus the character of the variation of the constants $^3J_{FF}$ as a function of the configuration is the opposite to that proposed for *threo*- and *erythro*-(LVI).[128]

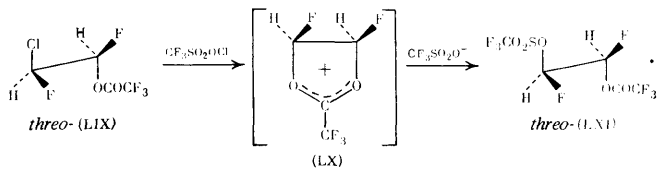
If the substrate molecule contains substituents which compete with the leaving halogen atom for the carbonium ion centre, like the phenyl substituent in stilbenes, then the electrophilic addition of ClF to such substrates involves the formation of *syn*-adducts together with the *anti*-adducts.[142] The involvement of bromine atoms in the chlorofluorination of *Z*- and *E*-1,2-dibromoethylenes is so great that in the chlorofluorination of the *E*-olefin by the hexachloromelamine–hydrogen fluoride system mainly the regioisomer (LVIII) is formed together with the pseudo-*syn*-adduct, namely *threo*-(LVII) (90 and 10% in the mixture of isomers—Scheme 12). The chlorination of this alkene by chlorine monofluoride in Freon-113 proceeds non-regioselectively and non-stereoselectively, but the pseudo-*syn*-adduct, i.e. *threo*-(LVII), predominates in the mixture of isomers.

Scheme 12



	erythro-(LVII) (*anti*-)	(LVIII)(regio-)	*threo*-(LVII) (pseudo-*syn*-)
Hexafluoromelamine-HF	<1%	90%	10%
ClF-Freon-113	15%	17%	68%

It is therefore doubtful if the addition of chlorine and bromine trifluoromethanesulphonates to 1,2-difluoro- and 1,2-dichloro-ethylenes[128] involves stereospecific *syn*-addition, because the entering halogens are more effective neighbouring groups than the substituents already present in the alkene molecules. The substitution of the chlorine atoms by the trifluoromethanesulphonate group on treatment of *erythro*- and *threo*-2-chloro-1,2-difluoroethyl-1-trifluoroacetates (LIX) with chlorine trifluoromethanesulphonate probably does indeed take place with retention of the configuration[129] but not as a consequence of cyclic synchronous substitution, the real reason being that the trifluoroacetate group present in the molecules of compound (LIX) maintains the configuration of the carbonium ion (LX):



threo-(LIX) (LX)

It is to be expected that in the absence from the substrate of neighbouring groups maintaining the configuration of the carbonium ion, the substitution of the halogens by the trifluoromethanesulphonate group will proceed non-stereospecifically (cf. subsection 4 above).

Reactions involving the electrophilic elimination of the halogen are characteristic not only of the heteroatomic reagents with electrophilic halogens mentioned above but also of molecular chlorine, bromine, and iodine monochloride in their interactions with alkyl iodides in inert salts at temperatures between −78° and 25 °C:[143–145]

$$RI + Hal_2 \xrightarrow{-78°} RHal + IHal;$$
$$Hal = Br, Cl.$$

The reaction is preceded by the formation of a complex between the alkyl iodide and the halogen, the decomposition of which results in the formation of a carbonium ion, which captures a halide anion. The typical carbonium ion rearrangements accompanying the substitution reaction confirm this mechanism. It has been shown in relation to the reaction of the optically active 2-iodo-octane with Br_2 and Cl_2 that the substitution takes place preferentially with inversion of the configuration.[143]

V. FLUORINATION BY HALOGEN POLYFLUORIDES AND THEIR INORGANIC COMPLEXES

Halogen polyfluorides are extremely dangerous to handle.[1-4] Chlorine trifluoride ignites wood, plastics, and even concrete and gives rise to an explosion on contact with the usual organic solvents at −100 °C.[146] Bromine trifluoride is somewhat less dangerous. Nevertheless, at the usual temperatures, it reacts explosively even with chlorocarbons. Iodine pentafluoride is not quite so reactive. Only highly fluorinated Freons can be mixed safely with halogen polyfluorides at moderate temperatures. Numerous attempts to employ halogen polyfluorides for the specific synthesis of organic fluorides have led investigators to the conclusion that a common disadvantage of all these reagents is that they are completely non-selective and give rise to a very complex mixture of products.[1,2,147] For some time, this reduced the interest in halogen polyfluorides. However, in subsequent years halogen polyfluorides and their complexes have again attracted attention as fluorinating agents.

Methods of synthesis in high yields of *N*-bromoperfluoropiperidine[148] by treating trichlorohexafluoropiperidine with BrF_3 at −50 °C and also of isomeric octabromotetrafluorocyclohexanes $C_6F_8Br_4$ by treating hexabromobenzene with ClF_3, IF_5, or IF_7 in bromine at temperatures between −10° and 60 °C have been patented.[149] When certain nitriles were treated with BrF_3 in anhydrous hydrogen fluoride at temperatures between −20° and −15 °C, the corresponding trifluoromethylalkanes were obtained in high yields.[150] 2,2-Difluoropropane has been obtained from acetone under the same conditions (93%):

$$RCN + BrF_3 \xrightarrow{HF} RCF_3 ;$$
$$R=Me,\ Et,\ CH_2Cl ;$$
$$MeCOMe + BrF_3 \xrightarrow{HF} MeCF_2Me .$$

Ethyl methyl ketone and isopropyl methyl ketone reacts with bromine trifluoride in hydrogen fluoride with dissociation of the carbon chain. On treatment of perfluoroalkyl iodides with chlorine or bromine trifluoride, bromine pentafluoride, and elemental fluorine in perfluorohexane or in the absence of solvents at temperatures between −60° and −80 °C, perfluoroalkyl iodide difluorides and tetrafluorides were obtained. The conditions of the synthesis and the properties of the products have been described in detail.[146] Iodine pentafluoride is ineffective in this reaction, while the reaction with ClF_3 proceeds in accordance with the equations

$$3R_FI + 2ClF_3 \rightarrow 3R_FIF_2 + Cl_2 ;$$
$$3R_FI + 4ClF_3 \rightarrow 3R_FIF_4 + 2Cl_2 ;$$
$$R_F=C_2F_5,\ C_4F_9,\ C_8F_{13},\ C_{10}F_2 .$$

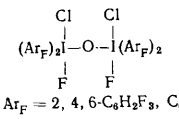
When elemental fluorine is used, three products are formed simultaneously:

$$C_4F_9I + F_2 \rightarrow C_4F_9IF_2 + C_4F_9IF_4 + (C_4F_9)_2I^+IF_6^- .$$

Freshly prepared perfluoroalkyl iodide difluorides are slow-melting solids; on standing, they are converted into insoluble, infusible products, to which the structure $R_2I^+Y^-$, where Y can be IF_4^-, IF_6^-, or IF_8^-, has been attributed on the basis of X-ray diffraction analysis. A method has been proposed for the synthesis of diarylbromonium salts having the general formula $(XC_6H_4)_2Br^+BF_4^-$ by treating arenes,[151] organomercury compounds,[152] or tetra-arylstannanes[153] with BrF_3 and boron trifluoride etherate in methylene chloride and acetonitrile at −70 °C.

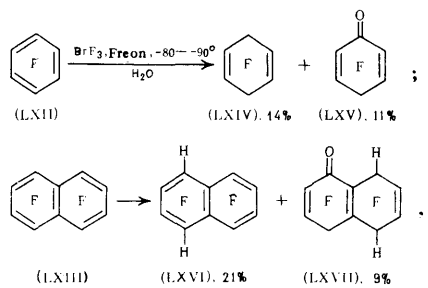
Interesting results have been obtained on treating aromatic polyfluoro-compounds with complexes of halogen fluorides.[154-157] Non-fluorinated arenes decompose and char on treatment with such complexes.[154]

Hexafluorobenzene and pentafluorobenzene do not react with IF_5 even at 120 °C. The reaction of trifluorobenzene and pentafluorobenzene with salts of the type $IF_4^+SbF_nCl_{6-n}$ in hydrogen fluoride, IF_5, or SO_2FCl at 15–50 °C with subsequent hydrolysis of the reaction mixture yielded aromatic derivatives of quinquevalent iodine—μ-oxotetrakis(polyfluoroaryl)dichlorodifluoroiodates:

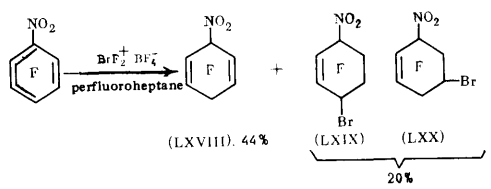


Ar_F = 2, 4, 6-$C_6H_2F_3$, C_6F_5 .

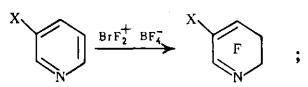
Bromine trifluoride reacts with pentafluorobenzene in Freon-114 or SO_2ClF with formation of bromopentafluorobenzene (27%); in an analogous reaction hexafluorobenzene (LXII) yields after hydrolysis perfluorocyclohexa-1,4-diene (LXIV) and hexafluorocyclohexa-2,5-dien-1-one (LXV); perfluoro-1,4-dihydronaphthalene (LXVI) and octafluoro-1-oxo-5,8-dihydronaphthalene (LXVII) are formed from octafluoronaphthalene (LXIII):[155]



Octafluorotoluene and 4*H*-heptafluorotoluene do not react with BrF_3 under these conditions, while pentafluoronitrobenzene and pentafluoropyridine do not react even at 20° to 30 °C. However, these compounds do react with difluorobromonium tetrafluoroborate $BrF_2^+BF_4^-$ at temperatures in the range between −80° and 0 °C. Pentafluoronitrobenzene is then converted into heptafluoro-1-nitrocyclohexa-1,4-diene (LXVIII) and a mixture of 4(5)-bromo-octafluoro-1-nitrocyclohex-2-enes (LXIX) and (LXX):



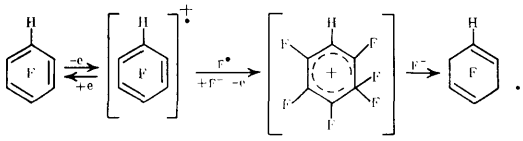
The fluorination of 3-halogenopyridines by this complex proceeds regiospecifically and leads to conjugated 3-substituted perfluoro-1-azacyclohexa-1,3-dienes:



X = Cl, F .

A similar study of the behaviour of aromatic polyfluoro-compounds in relation to BrF_3 and BrF_2^+ led Bardin et al.[155] to the conclusion that these reagents differ little in their electrophilicities, but the BrF_2^+ cation is a much stronger oxidant. Evidence is adduced in support of the view that the reactions of aromatic fluoro-compounds with bromine trifluoride and its complexes proceed via the one-electron

oxidation of the aromatic hydrocarbons with formation of radical-cations and their subsequent fluorination:[155–157]



It has been shown[158] that polyfluoroarenes are fluorinated via an analogous mechanism with xenon fluoride in hydrogen fluoride and by xenon fluoride complexes.

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It follows from the data examined that halogen fluorides are promising fluorinating agents which are suitable for the synthesis of practically important organofluorine products. The development of organic synthesis of the basis of these reagents is only just beginning.

From the preparative standpoint, we believe that chlorine monofluoride is of greatest interest. This applies particularly to the substitutional fluorination reactions of organic bromo- and chloro-derivatives. The waste products in the fluorination of such compounds with hydrogen fluoride are hydrogen halides, whose utilisation constitutes a difficult problem. In the fluorination reactions with the aid of ClF the side products are molecular halogens, which can be employed in the synthesis of the initial substrates.

In contrast to the majority of other fluorinating agents, chlorine monofluoride has the unique ability to introduce successively into an organic molecule one, two, and more fluorine atoms by substitutional fluorination. This constitutes yet another advantage of this interesting reagent.

The theoretical aspects of the reactions of halogen monofluorides and polyfluorides are also of undoubted interest. Chlorine monofluoride and the related compounds of the type HalY, where Y is a residue of a strong acid, not only add to multiple bonds but also abstract halogens from organic halogeno-derivatives under mild conditions via an electrophilic mechanism, which is usually not characteristic of the majority of other electrophiles (for example, HHal, RSHal, etc.). This group of reagents does not fit the classification of electrophiles which provides for their subdivision into two categories—strong and weak—depending on whether or not skeletal rearrangements take place following their addition to the $>C=C<$ bond.[159]

There is apparently no need for such a general classification of all electrophiles. The reactions of carbonium ions, occurring in the second stages of electrophilic processes, are associated solely with the characteristics of the structure of these intermediates and with their tendency to rearrange under particular conditions.

The unambiguous demonstration of a two-stage mechanism of the addition of ClF to the majority of unsaturated compounds in a non-polar medium[108] makes it impossible to agree with the conclusion that the initial molecules interact intermolecularly without the conversion of the intermediate molecular complexes into carbonium ions in non-polar media.[160] This conclusion was reached[160] on the basis of a theoretical study of the mechanism of the electrophilic addition reactions from the standpoint of the conservation of orbital symmetry.

It is to be expected that in the immediate future halogen fluorides will occupy their due place both in the industrial synthesis of organofluorine products and in theoretical organic chemistry.

REFERENCES

1. W.R.Musgrave, in "Advances in Fluorine Chemistry" (Translated into Russian), Izd.Khimiya, Moscow–Leningrad, 1964, Vols.I and II, p.41.
2. N.S.Nikolaev, V.F.Sukhoverkhov, Yu.D.Shishkov, and I.R.Alenchikova, "Khimiya Gadoidnykh Soedinenii Ftora" (The Chemistry of Fluorine Halides), Izd. Nauka, Moscow, 1968.
3. K.O.Christe, IUPAC XXIV Int.Congr.Pure Appl. Chem., 1974(4), 115.
4. W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, pp.109, 388.
5. N.Ishikawa and Y.Kobayshi, "Fluorine Compounds. Their Chemistry and Use" (Translated into Russian), Izd.Mir, Moscow, 1982, p.75.
6. L.S.Boguslavskaya, Uspekhi Khim., 1972, **41**, 1591 [Russ.Chem.Rev., 1972(9)].
7. L.Domange and S.Heuforfer, Compt.rend., 1948, **226**, 920.
8. G.P.Gambaretto and M.Napoli, J.Fluor.Chem., 1976, **7**, 569.
9. H.Schmitz and H.Schumacher, Z.Naturforsch., 1947, **2a**, 362.
10. Yu.I.Petrov, F.M.Mukhametshin, and A.D.Stepukhovich, Kinetika i Kataliz, 1976, **17**, 1347.
11. H.Schmitz and H.Schumacher, Z.Naturforsch., 1947, **2a**, 359.
12. M.A.Gambardella, A.W.Jache, and S.Kongpricha, US P.3 446 592, 1969.
13. A.W.Jache and J.J.Pitts, US P.3 451 775, 1969.
14. D.F.Smith, Science, 1963, **141**, 1039.
15. R.Gatti, R.L.Krecer, J.E.Sicre, and H.J.Schumacher, J.Inorg.Nuclear Chem., 1966, **28**, 655.
16. O.Ruff and A.Braida, Z.anorg.Chem., 1933, **214**, 81.
17. O.Ruff, Angew.Chem., 1933, **47**, 739.
18. R.A.Frey, R.L.Redington, and A.L.Aljibury, J.Chem. Phys., 1971, **54**, 344.
19. K.O.Christe, E.C.Curtis, and D.Pilipovich, Spectrochim.Acta, 1971, **27A**, 231.
20. L.Stein, "Halogen Chemistry", Acad.Press, New York, 1967, Vol.1, p.133.
21. A.J.Gordon and R.A.Ford, "A Chemist's Companion" (Translated into Russian), Izd.Mir, Moscow, 1976, p.134.
22. H.Selig and H.Holzman, Israel J.Chem., 1969, **7**, 417.
23. H.H.Hyman, T.Surles, L.A.Quarterman, and A.Popov, J.Phys.Chem., 1970, **74**, 2038.
24. T.Cyr and S.Brownstein, J.Inorg.Nuclear Chem., 1977, **39**, 2143.
25. G.A.Olah, M.Nojiama, and J.Kerekes, Synthesis, 1973, 780.
26. G.A.Olah, J.T.Welch, Y.D.Vankar, M.Nojiama J.Kerekes, and J.A.Olah, J.Org.Chem., 1979, **44**, 3872.
27. N.B.Mel'nikova, Ya.B.Yasman, L.S.Boguslavskaya, and V.R.Kartashov, Zhur.Org.Khim., 1980, **16**, 2026.
28. L.D.Hall and J.F.Manville, Canad.J.Chem., 1969, **47**, 361.
29. L.D.Hall and D.L.Jones, Canad.J.Chem., 1973, **51**, 2902.
30. L.E.Eckes and M.Hanack, Synthesis, 1978, 217.
31. L.S.Boguslavskaya, T.V.Morozova, and A.P.Voronin, Zhur.Org.Khim., 1978, **14**, 1442.
32. S.Hamman and C.G.Beguin, J.Fluor.Chem., 1979, **13**, 163.
33. A.K.Bose, K.G.Das, and P.T.Funke, J.Org.Chem., 1964, **29**, 1202.

34. L.S.Boguslavskaya et al.. Zhur.Org.Khim., 1969, **5**, 1932.
35. M.Zupan and A.Poliak, J.Chem.Soc., Perkin Trans.I, 1976, 971.
36. F.Weber, H.Giese, and N.Westphal, Z.Chem., 1975, **15**, 475.
37. L.S.Boguslavskaya, A.P.Voronin, K.V.Yarovykh, and A.P.Sineokov, Zhur.Org.Khim., 1975, **11**, 257.
38. F.L.M.Pattison, D.A.V.Peters, and F.H.Dean, Canad.J.Chem., 1965, **43**, 1689.
39. L.S.Boguslavskaya, N.B.Mel'nikova, A.P.Voronin, and V.R.Kartashov, Zhur.Org.Khim., 1978, **14**, 1401.
40. F.H.Dean and F.L.M.Pattison, Canad.J.Chem., 1965, **43**, 2465.
41. L.S.Boguslavskaya, A.N.Chernov, and E.N.Krom, Zhur.Org.Khim., 1980, **16**, 1640.
42. N.Craig, J.Phys.Chem., 1970, **74**, 4520.
43. G.S.Henderson and A.Gajar, J.Org.Chem., 1971, **36**, 3834.
44. P.W.Kent, F.O.Robson, and V.A.Welsh, J.Chem.Soc., 1963, 3273.
45. P.W.Kent and J.E.G.Barnett, J.Chem.Soc., 1964, 6196.
46. K.B.Wood, P.W.Kent, and D.Fisher, J.Chem.Soc., 1966, 912.
47. P.W.Kent and M.R.Freeman, J.Chem.Soc., 1966, 910.
48. L.D.Hall, D.L.Jones, and J.F.Manville, Chem.Ind. (London), 1967, 1787.
49. F.H.Dean, D.R.Marshall, E.W.Warnhoff, and F.L.M.Pattison, Canad.J.Chem., 1967, **45**, 2279.
50. A.Gregorovic and M.Zupan, Coll.Czech.Chem.Comm., 1977, **42**, 3192.
51. T.I.Limasova, A.G.Rumyantseva, M.I.Kollegova, S.G.Chernyakhovskaya, E.I.Berus, and V.A.Barkhash, Zhur.Org.Khim., 1971, **7**, 750.
52. B.E.A.Dear, J.Org.Chem., 1970, **35**, 1703.
53. M.Zupan, Synthesis, 1976, 473.
54. R.D.Chambers, W.R.Musgrave, and J.Savari, Proc.Chem.Soc., 1961, 113.
55. R.D.Chambers, W.R.Musgrave, and J.Savari, J.Chem.Soc., 1961, 3779.
56. E.S.Lo and J.D.Readio, J.Org.Chem., 1970, **35**, 2051.
57. V.S.Yuminov, L.N.Pushkina, and S.V.Sokolov, Zhur. Obshch.Khim., 1967, **37**, 375.
58. R.Pews and D.Garth, US P.3 651 155, 1972.
59. L.A.Quarterman, H.H.Hyman, and J.J.Katz, J.Phys. Chem., 1957, **61**, 912.
60. R.A.Devis and E.R.Larsen, J.Org.Chem., 1967, **32**, 3478
61. S.Rozen and M.A.Brand, Tetrahedron Letters, 1980, 27, 4543.
62. C.J.Schack and K.O.Christe, Israel J.Chem., 1978, 17, 20.
63. I.L.Knunyants and L.S.German, Izv.Akad.Nauk SSSR, Ser.Khim., 1966, 1065.
64. J.W.Hamersma and F.F.Caserio, US P.3 712 913, 1973.
65. V.Heasley, D.F.Shellhamer, R.K.Gipe, H.C.Wiese, M.L.Oakes, and G.E.Heasley, Tetrahedron Letters, 1980, 21, 4133.
66. L.S.Boguslavskaya et al., Zhur.Org.Khim., 1969, **5**, 11.
67. L.S.Boguslavskaya et al., Zhur.Org.Khim., 1972, **8**, 1147.
68. L.S.Boguslavskaya and A.B.Bulovyataova, Zhur.Org. Khim., 1971, **7**, 443.
69. L.S.Boguslavskaya et al., Zhur.Org.Khim., 1971, **7**, 1338.
70. L.S.Boguslavskaya and V.S.Etlis, Zhur.Org.Khim., 1971, **7**, 1811.
71. L.S.Boguslavskaya, N.B.Melnikova, A.P.Voronin, and V.R.Kartashov, J.Fluor.Chem., 1978, **12**, 257.
72. D.A.Aronovich, L.S.Boguslavskaya, N.N.Trofimov, and A.P.Voronin, Zhur.Org.Khim., 1975, **11**, 695.
73. L.S.Boguslavskaya et al., Zhur.Org.Khim., 1974, **10**, 2067.
74. L.S.Boguslavskaya et al., Zhur.Org.Khim., 1972, **8**, 1139.
75. L.S.Boguslavskaya, K.V.Yarovykh, and A.P.Sineokov, Zhur.Org.Khim., 1973, **9**, 231.
76. N.N.Chuvatkin, T.V.Morozova, and L.S.Boguslavskaya, Zhur.Org.Khim., 1983, **19**, 1107.
77. K.O.Christe, Inorg.Chem., 1972, **11**, 1220.
78. C.J.Schack, Inorg.Chem., 1967, **6**, 1938.
79. C.J.Schack and W.Maya, J.Amer.Chem.Soc., 1969, **91**, 2902.
80. D.E.Young, J.R.Anderson, D.E.Gould, and W.B.Fox, J.Amer.Chem.Soc., 1970, **92**, 2313.
81. A.Majid and J.M.Shreeve, Inorg.Chem., 1974, **13**, 2710.
82. C.T.Ratchlife et al., J.Amer.Chem.Soc., 1971, **93**, 3886.
83. N.Walker and D.D.Des Marteau, J.Amer.Chem.Soc., 1975, **97**, 13.
84. C.J.Schack and K.O.Christe, J.Fluor.Chem., 1978, **12**, 325.
85. E.N.Krom, N.N.Chuvatkin, L.S.Boguslavskaya, and V.R.Kartashov, USSR P.789 503, 1980; Ref.Zhur. Khim., 1981, 14N20.
86. J.Katsuhara and D.D.Des Marteau, J.Amer.Chem.Soc., 1979, **101**, 1035.
87. M.Bougon, M.Carles, and J.Aubert, Compt.rend., 1967, **265C**, 179.
88. G.P.Gambaretto and M.Napoli, J.Fluor.Chem., 1976, **7**, 569.
89. K.E.Peterman and J.M.Shreeve, Inorg.Chem., 1975, **14**, 1223.
90. A.F.Clifford and G.R.Zailenga, Inorg.Chem., 1969, **8**, 979.
91. C.J.Schack and R.D.Wilson, Inorg.Chem., 1970, **9**, 311.
92. C.J.Schack et al., J.Amer.Chem.Soc., 1969, **91**, 2907.
93. S.I.Yu and J.M.Shreeve, Inorg.Chem., 1976, **15**, 14.
94. D.D.Moldavskii and V.G.Temchenko, Zhur.Obshch. Khim., 1969, **39**, 1393.
95. G.U.Sprenger, K.J.Wright, and J.M.Shreeve, Inorg. Chem., 1973, **12**, 2800.
96. R.F.Swindell, R.M.Laborowski, and J.M.Shreeve, Inorg.Chem., 1971, **10**, 1635.
97. R.J.Kirchmeier, U.L.Lasouris, and J.M.Shreeve, Inorg.Chem., 1975, **14**, 592.
98. D.E.Gould, L.R.Anderson, D.E.Young, and W.B.Fox, J.Amer.Chem.Soc., 1969, **91**, 1310.
99. R.Veyre, M.Quenault, and C.Eyraud, Compt.rend., 1969, **268C**, 1480.
100. F.M.Makhametshin, Uspekhi Khim., 1980, **49**, 1261 [Russ.Chem.Rev., 1980(7)].
101. R.I.Kirchmeier, G.N.Sprenger, and J.M.Shreeve, Inorg.Nuclear Chem.Letters, 1975, **11**, 699.
102. J.B.Hynes and T.E.Austin, Inorg.Chem., 1966, **5**, 488.
103. D.E.Joung, I.R.Anderson, and W.B.Fox, Chem. Comm., 1970, 395.
104. K.E.Peterman and J.M.Shreeve, Inorg.Chem., 1974, **13**, 2705.
105. G.P.Gambaretto, Chimica e Industria, 1973, **55**, 18.
106. G.P.Gambaretto and M.Napoli, Gazzetta, 1974, **104**, 1291.

107. L.S.Boguslavskaya, N.N.Chuvatkin, I.Yu.Panteleeva, L.A.Ternovskoi, and E.N.Krom, Zhur.Org.Khim., 1980, **16**, 2525.
108. L.S.Boguslavskaya, N.N.Chuvatkin, and I.Yu.Panteleeva, Zhur.Org.Khim., 1982, **18**, 2082.
109. D.D.Moldavskii and V.G.Temchenko, Zhur.Org.Khim., 1973, **9**, 673.
110. E.M.Rokhlin, E.G.Abduganiev, and U.Utebaev, Uspekhi Khim., 1976, **45**, 1177 [Russ.Chem.Rev., 1976(7)].
111. L.S.Boguslavskaya, N.N.Chuvatkin, I.Yu.Panteleeva, and L.A.Ternovskoi, Zhur.Org.Khim., 1982, **18**, 938.
112. T.V.Morozova, N.N.Chuvatkin, I.Yu.Panteleeva, and L.S.Boguslavskaya, Zhur.Org.Khim., 1984, **20**, 1379.
113. N.N.Chuvatkin, I.Yu.Panteleeva, and L.S.Boguslavskaya, Zhur.Org.Khim., 1982, **18**, 946.
114. R.I.Gillespie, IUPAC XXIV Int.Congr.Pure Appl. Chem., 1974(4), 143.
115. R A. De Marco, T.A.Kovacina, and W.B.Fox, J.Fluor. Chem., 1975, **6**, 93.
116. G.C.Show, D.L.Seaton, and E.R.Bissel, J.Org.Chem., 1961, **26**, 4765.
117. J.Muray, J.Chem.Soc., 1959, 1884.
118. L.S.Boguslavskaya, Zhur.Org.Khim., 1982, **18**, 222.
119. R.Filler, "Fluorine-Containing Drugs", London–Chichester, 1979, p.123.
120. J.M.Shreeve, Acc.Chem.Res., 1973, **6**, 387.
121. A.V.Fokin, A.D.Nikolaeva, Yu.N.Studnev, A.I.Rapkin, N.A.Proshin, and L.D.Kuznetsova, Izv.Akad. Nauk SSSR, Ser.Khim., 1975, 1000.
122. A.V.Fokin, Yu.N.Studnev, A.I.Rapkin, K.I.Posevina, T.M.Potarina, and O.V.Verenikin, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2369.
123. A.V.Fokin, Yu.N.Studnev, L.D.Kuznetsova, and I.N.Krotovich, Uspekhi Khim., 1982, **51**, 1258 [Russ. Chem.Rev., 1982(8)].
124. A.V.Fokin Yu.N.Studnev, and A.I.Rapkin, J.Fluor. Chem., 1981, **18**, 553.
125. C.J.Schack and K.O.Christe, J.Fluor.Chem., 1980, **16**, 63.
126. C.J.Schack and K.O.Christe, J.Fluor.Chem., 1979, **14**, 519.
127. J.Katsuhara and D.D.Des Marteau, J.Amer.Chem.Soc., 1979, **101**, 1039.
128. J.Katsuhara and D.D.Des Marteau, J.Org.Chem., 1980, **45**, 2441.
129. J.Katsuhara and D.D.Des Marteau, J.Amer.Chem. Soc., 1980, **102**, 2681.
130. N.Walker and D.D.Des Marteau, J.Amer.Chem.Soc., 1975, **97**, 13.
131. C.J.Schack, D.Pilipovich, and J.F.Hon, Inorg. Chem., 1973, **12**, 897.
132. C.J.Schack, D.Pilipovich, and K.O.Christe, Inorg. Chem., 1975, **14**, 145.
133. L.R.Anderson, D.E.Young, D.E.Gould, R.Juurik-Hogen, D.Nuechterlein, and W.B.Fox, J.Org.Chem., 1970, **35**, 3730.
134. O.Lerman and S.Rozen, J.Org.Chem., 1980, **45**, 4122.
135. S.Rozen and J.Menahem, Tetrahedron Letters, 1979, 725.
136. D.H.R.Barton, R.H.Hesse, G.P.Jackman, L.Ogunkoya, and M.M.Pechet, J.Chem.Soc., 1974, 739.
137. S.Rozen and O.Lerman, J.Org.Chem., 1980, **45**, 672.
138. S.Rozen, O.Lerman, and M.Kol, Chem.Comm., 1981, 443.
139. R.F.Merritt, J.Amer.Chem.Soc., 1967, **89**, 609.
140. A.V.Fokin, Yu.N.Studnev, I.N.Krotovich, L.D.Kuznetsova, and O.V.Verenikin, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 806.
141. M.Hudlicky, J.Fluor.Chem., 1979, **14**, 189.
142. L.S.Boguslavskaya and L.A.Ternovskoi, Zhur.Org. Khim., 1983, **19**, 1881.
143. F.M.Beringer and H.S.Schultz, J.Amer.Chem.Soc., 1965, **77**, 5533.
144. R.M.Keefer and L.J.Andrews, J.Amer.Chem.Soc., 1953, **75**, 543.
145. R.M.Keefer and L.J.Andrews, J.Amer.Chem.Soc., 1954, **76**, 253.
146. C.S.Rondestvedt, J.Amer.Chem.Soc., 1969, **91**, 3054.
147. A.K.Barber, L.I.Belph, and M.V.Baxton, in "Advances in Fluorine Chemistry" (Translated into Russian), Izd.Khimiya, Leningrad, 1970, Vols.III and IV, p.134.
148. S.A.Mazalov and S.V.Sokolov, USSR P.172 816, 1965; Ref.Zhur.Khim., 1966, 23N280.
149. R.G.Pews and P.A.Davis US P.3 651 155, 1972).
150. T.E.Stevens, J.Org.Chem., 1961, **26**, 1627.
151. A.N.Nesmeyanov, A.N.Vanchikov, I.N.Lisichkina, N.S.Khrushcheva, and T.P.Tolstaya, Dokl.Akad. Nauk SSSR, 1980, **254**, 652.
152. A.N.Nesmeyanov, A.N.Vanchikov, I.N.Lisichkina, V.V.Lazarev, and T.P.Tolstaya, Dokl.Akad.Nauk SSSR, 1980, **255**, 1136.
153. A.N.Nesmeyanov, A.N.Vanchikov, I.N.Lisichkina, V.V.Grushin, and T.P.Tolstaya, Dokl.Akad.Nauk SSSR, 1980, **255**, 1386.
154. V.V.Bardin, G.G.Furin, and G.G.Yakobson, Zhur. Org.Khim., 1980, **16**, 1256.
155. V.V.Bardin, G.G.Furin, and G.G.Yakobson, Zhur. Org.Khim., 1981, **17**, 999.
156. T.Bastock, M.Hartley, A.Pedler, and J.Tatlow, J.Fluor.Chem., 1975, **6**, 331.
157. T.Bastock, A.Pedler, and J.Tatlow, J.Fluor.Chem., 1976, **8**, 11.
158. V.V.Bardin, G.G.Furin, and G.G.Yakobson, Zhur. Org.Khim., 1982, **18**, 604.
159. N.S.Zefirov, N.K.Sadovaja, A.M.Maggeramov, I.V.Bodrikov, and V.R.Kartashov, Tetrahedron 1975, **31**, 2948.
160. I.A.Ioffe et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 1126.