Chem. Rev. **1996,** *96,* 3269−3301 **3269**

The Chemistry of Highly Fluorinated Carbocations[†]

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Received July 5, 1996 (Revised Manuscript Received October 2, 1996)

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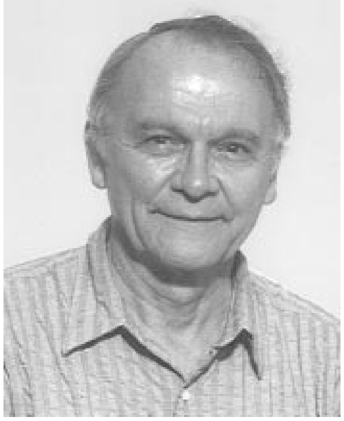

Carl G. Krespan (born 1926) received his B.S. from the University of Rochester, 1948, and his Ph.D. from the University of Minnesota, 1952. He has spent his entire professional carrier conducting research for the DuPont Company as research chemist, supervisor, or division head, and recently received DuPont's Pederson Award for technical excellence. Earlier he received the ACS award for Creative Work in Fluorine Chemistry. He has published some 160 papers, patents, reviews and chapters, largely in the field of organofluorine chemistry. His research has encompassed new synthetic methods and novel structures in both the fluorinated small molecules and fluoropolymer areas. His involvement with the ACS Division of Fluorine Chemistry includes two terms as chairman and the organization (with Professor Alan Clifford) of the First Winter Fluorine Conference.

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I. Introduction

The advent in recent decades of a new catalysts and improved systems for the generation of fluorocarbocations has been coupled with a better understanding of their reaction patterns. Little wonder,

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[†] Publication no. 7460.

S0009-2665(94)01144-1 CCC: $25.00 © 1996 American Chemical Society

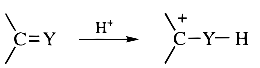
then, that these intermediates have become increasingly important in organofluorine chemistry. The following pages testify that the cation chemistry of the original Swarts reaction for replacement of chlorine with fluorine has proliferated to the point where fluorinated carbocations are useful intermediates in nearly all branches of synthetic organofluorine chemistry.

The present account seeks to cover the more recent developments in polyfluorinated carbocation chemistry, commencing from the status as reported in the many reviews that are cited. Emphasis is placed on the synthetic aspects of the newer work, and coverage through 1995 is attempted. The field is broad, so we offer our regrets in advance to any whose work has been omitted inadvertently.

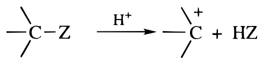
II. Methods for Generation of Polyfluorinated Carbocations

There are three general methods employed in fluoroorganic synthesis for generation of carbocations and cationic species.

(A) Formation of positively charged species can occur in highly acidic media by protonation of multiple bonds (C=C, C=O, C=N, etc.) (eq 1) or of heteroatoms with unshared electron pairs (—F, —Cl, —Br, —O—, —S—, —Se—, etc.) (eq 2).



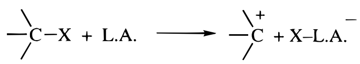
(1)



(2)

Strong protic acids having acidities $-H_0$ in the range 12−15 are often referred to as “superacids”[1] and include compounds such as anhydrous HF, $HOSO_2F$, and $HOSO_2CF_3$. The acidity of such protic acids, which correlates with electrophilicity of H^+ in this system, can be significantly increased (up to a value of $-H_0 = 22$) by addition of selected Lewis acids, including SbF_5, AsF_5, TaF_5, NbF_5, and BF_3. However, the low basicity of polyfluorinated materials usually limits this method to carbocation formation from nonfluorinated compounds (some alcohols, aromatics), relatively “basic” fluorinated substrates such as mono- and dihaloalkanes, and fluoroethylenes such as $CH_2{=}CF_2$.[2] More information on this subject can be found in two reviews,[3,4] and data on the preparation, handling, and use of superacids for generation of carbocations are summarized in a book[1] describing the ground-breaking work of Olah and coworkers.

(B) Direct interaction of a strong Lewis acid with a fluorinated substrate can result in formation of a cation or cationic species either by abstraction of halogen anion (usually F^-) from a substrate (eq 3) or by formation of a zwitterionic intermediate as a result of coordination of the Lewis acid with an unshared electron pair on a multiply bonded heteroatom (eq 4).



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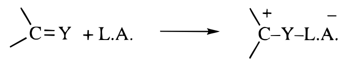
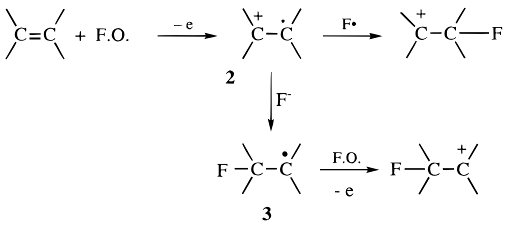


(4)

The difference between these two mechanisms may seem marginal, since the first stage of process 3 also involves interaction between an unshared electron pair on halogen and a vacant orbital of the Lewis acid. However, in the first case the carbocation and counter anion can exist under appropriate conditions as a separated pair, while in process 4 the whole zwitterionic complex is necessarily involved in the reaction with organic substrate. The ratio of substrate to Lewis acid is important, especially for the generation of long-lived poly- and perfluorinated carbocations,[5] since Lewis acids such as SbF_5 have a tendency to form polynuclear anions $Sb_nF_{5n+1}^-$ (**1**), where *n* depends significantly on the polarity of the medium. $Sb_2F_{11}^-$, for example, is the predominant anionic species for 20−40 mol % SbF_5 in HF.[6] As a result of delocalization of negative charge, anions **1** have reduced nucleophilicity, which may be defined as the ability to donate F^- to positively charged species such as carbocation or H^+. As a result ions **1** have a much greater ability, relative to SbF_6^-, to stabilize carbocations. The presence of ions **1** in solutions of SbF_5 in HF is responsible for the dramatic increase of HF acidity from $-H_0$ 11 (14.5 for extremely dry HF[7]) to 20.5 for a 1 M solution of SbF_5 in HF.[1]

(C) Indirect generation of carbocations can result from reaction between strong fluorooxidizers and unsaturated substrates. In this process carbocations can be generated either by addition of a fluorine atom to radical−cation **2** formed in the first stage of the reaction or by oxidation of the radical **3** derived from the interaction of the radical−cation **2** with fluoride anion. Depending on the reactivity of the substrate, the balance between carbocationic and radical branches in this mechanism can be shifted to one or the other side. The carbocationic mechanism is more likely to predominate in the reactions of hydrocarbons, for example fluorination of alkanes and aromatics over CoF_3, MnF_3, or CeF_4.[8] However, there are indications[9] that fluorination of poly- and perfluorocompounds such as hexafluorobenzene and pentafluoropyridine by CoF_3 proceeds as a radical process. This mechanism was proposed or may be applied to many reactions of hydrocarbons and polyfluorinated unsaturated compounds with: elemental fluorine[10,11] and halogen fluorides and their salts with Lewis acids $XF_n^+MF_m^-$ (where X = Cl, Br, or I and M = Sb, B, As, etc.);[12] metal fluorides in a high valence state (CoF_3, $NaCoF_4$, $KCoF_4$, MnF_3, CeF_4, PbF_4, etc.);[8,13] XeF_2 and other fluorides of noble gases and their salts with Lewis acids;[12,14] antimony,[15] vanadium,[15,16] and bismuth pentafluorides;[15] and



(5)

some transition metal hexafluorides, such as PtF_6, IrF_6, etc. It should be mentioned that although the oxidative process is the least studied mechanistically of the three, it is important, since there are a number of commercial processes for the manufacture of fluorocarbons based on the use of such reagents, particularly CoF_3.[17]

All these data indicate the importance of making the right choice of Lewis acid, either for the generation of stable, long-lived fluorinated carbocations or for use as a catalyst in the synthesis of fluorinated materials. The Lewis acid may be used to solve problems in several different ways.

A Lewis acid catalyst may be added to a strong protic acid (HF, $HOSO_2F$, sometimes CF_3SO_2OH) to generate a super acid, an efficient medium for electrophilic reactions involving the moderate electrophile H^+. This approach allows formation of positively charged species under mild conditions, and the counter anion of the medium (F^-, FSO_2O^-, $CF_3SO_2O^-$) is usually also involved in the reaction. The method was shown to be an extremely efficient way to generate a variety of hydrocarbon cations[18] and was also used for conjugate additions across the C=C bond. Antimony, tantalum, niobium, and arsenic pentafluorides (sometimes BF_3) are catalysts of choice.

Synthesis of highly reactive carbocationic species from poly- and perfluorinated materials or running electrophilic reactions involving such species as intermediates usually requires strong Lewis acids as neat reagents. In many cases an excess of one of the starting materials can be used as a reaction medium, and sometimes solvents such as SO_2 or SO_2ClF may also be used, although interaction between the solvent and Lewis acid can reduce the activity of the latter. Antimony pentafluoride, aluminum chlorofluoride, and sometimes $AlCl_3$ or $AlBr_3$ are the catalysts most used in these reactions.

Although some Lewis acids are used in fluorinations such as the Swarts reaction for replacement with fluorine of other halogen atoms, it should be noted that the term "fluorination" is broad enough to encompass oxidative fluorination. Such fluorinations include addition of elemental fluorine across a C=C bond and fluorination of C−H bonds by the action of fluorooxidizers such as halogen fluorides, fluorides of noble gases, and fluorides of metals in their higher valance states. The relationship between Lewis acidity and fluorooxidative properties of different fluorides are neither straightforward nor well-defined, but many fluorides do possess both properties. For example, SbF_5, one of the strongest Lewis acids, is also a quite strong fluorooxidizer.[15]

III. Characteristics of Some Strong Lewis Acids

The best choice of Lewis acid is often crucial to the successful solution of a synthetic problem. In order to make this choice easier, some characteristics of the most commonly used, commercially available Lewis acids are given below. Much of the physical data was taken from the Merck Index, Eleventh Edition.

Aluminum Chloride. A white solid when pure, commercial materials are very often colored (yellow to greenish), but can be purified by sublimation. It fumes in air and is very moisture-sensitive (*keep protected from moisture*), forms hydrates which are far less active as a Lewis acid, combines with water with *explosive violence* and liberation of much heat, and is soluble in solvents such as benzene, nitromethane, CCl_4, $CHCl_3$, 1,2-dichloroethane, and benzophenone. The activity of $AlCl_3$ as a catalyst in many reactions *strongly* depends on the purity (presence of other metals) and degree of hydration. For use as a catalyst, material of high purity and high surface area or freshly sublimed $AlCl_3$ is recommended. It is the catalyst of choice for Friedel−Crafts-type reactions and is effective in the condensation of chloromethanes and some chloroolefins with chloroethylenes[19,20] (Prins reaction), of selected fluoromethanes with fluoroolefins (for scope and limitations of this reaction see ref 21), and for isomerization of chloro- and bromofluoroethanes (for references see ref 22). $AlCl_3$ is a very effective reagent for exhaustive exchange of fluorines in hexafluoropropene[23] and cyclic fluoroolefins (for references see ref 24). It is also the starting material for preparation of the extremely active catalyst, aluminum chlorofluoride[25,26] (see below).

Aluminum Bromide. White to yellowish-red with mp 97 °C, bp 250−270 °C, and $d^4{}_{18}$ 3.205, $AlBr_3$ is hygroscopic, so that handling and storage are the same as for $AlCl_3$. It is more soluble than $AlCl_3$ in organic solvents such as alkanes, benzene, toluene, etc. When used for the isomerization of chloro- and bromoethanes (see ref 22), it is a more effective catalyst than $AlCl_3$. The use of $AlBr_3$ in the isomerization of *F*-1,2-dibromopropane[27] and *F*-2,3-dibromobutane[28] to the corresponding *gem*-dibromides was reported recently. It is also a reagent for nonselective exhaustive exchange of fluorine atoms in cyclic fluoroolefins (see ref 24).

Aluminum Chlorofluoride $AlCl_xF_y$ *($x = 0.05-0.3$, $y = 2.7-2.95$) (ACF).* The preparation of amorphous, high surface area material was described recently in the patent literature by exchange reactions of high purity $AlCl_3$ with selected haloalkanes (CFC-11, -12, -22,[25,26] -113[29]) or with a fluoroolefin such as hexafluoropropene.[26] The exothermic reaction results after isolation in a cream colored, free-flowing, light powder,[26] which is extremely sensitive to moisture and should be handled in a dry box, since even short exposure of the catalyst to moist air destroys its activity. The ratio of chlorine to fluorine in ACF can vary significantly; properly prepared and stored, the catalyst is extremely active, in some reactions even more active than antimony pentafluoride. ACF has been used for condensation of various fluoromethanes[30,31] and fluoroolefins[26,32] with tetrafluoroethylene, preparation of fluorinated oxetanes by reaction of hexafluoroacetone with fluoroethylenes,[33] and isomerization of dichlorides of several fluoroolefins.[34] On the basis of literature data, ACF is not only as effective as one of the strongest Lewis acids, SbF_5, it also has other advantages. The absence of either the powerful oxidative properties typical of SbF_5 or the pronounced ability to cause replacement of halogen atoms by fluorine, in combination with availability and low toxicity make this catalyst superior to antimony pentafluoride in most applications.

Antimony Pentafluoride and Antimony(V) Chlorofluorides. SbF_5 is a viscous liquid, bp 141 °C, mp 8.3 °C, $d^{25.8}$ 3.097, that reacts violently with water, is slowly hydrolyzed in air (*keep protected from moisture*), but in the absence of moisture may be stored and handled in glass. As a strong oxidant and Lewis acid, SbF_5 is very reactive toward most organic compounds. It is soluble in anhydrous HF, SO_2, SO_2ClF, and unreactive organic materials such as perfluorinated alkanes, tertiary amines, and ethers. As one of the strongest and the most frequently used Lewis acids, it has been employed for a variety of the reactions.[4,15,35,36] However, it should be kept in mind that SbF_5 is able to cause formation of side products because of its ability to (a) fluorinate double bonds of olefins and fluoroaromatics and (b) act as a potent reagent for exchange of other halogens by fluorine. Depending on the problem to be solved, the reactivity of antimony chlorofluorides may be significantly modified by varying the valence of antimony (SbF_3 is a weak fluorinating agent relative to SbF_5) and the ratio of chlorine atoms to fluorine atoms.

The activity of antimony fluorides as fluorinating agent and as Lewis acid rank as follows:[37] $SbF_5 > SbF_3Cl_2 > SbCl_5 + SbF_3 > SbF_3$. Thus, SbF_3 is widely used for exchange of the reactive halogens attached to silicon or phosphorus,[38] but the fluorination of most carbon−chlorine bonds require the use of Sb^{5+} compounds. In practice, the pentavalent fluorinating agent is either generated *in situ* by reaction of SbF_3 with small amounts of Cl_2 or Br_2 or by the addition $SbCl_5$ to HF or SbF_3.[39] The individual antimony chloro fluorides, SbF_3Cl_2 and SbF_4Cl,[38] have also been isolated, characterized, and used in Swarts reactions.

Boron Trifluoride. A colorless gas, bp −100.4 °C, mp −127.1 °C, BF_3 fumes in moist air and is a relatively weak Lewis acid. BF_3 is therefore not frequently used in fluoorganic synthesis by itself, but its low cost and ability to significantly enhance the acidity of acids such as $HOSO_2F$, $HOSO_2CF_3$, and HF make it a valuable catalyst for use in superacid media.

Phosphorus and Arsenic Pentafluorides. PF_5 is a colorless gas, bp −84.6 °C, mp −93.8 °C, that hydrolyzes readily and gives complexes with amines, sulfoxides, and other organic bases. It is soluble in common organic solvents.

AsF_5 is also a colorless gas, bp −53.2 °C, mp −79.8 °C, instantly hydrolyzed by water, soluble in benzene and ether; it is *quite toxic*.

Both are fairly strong Lewis acids without appreciable oxidative power. They may be used in combination with HF or $HOSO_2F$, but their use as catalyst in fluoroorganic synthesis has been limited. However, both compounds are often used for the preparation of stable hexafluorophosphate and hexafluoroarsenate salts.

Tantalum and Niobium Pentafluorides.[15] TaF_5 is a white solid, mp 96 °C, bp 229.2 °C, d^{15} 4.98, and NbF_5 is a white solid, mp 79.5 °C, bp 234.5 °C, d^{25} 3.29. In contrast to SbF_5, VF_5, and BiF_5, neither compound possesses oxidative properties. Both are readily soluble in aromatic hydrocarbons, pyridine, and most common organic solvents, forming complexes with them. Both pentafluorides have limited solubility in HF (for TaF_5 it is 0.9% at 19 °C[40]), but both are able to increase dramatically the acidity of protic acids (reported $-H_0$ for 0.6 mol % of TaF_5 in HF is 18.85[41]). TaF_5 is a weaker Lewis acid than SbF_5; however, it is a stronger Lewis acid than NbF_5;[41] both are widely used in combination with HF, especially for fluorination of chlorocarbons.

Bismuth and Vanadium Pentafluorides.[15] VF_5 is a colorless, viscous liquid, when it is absolutely pure; the technical product is slightly yellow and quite similar in *physical* properties to SbF_5; mp 19.5 °C, bp 48 °C, d^{19} 2.18; quite soluble in HF, SO_2ClF, $CFCl_3$, ClF_3, BrF_3, and BrF_5, but poorly soluble in perfluorocarbons. VF_5, in contrast to SbF_5, is a very weak Lewis acid, but it is an extremely potent oxidizer which was employed for the oxidative fluorination of a variety of fluorinated materials under mild conditions.[15,16] *Caution! VF_5 reacts violently with most organic compounds; it should be handled carefully and by trained personnel only.*

BiF_5 is a white solid, mp 151.4 °C, bp 230 °C, d^{25} 5.52, with a low solubility in most organic and inorganic solvents, including HF.[15] It is a strong Lewis acid, but a much stronger oxidizer comparable with VF_5. Experimental data on its use in synthesis are limited. *Caution! BiF_5 may react violently with many organic compounds; it should be handled carefully and by trained personnel.*

IV. Reactions

A. Alkylation

1. Of Fluoroolefins

Early alkylations via halocarbocations were those in which carbon tetrachloride was added to simple fluoroolefins with aluminum chloride as catalyst, a straightforward example being with tetrafluoroethylene (TFE) as the olefin.[42]

$$\mathrm{CCl_4 + CF_2{=}CF_2 \xrightarrow[100^\circ C]{AlCl_3} CCl_3CF_2CF_2Cl} \tag{6}$$

Detailed studies of the scope of this reaction with $AlCl_3$ as catalyst have been reported, notably by Paleta,[43,44] and the subject has been reviewed.[21] More recent work on the use of halofluoroalkanes as alkylating agents has emphasized the advantages in activity and selectivity accruing from the use of ACF ($AlCl_xF_y$) as catalyst. The catalyst ACF can be prepared separately or, often, generated *in situ* by preliminary Cl/F exchange of $AlCl_3$ with halofluoroalkane.

The following moderate yield reactions are examples.[25,30,31]

$$\mathrm{CHFCl_2 + CF_2{=}CF_2 \xrightarrow[30^oC]{ACF} \underset{3}{CF_3CF_2CHCl_2} \; + \; \underset{2}{ClCF_2CF_2CHFCl}} \tag{7}$$

$$\mathrm{+\ CF_3CCl_2CHF_2}$$

$$\mathrm{CF_2Cl_2 + CF_2{=}CF_2 \xrightarrow[30\text{-}40^oC]{ACF} CF_3CF_2CFCl_2 \xrightarrow{C_2F_4} CF_3CF_2CCl_2CF_2CF_3} \tag{8}$$

$$\mathrm{ClCF_2CFCl_2 + CF_2{=}CF_2 \xrightarrow[40^oC]{ACF} ClCF_2CCl_2CF_2CF_3} \tag{9}$$

Equation 7 illustrates the lack of selectivity occasionally observed with ACF in activation of carbon−

halogen bonds. Although there is a preference evident for cleavage of the C−F bond over a C−Cl bond, the same as was observed previously with $AlCl_3$ catalyst and substrates such as $CFCl_3$, formation of carbocation $CHFCl^+$ competes well with formation of $CHCl_2^+$.

A byproduct, $CF_3CCl_2CHF_2$, is usually formed in this reaction (eq 7), and prolonged exposure of the product to ACF causes the amount of this isomerization product to increase with concomitant near disappearance of $ClCF_2CF_2CHFCl$.[25] Clearly, ACF is capable of causing deep-seated isomerizations of chlorofluoroalkanes, in the present case leading to an equilibrium mixture composed essentially of the two most stable isomers. Note that here, as with the alkenylation reaction, isolated hydrogen atoms are unaffected. See section IV.F.1 for other examples of halogen migration.

Equation 9 is particularly interesting in that $ClCF_2CFCl_2$ isomerizes readily in the absence of fluoroolefin acceptor (*vide infra*), indicating that the lifetime of complex **4** is sufficiently long for TFE to intercept it. The $ClCF_2CFCl_2$ adsorbed on the catalyst surface is portrayed for simplicity as forming fully ionized complex **4**, even though the adsorbed species may actually contain a highly polarized C−F bond.

$$ClCF_2CFCl_2 + ACF \longrightarrow \underset{\mathbf{4}}{ClCF_2CCl_2^+\,ACF_2^-} \xrightarrow{TFE}$$

$$ClCF_2CCl_2CF_2CF_2^+\,ACF_2^- \longrightarrow ClCF_2CCl_2CF_2CF_3 + ACF \qquad (10)$$

Although ACF is often superior to SbF_5 in Lewis acid-catalyzed reactions, condensations that form appreciable amounts of hydrogen halide as byproduct result in rapid deactivation of ACF. Thus, SbF_5 is the catalyst of choice in cases such as the following, taken from an excellent review[4] of Russian work, published in 1984.

$$CH_3CF_3 + CF_2{=}CF_2 \xrightarrow{SbF_5} \underset{(90\%)}{CF_3CF_2CF_2CH_3} \qquad (11)$$

$$(CH_3)_3CCl + CF_2{=}CFCl \xrightarrow{HF,\ SbF_5} \underset{1}{(CH_3)_3CCFClCF_3} + \underset{:\ \ 1}{(CH_3)_3CCF_2CF_2Cl} \qquad (12)$$

2. Of Other π Systems

A mixture of CCl_4/HF has been used for trifluoromethylation of aromatic hydrocarbons. The reaction originaly discovered in DuPont for naphthalene was latter extended by Marhold and Klauke to benzene, alkylbenzenes, and monhalobenzenes providing a valuable route to corresponding benzotrifluorides. This reaction was reviewed.[17b]

Some activated carbonyl compounds can be used as alkylating agents. Chloral, for example, has been added to certain hydrocarbon olefins in the presence of $SnCl_4$, $AlCl_3$, or $FeCl_3$[45−47] to enhance its electrophilicity. Fluorinated carbonyl compounds are even more active toward hydrocarbon olefins. Hexafluoroacetone (HFA) and nitropentafluoroacetone give an ene reaction with isobutene at room temperature,[48] and the reaction of HFA with less reactive ethylene, propene, or cyclohexene proceeds in the presence of the catalyst $AlCl_3$.[49]

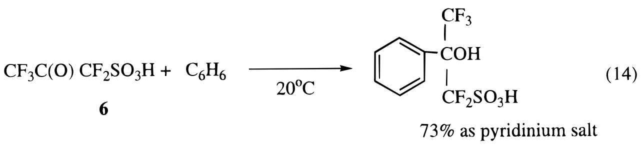
The reaction of HFA with aromatic compounds is referred to as the Knunyants reaction.[50] Activated compounds such as aniline can be alkylated thermally,[51] but this reaction is usually carried out under Friedel−Crafts conditions with $AlCl_3$ or BF_3 as catalyst.[52] In the presence of $AlCl_3$, reaction of HFA with benzene proceeds rapidly at room temperature and results in the formation of carbinol **5** in 94% yield;[53] *m*-bis(hexafluoroisopropyl)benzene is prepared at the higher temperatures.

More details can be found in two reviews on of the chemistry of HFA.[52,54]

$$C_6H_6 + (CF_3)_2C{=}O \xrightarrow[20\ ^\circ C]{AlCl_3} \underset{\mathbf{5}\qquad 94\%}{C_6H_5C(CF_3)_2OH} \qquad (13)$$

Friedel−Crafts types of condensations with aromatics are also efficiently catalyzed by perfluoroalkylsulfonic acids.[55,56] The use of Nafion sulfonated fluoropolymer as catalyst is particularly convenient, since the insoluble catalyst can be removed after reaction by simple decantation.[55]

Even examples of self-catalyzed additions of a fluoro ketone to aromatics under mild conditions are provided by the use of *F*-2-ketopropanesulfonic acid (**6**), for example with benzene.[56]

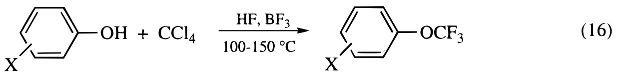


The imine of hexafluoroacetone (**7**) is much less reactive toward unsaturated compounds. Compound **7** reacts with isobutene only at elevated temperature and in the presence of Lewis acid.[48] Reaction of **7** and benzene catalyzed by $AlCl_3$ is slow even at 200 °C.[57]

$$C_6H_6 + \underset{\mathbf{7}}{(CF_3)_2C{=}NH} \xrightarrow[200\ ^\circ C,\ 12\ h]{AlCl_3} \underset{12\%}{C_6H_5C(CF_3)_2NH_2} \qquad (15)$$

3. At Heteroatoms

Carbon tetrachloride has been employed as alkylating agent in a number of other reactions. The interaction between CCl_4 and various phenols in anhydrous hydrogen fluoride was developed as a general method of preparation of CF_3O-substituted aromatic compounds bearing at least one electron-withdrawing substituent X.[58]



Recently it was found that this reaction can be used for the trifluoromethylation of β-fluorinated alcohols.[59]

$$R_fCHXOH + CCl_4 \xrightarrow[100\text{-}150\ ^\circ C]{HF\ cat.} R_fCHXOCF_3 \qquad (17)$$

$$(X = H, R_f)$$

Both reactions proceed rapidly and in good yield only at elevated temperatures and are catalyzed efficiently by BF_3. A simplified reaction mechanism would involve formation of CCl_3^+ carbocation as an intermediate, alkylation of phenol or alcohol at oxygen, and conversion of the resulting $-OCCl_3$ group into $-OCF_3$ by exchange with HF.

$$CCl_4 + HF \xrightarrow{-HCl} [CCl_3^+] \xrightarrow{ROH} ROCCl_3 \xrightarrow{3\,HF} ROCF_3 + 3\,HCl \qquad (18)$$

Carbocation $CFCl_2^+$ may also be an intermediate, since both trifluoromethylation reactions also proceed with $CFCl_3/HF/BF_3$ as reagent. In this connection the formation of trihalomethyl carbocations CX_3^+ (X = Cl, Br, I) by reaction of the corresponding halomethanes with SbF_5 in SO_2ClF as a solvent was recently reported.[60]

$$CX_4 + SbF_5 \xrightarrow[-78\ ^\circ C]{SO_2ClF} \overset{+}{C}X_3\ \overset{-}{Sb_nF_{5n+1}} \qquad (19)$$

On the other hand, Cl/F exchange on CCl_4 with HF/BF_3 was found not to proceed under reaction conditions, mitigating against straightforward formation of CCl_3^+ as intermediate. So instead, a transition state involving the hydroxylated substrate in a push–pull type of mechanism has been proposed.[58]

Reaction of carbon tetrachloride in the presence of $AlCl_3$ with polyfluoroanilines[61,62] or *N*-pentafluorophenylhydrazine (**63**) was used for the preparation a large number of the corresponding imidoyl chlorides **8** and **9**.

$$p\text{-}XC_6F_5NH_2 + CCl_4 \xrightarrow[80\ ^\circ C]{AlCl_3} \underset{\mathbf{8}\quad 50\text{-}80\%}{p\text{-}XC_6F_5N{=}CCl_2} \qquad (20)$$

(X = F, Br, Cl, NO_2, CN, CH_3)

$$C_6F_5NHNH_2 + CCl_4 \xrightarrow[80\ ^\circ C]{AlCl_3} \underset{\mathbf{9}}{C_6F_5NHN{=}CCl_2} \qquad (21)$$

More details on these reactions can be found in a review on the methods of synthesis of compounds containing the halogenoimidoyl group.[64] The same authors reported that the $CCl_4/AlCl_3$ system can also be used for the alkylation of pentafluorophenol (**10**), some fluoro alcohols,[65] and pentafluorothiophenol (**11**).[66] In sharp contrast to the reaction of CCl_4 in HF, the above-mentioned process does not stop at the stage of monoalkylation. Reaction of **10** with CCl_4 results in the formation of a mixture of **12**, **13**, and **14**.

$$\underset{\mathbf{10}}{C_6F_5OH} + CCl_4 \xrightarrow[80\ ^\circ C,\ 4\ h]{AlCl_3} \underset{\mathbf{12}}{C_6F_5OCCl_3} + \underset{\mathbf{13}}{(C_6F_5O)_2C{=}O} + \underset{\mathbf{14}}{(C_6F_5O)_3CCl} \qquad (22)$$

Reaction of **11** with CCl_4 is more selective and bis[(perfluorophenyl)thio]methane **15** was isolated in 60% yield.

$$\underset{\mathbf{11}}{C_6F_5SH} + CCl_4 \xrightarrow[60\text{-}70\ ^\circ C,\ 6\ h]{AlCl_3} \underset{\mathbf{15},\ 60\%}{(C_6F_5S)_2CCl_2} \qquad (23)$$

B. Alkenylation of Fluoroolefins

Condensation of polychlorinated compounds with chloroethylenes in the presence of aluminum chloride, known as the Prins reaction, was discovered in the beginning of this century.[67] Interaction between polychloropropenes and chloroethylenes results in the formation of polychloropentenes-1,[68] an example of alkenylation of a chloroolefin.

$$CCl_2{=}CXCCl_3 + CYCl{=}CCl_2 \xrightarrow{AlCl_3} CCl_2{=}CXCCl_2CClYCCl_3 \qquad (24)$$

X,Y=H,Cl

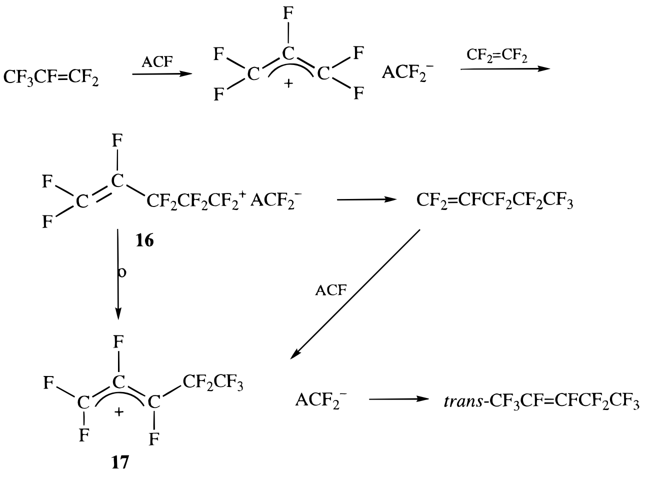
The condensations of CCl_4 and other polyhaloalkanes with fluoroolefins that were cited in section IV.A.1 are mediated by halocarbocations formed by interaction of the polyhaloalkanes with strong Lewis acids. In similar fashion, fluoroalkenes having allylic fluorine atoms can give fluoroallyl cations with strong Lewis acids,[5] and these cations condense readily with fluoroolefins. Such reactions were first observed in 1971 with SbF_5 as catalyst,[69] and a review[4] summarizing SbF_5-catalyzed electrophilic additions to fluoroolefins was published in 1984. More recently, work with ACF as catalyst has appeared,[26,32] affording ready access to a variety of higher molecular weight fluoroolefins. The presence of vinylic hydrogen and chlorine is tolerated well in these reactions, so that a large number of per- and polyfluoroolefins of varied structures can be synthesized.

The simplest form of the method is the highly selective condensation of hexafluoropropene (HFP) with tetrafluoroethylene (TFE) to give *F*-pentene-2 in high yield. Reactions catalyzed by ACF (amorphous aluminum chlorofluoride), either performed or generated *in situ*, give an 89% *trans*/11% *cis* mixture of *F*-pentene-2 isomers, whereas those catalyzed by SbF_5 are reported to be surprisingly stereospecific with almost exclusive formation of *trans* isomer.[69]

$$CF_3CF{=}CF_2 + CF_2{=}CF_2 \xrightarrow{cat.} \underset{90\text{-}95\%}{CF_3CF{=}CFCF_2CF_3} \qquad (25)$$

The mechanism proposed for this reaction using SbF_5[69] has been extended in the studies with ACF[32] to accommodate the possibility of a 1,3-fluoride shift occurring on the catalyst surface without necessarily forming *F*-pentene-1 as an intermediate. Scheme 1

Scheme 1



illustrates the one-step and two-step routes proposed for formation of *trans* product; *cis* product arises fromthe cation isomeric with **17** as intermediate. Evidence for the occurrence of cation **16** as a discrete intermediate at least in part is the formation of *F*-methylcyclobutane in low yield via cyclization of (**16**) (*vide infra*).

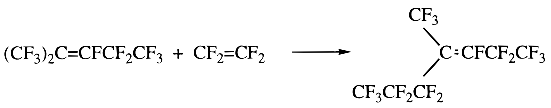
Many of the fluoroallylcarbocationic condensations reported are common to both SbF_5 and ACF. With ACF, however, reactions can proceed at somewhat lower temperatures, and some substrates of low reactivity respond to ACF catalysis, but not to SbF_5. For example, *F*-pentene-2 is of much lower reactivity toward ACF than is HFP, so that selective condensation of HFP with TFE is observed. In the absence of HFP, however, ACF (but not SbF_5) will catalyze the addition of *F*-pentene-2 to TFE, proceeding selectively to form linear *F*-heptene isomers in 80% yield (eq 26).[26] The heptene product mixture is essentially that obtained by isomerization of *F*-heptene-1 over ACF at 25 °C, indicating this composition is the equilibrium mixture derived from ACF at low temperature.[70] Both ACF and SbF_5 are effective isomerization catalysts for fluoroolefins, generally moving double bonds by a series of 1,3-fluoride shifts (see section IV.F.3). The following selection indicates the range of products available using ACF as catalyst.

$$CF_3CF{=}CF_2 + 2\,CF_2{=}CF_2 \longrightarrow CF_3CF{=}CF(CF_2)_3CF_3 + CF_3CF_2CF{=}CF(CF_2)_2CF_3 \qquad (26)$$

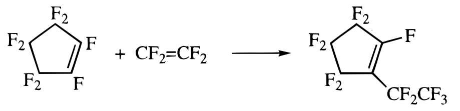
$$CF_3CH{=}CF_2 + CF_2{=}CF_2 \longrightarrow trans\text{-}CF_2CH{=}CFCF_2CF_3 \qquad (27)$$

$$CF_3CCl{=}CClCF_3 + CF_2{=}CF_2 \longrightarrow CF_3CF_2CF_2CCl{=}CClCF_3 \xrightarrow{TFE} CF_3CF_2CF_2CCl{=}CClCF_2CF_2CF_3 \qquad (28)$$

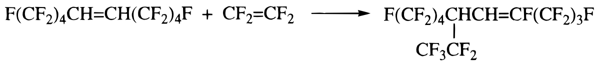
$$CF_3CCl{=}CCl_2 + CF_2{=}CF_2 \longrightarrow CF_3CF_2CF_2CCl{=}CCl_2 + CF_3CF_2CFClCCl{=}CCl_2 + CF_3CF_2CF{=}CClCCl_3 \qquad (29)$$



(30)



(31)



$$F(CF_2)_4CH{=}CH(CF_2)_4F + CF_2{=}CF_2 \longrightarrow F(CF_2)_4CH(CF_2CF_3)CH{=}CF(CF_2)_3F \qquad (32)$$

More recent work with SbF_5 as catalyst has shown that activated olefins such as *F*-2-alkoxypropenes react readily with TFE, forming *F*-2-alkoxy-2-pentenes **18** and **19**.[71]

$$CF_2{=}C(OR_f)CF_3 + CF_2{=}CF_2 \xrightarrow[SbF_5]{30°C} CF_3C(OR_f){=}CFC_2F_5 \qquad (33)$$

18, $R_f = CF_3$ (70%)
19, $R_f = n\text{-}C_3F_7$ (64%)

Despite the fact that antimony pentafluoride causes rapid cyclodimerization of *F*-pentadiene-1,3 at elevated temperatures,[72] the corresponding *F*-pentadienyl cation formed with excess of SbF_5 and diene at 20 °C[73] is reactive enough to attack TFE. The reaction results in formation of *F*-heptadiene-2,4 (**20**) along with some *F*-nonadiene-3,5 (ratio 85:15). Heptadiene **20** was isolated in 77% yield as a mixture of 75% *E*,*E*-, 17% *Z*,*E*-, and 8% *E*,*Z*-isomers; *Z*,*Z*-isomer was not found in the mixture.[74]

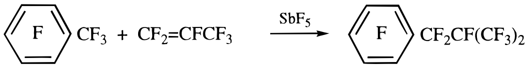
$$CF_2{=}CFCF{=}CFCF_3 + TFE \xrightarrow[SbF_5]{20°C} \underset{\mathbf{20}}{CF_3CF{=}CFCF{=}CFC_2F_5} + C_3F_7CF{=}CF\text{-}CF{=}CFCF_2CF_3 \qquad (34)$$

Reaction of *F*-hexadiene-2,4 with TFE at 50 °C led to formation of a mixture of 60% *F*-octadiene-3,5 (**21**) and 40% *F*-octadiene-2,4 (**22**).[74] Although perfluorinated dienes are known to undergo intramolecular cyclization with SbF_5[75] (see section IV.F.3), no cycloolefin formation was noted in the reaction of perfluoropentadiene and perfluorohexadiene with TFE.

$$CF_3CF{=}CFCF{=}CFCF_3 + TFE \xrightarrow[SbF_5]{50\ °C,\ 6\ h} \underset{\mathbf{21}}{CF_3CF{=}CFCF{=}CFC_3F_7} + \underset{\mathbf{22}}{C_2F_5CF{=}CFCF{=}CFC_2F_5} \qquad (35)$$

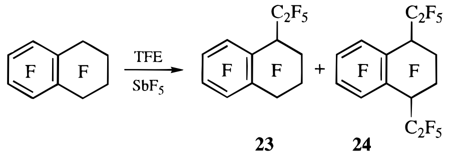
total yield 50%

Benzylic, as well as allylic, fluorides can be condensed with a fluoroolefin, as illustrated by eq 36 with *F*-toluene.[76]



(36)

Perfluorinated benzocycloalkanes also react with fluoroolefins in the presence of SbF_5 at room temperature and atmospheric pressure with formation of mixtures of mono- and disubstituted products. *F*-Tetralin reacted with TFE with formation of a mixture of *F*-1-ethyltetralin (**23**) and *F*-1,4-diethyltetralin (**24**) in the ratio 9:1.[77]

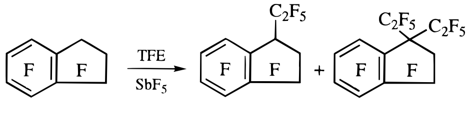


(37)

23 **24**

9 : 1

Reaction of *F*-indan with TFE led to formation of monosubstituted **25** and disubstiuted indan **26** in a ratio 54:46.[77] In contrast to the result with *F*-tetralin, *F*-diethylindan **26** has both *F*-ethyl groups connected to the same carbon.

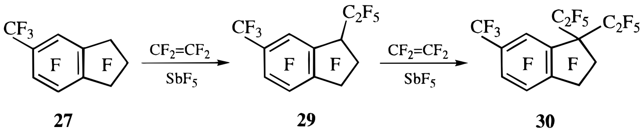


(38)

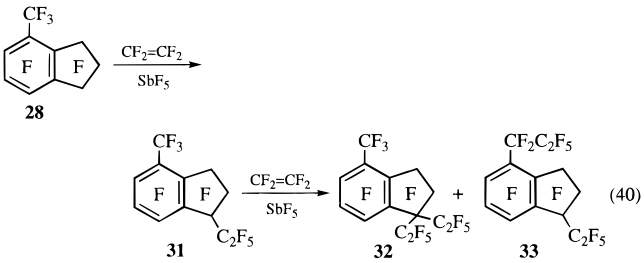
25 **26**

54 : 46

Similar results were observed for the reaction of *F*-methylindans **27** and **28** with TFE.[77] In the products, the perfluoroethyl groups are connected to the carbon of the five-membered ring that is in a *meta* position to the CF_3 group.



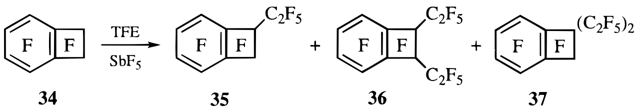
(39)



(40)

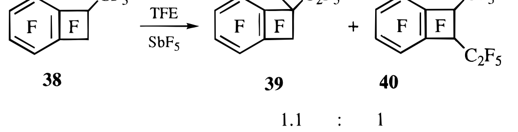
Thus, compound **27** gave *F*-1-ethyl-6-methylindan (**29**) and *F*-1,1-diethyl-6-methylindan (**30**). Isomeric indan **28** in reaction with TFE gives a mixture of *F*-1-ethyl-4-methylindan (**31**), *F*-1,1-diethyl-4-methylindan (**32**), and *F*-4-propyl-1-ethylindan (**33**), the latter formed as a result of insertion of TFE into the CF_3 group of indan **31**. Condensation of *F*-indan with CFCl═CFCl in the presence of SbF_5 at low temperature, followed by dechlorination of mono- and dialkylindans was used as a route for the synthesis of *F*-1-vinylindan and a mixture of *F*-1,1- and 1,3-divinylindans.[78] In the same work, reaction between *F*-indan and chlorotrifluoroethylene was described.

Although the reaction between *F*-benzocyclobutane (**34**) and TFE with SbF_5 catalyst also gives a mixture of mono- (**35**) and disubstituted (**36** and **37**) products (ratio 89:11), it was demonstrated[79] that *F*-diethylcyclobutanes **36** and **37** form as a mixture of 1,1- and 1,2-isomers. Absence of interconversion between **36** and **37** under reaction conditions was confirmed in a separate experiment. Reaction between chlorotrifluoroethylene and **34** gave a result similar to reaction with TFE.



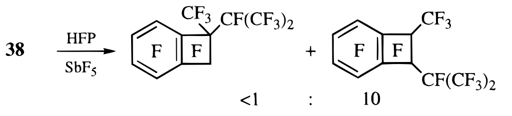
(41)

An increase in the volume of the perfluoroalkyl group introduced into *F*-benzocyclobutane can drastically change the ratio between *F*-1,1- and *F*-1,2-dialkylbenzocyclobutanes. Reaction, for example, between *F*-1-methylbenzocyclobutane (**38**) and TFE (0−10 °C, 4.5 h) leads to formation of almost equal amounts of 1,1- (**39**) and 1,2- (**40**) isomers.



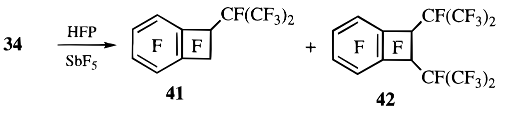
(42)

However, in the reaction of **38** with HFP, the 1,2-isomer is a major product.



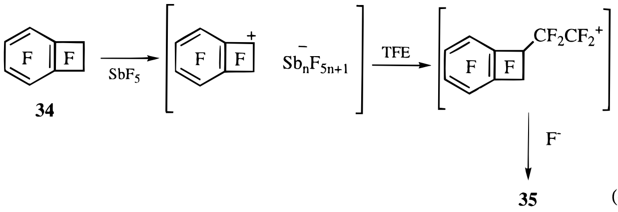
(43)

Interaction between *F*-benzocyclobutane (**34**) and HFP provides another example. Reaction carried out in a sealed tube (22 °C, 45 h) results in the formation of *F*-1-isopropylbenzocyclobutane (**41**) and *F*-1,2-diisopropylbenzocyclobutane (**42**). Formation of 1,1-isomer was not observed.



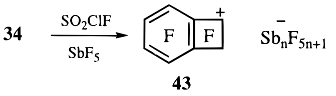
HFP = CF_2=$CFCF_3$ (44)

Interaction of polyfluorobenzocycloalkanes with TFE probably proceeds via the benzylic cations. Thus the reaction of *F*-benzocyclobutane with TFE may be represented by the following sequence.[77,79]



(45)

F-1-Benzocyclobutenyl cation (**43**) was generated by treating benzocyclobutane **34** with SbF_5 in SO_2-ClF, and the structure of the carbocation was confirmed by ^{19}F NMR.[77,79]



(46)

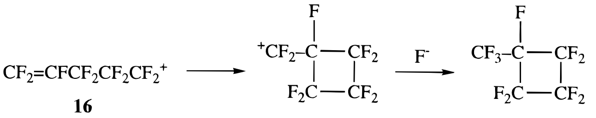
The observed values of coupling constants and chemical shifts are in a good agreement with those for the polyfluorobenzyl cations.[80,81] An attempt to detect by ^{19}F NMR *F*-1-indanyl and *F*-1-tetralinyl cations under similar conditions failed.[77] However the formation of stable 1-chlorooctafluoroindan-1-yl carbocation in the reaction of 1,1-dichlorooctafluoroindane with SbF_5 was reported recently.[82]

In separate experiments it was demonstrated that *F*-diethylbenzocycloalkanes **24** and **26** are formed stepwise by reaction of the monoderivative with a second mole of TFE. Reaction proceeds via the corresponding benzylic carbocation. The different orientations in reactions of *F*-tetralin **23**, *F*-indan **25**, and *F*-benzocyclobutane **35** was explained by the authors as being a result of competition between of electronic and steric factors in the corresponding intermediate stabilized carbocations.

C. Electrophilic 2+2 Cycloaddition

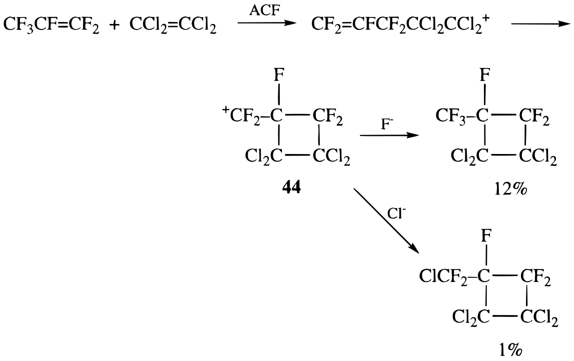
1. Olefin Cyclodimerization

As reported in section IV.B, addition of HFP to TFE catalyzed by ACF produces a small amount (<0.5% yield) of *F*-methylcyclobutane in a reaction viewed as involving intramolecular addition of the cationic carbon in **16** to an olefinic carbon (eq 47). This appears to be the first reported 2+2 cycloadditon of fluoroolefins catalyzed by a Lewis acid.



(47)

Extension of the reaction to tetrachloroethylene provided further support for the proposed mechanism with an indication that an intermediate such as **44** is also a discrete entity which may be capped with either chlorine or fluorine.[32]

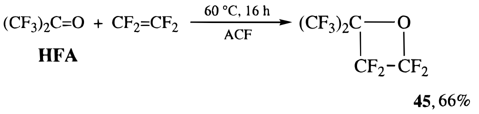


(48)

2. Cycloaddition of Hexafluoroacetone to Fluoroethylenes

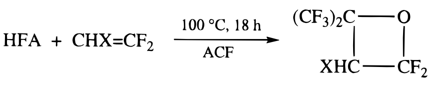
This reaction is mechanistically related to the Prins addition of formaldehyde to olefins in acidic media. In fact, 2*H*,2*H*-tetrafluorooxetane was isolated as a byproduct in the reaction of TFE with paraform in HF.[83] Antimony pentafluoride catalyzes the reaction of 1,1,3-trichlorotrifluoroacetone with TFE or $CFH=CF_2$ to produce a difficult to separate mixture of the corresponding oxetane and polyfluoropentanone-2, but the reaction of hexafluoroacetone and TFE under similar conditions failed.[4]

Recently it was reported that reaction of hexafluoroacetone (HFA) with TFE catalyzed by aluminum chlorofluoride (ACF) produces *F*-2,2-dimethyloxetane (**45**) in high yield.[33]



(49)

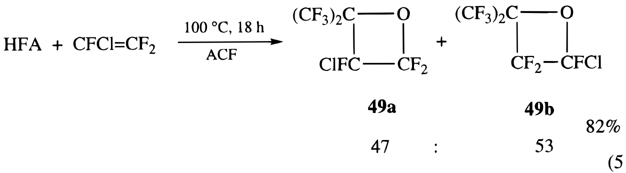
Polytetrafluoroethylene is the only byproduct formed. Trifluoroethylene and 2-chloro- and 2-bromo-1,1-difluoroethylenes all react with HFA regiospecifically to give monohydrooxetanes **46**−**48** in 91−98% yield. The formation of only one isomer, in sharp contrast to the earlier photochemical process,[84] is consistent with an electrophilic mechanism.



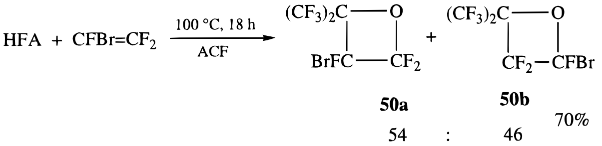
(50)

46, X = F, 98%
47, X = Cl, 98%
48, X = Br, 91%

Electrophilic addition to chloro- and bromotrifluoroethylenes is not regiospecific,[4] so it is not surprising that in cycloaddition reactions of these olefins with HFA, both possible isomers are formed.

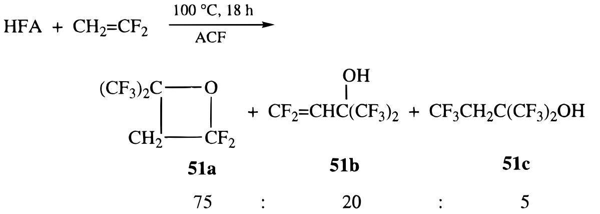


(51)



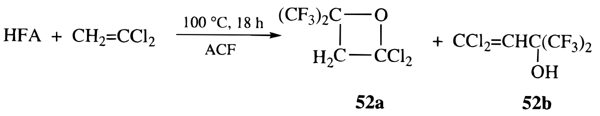
(52)

Reaction between HFA and vinylidene fluoride is more complicated, giving a mixture of a single oxetane **51a** and two alcohols **51b**,**c**. Pure oxetane may be isolated either by distillation or by washing the reaction mixture with dilute NaOH.



(53)

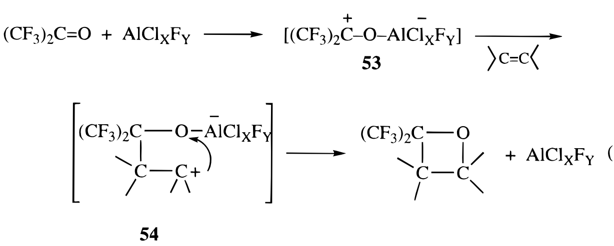
Reaction of HFA and vinylidene chloride also gives a mixture of oxetane **52a** and alcohol **52b**.



(54)

HFA is the most active of the acyclic halo ketones, and ACF the most active catalyst for this reaction. $AlCl_3$ and NbF_5 were tested as catalysts and found to give only traces of the product in reaction of HFA with trifluoroethylene.[33]

A proposed mechanism of the cycloaddition reaction of HFA with ethylenes includes generation of zwitterion **53** as a result of coordination of HFA with catalyst, then electrophilic attack of **53** on olefin with intermediate formation of **54**. Intramolecular cyclization of **54** gives the product oxetane.



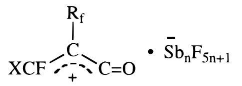
(55)

D. Acylation

Anhydrides and acyl halides of perfluorocarboxylic acids react with pentafluorobenzene in the presence of antimony pentafluoride, giving the corresponding ketones.[85] This reaction has been reviewed.[36] However, more electron-deficient substrates, for example tetrafluoroethylene, do not interact with acyl fluorides in the presence of either SbF_5[86] or ACF[87] as catalyst. Furthermore, all attempts to observe saturated perfluoroacylium cations failed.[88,89]

$$R_fC(O)X + C_6F_5H \xrightarrow{SbF_5} R_fC(O)C_6F_5 \qquad (56)$$

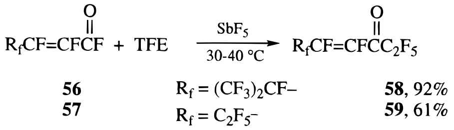
Recently it was found that stable acylium carbocations **55a**−**c** can be generated by SbF_5 from acyl fluorides of α,β-unsaturated perfluorocarboxylic acids.[86]



(57)

55a, X = F, $R_f = CF_3$
55b, X = C_2F_5, $R_f = CF_3$
55c, X = *i*- C_3F_7, R_f = *n* -C_3F_7

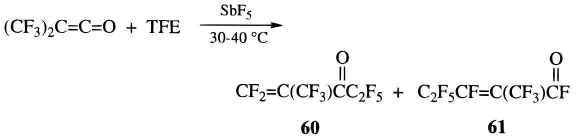
In contrast to acyl fluorides of saturated perfluoro acids, the acyl fluorides of α,β-unsaturated acids are able to acylate fluoroolefins in the presence of SbF_5. Reactions between acyl fluorides **56** and **57** and TFE proceed at 30−40 °C and atmospheric pressure, giving ketones **58** and **59**, respectively.[86]



$$R_fCF{=}CFC(O)F + TFE \xrightarrow[30\text{-}40\ °C]{SbF_5} R_fCF{=}CFC(O)C_2F_5 \qquad (58)$$

56 $R_f = (CF_3)_2CF–$ **58**, 92%
57 $R_f = C_2F_5–$ **59**, 61%

The compound **56** was also used in reactions with 1,2-dichlorodifluoroethylene and with HFP, the corresponding ketones having been isolated in high yield. The vinyl ketones obtained from these reactions exist as a mixture of *trans* and *cis* isomers with *trans* isomers the major components (85−93%, depending on the structure of the ketone). Even bis(trifluoromethyl)ketene reacts with TFE in the presence of SbF_5, producing a mixture of vinyl ketone **60** and acyl fluoride **61**.

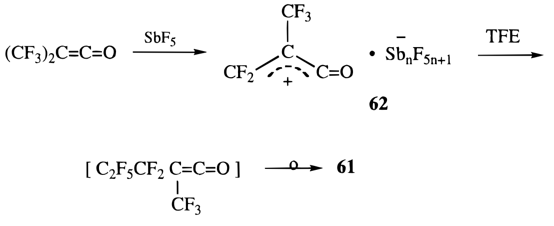


$$(CF_3)_2C{=}C{=}O + TFE \xrightarrow[30\text{-}40\ °C]{SbF_5} CF_2{=}C(CF_3)C(O)C_2F_5 + C_2F_5CF{=}C(CF_3)C(O)F \qquad (59)$$

60 **61**

yield of mixture 58%

The formation of acyl fluoride **61** in this reaction was explained[86] as being a result of isomerization of **60** catalyzed by SbF_5, a process which was earlier observed for certain vinyl ketones[90] (see section IV.F.4). However, the formation **61** can also be explained as a result of isomerization of ketene **63** derived from the attack of asymmetric, long-lived[91] carbocation **62** on TFE by the CF_2 end.



62

63

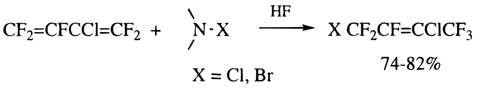
(60)

E. Halonium Ion Sources with Fluorinated Olefins

Conjugate additions to fluoroolefins by electrophilic species generated in anhydrous HF include halogenation, nitrofluorination, and reaction with formaldehyde and have been reviewed in detail.[92] A recent improvement of this method involves the use of BF_3 or TaF_5 rather than SbF_5 as additive to enhance HF acidity. The system TFE/ICl/HF/BF_3 results in a high-yield conjugate addition (eq 61). Other reactive olefins, such as terminal fluoroolefins and trifluorovinyl ethers, also participate in the reaction.[93]

$$CF_2{=}CF_2 + ICl + HF \xrightarrow{BF_3} CF_3CF_2I + HCl \qquad (61)$$

Conjugate 1,4-additions to fluorinated 1,3-dienes have also been observed[94] (eq 62).



$$CF_2{=}CFCCl{=}CF_2 + \ \rangle N\text{-}X \xrightarrow{HF} XCF_2CF{=}CClCF_3 \qquad (62)$$

X = Cl, Br 74-82%

The clean preparation of halogen fluorides of the type XF (X = I, Br) directly from the elements has made these reagents more readily available.[95,96] Their reactions with fluoroolefins are generally regioselective with halonium ion addition as the first step.

Halooxygenation of fluoroolefins, accomplished by treatment with neat hypohalite, is also viewed as an electrophilic attack, presumably with transfer of halonium ion to the olefins to give fluorocarbocationic intermediates. Most of the work has been carried out with the halogen fluorosulfates, $XOSO_2F$, because of their availability and has been reviewed [97]. In reactions of the type shown in eq 63, reactivity varies strongly with the identity of X in the order: Cl > Br > I.

$$XOSO_2F + CF_3CF{=}CF_2 \xrightarrow[\text{Solvent}]{} CF_3CFXCF_2OSO_2F \qquad (63)$$

X = Cl, Br, I

Perfluoroalkyl hypohalites R_fOX and triflates CF_3SO_2OX (X = Cl, Br) have also been added to fluoroethylenes; in both cases the reactivity is high and addition proceeds readily even at the low temperature mandated by the thermal stability of the reagents. A polar mechanism was proposed for these reactions.[98−101]

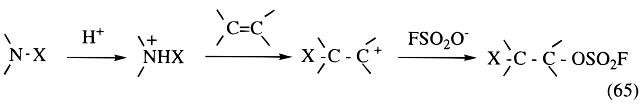
The fluorosulfates **64** were also prepared by reactions of the olefins TFE and HFP with a solution of *N*-halogen compound (hexachloromelamine or *N*-bromosuccinimide) in FSO_3H.[102]

$$YCF{=}CF_2 + \ \rangle N\text{-}X \xrightarrow[20°C]{FSO_2OH} XCFYCF_2OSO_2F \qquad (64)$$

64, 47-78%

X = Cl, Br

The reaction proceeds rapidly at room temperature and atmospheric pressure. Despite a similarity with the addition of $XOSO_2F$ to a C=C bond (eq 63), the above process differs mechanistically since it proceeds by electrophilic *conjugate* addition rather than through the addition of *in situ* generated of halogen fluorosulfate.[102]



$$\rangle N\text{-}X \xrightarrow{H^+} \rangle \overset{+}{N}HX \xrightarrow{\rangle C=C\langle} X\text{-}C\text{-}C^+ \xrightarrow{FSO_2O^-} X\text{-}C\text{-}C\text{-}OSO_2F$$

(65)

Halooxygenation of a fluorinated double bond is also achieved by conjugate addition of, for example, I_2 and SO_3 (eq 66), and can be used to prepare iododifluoroacetyl fluoride.[103]

$$CF_2{=}CF_2 + I_2 + n\,SO_3 \longrightarrow ICF_2CF_2OSO_2Y \xrightarrow{KF} ICF_2C(O)F \qquad (66)$$

Y= sulfonic anhydride residues

Interaction of iodine and mercuric acetate with perfluoroalkylethylenes is an older method for halooxygenation of these olefins,[104] which are unreactive toward the usual reagents for halohydrin or epoxide formation.

$$R_fCH{=}CH_2 + I_2 + Hg[OC(O)CH_3]_2 \longrightarrow R_fCHICH_2OC(O)CH_3 \qquad (67)$$

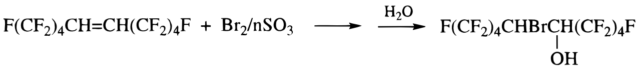
A new method that avoids the use of mercury to provide a driving force relies on the reagent X_2/nSO_3 ($X = I$, Br, CI; $n = 3$ or more).[105] Pure SO_3 does not attack $R_fCH{=}CH_2$ readily at either the double bond or allylic fluorine, although the latter reaction is catalyzed by BX_3 (see section IV.H.2). The combination X_2/SO_3, however, provides a halonium ion capable of ready addition to the double bond at 25 °C to generate carbocation **65** having the expected orientation. Combination of **65** with the counterion establishes the C−O bond. Subsequent redox reactions regenerate X^+ (or X_2) along with intermediate anions from addition of varying numbers of SO_3 molecules and the loss of one molecule of SO_2. Stable products **67** form by combination of the resulting polysulfuric anhydride anion **66** with another halogenated carbocation. Simple dialkyl sulfates (**67**, $n = 1$) tend to form without excess SO_3 present, a result usually to be avoided if the goal is halohydrin synthesis, since the sulfates hydrolyze with difficulty.

$$R_fCH{=}CH_2 + X^+ \longrightarrow \underset{\mathbf{65}}{R_fCHXCH_2+} \xrightarrow{{}^-OSO_2X}$$

$$\longrightarrow R_fCHXCH_2OSO_2X \xrightarrow{n\,SO_3} \underset{\mathbf{66}}{R_fCHXCH_2(OSO_2)_nO^-} + SO_2 + X^+ \xrightarrow{\mathbf{65}}$$

$$\longrightarrow \underset{\mathbf{67}}{R_fCHXCH_2(OSO_2)_nOCH_2CHXR_f} \qquad (68)$$

Derivatization of 1,2-bis(perfluoroalkyl)ethylenes is even more difficult, since their response to electrophiles is lower than for the monosubstituted ethylenes, and steric factors can also play a role. An indication of the presence of steric constraints is the failure of 1,2-bis(perfluorobutyl)ethylene to add bromine, despite determined efforts.[106] Reactivity of the olefin toward Br^+ is retained; however, since the bromooxygenation reaction with Br_2/nSO_3 followed by hydrolysis gives bromohydrin **68** in good yield.



$$F(CF_2)_4CH{=}CH(CF_2)_4F + Br_2/nSO_3 \longrightarrow \xrightarrow{H_2O} F(CF_2)_4CHBr\underset{\displaystyle OH}{\underset{|}{C}}H(CF_2)_4F$$

68, 78%

(69)

The availability of the perfluoroalkylated halohydrins renders the corresponding epoxides also available by treatment with strong base.[105] This route to such epoxides is useful, since conventional methods fail with the perfluoroalkylethylenes.

F. Isomerization

1. Halogen Migration

Fluorinated polyhalofluoroalkanes with halogens on different carbons, when treated with Lewis acids, tend to isomerize to give geminal isomers. This reaction is particularly effective for isomerization of fluoroethanes. Commonly used Lewis acids in this reaction are $AlCl_3$ and $AlBr_3$, and the latter catalyst is by far the more efficient one. Isomerization of halofluoroethanes was studied in great detail in the 1960s, and the data on this reaction have been summarized.[22] Only recently reported work will be discussed here. Isomerization of 1,2-dihalotetrafluoroethanes is more difficult than isomerization of trihalo- and tetrahaloethanes, isomerization of bromofluoro alkanes is generally easier than the same process for chlorofluoroalkanes, and isomerization of the ethanes is much easier than isomerization of similarly substituted propanes and higher alkanes. Isomerization of *F*-1,2-dibromoethane (**69**) was reported recently where aluminum chloride specially activated by reaction with CF_3CFBr_2 (**70**) was used as a catalyst.[107] Although the isomerization of *F*-1,2-dichloroethane into CF_3CFCl_2 was claimed to occur near 25 °C with this catalyst, no experimental details were given and the present authors have been unable to demonstrate the reaction.

$$\underset{\mathbf{69}}{CF_2BrCF_2Br} + AlCl_3 + CF_3CFBr_2 \xrightarrow[\text{reflux, 8h}]{} \underset{\mathbf{70}}{CF_3CFBr_2} \qquad (70)$$

Aluminum chloride is a good catalyst for isomerization of *F*-1,2-dibromopropane (**71**). However, complete conversion of starting material and reasonable yields of *F*-2,2-dibromopropane (**72**) in this reaction require prolonged reaction time at elevated temperature, a consequence of moving from a 2-carbon to a 3-carbon substrate.[27]

$$\underset{\mathbf{71}}{CF_3CFBrCF_2Br} + AlCl_3 \xrightarrow[\text{150 °C, 9 d}]{} \underset{\mathbf{72}}{(CF_3)_2CBr_2} \qquad (71)$$

According to a recent patent,[108] the conditions for the isomerization of **71** are milder and reaction time is much shorter (only a few hours) when aluminum chlorofluoride $AlCl_xF_y$ or aluminum bromofluoride $AlBr_xF_y$, generated *in situ* by reaction of $AlCl_3$ or $AlBr_3$ with compounds such as $CFCl_3$ or $CHCl_2F$, is used as a catalyst.

$$\mathbf{71} \xrightarrow[\text{50 °C, 4 h}]{AlCl_xF_y \text{ or } AlBr_xF_y} \mathbf{72} \qquad (72)$$

Surprisingly, the same patent claims an efficient isomerization of *F*-1,2-dichloropropane (**73**) using exactly the same conditions as for dibromopropane **71**. Although this transformation of dichloride **73** does proceed sluggishly under the conditions described, newer work[34] has established that small amounts of fluoroolefins such as HFP as promoter produce a striking increase in rate of isomerization to *gem*-dichloride **74**.

$$\underset{\mathbf{73}}{CF_3CFClCF_2Cl} \xrightarrow[130\ °C,\ 4\ h]{ACF,\ HFP} \underset{\mathbf{74},\ 100\%}{CF_3CCl_2CF_3} \qquad (73)$$

Heightened activity of ACF in the presence of a fluoroolefin promoter is also observed in the isomerization of *F*-1,2-dichloroethane, and isomerizations of several higher *vic*-dichlorides were also reported.[34] An example is that of 2,3-dichlorobutane **75**.

$$\underset{\mathbf{75}}{CF_3CFClCFClCF_3} \xrightarrow[130\ °C,\ 5\ h]{ACF,\ HFP} \underset{96\%}{CF_3CCl_2CF_2CF_3} \qquad (74)$$

Reaction of 2,3-dibromoperfluorobutane (**76**) with $AlCl_3$ at 85−90 °C is reported to give 2,2-dibromobutane (**77**), isolated in 71% yield, again illustrating the relative ease of rearrangement of dibromides.[28] At least one example of isomerization of a 1,3-dichloride to form *gem*-dichloride **78** has appeared, indicating that many more such deep-seated rearrangements are possible.[25]

$$\underset{\mathbf{76}}{CF_3CFBrCFBrCF_3} \xrightarrow[90\ °C]{AlCl_3} \underset{\mathbf{77},\ 71\%}{CF_3CBr_2CF_2CF_3} \qquad (75)$$

$$ClCFHCF_2CF_2Cl \xrightarrow[160\ °C,\ 8\ d]{ACF} \underset{\mathbf{78}}{CHF_2CCl_2CF_3} \qquad (76)$$

2. Double-Bond Migration

In 1978 SbF_5 was found to be an effective catalyst for the isomerization of fluoroolefins. The treatment of terminal fluoroolefins with SbF_5 results in migration of the double bond.[109] The main findings can be formulated as follows.[4] Interaction of a perfluoroalkene-1 with SbF_5 under conditions allowing control of this exothermic reaction results in the exclusive formation of olefin with the double bond in the 2-position. The process is stereoselective and *trans* isomer is always the major product (80−95%) in the mixture. A similar 1,3-fluoride shift accompanied by double-bond migration is induced by ACF and was recently reported (see section IV.B).[70]

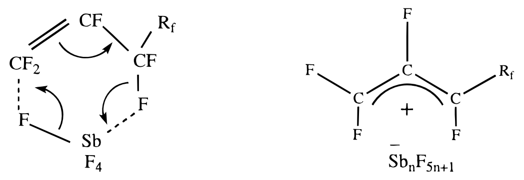
$$R_fCF_2CF{=}CF_2 \xrightarrow[exothermic]{SbF_5} R_fCF{=}CFCF_3 \qquad (77)$$

$$R_f = CF_3 - C_8F_{17},\ 95\text{-}100\%$$

Since migration of the double bond of a perfluoroolefin as catalyzed by SbF_5 involves concomitant migration of fluorine, the stereochemical control in this reaction was rationalized[109] as being due to the formation of a 6-membered ring transition-state complex **79** between the olefin and SbF_5, which determines the preferred geometry of the final product. At the other extreme from the concerted process would be a tight dipolar complex **80** (Scheme 2) as an intermediate in which charges are well stabilized. The actual mechanism may well involve partial charge separation in the intermediate or transition state.

The exclusive formation of *cis* isomers of 1-*H*-perfluoroalkenes-1 by isomerization with SbF_5 was explained using the same concerted mechanism.[110,111] Note that the presence in the molecule of such atoms as Cl or H favors the migration of the double bond to these atoms, even past the Δ^2 position.[109]

Scheme 2



79 **80**

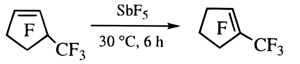
$$CF_2{=}CFCF_2CFHCF(CF_3)_2 \xrightarrow{SbF_5} CF_3CF_2CF{=}CHCF(CF_3)_2 \qquad (78)$$

This tendency is so strong that in butene **81** the double bond migrates from one end of the molecule to the other terminal position.[110]

$$\underset{\mathbf{81}}{CF_2{=}CFCF_2CF_2H} \xrightarrow[exothermic]{SbF_5} \underset{quant.,\ 100\%\ cis\ isomer}{CF_3CF_2CF{=}CFH} \qquad (79)$$

However, the amount of 1-*H*-perfluoroalkene-1 in the final product does depend on the chain length of the olefin. Recently published work[111] shows that the amount of $CFH{=}CF(CF_2)_nCF_3$ in the equilibrium mixture of olefins derived from the isomerization of ω-*H*-perfluoroalkenes-1 by SbF_5 at 50−100 °C decreases from 100% $n = 1$, 75% for $n = 2$, 18% for $n = 3$ to 6% for $n = 4$. In contrast to the isomerization of perfluoroolefins, where yields are practically quantitative,[109] typical yields in the isomerization of $HCF_2(CF_2)_nCF{=}CF_2$ olefins are lower (88−95%) because of partial dimerization of these fluorolefins. The structures of these dimers were not determined.[111]

Cyclic fluoroolefins provide further good examples of the general tendency of double bonds to migrate so as to minimize the number of vinylic fluorine atoms. For example, *F*-3-methylcyclopentene (**82**) readily isomerizes to the more stable *F*-1-methylcyclopentene (**83**) under the action of SbF_5.[112]



82 **83** quant. (80)

Another example demonstrating the same principle was found recently.[70] ACF causes rapid conversion of *F*-4-methylpentene-2 (**84**) to *F*-2-methylpentene-2 (**85**) in a reaction that has not been reported with SbF_5.

$$\underset{\mathbf{84}}{(CF_3)_2CFCF{=}CFCF_3} \xrightarrow[25\ °C,24\ h]{ACF} \underset{\mathbf{85}}{(CF_3)_2C{=}CFCF_2CF_3} \qquad (81)$$

At elevated temperature SbF_5 can cause the migration of the double bond beyond the 2-position. Prolonged heating of *F*-hexene-2 (**86**) or *F*-heptene-2 (**87**) with a catalytic amount of SbF_5 leads to formation of equilibrium mixtures containing 75−80% of Δ^3-olefin and 20−25% of Δ^2-olefin.[4]

$$CF_3CF{=}CFCF_2R_f \rightleftharpoons C_2F_5CF{=}CFR_f \qquad (82)$$

$$\mathbf{86}, R_f = C_2F_5$$
$$\mathbf{87}, R_f = n\text{-}C_3F_7$$

Surprisingly, the result of the reaction of *F*-heptene-1 with ACF catalyst is different. Fast (within 1 h at 25 °C) migration of the terminal double bond is followed by slower enrichment of the reaction mixture with Δ^3-olefin, still at 25 °C (70 h).[70] Furthermore, the observed ratio Δ^3- to Δ^2-olefins in the final mixture (95:5) was quite different from that reported for reaction **87** with SbF_5. This finding probably reflects the difference between homogeneous (SbF_5) and completely insoluble, heterogeneous (ACF) catalysis. The surprising ease with which ACF moves the double bond to the Δ^3 position as compared to SbF_5 is a further indication that ACF has very strong Lewis acid sites.

Perfluorinated dienes behave similarly to fluoroolefins with SbF_5. Controlled reaction between a terminal diene and the catalyst results in formation of diene containing both double bonds in the 2-position.[75,113] As in the case of fluoroolefins, this process is stereoselective and a typical reaction mixture contains 75−80% of *trans*−*trans* isomer and 20−25% of *cis*−*trans* isomer. No *cis*−*cis* isomers were found.

$$CF_2{=}CFCF_2(CF_2)_nCF_2CF{=}CF_2 \xrightarrow[0\text{-}20\ °C]{SbF_5} CF_3CF{=}CF(CF_2)_nCF{=}CFCF_3 \qquad (83)$$

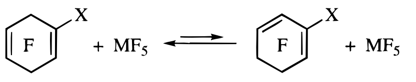
$$n = 0,2,4,6,8,10$$

At elevated temperatures double bonds tend to migrate further inside the diene molecule. The formation of conjugated dienes **21** and **22** was reported in the reaction of **88** with SbF_5,[75] but conditions strenuous enough for preparation of these compounds left only residual amounts in the reaction mixture, which contained mainly cycloolefins derived from cyclization of the dienes (see section IV.F.3 for details).

$$\underset{\mathbf{88}}{CF_3CF{=}CF(CF_2)_2CF{=}CFCF_3} \xrightarrow[90\ °C,\ 3\ h]{SbF_5} \underset{\mathbf{21}}{CF_3CF{=}CFCF{=}CFC_3F_7}$$

$$+ \underset{\mathbf{22}}{C_2F_5CF{=}CFCF{=}CFC_2F_5} + \text{cycloolefins} + \text{others} \qquad (84)$$

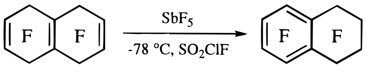
The migration of double bonds in perfluorinated dienes apparently proceeds in stepwise fashion, but the data are not sufficient to determine whether conjugated or nonconjugated diene is more stable in the presence of Lewis acid. The reaction of fluorocyclohexadienes with Lewis acids gave an unexpected result. It was demonstrated that SbF_5 or NbF_5 cause interconversion between fluorinated dienes **89** and **90**, but the equilibrium is significantly shifted toward *nonconjugated* 1,4-isomer.[114]



(85)

	89	**90**
X = F	92	8
X = H	85	15
X = CH$_3$	85	15

Reaction of SbF_5 with cyclic diene **91** in SO_2ClF as solvent gives *F*-tetralin **92** as the sole product even at low temperature, indicating that an aromatized product is favored when feasible.[114]



91 **92** quant. (86)

In some cases Lewis acids can cause the rearrangement of diene into allene. This transformation, as catalyzed by fluoride ion, is well known,[115] but the first example of electrophilic diene−allene rearrangement was reported in 1981.[116] High-yield formation of allene **95** in the reaction between diene **93** and SbF_5 was observed. As it was shown in the same work, this process involves transformation of starting material into a mixture of *cis*−*trans* isomers of diene **94** and isomerization of **94** into allene in a second step.

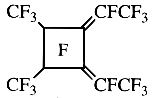
$$\underset{\mathbf{93}}{(CF_3)_2C{=}CFCF{=}CF_2} \xrightarrow[0\text{-}5\ °C]{SbF_5} \underset{\mathbf{94}}{CF_2{=}C(CF_3)CF{=}CFCF_3} \xrightarrow[20\ °C]{SbF_5}$$

$$\longrightarrow \underset{\mathbf{95}}{(CF_3)_2C{=}C{=}CFCF_3} \qquad (87)$$

Diene−allene interconversion appears to be typical for polyfluorodienes containing a trifluorovinyl group. Formation of cyclobutane **97** in a reaction of *F*-pentadiene-1,3 with SbF_5 was explained as being a result of thermal cyclodimerization of *F*-1,3-dimethylallene (**96**) formed as an intermediate.[72]

$$CF_2{=}CFCF{=}CFCF_3 \xrightarrow{SbF_5}$$

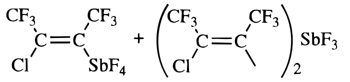
$$\underset{\mathbf{96}}{[CF_3CF{=}C{=}CFCF_3]} \longrightarrow$$



97 (88)

Recently it was found that the reaction of SbF_5 with excess *F*-2-chlorobutadiene-1,3 (**98**) in SO_2ClF as solvent gives the mixture of antimonates **99a**,**b**, isolated in 84% yield.[94]

$$\underset{\mathbf{98}}{CF_2{=}CClCF{=}CF_2} + SbF_5 \xrightarrow[SO_2ClF]{}$$



99a **99b** (89)

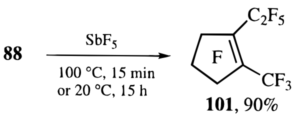
Again, the mechanism proposed for this reaction starts with transformation of diene **98** into allene **100** and then electrophilic addition of antimony pentafluoride across the terminal C=C of the allene (eq 90). The analogous formation of $CF_3C(BF_2){=}CF_2$ was reported earlier in the reaction of tetrafluoroallene with BF_3.[117]

$$\mathbf{98} \xrightarrow{SbF_5} \underset{\mathbf{100}}{[\ CF_3CCl{=}C{=}CF_2\ ]} \xrightarrow{SbF_5} \mathbf{99a} + \mathbf{99b} \qquad (90)$$

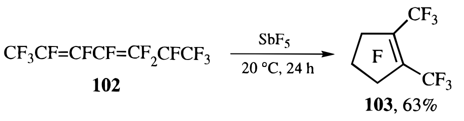
The nature of the Lewis acid is critical in the reactions of fluorodienes and can drastically affect the result. For example, reaction of *F*-butadiene-1,3 with ACF catalyst produces *F*-butyne-2 in quantitative yield,[70] a transformation not observed with SbF_5 and, in fact, the only reported example of a direct electrophilic diene−acetylene rearrangement.

3. Cyclization of Perfluorodienes

Heating of some perfluorinated dienes with *excess* of SbF_5 gives *F*-1,2-dialkylcyclopentenes as a result of intramolecular cyclization of diene. Although this type of transformation has been known for hydrocarbon dienes and polyenes for a long time,[118] the first example of such cyclization of perfluorinated dienes was reported in 1982.[113] Reaction between diene **88** and a 2- to 3-fold excess of SbF_5 proceeds rapidly (15 min) at 100 °C or slower (10−15 h at room temperature), giving *F*-1-methyl-2-ethylcyclopentene (**101**) in high yield. Similarly, *F*-heptadiene-2,4 (**102**) was converted into *F*-1,2-dimethylcyclopentene (**103**).[74]

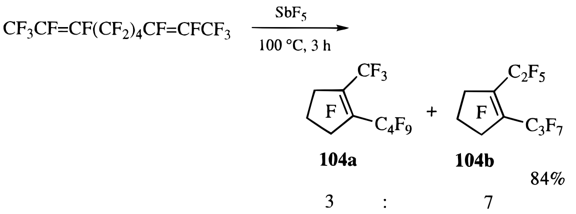


(91)



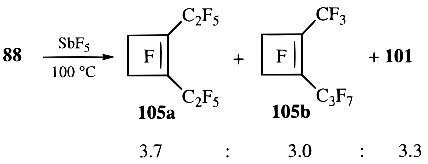
(92)

Cyclization of longer chain dienes proceeds only at elevated temperature to form mixtures of isomeric cyclopentene such as **104a**,**b**.



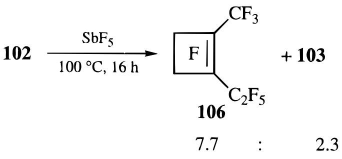
(93)

A remarkable feature of the reaction of perfluorodienes with SbF_5 is that the composition of the final mixture of products can depend strongly on the amount of SbF_5 used. Reaction of fluorodienes with a catalytic amount of SbF_5 caused formation of *F*-1,2-dialkylcyclobutenes as the main reaction. As was shown,[75] heating of the mixture of diene **88** and SbF_5 (molar ratio 3.4:1) leads to the formation of a mixture of cyclobutenes **105a**,**b** and cyclopentene **101** in the ratio 3.7:3.0:3.3.



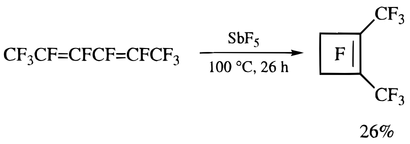
(94)

A similar reaction of diene **102** (molar ratio diene: SbF_5 4.9:1) gave the mixture of cyclobutene **106** and cyclopentene **103** in 77:23 ratio, isolated in 80% yield.



(95)

Surprisingly, the reaction of *F*-hexadiene-2,4 with SbF_5 is not sensitive to the amount of SbF_5; *F*-1,2-dimethylcyclobutene is the only product, isolated in modest yield.[75]

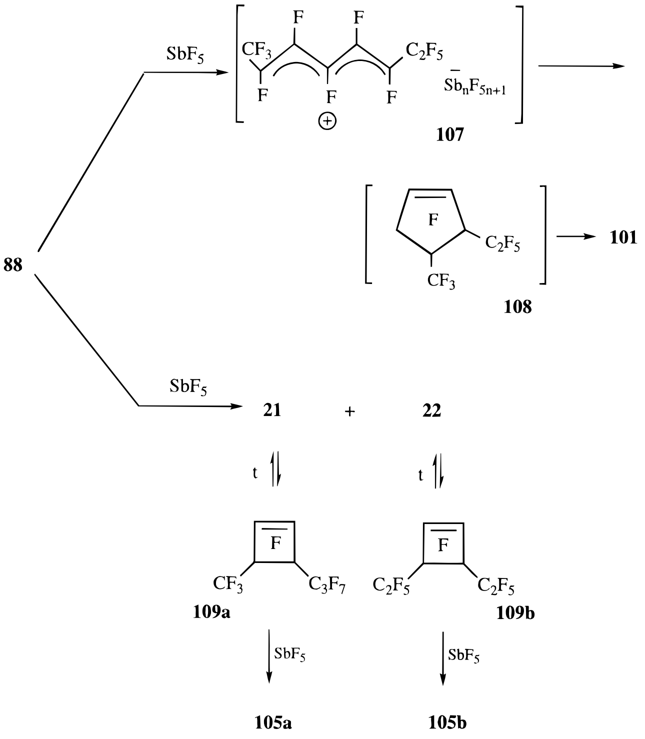


(96)

The formation of cyclopentenes from perfluorodienes with excess of SbF_5 results from concerted 1,5-cyclization of the corresponding 1,5-dialkylcyclopentadienyl cation **107** formed as an intermediate. Excess of SbF_5 in this reaction is necessary for the formation of polynuclear counter anions, $Sb_nF_{5+1}^-$, which are known to be far less nucleophilic than SbF_6^-. Lewis acid-catalyzed migration of the double bond in cyclopentene **108** gives the final product. The proposed mechanism[75] is in a good agreement with the experimental data, and it explains the higher reactivity of short-chain dienes and also the formation of isomeric cyclopentenes in reactions of dienes with a number of carbons greater than 8.

Formation of perfluorocyclobutenes in reactions of dienes with catalytic amounts of SbF_5 is probably a variant of the well-known thermal cyclization of conjugated perfluorodienes (for a review, see ref 119) (Scheme 3).

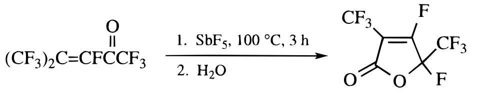
Scheme 3



SbF_5 plays a multiple role in this reaction.[75] It causes the isomerization of starting diene **88** into a mixture of conjugated dienes **21** and **22**. It probably also causes conversion of *trans*−*trans* and *trans*−*cis* isomers of dienes **21** and **22** into *cis*−*cis* isomers, since it was shown[119] that the activation energy for thermal cyclization of *trans*−*trans* *F*-hexadiene-2,4 is 21.5 kcal/mol higher than for the same process involving *cis*−*cis* isomers, and a noticeable rate of cyclization of *trans*−*trans* and *trans*−*cis* *F*-hexadienes can be achieved only at temperatures higher than 200 °C. Finally, SbF_5 is also responsible for the isomerization of 3,4-dialkylcyclobutenes **109a**,**b**, initially formed in reversible thermal cyclization of **21** and **22**, into 1,2-dialkylcyclobutenes **105a**,**b**. This step is irreversible, and it drives the several equilibria in this complicated system to the formation of the final products. The ratio between cyclobutenes and cyclopentenes in the final product is directly related to the amount of SbF_5 used, since it regulates the ratio between carbocationic and thermal routes.

4. Isomerization of Fluorinated Ketones, Diketones, and N-Fluoroimines

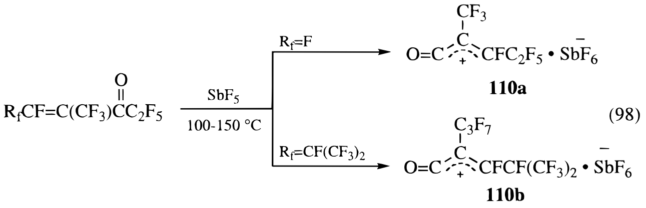
Antimony pentafluoride was shown to isomerize perfluorinated vinyl ketones.[90] The result of the reaction depends greatly on the structure of starting ketone. Ketones having a CF_3 group in the position β to the carbonyl group undergo intramolecular cyclization to give, after hydrolysis, derivatives of 2,5-dihydrofuran. This type of isomerization was observed earlier for perchlorovinyl ketones.[120] An example is given in eq 97.[90]



(97)

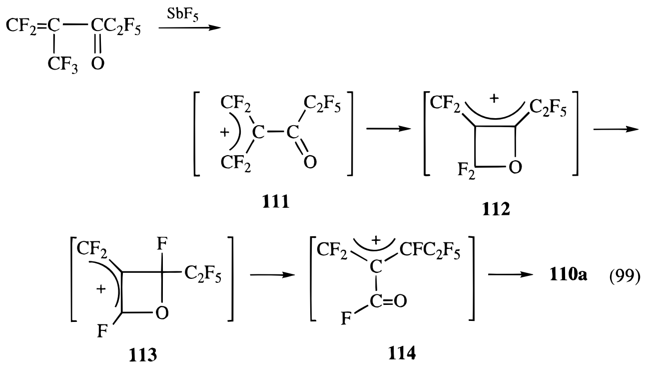
86%

Vinyl ketones having a CF_3 group in the position α to the carbonyl were converted by SbF_5 into stable acylium salts **110a**,**b**.[90]



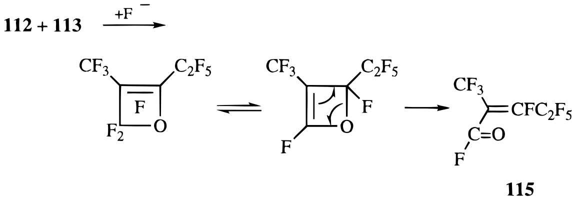
(98)

The mechanism proposed for this unusual rearrangement involves attack at allylic fluorine to form allyl cation **111**, its cyclization into cation **112**, rearrangement of this intermediate into **113**, and ring opening of **113** to give allyl cation **114**, which further rearranges into final acylium cation.



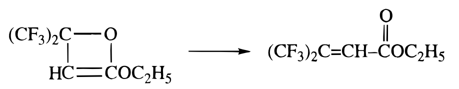
(99)

As has been suggested for the alkenylation of fluoroolefins with ACF as catalyst (see section IV.B), a dual mechanism involving either the carbocation rearrangement by 1,3-shift of fluorine as shown in eq 99, or the formation of discrete intermediates by addition of fluoride with a subsequent 1,3-fluorine shift and concerted ring opening to form acid fluoride **115** as shown in eq 100 may be occurring, reaction with SbF_5 then gives acylium ion **110a** in a final irreversible step (see also section IV.D for acylium ion formation and reaction).



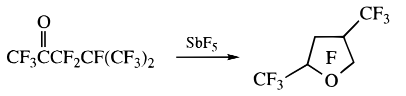
(100)

Electrocylic ring opening of oxetes is a known transformation, as illustrated in eq 101.[121]



(101)

An unusual reaction of perfluorinated ketones was reported recently.[122] Interaction of ketones having a CF_3 group β to the carbonyl group with SbF_5 results in high yield formation of perfluoroalkyloxolanes. Compound **116** was converted into oxolane **117** by heating with a catalytic amount of SbF_5.

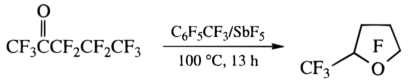


(102)

116

117, 84%

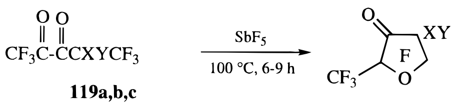
Linear *F*-pentanone-2 is less reactive, and under similar conditions the yield of corresponding oxolane **118** does not exceed 2–3%. However, the use of a $C_6F_5CF_3/SbF_5$ catalytic system allows significant improvement in the yield of *F*-2-methyloxolane (**118**).



(103)

118, 76%

No reaction was observed under similar conditions for $(CF_3)_2CFC(O)C_2F_5$, $(CF_3)_2CFC(O)CF_2CF_2C(CF_3)_3$, or $CF_3C(O)C_5F_{11}$,[122] indicating the presence of a β-CF_3 group to give a 5-membered ring is essential. Reactions of perfluoro-α-diketones provide especially clear evidence of the need for a CF_3 group β to carbonyl. Perfluoro-α-diketones R_f C(O)C(O)CF_3 (**119a**–**c**) were converted into the corresponding oxolanones (**120a**–**c**) by reaction with SbF_5.

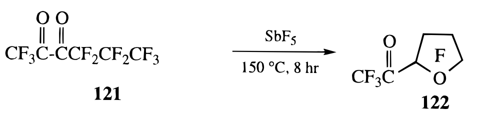


(104)

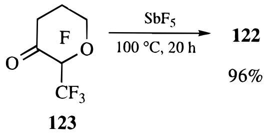
119a,b,c

120a, X = Y = F , 63%
120b, X = F, Y = CF_3 , 81%
120c, X = Y = CF_3, 80%

Similarly, diketone **121** was converted at 150 °C into *F*-2-acetyldioxolane (**122**).[122] The same product was prepared in high yield when cyclic ether **123** was reacted with SbF_5 at 100 °C.

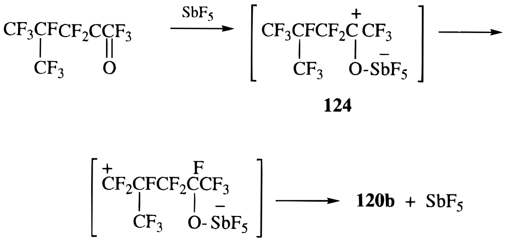


(105)



(106)

The mechanism advanced for cyclization of fluorinated ketones and diketones includes formation of zwitterion complex **124** and 1,4-shift of fluorine followed by ring closure into product **120b**.

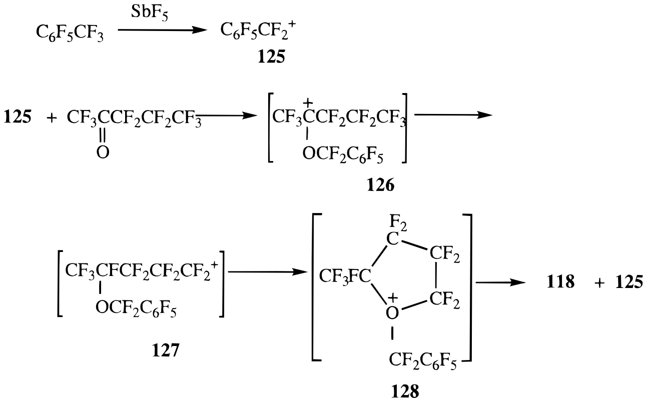


(107)

Acceleration of some reactions in the presence of *F*-toluene[122] and *F*-isobutene[123] was explained as being a result of initial attack on the carbonyl oxygen of low nucleophilicity by a carbocation more electrophilic than SbF_5, e.g. *F*-benzyl cation **125** formed in the reaction of $C_6F_5CF_3$ with SbF_5.[80,81] This effect merits further exploration. As in the previous mechanism, carbocation **126** rearranges into cation **127**.

The last stage includes cyclization of **127** with formation of oxonium cation **128** and its cleavage leads to recovery of $C_6F_5CF_2^+$ and formation of product oxolane (Scheme 4).

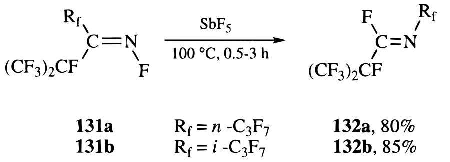
Scheme 4



Although *N*-fluoroimines of per- and polyfluoroketones have been known for over 40 years (methods of preparation and chemistry of *N*-fluoroimines have been covered in several reviews[124,125]), the reactions of this class of compound with Lewis acids were only recently studied. It was reported that imine **129** reacts exothermically with SbF_5, producing *F*-2-azabutene-2 (**130**) in high yield.[126]

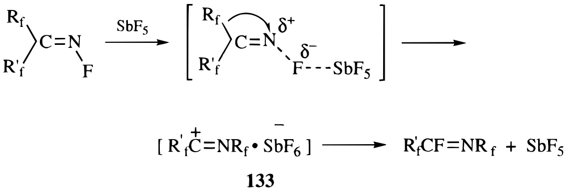
$$\underset{\mathbf{129}}{(CF_3)_2C{=}NF} \xrightarrow[\text{exotherm}]{SbF_5} \underset{\mathbf{130},\ \text{quant.}}{CF_3N{=}CFCF_3} \qquad (108)$$

Higher *N*-fluoroimines **131a**,**b** are less reactive toward SbF_5 and do not rearrange at ambient temperature, but at 100 °C rapidly rearrange into imines **132a**,**b**, respectively.[127]



(109)

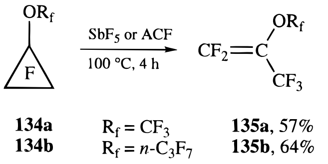
^{19}F NMR studies revealed that this reaction is sterospecifc and, as in the Beckman rearrangement,[128] only the perfluoroalkyl group *trans* to fluorine of N−F migrates in the course of the reaction. The mechanism, similar to that of Beckman rearrangement, includes polarization of the N−F bond by the Lewis acid, migration of perfluoroalkyl group with generation of stable immonium carbocation **133**, and combination with fluoride ion to give the corresponding imidoyl fluoride.[126,127]



(110)

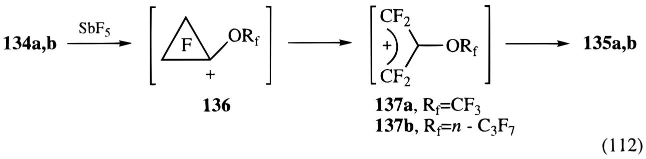
5. Ring-Opening Reactions of Polyfluorocyclopropanes

Fluorinated alkoxycyclopropanes **134a**,**b** can be readily converted into vinyl ethers **135a**,**b** by SbF_5[129] or by ACF[70] at elevated temperature.



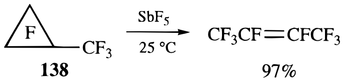
(111)

The reaction probably proceeds through the formation of cyclic carbocation **136** as an intermediate or transition state on the way to stable allyl cation **137a**,**b**. Allyl cations **137a**,**b** were recently observed by ^{19}F and ^{13}C NMR as long-lived species.[71]

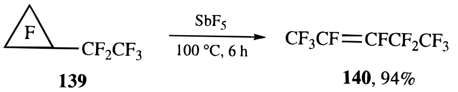


(112)

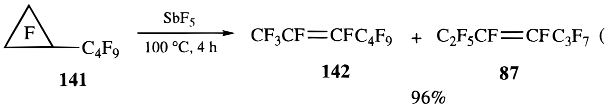
The nature of the substitutents has a significant effect on the reactivity of the cyclopropane. Reaction of *F*-methylcylopropane (**138**) with SbF_5[129] or with ACF[70] proceeds at only 20 °C, giving *F*-butene-2 instead of the *F*-isobutene expected from the mechanism above. Reaction of *F*-alkylcyclopropanes **139** and **141** with SbF_5 results in a high yield of linear fluoroolefins **140**, **142**, and **86** but requires prolonged heating to do so (see section IV.F.2 for the discussion of the migration of C=C in fluoroolefins).



(113)

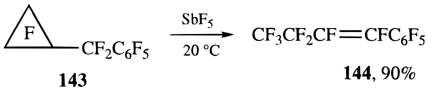


(114)



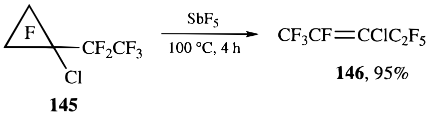
(115)

At the same time, reaction of *F*-benzylcyclopropane (**143**) with SbF_5 giving the olefin **144** is exothermic, strongly suggesting that the initial step is abstraction of a benzylic fluorine by the catalyst.



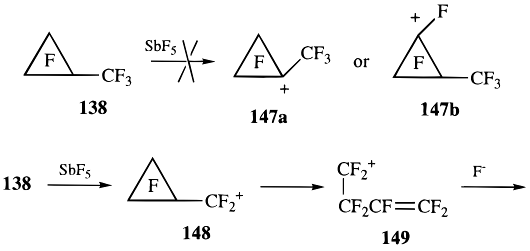
(116)

The presence of Cl rather than F α to the perfluoroalkyl substitutent does not alter the reaction course. Despite rather harsh conditions (100 °C), *F*-3-chloropentene-2 (**146**) was shown to be the only product of the reaction of **145** with SbF_5. The product of chlorine replacement *F*-pentene-2 does not form in this reaction.[129]



(117)

Experimental data obtained on the ring-opening reaction of alkylcyclopropanes **138**, **139**, **141**, **143**, and **145** indicate that the mechanism of this reaction is indeed different from that of isomerization of alkoxycyclopropanes **134a**,**b**. The pronounced ability of the nonfluorinated cyclopropane ring to stabilize a carbocationic center was demonstrated long ago.[130] Although there are no published experimental data on the ability of the polyfluorinated cyclopropane ring to stabilize a positive charge, it is reasonable to postulate that a perfluorinated cyclopropane ring is able to delocalize a positive charge, even though it may not be as effective as a nonfluorinated group. The mechanism proposed for the isomerization of *F*-alkylcyclopropanes[129] is based on this assumption. Using **138** as an example, the first step is ionization of the C−F bond leading to the formation of cyclopropylmethyl carbocation **148**, which is evidently more stable than cyclopropyl cations **147a**,**b**. The electrocyclic ring-opening reaction produces carbocation **149** and stabilization of the latter by addition of fluoride ion and a Lewis acid-catalyzed 1,3-fluorine shift leads to final product. Thus the sequence cyclopropanation of fluoroolefin and electrophilic isomerization of cyclopropane can be a useful tool for increasing the carbon chain of fluoroolefins by one CF_2 unit.

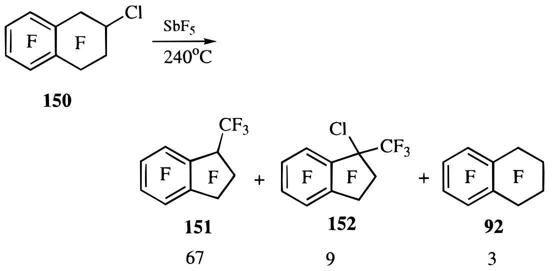


(118)

$$CF_3CF_2CF{=}CF_2 \xrightarrow{SbF_5} CF_3CF{=}CFCF_3 \qquad (119)$$

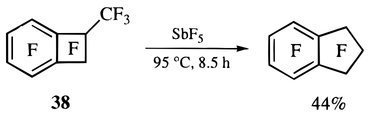
6. Rearrangements of Polyfluorinated Benzocycloalkanes

There is no report on the reaction of fluorinated cycloalkanes with strong Lewis acids. However, the effect of SbF_5 on benzocycloalkanes has been studied intensively. Early work in 1979 reported[131] ring contraction of *F*-2-chloro- (**150**) and *F*-2-bromotetralin to occur with SbF_5. For example tetralin **150** gave a mixture of indans **151** and **152** and small amounts of *F*-tetralin (**92**). Reactions of *F*-1,2-dichloro-, *F*-2,3-dichloro-, *F*-1,2,3,4-tetrachloro-, and *F*-1,1,4,4-tetrachlorotetralins with excess of SbF_5 give similar results.

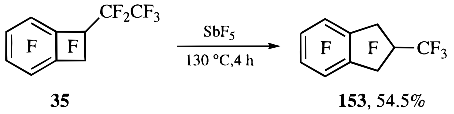


(120)

Heating fluorinated alkylbenzocyclobutanes with SbF_5 converts them into indans.[132−136] Thus the reaction of *F*-1-methylbenzocyclobutane (**38**) with SbF_5 results in formation of *F*-indan and reaction of *F*-1-ethylbenzocyclobutane (**35**) leads to *F*-2-methylindan (**153**).[132] It was also demonstrated that **153** is not formed by treatment of isomeric *F*-2-methylindan with SbF_5, indicating that not only does the indan nucleus tend strongly to form, but also that it is stable once formed.

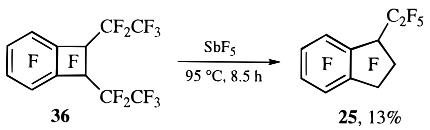


(121)



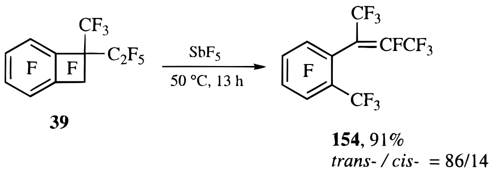
(122)

Dialkylbenzocyclobutane **36** does not react with SbF_5 at 50 °C, but at 95 °C gives a low yield of indan **25**.[136] The same reaction at higher temperature produces a complex mixture of six compounds.



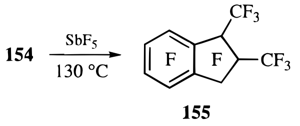
(123)

F-1-Methyl-1-ethylbenzocyclobutane (**39**) is more active toward SbF_5, affording styrene **154** in high yield at only 50 °C.[134]



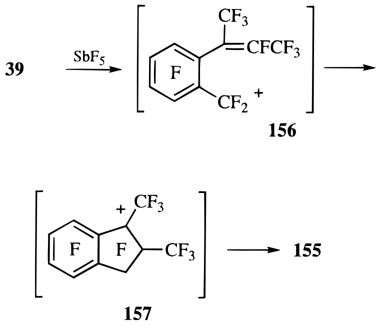
(124)

At higher temperature styrene **154** undergoes intramolecular cyclization to form *F*-1,2-dimethylindan (**155**).[133,134]



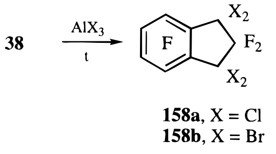
(125)

Similar formation of the corresponding styrenes as intermediates was observed in reactions of SbF_5 with *F*-1-ethyl-,[135] *F*-1-isopropyl-, *F*-1-methyl-1-isopropyl-, and *F*-1-methyl-2-isopropylbenzocyclobutanes.[136] The mechanism of cyclization of the styrenes involves formation of benzylic carbocation **156**, electrophilic intramolecular attack on the double bond, and stabilization of the intermediate cation **157** by addition of fluoride ion from the counteranion.



(126)

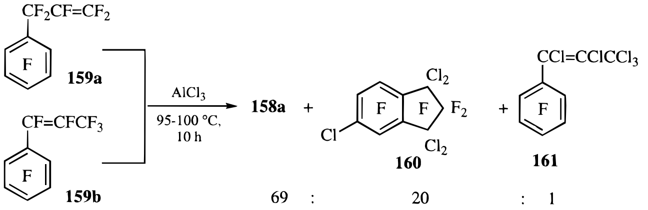
Aluminum chloride or bromide as catalyst with benzocyclobutane **38** also results in ring expansion, but not surprisingly the primary product, *F*-indan, exchanges benzylic fluorine with the aluminum halides giving tetrachloro or tetrabromo derivatives **158a**,**b** as major products.[132]



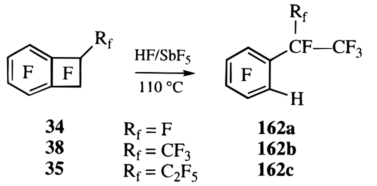
(127)

Ring closure reactions with formation of 5-membered rings have also been observed.[137] Interaction of either *F*-allyl- **159a** or *F*-propenylbenzene **159b** with aluminum chloride results in the formation of chloroindan **158a** as well as **160** and **161**.

As an aside, it has also been shown that *F*-benzocyclobutanes **34**, **38**, and **35** are sufficiently basic to be protonated by a solution of "$HSbF_6$" in HF, the products being *F*-*o*-*H*-alkylbenzenes **162a**−**c** from net addition of HF. The ease of reaction decreases in the order **34** > **38** > **35**. *F*-Dialkylbenzocyclobutanes, *F*-indan, and *F*-tetralin do not react with HF/SbF_5 under similar conditions.[138]



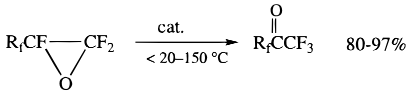
(128)



(129)

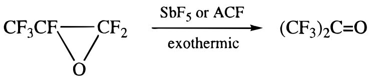
7. Heterocyclic Compounds

a. Oxiranes. Polyfluoro 1,2-epoxides are isomerized by strong Lewis acids into polyfluoro-2-alkanones, usually in high yield.



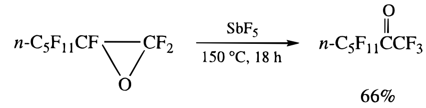
$$\mathrm{R_fCF\overset{}{\underset{O}{-}}CF_2} \xrightarrow[<20\text{–}150\ °C]{\text{cat.}} \mathrm{R_f\overset{O}{\overset{\|}{C}}CF_3} \quad 80\text{-}97\% \tag{130}$$

Conditions can vary greatly depending on the Lewis acid and the size of the fluoroalkyl group. Reaction of hexafluoropropene oxide either with SbF_5[139,140] or ACF,[70] for example, is exothermic and produces hexafluoroacetone.



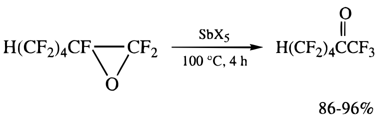
$$\mathrm{CF_3CF\underset{O}{-}CF_2} \xrightarrow[\text{exothermic}]{SbF_5\text{ or ACF}} \mathrm{(CF_3)_2C{=}O} \tag{131}$$

However, isomerization of *F*-1,2-epoxyheptane by SbF_5 proceeds only at elevated temperature.[139]



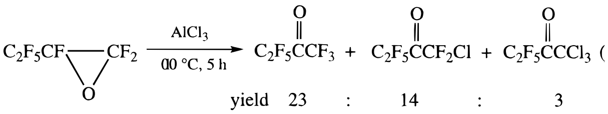
$$n\text{-}\mathrm{C_5F_{11}CF\underset{O}{-}CF_2} \xrightarrow[150\ °C,\ 18\ h]{SbF_5} n\text{-}\mathrm{C_5F_{11}\overset{O}{\overset{\|}{C}}CF_3} \quad 66\% \tag{132}$$

Both antimony pentafluoride and pentachloride were employed for isomerization of *F*-6-*H*-1,2-epoxyhexane.[141]



$$\mathrm{H(CF_2)_4CF\underset{O}{-}CF_2} \xrightarrow[100\ °C,\ 4\ h]{SbX_5} \mathrm{H(CF_2)_4\overset{O}{\overset{\|}{C}}CF_3} \quad 86\text{-}96\% \tag{133}$$

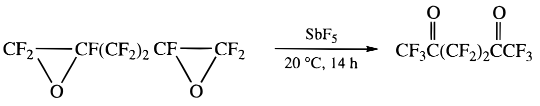
Aluminum chloride has also been used for the isomerization of 1,2-epoxides,[142] but the reaction does not have synthetic value since it leads to a mixture of chloro fluoro ketones formed by a secondary reaction of product ketone with $AlCl_3$ (see section IV.H.1 for halogen exchange reactions).



$$\mathrm{C_2F_5CF\underset{O}{-}CF_2} \xrightarrow[00\ °C,\ 5\ h]{AlCl_3} \mathrm{C_2F_5\overset{O}{\overset{\|}{C}}CF_3} + \mathrm{C_2F_5\overset{O}{\overset{\|}{C}}CF_2Cl} + \mathrm{C_2F_5\overset{O}{\overset{\|}{C}}CCl_3} \tag{134}$$

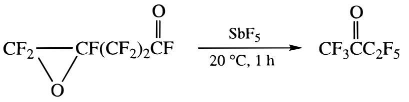
yield 23 : 14 : 3

Reactions of 1,2-epoxides with Lewis acids have been reviewed.[36] However, the development of new methods of preparation of fluoroepoxides by the reaction of fluoroolefins with sodium and calcium hypochlorites[143] or sodium hypobromite[144] has significantly increased the availability and hence the number of publications on reactions of fluorinated epoxides. As was shown recently, SbF_5 is an effective catalyst for the isomerization of diepoxides into diketones.[145] Mild reaction conditions and high yields of ketone **163** make this reaction attractive from a synthetic point of view.


(135)

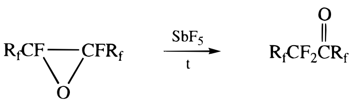
163, 95%

Interaction of **164** with SbF_5, despite mild reaction conditions, is accompanied by decarbonylation, and results in a high yield of ketone **165**.[145] This result is unusual, since linear perfluoroacyl fluorides (except $CF_3C(O)F$) undergo decarbonylation reactions only at elevated temperature.


(136)

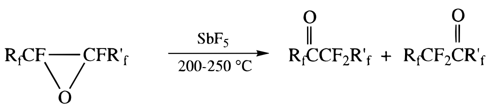
164 **165**, 78%

Epoxides of internal fluoroolefins are less reactive toward SbF_5, but usually can be converted into ketones at temperatures over 150 °C. Reaction of symmetrical epoxides leads to formation of only one product. The rate of isomerization depends on the size of perfluoroalkyl groups in the epoxide. Thus isomerization of **166** proceeds at 150 °C, but acceptable conversion of **168** into ketone can only be achieved at temperatures >200 °C.[146] *F*-Cyclohexene epoxide[147] is more easily rearranged than either **166** or **168**.


(137)

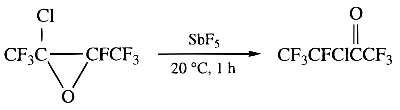
166 $R_f = CF_3$ **167**, 93%, t = 150 °C
168 $R_f = C_2F_5$ **169**, 95%, t = 250 °C

Epoxides containing two different perfluoroalkyl groups react with SbF_5 to produce a mixture of equal amounts of two isomeric ketones **170a**,**b** in high yields.[148] ACF is also an effective catalyst for such isomerizations, as has been demonstrated, for example, with *F*-2,3-epoxypentane.[70]


(138)

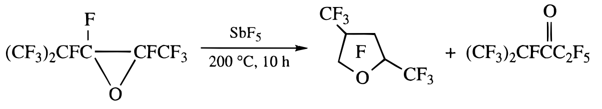
170a,b, 95-97%

Replacement of one of the fluorines in the ring with chlorine activates the epoxide toward the action of Lewis acid, so that isomerization of **171** into ketone **172** proceeds even at room temperature.[148]


(139)

171 **172**, 86%

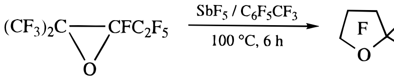
Reaction of oxide **173** with freshly distilled antimony pentafluoride, essentially free of trace HF, was recently shown to result in formation of a 1:1 mixture of oxolane **117** and ketone **116**[149] (see also section IV.F.4).


(140)

173 **117** **116**

yield of mixture 90%

Epoxides bearing three perfluoroalkyl groups attached to the ring are extremely resistant to the action of strong Lewis acids. No reaction was observed between **174** and SbF_5 at 300 °C.[150] However, later it was found that in the presence of SbF_5/C_6F_5-CF_3 system, epoxide **174** can be converted into oxolane **175** in high yield at only 100 °C.[122] This effect can be viewed as a result of intervention by cation **125** in a manner similar to that proposed for ketone cyclization (see section IV.F.4).

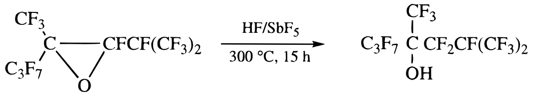

(141)

174 **175**, 83%

Very strong protic acids can also cause ring opening. With a mixture of hydrogen fluoride and SbF_5 at 300 °C, epoxides **174** and **176** added HF to give alcohols **177** and **178** in moderate yield.[150,151]

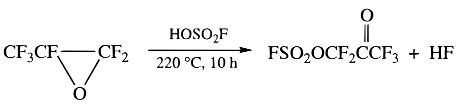
$$\mathbf{174} \xrightarrow[300\ ^\circ C,\ 12\ h]{HF/SbF_5} C_3F_7C(CF_3)_2OH \qquad (142)$$

177 40%


(143)

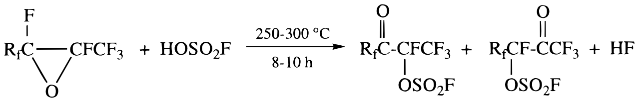
176 **178** 26%

Fluorosulfonic acid is able to add to **179** with ring opening at 200–220 °C without Lewis acid present.[152] In the presence of CrO_3, reaction proceeds to give **180** even at 25 °C and 1 atm.


(144)

179 **180**, 92%

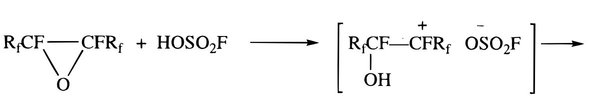
Epoxides of the internal fluoroolefins **181**–**183** react with $HOSO_2F$ at 250–300 °C giving 1:1 mixtures of two isomeric fluorosulfonato ketones.[153,154] Combination of this process with the known reaction of ketones **184a**,**b**–**186a**,**b** with CsF provides a convenient synthetic route to perfluoro-α-diketones that are otherwise difficult to obtain.



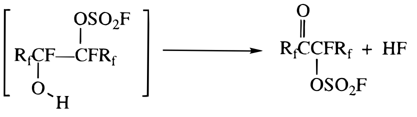
181 $R_f = -CF_3$ **184a**, **b**, 60%
182 $R_f = -C_2F_5$ **185a**, **b**, 55%
183 $R_f = -CF(CF_3)_2$ **186a**, **b**, 10%

(145)

The proposed mechanism for reactions of fluorinated epoxides with Lewis and protic acids includes coordination of Lewis acid with the oxirane oxygen (protonation in case of protic acid), ring opening with formation of carbocation **187** in the example, and stabilization of this species by addition of fluoride ion or counterion.[148] 1,2-Migration of fluorine in the cation is ruled out by calculational evidence[32] as well as by lack of precedent.

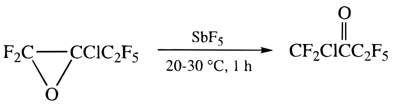


187



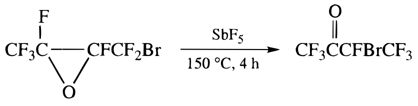
(146)

This mechanism accounts for the formation of equal amounts of isomeric ketones in reactions of nonsymmetrical epoxides. Additional evidence in favor of the carbocation mechanism is 1,2-migration of halogen atoms observed in isomerization of *F*-2-chloro-1,2-epoxybutane (**188**) and *F*-1-bromo-2,3-epoxybutane (**189**).[155]



(147)

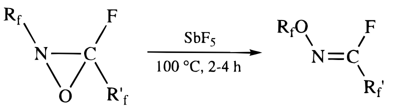
188 75%



(148)

189 20%

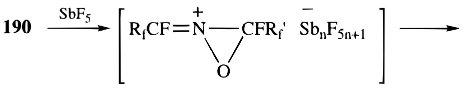
b. Oxaziridines, Diaziridines, Oxetanes. The simplest perfluorooxaziridine, *F*-2-methyloxaziridine, produces a dimer of unknown structure on heating with SbF_5.[156] However, as was shown recently, higher homologs oxaziridines **190** rearrange with SbF_5.[157] Reaction proceeds at 100 °C and results in formation of the corresponding alkoxyimines as single products. No evidence was found for the formation of dimeric products or nitrones, as reported[158] for the reaction of certain hydrocarbon oxaziridines with Lewis and protic acids.



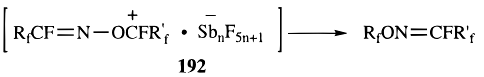
(149)

190 88-91%

The mechanism of the isomerization is similar to that proposed for the isomerization of cyclic tertiary perfluoroamines by SbF_5[159] (see section IV.F.7.c) and involves formation of immonium cation **191** as a result of abstraction by SbF_5 of fluoride from the CF_2 group, then ring opening leading to formation of final product through carbocation **192**.



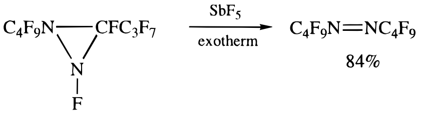
191



(150)

192

Perfluorodialkyldiaziridine (**193**) undergoes isomerization into *F*-azobutane in contact with SbF_5.[127]

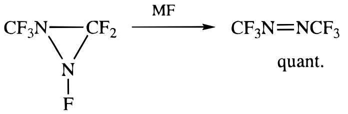


(151)

84%

193

The isomerization of *F*-*N*-methyldiaziridine into hexafluoroazomethane, observed earlier[160] upon contact with metals pretreated with fluorine gas, may well be in the same category, fluorides of Ni, Cr, or Fe being responsible for the isomerization.

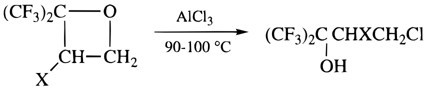


(152)

quant.

194

The reaction of 2,2-bis(trifluoromethyl)polyfluorooxetanes with $AlCl_3$ was published several years ago.[161] In most cases ring-opening reactions are accompanied by formation of chlorine-containing products.



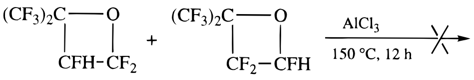
(153)

194a X = H **195a**, 45%
194b X = CF_3 **195b**, 48%

Fluorooxetane **51a** containing two fluorines on the ring produces with $AlCl_3$ a mixture of dichlorooxetane **52a** and dichlorovinyl carbinol **52b**. Further accumulation of fluorines in the oxetane drastically decreases its reactivity toward $AlCl_3$; isomeric oxetanes **46** and **196** do not interact with $AlCl_3$ even on prolonged heating.

$$\mathbf{51a} \xrightarrow[70\ ^\circ C,\ 8\ h]{AlCl_3} \mathbf{52a} + \mathbf{52b}, \quad (154)$$

yield 25% 20%



(155)

46 **196**

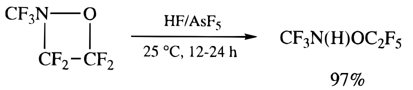
A few years ago the preparation of alcohol **197** was reported, on the basis of ring opening of *F*-2,2-dimethyloxetane (**45**) by a mixture of HF and SbF_5.[162]

Reaction proceeds under relatively mild conditions and produces alcohol **197** in excellent yield. At room temperature this reaction is slow (11% conversion after 36 h) and other Lewis acids, such as AsF_5, are not active. Interestingly, oxetane **45** is much more active in this reaction than perfluorinated epoxide **174** (see previous section) which produces the closely related alcohol **177** in moderate yield only at 300 °C.[150]

$$\mathbf{45} \xrightarrow[55\ ^\circ C,\ 17\ h]{HF/SbF_5} C_2F_5C(CF_3)_2OH \qquad (156)$$

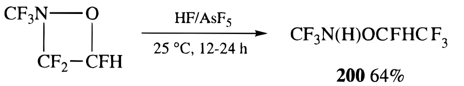
197, 90%

This reaction was also used for conversion of polyfluorinated oxazetidines into derivatives of hydroxylamines. In contrast to the result with oxetane, AsF_5 gave better yields of the products than SbF_5, and even BF_3 showed some catalytic activity. The ratio of heterocyclic compound to Lewis acid is also said to be important, and the best result was achieved when a 2-fold molar excess of AsF_5 to **198** was used.[162]

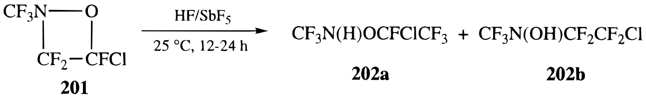


198 97% (157)

Reaction of monohydrooxazetidine **199** with HF/AsF_5 is straightforward, giving only **200**, isolated in 64% yield. However, the ring-opening reaction of chlorooxazetidine **201** under similar conditions leads to formation of two isomers **202a**,**b**.



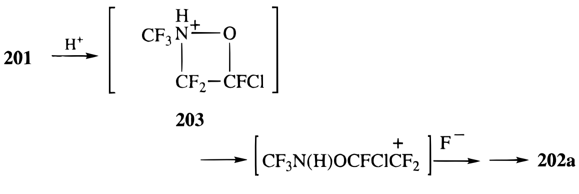
199 **200** 64% (158)



201 **202a** **202b**

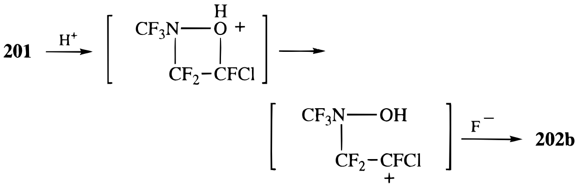
Yield 37% 27% (159)

The mechanism for the ring opening probably involves protonation of nitrogen by the strong acid and rearrangement of the resulting ammonium cation **203** into carbonium ion **204**. Stabilization of this species by addition of F^- leads to the final product.



203 **204** (160)

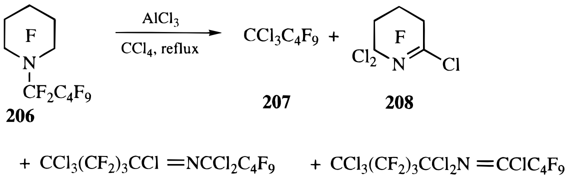
In the case of chlorooxazetidine **201**, isomeric product **202b** is probably the result of a concurrent process, protonation of oxygen and ring opening, which leads to the formation of **202b** through carbocation **205** as intermediate.



205 (161)

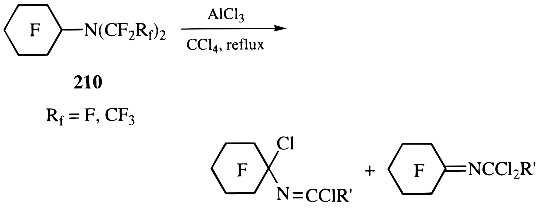
c. Cyclic Amines. Despite the well-known chemical inertness of perfluorinated tertiary amines, these compounds will react with strong electrophiles such as SO_3[163] or H_2SO_4.[164]

Reaction of aluminum chloride with *F*-*N*-amylpiperidine (**206**) was reported in the 1960s to cause ring opening with concomitant Cl/F exchange.[165,166] Reaction proceeds at 60−70 °C in CCl_4 as solvent and leads to a mixture of small amounts of trichloropentane **207** and cyclic imine **208** along with two isomeric products of ring opening, imidoyl chlorides **209a**,**b**, isolated in 65−70% yield. The ring-opening reaction of perfluorinated *N*-alkylpiperidines and -pyrrolidines[167,168] by $AlCl_3$ followed by alkaline hydrolysis of the imidoyl chlorides was used to determine the structure of cyclic amines obtained from electrochemical fluorinations.



206 **207** **208** **209a** **209b** (162)

Reaction between perfluorinated trialkylamines **210** and $AlCl_3$ proceeds differently through a stage of dealkylation and results in the formation of a mixture of isomeric imidoyl chloride **211a** and imine **211b**.[169,170]



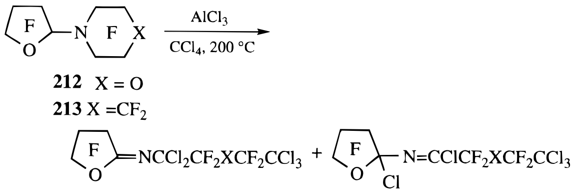
210

R_f = F, CF_3

211a **211b** (163)

R' = Cl, CF_3

Higher reactivity toward $AlCl_3$ of cyclic amines compared to cyclic ethers was demonstrated in reactions of perfluorinated aminotetrahydrofurans **212** and **213**.[171]



212 X = O
213 X =CF_2

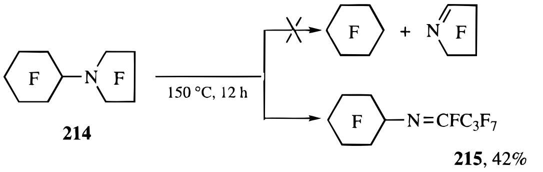
(164)

A unique reaction of imidoyl chlorides **209a**,**b** with excess of SbF_5 or a mixture of SbF_5/HF is the only known example of intramolecular cyclization involving a C=N bond. Reaction gives piperidine **206** in 70−80% yield. A necessary condition of this reaction appears to be the presence of terminal CCl_3 and C=N groups in the same molecule.[165,166] Attempts to prepare tertiary amines from imidoyl chlorides having no terminal CCl_3 groups failed.

$$\mathbf{209\ a,b} \xrightarrow{SbF_5,\ 160\ °C} \mathbf{206} \qquad (165)$$

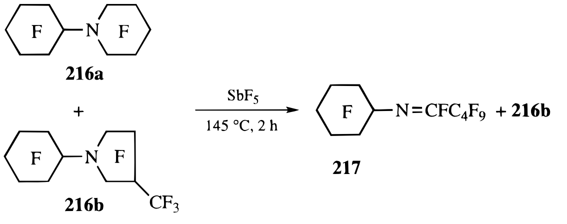
70-80%

Tertiary perfluoroalkyl amines do not react with Lewis acids such as $TiCl_4$, $SbCl_5$, $SnCl_4$, and $FeCl_3$ up to 160 °C.[165,166] However, SbF_5 was recently found to be a true isomerization catalyst for heterocyclic perfluoro-*N*-cycloalkylamines, affording the corresponding imidoyl fluorides at about 150 °C.[172] Reaction of *F*-*N*-cyclohexylpyrrolidine (**214**) with SbF_5 requires a higher temperature than the reaction of aliphatic fluorinated amines (see section IV.G.3). The reaction gives imine **215** cleanly, with no products of a dealkylation reaction, *F*-1-azapentene or *F*-cyclohexane being formed.



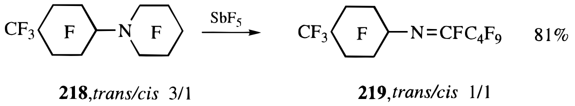
(166)

Unsubstituted cyclic amines appear to be more active in the reaction with antimony pentafluoride. Thus, a mixture of **216a**,**b** exposed to SbF_5 at 140−145 °C gave isomerized *N*-cyclohexylpiperidine **217**, while *N*-methylpyrrolidine **216b** was recovered unchanged.

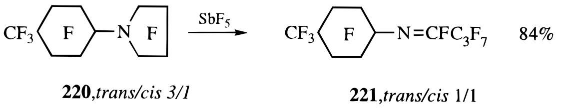


(167)

On the other hand, the presence of a perfluoroalkyl group in the alicyclic fragment of the molecule does not interfere with isomerization; no difference was found in the reactivity of amines **218** and **220** at 140−160 °C. This reaction is sterospecific, giving only *anti* isomers of the imidoyl fluorides **219** and **221**. *Cis*−*trans* isomerization in the substituted cylohexane fragment also accompanied this reaction; the ratio of *trans* and *cis* isomers changed from 3:1 to 1:1 in the course of the reaction. Another interesting feature of the reaction of perfluoroamines with SbF_5 is that only amines with an alicyclic fragment connected to nitrogen undergo isomerization. Perfluoroalkylpiperidines with SbF_5, in sharp contrast to their reaction with $AlCl_3$ (see above), undergo cleavage with loss of perfluoroalkane and formation of cyclic imine (see section IV.G.3, eq 198).



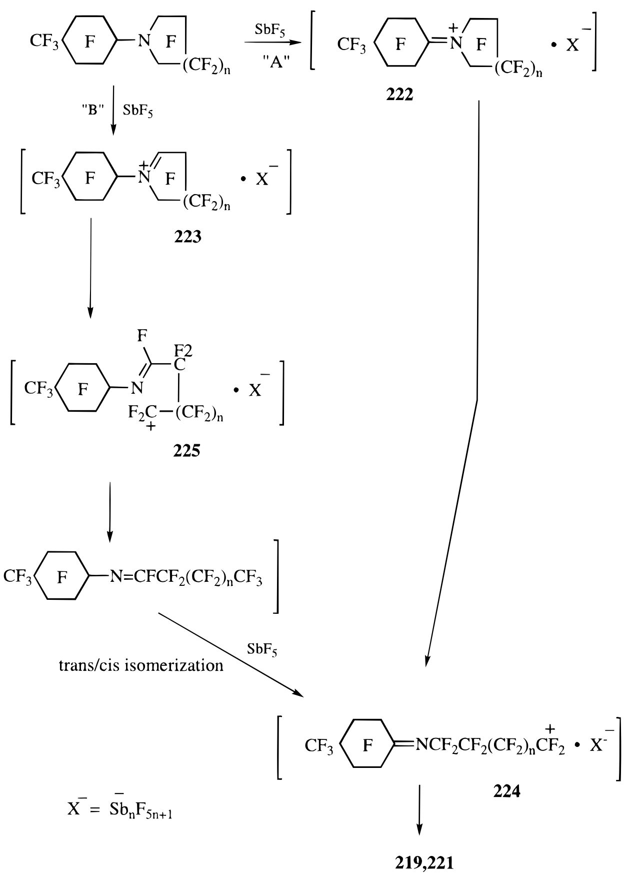
(168)



(169)

Isomerization of cyclic amines **214**, **216**, **218**, and **220** induced by SbF_5 involves formation of iminium cation **222** (route "A") or **223** (route "B") and isomerization of this intermediate into the carbocation **224** or **225**[172] (Scheme 5).

Scheme 5



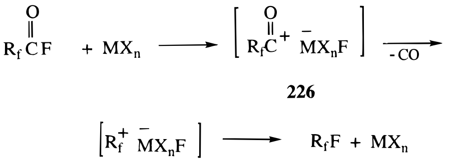
Reaction of imminium cation **224** with counteranion is probably responsible for the observed *cis*−*trans* isomerization. Cation **224** clearly has one planar section at the exocyclic carbon−nitrogen double bond. The addition of fluoride ion to it can proceed equally well from the top or from the bottom, which leads to the formation of equal amounts of *trans* and *cis* isomers.

G. Elimination Reactions

1. Decarbonylation

Perfluorinated acyl fluorides are resistant to the action of strong Lewis acids and usually do not interact with them at 20−50 °C,[86] but at higher temperatures they have a tendency to lose CO.[60,173] The generalized mechanism includes ionization of the acyl fluoride C−F bond to generate acylium cation

226, which then readily loses CO. Perhaps the most effective catalyst is SbF_5.

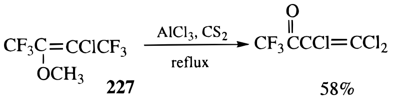


$$\mathrm{R_f}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} + \mathrm{MX_n} \longrightarrow \underset{\mathbf{226}}{\left[\mathrm{R_f}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{+}\ \overset{-}{\mathrm{MX_nF}}\right]} \xrightarrow[-\mathrm{CO}]{}$$

$$\left[\mathrm{R_f^+}\ \overset{-}{\mathrm{MX_nF}}\right] \longrightarrow \mathrm{R_fF} + \mathrm{MX_n} \qquad (170)$$

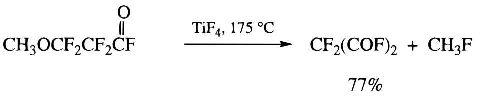
2. Cleavage of Ethers, Esters, and Anhydrides

Perfluorinated cyclic and linear ethers are usually more stable toward Lewis acids than perfluoroacyl fluorides or perfluorinated amines (see sections IV.G.1 and IV.G.3) and react, for example with $AlCl_3$, only at 175−220 °C.[174,175] However, partially fluorinated ethers are much more sensitive to electrophilic reagents, and primary ethers can be readily converted into esters by the action of H_2SO_4[176] and cleaved to acyl chlorides[177] or acyl fluorides[178] by the action of $HOSO_2Cl$, $HOSO_2F$, or SO_3. Aluminum chloride was shown to cleave secondary fluorinated vinyl ether **227** at low temperature,[179] but $AlCl_3$ is also prone to exchanging chlorine for fluorine.



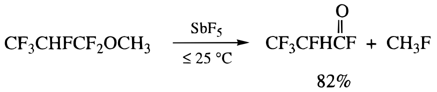
$$\underset{\mathbf{227}}{\mathrm{CF_3}\underset{\mathrm{OCH_3}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CClCF_3}} \xrightarrow[\text{reflux}]{\mathrm{AlCl_3,\ CS_2}} \underset{58\%}{\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CCl{=}CCl_2}} \qquad (171)$$

This secondary reaction is avoided when fluoride catalysts are used. Titanium tetrafluoride at 175 °C cleaves *F*-3-methoxypropionyl fluoride into CH_3F and *F*-malonyl fluoride, isolated in 77% yield.[180]

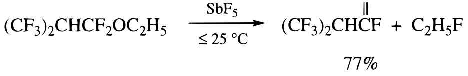


$$\mathrm{CH_3OCF_2CF_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} \xrightarrow{\mathrm{TiF_4,\ 175\ ^\circ C}} \underset{77\%}{\mathrm{CF_2(COF)_2 + CH_3F}} \qquad (172)$$

A number of fluorides have been found to be active catalysts for this type of the reaction.[181] Antimony pentafluoride is one of the most effective catalysts, as it was shown to cause cleavage of polyfluorinated ethers at room temperature or below. The reaction is exothermic, can be run neat, and usually evolves alkyl fluoride as a gas.

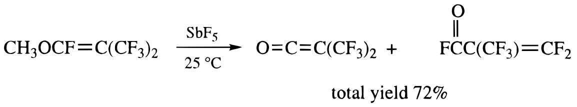


$$\mathrm{CF_3CHFCF_2OCH_3} \xrightarrow[\le 25\ ^\circ\mathrm{C}]{\mathrm{SbF_5}} \underset{82\%}{\mathrm{CF_3CFH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F}} + \mathrm{CH_3F} \qquad (173)$$



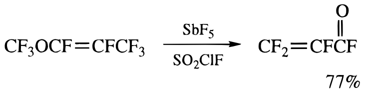
$$\mathrm{(CF_3)_2CHCF_2OC_2H_5} \xrightarrow[\le 25\ ^\circ\mathrm{C}]{\mathrm{SbF_5}} \underset{77\%}{\mathrm{(CF_3)_2CH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F}} + \mathrm{C_2H_5F} \qquad (174)$$

The reaction of terminal vinyl ethers with SbF_5 leads, depending on the structure, to formation of acryloyl fluorides and/or ketenes. Equations 175 and 176 provide examples.



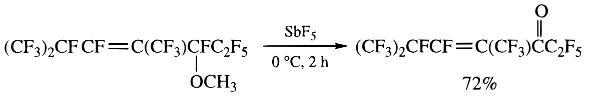
$$\mathrm{CH_3OCF{=}C(CF_3)_2} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{SbF_5}} \mathrm{O{=}C{=}C(CF_3)_2} + \mathrm{F}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{C(CF_3){=}CF_2} \qquad (175)$$

total yield 72%



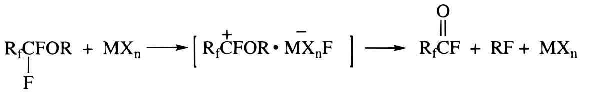
$$\mathrm{CF_3OCF{=}CFCF_3} \xrightarrow[\mathrm{SO_2ClF}]{\mathrm{SbF_5}} \underset{77\%}{\mathrm{CF_2{=}CF}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F}} \qquad (176)$$

Fluorinated vinyl ketones can be prepared by reactions of higher unsaturated ethers with antimony pentafluoride,[90] for example:



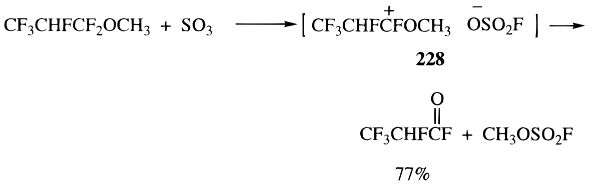
$$\mathrm{(CF_3)_2CFCF{=}C(CF_3)}\underset{\mathrm{OCH_3}}{\underset{|}{\mathrm{C}}}\mathrm{FC_2F_5} \xrightarrow[0\ ^\circ\mathrm{C},\ 2\ \mathrm{h}]{\mathrm{SbF_5}} \underset{72\%}{\mathrm{(CF_3)_2CFCF{=}C(CF_3)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{C_2F_5}} \qquad (177)$$

The generally accepted mechanism for these reactions, proposed in ref 181, is heterolysis of a C−F bond α to ether oxygen initiated by coordination of Lewis acid to F, followed by loss of alkyl cation.



$$\mathrm{R_f}\underset{\mathrm{F}}{\underset{|}{\mathrm{C}}}\mathrm{FOR} + \mathrm{MX_n} \longrightarrow \left[\mathrm{R_f}\overset{+}{\mathrm{C}}\mathrm{FOR}\cdot\overset{-}{\mathrm{MX_nF}}\right] \longrightarrow \mathrm{R_f}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F} + \mathrm{RF} + \mathrm{MX_n} \qquad (178)$$

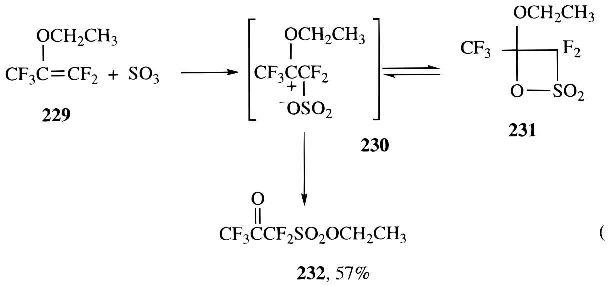
Cleavage of saturated ethers by SO_3 is not catalytic, since it is accompanied by the formation of alkyl fluorosulfate, providing confirmation of the presence of an intermediate cation such as **228**.[178]



$$\mathrm{CF_3CHFCF_2OCH_3 + SO_3} \longrightarrow \underset{\mathbf{228}}{\left[\mathrm{CF_3CHF}\overset{+}{\mathrm{C}}\mathrm{FOCH_3}\ \ \overset{-}{\mathrm{OSO_2F}}\right]} \longrightarrow$$

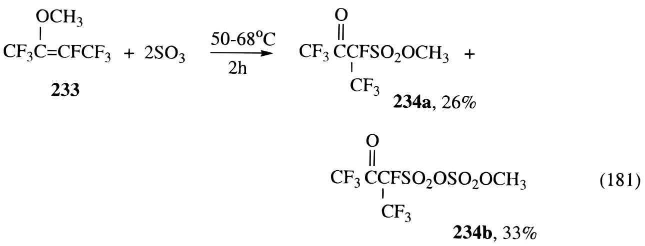
$$\underset{77\%}{\mathrm{CF_3CHF}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{F}} + \mathrm{CH_3OSO_2F} \qquad (179)$$

The methyl fluorosulfate, itself a potent methylating agent, arises from methylation of fluorosulfate anion by cation **228**, an even stronger methylating agent. This interpretation is confirmed by results reported with fluorovinyl ethers and SO_3. Acyclic ethers tend to undergo facile cycloadditions with SO_3 at low temperature, but the cycloadducts are unstable near 0 °C and rearrange to ketofluoroalkyl sulfonate esters.[182] For example, vinyl ether **229** cycloadds SO_3 exothermically and with a regiospecificity opposite to that of *F*-propene to give sultone **231**. At temperatures near 25 °C, the zwitterionic intermediate **230** is evidently in equilibrium with sultone, allowing the very reactive cationic center to transfer ethyl cation to the sulfonate group, giving the final product.

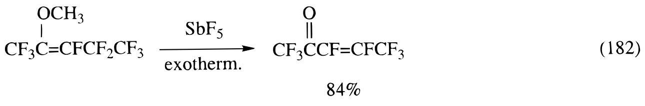


(180)

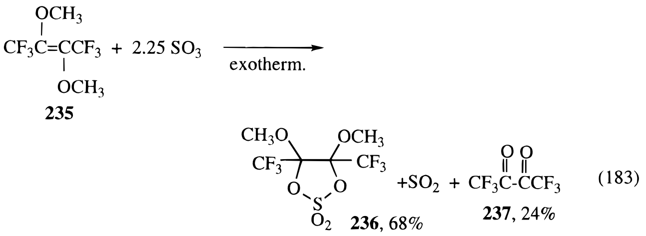
Fluorovinyl ethers having an internal double bond react similarly with SO_3 to form ketofluoroalkyl sulfonate esters, e.g. **234a** from **233**. In this case, excess of SO_3 and heating were required to promote reaction; mixed anhydride **234b** was also obtained due to the excess of SO_3 employed.[182]



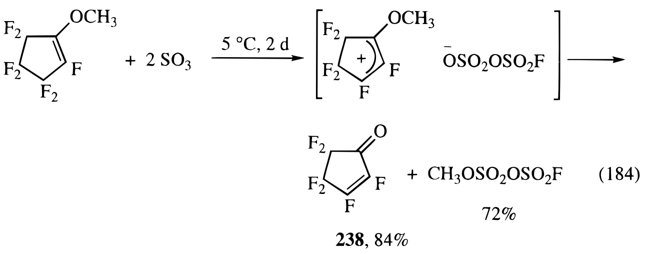
In contrast, as indicated above, SbF_5 cleanly converts an internally unsaturated fluorovinyl ether to the vinyl ketone. An example using an unbranched vinyl ether is shown in eq 182.



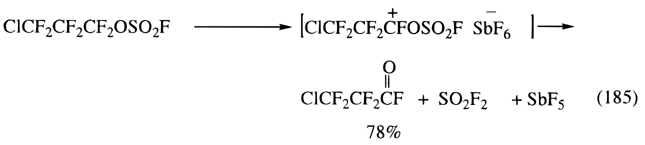
Yet another reaction path was observed on treatment of the vinylic dimethoxy ether **235** with SO_3.[182] The reaction provides a good route to *F*-biacetyl (**237**), since cyclic sulfate **236** is converted to **237** in high yield by heating with concentrated H_2SO_4.



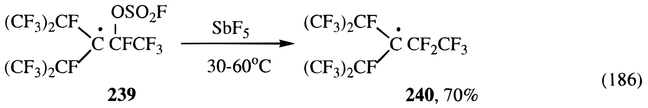
Surprisingly, cyclic fluorovinyl ethers are also cleaved by SO_3, but follow a different reaction path involving abstraction of allylic fluorine by SO_3, then intermolecular transfer of the alkyl group with formation of α,β-unsaturated ketones such as **238**.[183] No indication of sulfonated products was found.

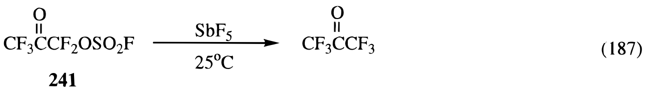


Cleavage of fluorosulfato esters can generally be accomplished by warming with a catalytic amount of SbF_5. Primary polyfluoroalkyl fluoro sulfates give acid fluorides and an equivalent amount of SO_2F_2.[184] This transformation is viewed as being initiated by coordination of SbF_5 to fluorine α to oxygen, labilizing the fluorine with development of a carbocationic center, as illustated in eq 185.

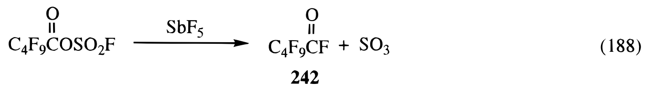


The presence of substituents strongly destabilizing to an adjacent cationic center, however, appears to redirect attack of SbF_5 to the fluorosulfato fluorine, leading to loss of SO_3. Such behavior was noted for the perfluorinated radical **239**[185] and for fluoroacetonyl fluorosulfate **241**.





Polyfluoroacyl fluorosulfates bear no fluorine on carbon α to oxygen, so their interaction with SbF_5 also occurs at the fluorosulfato fluorine atom and leads to polyfluoroacyl fluorides such as **242** and sulfur trioxide.



$$C_4F_9C(O)OSO_2F \xrightarrow{SbF_5} C_4F_9C(O)F + SO_3 \quad (188)$$

This is a catalyzed, low-temperature version of the known thermal dissociation which is reversible at lower temperatures and can be used to synthesize polyfluoroacyl fluorosulfates (see section IV.H.2).

A case of SbF_5 catalyzed elimination that proceeds through coordination to oxygen appears to be that of the conversion of triflic anhydride to trifluoromethyl triflate.[186]

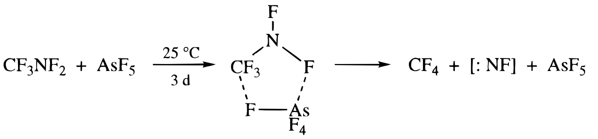
$$(CF_3SO_2)_2O \xrightarrow{SbF_5} CF_3SO_2OCF_3 \qquad (189)$$

3. Cleavage of Amines

Perfluorinated amines are essentially neutral compounds of pH 7 due to the strong electron-withdrawing effect of the perfluoroalkyl groups, which drastically reduce electron density at nitrogen. Even so, the presence of an unshared electron pair on nitrogen is reflected in activation of fluorine atoms in the position α to nitrogen, much the same as in polyfluoro ethers. As a result, a number of reactions with strong electrophiles are known for fluorinated amines. Examples of reactions with strong Lewis acids have now been found for practically all groups of polyfluoroamines, including CF_3ONF_2, SF_5NF_2, $ClNF_2$,[187] R_f-NF_2,[126] $(R_f)_2NF$, and $(R_f)_3N$.[188-191] All have basically the same mechanism involving coordination of Lewis acid at fluorine to form a positively charged nitrogen species, then decomposition of the intermediate into perfluoroalkane and either a stable nitrogen-containing transient species (for example, :N−F) or an imine. In the case of perfluoroamines containing the $-NF_2$ group, reaction starts with ionization or polarization of a weak N−F bond.

$$R_fNF_2 \longrightarrow \left[R_f\overset{+}{N}F\right] \longrightarrow R_fF + [:NF] \longrightarrow FN{=}NF \qquad (190)$$

As proposed in ref 187, the actual mechanism of decomposition of R_fNF_2 by Lewis acids likely involves formation of a bimolecular cyclic complex and transfer of fluorine inside the complex to produce the observed products. Perfluorinated amines containing the NF_2 group are extremely sensitive to the action of Lewis acids. Thus CF_3NF_2 slowly decomposes under the action of AsF_5 even at −78 °C.[187] At ambient temperature the reaction results in almost quantitative formation of CF_4 and N_2F_2.


(191)

N_2F_2 exists as a mixture of *cis* and *trans* isomers, but only the *cis* isomer forms an adduct with AsF_5.[187] In this reaction of gaseous *trans*-N_2F_2 and the salt $N_2F^+AsF_6^-$ was rationalized by postulating formation of both isomers.

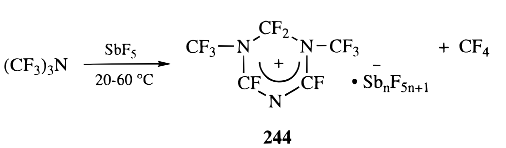
Secondary perfluoroamines are even more stable toward the much stronger Lewis acid, SbF_5. An increase in the number of perfluoroalkyl groups attached to N increases the strength of the N−F bond and, in the case of perfluorodialkylamines, causes reaction with SbF_5 to proceed via ionization of a C−F bond of an α-CF_2 group. Reaction between $(R_f)_2NF$ and antimony pentafluoride carried out at 70−100 °C resulted in formation of perfluoroalkane and *N*-fluoroimine.[126]

$$R_f'CF_2N(F)R_f \xrightarrow[\text{70-100 °C, 10-12 h}]{SbF_5} [R_f'CF{=}\overset{+}{N}(F)R_f\ \overset{-}{Sb_nF_{5n+1}}] \longrightarrow \underset{\text{20-80\%}}{R_fF + R_f'CF{=}NF} \qquad (192)$$

Secondary amines with a branched substituent are more active in this reaction. Exothermic reaction was observed when amine **243** was treated with SbF_5, giving hexafluoroethane and *F*-2-azabutene-2 (**130**).[126] As was demonstrated, this reaction involves formation of the *N*-fluoroimine of hexafluoroacetone **129** and isomerization of this intermediate into **130** (see section IV.F.4 for details).

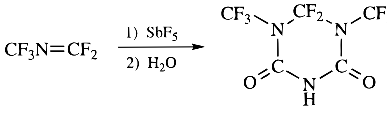
$$\underset{\mathbf{243}}{(CF_3)_2CF\,N(F)C_2F_5} \xrightarrow[\text{exotherm}]{SbF_5} C_2F_6 + \underset{\mathbf{130}}{CF_3N{=}CFCF_3} \qquad (193)$$

Reaction of *F*-trimethylamine with SbF_5 proceeds even at room temperature, producing CF_4 and salt **244** in nearly quantitative yield.[188]


(194)

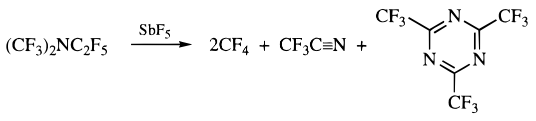
244

Salt **244** forms as a result of trimerization of *F*-2-azapropene, which is a primary product from cleavage of starting amine. Cyclic imide **245** was isolated from a reaction of *F*-2-azapropene with SbF_5 after hydrolysis of the reaction mixture.[192]


(195)

245

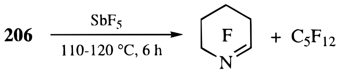
Tertiary amines having two CF_3 groups tend to lose both as CF_4. For example, *F*-dimethylethylamine reacts with SbF_5 to form a mixture of CF_4, CF_3CN, and triazine **246**.[188]


(196)

246

Higher tertiary amines are even less reactive toward antimony pentafluoride. Reasonable rates of reaction can be achieved at 120−130 °C to give a mixture of perfluoroalkane and imidoyl fluoride **247**. Perfluoro-*N*-alkylpiperidines with SbF_5 eliminate the N-alkyl group to form cyclic imine (eq 198).[190]

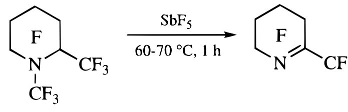
$$R_f'CF_2N(R_f)_2 \xrightarrow[\text{120-130 °C}]{SbF_5} R_fF + \underset{\substack{\mathbf{247}\\ \text{60-67\%}}}{R_f'CF{=}NR_f} \qquad (197)$$


(198)

80%

Reaction of SbF_5 with amines containing one CF_3−N fragment proceeds at a lower temperature and results in elimination of CF_4.[190,191] There are several examples which clearly show that the rate of reaction with SbF_5 for cyclic amines containing α-fluorine attached to tertiary carbon is much enhanced, as was seen earlier with acyclic tertiary amines. These two effects combine to make amine **248**[191] the most readily reacted isomer among other *F*-dimethylpiperidines.

$$(C_4F_9)_2NCF_3 \xrightarrow[\text{100 °C, 2 h}]{SbF_5} CF_4 + \underset{\text{92\%}}{C_3F_7CF{=}NC_4F_9} \qquad (199)$$


(200)

248

4. Dehydrofluorination by Lewis Acids

The tendency of polychloroalkanes to lose HCl in reactions catalyzed by $AlCl_3$ was discovered by Prins.[20]

$$CCl_3CHClCCl_3 \xrightarrow[\text{70-90 °C}]{AlCl_3} \underset{\text{90\%}}{CCl_3CCl{=}CCl_2} \qquad (201)$$

Polyfluoroalkanes are generally more resistant to the action of acids, but there are several reported examples of this type of reaction. Di- and polyhydrofluoroalkanes with SbF_5 at elevated temperatures are reported to form olefins.[193−195]

Both of these types of elimination of HF probably involve formation of carbocations as intermediate. In fact, the formation of quite stable[195] polyfluorinated allyl (**249**, $n = 1$) and polyenyl cations (**249**, $n = 2, 3$) as a result of the action of SbF_5 on fluoroalkanes has been reported. These cations were generated by

$$(CF_3)_2CFCH_2CF_3 \xrightarrow[120\ °C,\ 2\text{-}3\ h]{SbF_5} \underset{100\%}{(CF_3)_2C{=}CHC_2F_5} \quad (202)$$

$$(CF_3)_2CFCH_2CF_2CF_2CH_2CF(CF_3)_2 \xrightarrow[120\ °C,\ 3\ h]{SbF_5}$$

$$\underset{(100\%)}{(CF_3)_2C{=}CHCF_2CF_2CH{=}C(CF_3)_2} \quad (203)$$

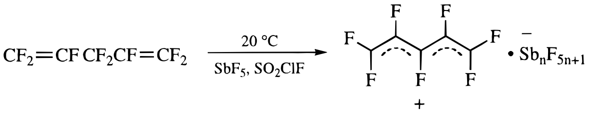
preparing uniform solutions of starting material in excess of antimony fluoride.

$$(CF_3)_2CFCH_2CF_2(CH_2CF_2)_nCH_2CF_3 \xrightarrow{SbF_5}$$

$$(CF_3)_2CFCH_2\overset{+}{C}F(CH{=}CF)_nCH_2CF_3 \bullet \overset{-}{Sb_n}F_{5n+1} \quad (204)$$

249, n = 1, 2, 3

Reported values of ^{19}F and ^{13}C chemical shifts and coupling constants of polyfluorinated allyl cation (**249**, $n = 1$) are in good agreement with those found for polyfluorinated allyl cations.[5] Structurally related longer chain alkanes appear to lead to the generation of cations (**249**, $n = 2, 3$),[195] the second and third long-lived polyfluorinated polyenyl cations to be reported. The first stable *F*-pentadienyl cation **250**, generated by action of SbF_5 on perfluoropentadiene-1,4 in SO_2ClF as a solvent, was reported two years earlier[73] (see section IV.F.2).



(205)

250

Perfluorinated cation **250** exists in solution as *F*-pentadienyl monocation in *s-trans*–*s-trans* configuration. However, on the basis of the ^{19}F and ^{13}C NMR data indicating a high symmetry, diallyl dication structure **252** was assigned to the product derived from the reaction of **251** with excess of SbF_5.[195] Structural factors clearly dictate preferential formation of mono- or dicationic products.

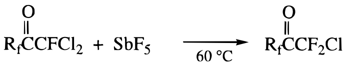
$$\underset{\mathbf{251}}{[(CF_3)_2CFCH_2CF_2CH_2CF_2]_2} \xrightarrow{SbF_5}$$

$$\underset{\mathbf{252}}{\left[(CF_3)_2CFCH_2\text{—}\overset{+}{\overline{CFCHCF}}\right]_2} \bullet 2\ \overset{-}{SbF_6} \quad (206)$$

H. Electrophilic Replacement of Activated Fluorine

1. Halogen Exchange

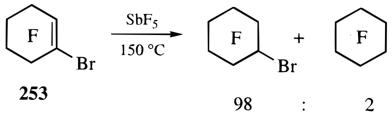
Introduction of fluorine by exchange reactions with organic halides is a well-studied reaction and numerous publications on the subject continue to appear. Replacement of chlorines in chloroorganic materials (readily available from exhaustive chlorination of the parent organic compounds) by reaction with anhydrous HF or antimony fluorides in the presence of Lewis acids is the process widely employed for preparation of fluorinated materials on a commercial scale. Summaries of such methods of fluorination can be found in refs 22 and 196. Neat antimony pentafluoride is also an effective reagent for replacement of moderately reactive Cl or Br atoms. For example, it was recently used for selective preparation of α-haloperfluoro-2-ketones by fluorination of α,α-dihaloperfluoroketones.[197]



$$R_f\overset{\overset{O}{\|}}{C}CFCl_2 + SbF_5 \xrightarrow[60\ °C]{} R_f\overset{\overset{O}{\|}}{C}CF_2Cl \qquad 78\text{-}88\% \qquad (207)$$

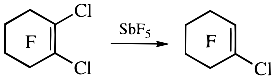
$R_f = CF_3, CF_2Cl, C_2F_5, C_3F_7, C_7F_{15}$

Reaction of *F*-1-bromocyclohexene (**253**) with SbF_5 at high temperature proceeds with fluorination of the C=C bond but with only a trace of *F*-cyclohexane produced as byproduct.[198]



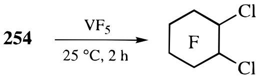
253 (208)

However, *F*-1,2-dichlorocyclohexene (**254**) with SbF_5 under similar conditions gives the product of replacement of one vinyl chlorine, cyclohexene **255**, as the sole product.



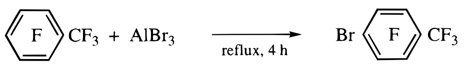
254 **255**, 46% (209)

Saturation of the double bond in cylohexene **254** without halogen replacement is best accomplished with VF_5,[16] since this reaction proceeds at room temperature and gives the desired product in high yield. Since VF_5 is a very weak Lewis acid, it does not cause an exchange reaction to occur. The mechanism proposed for fluorination of C=C bonds with VF_5 involve a single electron transfer from unsaturated substrate to vanadium pentafluoride as the initial step.[114]



89% (210)

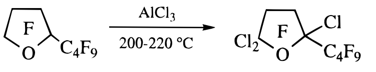
Interaction of fluorinated materials containing activated fluorines with aluminum halides AlX_3 results in the reverse exchange reaction, replacement of fluorine atoms with halogen. Reaction of HFP with $AlCl_3$ is not selective and results in formation of a mixture of chlorofluoropropenes, tending to give *F*-2-chloropropene as final product after exchange of all allylic fluorines.[199] However, in reactions of *F*-cyclobutene and *F*-cyclopentene with $AlCl_3$ and $AlBr_3$, complete halogen exchange can be achieved under certain conditions. Exchange of activated fluorine atoms has also been reported with substrates such as *F*-1-methylbenzocyclobutane and *F*-indan with $AlCl_3$ and with $AlBr_3$.[132] An unusual transformation reported recently is the direct reaction of $AlBr_3$ with *F*-toluene to form *F*-4-bromotoluene.[200] In contrast, the same reaction in acetyl bromide as a solvent leads to substitution of fluorines in the CF_3 group only.



54%

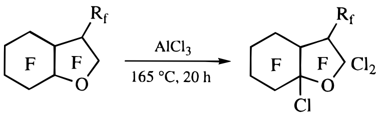
(211)

Perfluorinated alkanes are very stable toward the action of strong Lewis acids, but fluorine atoms are activated by an α-heteroatom, for example oxygen, and can be exchanged with $AlCl_3$ among other reagents.[201−205]



51%

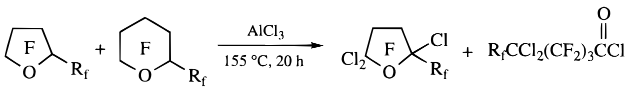
(212)



39-71%

(213)

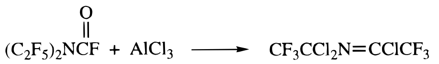
Perfluorinated oxanes tend to be less stable toward $AlCl_3$,[164] as was shown by reaction of a mixture of **256** and **257** with $AlCl_3$ at 155 °C. The chlorooxolane **258** was again formed along with acyl chloride **259**, a result of a ring-opening reaction of **257**.



256 **257** **258** **259**

(214)

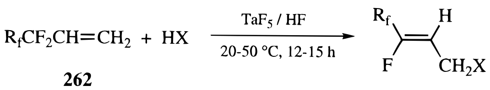
Reaction of oxetane **51a** with $AlCl_3$ to form both chlorooxetane and ring-opened alcohol **52b** is another example (eq 154). Carbamoyl fluoride **260** with $AlCl_3$ gives chlorinated imine **261** as a result of decarbonylation of **260** and formation of **261** by exchange of α-fluorines with $AlCl_3$.[205]



$$(C_2F_5)_2N\overset{\overset{\displaystyle O}{\|}}{C}F + AlCl_3 \longrightarrow CF_3CCl_2N{=}CClCF_3 \qquad (215)$$

260 **261**, 39%

An unusual example of halogen exchange with creation of a vinyl fluoride was found recently for perfluoroalkylethylenes **262**. Reaction of these olefins with hydrogen chloride or bromide in anhydrous HF as a solvent in the presence of Lewis acid results in replacement of one of the allylic fluorines to form allyl chlorides **263a** or allyl bromides **263b**.[206]



(216)

262

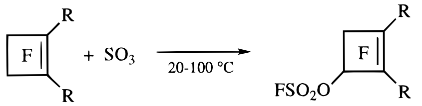
50-70%

263a, X = Cl
263b, X = Br

Allyl chlorides **263a** were also obtained in high yield by reaction of alkylethylenes **262** with chlorosulfonic acid in the presence of NbF_5 or TaF_5. SbF_5 is inactive in this reaction with $ClSO_3H$.[206]

2. Insertion of Sulfur Trioxide

The reaction between SO_3 and terminal fluoroolefins normally results in cycloadditon with formation of β-sultones and has been reviewed.[207] The first indication that the course of reaction of fluoroolefins with SO_3 can be different was reported in 1976.[208] It was demonstrated that the reaction of cyclobutenes **264** with stabilized sulfur trioxide leads to insertion of SO_3 into an allylic C−F bond with formation of the corresponding fluorosulfates **265** in 74−91% yield.



(217)

264 R = F, Cl, H **265**

The presence of a vinylic alkoxy group directs the reaction to yet another course[183] (see section IV.G.2).

Reaction of hexafluoropropene (HFP) with pure, distilled SO_3 at temperatures up to 100 °C leads to formation of β-sultone in high yield as the sole product,[207] but the presence of 0.5−2 mol % of BF_3 in the sulfur trioxide [B_2O_3 or $B(OCH_3)_3$ may be used as well] changes the direction of the reaction to one in which F-allyl fluorosulfate **266** is formed as the principal product.[209,210] It is an important reagent for the synthesis of F-allyloxy compounds[209,211] and F-glycidyl ethers.[212]

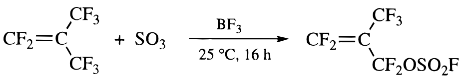
$$CF_2{=}CFCF_3 + SO_3 \xrightarrow[20\text{-}100\ °C]{BF_3} CF_2{=}CFCF_2OSO_2F + FSO_2OCF_2CF{=}CFOSO_2F$$

266, 50-60% **267**, *Z/E* 1:1.3

$$\left[+\ CF_2{=}CFCF(OSO_2F)_2\right] + FSO_2OSO_2F + FSO_2OSO_2OSO_2F \qquad (218)$$

268 **269a** **269b**

Attainment of 50−60% yields requires an excess of F-propene to be present, minimizing the occurrence of multiple substitutions. F-1,3-Bis(fluorosulfato)propene (**267**) was isolated in low yield from a reaction of nearly equivalent amounts of F-propene and SO_3, along with fluorosulfonic anhydrides **269a**,**b** and unidentified carbonyl compounds.[210] These latter products are attributed to the formation of unstable F-3,3-bis(fluorosulfato)propene-1 (**268**), which decomposes to give acid fluoride and derivatives. Later it was demonstrated[213] that F-isobutene under similar conditions forms F-methallyl fluorosulfate (**270**) in 71% yield.



$$CF_2{=}C\genfrac{}{}{0pt}{}{\diagup CF_3}{\diagdown CF_3} + SO_3 \xrightarrow[25\ °C,\ 16\ h]{BF_3} CF_2{=}C\genfrac{}{}{0pt}{}{\diagup CF_3}{\diagdown CF_2OSO_2F} \qquad (219)$$

270, 71%

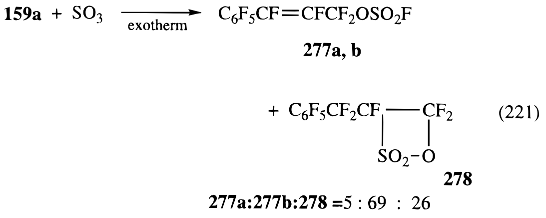
The reaction conditions of this process depend on the structure of the unsaturated compound. Interaction between SO_3 and compounds known to give stable carbocations, such as F-toluene (**271**), F-4-bromotoluene (**272**), or 3,3,3-trifluorotrichloropropene-1 (**273**) proceeds at 100 °C without a catalyst[214] and results in formation of the corresponding fluorosulfates **274**−**276** in 28−94% yield.

$$RCF_3 + SO_3 \xrightarrow[100\ °C,\ 20\ h]{} RCF_2OSO_2F \quad (220)$$

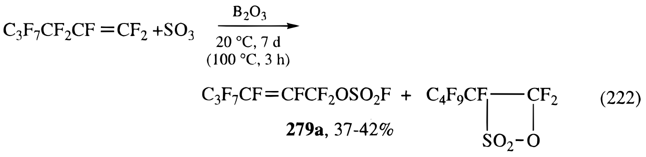
28-94%

271	R = C_6F_5–	**274**
272	R = 4-BrC_6F_4–	**275**
273	R = CCl_2=CCl–	**276**

F-Allylbenzene **159a** reacts with SO_3 exothermally giving a mixture of *cis*- (**277a**) and *trans*- (**277b**) fluorosulfate and sultone **278** in a ratio 5:69:26.

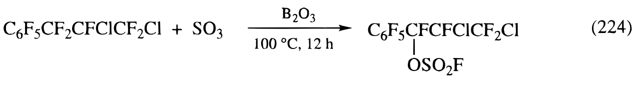


The formation of fluorosulfates **279a**−**c** in reactions of *F*-heptene-1, *F*-hexene-1, and *F*-*β*,*γ*-dichloropropylbenzene with sulfur trioxide also occur only in the presence of a catalyst.[210,214]



$$C_4F_9CF_2CF{=}CF_2 + SO_3 \xrightarrow[100\ °C,\ 4\ d]{B(OCH_3)_3} E\text{-}C_4F_9CF{=}CFCF_2OSO_2F \quad (223)$$

279b, 29%



$$C_6F_5CF_2CFClCF_2Cl + SO_3 \xrightarrow[100\ °C,\ 12\ h]{B_2O_3} C_6F_5\underset{\displaystyle OSO_2F}{\underset{|}{C}}FCFClCF_2Cl \quad (224)$$

279c, 58%

According to one study, higher internal Δ^2 perfluoroolefins do not interact with SO_3 in the presence of BF_3, but a stronger Lewis acid, antimony pentafluoride, catalyzes the transformation of perfluoro-2-alkenes into the corresponding allyl fluorosulfates **285**−**289**.[215,216]

$$R_fCF{=}CFCF_3 + SO_3 \xrightarrow[75\text{-}80\ °C,\ 2\ h]{SbF_5} R_fCF{=}CFCF_2OSO_2F \quad (225)$$

280	R_f = C_2F_5-	**285**, 87%
281	n-C_3F_7-	**286**, 93%
282	*i*- C_3F_7-	**287**, 93%
283	*t*- C_4F_9-	**288**, 89%
284	*n*- C_5F_{11}-	**289**, 87%

In contrast to these results with higher internal fluoroolefins, boron catalysis does promote reaction of *F*-butene-2 with SO_3 at 100−150 °C, although reaction is slow and several days are required.[210] The reaction of equimolar amounts of *F*-butene-2 and SO_3 produces 1-fluoro *F*-2-butenesulfate (**290**) along with fluoro acylsulfate **291** and $FSO_2OSO_2OSO_2F$ (**269b**), all in low yield.

$$CF_3CF{=}CFCF_3 + SO_3 \xrightarrow[150\ °C,\ 5\ d]{B(OCH_3)_3} CF_3CF{=}CFCF_2OSO_2F \xrightarrow{SO_3}$$

290, 4:1 *E/Z*
16% yield, 5% conv.,

$$CF_3CF{=}CFCO_2SO_2F + FSO_2OSO_2OSO_2F \quad (226)$$

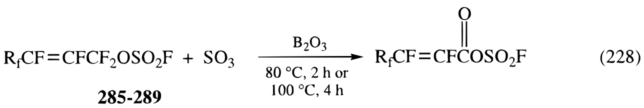
291, 7:3 *E/Z*

F-2,3-Dichlorobutene-2 reacted much more readily than *F*-butene-2 and gave a moderate yield of insertion product **292** even though an excess of SO_3 was employed.[210]

$$CF_3CCl{=}CClCF_3 + 2\,SO_3 \xrightarrow[15\ h]{100\ °C} CF_3CCl{=}CClCF_2OSO_2F \quad (227)$$

292,7:3 *E/Z*, 37%

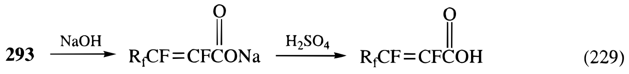
As was noted for the monofluorosulfation of *F*-propene, a high yield of fluorosulfate in the reactions of Δ^2-fluoroolefins depended on the use of excess of fluoroolefin, because further reaction of allyl sulfates **285**−**289** with excess of SO_3 leads to formation of fluoro acylsulfates **293**.[210,216,217] Compounds **293** were not isolated, but were converted into unsaturated acids **294** in isolated yields of 70−92%.[216]



$$R_fCF{=}CFCF_2OSO_2F + SO_3 \xrightarrow[80\ °C,\ 2\ h\ or\ 100\ °C,\ 4\ h]{B_2O_3} R_fCF{=}CF\overset{\displaystyle O}{\overset{\|}{C}}OSO_2F \quad (228)$$

285-289

293



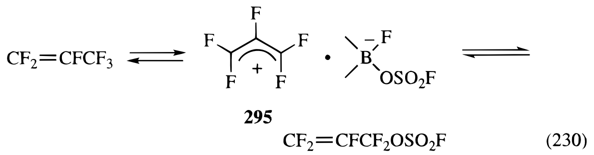
$$\mathbf{293} \xrightarrow{NaOH} R_fCF{=}CF\overset{\displaystyle O}{\overset{\|}{C}}ONa \xrightarrow{H_2SO_4} R_fCF{=}CF\overset{\displaystyle O}{\overset{\|}{C}}OH \quad (229)$$

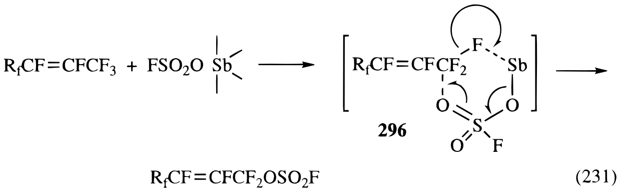
294 70-92%

This controlled hydrolysis of the trifluoromethyl group of perfluoro-2-alkenes by the use of excess SO_3 provides a good synthetic route to perfluorinated unsaturated acids not readily available by other routes and useful intermediates for the synthesis of a variety usaturated compounds.[218]

The mechanism of the insertion of SO_3 into an activated C−F bond is still not clear. This process includes at least two stages: formation of the catalytic complex by reaction of SO_3 with Lewis acid, and replacement of activated fluorine by an FSO_2O− group. The structure of the catalyst formed in the reaction of BF_3 with SO_3 was not determined, but evidence for formation of boroxin-type catalyst was obtained.[210] The structure of the catalyst complex formed by reaction of SbF_5 and SO_3 can probably be represented as $Sb(OSO_2F)_nF_{5-n}$.[216] The replacement of activated fluorine atom in a substrate by the action of catalyst containing FSO_2O− groups may proceed either as a reaction of virtually free carbocation **295**[209,210] generated by abstraction of fluorine from olefin by the Lewis acid[5] or possibly as a concerted process involving a transitional complex such as **296** of the olefin with Lewis acid.[215,216] The first or second mechanism could be realized depending on the structure of fluoroolefin and nature of Lewis acid.

Sulfur trioxide also inserts into the carbon−halogen bond of acyl fluorides and acyl chlorides to form mixed anhydrides **297**.[216,219] Reactions of acyl fluorides proceed at 25 °C, exothermically in some cases, to give the acyl fluorosulfates as thermally

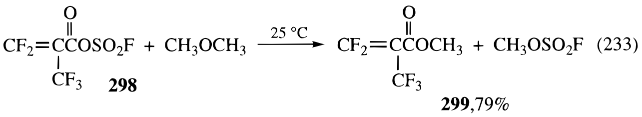




unstable products which revert to starting materials at temperatures above 100 °C, but which can be isolated in 70–80% yield by fractionation under vacuum.[219]

$$R_fCOX + SO_3 \rightleftharpoons \underset{\mathbf{297}}{R_fCOOSO_2X} \qquad (232)$$

Enhanced reactivity for the acyl fluorosulfates as compared to the corresponding acyl halides is demonstrated by their attack on dialkyl ethers to form esters, as illustrated by the reaction of fluoro *F*-methacryloylsulfate (**298**) with dimethyl ether to give methyl *F*-methacrylate (**299**).[219] Compound **299** is not formed from methanol and *F*-methacryloyl fluoride, since Michael addition to the C═C predominates.

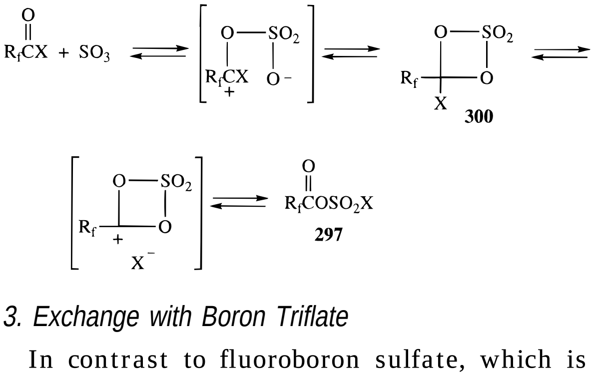


$$\underset{\mathbf{298}}{CF_2{=}\underset{CF_3}{C}\overset{O}{\overset{\|}{C}}OSO_2F} + CH_3OCH_3 \xrightarrow{25\,°C} \underset{\mathbf{299},79\%}{CF_2{=}\underset{CF_3}{C}\overset{O}{\overset{\|}{C}}OCH_3} + CH_3OSO_2F \qquad (233)$$

Aroyl halides undergo a similar insertion reaction with SO_3, but carbonyl fluoride proved to be a unique case in which both of the acyl–F bonds react, leading ultimately to pyrosulfuryl fluoride as the major product.

$$COF_2 + SO_3 \longrightarrow \underset{40\%}{FSO_2OSO_2F} + \underset{12\%}{FSO_2OSO_2OSO_2F} + CO_2 \qquad (234)$$

The absence of decarbonylation products and the lack of a need for the presence of catalyst led to the proposal that unstable cycloadducts **300** form as intermediates that rearrange to the observed acyl halosulfates in a series of reversible steps.[219]



3. Exchange with Boron Triflate

In contrast to fluoroboron sulfate, which is not stable under normal conditions and decomposes producing boroxin-type materials,[209] boron triflate **301** is reasonably stable and can be prepared by reaction of BX_3 (X = Cl or Br) with $HOSO_2CF_3$.[220,221] It was found that **301** is a strong Lewis acid capable of generating some stable carbocations and of catalyzing Friedel–Crafts aromatic substitution.[220,221]

Recently it was demonstrated that **301**, acting as a Lewis acid, is able to react with polyfluorinated compounds having sufficiently activated fluorine atoms, converting them into the corresponding triflates and boron trifluoride. In reactions between **301** and chlorotrifluoromethane or 1,1,2-trichlorotrifluoroethane, the triflates **302** and **303** were isolated in 90% and 44% yield, respectively.[222] 1,2-Dichlorotetrafluoroethane does not react with **301** under similar conditions.

$$\underset{\mathbf{301}}{B(OSO_3CF_3)_3} + CCl_3F \xrightarrow{25\,°C} \underset{\mathbf{302},\ 90\%}{CCl_3OSO_2CF_3} + BF_3 \qquad (236)$$

$$\mathbf{301} + CF_2ClCFCl_2 \xrightarrow{25\,°C} \underset{\mathbf{303},\ 44\%}{CF_2ClCCl_2OSO_2CF_3} + BF_3 \qquad (237)$$

Both $CF_2BrCFClBr$ and $CFCl_2CFCl_2$ are reactive, but exchange with **301** is accompanied by halogen migration.

$$\mathbf{301} + CFClBrCF_2Br \xrightarrow[25\,°C]{} \underset{68\%}{CBr_2ClCF_2OSO_2CF_3} + BF_3 \qquad (238)$$

$$\mathbf{301} + CFCl_2CCl_2F \xrightarrow[25\,°C]{} \underset{71\%}{CCl_3CFClOSO_2CF_3} + BF_3 \qquad (239)$$

Some fluoroolefins are more reactive toward **301** than these fluoroalkanes. Hexafluoropropene interacts even at 0 °C with **301**, giving *F*-allyl triflate (**304**).

$$\mathbf{301} + CF_2{=}CFCF_3 \xrightarrow[0\,°C,\ 5\,h]{} \underset{\mathbf{304},\ 68\%}{CF_2{=}CFCF_2OSO_2CF_3} \qquad (240)$$

Under similar conditions *F*-toluene (**271**) was converted into *F*-benzyl triflate (**305**), while olefins **273** and **306** interact with **301** at room temperature giving triflates **307** and **308**, respectively.

$$\mathbf{301} + \mathbf{271} \xrightarrow[0\,°C]{} \underset{\mathbf{305},\ 30\%}{C_6F_5CF_2OSO_2CF_3} \qquad (241)$$

$$\mathbf{301} + XCCl{=}CClCF_3 \xrightarrow[25\,°C,\ 2\text{-}4\,h]{} XCCl{=}CClCF_2OSO_2CF_3 \qquad (242)$$

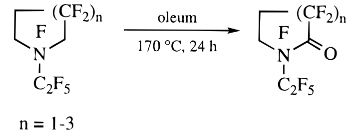
273	X=Cl	**307**, 63%
306	X=CF_3	**308**, 55%

4. Other Halogen/Oxygen Exchanges

Hydrolysis of fluoroalkyl groups by treatment with strong protic and Lewis acids, usually followed by water, is a common reaction, reported for many different types of fluorinated substrates. Detailed descriptions and numerous examples are given in ref 223. Here we discuss some recently published examples.

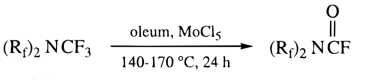
Cyclic perfluoroamines hydrolyze by reaction with oleum to form the corresponding lactams.[224] The reaction is selective and the products were isolated in 49–65% yield. The reactivity of such heterocycles toward fuming sulfuric acid decreases in the order:

pyrrolidino > morpholino > hexamethylenimino = piperidino.



(243)

Perfluorotriethylamine is far less reactive toward oleum and does not react up to 170 °C.[225] However, bis(perfluoroalkyl)-*N*-(trifluoromethyl)amines **309** under similar conditions were converted into the corresponding carbamoyl fluorides **310** in 40−60% yields. Lewis acids such as $HgSO_4$, PCl_5, P_2O_5, and especially $MoCl_5$ were found to serve as catalysts.

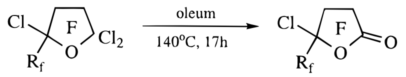


$$(R_f)_2NCF_3 \xrightarrow[140\text{-}170\ ^\circ C,\ 24\ h]{\text{oleum, } MoCl_5} (R_f)_2N\overset{O}{\overset{\|}{C}}F \quad (244)$$

309 **310**, 40-57%

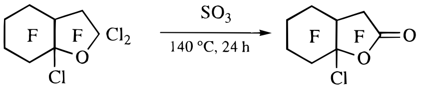
The proposed mechanism for these reactions, logically enough, includes insertion of SO_3 into an activated C−F bond of, for example, the CF_3 group of an amine, followed by removal of a second fluorine and elimination of SO_2F.

Cyclic ethers containing a $-CCl_2-$ group in the α-position to oxygen (compounds available from the reaction of perfluoroethers with anhydrous $AlCl_3$; see section IV.H.1) can also be converted into the corresponding lactones by reaction with SO_3.[226,227]



(245)

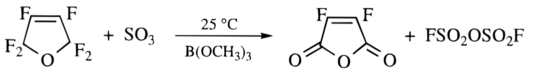
258 70-75%



(246)

74%

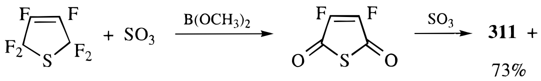
Perfluorinated ethers are much more resistant to hydrolysis or exchange with oxygen, but suitably activated α-fluorine in a perfluoro ether can react with SO_3 at 25 °C in the presence of a boron catalyst, as indicated by the following synthesis of difluoromaleic anhydride **311**.[228]



(247)

311, 53%

Fluorine α to sulfide in the related compound, *F*-2,5-dihydrothiophene, is similarly replaced by oxygen through reaction with $SO_3/B(OCH_3)_3$ catalyst at low temperature.[228] The intermediate thiol anhydride **312** can then be oxidized by excess SO_3 in a second stage to afford **311** directly and in good yield, making the reaction a convenient new synthesis of this useful anhydride.

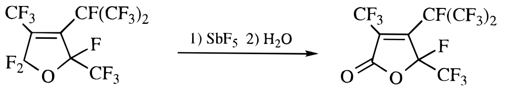


(248)

312 73%

Such reactions with SO_3 very likely proceed through fluorosulfato derivatives formed by addition of fluoro sulfate to an intermediate carbocation to give the SO_3 insertion product. As has been noted above,[228] when multiple insertion reactions occur to give 1,1-bis(fluoro sulfato) derivatives, reaction easily proceeds further to produce a carbonyl derivative and pyrosulfuryl fluoride. Thus, the oxygenation reaction is an extension of the SO_3 insertion reaction (see section IV.H.2).

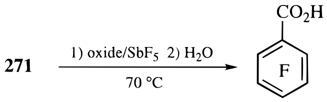
Products of hydrolysis often form in the reactions involving carbocations as intermediates, since the last step of the process usually involves workup of the reaction mixture with water to destroy a catalyst, as in eq 249.[91]



(249)

20% conv.

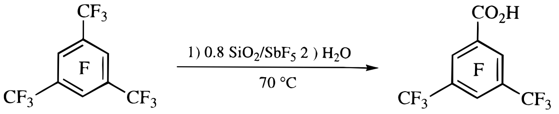
Selectivity in hydrolysis can be significantly improved by the use of such oxygen-containing compounds as SiO_2, Sb_2O_5, or Al_2O_3 in conjunction with the Lewis acid. *F*-Toluene was reacted with these compounds in the presence of 1.5−2 equiv of SbF_5. For the control experiment with 2 equiv of SbF_5, the yield did not exceed 20−25%.



(250)

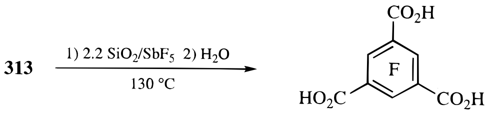
oxide = SiO_2 (85%), Sb_2O_5 (73%),
Al_2O_3 (38%)

This reaction can also be selective in that depending on the conditions, the product of the hydrolysis of one or three CF_3 groups in **313** were isolated in 67% and 87% yield, respectively.



(251)

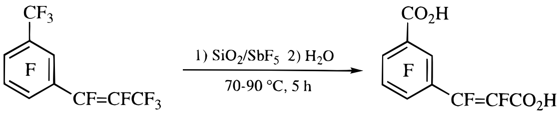
313 67%



(252)

86%

Both CF_3 groups in compound **314** are equally reactive toward hydrolysis by SiO_2/SbF_5, and diacid **315** (mixture of *trans* and *cis* isomers) was isolated in 80% yield.



(253)

314 **315**

V. Conclusions

The last 20 years or so has been a period of vigorous growth in studies of the formation and characterization of fluorocarbocations. The demonstrated reality of such cations as intermediates in a range of reaction types seems to have reinforced the natural optimism of fluorine chemists about such intermediates. Thus the extensive body of new synthetic fluorine chemistry has also appeared.

Advances in NMR spectroscopy have made it a particularly effective means for identifying relatively stable fluorocarbocations and for the elucidation of structural details. At the same time, expansion of the number of Lewis acids readily available and having a range of acidities and other properties (aluminum chloro fluoride is a notable example) has been accompanied by the appearance of new reagent systems (anhydrous HF and solutes come to mind). It is therefore possible to exercise better control of reaction conditions and reagent characteristics, allowing the improved syntheses.

We are confident that significant development of this broad and active field will continue apace.

VI. Acknowledgments

The successful development of the chemistry of fluorinated carbocations can be traced to discoveries by many chemists working in this field. We should like to single out two pioneers upon whose work much of our present knowledge is based. Dr. Victor Weinmayer established the utility of anhydrous HF as a reaction medium. In early work the group of professor Lev Solomonovich German used SbF_5 as a reagent for the formation of fluorinated carbocations and elucidation of a remarkable body of chemistry.

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