

Fluorinated allylic cations as actual intermediates in reactions of organofluorine compounds

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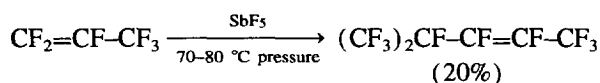
Abstract

This review presents the results of the studies of fluorinated allyl cations in reactions of organofluorine compounds conducted during 1972–1993. The probable mechanisms of the reactions are considered.

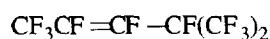
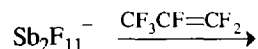
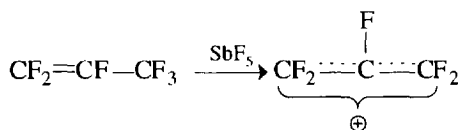
Keywords: Fluorinated allylic cations; Organofluorine compound reactions; Intermediates; NMR spectroscopy

1. Introduction

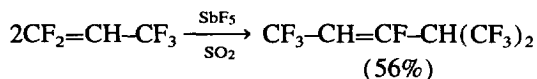
In 1972, I.L. Knunyants and coworkers discovered the electrophilic dimerization of hexafluoropropene (HFP) [1]. They showed that under the action of antimony pentafluoride and increased pressure at 70–80 °C, HFP dimerizes to form 4-trifluoromethylperfluoro-2-pentene as one of the reaction products.



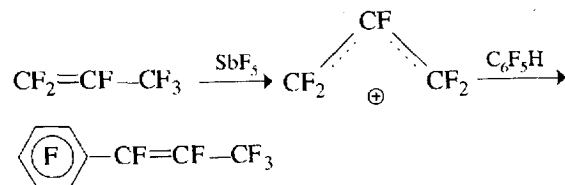
For the first time the assumption was made of the involvement of a perfluoroallyl cation in this reaction as an attacking particle [1].



2H-Pentafluoropropene dimerizes in a similar manner under milder conditions [1].

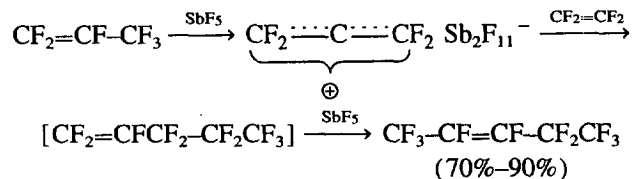


Later R.D. Chambers and coworkers reported similar results [2]. Additionally, it was found [3] that HFP reacted with pentafluorobenzene in the presence of SbF_5 to form perfluoropropenylbenzene among the reaction products [3]. The authors also assumed that the perfluoroallyl cation was also involved in this reaction.



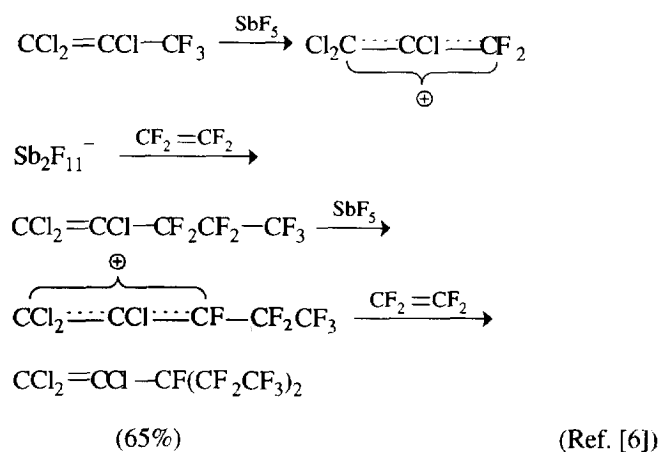
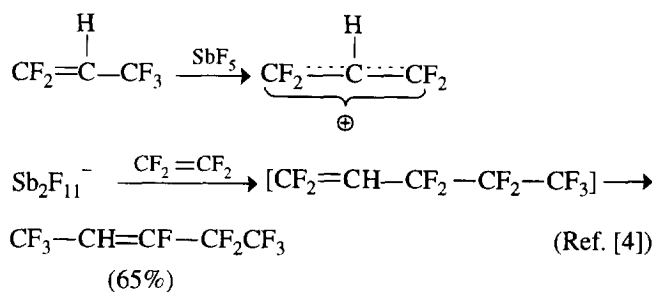
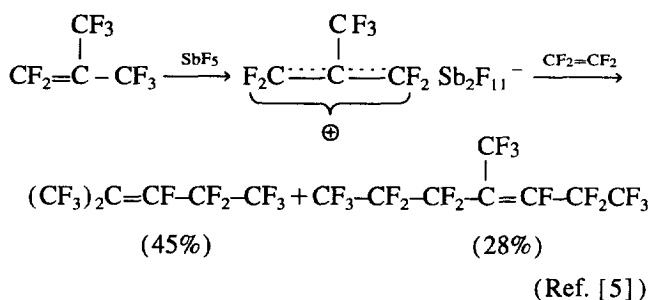
2. Electrophilic alkenylation of fluoroethylenes

The hypothesis for existence of fluorinated allyl cations in solution suggested that many of C_3 – C_4 fluoroolefins would be sufficiently convenient precursors of the corresponding allyl cations which could be used for electrophilic alkenylation of fluoroethylenes. In fact, it was found that under the action of SbF_5 as a catalyst, HFP reacted with tetrafluoroethylene (TFE) to give perfluoro-2-pentene preferably in the form of the *trans* isomer [4].

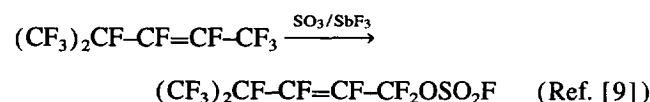
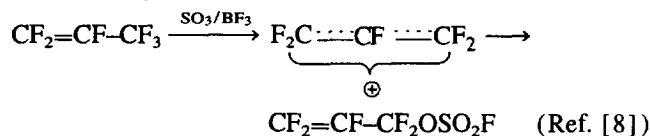


The scheme for this reaction is analogous to the scheme for the electrophilic dimerization of HFP presented above.

The primary step of the reaction also involves the formation of the perfluoroallyl cation from HFP under the action of SbF_5 . The last step includes the migration of the double bond in the intermediate terminal olefin from position 1 to the interior of the chain under the action of SbF_5 [4]. Perfluoroisobutene [5], trifluorotrchloropropene [6], dichloroperfluoroisobutylene [6], 2*H*-pentafluoropropene [4], 1*H*-pentafluoropropene [7], etc. were successfully used as the precursors of corresponding allyl cations and, therefore, as alkylating agents.



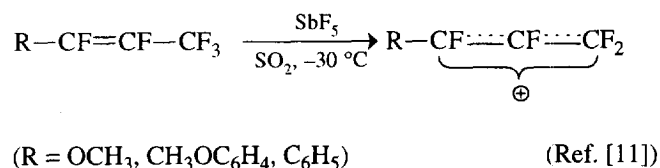
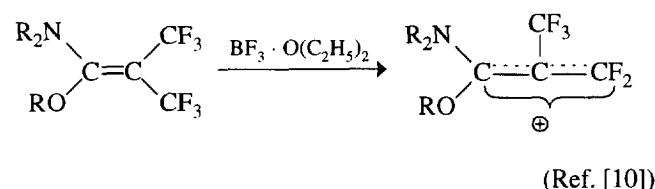
Reaction of electrophilic fluorosulphonation discovered in the 1980s is likely to occur involving the corresponding allyl cations [8,9]:



Thus, the hypothesis for the involvement of fluorinated allyl cations in the reactions of organofluorine compounds proved to be sufficiently fruitful and made it possible to extend a set of methods available for the synthesis of some types of fluoroaliphatic compounds including the higher fluoroolefins.

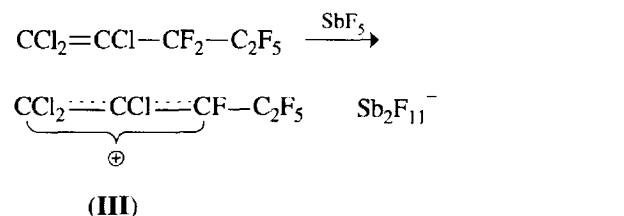
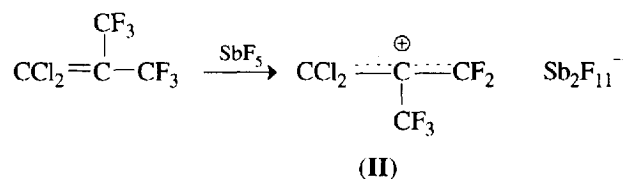
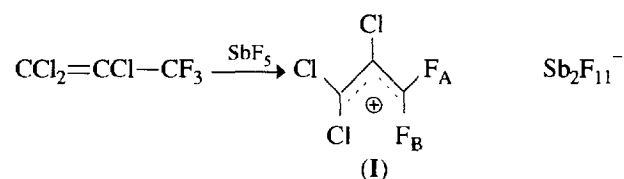
3. Detection of fluorinated allyl cations by NMR spectroscopy

The problem of detecting fluorinated allyl cations has its own history. In the 1970s, the first representatives of fluorinated allyl cations were obtained containing strong electron-donor substituents in position 1 of the allylic triad [10,11].



Several research groups attempted to record the perfluoroallyl cations by the NMR method, but failed.

We have ascertained that fluorochlorinated olefins, such as trifluorotrchloropropene, 1,1-dichloroperfluoroisobutene and trichloroperfluoro-1-pentene, can easily form the corresponding allyl cations (by the action of SbF_5) which are recorded by the NMR method at the common operating temperatures of NMR spectrometers [12].

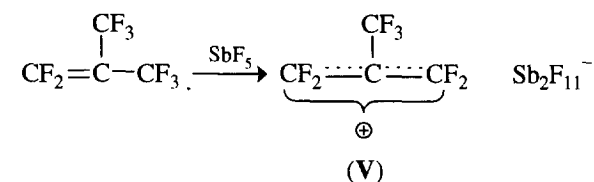
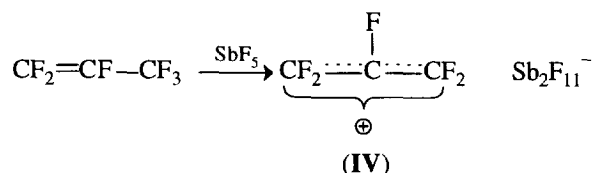


For example, the ^{19}F NMR spectrum of a trichlorotrifluoropropene solution in excess SbF_5 contains no signals of the starting olefin, but includes the AB system significantly shifted downfield with respect to the precursor ($F_A = -101$ ppm, $F_B = -93$ ppm; CF_3COOH as internal standard).

The presence of the AB system unambiguously points to the appearance of a positive charge in the molecule. This is the reason why the bond order between the C-2 and C-3 atoms increases, resulting in the magnetic nonequivalence of the fluorine atoms in cation **I**. There are three resonance signals in the ^{13}C NMR spectrum of this cation whose multiplicity is significantly distinct from the multiplicity of the starting olefin signals. Two of these signals, assigned to C-1 and C-3, are shifted markedly downfield with respect to the precursor (51 and 74.7 ppm, respectively), whereas the position of the C-2 signal remained unchanged. In addition, we have observed a significant increase in the absolute values of the spin-spin coupling constants (SSCC) $J(^{13}\text{C}-^{19}\text{F})$ of cation **I** in comparison with the olefin. We have also observed similar changes in the NMR spectra of cations **II** and **III**.

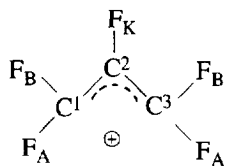
Such changes in the chemical shifts of the ^{13}C carbon nuclei in cations **I–III** are consistent both with theoretical notions about the positive charge distribution in allyl cations and with experimental data obtained for hydrocarbon allyl cations [13].

Perfluorinated allyl cations, such as perfluoroallyl (**IV**) and perfluoromethylallyl (**V**) cations, have also been characterized via their ^{19}F and ^{13}C NMR spectra [14,15].



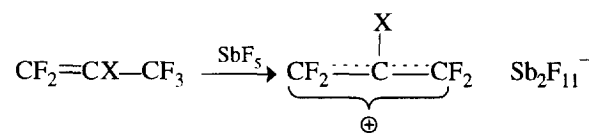
In contrast to the spectra of cations **I**, **II** and **III**, those of cations **IV** and **V** can be recorded at temperatures lower than 0°C using SO_2FCl or perfluorocyclobutane as the solvent. It should be emphasized that in the spectra of **IV** and **V**, the signals of their precursor olefins were observed at temperatures even lower than -40°C . The NMR spectra of cations **IV** and **V** also contain downfield multiplets; however, these spectra are not first order. In connection with this, the complete analysis of the spectra was implemented using iterative calculations. The assumption that the spin system of cation **IV** is related to the AA'BB'K type makes it possible to achieve a good agreement between the theoretical and experimental ^{19}F NMR spectra for cation **IV**. The presence of such a system confirms the elimination of fluorine anion from the

starting olefin resulting in an appearance of symmetry in the ^{19}F NMR spectrum of cation **IV**.



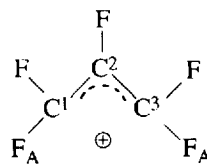
The ^{13}C NMR spectrum of cation **IV** contains a downfield multiplet at 170 ppm which may be considered to be the X part of an ABCDKX system related to the resonance of one of the carbon nuclei (C-1 or C-3).

The ^{13}C and ^{19}F NMR spectra for other fluorinated allyl cations with various substituents in position 2 were recorded and calculated in a similar manner [14].



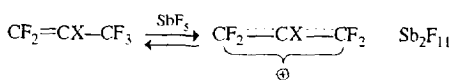
X = H (**VI**), Cl (**VII**), Br (**VIII**)

Examination of the NMR spectra of cations **IV–VIII** allows us to state that the following changes are observed in this case as one goes from the olefin to the cation. The signals of carbon atoms C-1 and C-3 of the allylic triad bearing the basic positive charge and the signals of fluorine nuclei at these carbon atoms are shifted sharply downfield, whereas the position of the signal corresponding to C-2 remains unchanged. In addition to the changes in chemical shift, the authors observed a marked increase in the SSCC values: $J(^{13}\text{C}_{1,3}-^{19}\text{F})$, $^2J(^{19}\text{F}-^{19}\text{F})$ and $^4J(\text{F}_{1a}-\text{F}_{3a})$.



The last mentioned constant is quite typical of fluorinated allyl cations. This value of this constant varies within the range 120–160 Hz and is more than twice the magnitude of the similar constant in α,α -difluoronaphthalene which contains no charge [14]. It should be noted that for all cations described above the signals of carbon nuclei C-1 and C-3 bearing the positive charge are more high field in comparison with the corresponding signals of the hydrocarbon allyl cations [13]. This difference is likely to be attributed to a partial compensation of the positive charge due to back-donation of the charge density from the fluorine atoms to the positively charged carbon atom. The high deshielding of the fluorine nuclei at C-1 and C-3 supports this assumption. The results of quantum chemical computations of fluorinated allyl cations also confirm the involvement of the fluorine atoms attached to C-1 and C-3 in the stabilization of the positive charge [16]. We could expect that a substituent in position

Table 1
Equilibrium thermodynamic parameters



[X = F, CF₃]

Cation	X	ΔH (kcal mol ⁻¹)	ΔS e.u.	ΔG (kcal mol ⁻¹)
IV	F	-5.9	-26.1	1.8
V	CF ₃	-4.6	-23.9	2.5

2 would have no marked effect on the stability of fluorinated allyl cations, because the positive charge in such cations is concentrated in positions 1 and 3. However, when the NMR spectra of these particles were recorded, it became apparent that this assumption was only valid on a limited scale.

Thus, under identical conditions (an olefin/SbF₅ mole ratio ≥ 2 ; solvent, SO₂ClF), the ¹⁹F NMR spectra of cations IV and V contain the signals of the olefin precursors even at low temperatures.

At the same time, no signals attributable to the corresponding olefins are observed in the spectra of cations VI–VIII in the temperature range -50 °C to +25 °C [17]. In this respect, the stability of cations IV–VIII relative to the substituent in position 2 was studied.

It emerged that the relative integral intensity of the signals arising from both the cations and their precursor olefins depended on the temperature. The existence of this dependence allowed us to obtain the equilibrium thermodynamic parameters for cations IV and V as listed in Table 1 [17].

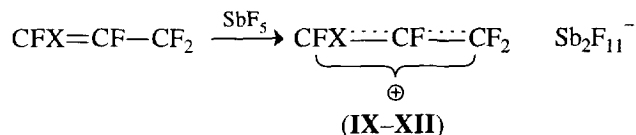
It follows from these data that the formation of cations IV and V is energetically profitable: the negative values of ΔS point to an increase in the order of the system resulting from the appearance of a charge. Cation IV is more stable than cation V by 1.3 kcal mol⁻¹. Similarly, cations VI, VII and VIII prove to be more stable than cations IV and V.

However, we failed to obtain equilibrium thermodynamic parameters for cations VI–VIII using NMR spectroscopy, because the equilibrium constant is more than unity in this case. In fact, we succeeded in estimating the relative stability

of cations VII and VIII from the kinetics of the reverse reaction (see Table 2).

The relative stability of cation VI was evaluated using the competing reaction method in the presence of an SbF₅ deficit. For this purpose we recorded the ¹⁹F NMR spectrum for a mixture of two olefins, i.e. 2*H*-pentafluoropropene and 2-chloropentafluoropropene, with SbF₅ in SO₂ClF solution at an olefin/olefin/SbF₅ molar ratio equal to 1:1:2. The spectrum recorded contained multiplets corresponding to cation VI and 2-chloropentafluoropropene. This indicates that cation VI has the highest thermodynamic stability in the series studied [17]. In summary, the results presented above lead to the following order of stability for fluorine-containing allyl cations (CF₂=CX=CF₂)⁺ depending on the nature of substituent in position 2: H > Cl > Br > F > CF₃. Thus, the stability of fluorinated allyl cations increases as both the acceptor ability and the bulk of the substituent in position 2 decrease. The latter is typical for the pairs of cations VII–VIII and IV–V.

The effect of substituents in position 1 of the allylic triad on the stability of fluorinated allyl cations was investigated via the example of the 1-substituted allyl analogues of the perfluoroallyl cation IV.

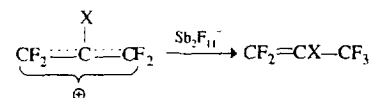


[X = H (IX), Cl (X), Br (XI), C₆F₅ (XII)]

These cations may also be prepared by the action of SbF₅ on the corresponding fluoroolefins in SO₂ClF solution and can be characterized via their ¹³C and ¹⁹F NMR spectra [18]. Again, the changes observed in the spectra were similar to those considered above, unambiguously confirming the elimination of the fluoride ion from the starting olefin. A significant downfield shift of the signals for the C(1)–F and C(3)–F fragments occurs, whereas the position of the lines for C(2)–F remains virtually unchanged. A marked increase in the SSCC values, i.e. ¹J(¹³C–¹⁹F), ²J(¹⁹F–¹⁹F) and ⁴J(¹⁹F–¹⁹F), was also observed.

According to the NMR spectra, cations IX–XI retain the configuration of their precursor olefins. In particular, cation

Table 2
Kinetic parameters for the interaction between the cations and the fluoride ion



(X = F, Cl, Br)

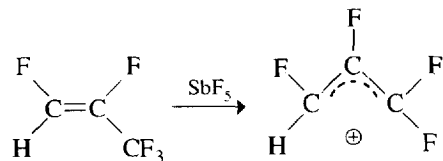
Cation	X	ΔE (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (e.u.)	ΔG (kcal mol ⁻¹)
IV	F	6.2	6.9	-8.4	9.4
VII	Cl	21.6	22.2	-12.1	25.5
VIII	Br	13.7	14.2	-15.0	18.7

Table 3
Thermodynamic parameters for the formation of cation IX

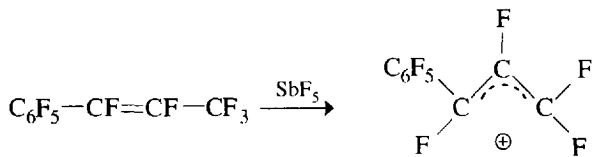
$$\text{CHF}=\text{CF}-\text{CF}_3 + \text{SbF}_5 \rightleftharpoons \underbrace{\text{CHF} \cdots \text{CF} \cdots \text{CF}_2}_{\oplus} \text{Sb}_2\text{F}_{11}^-$$

ΔH (kcal mol ⁻¹)	ΔS (e.u.)	ΔG (kcal mol ⁻¹)
4.3 ± 0.2	-26 ± 1.8	-2.6 ± 0.2

IX (X = H) exists in the form of the *cis* isomer and cations X and XI in the form of mixtures of the *cis* and *trans* isomers in the same ratios as their olefin precursors.



The only exceptions was cation XII (X = C₆F₅), which was observed in the form of the *trans* isomer in solution independent of its precursor configuration [19].



As would be expected, cations IX–XII differ markedly in terms of their stability. In the ¹⁹F NMR spectrum of a mixture of 1*H*-pentafluoropropene with SbF₅ (olefin SbF₅ mole ratio = 1:2, solvent, SO₂ClF), the signals of both the cation IX and its olefins precursor were observed even at -50 °C, the relative integrated intensities of the cation and its olefin signals depending on temperature. For instance, in the temperature range -50 to 10 °C, the molar concentration of cation IX decreased from 33% to 15%. Under the same conditions, the ¹⁹F NMR spectra of cations X–XII contained no signals corresponding to olefins.

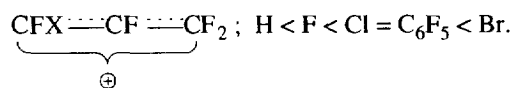
The existence of the temperature dependence of the integral intensity of the signals of the olefin and cation (in the ¹⁹F NMR spectra) makes it possible to calculate the equilibrium constant for the formation of cation IX and to derive the thermodynamic parameters for this equilibrium [18] (Table 3).

It follows from these data that the stability of cation IX is lower than that of the perfluoroallyl cation by 1.6 kcal mol⁻¹; this is consistent with theoretical *ab initio* calculations for allyl cations [16]. According to these calculations, the replacement of the hydrogen atom by a fluorine in position 1 of the allylic triad stabilizes the corresponding allyl cation by 2.8 kcal mol⁻¹ whereas the same replacement (H by F) in position 2 destabilizes the cation by 15.8 kcal mol⁻¹ [16]. Therefore, the experimental evidence indicates that in allyl

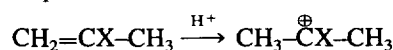
cations the fluorine atom attached to C-1 and C-3 (bearing the major positive charge) acts overall as an electron donor and thus stabilizes the positive charge by a 'back-donation' mechanism.

The relative stability of cations X–XII was estimated using competing reactions. For this purpose the ¹⁹F NMR spectra were recorded at +7 °C for mixtures of two fluoroolefins with an SbF₅ deficit. It was found that cation X (X = Cl) was more stable than cation IV (X = F) (integrated intensity ratio 3:1); and cation XI (X = Br) was more stable than cation X (integrated intensity ratio 4:1). The stability of cation XII (X = C₆F₅) was equal to that of cation X (integrated intensity ratio 1:1) and was significantly lower than the stability of cation XI (integrated intensity ratio 4:1).

Thus, based on quantitative and qualitative data, we may propose the following stability order for fluorinated allyl cations depending on the nature of the substituent in position 2:



As mentioned above, a fluorine atom in positions 1 and 3 of the allylic triad behaves as an electron donor, i.e. the strong inductive destabilization of the cation by fluorine is compensated by back-donation of the charge density on the positively charged carbon. It is generally assumed that both these effects decrease as one goes from fluorine to iodine. This statement is supported experimentally, for example, by the kinetics of protonation of 2-substituted propenes with trifluoroacetic or sulphuric acids [20], i.e.

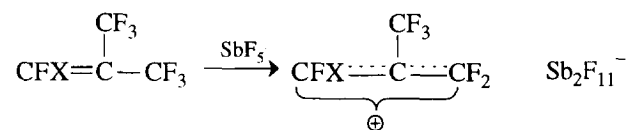


(X = H, F, Cl, Br)

where the sequence F > Cl > Br > H is observed. However, as the charge demand changes (for example, in the case of substituted methyl cations in the gaseous phase) the order of positive charge stabilization with halogens changes as follows: I > Br > Cl > F [20].

Hence, for 1-substituted fluorinated allyl cations, the stability order for the substituents F, Cl and Br is in good qualitative agreement with the stability of the ⁺CH₂X cations in the gaseous phase. This is likely to be associated both with the decreasing electron-withdrawing properties of the substituents and the increasing polarizability in going from fluorine to bromine.

The improved stabilization of the positive charge with more 'heavy' halogens than fluorine is also observed in the series of 1-substituted analogues of the perfluorometallyl cation [21], i.e.



[X = F, Cl, Br, I; X = OCH₃ (XIII)]

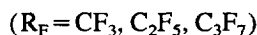
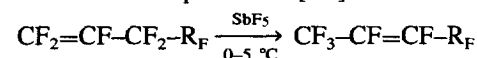
where the sequence $F < Cl < Br < I < OCH_3$ is observed. Note that the stability of the most stable in this series, i.e. cation **XIII**, is close to the stability of cation **VI** [21]. Therefore, the absence of an electron-withdrawing substituent in position 2 of fluorinated allyl cations is virtually equivalent to the introduction of a strong electron-donor group in position 1 [21].

As mentioned above, the 2-chloro- and 1-chloro-fluoroallyl cations **VII** and **X** are more stable than their perfluorinated analogue **IV**. Using the method of competing reactions, we have found that cation **VII** is more stable than cation **X** (integrated intensity ratio 2:1 in ^{19}F NMR spectrum) [18]. Hence, the presence of substituents such as H and Cl in position 2 of the fluoroolefin precursors of the corresponding allyl cations results in a greater energetic gain in the formation of allyl cations than the presence of the same substituents in position 1.

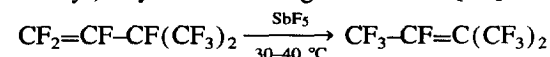
It is worth noting that we failed to observe the formation of the corresponding allyl cations from internal perfluoroolefins such as perfluoro-2-butene and perfluoro-2-pentene using ^{19}F NMR spectral techniques. Apparently, the presence of the electron-withdrawing perfluoroalkyl group in position 1 of the allylic triad leads to a significant decrease in the stability of the allyl cation. It is probably for this reason that we were unsuccessful in using these olefins as alkenylating agents [4,5].

4. Migration of the multiple bond in fluoroolefins catalyzed with SbF_5

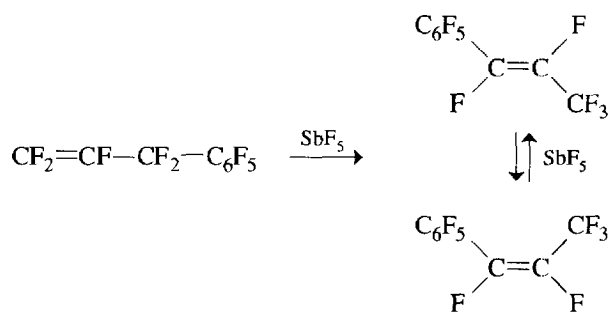
The last step of the scheme for electrophilic alkenylation presented above includes the migration of the multiple bond in the intermediate terminal olefin to the interior of the chain. This step has been confirmed experimentally. Thus, under mild conditions terminal olefins such as perfluoro-1-pentene, perfluoro-1-hexene, etc. readily isomerize in the presence of an SbF_5 catalyst to give the corresponding olefins with the double bond in position 2 [22].



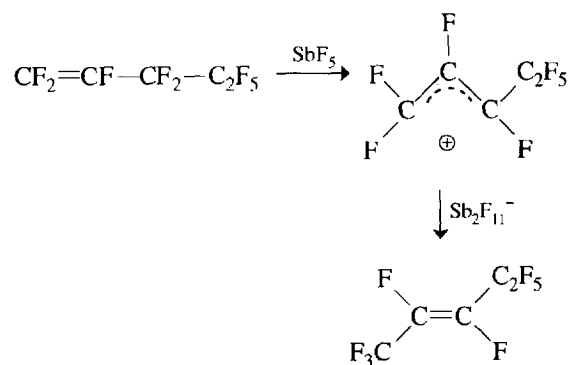
Perfluoroisopropylethene rearranges into tris(trifluoromethyl)ethylene on heating to 30–40 °C [22].



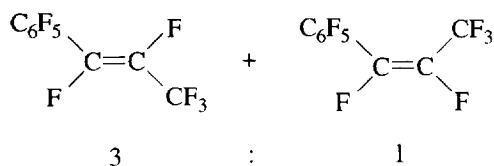
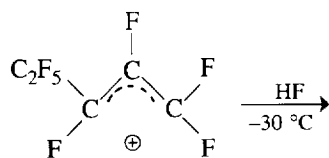
Note that in all of the cases indicated above the isomerization of 1-olefins into 2-olefins occurs stereospecifically, leading almost exclusively to the *trans* isomers [22]. The only exception is perfluoroallylbenzene which is converted to a 1:1 mixture of *cis*- and *trans*-perfluoropropenylbenzenes under the action of catalytic amounts of SbF_5 . Pure *cis*- and *trans*-perfluoropropenylbenzenes again form the same mixture of isomers in the same ratio when treated with SbF_5 [22].



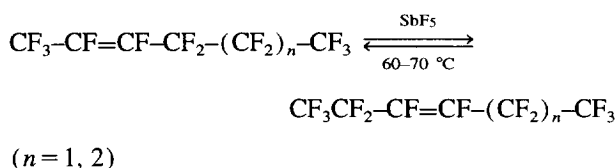
Migration of the double bond in fluoroolefins under the action of the fluoride ion, which occurs via intermediate formation of carbanions, has been reported previously [23]. Since SbF_5 is one of the most active electron acceptors, it is obvious that the migration of the double bond in olefins catalyzed SbF_5 occurs via intermediate formation of the corresponding allyl cation or via a transition state which is similar to the allyl cation in its structure.



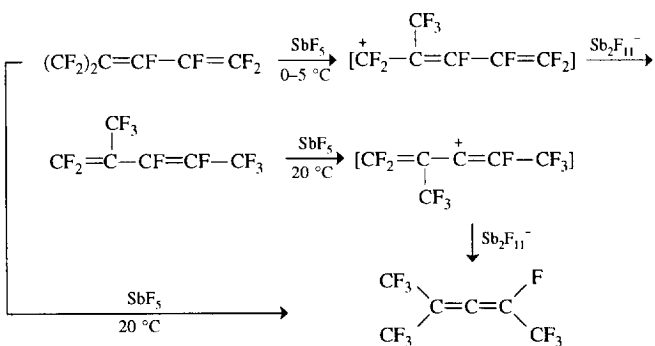
As mentioned above, the SSCC $^4J(^{19}\text{F}-^{19}\text{F})$ is very significant for fluorinated allyl cations. Its large value demonstrates the significant contribution made by the interaction through space which requires the maximal proximity of substituents attached to C-1 and C-3 which occurs in the '*cis*' position. From this viewpoint, the presence of any group more bulky than fluorine in this configuration will result in additional steric hindrance and destabilization of the corresponding allyl cation. Thus, the *trans* isomers are more stable for perfluorinated allyl cations, and this determines the stereochemistry of migration of the double bond in aliphatic perfluoroolefins. The formation of *cis*- and *trans*-perfluoropropenylbenzenes in equal amounts in the rearrangement of perfluoroallylbenzenes is likely to be attributed to a substantial decrease in the rotation barrier around the pseudo-double bond in cation **XII**. It should be noted that fast quenching of a solution of cation **XII** in SO_2ClF with HF at -30°C leads to the marked predominance of the *trans*-olefin in the reaction mixture (3:1). Thus, the *trans* isomer is a product of kinetic control.



It was found that refluxing 2-perfluoroolefins with a catalytic amount of SbF_5 resulted in an equilibrium fluoroolefin mixture containing 75%–80% 3-olefin and 20%–25% 2-olefin [24].

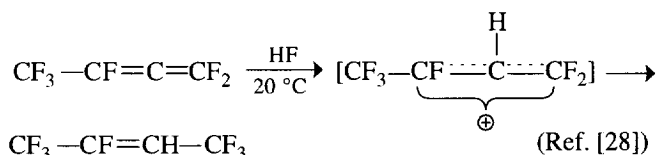
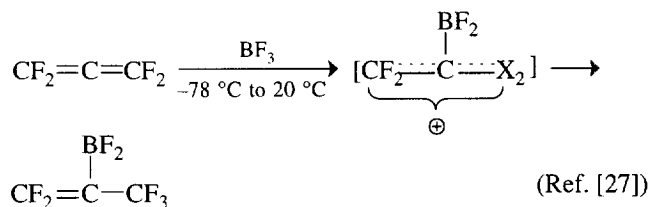
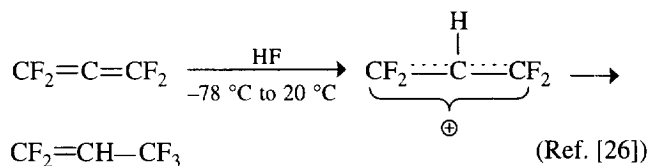


Migration of the multiple bond catalyzed by SbF_5 was also observed in the perfluorinated diene series. For example, perfluoro-2-methyl-2,4-pentadiene isomerizes under the action of SbF_5 at 0–5 °C to give perfluoro-2-methyl-1,3-pentadiene, the latter product isomerizing quantitatively into tris(trifluoromethyl)fluoroallene at 20 °C [25].



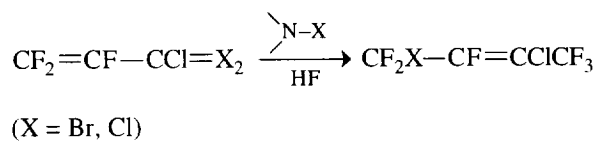
5. Fluorinated allyl cations as intermediates in electrophilic addition reactions to fluorinated allenes and dienes

Perfluoroallenes are known to add electrophilic reagents, for example HF and BF_3 , readily, with the initial attack of an electrophile directed at the central carbon atom of the allene system [26–28].

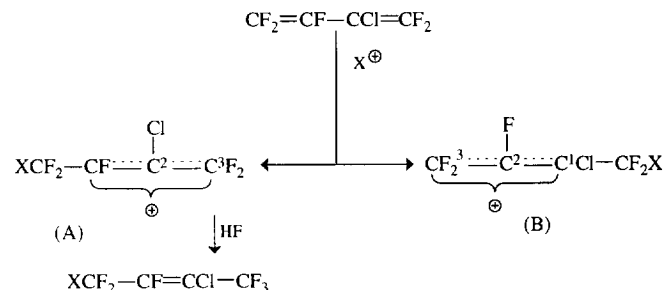


The orientation of the addition of the electrophilic agents to the fluorinated allenes is likely to be associated with the formation of relatively stable allyl cations in the first step.

Recently, it has been shown that the electrophilic bromofluorination and chlorofluorination of 2-chloropentafluorobutadiene occur exclusively at the 1,4-position in a strictly regioselective manner, i.e. the initial attack of the electrophile is directed towards the difluoromethylene moiety of the trifluorovinyl group in the starting diene [29].

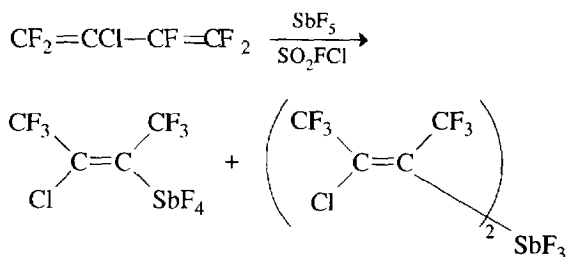


It is probable that in this case the regioselectivity of addition is connected with the stability of the intermediate allyl cation. For example, attack of the electrophile at the $\text{CF}_2=\text{CF}$ group of the starting diene leads to the formation of relatively stable cation A which contains a chlorine atom in position 2 of the allylic triad.

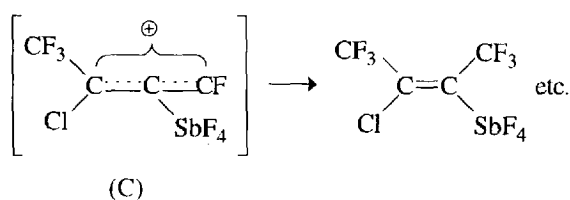
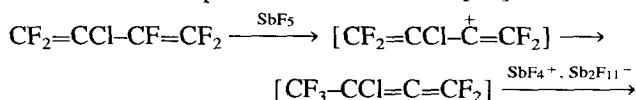


The initial attack of an electrophile at the $\text{CF}_2=\text{CFCl}$ group will form cation B containing chlorine and fluorine atoms in positions 1 and 2 of the allylic triad, respectively; this makes cation B less stable than cation A.

It turned out that 2-chloroperfluorobutadiene did not react with anhydrous HF, $\text{CF}_3\text{SO}_3\text{H}$ and HSO_3F . But 2-chloropentafluorobutadiene readily added SbF_5 in a solution of SO_2ClF to form a mixture of vinylic antimony derivatives.



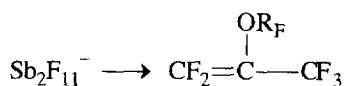
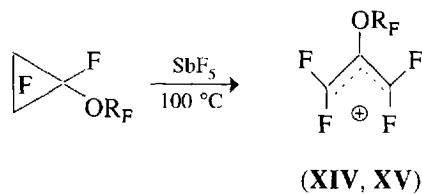
Isomerization of the diene apparently occurs in the first step to yield the corresponding allene, the latter being attacked at the central carbon atom by electrophilic SbF_4^+ to form the allyl cation C as an intermediate. Stabilization of cation C with fluoride ion derived from the medium results in one of the final products of the reaction [29].



6. Isomerization of fluorinated cyclopropanes under the action of SbF_5

Ring-opening of halo-substituted cyclopropanes under the action of Lewis acids is one method for generating allylic cations [30]. It is commonly supposed that opening of the three-membered ring to yield the allylic cation occurs synchronously as a concerted disrotation process [30].

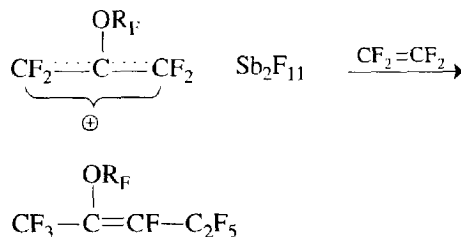
Apparently, perfluoroalkoxypropanes which isomerize into perfluoro-2-alkoxypropenes [31] under the action of SbF_5 at 100 °C react in a similar manner [31].



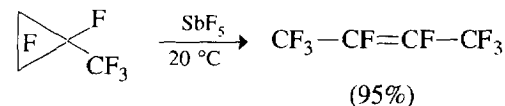
($\text{R}_F = \text{CF}_3, \text{C}_3\text{F}_7$)

Cations XIV ($\text{R} = \text{CF}_3$) and XV were recorded by NMR spectroscopy in the interaction of the corresponding olefins with SbF_5 in an SO_2ClF solution [31].

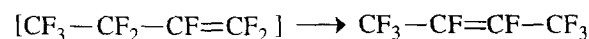
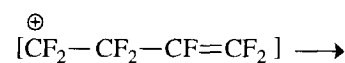
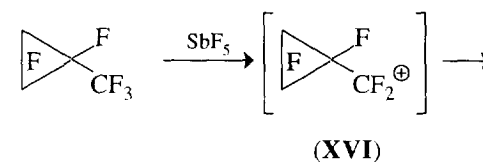
Using competing reactions, we have ascertained that cation XIV is less stable than perfluoroallylic cation IV, its stability being equal to that of the perfluoromethallylic cation V. Cations XIV and XV react with tetrafluoroethylene to form 2-perfluoroalkoxy-substituted perfluoro-2-pentenes [32].



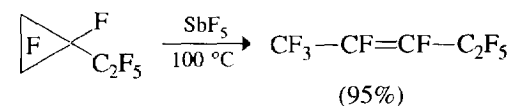
However, replacement of the perfluoroalkoxy group in the cyclopropane ring by the trifluoromethyl group changes significantly both the direction of the ring-opening and the reaction conditions. For example, perfluoro(methylcyclopropane) isomerizes to perfluoro-2-butene under the action of SbF_5 even at 20 °C [31].



In this case the first step in the ring-opening is heterolysis of the C–F bond in the CF_3 group of the starting cyclopropane, resulting in the formation of the cyclopropyl-substituted carbenium ion XVI as a probable intermediate. Opening of cation XVI occurs with cleavage of the attached bond in the cycle and finally leads to perfluoro-2-butene. Various attempts failed to record cation XVI by NMR methods over the temperature range –60 °C to –30 °C [31].

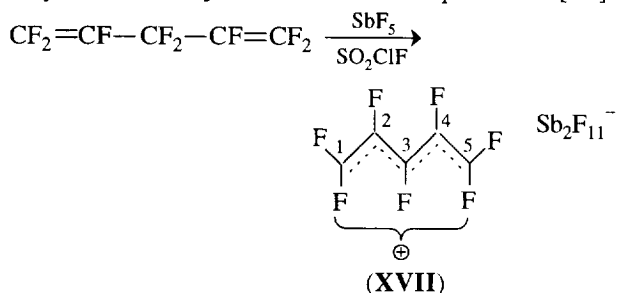


It follows from the scheme proposed that an increase in the length of the perfluoroalkyl chain in perfluorocyclopropanes, which is equivalent to the introduction of an electron-withdrawing substituent at the reaction centre, makes the isomerization conditions significantly more drastic. In particular, perfluoro(ethylcyclopropane) reacts with SbF_5 giving only perfluoro-2-pentene at 100 °C [31].



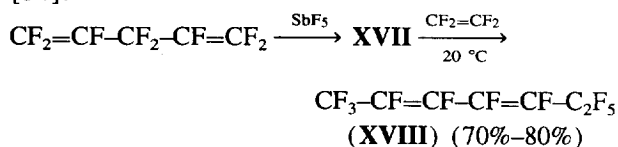
7. The perfluoropentadienyl cation

It may be expected that, like allyl cations, perfluorinated dienyl cations would be reasonably stable in a slightly nucleophilic medium. In fact, when pentafluoro-1,4-pentadiene is allowed to interact with an excess of SbF_5 in an SO_2ClF solution, the perfluoropentadienyl cation is formed which may be detected by the ^{19}F NMR technique at 0°C [33].

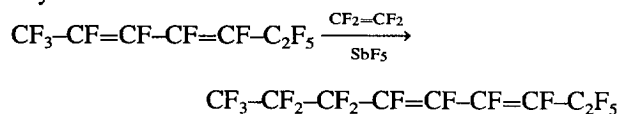


The ^{19}F NMR spectrum of cation **XVII** contained no signals of the precursor, but included four complicated multiplets in the region $\delta - 64$ ppm to 102 ppm (CF_3COOH used as internal reference). A complete analysis of the spectrum for the seven-spin system formed by the ^{19}F nuclei was performed using the iterative method. It was ascertained that the signals of the fluorine nuclei at C-1 and C-5 are in the lower field. It follows from SSCC values that cation **XVI** has a W (*s-trans,s-trans*) structure. This structural is also supported by quantum chemical MNDO studies. According to such calculations, the positive charge in cation **XVII** is localized on the C-1, C-3 and C-5 atoms, with the maximal positive charge concentrated on C-1 and C-5.

Like fluorinated allyl cations, cation **XVII** reacts with tetrafluoroethylene to afford perfluoro-2,4-heptadiene (**XVIII**) [34].



It should be noted that diene **XVIII** is capable of being condensed with tetrafluoroethylene in the presence of SbF_5 to form perfluoro-3,5-nonadiene [34], despite the fact that the intermediate perfluorinated dienyl cation contains the electron-withdrawing group in the resonance position. The existence of a longer chain for positive charge distribution in the dienyl cations apparently makes them less sensitive towards the effect of electron-withdrawing substituents than allyl cations.

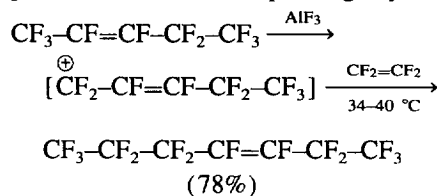


8. Recent developments

As mentioned above, under comparable conditions internal perfluoroolefins such as perfluoro-2-butene, perfluoro-2-pen-

tene, etc. do not react with antimony pentafluoride to form allyl cations, and probably for this reason they cannot be used as alkenylating agents.

However, Krespan has recently found that modified AlF_3 of formula $\text{Al}_1\text{F}_{2.9}\text{Cl}_{0.1}$, prepared from AlCl_3 by replacement (exchange) of chlorine by fluorine, is likely to be a stronger Lewis acid than SbF_5 [35]. This catalyst makes it possible to use internal olefins (for example, perfluoro-2-pentene) as precursors for the corresponding allyl cations.



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