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Stable Carbocations. CXXXI.[1] Intermolecular Fluorine Exchange of the Methylfluorocarbenium and Dimethylfluorocarbenium Ions in $HF-SbF_5-SO_2ClF$ Solution

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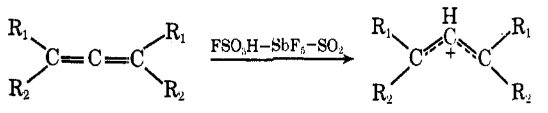
Protonation of allene, methylacetylene, and 2-fluoropropene as well as ionization of 2,2-difluoropropane in $HF-SbF_5-SO_2ClF$ solution all gave the dimethylfluorocarbenium ion which underwent rapid fluorine exchange with the superacid system. The fluorine exchange reaction of the dimethylfluorocarbenium ion as well as that of the methylfluorocarbenium ion was studied by ^1H, ^{19}F, and ^{13}C nmr spectroscopy.

In previous studies, protonation of substituted allenes in $FSO_3H-SbF_5-SO_2$ solution leading to the formation of the corresponding allylic cations was reported.[3]



$R_1 = CH_3$; $R_2 = H, CH_3$
$R_1 = R_2 = CH_3$

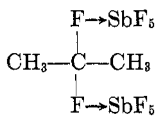
Protonation of the parent allene in "superacid" media has not been achieved previously. If the protonation were to take place on the sp-hybridized central carbon atom, the allyl cation would be generated. Alternatively, protonation on the terminal carbon atoms would give a vinyl cation. The direct observation of the allyl cation by nmr studies has been reported, although with poor resolution.[4a] The observation of vinyl cations as stable long-lived intermediates has not yet been achieved, although Olah and Pittman studied alkynylcarbenium ions which are mesomeric with allenyl cations.[4b] On the other hand, in a series of solvolytic studies it was concluded that vinyl cations were involved.[5] Presently, we wish to report the results of direct protonation of allene, methylacetylene, and acetylene in $HF-SbF_5-SO_2ClF$ solution resulting in the formation of the dimethylfluorocarbenium and methylfluorocarbenium ion, respectively, which undergo intermolecular fluorine exchange with the solvent system.

The intermolecular fluorine exchange reaction of the acetyl cation with acetyl fluoride was reported by Lunazzi and Brownstein.[6] In our laboratories, methyl and ethyl fluoride were found to exchange intramolecularly with antimony pentafluoride *via* the formation of donor-acceptor complexes, $RF \rightarrow SbF_5$ ($R = CH_3$ and C_2H_5). In the case where alkyl fluorides with antimony pentafluoride form stable ions (*e.g.*, isopropyl and *tert*-butyl cations), the possibility of an intermolecular fluorine exchange reaction (between carbenium ion and excess alkyl fluoride) was studied recently in our laboratories.[7] It was found, however, that only C-alkylated products were formed instead of fluorine exchange. This result is consistent with our unsuccessful attempts to prepare dialkylfluoronium ions. In order to study the possibility of intermolecular fluorine exchange reactions fluorocarbenium ions seem to be the appropriate species.

Results and Discussion

Pmr Spectra.—We carried out protonation of allene (I), methylacetylene (II), and 2-fluoropropene (III) as well as ionization of 2,2-difluoropropane (IV) in $HF-SbF_5-SO_2ClF$ (5/1 mol/mol) solution. Under conditions of stable ion formation, all gave an identical species displaying in the pmr spectra a sharp singlet absorption at δ 3.83. These results gave no indication that either the vinylic propynium ion V or the allyl cation was generated as a long-lived species, and a rapid exchange process Va ⇌ Vb must be considered. It seems unlikely that V could be generated from IV with $HF-SbF_5-SO_2ClF$. The nmr data can be best interpretated as either the dimethylfluorocarbenium ion VI exhibiting rapid fluorine exchange with the superacid system or as the formation of the antimony pentafluoride complex of 2,2-difluoropropane (VII). The later possibility can be excluded because the proton resonance (δ 3.83) is shifted upfield or downfield upon addition of HF and IV or SbF_5, respectively. Complex VII should have a definite proton shift, as in the methyl fluoride-antimony pentafluoride complex,[8] independent of excess IV or SbF_5.

$$\underset{\text{Va}}{{}^*CH_3\overset{+}{C}{=}CH_2} \rightleftharpoons \underset{\text{Vb}}{{}^*CH_2{=}\overset{+}{C}CH_3}$$



$$CH_3-\overset{F\rightarrow SbF_5}{\underset{F\rightarrow SbF_5}{C}}-CH_3$$

VII

The dimethylfluorocarbenium ion VI generated from IV in SbF_5-SO_2ClF shows a methyl doublet at δ 4.0 (J_{HF} = 26 Hz).[9] The doublet is shifted and collapsed to a sharp singlet at δ 3.83 when a fivefold amount of HF (relative to SbF_5) was added to the above solution. The singlet absorption shifted further upfield as more HF was added. Finally, the singlet absorption is found at δ 1.88 when a large excess of HF was added to the solution of VI. When this solution was allowed to warm to 25° in a closed system, the only product which could be collected was IV. IV itself was not ionized in

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(1) Part CXXX: G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, in press.

(2) Postdoctoral research associate, 1969–1971.

(3) (a) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6082 (1968); (b) C. U. Pittman, Jr., *Chem. Commun.*, 120 (1969).

(4) (a) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 5682 (1964); (b) G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 5632 (1965).

(5) For a review on vinyl cations in solvolysis reactions, see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970).

(6) L. Lunazzi and S. Brownstein, *J. Amer. Chem. Soc.*, **91**, 3034 (1969).

(7) G. A. Olah and Y. K. Mo, *ibid.*, in press.

(8) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *ibid.*, **91**, 2122 (1969).

(9) G. A. Olah, R. D. Chambers, and M. B. Comisarow, *ibid.*, **89**, 1268 (1967).

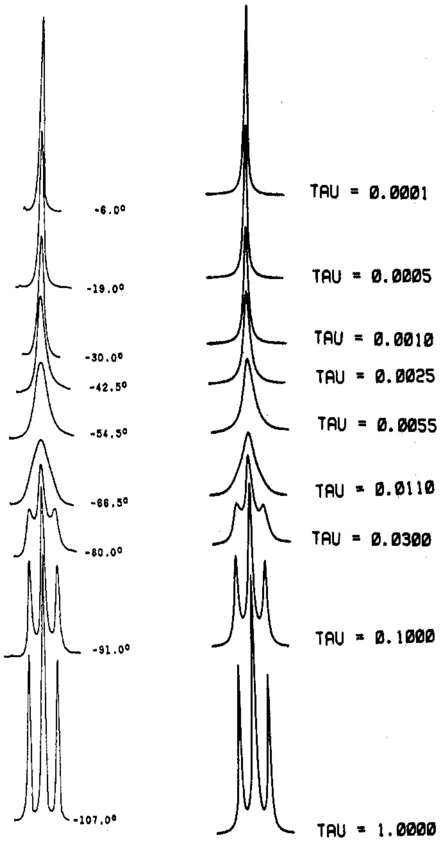

Figure 1.—Temperature-dependent pmr spectra of IV–SbF_5–HF (25:1:1) in SO_2ClF solution (left) and calculated spectra (right).

HF–SO_2ClF solution. Its pmr spectrum, showing a triplet at δ 1.63 (J_{HF} = 18 Hz) remained unchanged from −80 to −20°. However, when this solution was mixed with SbF_5–SO_2ClF (1/20 mol ratio to HF) at −78°, the pmr spectrum showed only one sharp singlet at δ 1.88. This singlet absorption became further deshielded as more SbF_5–SO_2ClF was added.

Further, we found that the singlet absorption observed between δ 1.88 and 3.83 is generally temperature independent between −100 and −20°, indicating that exchange reaction rates of ion IV with the superacid solvent media are more rapid than the nmr time scale. However, when the solution of IV–SbF_5–HF in SO_2ClF has a ratio of 25:1:1 and of 1:1:0.88, variable temperature pmr and fmr spectra could be observed (Figures 1–4, respectively).

Mechanism.—Before discussing the results of kinetic studies of the fluorine exchange reactions, it seems appropriate to discuss the mechanism of the exchange reaction. The nmr data discussed indicate that IV and ion VI as well SbF_5 and HF are involved in the exchange reactions. IV can be ionized to VI when IV is dissolved in SbF_5–SO_2ClF (eq 1). Ion VI itself can react with fluoride ion from HF and regenerate IV (eq 2). HF also interacts with SbF_5 (eq 3). Consequently, the equilibrium of eq 1 is shifted to the left. Finally, IV can fluorine exchange with ion VI (eq 4) but it does not affect the equilibrium of eq 1.

$$\underset{\text{IV}}{CH_3CF_2CH_3} + SbF_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{VI}}{CH_3\overset{+}{C}FCH_3} + SbF_6^- \quad (1)$$

$$\underset{\text{VI}}{CH_3\overset{+}{C}FCH_3} + HF \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{IV}}{CH_3CF_2CH_3} + H^+ \quad (2)$$

$$SbF_5 + HF \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} SbF_6^- + H^+ \quad (3)$$

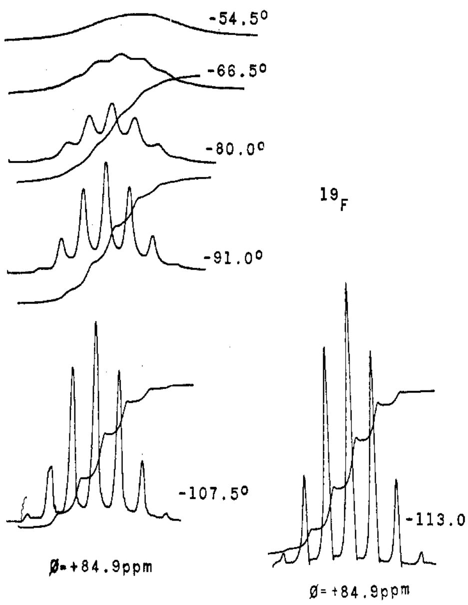

Figure 2.—Temperature-dependent fmr spectra of IV–SbF_5–HF (25:1:1) in SO_2ClF solution.

$$\underset{\text{IV}}{CH_3CF_2CH_3} + \underset{\text{VI}}{CH_3\overset{+}{C}FCH_3} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{\text{VI}}{CH_3\overset{+}{C}FCH_3} + \underset{\text{IV}}{CH_3CF_2CH_3} \quad (4)$$

The rate of forward and backward reactions 1–4 depend upon the relative concentration of each species. In the absence of HF and excess of SbF_5, IV is completely ionized to ion VI, and the equilibrium is shifted to the right ($k_1 \gg k_{-1}$). However, when HF was added to the above solution, reactions 2 and 3 became important. A fluorine exchange reaction between IV and the superacid medium occurs and washes out the proton–fluorine coupling when the exchange rate is greater than $1/J_{HF}$.[10] Equilibra (1–4) thus can account for the observation of the singlet absorption at δ 3.83 when I, II, and III were protonated or IV was ionized in HF–SbF_5–SO_2ClF (5/1 mol/mol) (eq 5).

$$\left.\begin{array}{l} H_2C{=}CCH_3\ (I) \\ CH_3C{=}CH_2\ (II) \\ CH_3CF{=}CH_2\ (III) \\ CH_3CF_2CH_3\ (IV) \end{array}\right\} \xrightarrow[(5/1\ \text{mol/mol}),\ -78°]{HF\text{–}SbF_5\text{–}SO_2ClF}$$

$$\underset{\text{VI}}{CH_3\overset{+}{C}FCH_3} + SbF_6^- \rightleftharpoons \underset{\text{IV}}{CH_3CF_2CH_3} + SbF_5 \quad (5)$$

Kinetics.—The relationship between the observed proton chemical shift (δ_{obsd}) and the concentrations of IV (C_{IV}) and VI (C_{VI}) can be expressed by eq 6.[11]

$$\delta_{obsd} = \delta_{VI} - \frac{n_{IV}C_{IV}}{n_{IV}C_{IV} + n_{VI}C_{VI}}(\delta_{VI} - \delta_{IV}) \quad (6)$$

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[10] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 151.

[11] One of the referees pointed out that eq 6, 7, and 8 are only valid if there is no change in chemical shift values with solvent composition. We have shown that change of the solvent composition (SbF_5 and HF) will affect the *average* proton chemical shifts but has negligible effect on proton shift of each individual IV and VI species (δ_{IV} and δ_{VI}). Thus, the pmr shifts themselves have practically no response to the solvent composition which only affects the relative amount of each species.

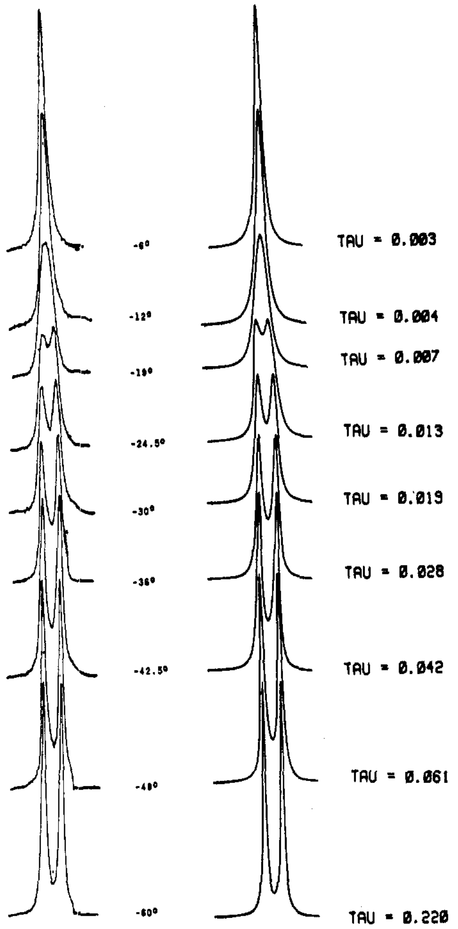

Figure 3.—Temperature-dependent pmr spectra of IV–SbF_5–HF (1:1:0.88) in SO_2ClF solution (left) and calculated spectra (right).

Since the number of labile protons in both IV and VI are equal ($n_{IV} = n_{VI}$) and the chemical shifts of IV and VI in the absence of exchange are known ($\delta_{VI} = 4.01$ and $\delta_{IV} = 1.63$), eq 6 can be simplified to eq 7. Alternatively, it can be expressed in terms of residence times of IV (τ_{IV}) and VI (τ_{VI}) since the $\tau_{IV}/\tau_{VI} = C_{IV}/C_{VI}$ relationship holds.[6] Equation 7 then becomes eq 8 as shown.

$$\delta_{obsd} = 4.01 - \frac{C_{IV}}{C_{IV} + C_{VI}} (2.38) \tag{7}$$

$$\delta_{obsd} = \delta\, 4.01 - \frac{\tau_{IV}}{\tau_{IV} + \tau_{VI}} (2.38) \tag{8}$$

In the case of the observed singlet at δ 3.83, the mole fraction $C_{IV}/C_{IV} + C_{VI}$ or the residence time fraction $\tau_{VI}/\tau_{IV} + \tau_{VI}$ is 0.0756. When more HF was added to the above solution, δ_{obsd} becomes smaller and the mole fraction $C_{VI}/C_{VI} + C_{IV}$ is increased. If $C_{VI} = C_{IV}$, $\delta_{obsd} = \delta\ 2.82$. For the other singlet observed at δ 1.88 (HF is in large excess), the mole fraction $C_{IV}/C_{VI} + C_{IV}$ is calculated to be 0.90.

In the presence of large excess of HF, reaction 4 is not important. We therefore conclude that the residence times of a species at each site, τ_{IV} and τ_{VI}, and the observed chemical shifts, δ_{obsd}, are totally dependent on the relative amount of HF. Thus, the exchange reaction can be regarded as pseudo first order.

As previously mentioned, when the solution of HF–SbF_5–IV in SO_2ClF has a ratio of 25:1:1, temperature dependent pmr and fmr spectra were observed. Thus the pmr spectra of a solution containing SbF_5 (3.5 mmol), HF (3.5 mmol), and IV (90.0 mmol) showed the coalescence of a triplet (of IV) to a singlet when the temperature was raised from −107 to −6° (Figure 1). The fluorine exchange reaction can be simplified as an equilibrium of IV and VI (eq 9). The relaxation time (τ) of this equilibrium is equal to $1/k$ or $1/k_{IV} + k_{VI}$ since it is a pseudo-first-order reaction.[12] The residence times of each site (IV and VI) are equal to $1/k_{IV}$ and $1/k_{VI}$, respectively (eq 10).

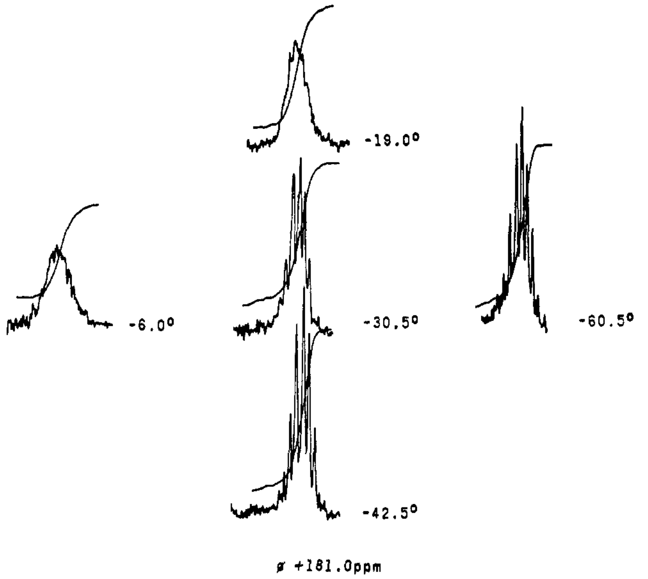

Figure 4.—Temperature-dependent fmr spectra of IV–SbF_5–HF (1:1:0.88) in SO_2ClF solution.

$$\mathrm{IV} \underset{1/\tau_{VI}}{\overset{1/\tau_{IV}}{\rightleftharpoons}} \mathrm{VI} \tag{9}$$

$$\tau_{IV} = 1/k_{IV},\ \tau_{VI} = 1/k_{VI} \tag{10}$$

Further, we also note that concentrations of IV and VI are related to k_{IV} and k_{VI} by eq 11 regardless of the mechanism of the exchange reaction. Consequently a simple equation (eq 12) can be derived to relate τ and the one directional rate constant, k_{IV}.

$$C_{IV}k_{IV} = C_{VI}k_{VI} \tag{11}$$

$$k = 1/\tau = k_{IV} + k_{VI} = K_{IV} + C_{IV}/C_{VI}k_{IV} = k_{IV}\left(\frac{C_{IV} + C_{VI}}{C_{VI}}\right)$$

$$k_{IV} = \frac{C_{VI}}{C_{IV} + C_{VI}} \frac{1}{\tau} \tag{12}$$

Theoretical spectra were calculated by the multiple sites exchange (MSE) program of Johnson.[13] The mean lifetimes, τ, were obtained by comparison of experimental (pmr) and calculated spectra (Figure 1). It should be noted that the chemical shifts (*ca.* δ 3.90) of experimental pmr spectra were temperature independent throughout the temperature range assessable in this study. Therefore, the mole fraction, $C_{VI}/C_{IV} + C_{VI}$, could be calculated from eq 8 and substituted into eq 12.

$$\frac{C_{VI}}{C_{IV} + C_{VI}} = \frac{4.01 - 3.90}{2.38} = 0.0462$$

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[12] F. A. Bovey in "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 187.

[13] C. S. Johnson, in "Advance in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965, p 33.

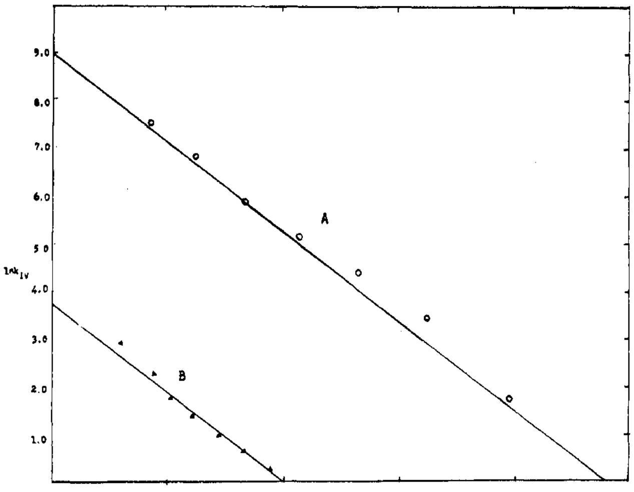


Figure 5.—Arrhenius plot of ln k vs. $1/T$.

A simple relation between k_{IV} and τ is shown in eq 13. The values of the Arrhenius activation energy, E_a, and the preexponential factor, A, were determined from the slope and intercepts of ln k_{IV} *vs.* $1/T$ plots (Figure 5, line A). It was found that $E_a = 7.62 \pm 0.9$ kcal/mol and $A = 10^{9.8 \pm 1.1}$.

$$k_{IV} = \frac{0.0462}{\tau} \qquad (13)$$

The temperature-dependent pmr spectra of the doublet ($CH_3\overset{+}{C}FCH_3$, VI) were recorded from a SO_2ClF solution containing SbF_5 (31.3 mmol), HF (31.3 mmol), and IV (27.5 mmol). The experimental and calculated spectra are displayed in Figure 3. By a similar approach, the one directional rate constants, k_{IV}, were obtained at different temperatures. A plot of ln k_{IV} *vs.* $1/T$ is shown in Figure 5 (line B). From the slope and the intercepts, the Arrhenius activation energy of 7.35 ± 0.8 kcal/mol and a preexponential factor of $10^{6.5 \pm 1.2}$ were obtained.

Other Systems.—In analogous studies we found that protonation of acetylene (VIII) and vinyl fluoride (IX) as well ionization of 1,1-difluoroethane (X) in excess of $HF-SbF_5-SO_2ClF$ (5/1 mol/mol) at −78° all gave similar species. These solutions displayed identical pmr spectra: a shielded three-proton doublet at δ 1.78 ($J_{HH} = 4.2$ Hz) and a deshielded one-proton quartet at δ 6.20 ($J_{HH} = 4.2$ Hz) (Figure 6, bottom trace). Both resonances were deshielded when SbF_5-SO_2ClF was added to the above solutions. These results can be well interpretated as $CH_3\overset{+}{C}HF$ (XI) exchanging fluorine with X (eq 14), a situation similar to the previously observed process.

$$\left.\begin{array}{l} HC{\equiv}CH\ (VIII) \\ H_2C{=}CHF\ (IX) \\ CH_3CHF_2\ (X) \\ CH_3CHCl_2\ (XII) \\ CH_3CHClNO_2\ (XIII) \\ CH_3CHFCl\ (XIV) \end{array}\right\} \xrightarrow[(5/1\ \text{mol/mol}),\ -78°]{HF-SbF_5-SO_2ClF}$$

$$\underset{XI}{CH_3\overset{+}{C}HF} + SbF_6^- \rightleftharpoons \underset{X}{CH_3CHF_2} + SbF_5 \qquad (14)$$

Furthermore, even 1,1-dichloroethane (XII), 1-chloronitroethane (XIII), and 1-chlorofluoroethane (XIV) reacted with $HF-SbF_5-SO_2ClF$ (5/1 mol/mol) at −78° to give the same equilibrium system of X and XI. Obviously, VIII reacted with 1 mol of HF to form IX and then further protonation of IX took place to give XI, but XI is highly reactive and was quenched by fluoride ion from the medium to form X. The equilibrium is then established. Both XII and XIII can be ionized in strong acid medium to give methylchlorocarbenium ion, $CH_3\overset{+}{C}HCl$ (XV). However, XV is not stable and will attack the gegenion (F^-) to give XIV. Further ionization of XIV will generate XI and will then equilibrate (eq 15). Similar halogen–fluorine exchange has been found in dimethylchlorocarbenium ion and dimethylbromocarbenium ion.[9]

$$\left.\begin{array}{l} CH_3CHCl_2\ (XII) \\ CH_3CHClNO_2\ (XIII) \end{array}\right\} \xrightarrow[(5/1\ \text{mol/mol}),\ -78°]{HF-SbF_5-SO_2ClF} \underset{XV}{CH_3\overset{+}{C}HCl} \xrightarrow{F^-}$$

$$\underset{XIV}{CH_3CHFCl} \xrightarrow{\text{ionized}} CH_3\overset{+}{C}HF \underset{SbF_5}{\overset{SbF_6^-}{\rightleftharpoons}} \underset{X}{CH_3CHF_2} \qquad (15)$$

The observation of the dependence of chemical shifts upon the relative concentration of SbF_5 and HF, which subsequently control the equilibrium (eq 15), has been discussed previously. No fluorine nmr resonance was detected from these reaction mixtures except those of the solvent, SO_2ClF and SbF_6^- (or $Sb_2F_{11}^-$).

Similarly, when a solution of X (53.0 mmol), SbF_5 (3.2 mmol), and HF (3.2 mmol) in SO_2ClF was prepared at −78°, temperature dependence of the nmr (^1H and ^{19}F) spectra was observed as shown in Figures 6 and 7. Due to the complexity of the spectra and the limits of accuracy of the multiple site exchange program, no attempt was made to calculate the rates of the exchange reaction at various temperatures.

Attempts to prepare methylfluorocarbenium ion XI either by protonation of IX with FSO_3H-SbF_5 or from XIV with SbF_5-SO_2ClF were reported previously to be unsuccessful.[9] Similarly, when we ionized X with excess of SbF_5-SO_2ClF at −80°, the pmr spectrum showed an upfield doublet at δ 4.32 ($J_{HH} = 1.8$ Hz) and a downfield quartet at δ 10.47 ($J_{HH} = 1.8$ Hz). These data are not consistent with the formation of ion XI, because both chemical shifts are too shielded for XI and also because of the absence of proton–fluorine coupling. In addition, no fmr resonance was observed except that of the solvent and acid systems. We therefore conclude that the two observed pmr signals are due to the exchange reaction of X and XI, in which the equilibrium was shifted further to the left (eq 15). It should be noted that the proton–proton coupling constant is smaller than that observed previously. When HF was added to this solution, both resonances became more shielded and the coupling constants were also increased. The two signals decreased in intensity as the temperature was increased and disappeared at −20° after 5 min. Apparently, decomposition (to unknown polymers) took place. In the presence of water, protonated acetaldehyde was the sole product observed (eq 16).

$$\underset{X}{CH_3CHF_2} \underset{SbF_6^-}{\overset{SbF_5}{\rightleftharpoons}} \underset{XI}{CH_3\overset{+}{C}HF} \xrightarrow{H_2O} CH_3{-}\underset{H}{\overset{+OH_2}{C}}{-}F \xrightarrow{-HF} CH_3\underset{+OH}{\overset{}{CH}} \qquad (16)$$

In addition, we found that difluoromethane was inert toward SbF_5-SO_2ClF or $FSO_3H-SbF_5-SO_2ClF$ at low temperature. Since the methylfluorocarbenium ion

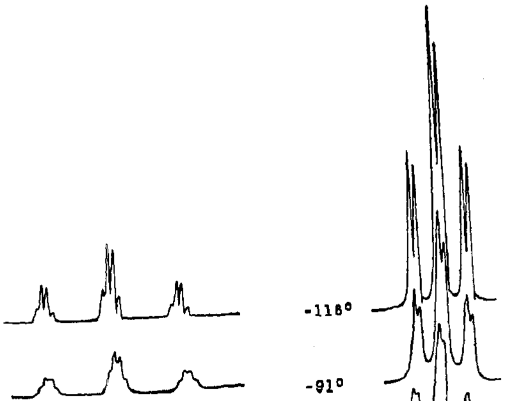
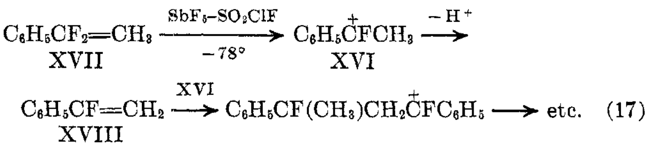


Figure 6.—Temperature-dependent pmr spectra of X–SbF$_5$–HF (16.5:1:1:) in SO$_2$ClF solution. (The bottom trace was obtained when a small amount of HF was added to the above solution at −78°.)

XI is not stable under our experimental conditions, $\overset{+}{C}H_2F$ should be even less stable. On the other hand, phenylmethylfluorocarbenium ion XVI has been directly observed as a stable long-lived species, but it polymerized with added α,α-difluorophenylethane ($C_6H_5CF_2CH_3$, XVII) instead of exchanging fluorine. Obviously, XVI, similarly to the styryl cation ($C_6H_5\overset{+}{C}HCH_3$), could deprotonate to form α-fluorostyrene ($C_6H_5CF{=}CH_2$, XVIII) and then polymerize (eq 17).



$$\underset{\text{XVII}}{C_6H_5CF_2{=}CH_3} \xrightarrow[-78^\circ]{SbF_5\text{–}SO_2ClF} \underset{\text{XVI}}{C_6H_5\overset{+}{C}FCH_3} \xrightarrow{-H^+}$$

$$\underset{\text{XVIII}}{C_6H_5CF{=}CH_2} \xrightarrow{\text{XVI}} C_6H_5CF(CH_3)CH_2\overset{+}{C}FC_6H_5 \longrightarrow \text{etc.} \qquad (17)$$

Fluorine-19 and Carbon-13 Nmr Spectra.—The fmr spectra of IV show a heptet (J_{HF} = 19 Hz) at φ 81.5 (from CFCl$_3$). Under the same conditions as those used when temperature-dependent pmr spectra were observed, fmr spectra were also recorded at various temperatures. These spectra are shown in Figure 2. It is important to note that the fluorine signals do not coalesce to a singlet, but broaden, reduce intensity, and finally at higher temperature merge into the base line. This is due to the fact that fluorine resonances disappear in the fluoroantimonate region when the exchange rates are more rapid than $1/J_{HF}$. This observation also provides support that the fluorine exchange between IV and VI (eq 4) is less important under these conditions. Hence, the exchange reaction is a pseudo first order with regard to both IV and VI.

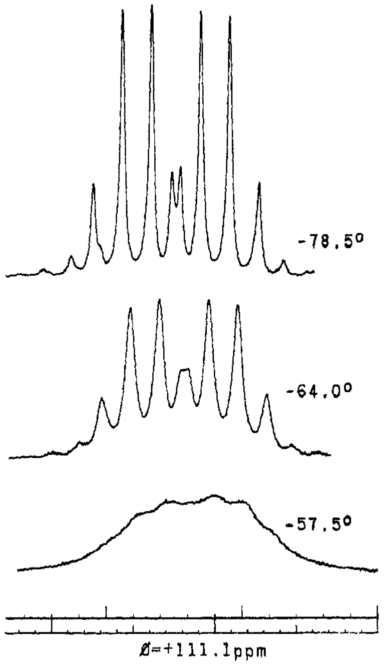


Figure 7.—Temperature-dependent fmr spectra of X–SbF$_5$–HF (16.5:1:1) in SO$_2$ClF solution.

Similarly, the fmr heptet (J_{HF} = 26 Hz) of VI also showed temperature dependence (Figure 4). The disappearance of the fluorine signals at higher temperature was also observed. Under conditions where a singlet was observed in the pmr spectrum between δ 1.88 and 3.83, no fmr resonance was observed, except those of solvent SO$_2$ClF and SbF$_6$.

Temperature dependent fmr spectra of X in HF–SbF$_5$–SO$_2$ClF are shown in Figure 7. Close similarities can be observed in Figures 2, 4, and 7.

The fluorine exchange systems were also studied by carbon-13 nmr spectroscopy. The carbon-13 chemical shifts of each system are tabulated in Table I. It should be noted the carbon shifts of –CF$_2$ and –CHF$_2$ carbon atoms are deshielded substantially as SbF$_5$ concentration is increased. However, the methyl carbons show only a small change of chemical shifts in the same series.

The C$_2$ carbon of VI has a cmr shift of δ ^{13}C − 142.0 (from CS$_2$). For comparison, it is only 6.5 ppm deshielded from the carbenium atom of the *tert*-butyl cation[14] indicating back donation from the fluorine atom to the carbenium center in ion VI.

Experimental Section

Materials.—All the compounds used were commercially available except 2,2-difluoropropane and α,α-fluoroethylbenzene which were prepared by methods described previously.[9]

Nmr Spectra.—The pmr and fmr spectra were obtained on a

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[14] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

TABLE I

CARBON-13 NMR SHIFTS OF FLUORINE EXCHANGING FLUOROCARBENIUM ION SYSTEMS[a]

$CH_3CF_2CH_3$ (IV)	$-CF_2$	$-CH_3$	CH_3CHF_2	$-CHF_2$	$-CH_3$
IV in SO_2ClF at −40°	+68.2	+167.4	X in SO_2ClF at −60°	+77.5	+174.6
IV in HF (excess)–SbF_5–SO_2ClF at −60°	+67.7	+168.1	X in HF (excess)–SbF_5–SO_2ClF at −60°	+71.8	+145.2
IV in HF–SbF_5–SO_2ClF (5/1 mol/mol) at −60°	−91.0	+157.3	X in HF–SbF_5–SO_2ClF (5/1 mol/mol) at −60°	−59.1	+140.4
IV in excess SbF_5–SO_2ClF at −60°	−142.0	+155.0			

[a] Carbon-13 shifts are in parts per million from external CS_2.

Varian Associates Model A-56-60A spectrometer equipped with variable temperature probes. Probe temperatures were calibrated before use. TMS and $CFCl_3$ in a capillary were used for proton and fluorine references, respectively. Carbon-13 spectra were obtained by the INDOR method described previously.[15]

Preparation of Ions.—Solutions of ions were prepared as described previously in this series, with concentrations and conditions given in text.

Registry No.—IV, 420-45-1; VI, 14665-81-7; X, 75-37-6; XI, 29526-61-2; HF, 7664-39-3; SbF_5, 7783-70-2; SO_2ClF, 13637-84-8.

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Vinylic Cations from Solvolysis. X. SN1 and Nucleophilic Addition–Elimination Routes for 9-(α-Haloarylidene)fluorenes

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The solvolysis of α-anisyl-β,β-diphenylvinyl chloride and bromide (1-Cl and 1-Br) in 80% EtOH in the presence of acetate, hydroxide, benzylthiolate, and *p*-toluenethiolate ions is mechanistically SN1. The solvolysis of 9-(α-haloarylidene)fluorenes (2 and 4) in 80% EtOH in the presence of acetate ion also follows the SN1 route. However, 2 and 4 react in the presence of *p*-toluenethiolate and benzylthiolate ions *via* the nucleophilic addition–elimination substitution route. Various criteria (the substituent effect, the solvent effect, the "element effect," the dependency on the nucleophile, and the kinetics) for differentiation between the two routes were investigated and discussed and the behavior of compounds 1 and 2 is compared.

Two of the important mechanisms of nucleophilic vinylic displacement of the leaving group X by the nucleophile Nu^- are the nucleophilic addition–elimination route[1-3] (Ad_N–El, eq 1) and the SN1 route[1,2,4,5]

$$RCX{=}CYR' + Nu^- \xrightarrow{\text{slow}} RCX(Nu)\bar{C}YR' \longrightarrow RC(Nu){=}CYR' + X^- \quad (1)$$

(eq 2). Other mechanisms such as the "elimination–

$$RCX{=}CR'R'' \xrightarrow[-X^-]{\text{slow}} R\overset{+}{C}{=}CR'R'' \xrightarrow{Nu^-} RC(Nu){=}CR'R'' \quad (2)$$

addition" routes[1-3] are dependent on the presence of an allylic or a vinylic hydrogen and are less general. The two mechanisms differ by many mechanistic criteria. The rate of the SN1 route is of a first order and is independent of added nucleophiles. This route is activated by electron-donating α substituents R, and it shows an "element effect" of the leaving group X and is accelerated by polar solvents. Both cis and trans isomers give the same product mixture.[6] The Ad_N–El route is of a second order and its rate is strongly nucleophile dependent. The reaction is activated by electron-attracting groups Y from the β position, it shows a small k_{Br}/k_{Cl} element effect, and its stereochemical outcome is retention of configuration.[1-3] No system which reacts by both routes is known. Competition between the powerfully SN1 activating α-*p*-dimethylaminophenyl group and the two Ad_N–El activating β-cyano groups of $p\text{-}Me_2NC_6H_4C(Cl){=}C(CN)_2$ resulted in the Ad_N–El route alone.[7] Indeed, the SN1 route often competes with the electrophilic addition–elimination route,[8] while the Ad_N–El route often competes with the elimination–addition routes.[1-3]

It was of interest to find a system capable of reacting under different conditions by both the SN1 and the Ad_N–El routes. Since triarylvinyl halides are known

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