Preparation of Solutions of Cations. Most of the ions discussed were prepared from carbinol precursors. Best results were obtained by freezing approximately 60 mg of the alcohol into the wall of a test tube containing about 1.5 ml of the acid solution at −78°. The alcohol is then gently washed into solution. Careful agitation at the start is usually required. Complete mixing is accomplished with a vortex mixer. Typical acid solutions were ~1:3 (v/v) SbF_5–SO_2ClF and saturated solutions (prepared at −10°) of SbF_5 in SO_2.

Quenching of Solutions of Ions. About 0.3 g of precursor alcohol was ionized as usual at −78°. The solution was allowed to stand at this temperature for 3.0 hr, at which time pmr showed no precursor remaining. The solution was added dropwise to a rapidly stirred solution of 100 ml of ice-water containing 5.0 g of K_2CO_3 and 25 ml of diethyl ether. The aqueous layer was repeatedly extracted with ether and reduced in volume. Glpc was generally carried out on a Perkin-Elmer Model 226 gas chromatograph using a 50 × 0.01 in. capillary polypropylene glycol "R" column at 60°. Products were identified by comparison with authentic samples. Ratios of cyclobutanol to cyclopropylcarbinol varied (see text).

Nuclear Magnetic Resonance Spectra. Proton spectra were recorded at 60 and 100 MHz on Varian Associates Model A56-60A and HA-100 spectrometers. Capillary TMS was used as reference. ^{13}C spectra were obtained by the indor method. The general technique employed has been described previously.[46] We have since modified the instrumentation. The proton (monitoring) signal was obtained at 100 MHz with a Varian HA-100 spectrometer. The 25.1-MHz frequency was obtained from a Monsanto 3100 Digital Frequency Synthesizer. Frequency sweeping was accomplished by means of the voltage ramp of a C-1024 time-averaging computer which in some cases was also used for signal accumulation by rapid (30–60 Hz sec^{-1}), repetitive sweeping through the 25.1 MHz region. ^{13}C shifts were calculated with respect to $^{13}CS_2$. Negative shifts indicate resonances downfield from $^{13}CS_2$.

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Friedel–Crafts Chemistry. VII.[1] The Methyl and Ethyl Fluoride–Antimony Pentafluoride Complexes. Structure and Alkylating Ability. Evidence for the Intermediacy of the Ethyl Cation

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Abstract: The $CH_3F{\rightarrow}SbF_5$ and $CH_3CH_2F{\rightarrow}SbF_5$ complexes were prepared at low temperature in SO_2 solution. Their structure was studied by spectroscopy (^1H, ^{13}C, ^{19}F nmr, laser Raman). Spectroscopic and isotopic labeling experiments show the intermediacy of the ethyl cation in solutions of ethyl fluoride and antimony pentafluoride. The alkylating power of methyl and ethyl fluoroantimonates is unmatched by that observed for any previously reported methylating or ethylating agent.

The interaction of primary and secondary alkyl halides with Lewis acid halides has been a topic of extensive study.[2-4] Literature of Friedel–Crafts alkylation reactions has indicated that in the presence of acid catalysts, alkyl halides undergo either limiting formation of an alkyl halide–Lewis acid halide complex or carbenium ion formation through heterolytic cleavage of the carbon–halogen bond. For these two possibilities, Friedel–Crafts alkylation can occur either *via* a displacement reaction of the alkyl halide–Lewis acid halides complex or a direct alkylation by the carbenium ion, respectively. In recent years, we found that tertiary and secondary alkyl halides in antimony pentafluoride solution generally form stable carbenium ion fluoroantimonates. We have also shown[3r] that an excess of primary (and, under certain conditions, secondary or even tertiary) alkyl halides (other than fluorides) yields dialkylhalonium ion salts with antimony pentafluoride. No primary alkylcarbenium ions were, however, ever observed.

Infrared spectroscopic studies of methyl chloride in $SnCl_4$ and $SbCl_5$ solution[3h] and studies of methyl fluoride in BF_3 solution[3d,n] indicate that these exist as slightly polarized donor–acceptor complexes. From their kinetic study, Brown, Pearsall, and Eddy[3b] concluded that Lewis acid halide catalyzed alkylation of

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aromatic hydrocarbons by primary alkyl halides involves a nucleophilic displacement reaction on the donor–acceptor complex. Roberts, Ropp, and Nevill[3c] have reported that ethyl halides yield with aluminum chloride almost complete scrambling of the α and β carbons of the ethyl group (as observed by ^{14}C label). This scrambling was consistent with the formation of an ethyl cation and/or an elimination–addition mechanism. In analogous experiments using excess benzene as solvent, no scrambling of the α and β carbons was observed.[3c,e] It was concluded that with excess benzene, alkylation occurs through displacement on an ethyl halide–aluminum halide complex or by very rapid (faster than 1,2 shift) reaction of ethyl cation (a very unlikely possibility). Nakane, Kurihara, and Natsubori have reported recently a study in which ethyl-*2*-^{14}*C* iodide and aluminum chloride in *n*-hexane were used as an alkylating mixture for benzene and toluene. In this case scrambling of 20% of the ^{14}C label from the α to the β carbon of the ethyl group in the ethyl aromatic product was found.[3q,5] Our studies of the ethylation of benzene and toluene[6] indicate that under the conditions used by Nakane scrambling may occur through exchanging diethyliodonium ion system. Thus, no conclusive evidence for the intermediacy of methyl and ethyl cations in the Lewis acid halide catalyzed alkylation of aromatics with methyl and ethyl halides has been reported.

Alternatively, evidence of the intermediacy of the ethyl cation in the solvolysis of ethyl tosylate is convincing.[7] A recent study of the solvolysis of CH_3CH_2OTs in 96% H_2SO_4 at 30° indicates <5% rearrangement after nine half-lives (nmr).[7a] Similar experiments with CH_3CH_2OTs and CD_3CH_2OTs in FSO_3H at 0° show small but measurable amounts of H(D) scrambling after 40% reaction. Almost statistical distribution of the deuterium label was observed before exchange of deuterium with solvent acid was detected.[7b] This was in marked contrast to the solvolysis of propyl tosylate, for which elimination–addition mechanism is predominate as shown by very rapid exchange of H(D) with protic solvents and by trapping of the intermediate olefin with Br_2. Roberts and Yancey have reported[7c] that ethyl cation formed possibly from diazotization of ethylamine must react with the solvent more rapidly than it undergoes intramolecular 1,2-hydrogen shift. In this case, only 1.5% scrambling of ^{14}C from the β to the α carbon of the ethyl group was observed. This is consistent only with greater reactivity of carbenium ions formed from diazonium salts (extremely reactive ["hot"] carbenium ions) than those obtained from alkyl halides with Lewis acids.

From our previous studies it was evident that primary alkylcarbenium ions are indeed so reactive that direct observation of the methyl and ethyl cations in significant concentration is not likely. This is true even for superacid media like SbF_5, FSO_3H-SbF_5 and HF-SbF_5. We have undertaken presently a detailed study of the methyl fluoride- and ethyl fluoride–antimony pentafluoride systems. We present now our findings on the properties and nature of solutions of CH_3F and CH_3CH_2F in SbF_5 or SbF_5–SO_2 and SbF_5–SO_2ClF as observed by nmr and laser Raman spectroscopy and the rather unique behavior of these systems.

Results

Preparation and Spectroscopic Study of Methyl and Ethyl Fluoride–Antimony Pentafluoride Complexes. Hydrogen-1 Nmr (Pmr) Spectra. I. Methyl Fluoride. To a solution of antimony pentafluoride in SO_2 was added CH_3F–SO_2 solution (0.9 CH_3F–SbF_5–$8SO_2$) at −78°. A clear colorless solution results. At −78° the pmr spectrum of this solution shows a sharp singlet at δ 5.56 and depending on the completeness of the reaction the separate doublet (J_{HF} = 45.7 Hz) at 4.50 of CH_3F. When the solution is allowed to stand at −78° or is warmed to −60°, the disappearance of the methyl fluoride doublet at δ 4.50 is accompanied by a 1:1 increase in the integrated area of the deshielded singlet at 5.56.

The pmr spectra of solutions prepared similarly with excess methyl fluoride–CH_3F–$SbF_5 > 1$ show the same deshielded singlet at δ 5.56 and doublet at 4.50 throughout the temperature range −70 to −95°. This indicates that there is no interaction (within the limits of the nmr time scale) between uncomplexed excess CH_3F and the species yielding the deshielded singlet in these solutions. The pmr results show that the stoichiometry of the reaction of methyl fluoride and antimony pentafluoride is limiting in SbF_5 at a mole ratio of 1:1. In addition the rate of exchange of fluorine is apparently independent of the concentration of the species yielding the deshielded singlet.

The CH_3F–SbF_5 complex can also be prepared in SO_2ClF solution (pmr δ 5.6 (s)). The solution also contains a second species showing a pmr singlet at δ 4.6 and found (by comparison with an authentic sample) to be the SbF_5 complex of methyl fluorosulfite, CH_3OSOF–SbF_5.

In FSO_3H–SO_2 and FSO_3H–SbF_5–SO_2 solution methyl fluoride forms methyl fluorosulfate, CH_3OSO_2F (δ 4.2, ϕ −31). Assignments were again made by comparison (and addition of) authentic samples in the same solvent system.

II. Ethyl Fluoride. To a solution of 1 ml of SbF_5 in 5 ml of SO_2 at −78° was added a solution of 0.25 ml of ethyl fluoride in 3 ml of SO_2 at −60° (1:3 EtF–SbF_5–8 SO_2). After stirring for 2 min at −78° the resulting mixture was clear and colorless. The pmr spectrum of this solution at −70° shows a well-resolved quartet at δ 6.22 (J_{HH} = 7.1 Hz; J_{HF} = 0 Hz) and a triplet at 1.94 (J_{HH} = 7.1 Hz; J_{HF} = 0 Hz). Solutions prepared with excess ethyl fluoride (EtF–$SbF_5 > 1$) show a separate doublet of quartets at δ 3.50 (J_{HH} = 7.1 Hz; J_{HF} = 47.0 Hz) and a doublet of triplets at 1.21 (J_{HH} = 7.1 Hz; J_{HF} = 28.4 Hz).

As with CH_3F, limiting stoichiometry in antimony pentafluoride of 1:1 mole C_2H_5F–SbF_5 ratio is observed. No change in the deshielded quartet and triplet was observed in the pmr spectra of ethyl fluoride–excess SbF_5 solutions on cooling to −100°. The ^{19}F exchange is also apparently independent of $CH_3CH_2F \rightarrow SbF_5$ concentrations. However, when a solution of ethyl fluoride in excess SbF_5–SO_2 is heated, reversible temperature-dependent pmr spectra shown in Figure 1

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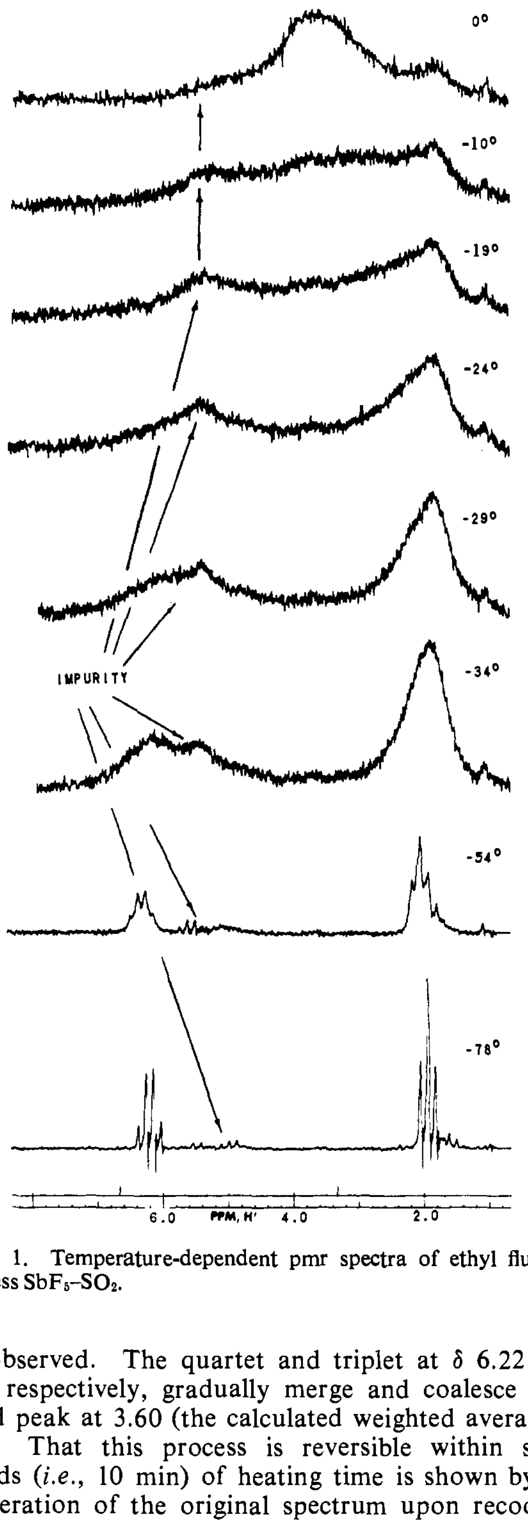

Figure 1. Temperature-dependent pmr spectra of ethyl fluoride in excess SbF_5–SO_2.

are observed. The quartet and triplet at δ 6.22 and 1.94, respectively, gradually merge and coalesce to a broad peak at 3.60 (the calculated weighted average is 3.65). That this process is reversible within short periods (*i.e.*, 10 min) of heating time is shown by the regeneration of the original spectrum upon recooling the mixture (with generally only less than 1% decomposition of the complex; see Figure 1).

The same proton exchange equilibrium and temperature dependence (Figure 1) are observed for ethyl fluoride in excess FSO_3H–SbF_5 or HF–SbF_5–SO_2.[8] In addition, the pmr signals of the protons of FSO_3H and HF in these solutions remain well resolved at approximately the same chemical shifts (*i.e.*, they show normal temperature-dependent shifts) throughout the entire range of temperatures reported in Figure 1. Thus if intermolecular proton exchange with the protic acids is occurring, it is not taking place at a rate fast enough to affect noticeably the rate of intramolecular proton scrambling in the ethyl group. That this is actually the case is shown by the reaction of CD_3CH_2F with excess FSO_3H–SbF_5 and HF–SbF_5 in SO_2 and that of CH_3CH_2F in excess FSO_3D–SbF_5 and DF–SbF_5 in SO_2.

When CD_3CH_2F is allowed to react with excess SbF_5–SO_2, FSO_3H–SbF_5–SO_2, or HF–SbF_5–SO_2 at −78°, fast equilibrium deuterium scrambling is evident from the pmr spectra of the resulting solutions. Based on the 2.09 protons present in the ethyl fluoride-d_3 precursor (determined from pmr integration), the values calculated for statistical scrambling of H and D are 0.84 proton at the α carbon and 1.25 protons at the β carbon. The experimentally observed values taken as an average for 12 integrals of the pmr signals for five different runs were for the α and β carbons, 0.77 ± 0.02 and 1.32 ± 0.04 protons (error limits represent maximum experimental deviations), respectively. This is consistent with nearly statistical D scrambling, with a small accompanying secondary deuterium isotope effect. Deuterium shows a small 1.06 ± 0.03% preference for the α carbon of the ethyl group in the ethyl fluoride–antimony pentafluoride complex. When the same reactions are run with $^{13}CH_3CH_2F$ (90%) a statistical 50:50 distribution of ^{13}C in the α and β carbon positions is shown by integration of the ^{13}C satellites in the pmr spectrum.

For the reaction of CH_3CH_2F with FSO_3D–SbF_5 and DF–SbF_5 at −78° in SO_2, there is no detectable incorporation of deuterium in the ethyl group at −78° over a 5-hr period. When these solutions are heated to −20° for a few minutes and recooled, observable incorporation of D into the ethyl group is noted in the pmr spectra. Thus, although protic acids do not affect the rate of intramolecular proton exchange in the ethyl group, a much slower intermolecular exchange of protons does occur with FSO_3H and HF.

On standing at −78°, gradual changes in the pmr spectrum of excess CH_3CH_2F in SbF–SO_2, FSO_3H–SbF_5–SO_2, and HF–SbF_5–SO_2 are noted. Appearance of a doublet of quartets at δ 5.23 (J_{HH} = 7.1 Hz; J_{HCSF} = 1.8 Hz) and a triplet at 1.61 (J_{HH} = 7.1 Hz) is accompanied by a concomitant 1:1 decrease in the integrated area of the originally observed deshielded quartet and triplet in the pmr spectrum of these solutions. These changes occur with no apparent variation in concentration of excess ethyl fluoride. By addition of an authentic sample, the newly formed species is shown to be ethanesulfonyl fluoride ($CH_3CH_2SO_2F$). The reaction with SO_2 proceeds slowly (with SbF_5, $t_{1/2}$ = 21 hr) at −78° until all of the species yielding the originally observed deshielded pmr quartet and triplet have been consumed. On the other hand, SO_2 in the CH_3F–SbF_5–SO_2 system—at least in the studied low-temperature range (<−20°)—does not react to form CH_3SO_2F regardless of the relative concentrations of the reagents.

Reaction of CH_3CH_2F with SbF_5 in SO_2ClF at −78° is very sensitive and, in our hands, a maximum of only 5% (v/v) concentration of the species yielding the deshielded quartet and triplet in the pmr spectrum is obtainable. Attempts to increase concentration of ethyl fluoride in these solutions lead to changes in the pmr

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(8) In FSO_3H–SbF_5–SO_2 or FSO_3H–SO_2 media, the slow formation of CH_3CH_2–OSO_2F occurs in the heated (−20 to 0°) CH_3CH_2F solutions (δ 5.1 (q), 1.7 (tr), J = 7.5 Hz),

spectrum consistent with condensation reaction of the CH_3CH_2F. The pmr signals of the ethyl protons of the CH_3CH_2F–SbF_5–SO_2ClF mixture at −78° are considerably broadened and are also slightly deshielded relative to the analogous mixture with SO_2 as solvent. The temperature dependence of the pmr spectrum in SO_2ClF appears to be analogous. However, broadening, merging, and coalescence occur at temperatures about 15° lower in this solvent. The deshielded quartet is observed at δ 6.30 (J_{HH} = 6.5 Hz; J_{HF} = 0 Hz) and the deshielded triplet at 2.06 (J_{HH} = 6.5 Hz; J_{HF} = 0 Hz). The C_2H_5F–SbF_5 complex can also be prepared when ethylene is dissolved in HF–SbF_5 (1:1) at −78°.[9]

Fluorine-19 Nmr (Fmr) Spectra. With SbF_5 (SO_2) the fmr spectra of excess ethyl fluoride and methyl fluoride (RF–$^1/_3SbF_5$) have very broad and unresolvable (−78 to 0°) absorptions (width about 1000 Hz) centered at +113 ppm (from CCl_3F). This type of signal is characteristic of an RF–SbF_5 system.[10] Excess ethyl fluoride appears as a characteristic fmr triplet (J_{HF} = 48 Hz) of quartets (J_{HF} = 28.4 Hz) centered at ϕ +270.5 (external capillary of CCl_3F (lit.[11] ϕ +271.9). Excess methyl fluoride in SbF_5–SO_2 shows a characteristic fmr quartet (J_{HF} = 45.7 Hz) at ϕ +271.9. The fmr spectra of CH_3F–$^1/_3SbF_5$–$8SO_2$ and CH_3CH_2F–$8SO_2$ solutions are essentially temperature independent through the range 0 to −100°.

Carbon-13 Nmr (Cmr) Spectra. The cmr shift of the $0.9CH_3F$–SbF_5–SO_2 system occurs at δ 117.8 (from CS_2) with $J_{^{13}C\text{-}H}$ = 166 Hz. The ^{13}C nmr parameters of CH_3F (in SO_2 solution) are δ 118.9 (from CS_2), $J_{^{13}C\text{-}H}$ = 149. There is, therefore, only a small deshielding ($\Delta\delta$ = 1.1) of the methyl carbon of methyl fluoride in SbF_5–SO_2. However, a substantial increase ($\Delta J_{^{13}C\text{-}H}$ = 15 Hz) in the $J_{^{13}C\text{-}H}$ coupling constant of the CH_3 group is observed.

The cmr shift of the α carbon atom of ethyl fluoride in SbF_5–SO_2 obtained by main peak enhancement of the pmr quartet at δ 6.22 is $\delta_{^{13}C}$ +104.0 (from CS_2) with $J_{^{13}C\text{-}H}$ = 162 Hz. Excess ethyl fluoride in the same solution shows an α carbon cmr shift of +107 and that obtained for ethyl fluoride in SO_2 is +109.0 (from CS_2) with $J_{^{13}C\text{-}H}$ = 150.0 Hz. Thus, as in the CH_3F–SbF_5–SO_2 case, a significant increase in J_{CH} ($\Delta J_{^{13}CH}$ = 12 Hz) and a small shift ($\Delta\delta$ = 2.0) of the α carbon cmr signal to lower field is observed.

Raman Spectra. The laser Raman spectrum of a $0.9CH_3F$–SbF_5–SO_2 solution[12] shows lines at 526, 653, 685, 738, 1008, 1150, 1330, 2863, and 2590 cm^{-1}. These lines are nearly identical with those obtained for the additive Raman spectra of SbF_5 and CH_3F in SO_2 solution. The intense line usually assigned to the υ_1 vibration of SO_2 in the $SO_2 \rightarrow SbF_5$ complex at 1106 cm^{-1} is not observed in the CH_3F–SbF_5–SO_2 spectrum. The similarities in the fundamental Raman-active vibrations of CH_3F and methyl fluoride in the $CH_3F \rightarrow SbF_5$ complex show that the weakening of the C–F bond in methyl fluoride is not sufficient to alter significantly the tetrahedral geometry the molecule possesses in neutral solution.

In a number of lines and line frequencies, the Raman spectrum of ethyl fluoride with excess SbF_5 (SO_2) is very similar to the additive spectra of ethyl fluoride in SO_2 and that of SbF_5. The $\Delta(\Delta\nu)$ for the C_α–F bond of ethyl fluoride in SO_2 (1004 cm^{-1}) and ethyl fluoride with excess SbF_5 in SO_2 (1000 cm^{-1}) is 4 cm^{-1}.

Reactions of Methyl and Ethyl Fluoride–Antimony Pentafluoride Complexes. The CH_3F–SbF_5–SO_2 and CH_3CH_2F–SbF_5–SO_2 solutions are extremely powerful new alkylating mixtures capable of methylating and ethylating n donor, π donor, and σ donor bases.

I. Alkylation of n Donor Bases. Equation 1 shows

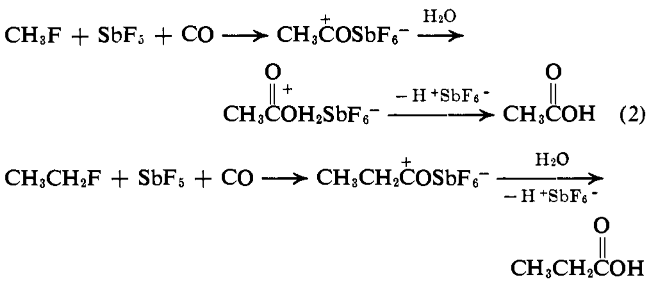
$$\mathrm{RF} + \mathrm{SbF_5} + (\mathrm{R'})_n\mathrm{Y}\!: \xrightarrow{\mathrm{SO_2}} (\mathrm{R'})_n\overset{+}{\mathrm{Y}}\mathrm{R}\cdot\mathrm{SbF_6}^- \qquad (1)$$

R = methyl, ethyl; Y = $-\ddot{\underset{..}{\mathrm{O}}}-$, $-\ddot{\underset{..}{\mathrm{S}}}-$, $-\underset{|}{\ddot{\mathrm{N}}}-$, $-\ddot{\underset{..}{\mathrm{Cl}}}\!:$, $-\ddot{\underset{..}{\mathrm{Br}}}\!:$, $-\ddot{\underset{..}{\mathrm{I}}}\!:$

R′ = alkyl, aryl; n = 1, 2, 3

the reaction of CH_3F and CH_3CH_2F and SbF_5–SO_2 with heteroorganic compounds. Reactions were performed by addition of an aliquot portion of CH_3F–SbF_5 (CH_3CH_2F–SbF_5) in SO_2 at *ca.* −60° to a calculated amount of heteroorganic n base substrate at −78°. At least two runs with each system, one with alkylating agent in excess and one with n-donor base in excess, were carried out. Alkylation of n-donor bases by CH_3F and especially CH_3CH_2F with SbF_5–SO_2 is unselective and vigorous. In fact, care must be taken to mix the reagents slowly with stirring to prevent side reactions from occurring. The "onium" products are generally formed with CH_3F and CH_3CH_2F in SbF_5–SO_2 with nearly quantitative yield, as analyzed by nmr spectroscopy. Table I summarizes a series of methylated and ethylated onium ions obtained.

Although carbon monoxide is a relatively weak base, it reacts readily with CH_3F–SbF_5 and C_2H_5F–SbF_5 under pressure (∼200 psi) to give in high yield the oxocarbenium ions. Hydrolysis of the resulting mixtures yields the corresponding carboxylic acids



$$\mathrm{CH_3F + SbF_5 + CO \longrightarrow CH_3\overset{+}{C}OSbF_6^- \xrightarrow{H_2O} CH_3\overset{\overset{\displaystyle O}{\|}}{C}\overset{+}{O}H_2SbF_6^- \xrightarrow{-H^+SbF_6^-} CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH} \qquad (2)$$

$$\mathrm{CH_3CH_2F + SbF_5 + CO \longrightarrow CH_3CH_2\overset{+}{C}OSbF_6^- \xrightarrow[-H^+SbF_6^-]{H_2O} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH}$$

Even SO_2 reacts, as mentioned previously, with C_2H_5F–SbF_5 to slowly give ethanesulfonyl fluoride, although this reaction was not observed (at least at the studied low temperatures < −20°) with CH_3F–SbF_5.

O-Alkylation of sulfur dioxide under the reaction conditions must be considered a rapid reversible process, as alkyl fluorosulfites were found to cleave with ease with loss of SO_2. Sulfur trioxide reacts with the complexes to give the corresponding fluorosulfates (CH_3OSO_2F and $C_2H_5OSO_2F$) which cleave only under more forcing conditions.

When CH_3F–SbF_5 (and C_2H_5F–SbF_5) is prepared in "wet" SO_2 the solution shows the presence of protonated methanol and dimethyl ether (identified through their well-known pmr spectral parameters), indicating

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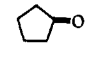
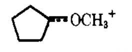
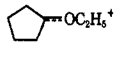
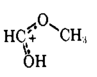
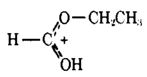
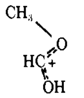
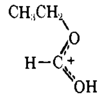
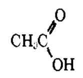
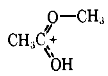
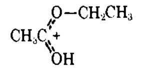
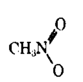
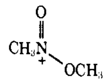
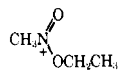
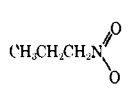
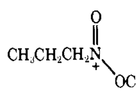
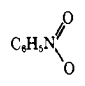
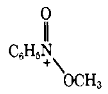
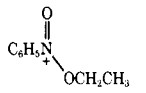
Table I. Representative Methylated and Ethylated Onium Ions Obtained with CH_3F–SbF_5 and C_2H_5F–SbF_5

Heteroorganic substrate	Methylated onium ion	Ethylated onium ion
$(CH_3)_2O$	$CH_3O(CH_3)_2^+$	$(CH_3)_2OC_2H_5^+$
$(C_2H_5)_2O$	$C_2H_5O(CH_3)(C_2H_5)^+$	$(C_2H_5)_3O^+$
CH_3OH	$CH_3O(CH_3)H^+$	$(C_2H_5)CO(CH_3)H^+$
$(CH_3)_2C{=}O$	$(CH_3)_2C\overline{\cdots}OCH_3^+$	$(CH_3)_2C\overline{\cdots}OC_2H_5^+$
$(C_2H_5)_2C{=}O$	$(C_2H_5)_2C\overline{\cdots}OCH_3^+$	$(C_2H_5)_2C\overline{\cdots}OC_2H_5^+$
		
$(C_6H_5)_2C{=}O$	$(C_6H_5)_2C\overline{\cdots}\ddot{O}CH_3^{+d}$	
$CH_3CH{=}O$	$CH_3CH\overline{\cdots}\ddot{O}CH_3$	$CH_3CH\overline{\cdots}OC_2H_5$
$C_6H_5CH{=}O$	$C_6H_5CH\overline{\cdots}\ddot{O}CH_3$	$C_6H_5CHC{=}OC_2H_5^+$
$HC(OH){=}O$		
		
		
		
		
		
$[(CH_3)_2CH]_2S$	$[(CH_3)CH]_2SCH_3^+$	
$(C_2H_5)_2S$	$(C_2H_5)_2SCH_3$	$(CH_3CH_2)_3S^+$
tert-BuS—H	*tert*-$BuSHCH_3^+$	*tert*-$BuSHC_2H_5^+$
$(C_2H_5)_3N$	$(C_2H_5)_3NCH_3^+$	$(CH_3CH_2)_4N^+$

O-methylation (ethylation)

$$CH_3F\text{-}SbF_5 + H_2O \xrightarrow{SO_2} CH_3\overset{+}{O}H_2\ SbF_6^- \underset{}{\overset{-H^+}{\rightleftharpoons}}$$

$$CH_3OH \xrightarrow[CH_3F\text{-}SbF_5]{} (CH_3)_2OH^+$$

The extremely high reactivity of CH_3F and CH_3CH_2F in SbF_5–SO_2 is further exemplified by their reaction with alkyl halides (RX where X = Cl, Br, I) to form the new and interesting species, dialkylhalonium ions. We

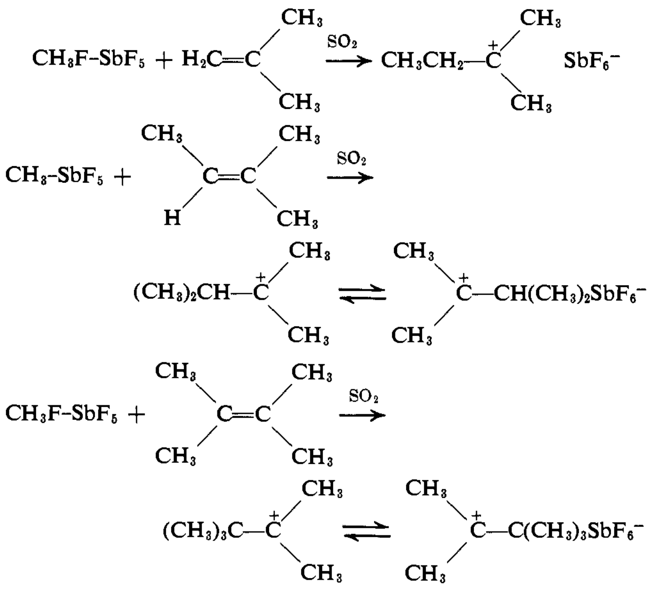
$$CH_3F + SbF_5 + RX \xrightarrow[SO_2ClF]{SO_2\text{ or}} R\overset{+}{X}CH_3 + SbF_6^- \qquad (3)$$

have recently reported the isolation and characterization of dimethylhalonium fluoroantimonate salts prepared by methylation with CH_3F in SbF_5–SO_2.[3r] Ethylation of alkyl halides with CH_3CH_2F in SbF_5–SO_2 occurs analogously to give ethyl alkylhalonium ions.[13]

In sharp contrast to alkyl chlorides, bromides, and iodides, alkyl fluorides are not n-alkylated and give no dialkylfluoronium ions (RFR^+). In all probability the reason is that fluorine as the most electronegative element is unable to acquire positive charge. Alkylation of alkyl fluorides consequently takes place on carbon (see subsequent discussion).

In each case shown in eq 1, alkylation leads to formation of "onium" ions quantitatively. No exchange between excess alkylating agents and onium ions is observed on the pmr time scale between 0 and −78°. As observed for dialkylhalonium ions,[3r] many of the fluoroantimonate salts of the onium ion products can be isolated upon evaporation of solvent, excess alkyl fluoride, and precursor alkyl halide.

II. Alkylation of π Bases. When solutions of olefins in SO_2 or SO_2ClF at ∼−60° are added slowly with stirring to a solution of excess CH_3F or CH_3CH_2F in SbF_5–SO_2, the formation of carbenium ions is observed. With mono- and dialkyl-substituted olefins significant side reactions such as polymerization and fluorination are observed. For 1,1-dialkyl, tri-, and tetraalkyl-substituted olefins, formation of the expected stable tertiary carbenium ion is predominant. For example, the reaction of isobutylene and tri- and tetramethylethylene with CH_3F in SbF_5–SO_2 yields tertiary amyl and tetra- and pentamethylethyl cations, respectively.



Alkylation of aromatic hydrocarbons such as benzene and toluene by CH_3F and CH_3CH_2F and SbF_5–SO_2ClF at −78° gives solutions whose pmr spectra indicate irreversible formation of the intermediate benzenium fluoroantimonate complexes.[14] These solutions give after quenching >70% yields of the monomethylated and monoethylated aromatics, respectively.[6]

$$RC_6H_5 + CH_3F\text{-}SbF_5 \xrightarrow[-78\text{ to }-60°]{SO_2ClF}$$

$$RC_6H_5CH_3^+SbF_6^- \xrightarrow[H_2O,\ 0°]{HCO_3Na} RC_6H_4CH_3$$

R = H or alkyl

Methylation of toluene at −78° with short (<1 min) reaction times gives 54% *o*-, 18% *m*-, and 28% *p*-xylene. Similar ethylations result in 39% *o*-, 19% *m*-, and 41% *p*-ethyltoluene. Dialkylated products are always present in the product mixture and generally vary from 1 to 10% depending on the concentration of reagents.

III. Alkylation of σ Bases (Including Self-Condensation). When methyl fluoride is dissolved in neat antimony pentafluoride at room temperature, a solu-

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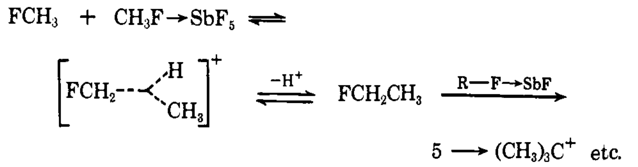
(13) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970).

(14) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, Chapter 20, p 837.

Table II. Nmr and Raman Spectroscopic Data of Methyl Fluoride and Ethyl Fluoride and Their Antimony Pentafluoride Complexes in Sulfur Dioxide Solution

	Nmr			Raman
	^{1}H (δ, TMS) [J_{H-F}]	^{19}F (δ, CCl$_3$F)	^{13}C (δ, ^{13}CS$_2$) [$J_{^{13}C-H}$]	C–F stretching frequency, cm^{-1}
CH_3F	4.50 [45.7]	270.5	119 [149]	1010
CH_3F-SbF_5	5.56 [0]	Exchanging	118 [166]	1008
Δδ [ΔJ]	1.06 [45.7]		[17]	$\Delta[\Delta\bar{\nu}] = 2$
CH_3CH_2F	3.50 [47.0]	271.9	103 [150]	1004
CH_3CH_2F-SbF_5	5.99 [0]	Exchanging	101 [162]	1000
Δδ [ΔJ]	2.49 [47.0]		2 [12]	$\Delta[\Delta\bar{\nu}] = 4$

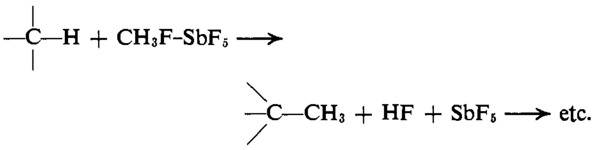
tion is formed whose pmr spectrum consists of a singlet at δ 5.50 and peaks at 4.35 and 12.5. The intensity of the latter two absorptions increases (at the probe temperature, +35°) with time. Quenching experiments indicated that the signal at δ 4.35 is the tertiary butyl cation and the peak at δ 12.5 was identified by control experiments as being due to HF. Thus methyl fluoride is seen to readily undergo a self-condensation reaction in neat SbF$_5$. Based on peak area integration for each mole of tertiary butyl cation, 3 mol of HF is formed. In a separate experiment, methylation of methyl fluoride by CH_3F-SbF_5 yielded identical results.



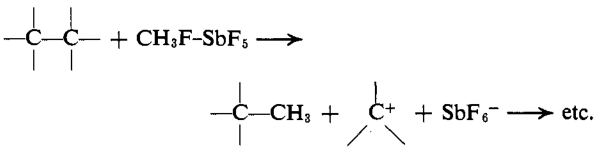
When methyl fluoride was treated with 1:1 HF-SbF$_5$ at 0° only the exchanging $CH_3F \rightarrow SbF_5$ complex (pmr singlet δ 5.50 (s)) is originally formed. The complex then slowly converts ($t_{1/2} \sim 1$ hr) to the tertiary butyl cation (singlet at δ 4.35). In FSOH-SbF$_5$, or when adding FSO$_3$H to the above solution, methyl fluorosulfate is formed, indicating that when incipient primary ions are formed they are such powerful electrophiles that they will O-alkylate fluorosulfonate to the corresponding covalent esters. For ethyl fluoride, dissolution in SbF$_5$ at room temperature leads to a more complex mixture than that formed with methyl fluoride. The pmr spectrum of the resulting solution consists of several resonances which were identified by quenching and control experiments to be due to tertiary amyl (~25%), tertiary hexyl (~25%), and tertiary butyl (~10%) cations. Approximately 40% of the products formed were not identified. Attempts to add ethyl fluoride in substantial concentrations to SbF$_5$-SO$_2$ClF even under carefully controlled low-temperature conditions lead to a solution analogous to that observed with neat SbF$_5$ at room temperature. The pmr spectra of these solutions show a very broad single line resonance at δ 6.9–7.5. The species yielding this pmr signal has been identified by control experiments to be HF exchanging with the system. Integration of the pmr spectra indicates that HF is formed in quantities consistent with the stoichiometry of the cation formation reactions. With SO$_2$ as solvent, the reaction proceeds smoothly at −78° to form the stable CH_3CH_2F-SbF_5-SO_2 solution discussed above.

Warming this solution to < −20° leads (with excess SbF$_5$) to the very slow formation of the tertiary amyl, tertiary hexyl, and tertiary butyl cations.

The self-condensation reactions of methyl and ethyl fluoride in SbF$_5$-SO$_2$ solution are specific examples of the alkylation of σ donor bases. In these cases the σ donor bases are the C–H and C–C bonds of the alkyl fluorides. The extraordinary reactivity of these alkylating mixtures is further exemplified by the fact that they slowly react with hydrocarbons such as neopentane and isobutane even at −78°. The reaction of CH$_3$F and CH$_3$CH$_2$F in SbF$_5$-SO$_2$ with a variety of alkanes gives alkylation products consistent with eq 4 and 5.



(4)



(5)

The overall process is, of course, more complicated as intermediate carbenium ions (eq 5) and newly formed hydrocarbons (eq 4 and 5) also undergo hydride transfer and alkylation, and the found higher molecular weight hydrocarbon ions undergo, in turn, fragmentation.[15]

Discussion

The Structure of CH$_3$F and CH$_3$CH$_2$F in SbF$_5$-SO$_2$ (and Related Media). I. Methyl Fluoride–Antimony Pentafluoride. Nmr and Raman spectroscopic data obtained for solutions of 0.9CH$_3$F-SbF$_5$ and 0.9CH$_3$-CH$_2$F-SbF$_5$ in SO$_2$ are summarized in Table II. The methylation reactions of CH$_3$F in SbF$_5$-SO$_2$ and related media show that the pmr singlet at δ 5.56 is due to a methyl group resonance. Lack of ^{19}F–H coupling and absence of an fmr chemical shift for the fluorine atom of CH$_3$F in these solutions are indicative of a rapid fluorine exchange involving the C–F and Sb–F bonds. Lack of interaction on the nmr time scale between the methyl group exchanging fluorine and excess methyl fluoride indicates that the fluorine exchange is occurring intramolecularly. The pmr and cmr results show that for both CH$_3$F and CH$_3$CH$_2$F the reaction with SbF$_5$ is limiting in SbF$_5$ at a mole ratio of 1:1. Antimony pentafluoride itself can form dimeric, trimeric, and possible higher polymeric anions, but addition of excess antimony pentafluoride yields no observable change in the pmr spectra of CH$_3$F-SbF$_5$-SO$_2$ solutions. These results show, therefore, that complex formation according to eq 6 is irreversible within the

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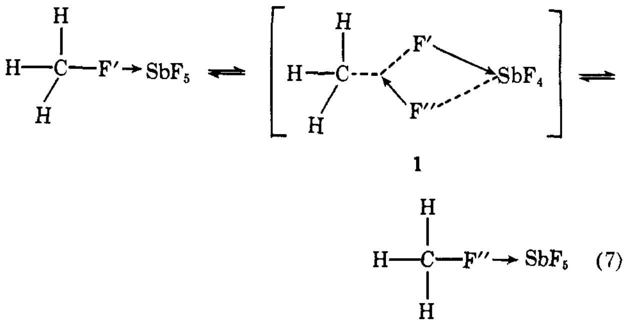
[15] The detailed discussion of the mechanism and products of these alkylation reactions will be reported separately.

$$CH_3F + SbF_5\text{–}SO_2 \longrightarrow CH_3F\text{–}SbF_5 \text{ (or } Sb_2F_{10}\text{, etc.)} + SO_2 \quad (6)$$

limits of the nmr time scale. This indicates that there is a strong and binding interaction between the fluorine atom of methyl fluoride and antimony pentafluoride. In addition, the lack of dependence of ^{19}F exchange, as observed, by nmr, on the concentration of the $CH_3F\rightarrow SbF_5$ complex indicates that an intermolecular exchange process involving two or more complex molecules is not a principle mechanism for fluorine exchange. On the other hand, only very small deshielding of the pmr and cmr shifts of the methyl group exchanging fluorine is observed. The only significant change observed is the increase of the $J_{^{13}C\text{–}H}$ coupling constant of the methyl exchanging fluorine (17 Hz). These increases in $J_{^{13}C\text{–}H}$ are consistent with an increase in the s character of the C–F carbon's molecular orbitals. This, of course, is consistent with an increase in sp^2 character of this carbon due to formation of an intermediate species of fluorine exchange that is highly polarized.[16]

Further evidence for both the strong binding of the fluorine atom of methyl fluoride to antimony pentafluoride and also for the lack of significant change in the C–F bond is obtained from the Raman spectra of CH_3F in $SbF_5\text{–}SO_2$. The Raman line at 1106 cm^{-1} observed usually for SO_2 in the $SO_2\rightarrow SbF_5$ complex is not found in the Raman spectrum of $0.9CH_3F\text{–}SbF_5\text{–}SO_2$. Methyl fluoride must, therefore, be a stronger n donor base than SO_2 in these solutions leading to exclusive formation of $CH_3F\text{–}SbF_5$ species. Similarities in the fundamental Raman-active vibrations of CH_3F and those spectroscopically detectable species from $CH_3F\text{–}SbF_5$ show that overall weakening of the C–F bond is not sufficient to alter significantly the tetrahedral geometry of methyl fluoride.

All of these data are consistent only with the formation of the tightly bound donor–acceptor complex $CH_3F\rightarrow SbF_5$ undergoing *rapid intramolecular fluorine exchange*. Thus far, we have not discussed the mechanism by which fluorine may be exchanged in the tightly bound $CH_3F\rightarrow SbF_5$ complex. Rapid intramolecular fluorine exchange and lack of significant change in the C–F bond of methyl fluoride are consistent only with the predominate species in $CH_3F\text{–}SbF_5\text{–}SO_2$ being tightly bound $CH_3F\rightarrow SbF_5$. *These highly polar species through which CH_3F undergoes fluorine exchange in these solutions—be they intermediate or transition states—must be present only in very small concentration in equilibria with $CH_3F\rightarrow SbF_5$.* Possible mechanisms by which fluorine can be exchanged intramolecularly are shown by eq 7 and 8. Equation 7 shows a transition state of the intramolecular nucleophilic exchange (substitution) of F′ by F″. This could be pictured to occur in one step *via* bimolecular nucleophilic frontside substitution. An alternate process for fluorine exchange is formation of an intermeduate intimate ion-pair complex[17] **2** (eq 8) in very small concentration, in rapid equilibrium with $CH_3F\text{–}SbF_5$ and its subsequent collapse allowing frontside exchange (analogous to SN] substitution).[18]



1

(7)

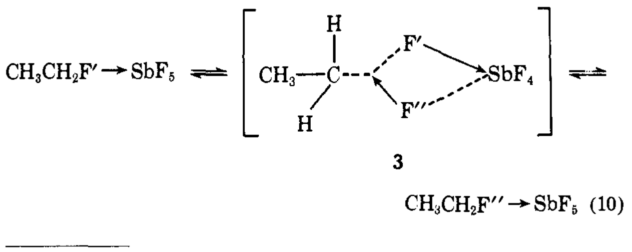
$$CH_3\text{—}F\rightarrow SbF_5 \rightleftharpoons CH_3^+SbF_6^- \quad (8)$$

2

Distinguishing between these two mechanistic possibilities of fluorine exchange is difficult and we have to rely on the analogy (apparent from spectral studies and chemical reactivity) between the methyl and ethyl fluoride–antimony pentafluoride complexes (see subsequent discussion). In any case it should be kept in mind that mechanisms 7 and 8 represent limiting cases and any degree of intermediate character between **1** and **2** should be possible.

II. Ethyl Fluoride–Antimony Pentafluoride. The reactions and low-temperature (−70 to −150°) nmr data of ethyl fluoride in $SbF_5\text{–}SO_2$ are analogous to those observed for $CH_3F\text{–}SbF_5\text{–}SO_2$. The slightly more deshielded pmr and cmr chemical shifts and very similar Δδ's (Table II) observed for CH_3CH_2F relative to CH_3F in $SbF\text{–}SO_2$ and related media are consistent with the greater ease of polarization and/or cleavage of the C_α–F bond of ethyl fluoride. A very similar $\Delta J_{^{13}C\text{–}H}$ (Table II) for the C_α–H in CH_3CH_2F (12 Hz) and that in CH_3F (17 Hz) is also observed. The Raman spectral data of $CH_3CH_2F\text{–}SbF_5\text{–}SO_2$ are completely analogous to those discussed for $CH_3F\text{–}SbF_5\text{–}SO_2$. With SbF_5, therefore, ethyl fluoride forms a similar tightly bound donor–acceptor complex ($CH_3CH_2F\rightarrow SbF_5$, eq 9) which undergoes rapid intramolecular fluorine exchange. Equations 10 and 11 show the two limiting pathways possible for fluorine exchange in $CH_3CH_2F\text{–}SbF_5$, which are entirely analogous to eq 7 and 8 previously discussed for the related fluorine exchange process in $CH_3F\text{–}SbF_5$.

$$CH_3CH_2F + SbF_5 \rightleftharpoons CH_3CH_2F\rightarrow SbF_5 \quad (9)$$



3

(10)

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(16) We have, however, observed instances in ^{13}C nmr studies where increases in $J_{^{13}C\text{–}H}$ of carbenium atoms were effected by factors other than increases in s character (*cf.* nonclassical ions).

(17) For a thorough discussion of the SNi mechanism see: J. March, "Advances in Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 268–269.

(18) Depictions and text book discussions of the SNi process have always indicated a frontside displacement.[17] We prefer to consider fluorine exchange by mechanism 8 as approaching backside attack by F″ on the methyl carbon. Such a process, possibly accompanied by simultaneous lengthening of the Sb–F′ and Sb–F″ bonds, seems to be a more acceptable alternative to frontside displacement where repulsion of the electrons in the Sb–F″ and C–F″ bonds in the transition state **1** would apparently be a highly unfavorable factor. It should be emphasized that there is no reason to consider a *single* preferred geometry of attack for all SNi type processes. Depending on conditions of individual systems, particularly steric considerations, a whole scope of intermediate geometries of the transition state should be possible, depending how far bonds in the transition state can be distorted.

$$CH_3CH_2F{\rightarrow}SbF_5 \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} CH_3CH_2{}^+SbF_6{}^- \qquad (11)$$

4

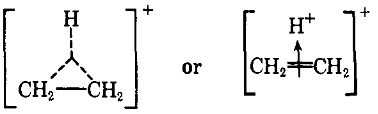
$$C'H_3C''H_2{}^+SbF_6{}^- \underset{-k_2}{\overset{k_2}{\rightleftharpoons}} C''H_3C'H_2{}^+SbF_6{}^- \qquad (12)$$

An additional exchange process, that of hydrogen and carbon scrambling involving equilibration through 1,2 hydrogen shift in the ethyl cation of the intimate ion pair **4**, is shown in eq 12. Rapid intramolecular scrambling of hydrogen and carbon of ethyl fluoride in excess SbF_5–SO_2, $FSO_3H(D)$–SbF_5–SO_2, and $H(D)F$–SbF_5–SO_2 is possible only through formation of an intimate ion pair **4**. If hydrogen and carbon exchange in the ethyl group involved primarily the intermediacy of distinct proton and ethylene (eq 13) inter- and intramolecular proton exchange should occur at approximately the same rate.[7b] Observed fast intramolecular and very slow intermolecular proton exchange is, therefore, consistent only with an intermediate ethyl cation.

$$CH_3CH_2F{\rightarrow}SbF_5 \rightleftharpoons CH_2{=}CH_2 + H^+SbF_6{}^- \qquad (13)$$

The structure of $[CH_3CH_2]^+$ is considered to be the classical equilibrating system (**5**) and not a bridged nonclassical ethyl cation (**6**). Recent theoretical calculations[19] have indicated that the classical equilibrating ethyl cation **5** is *ca.* 11 kcal/mol more stable than the nonclassical ethyl cation **6**. On the basis of distortion energy, it was also suggested[19a] that the more highly substituted alkylcarbenium ions are fairly reliable models for the behavior of the ethyl cation. It has been indeed shown conclusively in our earlier experimental work[20] that stable, long-lived higher substituted alkylcarbenium ions, such as the dimethylisopropyl and dimethyl-*tert*-butylcarbenium ions, are classical equilibrating systems.

$$C'H_3C''H_2{}^+ \rightleftharpoons C''H_3C'H_2{}^+$$



6

The observed deuterium isotope effect (*i.e.*, 1.06% preference of ^1H for C_β) is too small to be related to ethyl cation formation.[21] The effect probably, however, is related to polarization of the H_3C_α–F bond through some process in the complex itself.

The combined spectroscopic studies and isotopic labeling experiments show that hydrogen, carbon, and fluorine exchange occur in $CH_3CH_2F{\rightarrow}SbF_5$ through equilibrium **12**. Thus, cleavage of the C_α–F bond of the complex yields the intimate ethyl cation ion pair **4** and reaction with the gegenion of the ion pair follows at a rate slower than 1,2-hydrogen shift.

III. As was mentioned earlier, analogy between $CH_3F{\rightarrow}SbF_5$ and $CH_3CH_2F{\rightarrow}SbF_5$ may allow drawing some distinction between mechanisms 7 and 8 for $CH_3F{\rightarrow}SbF_5$. The nearly identical spectroscopic characteristics of these two systems stress their very similar chemical nature. The fact that there is little precedent for the formation of transition states such as **1** and since we obtained direct evidence for the intermediacy of ion pair **4** in the $CH_3CH_2F{\rightarrow}SbF_5$ case could suggest that fluorine exchange in $CH_3F{\rightarrow}SbF_5$ is also occurring through ion pair **2**, although no direct experimental evidence is available as obviously no exchange processes can be observed in the methyl system.

The CH_3F–SbF_5 and C_2H_5F–SbF_5 complexes[22] are in our experience the most reactive methylating and ethylating agents known. Their reactivity surpasses more conventional Friedel-Crafts systems,[23] trialkyloxonium ions,[24] dialkylhalonium ions,[3o,3r,12,25] alkyl fluorosulfonates,[26] and other alkylating systems. In their chemical reactivity they truly behave like methyl and ethyl fluoroantimonates, respectively.

Finally it should be mentioned that fragmentative ionization of fluoroformates and fluorosulfites by antimony pentafluoride, found by Olah and Bollinger[27] as a suitable method to generate carbenium ions, gives in the case of methyl and ethyl esters the CH_3F–SbF_5 and C_2H_5F–SbF_5 complexes, respectively. The corresponding fluorosulfates and trifluoromethanesulfonates also cleave to the same complexes *via* disproportionation. Details of the fragmentative and disproportionative behavior, as well as alkylating ability, of these esters will be reported in full separately.

Experimental Section

Materials. Antimony pentafluoride was obtained from the Allied Chemical Co. and was twice distilled before use. Argentous fluoride was obtained from the Harshaw Chemical Co. Methyl and ethyl fluoride were commercially available (Matheson Gas Products and Pierce Chemical, respectively).

Deuterated and ^{13}C-labeled ethyl iodide were obtained from Merck Sharp and Dohme, Ltd., Montreal, Canada. Labeled ethyl fluoride was prepared by the general method of Moissan[28] using halogen exchange of the corresponding iodide with argentous fluoride. The halogen exchange reactions were carried out in small stainless steel pressure cylinders. Nmr spectra of the labeled ethyl fluoride products showed that no scrambling had occurred during the halogen exchange process.

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[19] (a) J. E. Williams, Jr., J. Buso, L. C. Allen, P. v. R. Schleyer, W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970); (b) M. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2144 (1970); (c) D. T. Clark and D. M. Lilley, *Chem. Commun.*, 549 (1970).

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

[21] A referee informed us that a similar isotope effect was also observed in Professor M. Saunder's work.

[22] We are depicting throughout this paper the $CH_3F{\rightarrow}SbF_5$ and $C_2H_5F{\rightarrow}SbF_5$ complexes as 1:1 compositions with monomeric SbF_5. It should be recognized, however, as discussed in detail by Gillespie (J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969); **48**, 3413 (1970)), and also in some of our preceding work (A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969)), that antimony pentafluoride complexes frequently also can have 1:2 (or 1:3) stoichiometry, due to the ease with which SbF_5 forms fluorine-bridged polymers. Similarly the gegenions in the fluoroantimonate complexes which are defined as monomeric $SbF_6{}^-$ can also be $Sb_2F_{11}{}^-$ (or $Sb_3F_{16}{}^-$). In SO_2, however, SbF_5 tends to form a monomeric 1:1 complex, SO_2–SbF_5, and thus subsequent monomeric complex (or ion) formation is possible. As the SO_2ClF–SbF_5 complex is much weaker in this solvent there is less tendency for polymeric SbF_5 complexes (or ions) as is the case in neat SbF_5.

[23] For a review see G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I–IV, Wiley-Interscience, New York, N. Y., 1963–1969.

[24] For a review see H. Meerwein in Houben-Weyl, "Methoden der organischen Chemie," 2nd Ed, Vol. VI/3, 6 Thieme Verlag, Stuttgart, 1965, pp 325–366.

[25] G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); **92**, 718, 2562 (1970).

[26] M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968), or M. G. Ahmed and R. W. Alder, *ibid.*, 1389 (1969).

[27] G A. Olah and J. M. Bollinger, to be published; see also G. A. Olah and J. A. Olah in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 765; G. A. Olah, *Chem. Eng. News*, 81 (Mar 27, 1967).

[28] M. Moissan, *C. R. Acad. Sci.*, 110, 952 (1890); *Ann. Chim. Phys.*, **19**, 272 (1891); F. Swarts, *Bull. Soc. Chim. Belg.*, **30**, 302 (1921).

^{1}H and ^{19}F Nmr Spectra. All pmr spectra were recorded at both 60 and 100 MHz using Varian Associates Model A56/60A and HA-100 spectrometers equipped with variable-temperature probes. ^{19}F nmr spectra were recorded at 56-MHz $\delta_{^1H}$ relative to TMS (δ ^{19}F relative to CCl_3F).

^{13}C Nmr Spectra. ^{13}C spectra were obtained by irradiation of the 100-MHz proton spectrum with a swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[20] ^{13}C shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard.

Raman Spectra. Raman spectra were recorded on a Cary-81 Raman spectrophotometer with laser source (50-mW gas laser using the 6328-Å He–Ne line) equipped with a variable-temperature Raman cell.[11]

Alkylation Reactions. Heteroorganic (n Donor) Bases. The bases used in these alkylation experiments were commercially available. Liquids were distilled and solids recrystallized to ensure purity. A general procedure for the alkylation reactions was used. A calculated amount of n donor base was added to an nmr tube and then cooled to −78° in a Dry Ice–acetone bath. An equivalent amount of the freshly prepared solution of RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2 (SO_2ClF) at *ca.* −60° was then added. The mixture was then stirred at *ca.* −40° until a clear, colorless solution was observed. Pmr spectra of these solutions[3r] were then used to identify the "onium" ions generated.

π Bases. To a solution of excess RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2(SO_2ClF) at −78° in an nmr tube was added with stirring 0.5 equiv of olefin or aromatic π base in SO_2 (SO_2ClF) at *ca.* −60°. The resulting solutions were clear and usually highly colored. These solutions were studied by pmr spectroscopy. In the case of aromatic alkylations the σ complexes were then quenched with aqueous $NaHCO_3$ at 0°. The resulting mixtures were extracted with diethyl ether and the combined extracts dried over $MgSO_4$. The methyl and ethyl aromatic products were then analyzed by capillary gas–liquid chromatography.

σ Bases (Alkanes). Reactions of RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2 with alkanes were run at low temperature according to the same procedure described above for n donor bases. Reactions run at room temperature (or above) were carried out in stainless steel, Teflon-lined pressure cylinders. Normal reaction time at room temperature was about 0.5 hr. At the termination of the reaction, gaseous products were collected and studied by mass spectroscopy. The residual solutions were quenched with $NaHCO_3$–H_2O at −78° and extracted with diethyl ether. The resulting ether solutions were studied by glc.

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5-Dibenzosemibullvalenylcarbinyl Carbene and Carbonium Ion. Some Observations on the Fate of Reactive Groups Attached to the Bridgehead Carbon of a Nonfluxional Semibullvalene

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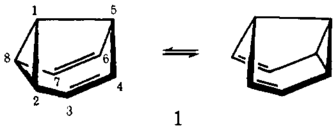
Abstract: The decomposition of 5-dibenzosemibullvalenylcarboxaldehyde tosylhydrazone (**7**) was examined under a variety of conditions. Under aprotic conditions in diglyme, benzo[*b*]fluorene (**8**) was the only product formed. Base-induced decomposition in protic ethylene glycol took an almost totally different course; **8** was again produced, but the 2-hydroxyethyl ether (**9**) predominated by a sizable margin. The reaction mechanisms which best correlate with these results are presented. It is concluded that the derived carbene is the reactive species in aprotic solvent and that the carbinyl cation intervenes in proton-donating media. Independent generation of diazonium ion **25** was found to give rise to a similar product distribution. Mechanistically revealing information was also derived from reactions of **7** in ethylene glycol-d_2. Insight into the behavior of the 5-dibenzosemibullvalenylcarbinyl cation was gained from acetolysis and deamination studies. Tosylate **10** was seen to solvolyze very slowly as a result of the adverse inductive effects of the attached phenyl and cyclopropane rings. Ring expansion was seen under both sets of conditions, with phenyl migrating to the exclusion of cyclopropyl. The factors underlying this phenomenon are discussed and other considerations relating to the neopentyl and rearranged tertiary cations are offered for consideration.

The semibullvalene molecule **1**, restricted for structural reasons to undergo the Cope rearrangement *via* a boatlike transition state,[1] exhibits an activation energy for degenerate rearrangement which is the lowest recorded to this time.[2-4] As a result, the rapid valence tautomerism of this hydrocarbon results



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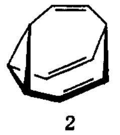
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in the equivalence of carbon atoms 2, 4, 6, and 8, and of 1 and 5 (3 and 7 remain vinyl throughout). Thus, any substituent attached to C_5 of **1**, for example, will be subject to rapid interconversion between two sites of

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(1) Stereochemically unconstrained acyclic 1,5-hexadienes are known to undergo Cope rearrangement preferentially *via* chair transition states. In a typical case, the boatlike form was shown to be at least 5.7 kcal/mol less stable than the chair counterpart: W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

(2) The 60-MHz nmr spectrum of 1 is invariant from −110 to +117°: H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. L. Sherwin, *J. Amer. Chem. Soc.*, 91, 3316 (1969).

(3) Recent MINDO/2 calculations have produced an estimated activation energy of 2.3 kcal/mol for the degenerate rearrangement of 1: M. J. S. Dewar and W. W. Schoeller, *ibid.*, 93, 1481 (1971).

(4) The free energy of activation for the degenerate Cope rearrangement of octamethylsemibullvalene has been measured, *ca.* 6.4 kcal mol: F. A. L. Anet and G. E. Schenk, *Tetrahedron Lett.*, 4237 (1970).