fonyl chloride in 10 ml of dichloromethane was added to a solution of 620 mg (2.70 mmol) of the dienamine **1** and 1.0 ml of triethylamine in 20 ml of dichloromethane at −15°, under nitrogen. After 2 hr at −15° and 12 hr at room temperature, the mixture was extracted with 5% hydrochloric acid, dried over magnesium sulfate, filtered, and concentrated under vacuum. Addition of 1:1 ether–ethyl acetate caused crystallization of products **15** and **16**. The white solid **15**, 100 mg (13% yield), mp 242–244°, was recrystallized from ethyl acetate and methanol to mp 244–246°: $\nu_{\max}^{\mathrm{KBr}}$ 1700 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ; nmr ($CDCl_3$) δ 1.10 (s, 3 H), 4.00 (m, 1 H), 5.50 (s, 1 H), and 7.30–7.70 (m, 5 H).

Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.92; H, 6.96; S, 10.06. Found: C, 67.82; H, 7.05; S, 10.33.

The yellow crystals of **16** were recrystallized from ethanol to give 200 mg (22% yield): mp 169–170°; $\nu_{\max}^{\mathrm{KBr}}$ 1570 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 226 and 393 mμ; nmr ($CDCl_3$) δ 1.04 (s, 3 H), 3.10 (t, 4 H), 3.65 (t, 4 H), 4.20 (m, 2 H), 6.22 (s, 1 H), and 7.30 (s, 5 H).

Anal. Calcd for $C_{22}H_{29}NO_3S$: C, 68.18; H, 7.54; N, 3.62; S, 8.28. Found: C, 68.18; H, 7.55; N, 3.65; S, 8.35.

An intermediate tricyclic enamine could be seen in the initial reaction product by $\nu_{\max}^{\mathrm{neat}}$ 1660 cm^{-1}. This absorption band was lost on hydrolysis or on heating. When the total reaction product mixture was heated for 2 hr at 80°, the ir spectrum changed to that of the ring expanded dienamine **16**. A solution of 50 mg of **16** in 30% aqueous acetic acid was heated at reflux for 1 hr. Extraction with dichloromethane and washing with aqueous sodium carbonate gave a crude product with $\nu_{\max}^{\mathrm{film}}$ 1660 and 1700 cm^{-1}. Trituration with ethyl acetate gave 25 mg (60% yield) of the ketone **15**.

(b) **Dienamine 2.**—This reaction was carried out without triethylamine. A solution of 880 mg (4.63 mmol) of benzylsulfonyl chloride in 10 ml of dichloromethane was added to 2.00 g (9.16 mmol) of dienamine **2** in 50 ml of dichloromethane at −20°, under nitrogen, during 1 hr. After 2 hr at this temperature and 10 hr at room temperature, the mixture was extracted with water; the organic phase was dried over magnesium sulfate and concentrated. Trituration with ethyl acetate gave three products: The bridged sulfone **17**, 350 mg (20% yield), mp 142–143°, was recrystallized from ethyl acetate and cyclohexane to mp 149–150°: $\nu_{\max}^{\mathrm{KBr}}$ 1450 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 215 mμ; nmr ($CDCl_3$) δ 1.5–2.9 (m, 16 H), 3.33 (m, 4 H), 4.52 (s, 1 H), 4.85 (s, 1 H), and 7.20–7.60 (m, 5 H).

Anal. Calcd for $C_{21}H_{27}NO_3S$: C, 67.27; H, 7.29; N, 3.75; S, 8.58. Found: C, 67.27; H, 7.48; N, 3.84; S, 8.98.

The keto sulfone **18**, 100 mg (7% yield), was recrystallized from ethanol to mp 232–233°: $\nu_{\max}^{\mathrm{KBr}}$ 1705 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ; nmr ($CDCl_3$) δ 4.15 (m, 1 H), 5.10 (s, 1 H), and 7.40 (s, 5 H).

Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.07; H, 6.62; S, 10.53. Found: C, 66.88; H, 6.51; S, 10.36.

The dienamine sulfone **19**, 80 mg (4% yield), was recrystallized from ethyl acetate and showed $\nu_{\max}^{\mathrm{KBr}}$ 1575 cm^{-1}: nmr ($CDCl_3$) δ 3.15 (t, 4 H), 3.80 (t, 4 H), 4.30 (t, 2 H), 6.40 (s, 1 H), and 7.40–7.48 (d, 5 H).

Reaction of Phenylsulfene with Dienol Ether 9.—The reaction was carried out as described for method a used with the dienamines. Only *trans*-stilbene, mp 123° (46% yield), and recovered dienol ether **9** were isolated.

Registry No.—**1**, 23088-12-2; **2a**, 23088-05-3; **2b**, 23088-06-4; **3**, 33527-50-3; **4**, 33527-51-4; **5**, 33527-52-5; **6**, 33527-53-6; **7**, 33527-54-7; **8**, 33527-55-8; **9**, 33527-56-9; **10**, 33527-57-0; **11**, 33527-58-1; **12**, 33527-59-2; **13**, 33527-60-5; **14**, 33527-61-6; **15**, 33527-62-7; **16**, 33527-63-8; **17**, 33527-64-9; **18**, 33527-65-0; **19**, 33527-66-1; *trans*-stilbene, 103-30-0.

Organic Fluorine Compounds. XXXIII.[1] Electrophilic Additions to Fluoro Olefins in Superacids

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A series of fluoro olefins (I–X) were studied in the superacid systems, SbF_5–HF–SO_2ClF, SbF_5–HSO_3F–SO_2ClF, or in HSO_3F at low temperature. Eight of the fluoro olefins (I–VIII) reacted with the acid systems to give the corresponding fluoride or fluorosulfonate addition products. A preparative method for preparation of α-fluoroethyl and α,α-difluoroethyl fluorosulfate in 90–95% yield was developed. No long-lived fluorocarbenium ion[2] intermediates were observed, even in these very low nucleophilicity acid systems, as they react rapidly with gegenions to give the observed covalent fluorides or fluorosulfates. Two of the fluoro olefins (IX and X) were found to be inert even in superacids. 1,1,1-Trihaloethanes, CH_3CX_3 (X = F and Cl), reacted with SbF_5–SO_2ClF at −80° to give the first stable methyldihalocarbenium ion, $CH_3C^+X_2$ (X = F and Cl).

Due to the high electronegativity of fluorine the replacement of hydrogen by fluorine in ethylene results in the withdrawal of electron density from the π-electron system. Consequently, most of the ionic reactions of fluoro olefins are due to nucleophilic attack. The ionic reactions of fluoro olefins have been reviewed by Chambers and Hobbs.[3] They concluded that electrophilic attack on fluoro olefins may only be achieved in the presence of strong Lewis acid catalyst. However, no direct evidence was provided for this assumption. With techniques developed in our laboratories for study of stable carbenium ions in superacids and for their low-temperature nuclear magnetic resonance spectroscopic study, we attempted the protonation of a series of fluoro olefins hoping to study their protolytic behaviors and thus directly observe, if possible, the related fluorocarbenium ion and to evaluate the possibility of ionic polymerization of fluoro olefins in superacids.

Results

Ten fluoro olefins ($R_1R_2C{=}CR_3R_4$) were selected for our studies (I–X). Two different superacid media with variable ratio of SbF_5–HF and SbF_5–HSO_3F in

$R_1R_2C{=}CR_3R_4$
I, $R_1 = R_2 = R_3 = H$; $R_4 = F$
II, $R_1 = R_2 = H$; $R_3 = R_4 = F$
III, $R_1 = R_3 = H$; $R_2 = R_4 = F$
IV, $R_1 = R_2 = R_3 = F$; $R_4 = H$
V, $R_1 = R_3 = H$; $R_2 = Cl$; $R_4 = F$
VI, $R_1 = R_2 = R_3 = F$; $R_4 = Cl$
VII, $R_1 = R_2 = R_3 = F$; $R_4 = Br$
VIII, $R_1 = R_2 = R_3 = F$; $R_4 = I$
IX, $R_1 = R_2 = R_3 = R_4 = F$
X, $R_1 = R_2 = R_3 = F$; $R_4 = CF_3$

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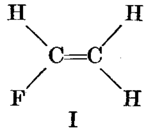
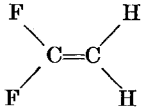
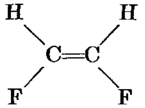
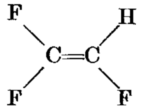
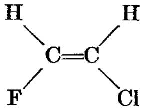
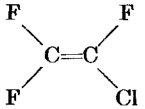
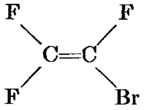
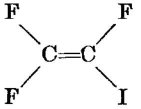
[1] Part XXXII: G. A. Olah and Gh. Mateescu, *J. Amer. Chem. Soc.*, **93**, 781 (1971).

[2] For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *ibid.*, **94**, 808 (1972).

[3] R. D. Chambers and R. H. Mobbs in "Advances in Fluorine Chemistry," Vol. 4, M. Stacey, J. C. Tatlow, and A. G. Sharpe," Ed., Butterworths, London, 1965.

TABLE I

PROTON AND FLUORINE NMR DATA OF FLUORIDE AND FLUOROSULFATE ADDITION PRODUCTS OF FLUORO OLEFINS

Fluoro olefin	Super acid system	Addition product	Pmr parameters[a]	^{19}F nmr parameters[b]
	SbF_5:HF (1:4)–SO_2ClF	CH_3CHF_2	1.78 (3 H, dt, J_{HF} = 21, J_{H-H} = 4 Hz) 5.90 (1 H, tq, J_{HF} = 57, J_{H-H} = 4 Hz)	+111.1 (2 F, dq, J_{HF} = 57, J_{HF} = 21 Hz)
I	HSO_3F–SO_2ClF	$CH_3CHFOSO_2F$	1.84 (3 H, dd, J_{HF} = 21, J_{H-H} = 4 Hz) 6.42 (1 H, dq, J_{HF} = 56, J_{H-H} = 4 Hz)	+118.7 (1 F, ddq, J_{HF} = 56, J_{HF} = 21, J_{FF} = 10 Hz) −42.0 (1 F, d, J_{FF} = 10 Hz)
	SbF_5:HF (1:4)–SO_2ClF	CH_3CF_3	2.01 (3 H, q, J_{HF} = 14 Hz)	+62.0 (3 F, q, J_{HF} = 14 Hz)
II	HSO_3F–SO_2ClF	$CH_3CF_2OSO_2F$	2.17 (3 H, t, J_{HF} = 14.5 Hz)	+64.6 (2 F, dq, J_{HF} = 14.5, J_{FF} = 9 Hz) −45.0 (1 F, t, J_{FF} = 9 Hz)
	SbF_5:HF (1:4)–SO_2ClF	CH_2F+CHF_2	4.84 (2 H, dtd, J_{HF} = 45, J_{HF} = 14, J_{HH} = 3.5 Hz) 5.31 (1 H, tdt, J_{HF} = 53, J_{HF} = 9.5, J_{HH} = 3.5 Hz)	+243.6 (1 F, ttd, J_{HF} = 45, J_{HF} = 9.5, J_{FF} = 1.7 Hz) +132.4 (2 F, ddt, J_{HF} = 54, J_{HF} = 14 Hz, J_{FF} = 17 Hz)
III	SbF_5:HSO_3F (1:4)–SO_2ClF	$CH_2FCHFOSO_2F$	4.98 (2 H, ddd, J_{HF} = 47, J_{HF} = 14, J_{HH} = 3.5 Hz) 7.78 (1 H, ddt, J_{HF} = 54, J_{HF} = 10, J_{HH} = 3.5 Hz)	+241.9 (1 F, tdd, J_{HF} = 47, J_{HF} = 10, J_{FF} = 19 Hz) +139.0 (1 F, m, −45.5 (1 F, d, J_{FF} = 8 Hz)
	SbF_5:HF (1:1)–SO_2ClF	CF_3CH_2F	4.50 (2 H, dq, J_{HF} = 46, J_{HF} = 8.5 Hz)	+242.8 (1 F, tq, J_{HF} = 46, J_{FF} = 15 Hz) +80.8 (3 F, qu, (dt), J_{HF} = 8.5, J_{FF} = 15 Hz)
IV	SbF_5:HSO_3F (1:1)–SO_2ClF	$CFH_2CF_2OSO_2F$	9.46 (2 H, dt, J_{HF} = 45, J_{HF} = 8.5 Hz)	+239.6 (1 F, tt, J_{HF} = 45, J_{FF} = 16.5 Hz) +83.6 (2 F, sex, J_{HF} = 8.5, J_{FF} = 16.5, J_{FF} = 9 Hz) −47.1 (1 F, t, J_{FF} = 9 Hz)
	SbF_5:HF (1:4)–SO_2ClF	CH_2ClCHF_2	3.82 (2 H, td, J_{HF} = 14, J_{HH} = 4 Hz) 6.11 (1 H, tt, J_{HF} = 56, J_{HH} = 4 Hz)	+86.5 (2 F, dt, J_{HF} = 56 Hz, J_{HF} = 14 Hz)
V	SbF_5:HSO_3F (1:4)–SO_2ClF	$CH_2ClCHFOSO_2F$	4.27 (2 H, dd, J_{HF} = 13, J_{HH} = 4 Hz) 6.81 (1 H, dt, J_{HF} = 54, J_{HH} = 4 Hz)	+128.1 (1 F, dtd, J_{HF} = 54, J_{HF} = 13, J_{FF} = 8 Hz) −42.9 (1 F, d, J_{FF} = 8 Hz)
	SbF_5:HF (1:1)–SO_2ClF	CF_3CHFCl	6.61 (1 H, dq, J_{HF} = 47, J_{HF} = 4 Hz)	157.9 (1 F, dq, J_{HF} = 47, J_{FF} = 11 Hz) 101.2 (3 F, dd, J_{HF} = 4, J_{FF} = 11 Hz)
VI	SbF_5:HSO_3F (1:4)–SO_2ClF	CF_3CHFCl		
	SbF_5:HF (1:1)–SO_2ClF	CF_3CHFBr	6.91 (1 H, dq, J_{HF} = 47, J_{HF} = 5 Hz)	+162.2 (1 F, dq, J_{HF} = 47, J_{FF} = 13.5 Hz) +81.8 (3 F, dd, J_{HF} = 5, J_{FF} = 13.5 Hz)
VII	SBF_5:HSO_3F (1:1)–SO_2ClF	CF_3CHFBr		
	SbF_5:HF (1:4)–SO_2ClF	CF_3CHFI	7.31 (1 H, dq, J_{HF} = 45, J_{HF} = 4.4 Hz)	+166.9 (1 F, dq, J_{HF} = 46, J_{FF} = 16.5 Hz) −78.8 (3 F, dd, J_{HF} = 5.5, J_{FF} = 16.5 Hz)
VIII	SbF_5:HSO_3F (1:4)–SO_2ClF	CF_3CHFI		

[a] Proton chemical shifts are referred to external capillary TMS in parts per million, d = doublet, t = triplet, q = quartet, qu = quintet, and sex = sextet. [b] Fluorine chemical shifts are referred to external capillary $CFCl_3$ in parts per million.

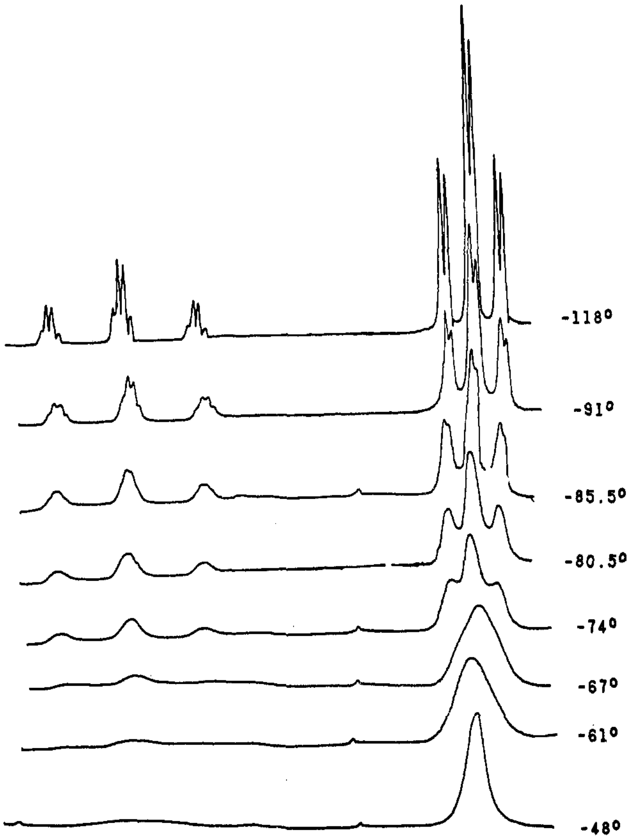


Figure 1a.—Temperature-dependent pmr spectra of fluorine exchange reaction in CH_3CHF_2–SbF_5–SO_2ClF system.

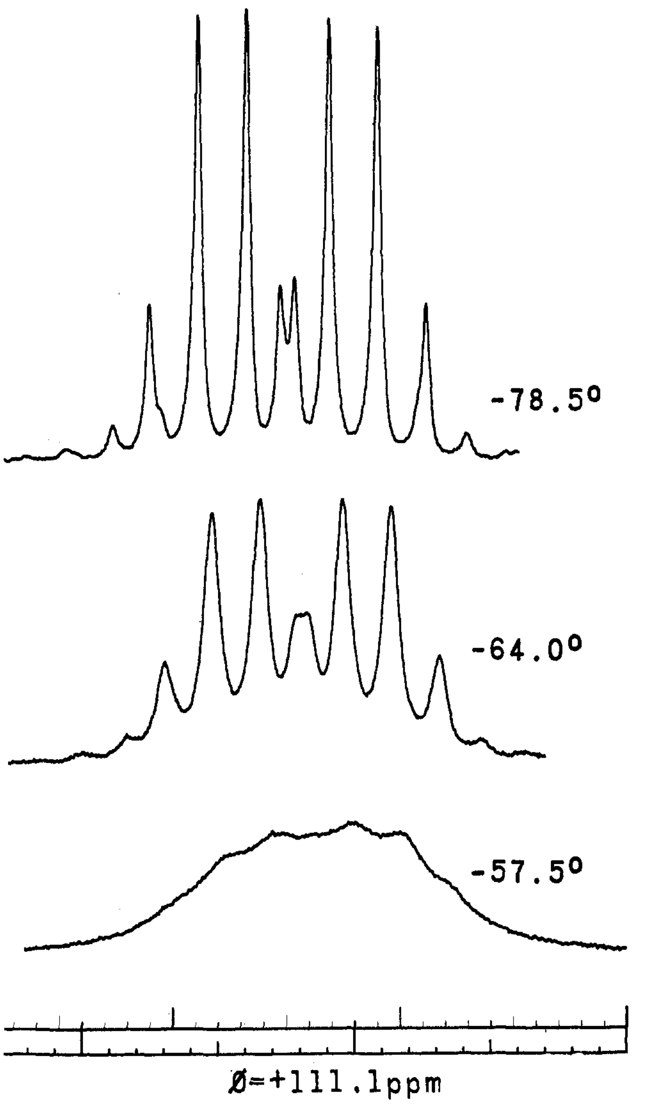


Figure 1b.—Temperature-dependent ^{19}F nmr spectra of fluorine exchange reaction in CH_3CHF_2–SbF_5–SO_2ClF system.

SO_2ClF or SO_2 were used. The results are summarized in Table I.

Vinyl Fluoride (I).—A solution of I in SO_2ClF reacted smoothly with fluorosulfuric acid at −78° to give α-fluoroethyl fluorosulfate, $CH_3CHFOSO_2F$. Alternatively, when I was bubbled into neat fluorosulfuric acid (until saturated) at −78°, $CH_3CHFOSO_2F$ was formed quantitatively as revealed by nmr spectra. A preparative yield of 95% was achieved by isolating the product by vacuum distillation, bp 33° (35 mm). Distillation at atmospheric pressure (bp 92–93°) gave a low yield due to decomposition to 1,1-difluoroethane (see subsequent discussion). In the pmr spectrum of $CH_3CHFOSO_2F$, the methyl group appears as a pair of doublets at δ 1.84 (3 H, $J_{HF} = 21$, $J_{HH} = 4$ Hz). The ^{19}F nmr spectrum of $CH_3CHFOSO_2F$ in HSO_3F–SO_2ClF showed a doublet at ϕ −42.0 ($J_{FF} = 10$ Hz) and a multiplet at ϕ 118.7. The low-field doublet is assigned to $-SO_2F$ and the multiplet to CH_3CHF. The latter is a A_3BMX system and should give a total of 16 lines (first-order spectrum). However, three lines coincide and only 13 lines are observed.

When I was dissolved in SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF at 78°, two products were obtained. The more predominant one is $CH_3CHFOSO_2F$, with 1,1-difluoroethane formed as the minor product. The chemical shifts and coupling constants in both the ^1H and ^{19}F nmr spectra of the solution corresponding to 1,1-difluoroethane were consistent with the spectral parameters of an authentic sample. When the temperature of the solution was raised to −20°, the intensity of both ^1H and ^{19}F signals of 1,1-difluoroethane increased substantially and the gaseous product obtained by distilling the reaction mixture at atmospheric pressure was exclusively 1,1-difluoroethane. This indicates that $CH_3CHFOSO_2F$ undergoes cleavage of SO_3 to give 1,1-difluoroethane. Further, when I was treated with SbF_5–HSO_3F (1/1 *M/M*)-SO_2ClF at −78° it gave 1,1-difluoroethane as a major product, and the concentration of the fluorosulfate was substantially decreased.

The reaction of I with SbF_5–HF–SO_2ClF is more complicated and the reaction conditions are very critical. The observed ^1H and ^{19}F nmr spectra are entirely dependent on the ratio of I, SbF_5, and HF. I reacted with a catalytic amount of SbF_5 in HF–SO_2ClF gave exclusively the HF addition product, *i.e.*, CH_3CHF_2. However, when the concentration of SbF_5 was increased

$$CH_2{=}CHF + HF\text{–}SO_2ClF \xrightarrow[SbF_5]{\text{catalytic}} CH_3\overset{+}{C}HF \underset{SbF_5}{\overset{HF}{\rightleftharpoons}} CH_3CHF_2$$

to about 5 mol % of I and HF kept at a concentration four times that of I, both the ^1H and ^{19}F nmr spectra became temperature dependent (Figure 1). When the mole ratio of SbF_5 to I was 10 mol %, the pmr spectrum of the solution showed a high-field doublet at δ 1.78 (3 H, $J_{HH} = 4$ Hz) and a low-field quartet at δ 6.20 (1 H, $J_{HH} = 4$ Hz). The ^{19}F nmr resonance of either I or CH_3CHF_2 is absent. Both the temperature dependent

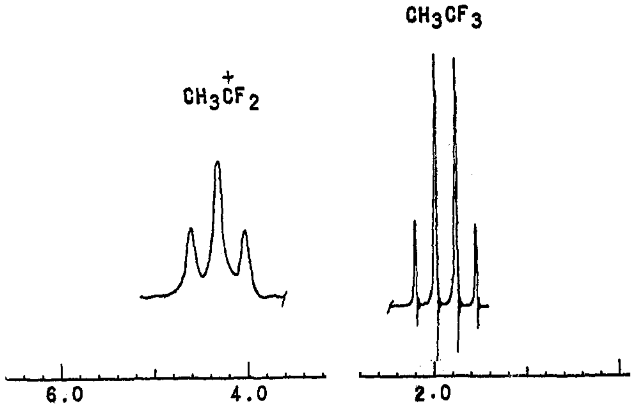
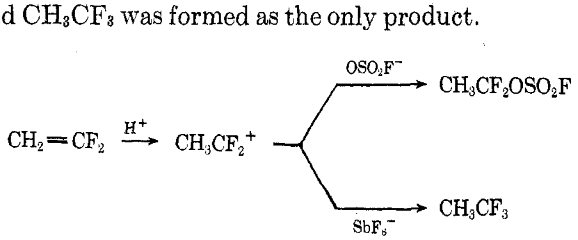


Figure 2a.—Pmr spectra of methyldifluorocarbenium ion and 1,1,1-trifluoroethane.

nmr spectra and the absence of proton–fluorine coupling indicate that CH_3CHF_2 exchanges its fluorines with $CH_3C\overset{+}{C}HF$ or SbF_5.

Furthermore, when 1,1-difluoroethane was ionized in SbF_5–SO_2ClF, with an excess of SbF_5 present, the pmr spectrum of the solution displayed a doublet at δ 4.32 (3 H, J_{HH} = 1.8 Hz) and a quartet at δ 10.47 (1 H, J_{HH} = 1.8 Hz). These two resonances disappeared when the temperature was raised above −40°. Polymer was found in the nmr tube. On the other hand, when CH_3CHF_2 was added gradually at −78° to the above solution mixture, the two resonances became shielded and the coupling constants were increased. The shielding and the increasing coupling constant were proportional to the amount of CH_3CHF_2 added. The same results (shielding of the two resonances and increasing of coupling constant) were obtained when HF was added to the solution mixture instead of CH_3CHF_2. The nature of the exchange reaction will be discussed subsequently.

Vinylidene Fluoride (II).—Reaction of II in HSO_3F–SO_2ClF at −60° led to the formation of α,α-difluoroethyl fluorosulfonate, $CH_3CF_2OSO_2F$. Isolated product in a preparative run was obtained in 90% yield, bp 25° (30 mm). Distillation at atmospheric pressure (bp 67–68°) gave only a low yield due to decomposition to 1,1,1-trifluoroethane. When II was treated with SbF_5–HSO_3F (1/10 *M*/*M*)–SO_2ClF, both the ^1H and ^{19}F nmr spectra indicated that $CH_3CF_2OSO_2F$ was formed as a major product, with CH_3CF_3 as the minor product. When SbF_5HSO_3F (1/4 *M*/*M*) -SO_2ClF acid system was used, $CH_3CF_2OSO_2F$ was not found and CH_3CF_3 was formed as the only product.



II reacted with HF at −50° in the presence of a catalytic amount of SbF_5 to give CH_3CF_3 quantitatively. The solution showed only a pmr quartet at δ 2.0 (3 H, J_{HF} = 14 Hz) and a ^{19}F nmr quartet at φ 62.0 (3 F, J_{HF} = 14 Hz). Pure CH_3CF_3 could be obtained by careful distillation of the solution. Protonation of II with SbF_5–HF (1/4 *M*/*M*) -SO_2ClF did not produce the difluoromethylcarbenium ion, $CH_3\overset{+}{C}F_2$, and again gave CH_3CF_3 as the major product. However, $CH_3\overset{+}{C}F_2$ was obtained by the treatment of CH_3CF_3 with SbF_5–SO_2ClF at −80°. The ion shows a pmr triplet at δ 4.50 (3 H, J_{HF} = 17 Hz) and a ^{19}F nmr quartet at φ −96.4 (2 F, J_{HF} = 17 Hz) (Figure 2).

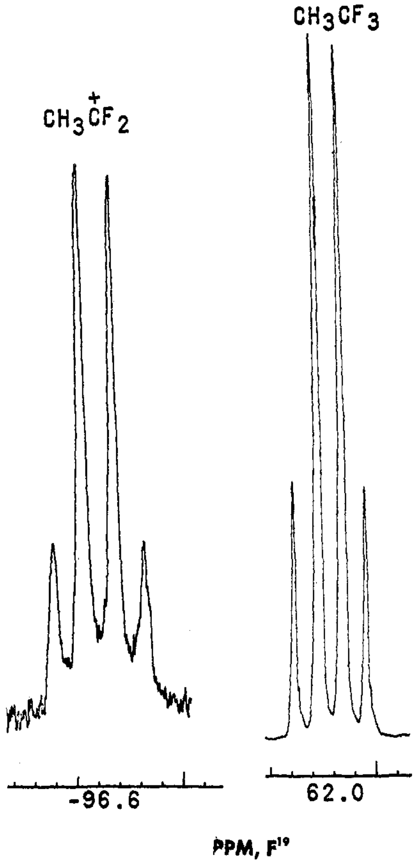


Figure 2b.—^{19}F nmr spectra of methyldifluorocarbenium ion and 1,1,1-trifluoroethane.

Similarly, when 1,1,1-trichloroethane was treated with SbF_5–SO_2ClF solution at −78°, the methyldichlorocarbenium ion, $CH_3\overset{+}{C}Cl_2$, was formed. It was evidenced by the substantial deshielding of the observed pmr resonance, singlet at δ 4.60 (1.70 ppm deshielded from the precursor, CH_3CCl_3). $CH_3\overset{+}{C}X_2$ (X = F and Cl) are the first directly observed alkyldihalocarbenium ions.

1,2-Difluoroethylene (III).—Protonation of III with neat HF or HSO_3F–SO_2 did not occur at −20°. When III was bubbled through a solution of SbF_5–HF (1/4 *M*/*M*) -SO_2ClF, both ^1H and ^{19}F nmr spectra of the resulting solution indicated that CHF_2CH_2F was the only product formed.

When III was treated with SbF_5–HSO_3F (1/4 *M*/*M*)–SO_2ClF it gave 1,2-difluoroethyl fluorosulfate, $CH_2FCHFOSO_2F$, which was stable at −20°. When the reaction mixture was distilled at atmospheric pressure, cleavage occurred and CH_2FCHF_2 was obtained. When III reacted with SbF_5–HSO_3F (1/1 *M*/*M*) -SO_2ClF at −78°, instead of giving $CH_2FCHFOSO_2F$, CH_2FCHF_2 was formed almost exclusively. When CH_2FCHF_2 was treated with SbF_5–SO_2ClF it showed no sign of reacting. This is expected since both $CH_2F\overset{+}{C}HF$ and $CHF_2\overset{+}{C}H_2$ would be extremely unstable.

Trifluoroethylene (IV) did not react with fluorosulfuric acid or hydrogen fluoride in SO_2ClF solution at −20°. However, when IV was treated with SbF_5–HF (1/4 *M/M*) in SO_2ClF at −78°, the resulting solution showed that CF_3CH_2F was formed as the only product. IV also reacted smoothly with SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF or SO_2 at −78°. The pmr spectrum of the solution at −80° showed a doublet of triplets at δ 4.96 (J_{HF} = 45.0 and 8.5 Hz). The ^{19}F nmr spectrum showed a high-field triplet of triplets at ϕ 239.6 (1 F, J_{HF} = 45.0, J_{FF} = 16.5 Hz), a sextet at ϕ 83.6 (2 F, J_{HF} = 8.5, J_{FF} = 16.5 and 9.0 Hz), and a deshielded triplet at ϕ −47.1 (1 F, J_{FF} = 9.0 Hz). These data are only consistent with $CH_2FCF_2OSO_2F$. 1,1,2-Trifluoroethyl fluorosulfate is not stable at higher temperature and cleaves at −50° to give CH_2FCF_3, which can be recovered from the distillate in high yield as the condensed gas. When IV was treated with SbF_5–HSO_3F (1/1 *M/M*) in SO_2ClF, only CH_2FCF_3 was found even at −78°.

CH_2FCF_3 is not ionized in SbF_5–SO_2ClF solution. This indicates that ions $CF_3\overset{+}{C}H_2$ and $CH_2F\overset{+}{C}F_2$ are unstable.

1-Chloro-2-fluoroethylene (V).—The behavior of V is similar to that of III in the super acid systems studied. CH_2ClCHF_2 was obtained when V was treated with SbF_5–HF (1/4 *M/M*) -SO_2ClF or SO_2. 1-Fluoro-2-chloroethyl fluorosulfonate, $CH_2ClCHFOSO_2F$, was obtained when V was treated with SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF or SO_2. The structure was confirmed by both pmr and ^{19}F nmr, respectively. As with III, V gave only CH_2ClCHF_2 when it was treated with SbF_4–HSO_3F (1/1 *M/M*) -SO_2ClF at −78°. V does not react with fluorosulfuric acid or hydrogen fluoride in SO_2ClF solution at −20°.

Highly pure CH_2ClCHF_2 could be obtained from the distillation of the V-SbF_5–HF (1/4 *M/M*) -SO_2ClF or V-SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF systems. A yet unidentified by-product was found in small amount when CH_2ClCHF_2 was allowed to stay in contact with SbF_5–SO_2ClF at −80° for prolonged periods of time.

Trifluorochloroethylene (VI) reacted either with SbF_5–HF (1/1 *M/M*) -SO_2ClF or SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF at −20° to give CF_3CHFCl exclusively. VI did not react either with HSO_3F–SO_2ClF or SbF_5–HF (1/4 *M/M*) -SO_2ClF. Similarly, **trifluorobromoethylene** (VII) reacted either with SbF_5–HF (1/1 *M/M*) -SO_2ClF or SbF_5–HSO_3F (1/1 *M/M*) -SO_2ClF at −10° to give CF_3CHFBr exclusively. Again the pmr spectrum showed a doublet of quartets at δ 6.9 (1 H, J_{HF} = 47.0 and 5.0 Hz). The ^{19}F nmr spectrum of the same solution showed a one-fluorine doublet of quartets at ϕ 162.2 (J_{HF} = 47.0 Hz, J_{FF} = 13.5 Hz) and a three-fluorine doublet of doublets at ϕ 81.8 (J_{HF} = 5.0 Hz, J_{FF} = 13.5 Hz). VII did not react either with HSO_3F–SO_2ClF or SbF_5–HF (1/4 *M/M*) -SO_2ClF at −15°. However, it reacted very slowly with SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF at −10° to yield CF_3CHFBr.

When **trifluoroiodoethylene** (VIII) was treated either with SbF_5–HSO_3F (1/4 *M/M*) -SO_2ClF or SbF_5–HF (1/4 *M/M*) -SO_2ClF at −30° for 1 hr, the solution showed in its pmr spectrum a doublet of quartets at δ 7.31 (J_{HF} = 46.0 and 5.5 Hz). The ^{19}F nmr spectrum of the same solution revealed a doublet of quartets at ϕ 166.9 (1 F, J_{HF} = 46.0, J_{FF} = 16.5 Hz) and a doublet of doublets at ϕ 78.8 (3 F, J_{HF} = 5.5 Hz, J_{FF} = 16.5 Hz). Thus the product formed is CF_3CHFI.

Tetrafluoroethylene (IX) and hexafluoropropene (X) did not react either with SbF_5–HF (1/1 *M/M*) -SO_2ClF or SbF_5–HSO_3F (1/1 *M/M*) -SO_2ClF at −5°. The solution did not show any proton resonance except the acid proton peak. The ^{19}F nmr spectra showed fluorine signals corresponding only to the unreacted starting materials.

Discussion

In all the investigated cases protonation of fluoro olefins in superacids did not give stable long-lived fluorocarbenium ions. However, results obtained indicate primary protonation according to the extended Markovnikov rule. Back-donation from the unshared fluorine electron pairs stabilizes the intermediate ions but they are still not sufficiently stable and are rapidly quenched by fluoride or fluorosulfate ions from the solvent systems. The ease of protolytic attack on the fluoro olefins was found to decrease with increasing fluorine substitution.

I and II showed similar chemical behavior toward the super acid systems at low temperature. Both I and II reacted with HF or HSO_3F in the presence of SbF_5 in SO_2ClF to give the HF or HSO_3F addition products. This indicates that electrophilic attack does occur and intermediate fluorocarbenium ions are formed. However, $CH_3\overset{+}{C}HF$ and $CH_3\overset{+}{C}F_2$ are not stable even in the low nucleophilic system and react rapidly with the counterions to form the addition products. In fact, $CH_3\overset{+}{C}HF$ was never directly observed (by nmr spectroscopy) even when ionization of CH_3CHF_2 was attempted with SbF_5–SO_2ClF. The reason for the instability of $CH_3\overset{+}{C}HF$ is that the monofluorocarbenium ion would be stabilized by only one fluorine atom (*via* back-donation of the lone-pair electrons to the electron-deficient carbon).[4] The pmr spectrum of CH_3CHF_2–SbF_5–SO_2ClF solution (−80°) displays a doublet at δ 4.32 (3 H, J_{HH} = 1.8 Hz) and a quartet at δ 10.47 (1 H, J_{HH} = 1.8 Hz), indicating that the carbenium ion $CH_3\overset{+}{C}HF$ exchanges fluorine with the solvent system (SbF_5–SO_2ClF). The possible mechanisms by which fluorine can be exchanged intramolecularly should be similar to those of methyl fluoride–antimony pentafluoride complex[5] and are shown by eq 1 and 2. Equation 1 represents a S_Ni process in which the transition state XI of the intramolecular nucleophilic displacement is shown by the substitution of F′ by F″. The second process for fluorine exchange is formation of an intermediate intimate ion-pair complex XII (eq 2) in very low concentration, in rapid equilibrium with $CH_3CHF_2 \rightarrow SbF_5$ and its subsequent collapse allowing front-side exchange (analogous to S_N1 substitution). The two mechanisms represent limiting cases and any

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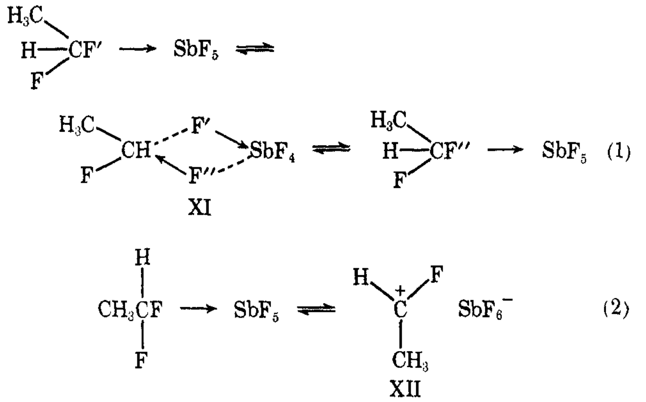
[4] One of the referees questioned that it is difficult to understand that ion $CH_3\overset{+}{C}HF$ is less stable than ion $CH_3\overset{+}{C}F_2$. We have separately studied the carbon-13 nmr of halocarbenium ion and found that halogen back-donation is related to the stability of halocarbenium ions. See G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, in press. Thus, direct experimental evidence was obtained to substantiate observed differing stabilities.

[5] G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); **94**, 156 (1972).

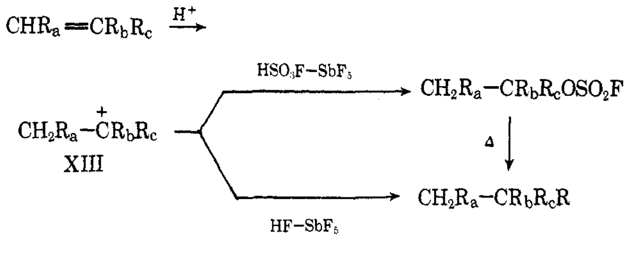


degree of intermediate character between XI and XII should be possible.

The increase in shielding of the resonance and of coupling constants when either HF or CH_3CHF_2 was added to the solution indicates that a change of the nature of the transition state is possible. It is also possible that intermolecular fluorine exchange may occur. The roles of HF and CH_3CHF_2 in this exchange reaction will be fully discussed elsewhere.[6]

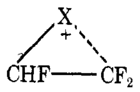
In the 1,1,1-trifluoroethane–SbF_5–SO_2ClF system, the first direct observation of an alkyldifluorocarbenium ion, *i.e.*, that of the methyldifluorocarbenium ion, was accomplished by nmr spectroscopy. The fluorine chemical shift of $CH_3\overset{+}{C}F_2$ (ϕ −96.4) is 87.9 ppm more shielded than that of $(CH_3)_2\overset{+}{C}F$, indicating that back-donation of fluorine lone-pair electrons is twice as much in $(CH_3)_2\overset{+}{C}F$.[7] Pmr spectra of the ion also agree with this observation, since the methyl resonance of $CH_3\overset{+}{C}F_2$ is only 0.31 ppm deshielded from the methyl resonance of $(CH_3)_2\overset{+}{C}F$.

Fluoro olefins III, IV, and V reacted with superacids in a similar fashion. Protonation occurred only when the reactions were carried out in the presence of high concentration of SbF_5 in HF–SO_2ClF or HSO_3F–SO_2ClF (*i.e.*, in the stronger super acids). The π bonds in III, IV, and V are inductively deactivated by the increasing number of fluorine atoms; therefore protonation takes place only in the strongest acid systems. Furthermore, the carbenium ions (XIII) formed by protonation in super acids are destabilized by the fluorine or chlorine atom (R_a) adjacent to electron-deficient carbon. In fact, XIII was never observed as a stable long-lived cation either upon protonation of fluoro olefins III, IV, and V or upon ionization of CH_2FCHF_2, CH_2FCF_3, and CH_2ClCHF_2 by SbF_5–SO_2ClF, even at −20°. The intermediate formed ions were rapidly quenched by the fluoride (fluorosulfonate) ion from the solution, leading to the Markovnikov addition products. However, the fluorosulfates (XIII-OSO_2F) were not stable at higher temperature, since $-OSO_2F$ is a good leaving group and exchanges readily to give the corresponding thermodynamically more stable fluorides (XIII–F).



The trifluorohaloethylenes (VI, VII, and VIII) when treated either with SbF_5–HF–SO_2ClF or SbF_5–HSO_3F–SO_2ClF gave similar HF addition products, $CHFXCF_3$ (X = Cl, Br, and I). As the reactions occurred only at higher temperature (from −30 to −15°), no fluorosulfate addition products ($CHFXCF_2OSO_2F$) were observed when the reaction was carried out in SbF_5–HSO_3F–SO_2ClF. This behavior is again caused by the substantial deactivation of the π bond by the four halogen atoms and the extreme instability of the corresponding carbenium ions, $CHFX\overset{+}{C}F_2$. In systems containing FSO_3H, fluorosulfates, $CHFXCF_2OSO_2F$ may be formed in the first step, but readily cleave to the corresponding fluorides.

The three trifluorohaloethylenes studied showed similar reactivity toward the superacid systems. Protolytic attack takes place again according to the extended Markovnikov's rule forming the more stable carbenium ion ($CHFX\overset{+}{C}F_2$), as the halogen atoms (Cl, Br, and I) can also stabilize the carbenium ion by neighboring group participation.[8] The alternative carbenium ion ($CHF_2\overset{+}{C}FX$) could not be stabilized in a similar way, as neighboring fluorine is unable to participate.



Neighboring halogen atom participation is important, as can be seen from the observed inertness of IX and X toward superacids. Although fluorine inductively has greater electron-withdrawing power than other halogens atoms, the π-electron donor system (*i.e.*, the basicity of the double bond) in $CF_2{=}CFX$ and $CF_2{=}CF_2$ or $CF_2{=}CFCF_3$ would be expected to be more or less the same. The difference in reactivity of $CF_2{=}CFX$ and IX or X indicates that neighboring halogens indeed play a significant role in influencing the protonation of fluoro olefins, through their ability to stabilize the carbenium ion intermediates.

Experimental Section

Materials.—All fluoro olefins used were commercially available in high purity from Peninsular Chemical Research Inc. Antimony pentafluoride (Allied Chemical Co.) was purified first by removing HF by refluxing while passing a stream of dry nitrogen through it and then distilling twice (bp 161–164°). Fluorosulfuric acid (Allied Chemical Co.) was also twice distilled after removing HF.

Nmr Spectra.—A Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe was used for all spectra. Both ^{19}F and ^1H coupling constant are believed accurate to ±0.1 Hz. Unless otherwise indicated, all proton chemical shifts (δ) are in SO_2ClF solvent from external (capillary) TMS. ^{19}F chemical shifts (ϕ) in SO_2ClF solvent are from external CCl_3F.

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[6] G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, in press.

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

[8] B. Capon, *Quart. Rev. (London)*, **18**, 45 (1964).

General Procedure of Reaction of Fluoro Olefins with Superacids.—Superacid solutions were prepared by dissolving SbF_5–HSO_3F (1/1 mol/mol) in an equal volume of sulfuryl chlorofluoride (Allied Chemical Co.) and cooling to −78°. Fluoro olefins were then introduced into the above solution also at −78°. The acid was always in slight excess over the fluoro olefins. Covalent fluorides were ionized in a solution prepared of antimony pentafluoride in sulfuryl chlorofluoride (1/1.5 v/v) at −78°.

α-Fluoroethyl and α,α-difluoroethyl fluorosulfates were prepared by introducing I and II into neat fluorosulfuric acid at −78°, respectively, until the solutions were saturated. The pure fluorosulfates were obtained by vacuum distillation. Yields are generally high (90–95%) and the fluorosulfates have the following boiling points: $CH_3CHFOSO_2F$, bp 33° (35 mm); $CH_3F_2OSO_2F$, bp 25° (30 mm). Spectral properties (^1H and ^{19}F nmr) and analytical data are in accordance with structures.

Registry No.—I, 75-02-5; II, 75-38-7; III, 1691-13-0; IV, 359-11-5; V, 460-16-2; VI, 79-38-9; VII, 598-73-2; VIII, 359-37-5; IX, 116-14-3; X, 116-15-4; α-fluoroethyl fluorosulfate, 33515-40-1; α,α-difluoroethyl fluorosulfonate, 460-95-7.

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The Mechanism of Benzophenone Reduction with the 2-Norbornyl Grignard Reagent

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The reduction of 0.5 equiv of benzophenone with a Grignard reagent from 2-*exo*-chloro-3-*exo*-deuterionorbornane is characterized by deuterium transfer. Carbonation of the unreacted Grignard reagent produces *endo*-norbornane-2-carboxylic acid. These results show that the benzophenone reduction occurs preferentially by a cis–exo eliminative transfer of D and MgCl.

In connection with our work on chiral Grignard reagents,[1-4] it was desirable to know more about the detailed mechanism of ketone reductions with some bicyclic Grignard reagents. A suitable system for a study of the type required appeared to be the reduction of benzophenone with a Grignard reagent from deuterium labeled 2-chloronorbornane.

Recent studies have revealed that the norbornyl Grignard reagent is a relatively slowly equilibrating mixture of epimers.[5-8] On the basis of nmr evidence, Krieghoff and Cowan[6] concluded that either *exo*- or *endo*-chloronorbornane gave an ethereal solution consisting, at equilibrium, of about a 54:46 mixture of endo–exo epimers of the Grignard reagent. Hill[5] similarly concluded that in THF norbornylmagnesium chloride was a 50:50 mixture of epimers. Jensen and Nakamaye[7] prepared norbornylmagnesium bromide in ether and using nmr found it to be a 59:41 mixture of endo–exo isomers. Carbonation of the equilibrium mixture gave a mixture of the epimeric acids, 56–60% the endo isomer. When the equilibrated Grignard reagent was allowed to react with 0.5 equiv of benzophenone at 0°, the nmr signal due to the exo isomer disappeared and the benzophenone was converted to the bromomagnesium salt of benzhydrol. Rapid carbonation of the unreacted Grignard reagent gave almost exclusively *endo*-2-norbornanecarboxylic acid. It was observed that the *endo*-norbornylmagnesium bromide remaining after reaction with benzophenone reequilibrated to the original equilibrium composition if allowed to stand for 1 day at room temperature. These workers also examined the Grignard reagent from norbornyl chloride and found it to be a 57:43 mixture of endo–exo isomers; the behavior toward benzophenone paralleled that of the Grignard reagent from norbornyl bromide.

Davies and Roberts[8] confirmed the results of Jensen and Nakamaye and found that *endo*-norbornylmagnesium bromide did not reequilibrate at 0° over a 3-hr period; at −78° the reagent was still about 95% the endo isomer after 5 days. They also observed that the reduction of benzophenone with equilibrated reagent did not take place at −15°, although an intense red-brown color (presumably due to a Grignard reagent–ketone complex) was produced at this temperature.

The experiments of Jensen and Nakamaye make it clear that the *exo*-norbornyl Grignard reagent reduces benzophenone much more rapidly than the endo isomer. These experiments do not, however, allow one to completely define the stereochemistry of the reduction process. We wanted to know the stereoselectivity associated with the transfer of hydrogen from C-3 of the Grignard reagent. In other words, does the reduction of benzophenone involve transfer of the exo magnesium and the exo hydrogen, the exo magnesium and the endo hydrogen, or a combination of these alternatives? The following experiments led to an answer to this question.

Addition of gaseous DCl to a pentane solution of norbornene[9] at −78° gave 2-*exo*-chloronorbornane in 81% yield. The amount, location, and orientation of deuterium in the chloride had to be rigorously determined (see below). Stille and coworkers treated 2,3-dideuterionorbornene with HCl in pentane at −78° and obtained approximately a 50:50 mixture of *endo*-

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(2) J. D. Morrison, D. L. Black, and R. W. Ridgway, *Tetrahedron Lett.*, 985 (1968).

(3) (a) J. D. Morrison, A. Tomash, and R. W. Ridgway, *ibid.*, 565 (1969); (b) J. D. Morrison and R. W. Ridgway, *ibid.*, 569 (1969).

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(5) E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966).

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