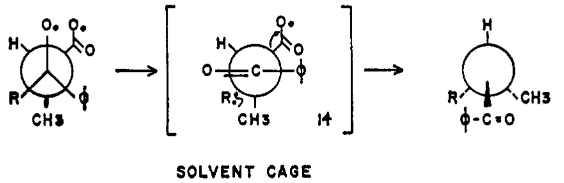
An alternative interpretation of the stereochemical data may involve complete β scission at the alkoxy radical site in the oxygen diradical forming first a solvent-caged radical pair (**14**) (Scheme IV). Before the radical pair diffuses from the solvent cage, the alkyl or phenyl radical displaces carbon dioxide by back-side attack at the asymmetric α carbon *via* a $S_{\mathrm{D}}R$ reaction.[8] Therefore, it was pertinent to examine the thermolysis of a peroxylactone in which the migrating group itself is asymmetric. Should β scission be effectively complete before decarboxylation has commenced, it would be expected that the asymmetric radical pair **14** would be extensively racemized, but not necessarily completely.[9]

Scheme IV. The $S_{\mathrm{D}}R$ Mechanism of the Rearrangement of Thermally Generated Oxygen Diradicals



The system chosen for this study was the peroxylactone derived from the optically active 3,5-diphenyl-3-hydroxy-4-methylvaleric acid (mp 160–160.5°; $\alpha^{24}\mathrm{D}$ +3.72° (ethanol)). The thermal decomposition of the optically active peroxylactone gave a 90% yield of the rearrangement ketone 1,4-diphenyl-3-methyl-1-butanone with an optical rotation of −12.6° in benzene. The configuration of the ketone was assigned as *R*-(−) by correlating it with benzylmethylacetic acid.[10] Since the synthetic ketone had an optical rotation of $\alpha^{29}\mathrm{D}$ −14.7° (benzene), the thermolysis ketone has a minimum optical purity of 93%. The configurational assignment and thus the assessment of the optical purity of this peroxylactone are still in progress. It is, therefore, possible that the optical purity of the rearrangement ketone is actually greater than 93%. Furthermore, the configurational assignment of this peroxylactone is important to assess whether the migration of the β-alkyl substituent proceeds stereospecifically *via* inversion or retention in view of the Woodward–Hoffmann theory of sigmatropic rearrangements.[11]

The stereochemical evidence compounded in this study along with the kinetic and product studies of the preceding communication[1] suggest that the β substituent in the oxygen diradical migrates *via* a nonclassical alkyl or phenyl bridge. The driving force for this novel process derives from the collaborated "push-pull" action between the alkoxy and carboxylate radical sites. To the best of our knowledge this is the first demonstration of a concerted rearrangement in radical reactions.

Acknowledgment. The financial assistance by the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation is gratefully acknowledged. We thank the Puerto Rico Nuclear Center for allowing us to use their polarimetric equipment.

---

(8) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 64.

(9) F. D. Greene and M. A. Berwick, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, ORGN-112.

(10) P. A. Levine and R. E. Marker, *J. Biol. Chem.*, 110, 299 (1935); K. B. Wiberg and T. R. Hutton, *J. Am. Chem. Soc.*, 78, 1640 (1956).

(11) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(12) Undergraduate Research Participant.

Waldemar Adam, Ying Ming Cheng
Carlos Wilkerson,[12] Wasi Ahmed Zaidi
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Received December 19, 1968

Friedel-Crafts Chemistry. III.[1]

Methyl Fluoride–Antimony Pentafluoride, a Powerful New Methylating Agent. Methylation Reactions and the Polycondensation of Methyl Fluoride

Sir:

Ever since Friedel and Crafts published their initial papers[2] on the reactions of alkyl halides and aluminum chloride, organic chemists have searched to clarify the exact nature of the complexes formed in the interaction of alkyl halides and Lewis acid halides.[3] In recent years, we found that alkyl halides in antimony pentafluoride solution generally form stable carbonium ion complexes. Methyl halides, however, failed to yield the methyl cation. Infrared spectroscopic studies of methyl chlorides in $SnCl_4$ and $SbCl_5$ solution[4] and studies of methyl fluoride in BF_3 solution[5] indicated that these exist as slightly polarized donor–acceptor complexes. We now wish to present our findings on the properties and nature of solutions of methyl fluoride in SbF_5 or SbF_5–SO_2 as observed by nmr and laser Raman spectroscopy and the rather unique chemical behavior of these systems.

When methyl fluoride is dissolved in SbF_5–SO_2 solution at −78° a clear, colorless liquid solution is obtained. The pmr spectrum shows the complex formed at −60° as a sharp singlet at δ 5.56 (external TMS capillary). If excess methyl fluoride is present it appears as a doublet (J_{HF} = 45.7 Hz) at δ 4.50. Raising the temperature of the solution (to −20°) brings about the disappearance of the methyl fluoride doublet with no change in the deshielded singlet. (The pmr spectrum of methyl fluoride in SO_2 solution is a doublet at δ 4.00, J_{HF} = 45.8 Hz.)

The ^{13}C nmr shift[6] of the CH_3F–SbF_5–SO_2 system occurs at δ 117.8 (from CS_2) with $J_{^{13}\mathrm{C-H}}$ = 166 Hz. The ^{13}C nmr parameters of CH_3F (in SO_2 solution) are δ 118.9 (from CS_2), $J_{^{13}\mathrm{C-H}}$ = 149 Hz. Since the $J_{^{13}\mathrm{C-H}}$ is proportional to the per cent s character[7], clearly the antimony pentafluoride strongly polarizes the C–F bond of methyl fluoride. At the same time the relatively small deshielding effect observed in the ^1H and ^{13}C chemical shifts indicates that no methyl cation is formed. The absence of hydrogen–fluorine coupling

---

(1) Part II: G. A. Olah, S. J. Kuhn, and D. G. Barnes, *J. Org. Chem.*, 29, 2685 (1964). (Note the change of the title of the series from "Selective Friedel-Crafts Reactions" to the more appropriate "Friedel-Crafts Chemistry.")

(2) C. Friedel and J. M. Crafts, *Compt. Rend.*, 84, 1392 (1877); C. Friedel and J. M. Crafts, *Bull. Soc. Chim. Fr.*, (2) 27, 482, 530 (1877).

(3) For a summary see G. A. Olah and M. Meier, "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, pp 623–765.

(4) H. M. Nelson, *J. Phys. Chem.*, 66, 1380 (1962).

(5) G. A. Olah, S. J. Kuhn, and J. A. Olah, *J. Chem. Soc.*, 2174 (1957); R. Nakane and T. Oyama, *J. Phys. Chem.*, 70, 1146 (1966).

(6) Drs. M. B. Comisarow and A. M. White have carried out the ^{13}C nmr studies.

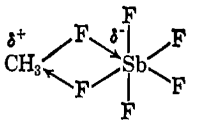
(7) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768 (1969).

indicates a rapidly exchanging donor–acceptor complex system.

The laser Raman spectrum of a CH_3F–SbF_5–SO_2 solution[8] contains lines at 526, 653, 685, 738, 1010, 1150, 1330, 2863, and 2950 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 ν_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. This indicates that CH_3F is a stronger n base than SO_2 in these solutions leading to the exclusive formation of a $CH_3 \rightarrow SbF_5$ donor–acceptor complex. Furthermore, the fact that there is no apparent interaction (*i.e.*, exchange) observed between excess CH_3F and the complex $CH_3F \rightarrow SbF_5$ on either the Raman or nmr time scale suggests a strong $CH_3F \rightarrow SbF_5$ bonding interaction. On the other hand, the similarities in the fundamental Raman-active vibrations of CH_3F and methyl fluoride in the $CH_3F \rightarrow SbF_5$ complex shows that the weakening of the C–F bond in methyl fluoride is not sufficient to significantly alter the tetrahedral geometry the molecule possesses in neutral solution.

Nmr and Raman data for the CH_3F–SbF_5 complex in SO_2 solution described above indicates a polarized donor–acceptor complex undergoing rapid fluorine exchange in what amounts to front-side attack (**1**).

The pmr spectrum of a 1:1 (mol:mol) antimony pentafluoride–methyl fluoride mixture in sulfur dioxide solution showed only a single peak for the complex with no evidence of excess CH_3F. Thus a 1:1 relationship is established, thereby supporting structure **1**.



1

In neat SbF_5 as solvent, clearly a dimeric (or polymeric) antimony pentafluoride would be the complexing agent, but the self-condensation reaction of methyl fluoride under these conditions (*vide infra*) does not allow the study of this system. To our knowledge, the CH_3F–SbF_5 complex is the first well-characterized example of a Friedel–Crafts donor–acceptor complex.

The methyl fluoride–antimony pentafluoride complex is a powerful new methylating agent capable of oxygen, sulfur, aromatic and aliphatic carbon, and even halogen substitution.

Dimethyl ether, for example, is methylated to the trimethyloxonium ion, dimethyl sulfide to the trimethylsulfonium ion (eq 1 and 2). Aromatic hydrocarbons

$$CH_3OCH_3 + CH_3F\text{–}SbF_5 \longrightarrow (CH_3)_3O^+SbF_6^- \qquad (1)$$

$$CH_3SCH_3 + CH_3F\text{–}SbF_5 \longrightarrow (CH_3)_3S^+SbF_6^- \qquad (2)$$

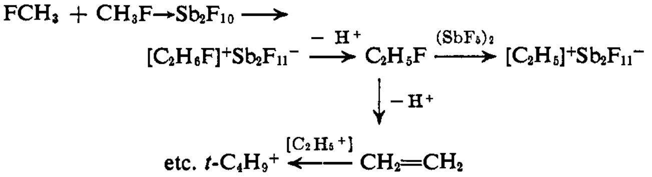
are methylated (eq 3) and even alkanes undergo methylation (eq 4). The powerful methylating ability of

$$ArH + CH_3F\text{–}SbF_5 \longrightarrow ArCH_3 + HF + SbF_5 \qquad (3)$$

$$RH + CH_3F\text{–}SbF_5 \longrightarrow RCH_3 + HF + SbF_5 \qquad (4)$$

CH_3F–SbF_5 toward saturated aliphatic carbon is further evidenced by its self-condensation reaction.

When methyl fluoride is dissolved in neat antimony pentafluoride at room temperature, a solution is formed whose pmr spectrum consists of a singlet at δ 5.50 and peaks at δ 4.35 and δ 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 *t*-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 *t*-butyl cation, 3 mol of HF is formed.



$$\begin{tikzcd}
FCH_3 + CH_3F \rightarrow Sb_2F_{10} \arrow[r] & {} & {} \\
{[C_2H_6F]^+Sb_2F_{11}^-} \arrow[r, "-\,H^+"] & C_2H_5F \arrow[r, "(SbF_5)_2"] \arrow[d, "-\,H^+"] & {[C_2H_5]^+Sb_2F_{11}^-} \\
\text{etc. } t\text{-}C_4H_9^+ & CH_2{=}CH_2 \arrow[l, "{[C_2H_5^+]}"'] &
\end{tikzcd}$$

The condensation reaction must occur in the following manner: methyl fluoride and antimony pentafluoride form an incipient methyl cation which then methylates a second molecule of methyl fluoride on carbon to form the $C_2H_6F^+$ species. The $C_2H_6F^+$ deprotonates to ethyl fluoride which then in SbF_5 ionizes to $C_2H_5^+$ which, in turn, is ready to condense to the *t*-butyl cation, *t*-hexyl cations, etc. In a separate experiment, methylation of ethyl fluoride yielded identical condensation results.

When methyl fluoride was treated with 1:1 HF–SbF_5 or 1:1 FSO_3H–SbF_5 at 0° only a single pmr absorption at δ 5.50 (s) is originally observed. This species then slowly converts ($t_{1/2} \sim$ 1 hr) to the *t*-butyl cation (singlet at δ 4.35).

When alkyl halides, other than the fluorides, are treated with CH_3F–SbF_5, n alkylation on halogen takes place and dialkylhalonium ions are formed. The following communication reports on this new reaction and its implications to Friedel–Crafts chemistry.[9]

Acknowledgment. Partial support of the work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

[8] For experimental conditions see G. A. Olah and A. Commeyras, *J. Amer. Chem. Soc.*, in press.

[9] G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).

[10] Postdoctoral Research Investigator.

George A. Olah, John R. DeMember,[9] Richard H. Schlosberg[10]
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received February 24, 1969

Friedel–Crafts Chemistry. IV.[1] Dialkylhalonium Ions and Their Possible Role in Friedel–Crafts Reactions

Sir:

In the extensive literature of Friedel–Crafts chemistry[2] the alkyl halide–Lewis acid system studied always showed 1:1 or 1:2 complex formation. No indication of 2:1 or 2:2 complex formation was obtained. Since dialkylhalonium ions were not previously

---

[1] Part III: G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969).

[2] G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I-IV, Interscience Publishers, New York, N. Y., 1963–1965.