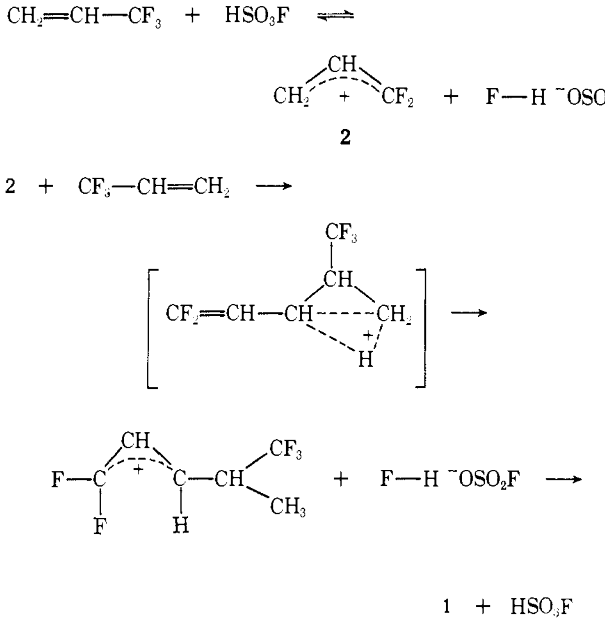
gration of one hydrogen from a terminal methylene on one monomeric unit to the terminal methylene carbon of its complement.[10]

If solvent assisted ionization of a fluorine–carbon bond, yielding the 1,1-difluoroallyl cation **2**, is allowed, these observations can be explained by the scheme shown in eq 3. Thus, dimerization would involve electrophilic attack of **2** on alkene to yield, after formal 1,3-hydrogen shift, an alkylated fluoroallyl cation.[11] Formation of dimer from the alkylated ion is the reverse of the first step.[12]



(3)

Since $CF_3CH{=}CH_2$ is not protonated in the super acid, HSO_3F, but does dimerize, apparently *via* the allylic ion **2**, one must question the detailed mode of apparent addition of other acids to this alkene.[2] Data pertinent to this question are reported in the accompanying communication.[13]

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[10] Note that $CF_3CH{=}CH_2$ is reportedly not polymerized by Friedel-Crafts catalysts; see A. Goldschmidt, *J. Amer. Chem. Soc.*, 73, 2940 (1951).

[11] We assume that the alkylation–hydrogen transfer is best formulated by an edge-protonated cyclopropane. Studies of product and kinetic isotope effects in dimerization of $CF_3CH{=}CD_2$ and isomeric $CF_3CH{=}CHD$ that are in progress should permit a more definitive characterization of this possible π route to protonated cyclopropane.

[12] The ambident nature of the allylic ions of this scheme provide several points of branching for the reaction path. None of these branching points appear to be significant in HSO_3F solvent; *cf.* ref 13.

[13] P. C. Myhre and G. D. Andrews, *ibid.*, 92, 7596 (1970).

[14] National Science Foundation Undergraduate Research Participant, Summer 1970.

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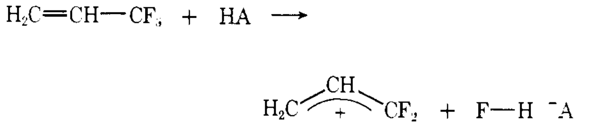
Electrophilic "Additions" of Strong Acids to 3,3,3-Trifluoropropene

Sir:

Henne and Kaye reported that hydrogen halides add to $CF_3CH{=}CH_2$ in the presence of aluminum halides to give the anti-Markovnikov adducts, $CF_3CH_2CH_2X$.[1] This report has been repeatedly cited as an instructive, albeit rare, example of the ability of electron-withdrawing substituents to reverse the normal direction of electrophilic addition to alkenes.[2] There are related observations, however, that cause one to suspect that apparent additions to $CF_3CH{=}CH_2$ may be more complex than the reported[1] products would indicate. For example, it is known that $CF_3CH{=}CH_2$ and related derivatives hydrolyze slowly in concentrated sulfuric acid media to yield carboxylic acids.[1,3] Also it is now known that the very strong acid, HSO_3F, does not add to $CF_3CH{=}CH_2$. Rather, HSO_3F catalyzes a dimerization of $CF_3CH{=}CH_2$ without transfer of solvent hydrogens to carbon [4,5]

These later observations seem best explained by reaction sequences in which solvent-assisted ionization is the initial step, eq 1. The apparent facility with which this ionization occurs in HSO_3F, and the absence of any evidence of proton addition to the double bond, has prompted a more complete investigation of the reactions of $CF_3CH{=}CH_2$ with other strongly acidic systems. We report here studies of the behavior of $CF_3CH{=}CH_2$ in HSO_3Cl, $HCl{-}AlCl_3$, and $HBr{-}AlBr_3$.



(1)

Trifluoropropene reacts smoothly with HSO_3Cl to yield 3-chloro-1,1-difluoropropyl chlorosulfate (**1**) as the major product, eq 2. Nmr spectra show the development of two absorption bands of nearly equal area, a triplet at *ca.* δ 3.8 and a multiplet at 2.8, as the $CF_3CH{=}CH_2$ absorption lines disappear. The rate of spectral change is first order in alkene, $k = 1.15 \times 10^{-4}\ sec^{-1}$ at 30°, 3 *M* alkene.[6] The dense oil isolated

$$CF_3{-}CH{=}CH_2 + 2HSO_3Cl \longrightarrow \underset{\mathbf{1}}{ClCH_2CH_2CF_2OSO_2Cl} + HSO_3F \qquad (2)$$

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[1] A. L. Henne and S. Kaye, *J. Amer. Chem. Soc.*, 72, 3369 (1950).

[2] (a) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, p 51; (b) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 226; (c) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan, New York, N. Y., 1961, p 187; (d) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 949; (e) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 518; (f) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, p 576; (g) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, p 187.

[3] E. Moller, Ed., "Methoden der organishen Chemie (Houben-Weyl)," Vol. 5, Part 3, Georg Thieme Verlag, Stuttgart, 1962, pp 469–476.

[4] P. C. Myhre and G. D. Andrews, *J. Amer. Chem. Soc.*, 92, 7595 (1970).

[5] Compare with acid catalysis in solvolysis of benzyl fluoride studied by C. G. Swain and R. E. T. Spalding, *ibid.*, 82, 6104 (1960).

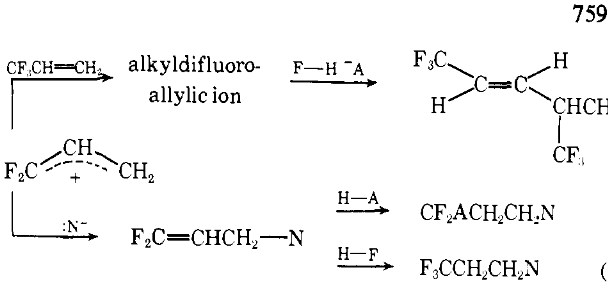
[6] A broad doublet, δ 4.5, develops rapidly and remains in essentially

by quenching reaction mixtures in aqueous methanol at −40° and distillation, bp 45–50° (2 mm), 50–60% (*Anal.* Calcd: C, 15.7; H, 1.8; Cl, 31.0. Found: C, 16.0; H, 2.1; Cl, 30.8.), exhibits an nmr spectrum almost identical with that observed in reaction mixtures.[7,8] Recognition of the high-field multiplet as a triplet of triplets was a structural key demonstrating the presence of only two fluorine atoms. The chemical shift of the low-field triplet indicates chlorine is attached to the terminal carbon bearing hydrogen. The hydrolytic stability of **1** indicates the attachment of the chlorosulfate group to carbon-bearing fluorine.[9] The mass spectrum of **1** shows no molecular ion, but fragmentation ions are observed corresponding to the masses and isotopic composition of $ClCH_2CH_2CF_2$-OSO_2, CF_2OSO_2Cl, $ClCH_2CH_2CF_2O$, and $ClCH_2$-CH_2CF_2. Additional confirmation of structure was obtained by hydrolysis of **1** in methanolic silver nitrate to yield methyl 3-chloropropanoate.

As Henne and Kaye have reported,[1] $CF_3CH{=}CH_2$ does not react with excess anhydrous HCl (6 equiv) at autogenous pressure, but upon addition of catalytic amounts of aluminum chloride, reaction takes place at ambient temperature. In marked contrast with the previous report,[1] we find not only $CF_3CH_2CH_2Cl$ but also $CF_2ClCH_2CH_2Cl$ as products. The mole ratio of products varied from *ca.* 60:40 to 45:55 upon variation of the $AlCl_3$ from 0.2 to 0.05 equiv. Products were analyzed and characterized by nmr and mass spectra of the mixture and subsequently separated by distillation, bp 45 and 80°, respectively (lit.[1,10] 45 and 81°).[11,12]

By contrast with our results in HCl–$AlCl_3$, mass spectral and nmr spectral analyses of products obtained by reaction of $CF_3CH{=}CH_2$ with HBr–$AlBr_3$ (1.0:4.5:0.05 equiv, darkened sealed tube, ambient temperature) revealed only $CF_3CH_2CH_2Br$ with no trace of $CF_2BrCH_2CH_2Br$.[1]

It seems clear that the kinds of the products obtained from reactions of $CF_3CH{=}CH_2$ with strong acids are varied. Under appropriate reaction conditions one may obtain apparent addition and addition–substitution products as well as those derived from hydrolysis and dimerization.[4] We suggest that the 1,1-difluoroallyl cation, formed by solvent-assisted ionization, eq 1, is the intermediate common to all of these reaction paths. Given this intermediate, the products formed in all acid media examined can be reasonably explained, as shown in eq 3, where we allow that the nucleophile, :N, may or may not correspond to the bulk solvent anion, A^-. Thus nucleophilic attack on the methylene carbon of the relatively stable allylic ion by alkene in the case of HSO_3F solvent, by chloride in the case of HSO_3Cl[13] or HCl–$AlCl_3$, and bromide in the case of HBr–$AlBr_3$ would yield either an alkylated ion (HSO_3F) or a 1,1-difluoro-1-alkene. It seems reasonable to assume that neutralization of a relatively stable allylic ion would be quite selective and the nucleophilic reactivity would parallel that normally observed in hydroxylic solvents.[14]



(3)

Additions of strong acids to 1,1-difluoro-1-alkenes are well documented.[15] We assume that difluorocarbonium ions formed in such additions would show much less selectivity and yield products corresponding more closely to the concentration of solvent nucleophiles. Such a center of positive charge may actually discriminate in favor of first-row nucleophiles, analogous to the order observed in nucleophilic additions to fluoroolefins.[16]

The degree of kinetic control in the addition stage (eq 3) remains to be determined. Thus, the differences in product distributions in the HCl–$AlCl_3$ system that we observe at ambient temperatures and Henne and Kaye observe at 100° may reflect more complete conversion of the $-CF_2Cl$ group to the more stable $-CF_3$ group at the higher reaction temperature.

An important result of these studies is our failure to find any evidence indicating that proton addition to $CF_3CH{=}CH_2$ is an available reaction path. Clear-cut evidence of the absence of such a process is found in the strongest acid system, HSO_3F; the nature of the products formed in other systems appears to constitute strong supporting evidence. We conclude that the formation of apparent anti-Markovnikov addition products in the reaction of $CF_3CH{=}CH_2$ with strong acids does not represent a valid basis for discussion of the relative stabilities of cationic intermediates resembling $CF_3C^+HCH_3$ or $CF_3CH_2CH_2^+$.[1,2]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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constant concentration (*ca.* 5–10%) during these kinetic runs. We assume that this absorption is attributable to $CF_2{=}CHCH_2Cl$.

(7) Spectral data were: ^1H nmr ($\delta^{TMS}_{CCl_4}$) 2.86 (triplet of triplets, $J_{H_2,H_3} = 7.1$, $J_{H_2,F} = 11.7$ Hz), 3.90 (triplet, H_3); ir (CCl_4) 2950 (w), 1430 (s), 600 (s) cm^{-1}.

(8) A high boiling component (bp 90–95° (2 mm)) is isolated in *ca.* 10% yield. This product has a strong nmr absorption line in the δ 2.8 region that obscures the multiplet structure of the main product in reaction mixtures.

(9) H. H. Gibbs, W. L. Edens, and R. N. Griffen, *J. Org. Chem.*, **26**, 4140 (1961).

(10) R. N. Hazeldine, *J. Chem. Soc.*, 3371 (1953).

(11) Spectral data were: ^1H nmr ($\delta^{TMS}_{CCl_4}$), $CF_3CH_2CH_2Cl$, 2.83 (quartet of triplets, $J_{H_2,F} = 11.8$ Hz, $J_{H_2,H_3} = 7.8$ Hz), 3.89 (triplet, H_3); $CF_2ClCH_2CH_2Cl$, 2.94 (triplet of triplets, $J_{H_2,F} = 12.1$ Hz, $J_{H_2,H_3} = 7.8$ Hz), 3.99 (triplet, H_3); mass spectrum, $CF_3CH_2CH_2Cl$, mol ions 132, 134; $CF_2ClCH_2CH_2Cl$, mol ions 148, 150, 152.

(12) Reactant $CF_3CH{=}CH_2$ was shown to be free of $CF_2ClCH{=}CH_2$[10] by mass spectral examination.

(13) Evidence for the existence of the equilibrium, $HSO_3Cl \rightleftharpoons HCl + SO_3$, at room temperature and below has been reported by W. Seaman, J. T. Woods, and H. N. Bank, *Anal. Chem.*, **22**, 549 (1950); see also S. C. Chackalackal and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 4815 (1966).

(14) C. G. Swain, C. B. Scott, and K. H. Lohmann, *ibid.*, **75**, 136 (1953).

(15) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Russ. Chem. Rev.*, **35**, 417 (1966).

(16) Reference 2b, pp 230–231.

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