Acknowledgment. This investigation was supported by Grant No. NB-08245 from the National Institutes of Health and funds provided by Eli Lilly.

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Received October 2, 1970

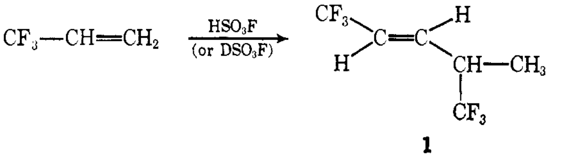
Solvolysis in Strong Acid Media. Solvolytic Dimerization of 3,3,3-Trifluoropropene

Sir:

This investigation had its origin in a study of the solvolytic behavior of $CF_3CH_2CH_2OTs$ and $CF_3CH(OTs)CH_3$ in strong acid media. Our intent was to find systems in which solvolysis of sufficiently destabilized secondary alkyl systems would proceed with hydrogen participation to yield primary alkyl derivatives. Solvolysis of CH_3CH_2OTs in HSO_3F occurs with apparent rate-limiting hydrogen participation,[1] and electrophilic addition of hydrogen halides to $CF_3CH{=}CH_2$ yields the anti-Markovnikov addition products.[2] Assuming these observations indicate both the feasibility of observing such a rearrangement and a molecular structure in which the normal carbonium ion stabilities have been inverted,[3] we anticipated that $CF_3CH_2CH_2OTs$ would solvolyze slowly in powerful ionizing solvents of low nucleophilicity to yield unrearranged product, while the secondary isomer, $CF_3CH(OTs)CH_3$, might solvolyze more rapidly with rearrangement to a primary alkyl derivative.

Our expectations were not completely realized. While observed rates of solvolysis are in accord with prediction, we found that neither $CF_3CH(OTs)CH_3$ nor $CF_3CH_2CH_2OTs$ solvolyze with detectable rearrangement (nmr) in solvent systems that include H_2SO_4, HSO_3Cl, HSO_3F, and $HSO_3F–SbF_5$.

Supporting investigations of the behavior of $CF_3CH{=}CH_2$ in HSO_3F revealed an apparent paradox. We do not observe addition of fluorosulfuric acid to 3,3,3-trifluoropropene. Rather, in freshly distilled HSO_3F solvent, $CF_3CH{=}CH_2$ undergoes dimerization to yield *trans*-1,1,1,5,5,5-hexafluoro-4-methyl-2 pentene (**1**) *without* incorporation of solvent protons, eq 1.



(1)

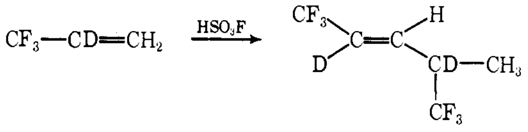
1

Dimerization proceeds cleanly as judged by the developing product nmr spectrum (*vide infra*); integration of nmr spectra of reaction mixtures yielded kinetic data demonstrating clear second-order dependence on alkene In freshly distilled HSO_3F containing 3 *M* alkene, observed rate constants are 1.5×10^{-4} l. mol^{-1} sec^{-1} at 30°. Rates of dimerization fall off dramatically upon addition of KSO_3F: 4.6×10^{-6} l. mol^{-1} sec^{-1} (0.43 *M* KSO_3F), 1.5×10^{-6} l. mol^{-1} sec^{-1} (0.85 *M* KSO_3F).[4]

The dimer **1** could be isolated in good yield (75–80%) by carefully quenching the reaction mixture in aqueous methanol at −40° followed by centrifugation of the dense organic layer and normal work-up; bp 64°; $d^{25°}{}_4$ 1.298. (*Anal.* Calcd: C, 37.2; H, 2.95; mol ion, 192. Found: C, 37.5; H, 3.15; mol ion, 192.) Structural characterization follows from the observed spectral properties.[5] The nmr spectrum of the vinyl proton region is noteworthy; the two high-field lines of the AB quartet are each split into quartets by vicinal fluorines, and the two low-field lines are each split into doublets of quartets by vicinal proton and stereospecific four-bond fluorine coupling [7]

Reaction of $CF_3CH{=}CH_2$ with DSO_3F gave nmr spectra identical with that found by reaction of alkene with HSO_3F. After 90% conversion, nmr spectra of solvent, reactant, and product regions showed no evidence of significant hydrogen exchange. Mass spectral analysis of product isolated at this degree of conversion showed that 96.4% of dimer contained no deuterium.[8]

Reaction of $CF_3CD{=}CH_2$[9] with HSO_3F afforded dimer labeled with deuterium at C-2 and C-4, eq 2. Thus the nmr spectrum shows only two bands, a broad singlet (3 H) at δ 1.3 and a very broad band at 6.4 (1 H); the mass spectrum shows the molecular ion at *m/e* 194 (>96% *1-d₂*) with a fragmentation pattern consistent with the structure shown, eq 2.



(2)

In summary, $CF_3CH{=}CH_2$ dimerizes stereospecifically in HSO_3F to yield an apparent Markovnikov addition product. Dimerization rates show marked acid catalysis; however, this catalysis does not involve transfer of solvent protons to olefinic carbon of reactant. Dimer must form from precursor by mi-

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(1) P. C. Myhre and E. Evans, *J. Amer. Chem. Soc.*, **91**, 5641 (1969).

(2) A. L. Henne and S. Kaye, *ibid.*, **72**, 3369 (1950).

(3) H. Bodot and J. Jullien, *Bull. Soc. Chim. Fr.*, 1488 (1962).

(4) Rates in HSO_3F also fall off rapidly with the "age" of the acid indicating a marked decelerating effect of trace amounts of water.

(5) Spectral properties were: ^1H nmr ($\delta^{TMS}_{CCl_4}$) 1.26 (doublet, 3 H, $J_{H,H}$ = 7 Hz, 4-CH_3); 2.95 (broad octet, 1 H, $J_{H,H-F}$ = 8 Hz, H_4); 5.80 (doublet of quartets, 1 H, J_{H_2,H_3} = 17.5 Hz, J_{H_2,CF_3} = 6.3 Hz); 6.42 (doublet of doublets of quartets, 1 H, J_{H_3,H_4} = 6.7 Hz, J_{H_3,CF_3} = 2.2 Hz). ^{19}F nmr at 94.5 MHz showed two bands of equal intensity separated by 7.4 ppm; the signal at high field was a simple doublet ($J_{F,H}$ = 8 Hz), and the signal at low field is a doublet of triplets (J_{F,H_2} = 6 Hz, J_{F,H_3} = 2 Hz).[6] Mass spectral characteristics (70 V) are: *m/e* 192 (28%, mol ion), 173 (22%, M − F), 123 (100% M − CF_3), 103 (24%, M − (CF_3,HF)), 95 (71%, M − CH_3CHCF_3); ir (CCl_4) 1680 (m), 1455 (m), 1370–1100 (s multiple bands), 1010 (m), 961 (m) cm^{-1}.

(6) We are grateful to Professor Kenneth Servis for examination of the ^{19}F nmr spectrum.

(7) A. A. Bothner-By, S. Castellano, and H. Günther, *J. Amer. Chem. Soc.*, **87**, 2439 (1965).

(8) We attribute the small amount of deuterium incorporation to a slow protonation–deprotonation or addition–elimination reaction.

$$\mathbf{1} + HA \rightleftharpoons \text{ion (or adduct)} \rightleftharpoons CF_3CH_2CH{=}C(CF_3)CH_3 + HA$$

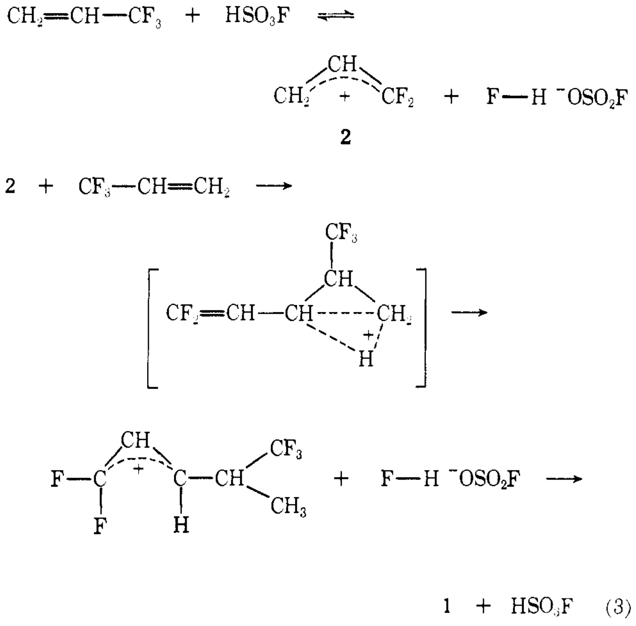
Evidence for this reaction includes (1) the observation of slow changes in the nmr spectrum of **1** (*ca.* 20% conversion in 7 days) with the development of a singlet at δ 1.85, a multiplet at ~3, and a triplet at 4.8, and (2) observation of similar spectral changes of **1** in D_2SO_4 and, in addition, the slow change of the methyl doublet of **1** (δ 1.26) to a broad singlet.

(9) $CF_3CD{=}CH_2$ was prepared by the sequence:

$$CF_3COCH_3 \xrightarrow{LiAlD_4} CF_3CD(OH)CH_3 \longrightarrow CF_3CD(OAc)CH_3 \xrightarrow{600°} CF_3CD{=}CH_2$$

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



(3)

1,3-hydrogen shift, an alkylated fluoroallyl cation.[11] Formation of dimer from the alkylated ion is the reverse of the first step.[12]

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]

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

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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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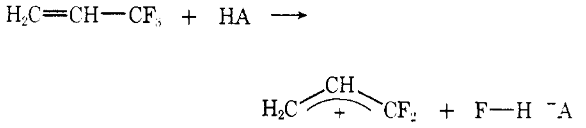
Received September 16, 1970

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



(1)

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, $HCl\text{-}AlCl_3$, and $HBr\text{-}AlBr_3$.

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

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

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

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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