A, **335**, 525 (1973).

(20) J. H. Dunn, C. M. Neher, and P. W. Trotter, U.S. Patent 2 635 122 (1953).
(21) M. J. Molera and E. Ariza, *An. R. Soc. Esp. Fis. Quim.*, **54**, 389 (1958).
(22) (a) P. Cadman and W. J. Engelbrecht, *Chem. Commun.*, 453 (1970); (b) F. Zabel, *Int. J. Chem. Kinet.*, **9**, 651 (1977).
(23) (a) A. A. Westenberg, J. H. Goldstein, and E. B. Wilson, Jr., *J. Chem. Phys.*, **17**, 1319 (1949); (b) E. Kloster-Jensen, *J. Am. Chem. Soc.*, **91**, 5673 (1969).
(24) Aa. S. Sudbo, P. A. Schulz, E. R. Grant, Y. R. Shen, and Y. T. Lee, *J. Chem. Phys.*, **68**, 1306 (1978).
(25) A. Gandini, C. Willis, and R. A. Bach, 13th Informal Conference on Photochemistry, Clearwater Beach, Fla., Jan 1978.
(26) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(27) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2599 (1954).
(28) (a) R. V. Ambartzumyan, N. V. Chekalin, V. S. Dolzhikov, V: S. Letokhov, and V. N. Lokaman, *J. Photochem.*, **6**, 55 (1976); (b) K. Nagai and M. Katayama, *Chem. Phys. Lett.*, **51**, 329 (1977).
(29) (a) L. D. Hanton and G. P. Semeluk, *Can. J. Chem.*, **44**, 2143 (1962); (b) P. M. Jeffers, *J. Phys. Chem.*, **76**, 2829 (1972).
(30) (a) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, pp 288–293; (b) W. F. Colby, *Phys. Rev.*, **47**, 388 (1935); (c) F. Stitt, *J. Chem. Phys.*, **8**, 56 (1940).
(31) (a) K. C. Kim, D. W. Setser, and B. E. Holmes, *J. Phys. Chem.*, **77**, 307 (1973); (b) K. C. Kim and D. W. Setser, *ibid.*, **78**, 2166 (1974).
(32) D. R. Keefer, J. E. Allen, Jr., and W. B. Person, *Chem. Phys. Lett.*, **43**, 394 (1976).
(33) The activation energy for cis–trans isomerization of β-d₁-vinyl chloride is not known, but should be intermediate between that of ethylene-d₂ (62

kcal/mol[34]) and 1,2-dichloroethylene (55 kcal/mol[29]). In any case, it must be less than that for HCl elimination (69 kcal/mol[22]).
(34) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).
(35) J. L. Lyman, *J. Chem. Phys.*, **67**, 1868 (1977).
(36) E. R. Grant, P. A. Schulz, Aa. S. Sudbo, Y. R. Shen, and Y. T. Lee, *Phys. Rev. Lett.*, **40**, 115 (1978).
(37) P. Carruthers and N. N. Nieto, *Am. J. Phys.*, **33**, 537 (1965).
(38) C. C. Jensen, R. D. Levine, and J. I. Steinfeld, *J. Chem. Phys.*, **69**, 1432 (1978).
(39) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).
(40) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, N.Y., 1972.
(41) (a) S. Narita, S. Ichinoke, and S. Enomoto, *J. Chem. Phys.*, **31**, 1151 (1959); (b) G. Varsanyi, *Acta Chim. Hung.*, **35**, 61 (1963).
(42) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967); see also E. Tschuikow-Roux and S. Kodama, *J. Chem. Phys.*, **50**, 5304 (1969).
(43) E. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 348.
(44) Aa. S. Sudbø, P. A. Schulz, Y. R. Shen, and Y. T. Lee, *J. Chem. Phys.*, **69**, 2312 (1978).
(45) P. J. Stang, *Acc. Chem. Res.*, **11**, 107 (1978); *Chem. Rev.*, in press.
(46) H. D. Hartzler in "Carbenes", Vol. II, R. A. Moss and M. Jones, Jr., Ed., Wiley-Interscience, New York, N.Y., 1975, pp 43–100.
(47) P. J. Stang, J. Davis, and D. P. Fox, *J. Chem. Soc., Chem. Commun.*, 17 (1975).
(48) (a) O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmaida, *J. Am. Chem. Soc.*, **92**, 6395 (1970); (b) R. J. Norstrom, H. E. Gunning, and O. P. Strausz, *ibid.*, **98**, 1454 (1976).
(49) I. Burak, T. J. Quelly, and J. I. Steinfeld, *J. Chem. Phys.*, to be published.

Substituent Effects of the Trifluoromethyl Group on Electrophilic Additions to Alkenes. Solvolysis of the Trifluoromethyl Group. Protonation of Alkenes Less Basic Than Ethylene, ρ^+ Values of Deactivated Styrenes, and Reactivity–Selectivity Effects

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Abstract: Rates of solvent addition to aryl-substituted α-trifluoromethylstyrenes $ArC(CF_3)=CH_2$ in aqueous sulfuric acid solutions at 25 °C were measured and correlated with the acidity function H_0 of the medium. When aryl is *p*-tolyl the observed reactivity is almost identical with that of ethylene, and for aryl equal to phenyl, *p*-chlorophenyl, and *m*-chlorophenyl the reactivities are distinctly less than that of ethylene. The styrene reactivities are correlated with those of other alkenes by our previously introduced equation $\log k_2 = -10.5\Sigma\sigma_p^+ - 8.92$, and extend the total range of reactivity covered by this equation to 22 orders of magnitude. Ethylene is less reactive than predicted by this equation but is still proposed to react by the same mechanism as the other alkenes, namely, rate-determining protonation on carbon. The low rate is attributed to the inadequacy of the standard σ^+ parameter of hydrogen to fully account for its minimal electron-donating ability in the absence of any other substituent. The reactivity of the styrenes themselves is correlated by the σ_p^+ parameters of the aryl substituents with $\rho^+ = -4.0$. Even in this situation of high electron demand the sensitivity of the reaction to the substituents as measured by the magnitude of ρ^+ is not greatly enhanced. These results show the operation of linear free energy relationships over vast differences in reactivities, with minimal influence of reactivity–selectivity effects.

The trifluoromethyl group is a valuable probe for the study of the interrelation of electronic substituent effects with organic structure, equilibria, and reactivity. Different measurements of the substituent effect of this group are best summarized by the various electronic Hammett σ values: σ_m, 0.42; σ_p, 0.54; σ_m^+, 0.52; σ_p^+, 0.61; σ_I, 0.38; σ_R, 0.18.[1,2] Steric problems with this group are minimized owing to its relatively small size and the absence of any conformational dependence of its substituent effect.

These substituent parameters all emphasize the powerful inductive electron-withdrawing effect of trifluoromethyl. The resonance electron-withdrawing ability of this group as manifested in its σ_R value of 0.18 has been ascribed to the no bond resonance shown in eq 1.[3] An alternative explanation of

$$(1)$$
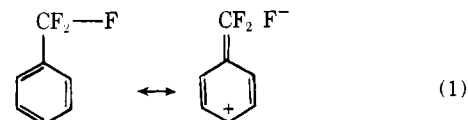
this phenomenon is that there is a selective p–π electron donation to the meta position of the benzene ring through resonance interactions as depicted in eq 2.[2] This effect would

$$(2)$$
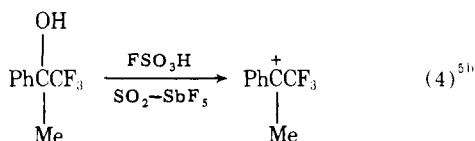
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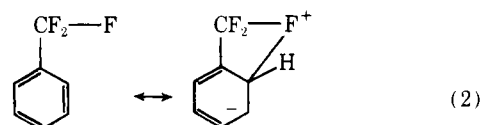
give a relatively lower electron density at the para position, causing the apparent resonance electron withdrawal from that position.
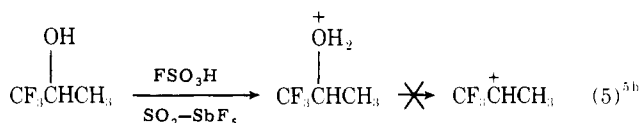
There is evidence that in certain circumstances this group can function as an electron donor. Thus measurements of the ESCA spectra of trifluoromethylbenzene and the bis(trifluoromethyl)benzenes indicate a net negative charge on the aromatic rings.[4] The mechanism proposed[4] for this interaction is shown in eq 3.

$$\langle\bigcirc\rangle\!-\!CF_3 \longleftrightarrow \langle\bigcirc\rangle\!-\!CF_2\!=\!F^+ \qquad (3)$$
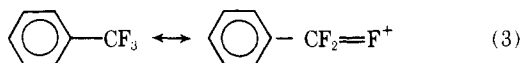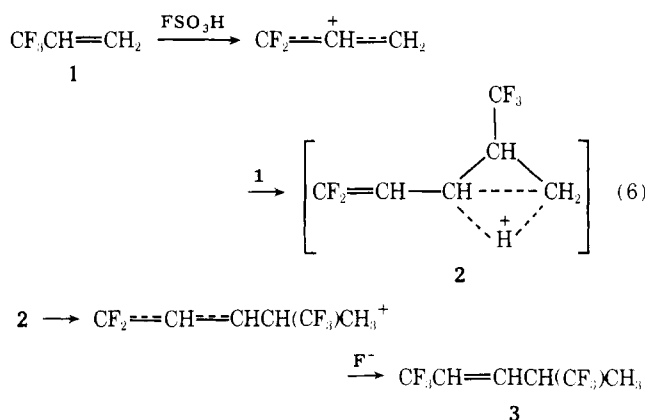
Carbonium ions bearing one trifluoromethyl substituent derived from the corresponding alcohols have been directly observed by NMR providing at least one phenyl group stabilizes the positive charge,[5] as shown in eq 4. However, if two

$$
\underset{\underset{Me}{|}}{\overset{\overset{OH}{|}}{PhCCF_3}} \xrightarrow[SO_2-SbF_5]{FSO_3H} \underset{\underset{Me}{|}}{\overset{+}{PhCCF_3}} \qquad (4)^{5b}
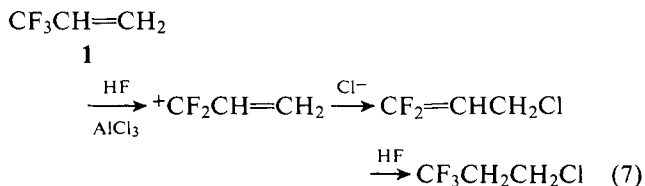$$

trifluoromethyl groups were present, or if a resonance electron-donating group was not present, corresponding treatment of the appropriate alcohols led to the formation of the protonated alcohols and the carbonium ions were not observed, e.g., eq 5.

$$
\underset{CF_3CHCH_3}{\overset{\overset{OH}{|}}{}} \xrightarrow[SO_2-SbF_5]{FSO_3H} \underset{CF_3CHCH_3}{\overset{\overset{+}{OH_2}}{|}} \quad\cancel{\longrightarrow}\quad \overset{+}{CF_3CHCH_3} \qquad (5)^{5b}
$$

Reported products of reactions of alkenes bearing the trifluoromethyl substituent with electrophilic reagents are in general not the normal products of ionic Markownikoff addition.[6] Thus the reaction product of 3,3,3-trifluoropropene (1) with DSO_3F is 3, with no incorporation of deuterium.[7] The outline of the mechanism proposed for reaction is given in eq 6. It was also concluded[7] that reported[8] examples of anti-

$$
\underset{\textbf{1}}{CF_3CH\!=\!CH_2} \xrightarrow{FSO_3H} CF_2\!\!=\!\!\overset{+}{CH}\!\!=\!\!CH_2
$$

$$
\xrightarrow{\textbf{1}} \left[CF_2\!=\!CH\!-\!\underset{\diagdown\,\overset{+}{H}\,\diagup}{\overset{\overset{\overset{CF_3}{|}}{CH}}{CH}}\cdots\cdots CH_2 \right] \qquad (6)
$$

$$\textbf{2}$$

$$\textbf{2} \longrightarrow CF_2\!=\!\!=\!CH\!=\!\!=\!CHCH(CF_3)CH_3^+$$

$$\xrightarrow{F^-} CF_3CH\!=\!CHCH(CF_3)CH_3$$

$$\textbf{3}$$

Markownikoff addition to **1** probably involve ionization-addition sequences (eq 7).

$$CF_3CH\!=\!CH_2$$
$$\textbf{1}$$

$$\xrightarrow[AlCl_3]{HF} {}^+CF_2CH\!=\!CH_2 \xrightarrow{Cl^-} CF_2\!=\!CHCH_2Cl$$

$$\xrightarrow{HF} CF_3CH_2CH_2Cl \qquad (7)$$

Quantitative studies of the effect of the trifluoromethyl group on the reactivity of alkenes have not been reported. We have recently been successful in correlating the reactivity of 1,1-disubstituted alkenes (eq 8) in protonation by eq 9, in which

$$
\underset{R_2}{\overset{R_1}{\diagdown}}C\!=\!CH_2 \xrightarrow{H^+} \underset{R_2}{\overset{R_1}{\diagdown}}{}^+\!C\!-\!CH_3 \qquad (8)
$$
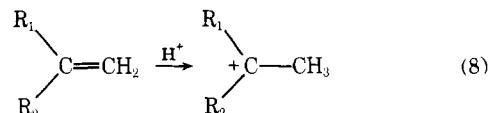
$$\log k_2 = -10.5\Sigma\sigma_p^+ - 8.92 \qquad (9)$$

the σ_p^+ constants of the substituents R_1 and R_2 are used.[9]

The least reactive alkene whose rate of protonation in solution has been observed is ethylene itself.[9] The observed rate of reaction of ethylene is, however, notably lower than predicted by eq 9, particularly when comparison is made at the standard extrapolated acidity $H_0 = 0.0$, equivalent to pH 0.0.[9] The actual reactivity of ethylene was measured at much higher acidity and at those acidities its reactivity was much closer to that of a model unreactive alkene, *p*-nitrostyrene. However, this latter compound was still 24 times more reactive than ethylene.
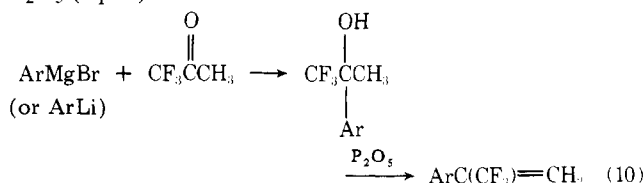
It appeared desirable to seek alkenes even less reactive than ethylene itself in protonation both as a guide to the mechanism of protonation of ethylene and as a critical test of the validity of eq 9. The trifluoromethyl group appeared to be the ideal probe for this purpose because its quantitative electron-withdrawing ability is thoroughly documented. Accordingly we have examined the reactivity of a series of α-trifluoromethylalkenes. Study of the reactivities of these highly deactivated species was expected to require rate measurements in highly acidic media, and thereby to provide a valuable connection with spectroscopic[5] and calorimetric[10] studies of stable ions in strong acids.

Study of a series of highly deactivated alkenes would also provide a quantitative comparison of the dependence of substituent effects on reactivity. A great deal of attention has recently been devoted to the question of variable sensitivity of developing carbonium ion centers to stabilization by substituents on the centers. In particular the change in sensitivity to the substituents, as measured by the variation of the ρ^+ values, has been found to increase in magnitude with the increasing "electron demand" of the carbonium ion center.[11]

Results

The reactivity of 2-trifluoromethylpropene (**4**) and 2-trifluoromethyl-2-propanol (CF_3CMe_2OH) in acid solution was observed by NMR. No change in the spectra was visible in 98% H_2SO_4 ($H_0 = -10.4$) but in chlorosulfuric acid ($ClSO_3H$, $H_0 = -13.8$) the resonances of **4** were converted to those of methacrylic acid ($CH_2\!=\!CMeCO_2H$). When the alcohol was treated with $ClSO_3H$ the spectrum changed to that of **4**, which then was converted to methacrylic acid. The alkene **4** was partly reacted with $D_2SO_4-ClSO_3H$ and the unreacted **4** and the product acid were recovered but no deuterium incorporation was observed in either compound.

α-Trifluoromethylstyrenes (**5–10**) were prepared by the method of Tarrant and Taylor.[12] The appropriate arylmagnesium bromide or aryllithium was reacted with 1,1,1-trifluoroacetone to give the corresponding 1-arylethanol (**11–16**) which was then dehydrated to the styrene by distillation from P_2O_5 (eq 10).

$$
ArMgBr + \underset{}{\overset{\overset{O}{\|}}{CF_3CCH_3}} \longrightarrow \underset{\underset{Ar}{|}}{\overset{\overset{OH}{|}}{CF_3CCH_3}}
$$
$$(or\ ArLi)$$

$$\xrightarrow{P_2O_5} ArC(CF_3)\!=\!CH_2 \qquad (10)$$

11	Ar = *p*-MeOC$_6$H$_4$	5
12	Ar = *p*-MeC$_6$H$_4$	6
13	Ar = Ph	7
14	Ar = *p*-ClC$_6$H$_4$	8
15	Ar = *m*-ClC$_6$H$_4$	9
16	Ar = *m*-CF$_3$C$_6$H$_4$	10

Table I. Acid-Catalyzed Hydration of $XC_6H_4C(CF_3){=}CH_2$ in H_2SO_4 at 25 °C

X	$[H_2SO_4]$, M^a	H_0	k_{eq}^{b}	k_{obsd}, s^{-1}	k_{hyd}, s$^{-1 c,d}$
p-MeO (**5**)	13.00	−6.71	2.20	1.59 × 10^{-3}	1.09 × 10^{-3}
	12.44	−6.39	(2.24)^e	6.52 × 10^{-4}	4.51 × 10^{-4}
	12.14	−6.21	(2.40)^e	4.85 × 10^{-4}	3.42 × 10^{-4}
	11.51	−5.81	3.03	1.84 × 10^{-4}	1.38 × 10^{-4}
	11.36	−5.74	(3.24)^e	1.39 × 10^{-4}	1.06 × 10^{-4}
	10.93	−5.47	(4.56)^e	7.31 × 10^{-5}	6.00 × 10^{-5}
	10.25	−5.07	9.49	2.44 × 10^{-5}	2.21 × 10^{-5}
p-Me (**6**)	15.00	−7.90	(0.316)^e	6.42 × 10^{-3}	1.54 × 10^{-3}
	14.30	−7.49	0.564	1.17 × 10^{-3}	4.22 × 10^{-4}
	14.05	−7.34	0.708	6.28 × 10^{-4}	2.60 × 10^{-4}
	13.40	−6.96	1.03	1.41 × 10^{-4}	7.15 × 10^{-5}
	13.09	−6.77	1.95	7.97 × 10^{-5}	5.27 × 10^{-5}
	12.44	−6.39	2.73	3.12 × 10^{-5}	2.28 × 10^{-5}
H (**7**)	15.90	−8.47	0.274	1.14 × 10^{-3}	2.46 × 10^{-4}
	15.90^f	−8.47	0.274	1.26 × 10^{-3} ^{f}	2.70 × 10^{-4}
	15.36	−8.14	0.436	2.86 × 10^{-4}	8.69 × 10^{-5}
	15.00	−7.91	0.511	1.83 × 10^{-4}	6.20 × 10^{-5}
	14.30	−7.49	0.846	3.51 × 10^{-5}	1.61 × 10^{-5}
	14.03	−7.32	(1.06)^e	1.72 × 10^{-5}	8.87 × 10^{-6}
p-Cl (**8**)	16.80	−9.09	0.053	6.68 × 10^{-3} ^{f}	3.36 × 10^{-4}
	16.34	−8.75	0.072	2.26 × 10^{-3} ^{f}	1.52 × 10^{-4}
	15.90	−8.47	0.086	4.42 × 10^{-4} ^{f}	3.50 × 10^{-5}
	15.90^f	−8.47	0.086	3.51 × 10^{-4} ^{g}	2.78 × 10^{-5}
	15.36	−8.14	0.154	9.48 × 10^{-5}	1.27 × 10^{-5}
	15.00	−7.91	(0.190)^e	4.48 × 10^{-5}	7.15 × 10^{-6}
m-Cl (**9**)	17.88	−10.18	(0.035)^e	1.25 × 10^{-2} ^{f}	4.24 × 10^{-4}
	17.50	−9.68	0.049	2.82 × 10^{-3} ^{f}	1.32 × 10^{-4}
	17.08	−9.31	0.054	4.76 × 10^{-4} ^{f}	2.44 × 10^{-5}
	16.80	−9.09	0.062	3.07 × 10^{-4} ^{f}	1.79 × 10^{-5}
	16.36	−8.76	0.092	1.02 × 10^{-4} ^{f}	8.63 × 10^{-6}
	16.36^g	−8.76	0.092	6.78 × 10^{-5} ^{g}	5.71 × 10^{-6}

^{a} Measured by titration. ^{b} K_{eq} = [alcohol]/[alkene] at equilibrium. ^{c} $k_{hyd} = K_{eq}k_{obsd}(1 + K_{eq})^{-1}$. ^{d} $k_{deh} = k_{obsd}(1 + K_{eq})^{-1}$; $k_{obsd} = k_{hyd}$ + k_{deh}. ^{e} Calculated by graphic interpolation of the plot of log K_{eq} vs. H_0. ^{f} k_{obsd} measured from the rate of disappearance of the alcohol. ^{g} k_{obsd} measured from the rate of disappearance of the alkene, but this point has not been included in the rate correlation.

The rates of reaction of the α-trifluoromethylstyrenes **5–9** at 25 °C were monitored by observing the decrease of the UV absorption maximum of the styryl chromophore. For **8** and **9** the rates of increase of the absorption beginning with the corresponding 1-arylethanols were observed. Only small amounts of addition product were present at equilibrium for **8** and **9** so much larger absorbance changes occurred beginning with the alcohols. The observed rates (Table I) beginning with the alcohol were 10–30% higher than with the alkene, although good first-order plots were obtained in all cases, with end points after 8–10 half-lives that remained constant within 2% during each additional half-life. For calculation of k_{hyd} and k_{deh} the k_{obsd} values derived from disappearance of the styrene were used for the *p*-MeO, *p*-Me, and H derivatives, and k_{obsd} values for reaction of the alcohol were used for the *p*-Cl and *m*-Cl substituted compounds.

Equilibrium constants K_{eq} = [alcohol]/[alkene] were measured in some cases by observing the equilibrium absorption obtained after 10 half-lives beginning with the alcohol or alkene. Values of K_{eq} that were not directly measured were derived from correlations of log ([alkene]/[alcohol]) vs. H_0.

The rate constants k_{hyd} and k_{deh} (eq 11) were calculated[13]

$$ArC(CF_3){=}CH_2 \underset{k_{deh}}{\overset{k_{hyd}}{\rightleftharpoons}} \underset{\underset{CF_3}{|}}{\overset{\overset{OH(S)}{|}}{Ar\overset{|}{C}CH_3}} \qquad (11)$$
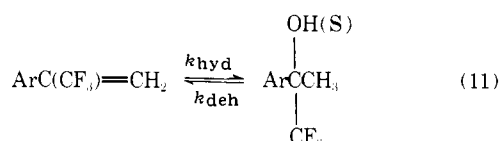
from the measured k_{obsd} and K_{eq} by the relations k_{hyd} = $K_{eq}k_{obsd}(1 + K_{eq})^{-1}$ and $k_{deh} = k_{obsd}(1 + K_{eq})^{-1}$ Particularly in the more concentrated acids much of the product is expected to be present as the sulfate ester, and this may contribute to

Table II. Correlation of Reactivities of Alkenes with H_0 in H_2SO_4 at 25 °C^a

alkene	γ^{b}	ϵ^{b}	k_2, M^{-1} s^{-1} ^{c}
$CH_2{=}CH_2$	−1.54	−14.83	1.24 × 10^{-13} ^{d}
p-AnisC(CF$_3$)=CH$_2$ (**5**)^f	−1.02	−9.79	1.62 × 10^{-10}
p-TolC(CF$_3$)=CH$_2$ (**6**)	−1.23	−12.61	2.48 × 10^{-13}
PhC(CF$_3$)=CH$_2$ (**7**)	−1.23	−14.05	8.97 × 10^{-15}
p-ClC$_6$H$_4$C(CF$_3$)=CH$_2$ (**8**)	−1.51	−17.15	1.20 × 10^{-15} ^{e}
m-ClC$_6$H$_4$C(CF$_3$)=CH$_2$ (**9**)	−1.25	−16.06	8.63 × 10^{-17}

^{a} Sums of $\Sigma\sigma_p^+$ for **5, 6, 7, 8, 9**, and **10** are 0.27, 0.37, 0.43, 0.45, 0.51, and 0.53, respectively. See ref 14. ^{b} From log $k_{obsd} = \gamma H_0 + \epsilon$, correlation coefficients 0.999, 0.994, 0.995, 0.993, and 0.988 for **5, 6, 7, 8**, and **9**, respectively. ^{c} $k_2 = k_{obsd}/h$ at $H_0 = 0$. ^{d} Calculated by assigning the k_2 value of ethylene as that of **6** divided by a statistical factor of 2. ^{e} Calculated by multiplying k_2 for **7** by the 8/7 reactivity factor of 0.134, which is the average value obtained within the range of experimental observation.

the differences observed in k_{obsd} depending on whether or not the alkene or alcohol is used as the substrate. Correlations of the derived k_{hyd} with the acidity function H_0 are given in Table II and illustrated in Figure 1, along with data for ethylene[9] for comparison.

Increasing amounts of the alkenes were present in equilibrium with the addition products as the acidity of the medium increased. As the equilibrium constants for addition decreased the percent error in determination of the alcohol concentration at equilibrium increased. This should particularly lower the reliability of k_{hyd} for the least reactive alkenes. This is apparent in the decreased correlation coefficients of the plots of log k_{hyd} vs. H_0 (Table II) and may be seen in Figure 1. It does appear that the deviations are not systematic but instead arise from
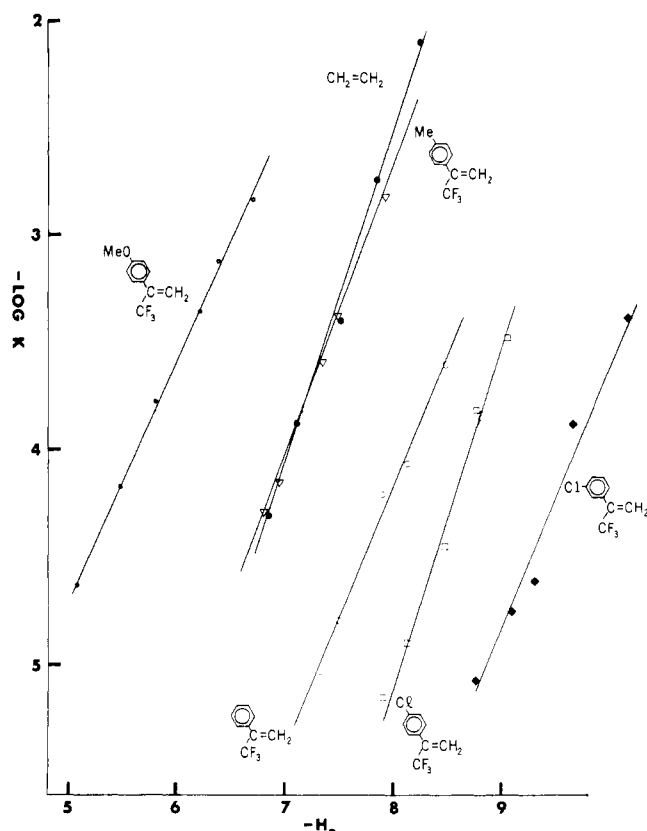
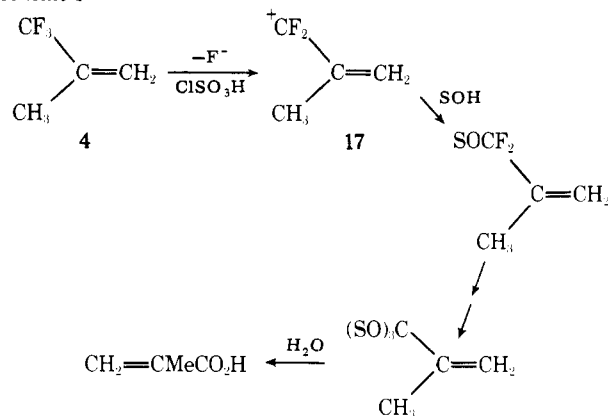**Figure 1.** Rates of acid-catalyzed solvent addition to α-trifluoromethyl-styrenes vs. H_0.

before it undergoes protonation. The cation $Me_2CF_3C^+$ is evidently formed from CF_3CMe_2OH in $ClSO_3H$ but is converted irreversibly to **4**. A plausible mechanism to form methacrylic acid from **4** is given in Scheme I. The cation **17** is stabilized by its allylic character and further the fluorines on the positively charged carbon stabilize the cation owing to their resonance electron-donating power ($\sigma_p^+ = -0.07$).[1b]

We have found[14] that the rate of formation of 2-chloroallyl cations by alkene protonations can be quantitatively predicted by eq 9 utilizing the σ_p^+ parameter for the halogen, and are testing if fluoro substituents also obey this relation.

The failure to observe equilibration of the m-trifluoro-methylstyrene **10** with its addition product similarly appears to result from destruction of **10** by another reaction. Solvolysis of the aryl trifluoromethyl group in **10** as found for **4** is the most likely choice for such a process. Solvolysis of trifluo-

romethylbenzene to benzoic acid in concentrated sulfuric acid has been reported.[6d,e]

The correlation of the reactivity of the α-trifluorostyrenes by eq 9 required derivation of k_2 values for these alkenes suitable for comparison. For the alkenes **5, 6, 7,** and **9** the slopes of plots of log k_{hyd} vs. H_0 fall in the range of -1.02 to -1.25, typical of values for other alkenes in general and styrenes in particular.[13,15-18] Therefore we have utilized the values of k_{hyd} derived from extrapolation of these plots to $H_0 = 0$ to derive values of k_2 for these alkenes. For **8** the slope is quite steep and gives rise to a value of k_{obsd} extrapolated to $H_0 = 0$ that is unrealistically low. Thus, although **8** is more reactive than **9** by a factor of 20 within the range of the actual experimental rate measurements, the order is reversed in the rates extrapolated to $H_0 = 0$. Therefore a k_2 value for **8** was derived by comparison to **7**. The details of this calculation are presented in Table II, and the correlations of all the k_2 values by eq 9 are shown in Figure 2.

The fit of the points for **5-9** to the previously derived correlation line shown in Figure 2 is reasonably good. Heretofore ethylene was the least reactive alkene toward protonation which had been examined, but alkenes **7-9** are all distinctly less reactive, even when the observed rate of ethylene is reduced by a statistical factor of 2 to account for the two equivalent sites for protonation. This result provides convincing further evidence for the validity of eq 9 for the correlation of alkene protonation, and for the generality of the mechanism of eq 8 of rate-determining protonation on carbon as the mechanism of alkene hydration.

The reactivity of ethylene has been the major deviation noted from eq 9.[9] We have argued previously[9] that this is at least partly due to the very steep slope of the correlation of log k_{hyd} for ethylene vs. H_0, and a consequent unrealistically low value of k_{hyd} for ethylene extrapolated to $H_0 = 0$. As may be seen in Figure 1 the reactivity of ethylene is almost identical with that of α-trifluoromethyl-p-methylstyrene (**6**) throughout the range of experimental observation. The sharper dependence of the ethylene rate on acidity results in ethylene being slightly

the random errors inherent in the difficulties in making these measurements.

The rate of addition of **10** could not be measured, as the absorbance of this compound in 17.5 M H_2SO_4 increased with time. When the alcohol **16** was treated with 17.5 M H_2SO_4 a smooth increase in absorbance indicating formation of **10** was observed, but a stable end point was not obtained. Instead the absorbance continued to increase past the value expected for 100% conversion to **10**. Evidently dehydration of **16** to **10** is occurring, but **10** is not stable under the reaction conditions and is consumed in a side reaction giving rise to a product with a high absorbance.

Discussion

The observed conversion of 2-trifluoromethylpropene (**4**) to methacrylic acid in chlorosulfuric acid and the failure to observe any deuterium incorporation in **4** recovered after partial reaction indicate that **4** is consumed by another reaction
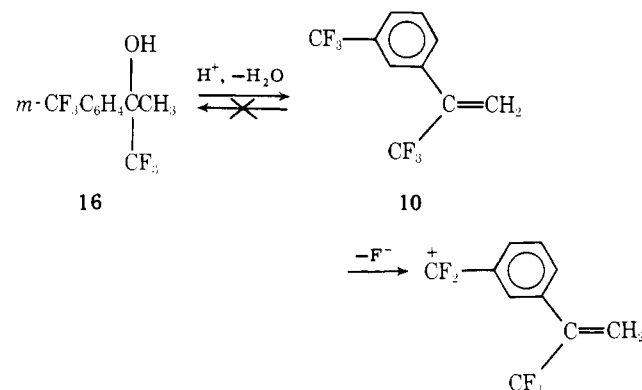
Scheme I

more reactive than **6** at the higher acidities and slightly less reactive at the lower acidities. However, when the rates are extrapolated to $H_0 = 0.0$, ethylene is a factor of 100 less reactive. Therefore a more realistic k_2 value for ethylene has been taken as that of **6** divided by the statistical factor of 2. This corrected value for ethylene is included in Figure 2.

The corrected rate of ethylene is still a factor of 10^4 smaller than predicted by eq 9. This deficiency in reactivity of ethylene is not an artifact of the data treatment. This may be illustrated by comparison with **6**, which has comparable reactivity to ethylene but whose $\Sigma\sigma_p^+$ value applicable to eq 9 is 0.37, predicting a much lower reactivity than ethylene. It is proper to ask the meaning of the deviation.

A change in mechanism for ethylene, such as formation of a π complex or concerted addition of the elements of water, can be excluded as the cause for the reactivity being less than expected. A different mechanism would intervene only if it were energetically more favorable and thus would be characterized by an enhanced rate. Similarly an unusual stabilization of ethylene in mineral acid leading to decreased reactivity can be excluded. The solubility of ethylene in $HClO_4$ decreases at higher acid concentrations, indicating that no special stabilization of the alkene occurs in strong acid.[19] Thus the failure of eq 9 to account for the low rate of ethylene apparently arises from a breakdown of the linear free energy correlation when applied to this totally unsubstituted compound. The σ_p^+ parameter of hydrogen $(= 0.0)$ is derived from the solvolysis of cumyl chloride, in which the hydrogen is substituted in the para position of a benzene ring. Apparently this substituent parameter is inadequate to describe the low stabilization available in the formation of the $C_2H_5^+$ involving only seven atoms.

Comparison with the gas-phase protonation of alkenes as included in Table III is also revealing in this regard. The heat of reaction in proton transfer to ethylene is 21.5 kcal/mol more than that to propene, which in turn exceeds the value for proton transfer for isobutylene by 12.0 kcal/mol.[20a] Thus the effect of successive methyl substitution on the heats of protonation of the simple alkenes is not additive in the gas phase but methyl substitution on the ethyl cation provides 9.5 kcal/mol more stabilization than the corresponding substitution on the 2-propyl cation. This high heat of protonation of ethylene in the gas phase parallels the low reactivity of ethylene in solution. For reference heats of reaction forming the simple alkyl cations from various sources are included in Table III. These other cases exhibit a smaller energy increment when the difference between isopropyl and ethyl cations is compared to that between *tert*-butyl and isopropyl.

The most recent calculations on the structure of the $C_2H_5^+$ ion in the gas phase favor a bridged structure,[20] but the effect of solvent has been proposed to favor an open ion.[20c]

There has recently been considerable discussion of the behavior of linear free energy relationships over extended ranges of reactivity.[11,21-24] One example[21] considers the additivity of substituent effects when more than one group is present. The argument is made[21] that additivity is not expected because one substituent perturbs the transition state so that the effect of an additional substituent is altered. This anticipated behavior (an example of the reactivity-selectivity principle[22]) was observed in the rate of elimination of 1-arylethyl esters.[21] Another example mentioned in the introduction is the "tool of increasing electron demand",[11] in which the electron supply in the transition state is correlated with ρ^+. Another widely cited method for the study of transition state structure is the Yukawa-Tsuno relation

$$\log k/k_0 = \rho\left[\sigma + r(\sigma^+ - \sigma)\right] \qquad (12)$$

This relation was designed to accommodate variable electronic supply by substituents but the need for this relation has been reexamined[23b] and it has been found superfluous for the
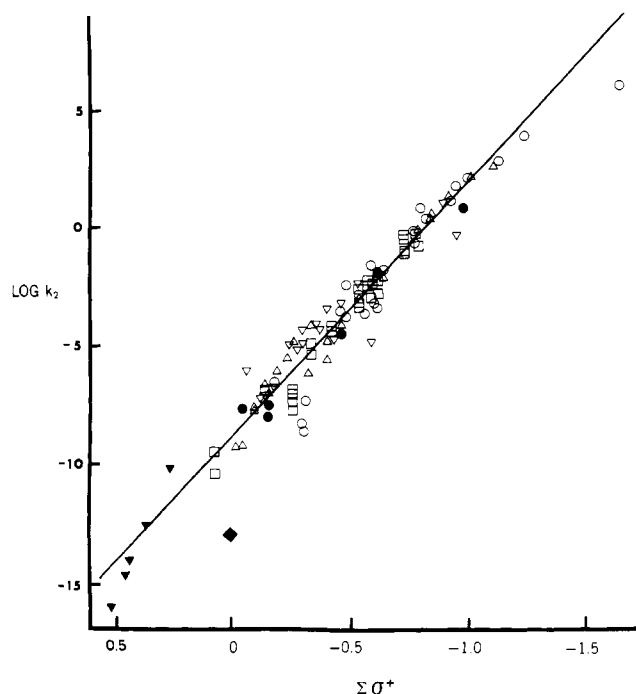
Figure 2. Correlation of acid-catalyzed hydration rates of alkenes vs. σ_p^+ substituent parameters ($\blacktriangledown$ (**5-9**), α-trifluoromethylstyrenes; $\blacklozenge$, ethylene).

analysis of a large body of solvolytic data. The absence of a reactivity-selectivity relation in a series of pyridine alkylations spanning a factor of 10^8 in reactivity has also been observed.[24a]

Our results allow several different comparisons of the applicability of linear free energy relationships to accommodate wide ranges of reactivity. These include both the entire group of alkenes and also subsets of substituted styrenes.

The correlation of the reactivity of the α-trifluoromethyl substituted styrenes **5-9** with variation in the aryl substituent requires a somewhat arbitrary choice of the acidity at which to make the comparison. As may be seen in Figure 1 the acidity dependences of the reactivity of these styrenes are not identical, and furthermore the reactivities of all were not measured at any one acidity so extrapolations are necessary to arrive at a common basis for comparison. The best correlation ($r = 0.984$) was found at $H_0 = -7.50$ with $\rho^+ = -4.00$. This acidity was near the center of the range at which the rates were actually measured. The ρ^+ value is compared in Table IV to those for other groups of α-substituted styrenes.

The precision of most of the correlations of styrene reactivities with the σ^+ values of the aryl substituents is only fair, as summarized in the correlation coefficients given in Table IV. In one example curvature in the plot was interpreted[15b] in terms of a saturation of the substituent effect for the more reactive compounds. A noticeable difference was obtained for the ρ^+ values for the α-H substituted styrenes by different groups of workers measuring rates for H_2SO_4- and $HClO_4$-catalyzed reactions, respectively. It is significant that a much better correlation coefficient was obtained in the latter case in which the comparison could be made at a common acidity at which all the rates were measured. It appears that the extrapolations that must be employed in most of the examples cited are one cause of the low precision in some of the correlations. Another factor that may be involved is steric interaction between the aryl ring and the α substituent, but no reliable estimate of the magnitude of this effect is available.

Having noted the need for discretion in the interpretation of the ρ^+ parameters it nevertheless appears that there is a significant trend in the data. For example, the ρ^+ value of -4.0

Table III. Comparative Gas-Phase Heats of Formation of Alkyl Cations from Various Sources

| | ΔH^{OR}_{react}, kcal/mol | | | | $\Delta\Delta H^{OR-R'}_{react}$, kcal/mol | | | |
	Me	Et	*i*-Pr	*t*-Bu	(Et − Me)	(*i*-Pr − Et)	(*t*-Bu − *i*-Pr)	ref
$R^+ + Br^- \rightarrow RBr$	−217.7	−181.9	−162.9	−148.7	35.8	19.0	14.2	a
$R^+ + H_2O \rightarrow ROH_2^+$	−66	−37	−22.8	−11.2	29	14.2	11.6	b
alkene + $H^+ \rightarrow R^+$		−159.5^e	−181.0	−193.0		21.5	12.0	c
ΔH_f	261	219	192	167	−42	−27	−25	d
$R^+ + R'H \rightarrow RH + R'^+$		−40	−18	0.0		22	18	f

^{a} R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5964 (1977). ^{b} K. Hiraoka and P. Kebarle, *ibid.*, **99**, 360 (1977). ^{c} Reference 20a. ^{d} F. P. Lossing, *J. Am. Chem. Soc.*, **99**, 7526 (1977); F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 755 (1970). ^{e} Calculated from the ΔH_f^0 of 12.54 for ethylene (*Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971)); the ΔH_f^0 of 366 for H^+ (*ibid.*, No. 26 (1969)); and the ΔH_f^0 for $C_2H_5^+$ of 219 (footnote d). ^{f} R' = *t*-Bu: M. Meot-Ner Mauntner and F. H. Field, *J. Am. Chem. Soc.*, **100**, 1356 (1978).

Table IV. Effect of Structure on Reactivity of ArCR=CH₂ in Acid-Catalyzed Hydration at 25 °C

R	σ_p^+ (R)	ρ^+	k_2, $M^{-1} s^{-1}$ (Ar = Ph)	ref	r^g
R_2N^a	−1.7	−1.1^b	6.24×10^7	15a	0.986
EtO	−0.83	−1.6^c	1.18×10^2	15c	0.975
MeO	−0.78	−1.7^c	5.45×10^1	15b	0.981
Me	−0.31	−2.9	9.67×10^{-5}	16	0.981
$(EtO)_2PO_2$	−0.13	−2.1	1.11×10^{-5}	17	0.999
AcO	−0.06	−1.9	9.9×10^{-6}	18	
H	0.0	−2.9^d	3.72×10^{-7}	16	0.993^h
H	0.0	−3.6^e	1.09×10^{-7}	13	0.998
CF_3	0.61	−4.0	8.97×10^{-15}	f	0.984^i

^{a} R_2N = *N*-morpholino. ^{b} A better correlation is obtained using σ parameters: $\rho = -1.3$, $r = 1.000$. ^{c} Curved correlations; straight line plots consisting only of points for aryl groups no more electron donating than phenyl give $\rho^+ = -2.2$ and -2.3 for R = EtO and MeO, respectively, with $r = 0.994$ and 0.995. ^{d} In H_2SO_4. ^{e} In $HClO_4$. ^{f} This work. ^{g} Correlation coefficients derived from the reported rates. ^{h} Omitting a point for *m*-NO₂. If this point is included ρ^+ is -3.31 and r is 0.977. ^{i} At $H_0 = -7.5$. At $H_0 = -7.0$ and -8.0 slopes were -4.1 and -3.9 with $r = 0.983$ and 0.983, respectively.

for the α-CF₃ series is distinctly greater than that of -1.7 to -2.3 for the α-MeO series. This is of course the expected result for the much greater stabilizing effect of the α-MeO group. By comparison the ρ^+ values observed in the solvolysis of ArCMe₂OPNB and ArC(c-Pr)MeOPNB are -4.72 and -2.78, respectively.[11c] The difference in the ρ^+ values for these substrates is comparable to those for the styrene protonations, although the σ^+ values of methyl (-0.31) and cyclopropyl (-0.47) differ by only 0.16 unit whereas those of MeO and CF₃ differ by 1.39 units. Variation of the α substituent leads to a change in reactivity of 10^{22} in the styrenes (Table IV) but the effect on ρ^+ is modest. Thus the protonation of styrenes does show an influence of the effect of electron demand on the value of ρ^+, but the magnitude of this effect is vastly compressed over that observed in solvolysis of esters. A theory has been proposed[11a] to predict values of ρ^+ and it will be of interest if it can account for this divergent behavior.

Inspection of Figure 2 reveals that a line defined only by the rates of **5–9** is clearly steeper than the overall correlation line. However, inclusion of **5–9** in the set of compounds which define the best correlation for the entire line[25] actually improves the overall correlation coefficient for this set from 0.969 to 0.984. This arises because **5–9** considerably extend the range of the correlation while bracketing the previous line.

The utility of our general correlation of rates, expressed in eq 9 and illustrated in Figure 2, depends on the additivity of substituent effects. This correlation now covers 22 orders of magnitude in reactivity, and correlates the data rather well without any clear evidence of curvature. Nonadditivity of substituent effects has been proposed as a criterion for the

operation of the reactivity–selectivity principle, so the linearity of Figure 2 argues against the applicability of this principle in this system. The "capricious" nature of this effect has been commented upon.[24a]

A recent discussion has appeared[24b] of the description of transition states by structure–reactivity coefficients. Two alternative types of behavior were discussed. In "Hammond"-type reactions the more endothermic reactions have more advanced transition states, whereas "anti-Hammond" behavior is characterized by an adjustment of the transition-state structure to take advantage of favorable substituent effects. Our work illustrates that the behavior of different systems on linear free energy correlations can be quite different. Thus in alkene protonations such correlations cover vast ranges in reactivity with only modest differences in sensitivities. In solvolytic reactions the effect of substituents varies depending on the electron supply at the electron-deficient center.

Another point regarding the reactivity of these deactivated alkenes should be addressed. If protonation at the β carbon is much slower than protonation of ethylene, why does not protonation occur at the α carbon to form a primary cation (eq 13)? One answer is that the β substituents destabilize the

$$R_2C{=}CH_2 \xrightarrow{H^+} R_2CH\overset{+}{C}H_2 \tag{13}$$

transition state leading to the cation in eq 13 even more than they destabilize formation of the alternative *tertiary* cation. We have considered the question of β-substituent effects previously and found that both an inductive electron-withdrawing effect of the substituent and its influence in stabilizing the ground state retard the rate of protonation.[26] A quantitative measure of the latter effect for the CF₃ group is not available but as a rough guide both phenyl and halogen individually cause rate retardation by factors of approximately 500. Protonation at the α carbon in the cases considered here can thus be crudely estimated as retarded by factors of 10^4–10^6.

Experimental Section

¹H NMR spectra were run using a Varian T-60 instrument with tetramethylsilane as an internal standard. Vapor phase chromatographic (VPC) separations were carried out using a Varian-Aerograph Model 920 instrument and a 3 m × 10 mm OV-17 column. Kinetic measurements were done using Cary 14 and 118 instruments.

2-Trifluoromethylpropene (**4**) was obtained from PCR and 1,1,1-trifluoroacetone and the aryl bromides were from Aldrich Chemical. 2-Trifluoromethyl-2-propanol was obtained from the reaction of methylmagnesium bromide with 1,1,1-trifluoroacetone.

2-Aryl-1,1,1-trifluoropropan-2-ols **11–16** were prepared by addition of the aryl Grignard or lithium reagents derived from the corresponding aryl bromides to 1,1,1-trifluoroacetone as has been described.[12] The crude alcohols were purified by VPC for kinetic and equilibrium studies. For preparation of the styrenes **5–10** the crude alcohols were mixed with P₂O₅ and heated at atmospheric pressure as described.[12] The material that distilled up to 170 °C was collected and then further fractions were obtained at the same pot temperature

and 20 Torr. The styrenes were purified by VPC and characterized as follows. **5:** NMR (CDCl₃) δ 3.76 (s, 3, OMe), 5.66 and 5.82 (each m, 2, =CH₂), and 6.84 and 7.36 (dd, 4, J = 8 Hz, A₂B₂ of Ar); mass spectrum *m/e* 202 (M⁺). **6:** NMR (CCl₄) δ 2.30 (s, 3, Me), 5.62 and 5.84 (each m, 2, =CH₂), and 7.08 and 7.30 (dd, 4, J = 8 Hz, A₂B₂ of Ar); mass spectrum *m/e* 186 (M⁺). **7:**[12] NMR (CCl₄) δ 5.68 and 5.90 (each m, 2, =CH₂) and 7.31 (s, 5, Ar). **8:** NMR (CCl₄) δ 5.64 and 5.88 (each m, 2, =CH₂) and 7.25 (s, 4, Ar); mass spectrum *m/e* 206 (M⁺). **9:** NMR (CCl₄) δ 5.74 and 5.98 (each m, 2, =CH₂) and 7.3 (m, 4, Ar); mass spectrum *m/e* 206 (M⁺). **10:**[12] NMR (CCl₄) δ 5.80 and 6.06 (each m, 2, =CH₂) and 7.6 (m, 4, Ar); mass spectrum *m/e* 240. The new compounds **5, 6, 8,** and **9** were further characterized by correct elemental analyses (C, H) and exact mass molecular ion determination.

Kinetics. Acid solutions were prepared by diluting concentrated H₂SO₄ with distilled water. Acid molarities were measured by titration with standard NaOH and were converted to acidity functions H_0 by the use of standard tables. For kinetic runs 3-mL acid solutions were equilibrated at 25.0 °C in 1-cm cells in the UV instrument and 2-μL samples of 0.2 M solutions of the alkene or alcohol were injected to give final concentrations of 4 × 10⁻⁴ M. The change in absorbance near the maxima was then monitored as a function of time. End points after 10 half-lives were stable to within 2% for each additional half-life. Equilibrium constants were calculated from the final absorbances obtained beginning with known concentrations of alkene or alcohol (λ_{max} (H₂O): **5,** 251; **6,** 244, **7,** 234; **8,** 242; **9;** 235; **10,** 231 nm). The alcohols showed no absorbance at these wavelengths. All rate constants were obtained in duplicate with agreement within ±5%.

The reactivity of **4** was monitored by condensing 0.05 g of the gaseous alkene in a tube contained in a dry ice–acetone bath and transferring the material to a cooled NMR tube and adding cooled ClSO₃H. Water (5%) was added to most of the samples to slow the rate of reaction for convenient NMR measurement. Over a time span of about 10 min the NMR spectrum was converted into that of methacrylic acid. When ClSO₃H was added to CF₃CMe₂OH the spectrum underwent conversion to that of **4** and then changed to that of methacrylic acid.

In a preparative experiment 1 g of the alcohol was stirred for 2 h with 20 mL of ClSO₃H in a sealed container. The contents were poured onto ice and extracted with CH₂Cl₂ which was then evaporated. The residue was identified as methacrylic acid by its NMR spectrum and elemental analysis of its cyclohexylamine salt.

To test for deuterium uptake 1 g of condensed **4** was added to a cooled ampule and 4 mL of a cold 1:1 mixture of ClSO₃H and D₂SO₄ was added. The heterogeneous mixture was shaken for 6 h and then the residual gaseous alkene was collected in a cold receiver after the ampule was opened and warmed. The liquid residue was diluted with water and extracted with CH₂Cl₂, which was evaporated. The mass spectra of the recovered alkene and the product methacrylic acid both showed no incorporation of deuterium.

References and Notes

(1) (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); (b) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(2) W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965); *Tetrahedron*, **27**, 945 (1971).
(3) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).
(4) S. A. Holmes and T. D. Thomas, *J. Am. Chem. Soc.*, **97**, 2337 (1975).
(5) (a) G. A. Olah and Y. K. Mo, *Adv. Fluorine Chem.*, **7**, 69 (1972); (b) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **88**, 3310 (1966).
(6) (a) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Usp. Khim.*, **35**, 417 (1966); (b) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Fluorine Chem. Rev.*, **3**, 45 (1969); (c) R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, **4**, 50 (1965); (d) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969; (e) Y. Kobayashi and I. Kumadaki, *Acc. Chem. Res.*, **11**, 197 (1978).
(7) P. C. Myhre and G. D. Andrews, *J. Am. Chem. Soc.*, **92**, 7595, 7596 (1970).
(8) A. L. Henne and S. Kaye, *J. Am. Chem. Soc.*, **72**, 3369 (1950).
(9) (a) W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 7233 (1977); (b) V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10**, 252 (1977).
(10) E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 2563, 5408 (1978).
(11) (a) W. L. Jorgensen, *J. Am. Chem. Soc.*, **99**, 3840 (1977); (b) E. N. Peters, M. Ravindranathan, and H. C. Brown, submitted for publication; (c) H. C. Brown, M. Ravindranathan, and C. G. Rao, *J. Am. Chem. Soc.*, **100**, 1218 (1978).
(12) P. Tarrant and R. E. Taylor, *J. Org. Chem.*, **24**, 238 (1959).
(13) W. M. Schubert and J. R. Keeffe, *J. Am. Chem. Soc.*, **94**, 559 (1972).
(14) W. K. Chwang, P. Knittel, K. M. Koshy and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3395 (1977).
(15) (a) P. Y. Sollenberger and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 4261 (1970); (b) G. M. Loudon and C. Berke, *ibid.*, **96**, 4508 (1974); (c) Y. Chiang, W. K. Chwang, A. J. Kresge, L. H. Robinson, D. S. Sagatys, and C. I. Young, *Can. J. Chem.*, **56**, 456 (1978).
(16) (a) N. Deno, F. A. Kish, and H. J. Peterson, *J. Am. Chem. Soc.*, **87**, 2157 (1965); (b) J.-C. Simandoux, B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 4402 (1972).
(17) R. D. Frampton, T. T. Tidwell, and V. A. Young, *J. Am. Chem. Soc.*, **94**, 1271 (1972).
(18) D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.*, **91**, 119 (1969).
(19) E. L. Purlee and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **78**, 5811 (1956).
(20) (a) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976); (b) H. Lischka and H.-J. Köhler, *ibid.*, **100**, 5297 (1978); (c) W. L. Jorgensen and J. E. Munroe, *Tetrahedron Lett.*, 581 (1977); (d) S. Nagase and K. Morokuma, *J. Am. Chem. Soc.*, **100**, 1666 (1978).
(21) E. Glyde and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1537, 1541 (1977).
(22) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).
(23) (a) T. J. Gilbert and C. D. Johnson, *J. Am. Chem. Soc.*, **96**, 5846 (1974); (b) C. D. Johnson, *J. Org. Chem.*, **43**, 1814 (1978); (c) I. Roberts, C. D. Johnson, and P. G. Taylor, *Tetrahedron*, **33**, 2123 (1977).
(24) (a) E. M. Arnett and R. Reich, *J. Am. Chem. Soc.*, **100**, 2930 (1978); (b) D. A. Jencks and W. P. Jencks, *ibid.*, **99**, 7948 (1977).
(25) Footnote 25, ref 9a. Compounds **5–9** in the current work constitute **98–102**, respectively, in the complete set.
(26) P. Knittel and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3408 (1977).