

Solvolysis of Vinyl Triflates. Effect of Alkyl Substituents, Solvents, and Added Nucleophiles¹

Richard H. Summerville,^{2a,d} Carol A. Senkler,^{2a} Paul v. R. Schleyer,^{*2a} Thomas E. Dueber,^{2b} and Peter J. Stang^{2c}

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, and University of Utah, Salt Lake City, Utah 84112. Received May 21, 1973

Abstract: Vinyl solvolyses are somewhat anomalous when compared with the behavior of saturated analogs. There is evidence of nucleophilic solvent involvement of alkyl-substituted vinyl substrates (m and l values are of intermediate magnitude and the effect of changes in solvent nucleophilicity at constant ionizing power is significant), but, in contrast, the carbonium ion character is high (ρ^* is large for alkyl substitution) and added strong nucleophile, Br^- , has no significant effect on rates or products. Furthermore, the accompanying paper shows that substitution occurs with only partial inversion; there is no evidence for an $\text{S}_{\text{N}}2$ reaction. Nucleophilicity effects are larger with substrates with trans β hydrogen than with trans β -alkyl groups. This anomalous behavior may be due to solvation of an ion pair, but this solvation appears to occur at the β hydrogen or at other sites but not directly at the rear of the carbon bearing the leaving group.

Although vinyl cations are less stable than comparably substituted aliphatic carbenium ions,^{1b} vinylic substrates seem to be less prone toward rear-side attack by solvent or nucleophiles.³ α -Phenethyl⁴ derivatives acetylyze with net inversion, but vinylic substrates bearing an α -aryl group react with nearly complete cis-trans randomization.⁵ Simple primary and secondary substrates react by $\text{S}_{\text{N}}2$ or ion-pair $\text{S}_{\text{N}}2$ pathways with considerable solvent assistance⁶ and complete inversion.^{6,7} In contrast, the acetylysis of alkyl-substituted vinyl substrates typically give only 30–40% inversion.^{1b,8} Extended Hückel calculations indicate the relative difficulty of $\text{S}_{\text{N}}2$ reactions in vinylic systems.⁹ When the $\text{S}_{\text{N}}1$ pathway is not available, vinylic in-plane $\text{S}_{\text{N}}2$ processes are not observed, rather various combinations of elimination-addition and addition-elimination.¹⁰

(1) (a) A preliminary account of part of this work has appeared: P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969). (b) A related study is presented in the following paper: R. Summerville and P. v. R. Schleyer, *ibid.*, **96**, 1110 (1974).

(2) (a) Princeton University; (b) University of Utah; (c) Princeton University, 1967–1969; present address, University of Utah; (d) National Science Foundation Predoctoral Fellow, 1969–1972.

(3) For reviews, see (a) P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 205 (1972); (b) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971); (c) Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, **92**, 4985 (1970); (d) H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 899; (e) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970).

(4) (a) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 4; (b) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions" American Chemical Society Monograph, No. 167, C. J. Collins and N. S. Bowman, Ed., Van Nostrand Reinhold, New York, N. Y., 1970, p 90.

(5) (a) Z. Rappoport and Y. Apeloig, *Proc. Isr. J. Chem.*, **7**, 34 (1969); (b) *J. Amer. Chem. Soc.*, **91**, 6734 (1969); (c) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970); (d) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971); (e) however, cf. G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970); (f) Z. Rappoport and Y. Houminer, *J. Chem. Soc., Perkin Trans. 2*, 1506 (1973).

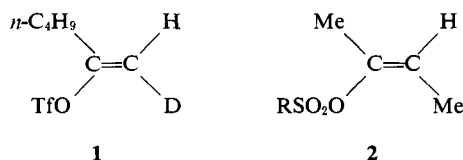
(6) See a recent review: D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972).

(7) (a) A. Streitwieser, Jr., and J. D. Walsh, *J. Amer. Chem. Soc.*, **87**, 3686 (1965); (b) A. Streitwieser, Jr., J. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965); (c) H. Weiner and R. A. Snee, *ibid.*, **87**, 287 (1965).

(8) (a) R. H. Summerville and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 3629 (1972); (b) J. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, **94**, 3627 (1972).

(9) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1953 (1971).

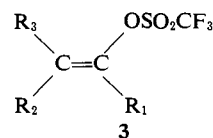
Despite this, there is some indication of solvent participation with alkylvinyl sulfonates bearing β hydrogen trans to the leaving group. In the accompanying paper^{1b,8a} it was shown that relatively unhindered **1** gave an unusually large per cent (80%) of net inversion on acetylysis. Dimethylvinyl sulfonates **2**



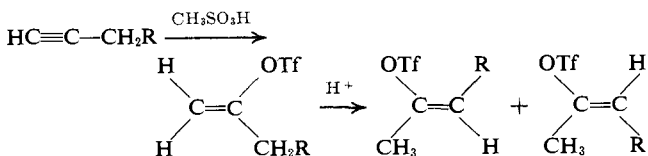
give >95% elimination suggesting attack by solvent on hydrogen.^{1,8a,11} In order to clarify the mechanism of solvolysis of simple alkylvinyl substrates, we have examined the effect of substituents, solvents, and added nucleophiles.

Results

A series of substrates (**3**) was prepared with varied alkyl



substituent patterns (Table I). Addition of triflic acid to terminal acetylenes at -30° , followed by careful neutralization to prevent acid-catalyzed rearrangement of the double bond, gave triflates with terminal double bonds.^{1b} This technique was also used to prepare the isomers of **16** and **18**. The tendency of vinyl triflates with terminal double bonds to isomerize was utilized to prepare the isomers of **8** and **14**. An attempt to



(10) For a review, see (a) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969); (b) Z. Rappoport and A. Gal, *J. Org. Chem.*, **37**, 1174 (1972).

(11) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **91**, 6194 (1969).

Table I. Rate Constants for Solvolysis of Vinyl Triflates

Compd	$\begin{array}{c} \text{R}_3 \qquad \text{OTf} \\ >\text{C}=\text{C}< \\ \text{R}_2 \qquad \text{R}_1 \end{array}$			Solvent	Temp, °C	k , sec ⁻¹ ^a	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu											
	R ₁	R ₂	R ₃																
4	CH ₃	H	H	80% EtOH	76.1	$4.95 \pm 0.28 \times 10^{-5}$	24.7	-7.7											
					100.1	$5.26 \pm 0.25 \times 10^{-4}$													
					75.0	4.43×10^{-5}													
				50% EtOH	76.1	$3.72 \pm 0.25 \times 10^{-4}$			24.9	-3.3									
					50.2	$1.95 \pm 0.05 \times 10^{-5}$													
					75.0	3.31×10^{-4}													
				97% TFE ^d	105.1	$7.73 \pm 0.18 \times 10^{-5}$					23.9	-14.7							
					75.2	$4.66 \pm 0.04 \times 10^{-6}$													
					75.0	4.57×10^{-6}													
5	<i>n</i> -Bu	H	H	90% EtOH	75.3	$5.70 \pm 0.11 \times 10^{-5}$	23.6	-9.1											
					80% EtOH	100.22							$1.30 \pm 0.04 \times 10^{-3}$						
						75.05							$1.22 \pm 0.08 \times 10^{-4}$						
				50% EtOH	75.0	1.21×10^{-4}			21.9	-10.1									
					75.2	$8.40 \pm 0.02 \times 10^{-4}$													
					62.0	$2.33 \pm 0.02 \times 10^{-4}$													
				HOAc ^b	75.0	8.25×10^{-4}					27.7	-5.1							
					125.4	$4.33 \pm 0.02 \times 10^{-4}$													
					103.1	$5.17 \pm 0.10 \times 10^{-5}$													
				97% TFE ^d	75.0	2.42×10^{-6}							22.9	-14.0					
					75.0	2.42×10^{-6}													
					89.9	$1.08 \pm 0.02 \times 10^{-4}$													
50% EtOH	75.4	$2.77 \pm 0.24 \times 10^{-5}$	21.9	-10.1															
	75.0	2.66×10^{-5}																	
	75.0	2.66×10^{-5}																	
6	<i>i</i> -Pr	H			H	50% EtOH	75.0	8.31×10^{-4}	24.0	-4.0									
							62.0	$3.71 \pm 0.01 \times 10^{-4}$											
							49.75	$3.84 \pm 0.01 \times 10^{-5}$											
7	<i>t</i> -Bu	H			H	50% EtOH	75.4	$9.14 \pm 0.16 \times 10^{-4}$	23.7	-4.8									
							50.4	$6.03 \pm 0.08 \times 10^{-5}$											
							75.0	8.78×10^{-4}											
(Z)-8	Me	H			Me	90% EtOH	75.24	$2.25 \pm 0.03 \times 10^{-4}$	23.8	-5.3									
							80% EtOH	76.1			$6.29 \times 0.20 \times 10^{-4}$								
								50.2			$3.72 \pm 0.05 \times 10^{-4}$								
			60% EtOH	75.0		5.63×10^{-4}	24.5	-0.70											
				74.96		$2.26 \pm 0.02 \times 10^{-3}$													
				53.05		$1.97 \pm 0.02 \times 10^{-4}$													
			50% EtOH	75.0		2.27×10^{-3}					23.2	-3.6							
				50.4		$2.44 \pm 0.05 \times 10^{-4}$													
				25.05		$1.05 \pm 0.01 \times 10^{-5}$													
			97% TFE ^d	75.0		2.03×10^{-3}							22.7	-12.0					
				100.0		$8.74 \pm 0.19 \times 10^{-4}$													
				75.15		$9.14 \pm 0.11 \times 10^{-6}$													
HOAc ^b	75.0	9.01×10^{-5}	28.3	-1.8															
	100.0	7.99×10^{-6}																	
	75.0	4.80×10^{-6}																	
CF ₃ CO ₂ D ^b	100.0	1.72×10^{-3}			25.5	-3.3													
	75.0	1.36×10^{-4}																	
	75.0	1.36×10^{-4}																	
(E)-8	Me	Me					H	80% EtOH	100.1	$2.48 \pm 0.08 \times 10^{-4}$	25.3	-7.7							
									76.2	$2.25 \pm 0.08 \times 10^{-5}$									
									75.0	1.98×10^{-5}									
								60% EtOH	99.92	$1.112 \pm 0.001 \times 10^{-3}$			26.4	-1.5					
									74.98	$8.13 \pm 0.04 \times 10^{-5}$									
									100.5	$1.83 \pm 0.04 \times 10^{-3}$									
			50% EtOH	75.5				$1.82 \pm 0.01 \times 10^{-4}$	23.2	-9.5									
				75.0				1.75×10^{-4}											
				75.0				1.75×10^{-4}											
			97% TFE ^d	100.0	$2.46 \pm 0.04 \times 10^{-4}$	25.1		-8.2											
				75.15	$2.15 \pm 0.05 \times 10^{-5}$														
				75.0	2.11×10^{-5}														
HOAc ^b	100.0	1.88×10^{-5}	30.3	+0.7															
	75.0	9.27×10^{-7}																	
	100.0	1.31×10^{-3}																	
CF ₃ CO ₂ D ^b	100.0	1.31×10^{-3}			26.9		0.0												
	75.0	9.01×10^{-5}																	
	75.0	9.01×10^{-5}																	
(Z)-9	Et	H							Me	50% EtOH	75.3	$4.50 \pm 0.04 \times 10^{-3}$	22.9	-2.6					
											(E)-9	Et			Me	H	50% EtOH	75.3	$9.78 \pm 0.34 \times 10^{-4}$
																		(Z)-10 ^c	<i>i</i> -Pr
49.75	$5.83 \pm 0.01 \times 10^{-4}$																		
(E)-10 ^c	<i>i</i> -Pr	Me				H		50% EtOH	75.0	8.35×10^{-3}	22.7	-3.4							
									75.3	$7.78 \pm 0.42 \times 10^{-3}$									
			49.75	$5.40 \pm 0.07 \times 10^{-4}$															
11	Me	Me	Me	80% EtOH		75.0		7.57×10^{-3}	25.3	-7.0									
						100.0		$3.33 \pm 0.04 \times 10^{-4}$											
					75.15	$2.75 \pm 0.03 \times 10^{-5}$													
					75.0	2.70×10^{-5}													

Table I (Continued)

Compd	$\begin{array}{c} R_3 \qquad \text{OTf} \\ \diagdown \quad / \\ >C=C< \\ / \quad \diagdown \\ R_2 \quad R_1 \end{array}$				Solvent	Temp, °C	k , sec ⁻¹ ^a	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
	R ₁	R ₂	R ₃						
12	Et	Me	Me	50% EtOH	60% EtOH	99.92	$1.64 \pm 0.03 \times 10^{-3}$	25.5	-3.4
						74.96	$1.30 \pm 0.02 \times 10^{-4}$		
						75.0	1.31×10^{-4}		
					50% EtOH	100.0	$2.82 \pm 0.20 \times 10^{-3}$		
						75.15	$2.98 \pm 0.03 \times 10^{-4}$		
						75.0	2.94×10^{-4}		
					97% TFE ^d	100.2	$3.71 \pm 0.02 \times 10^{-4}$		
						74.85	$4.33 \pm 0.03 \times 10^{-5}$		
						75.0	4.39×10^{-5}		
					HOAc ^b	100.0	2.00×10^{-5}		
						75.0	1.05×10^{-5}		
					13	<i>i</i> -Pr	Me		
49.75	$1.14 \pm 0.01 \times 10^{-4}$								
75.0	2.23×10^{-4}								
<i>(Z)</i> -14	Me	H	Et	50% EtOH	49.90	$1.77 \pm 0.02 \times 10^{-4}$	22.7	-1.0	
					25.00	$8.51 \pm 0.03 \times 10^{-5}$			
					75.00	2.45×10^{-2}			
<i>(E)</i> -14	Me	Et	H	50% EtOH	75.00	$3.22 \pm 0.02 \times 10^{-3}$	21.9	-7.2	
					49.75	$2.50 \pm 0.04 \times 10^{-4}$			
					75.00	5.20×10^{-4}			
<i>(Z)</i> -15	Me	H	<i>i</i> -Pr	50% EtOH	88.90	$1.90 \pm 0.02 \times 10^{-3}$	22.6	-8.8	
					75.06	$5.23 \pm 0.03 \times 10^{-4}$			
					75.00	5.20×10^{-4}			
<i>(E)</i> -15	Me	<i>i</i> -Pr	H	50% EtOH	49.75	$4.75 \pm 0.02 \times 10^{-4}$	23.4	-1.6	
					31.86	$5.31 \pm 0.01 \times 10^{-5}$			
					75.0	7.18×10^{-3}			
<i>(Z)</i> -16	Et	H	Et	60% EtOH	75.20	$1.37 \pm 0.03 \times 10^{-3}$	22.6	-6.9	
					49.75	$9.65 \pm 0.02 \times 10^{-5}$			
					75.0	1.35×10^{-3}			
<i>(E)</i> -16	Et	Et	H	60% EtOH	74.96	$4.27 \pm 0.06 \times 10^{-3}$	22.1	-6.2	
					50.01	$3.36 \pm 0.02 \times 10^{-4}$			
					75.0	4.29×10^{-3}			
17	CD ₃	Me	Me	60% EtOH	74.96	$1.02 \pm 0.01 \times 10^{-3}$	23.9	-3.9	
					49.95	$6.54 \pm 0.04 \times 10^{-5}$			
					75.0	1.02×10^{-3}			
<i>(Z)</i> -18	Me	D	Me	60% EtOH	74.96	$9.12 \pm 0.04 \times 10^{-5}$	74.96	1.12 ± 0.10 × 10 ⁻⁴	
					74.96	$1.12 \pm 0.10 \times 10^{-4}$			
<i>(E)</i> -18	Me	Me	D	60% EtOH	74.96	$6.61 \pm 0.04 \times 10^{-5}$	74.96	$6.61 \pm 0.04 \times 10^{-5}$	

^a Determined conductimetrically unless other indicated. Error limits are average deviations of duplicate determinations. All runs were buffered with 1 equiv of 2,6-lutidine. ^b Reference 8a. ^c Determined by glc. ^d Trifluoroethanol.

prepare **11** from isopropylacetylene in this manner led to decomposition. Triflates **9–13**, **15**, and **17** were prepared from the appropriate ketone and triflic anhydride in the presence of sodium carbonate or 2,6-lutidine buffer.¹² The assignment of *Z* and *E* stereochemistry¹³ was made on the basis of nmr chemical shifts and the relative position of the infrared absorption of the carbon-carbon double bond.^{1b} Rate constants and activation parameters for triflate solvolyses are listed in Table I and relative rates in Table II. In order to interpret these data, it is necessary to make corrections for varying ground-state stabilities. Series I and II (Table II) are similar in having the α -alkyl group cis to a hydrogen; their ground-state strains should be comparable. Series III and IV both have the α -alkyl group cis to methyl and their ground-state strains should also be comparable. The relative stabilities of *Z* (series II) and *E* (series III) isomers can be determined directly by equilibration, at least in principle, and the resulting data applied also to the interpretation of ground-state steric effects in series I and IV. Unfortunately, except

for (*Z*)-**8** and (*E*)-**8** which give a *Z/E* ratio of 1.33 at 75°, triflates decompose rather than equilibrate in the presence of strong acid. Enol acetates, which equilibrate readily,¹⁴ were chosen as models for the steric effects in triflates.¹⁵ Acid equilibration at 75° gave *Z/E* isomer ratios of 2.9 for **20**, 6.15 for **21**, and 20.5 for **22**. The relative ratios should correct, at least somewhat, for the use of acetates instead of triflates; based on 1.0 for **20**, these ratios are 2.1 for **21** and 7.1 for **22**.

During the solvolysis of series III and IV compounds, the α -alkyl substituent bends away from the cis β -methyl group, and ground-state strain is relieved. Hence, the solvolysis rates of these compounds should be enhanced sterically, relative to corresponding members of series I and II. These steric enhancements can be corrected by dividing the relative rates of each compound of series III and IV by the appropriate *Z/E* ratio. (Of course, this treatment is an extreme since it assumes that all of the ground-state strain is relieved in the transition state.) The resulting values are shown in parentheses in Table II. Since differences in the β sub-

(12) T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970).

(13) J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(14) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(15) In some cases, acetates, trifluoroacetates, and trimethylsilyl ethers give similar *Z/E* ratios under similar conditions; see (a) ref 8a; (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

Table II. Relative Rates of Solvolyses of Substituted Vinyl Triflates in 50% EtOH at 75°

Series	R ₁	R ₂ = C=C < OTf			<i>k</i> rel				
		R ₂	R ₁	R ₃	Me	Et	<i>n</i> -Bu	<i>i</i> -Pr	<i>t</i> -Bu
I	Varied	H	H	H	1		2.49	2.51	2.65
II	Varied	H	Me	Me	1	1.3		2.46	
III ^a	Varied	Me	H	H	1	5.59		44.5	
IV	Varied	Me	Me	Me	1	7.58		83.3	
V	Me	H	Varied	Varied	(1) ^b	(3.54) ^b		(11.7) ^b	
VI	Me	Varied	H	H	1	2.97		7.71	

^a 75.3°. ^b Corrected for ground-state steric effects (see text).

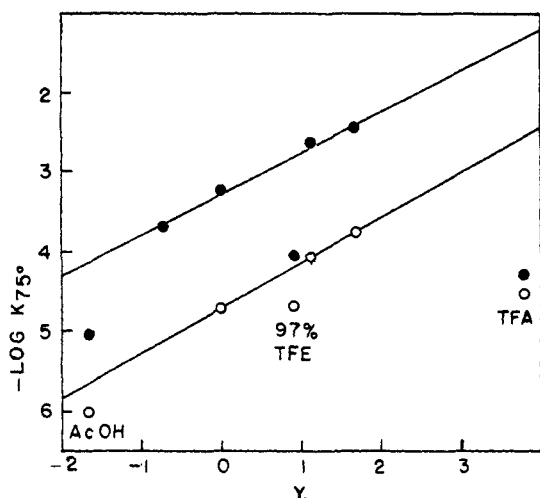
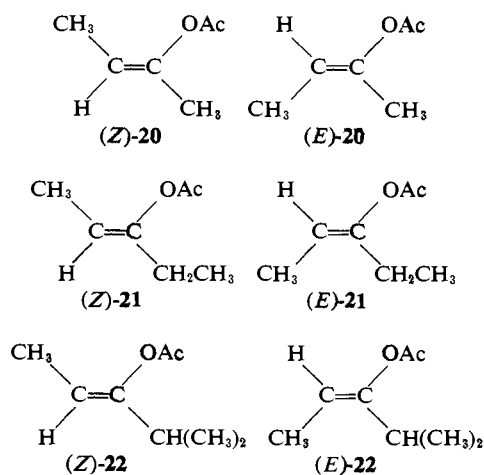


Figure 1. Plot of $-\log k (75^\circ)$ for solvolysis of (*Z*)-2-buten-2-yl triflate [(*Z*)-8] (●) and (*E*)-2-buten-2-yl triflate [(*E*)-8] (○) vs. *Y*. The lines represent the least-squares fit for the aqueous ethanol solvents.



stituents employed have little effect on enol acetate equilibria,¹⁴ no corrections were applied to series V and VI.

Although the number of data points (Table II) is limited, the relative rates of series VI as well as the corrected relative rates of both series III and IV correlate very satisfactorily with σ^* constants¹⁶ (correlation coefficient >0.999); values for ρ^* are -4.2 , -5.6 , and -4.7 , respectively. The ρ^* values for uncorrected rates of series III and IV were -8.6 (correlation coefficient

(16) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

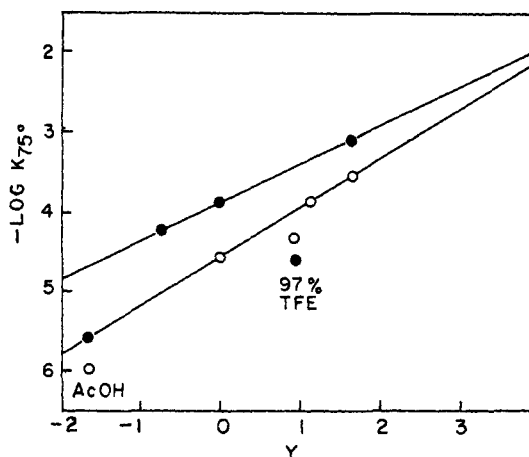


Figure 2. Plot of $-\log k (75^\circ)$ for solvolysis of 3-methyl-2-buten-2-yl triflate (**11**) (○) and 1-hexen-2-yl triflate (**5**) (●) vs. *Y*. The lines represent the least-squares fit for the aqueous ethanol solvents.

coefficient 0.996) and -10.8 (correlation coefficient 0.999), respectively. Series I (correlation coefficient = 0.89), II (correlation coefficient 0.96), and V (correlation coefficient 0.83) correlated poorly with σ^* giving lower ρ^* values of -1.4 , -2.0 , and -1.7 , respectively.

The rates of solvolysis of (*Z*)-8, (*E*)-8, and **11** in aqueous ethanol are well correlated with Winstein-Grunwald *Y* values¹⁷ (Figures 1 and 2). However, weakly nucleophilic solvents, acetic acid and trifluoroethanol, give solvolysis rates lower than expected on this basis. These deviations do not appear to be a leaving group effect. Triphenylvinyl triflate, which solvolyzes by an S_N1 pathway, reacts only 1.6 times faster in 98% ethanol than in acetic acid,¹⁸ a less nucleophilic solvent with the same *Y* value. The *Y* value for 97% trifluoroethanol, which is dependent on the leaving group and substrate type,¹⁹ was determined to be 0.93 for triflates using the average of data from **23** and **24**. These compounds must solvolyze by a limiting mechanism because solvent is blocked from backside at-

(17) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); (d) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957); (e) see also T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

(18) W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, **92**, 5457 (1970).

(19) (a) D. E. Sunko, I. Szele, and M. Tomić, *Tetrahedron Lett.*, 1827 (1972); (b) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5977 (1970); (c) Z. Rappoport, private communication.

Table III. Mechanistic Criteria for Solvolysis of Vinyl Triflates at 75°

Compd	m^a (aq ethanol)	m^b	ρ^b	$(k_{\text{ROH}}/k_{\text{AcOH}})_Y^c$	$(k_{\text{ROH}}/k_{\text{TFE}})_{Y=0.93}^d$
4	0.52	0.70	0.41		30
5	0.48	0.71	0.32	7.5	11.9
(Z)- 8	0.52	0.71	0.40	15.9	15.9
(E)- 8	0.57	0.76	0.15	2.3	3.0
11	0.62	0.85	0.12	2.5	2.2
23	0.77 ^g				1.12 ^g
24	0.66 ^g				0.92 ^g
MeOTs	0.23 ^h	0.30 ^k	1.00 ^k	97 ^h	
2-PrOTs	0.46 ⁱ	0.61 ^k	0.35 ^k	4.2 ⁱ	12.3 ^j
2-Adamantyl OTs	0.78 ⁱ	1.0 ^l	0.0 ^l	0.19 ^j	0.21 ^{i,m}

^a Calculated from $\log(k/k_0) = mY$ using only aqueous ethanol solvents. ^b Calculated for all solvents except 60% EtOH and CF₃CO₂H using $\log(k/k_0) = mY + lN$ (ref 17b,d) with 2-adamantyl tosylate and methyl tosylate as standards (ref 17e). The usual Y values for triflates in AcOH (-1.64) and 97% TFE (0.93) were multiplied by 0.78 to place them on the tosylate scale. ^c Aqueous ethanol, $Y = -1.64$. ^d Rates were calculated using the mY relationship and the rate constants for other aqueous ethanol mixtures (Table I). ^e Aqueous ethanol, $Y = 0.93$. ^f 97% w/w trifluoroethanol ($Y = 0.93$). ^g Calculated from data in ref 20. ^h Reference 27a, p 64. ⁱ Calculated from data in ref 31. ^j Calculated from data in ref 28. ^k 50°. ^l 25°. ^m R. E. Hall, A.B. Thesis, Princeton University, 1970.

Table IV. Products of Solvolysis of Vinyl Triflates

Compd	Solvent	Temp, °C	Normalized product compositions, ^a %				
			Allene	Acetylene	Ketone	Others	
5	90% EtOH	100	17.6	73.0	9.0		
	80% EtOH	100	17.5	70.7	11.8		
	50% EtOH	100	18.6	62.8	18.6		
	30% EtOH	100	17.9	57.2	25.0		
	97% TFE	100	17.0	61.8	21.2		
	AcOH	100	21.7	60.8	17.5		
7	50% EtOH	75		75	2	23 ^e	
	80% EtOH	105		98.9	1.1		
	50% EtOH	105		97.3	2.7		
	97% TFE	105	1.6	95.4	3.0		
	AcOH	101		95.3		4.7 ^e	
	TFA	75		91.3		8.7 ^d	
(E)- 8	80% EtOH	75	15.7	56.4	27.7		
		105	12.8	56	31		
	60% EtOH	75	19	53	28		
	50% EtOH	75	7.3	51.4	41.8		
	97% TFE	105	3.1	92.0	4.9		
	AcOH	100	4.7	77.6		17.7 ^e	
	TFA	75		95.0		5.0 ^d	
	11	60% EtOH	75	44		56	
		CD ₃ CO ₂ D	100	37 ^e			63 ^{e,f}
		80% MeOD	100	38 ^f		62 ^f	
50% pyridine		100	36 ^e		64 ^f		
(Z)- 16	60% EtOH	75	6.8	89.8	3.4		
(E)- 16	60% EtOH	75	34.6	48.8	16.6		

^a Determined by glc unless otherwise indicated. ^b M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, **92**, 3802 (1970). ^c Rearrangement products. ^d Enol trifluoroacetates. ^e Enol acetates. ^f Determined by nmr.



tack.^{20,21} The m values for aqueous ethanol, m and l values determined for the more complete Winstein-Grunwald equation $\log(k/k_0) = mY + lN$,^{17b,d,e}

(20) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *ibid.*, **93**, 1513 (1971).

(21) The Y value used for trifluoroacetic acid (3.8) was calculated for a vinyl tosylate [Z. Rappoport and J. Kaspi, *Tetrahedron Lett.*, 4039 (1971)] as other substrates give different values [Z. Rappoport, private communication]. Also, triflate/tosylate ratios, usually constant $\sim 10^5$,²² may be abnormally low in trifluoroacetic acid.²³

(22) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969).

(23) G. A. Dafforn and A. Streitwieser, Jr., *Tetrahedron Lett.*, 3159 (1970).

values of $(k_{\text{ROH}}/k_{\text{AcOH}})_Y$ and $(k_{\text{ROH}}/k_{\text{TFE}})_{Y=0.93}$ for vinyl triflates along with methyl, 2-propyl, and 2-adamantyl tosylates, are listed in Table III. Product analyses as determined by glc or nmr are given in Table IV. No substrate isomerization was detected during these reactions.

Concerted elimination in (Z)-**8**, if present, should be sensitive to added base; hence, the effect of 0.115 M NaOH on the reaction of vinyl triflates including cyclohexenyl triflate (**25**) and phenyl triflate (**26**) in 50% di-



oxane was examined. The rate and product data for these reactions are presented in Table V.

The tendency of **4** and **11** to react with strong nucleo-

Table V. Effect of 0.115 M NaOH on the Solvolyses of Vinyl Triflates in 50% Dioxane at 49.9°

Compd	10 ⁴ k, sec ⁻¹	10 ⁴ k _{OH} , sec ^{-1a,c}	Normalized product composition, ^e %	
			Al-lene	Acet-yene Ketone
(Z)-8	2.30 ± 0.01 ^b		98	~2
(E)-8	0.077 ± 0.01 ^b	9.35 ± 0.87	48	52
25	0.000003 ^d	4.78 ± 0.73	8	~2
26	NR ^e	2.46 ± 0.11		~98
		≥100		100
				100 ^e

^a Pseudo-first-order rate constant. ^b Determined by conductance. ^c Determined by glc. ^d In 60% EtOH, calculated from data in ref 20. ^e Phenol.

Table VI. Rate Constants and Products from Vinyl Triflate Solvolyses in Trifluoroethanol at 90.05°^a

Triflate	Salt (concn)	10 ⁴ k, sec ^{-1 b}	k rel	Normalized product composition, % ^b			
				Allene	Acetylene	Ether	Bromide
4	LiClO ₄	1.45 ± 0.01	1	9.8 ± 1.2	72.1 ± 0.4	18.1 ± 0.8 ^c	
	(0.137 M)	3.30 ± 0.04	2.27	11.0 ± 0.6	77.1 ± 1.4	11.8 ± 1.9 ^c	
	LiBr	3.22 ± 0.14	2.22	8.7 ± 0.7	68.2 ± 2.6	14.6 ± 2.4 ^c	8.5 ± 0.8
11	LiClO ₄	15.65 ± 0.05	1	38.7 ± 0.7		61.3 ± 0.7	
	(0.137 M)	39.8 ± 0.6	2.55	36.2 ± 0.5		63.8 ± 0.5	
	LiBr	33.1 ± 1.0	2.12	31.1 ± 0.5		64.6 ± 0.5	4.3 ± 0.0

^a 0.02 M substrate, 0.04 M in 2,6-lutidine. ^b Determined by glc. Error limits are average deviations of duplicate determinations. ^c Acetone was the isolated product.

philes²⁴ was probed in trifluoroethanol in the presence of bromide ions;²⁵ perchlorate ions were used as a non- or weakly nucleophilic reference (Table VI). In order to check the effectiveness of 0.137 M bromide ion as nucleophile, 2-propyl tosylate was solvolyzed under the conditions used for the vinyl triflates and found to give more than 50% 2-propyl bromide.

Discussion

Substituent Effects. The magnitude of substituent effects measured by the Taft ρ^* ¹⁶ is proportional to the degree of charge development in solvolysis reactions.²⁷ For simple aliphatic secondary systems ρ^* varies from nearly 0 in ethanol²⁸ to -7 in trifluoroacetic acid;²⁹ in 50% ethanol the value is -1.6 at 75°. ³⁰ The ρ^* for saturated tertiary chlorides in 80% ethanol is -3.3.^{27a} The uncorrected ρ^* values, -8.6 and -10.1, for the vinyl

(24) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1969; (b) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(25) The often used nucleophile, azide ion,²⁶ could not be employed because the product vinyl azides are unstable above room temperature; see A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

(26) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971).

(27) Reviews: (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964.

(28) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).

(29) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965).

(30) In 50% EtOH at 75°, the relative rates of 2-propyl,³¹ 2-butyl,³² and 3-pentyl³² tosylates are 1.0, 1.50, and 2.05, respectively.

(31) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(32) T. W. Bentley, unpublished data.

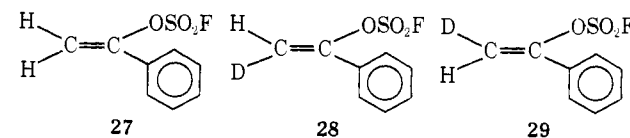
series III and IV are large. Even with correction for steric effects, the solvolyses of series III, IV, and VI have an average ρ^* of -4.8, indicating a greater response to electron-donating substituents than the tertiary chlorides. *Ab initio* calculations indicate that vinyl cations should have larger substituent effects than aliphatic carbenium ions in the gas phase.³³ Substrates with an alkyl group trans to the triflate and substrates with hydrogen trans to the leaving group are clearly divided into two sets by their magnitude of response to substituent effects. The latter set, series I, II, and V, gives ρ^* 's only slightly larger than the saturated secondary systems under these conditions.³⁰ This is certainly consistent with the possible presence of nucleophilic assistance.

Deuterium isotope effects in vinylic solvolyses are

larger than in saturated systems. For reaction of **11** and **17** in 60% ethanol at 75°, $k_{\text{CH}_3}/k_{\text{CD}_3}$ is 1.44. For *tert*-butyl chloride at 25° in 60% ethanol, $k_{\text{CH}_3}/k_{\text{CD}_3}$ is 1.33; a lower value would be expected at 75°. ^{4b} However, $k_{\text{CH}_3}/k_{\text{CD}_3}$ for isopropyl tosylate, which is 1.2 or less in aqueous ethanol,^{4b} does reach 1.46 in trifluoroacetic acid.³⁴

Of particular interest is the magnitude of the effect of substituent changes (R_2 in **3**) trans to the leaving group. These effects are almost as large as those at the α carbon despite the extra bond between the substituent group and the reaction center. This greater demand on the position trans to the leaving group is also reflected in the magnitude of isotope effects. For (Z)-**8** and (Z)-**18** in 60% ethanol at 75°, $k_{\text{H}}/k_{\text{D}}$ is 2.02 while for (E)-**8** and (E)-**18** the isotope effect is 1.23.

Although the magnitude of the former value suggests a primary isotope effect in a concerted elimination,³⁵ an analogous spread in cis and trans isotope effects was observed by Maness and Turrentine for **27**, **28**, and **29** which do not eliminate.³⁶ The rate of



(33) L. Radom, R. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(34) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

(35) Reference 4b, p 213.

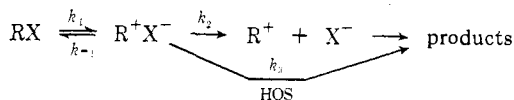
(36) D. D. Maness and L. D. Turrentine, *Tetrahedron Lett.*, 755 (1973).

acetolysis of **27** at 53° was 1.57 times faster than **28** and 1.10 times faster than **29**. These results suggest that the transition state for ionization of vinyl substrates is bent with the electron deficient orbital interacting with the trans substituent.³⁷

The substituent effects in these vinylic systems, although quite large, are less than those observed for 1-cyclohexenyl triflate where each methyl substituent in the 2, 3, or 6 position increases the rate by approximately a factor of 10.²⁰ This may be due to ground-state steric strain, or it may be due to ion pair behavior.

For a simple model process involving competitive solvent capture or dissociation of an ion pair (Scheme I), the observed rate constant, k_T , is given by eq 1. If

Scheme I



$$k_T = k_1(k_2 + k_3)/(k_{-1} + k_2 + k_3) \quad (1)$$

there is no solvent attack on the ion pair (*i.e.*, k_3 is negligible), eq 2 pertains. If substituents influence k_2

$$k_T = k_1k_2/(k_{-1} + k_2) \quad (2)$$

more than k_1 or k_{-1} , then the larger the relative magnitude of k_3 (solvent participation), the smaller the substituent effect on k_T . However, even when there is no solvent attack on the ion pair (eq 2), the degree to which changes in k_2 are reflected in k_T may depend on the magnitude of k_{-1} . This occurs when $k_{-1} \gg k_2$; then $k_T \approx k_1k_2/k_{-1}$ and any changes in k_2 affect k_T directly. Thus, if k_{-1} for cyclohexenyl triflate is greater than k_{-1} for the acyclic analog, the smaller acyclic substituent effects observed do not necessarily indicate solvent participation. This might result if bending destabilizes an ion pair less than a dissociated ion, so that internal return predominates in the cyclic substrates. When $k_{-1} \ll k_2$, $k_T \approx k_1$ and changes in k_2 or k_{-1} have no effect on k_T . Unfortunately, there is no way at present to determine k_1 , k_{-1} , and k_2 (eq 2) in these systems.

Solvent Effects. A variety of criteria, listed in Table III, provide information concerning the mechanism of solvolysis reactions.^{17,19a,29,38} These criteria divide the vinyl triflates we have studied into the same two sets as did the effects of substituents. At 75° the aqueous ethanol m values of cyclic vinyl triflates **23** and **24** (0.77 and 0.66)²⁰ are near that of 2-adamantyl tosylate (0.78), a secondary substrate which solvolyzes by a limiting mechanism.^{28,38,39} The aqueous ethanol m values of

4, **5**, and (*Z*)-**8** (0.52, 0.48, and 0.52) are lower and approach that of 2-propyl tosylate (0.46), a substrate which reacts with considerable solvent assistance.²⁶ The relative rates in solvents of differing nucleophilicity but similar ionizing power, $(k_{\text{ROH}}/k_{\text{AcOH}})_Y$ and $(k_{\text{ROH}}/k_{\text{TfE}})_{Y=0.93}$, and the l values also suggest that the reactions of acyclic vinyl triflates **4**, **5**, and (*Z*)-**8** depend on solvent nucleophilicity. Indeed, the l values suggest that these vinyl triflates are as responsive to nucleophilicity as 2-propyl tosylate! The companion paper^{1b} shows that the acetolyses of these vinyl triflates do not involve an addition-elimination mechanism. The change in solvent from 50% aqueous ethanol to 97% trifluoroethanol results in an increase of the **5**:**4** rate ratio at 75° from 2.4 to 6. The increase in magnitude of substituent effects in saturated secondary tosylates in solvents of low nucleophilicity and high ionizing power due to the more ionic nature of the reactions is analogous.²⁹

Product analyses (Table IV) provide little clear-cut mechanistic information. **5**, (*Z*)-**8**, and (*E*)-**8** tend to form more ketone product as the fraction of water is increased in aqueous alcohol mixtures, but a similar trend toward more substitution product is observed for *tert*-butyl chloride.⁴⁰ Triflate (*Z*)-**8** with H and OTf trans gives >90% elimination; the product composition from (*E*)-**8** approaches that of (*Z*)-**8** as solvent ionizing power increases or solvent nucleophilicity decreases.^{40,41} Oddly, substrates most sensitive to solvent nucleophilicity, **5** and (*Z*)-**8**, show the smallest product change in going from 50% ethanol to 97% trifluoroethanol.

Reactions with Added Base or Nucleophile. If the reaction of (*Z*)-**8**, which gives >90% 2-butyne, proceeds by an E2 elimination with solvent as base, dramatic acceleration by the strong base OH⁻ would be expected. In fact, the results in Table V show that a change of mechanism to S-O cleavage occurs. The rates of the three vinyl triflates (*Z*)-**8**, (*E*)-**8**, and **25**, which vary by 10⁶ in the absence of base, are within a factor of 4 in the presence of OH⁻. The solvolytically inert²² phenyl triflate, **26**, reacts much more rapidly with OH⁻ since phenoxide (pK_a = 9.9) is a better leaving group than the enolate ions (pK_a ~ 15).⁴² Nucleophilic attack on sulfur has been observed for phenyl,⁴³ vinyl,⁴⁴ and saturated⁴⁵ tosylates, and for trifluoroethyl triflate.⁴⁶ The rate of elimination from (*Z*)-**8** in the presence of 0.115 M sodium hydroxide is only a factor of 2

(40) (a) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963); (b) F. Spieth, W. C. Ruebsamen, and A. R. Olson, *ibid.*, **76**, 6253 (1954); (c) K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty, and L. I. Woolf, *J. Chem. Soc.*, 2043 (1948); (d) G. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1211 (1968).

(41) For a similar trend in a saturated system, see V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4848 (1969).

(42) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 11, 41; (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, p 494.

(43) J. Ferns and A. Lapworth, *J. Chem. Soc. Trans.*, 101, 273 (1912); C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951); J. F. Bunnett and J. Y. Bassett, Jr., *J. Amer. Chem. Soc.*, **81**, 2104 (1959); *J. Org. Chem.*, **27**, 1887, 2345 (1962); T. J. Broxton, Y. C. Mac, A. J. Parker, and M. Ruane, *Aust. J. Chem.*, **19**, 521 (1966).

(44) N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem. Commun.*, 1044 (1969).

(45) P. Gassman, J. M. Hornback, and J. M. Pascone, *Tetrahedron Lett.*, 1425 (1971); F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, **73**, 5004 (1951).

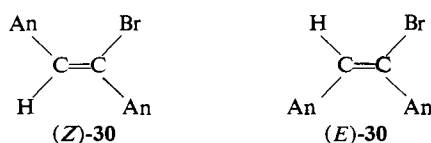
(46) A. Mendel, *J. Org. Chem.*, **31**, 3445 (1966).

(37) A similar trans effect is operative in saturated systems: (a) R. C. Bingham and P. v. R. Schleyer, *Tetrahedron Lett.*, 23 (1971); (b) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971); (c) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(38) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970).

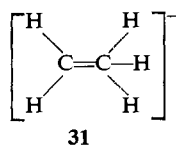
(39) Although triarylvinylic substrates give low m values, steric hindrance to solvation by bulky β substituents has been invoked to explain this anomaly as the mechanism of these substrates is clearly SN1. If the bulky substituents are removed the m values approach those for saturated tertiary systems; see (a) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973); (b) *J. Amer. Chem. Soc.*, **91**, 5246 (1969); (c) Z. Rappoport and M. Atidia, *Tetrahedron Lett.*, 4085 (1970); *J. Chem. Soc., Perkin Trans. 2*, 3216 (1972); Z. Rappoport and J. Kaspi, *J. Amer. Chem. Soc.*, submitted for publication.

faster than that in neutral solution. This compares with an increase of 780 observed for (*Z*)-**30** with 0.5 *N* sodium hydroxide in 80% ethanol.^{39c} The reaction of (*E*)-**30** in 80% ethanol was not accelerated in the pres-



ence of base. Similarly, base had little effect on the rate of reaction of α -bromo-*p*-aminostyrene in 50% dioxane.^{47a} The acceleration observed for the reaction of (*Z*)-**8** in the presence of hydroxide ion seems too small to be consistent with a concerted elimination, but may indicate elimination from an ion pair.⁴⁷

The trifluoroethanolyses of **4** and **11** are as fast or faster in the presence of lithium perchlorate than lithium bromide, indicating little sensitivity to a strong nucleophile. In contrast to 2-propyl tosylate, which gave ~50% 2-propyl bromide under these conditions, there is little bromide incorporated in the products from **4** or **11**. While vinyl solvolysis rates are somewhat sensitive to solvent nucleophilicity, they do not appear to be affected by strong nucleophiles. This fact and the incomplete inversion observed in the products indicate that the solvolyses of acyclic vinyl triflates involve competition between solvent capture and dissociation of an ion pair; also, vinylic substrates are not as susceptible to backside $\text{S}_{\text{N}}2$ reactions as saturated secondary substrates.^{1b,9} The shorter bonds in the vinylic systems, $\text{sp}^2\text{-sp}^2$ and $\text{sp}^2\text{-sp}^3$ vs. the $\text{sp}^3\text{-sp}^3$ bonds in saturated secondary substrates, mean that substituents in the vinylic substrates will have larger effects in stabilizing cationic intermediates and in sterically hindering in-plane $\text{S}_{\text{N}}2$ transition states.^{33,48} Extended Hückel calculations indicate the transition state for hydride attack on ethylene (**31**) will have both entering and leaving hydride ions



bent away from the β -CH bonds.⁹ Vinylic $\text{S}_{\text{N}}2$ reactions are not observed under forcing conditions due to the relative ease of addition-elimination and elimination-addition pathways. However, rate-determining participation does occur with some intramolecular nucleophiles.⁴⁹ Thus, it is possible that the parent vinyl triflate or primary vinyl triflates will react by an in-plane $\text{S}_{\text{N}}2$ -like mechanism.

Conclusion

Our evidence indicates that solvolysis reactions of alkyl-substituted vinyl triflates proceed through ion-pair pathways. There is no evidence of direct $\text{S}_{\text{N}}2$ or $\text{E}2$ reactions of vinyl substrates with a strong nucleophile, Br^- , or a strong base, OH^- . However, indirect mechanistic criteria (*l* and *m* values and dependence on

solvent nucleophilicity at constant ionizing power) suggest that solvent nucleophilicity is important in these reactions, particularly in substrates with β hydrogen trans to the leaving group. Since the accompanying paper^{1b} shows that only partial inversion is observed in these reactions, the nucleophilic sensitivity of vinylic substrates must be due to specific solvation of a trans β hydrogen or other site not directly at the rear of the reacting carbon.

Experimental Section

All boiling points are uncorrected. Nmr spectra were taken on a Varian A60-A spectrometer using tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin-Elmer Model 237 B grating spectrometer. Preparative gas chromatography was performed on a Varian Aerograph Model 90-P gas chromatograph using the following columns: A, 0.375 in. \times 15 ft 20% Carbowax 20M on 45-60 Chromosorb W; B, 0.375 in. \times 6 ft 20% Carbowax 20M on 45-60 Chromosorb W; C, 0.25 in. \times 3 ft 20% Carbowax 20M on 45-60 Chromosorb W; D, 0.375 in. \times 15 ft 20% FFAP on 45-60 Chromosorb W; E, 0.375 in. \times 15 ft 15% SF-96 on 60-80 Chromosorb W. Analytical gas chromatography was performed on a Varian Aerograph Model 1520 or a Perkin-Elmer Model 810 instrument equipped with flame ionization detector using the following columns: F, 0.125 in. \times 10 ft 10% Carbowax 20M on 80-100 Chromosorb W; G, 0.125 in. \times 17 ft 10% Carbowax 20M on Chromosorb W; H, 0.125 in. \times 10 ft 10% QF-1 on 60-80 Chromosorb G. Microanalyses were performed by Hoffmann-La Roche, Inc., Nutley, N. J. Analytical samples for all vinyl triflates were collected from column C at 50° with gas chromatograph injector and detector temperatures no higher than 100°.

Materials. Trifluoromethanesulfonic (triflic) acid⁵⁰ was purchased from 3M Co. and converted to the anhydride with P_2O_5 .⁵¹ Acetylenes were purchased from Farchan Research Laboratories. 3-Methyl-1,3-butadiene, 2-bromopropene, 3-pentanone, 4-methyl-2-pentanone, and 2,4-dimethyl-3-pentanone were obtained from Aldrich Chemical Co. 2-Methyl-3-pentanone, 2-hexanone, and 3-hexanone were purchased from Chemical Samples Co. Ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.⁵² Dioxane was purified by the method of Fieser.⁵³ The purified solvent was stored over sodium and distilled shortly before use. For conductance experiments, commercial 2,2,2-trifluoroethanol (Matheson Coleman and Bell) was distilled from aqueous potassium carbonate, dried with P_2O_5 , and fractionally distilled through a 24-in. vacuum-jacketed column packed with glass helices, bp 73.5-74.5°.⁴¹ Commercial trifluoroethanol (Aldrich Gold Seal) was used without further purification for glc experiments because it contained the least amount of volatile impurities ($\sim 10^{-3}$ *M*). These impurities, present in all commercial trifluoroethanol, could not be removed by distillation.

Synthesis of Vinyl Triflates. The procedure used to prepare vinyl triflates that might be sensitive to excess acid is illustrated in the preparation of propen-2-yl triflate.

Propen-2-yl Triflate (4). Propyne (4.0 g, 0.10 mol) was condensed in a vial and added to 20 ml of pentane in a 50-ml round-bottomed flask equipped with magnetic stirrer and cooled to -30°. Trifluoromethanesulfonic acid (8.0 g, 10.2 mmol) was added dropwise over 15 min. The cooling bath was then removed and as the reaction warmed to 0°, saturated NaHCO_3 (15 ml) was added. After this mixture had stirred for 5 min, the aqueous layer was removed with a transfer pipet. The organic layer was washed twice with saturated NaHCO_3 in this manner and dried over K_2CO_3 . The pentane was distilled at atmospheric pressure and the residue distilled to give 6.8 g (67%) of **4**: bp 25-27° (15 mm); nmr (CCl_4) δ 2.12 (s, 3 H, CH_3), 4.97 (m, 1 H, vinylic H trans to OTf), 5.07 (d, $J = 3.5$ Hz, 1 H, vinylic H cis to OTf); ir (thin film) 1678 ($\text{C}=\text{C}$), 1413, 1251, 1220, 1170, 1135, 1006, 943, and 890 cm^{-1} .

Anal. Calcd for $\text{C}_4\text{H}_5\text{F}_3\text{O}_3\text{S}$: C, 25.27; H, 2.65. Found: C, 25.13; H, 2.60.

(47) (a) C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, **59**, 2060 (1971). (b) The rate of hydrolysis of 2-propyl benzenesulfonate in 56% acetone is increased only 8% by 0.1 *N* NaOH at 50°: E. Tommila and J. Juttla, *Acta Chem. Scand.*, **6**, 844 (1952).

(48) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 265 (1968).

(49) P. E. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, **95**, 2683, 2686 (1973), and references cited therein.

(50) For information, see Minnesota Mining and Manufacturing Co., Technical Information, "FC-24-Trifluoromethanesulfonic acid."

(51) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(52) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(53) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941.

placed in a 100-ml flask with a reflux condenser and heated to reflux. At 10-hr intervals the mixture was cooled and the aqueous layer drawn off and replaced with fresh D₂O and P₂O₅. The procedure was repeated six times, then the aqueous layer was saturated with NaCl. The organic layer was separated, dried (K₂CO₃), and distilled to give 15 g of ketone, bp 91–95°, 98% deuterated by nmr.

3-Methyl-2-buten-2-yl Triflate-1,1,1-d₃ (17). Reaction of the deuterated ketone (1.5 g, 0.017 mol), sodium carbonate (1.5 g, 0.014 mol), and (CF₃SO₂)₂O (7.0 g, 0.025 mol) in 10 ml of pentane gave 1.1 g (29%) of **17**, bp 44–48° (15 mm) [nmr (CCl₄) δ 1.80 (broad s); ir (thin film) 1700 (C=C), 1450, 1405, 1257, 1202, 1135, 1080, and 994 cm⁻¹], 93.5% deuterated by nmr.

Attempted Equilibration of Vinyl Triflates. A 20-ml portion of each isomer of 2-buten-2-yl triflate (**8**) was sealed with 0.5 ml of triflic acid in five ampoules of 3-mm Pyrex tubing. After equilibrating at 75°, ampoules were removed at 3-hr intervals. The contents, 10 μl, were dissolved in 1 ml of pentane, shaken with 20 mg of NaOAc to remove strong acid and analyzed on glc column G at 75°. After 9 hr, the mixtures from (*Z*)-**8** and (*E*)-**8** showed equivalent ratios of 1.33 ± 0.02:1. Exposure of **6** as well as the inseparable mixtures of 2-penten-3-yl triflate (**9**) and 4-methyl-2-penten-3-yl triflate (**10**) to these conditions gave numerous decomposition peaks on the glc.

Preparation and Equilibration of Enol Acetates. Enol acetates were prepared by literature methods from 2-butanone,^{15b} 3-pentanone,¹⁴ and 2-methyl-3-pentanone.¹⁴ The isomers were separated on glc column A at 90°. A solution of enol acetate predominating in each isomer (10 μl), acetic anhydride (10 μl), and triflic acid (0.5 μl) in 1 ml of carbon tetrachloride was sealed in 0.2-ml portions in ampoules of 5-mm Pyrex tubing. After they equilibrated at 75°, ampoules were removed at 5-min intervals. The contents were shaken with ~20 mg of NaOAc to remove acid and analyzed on the glc column G. All isomers were fully equilibrated after 10 min; a slower decomposition process then occurred over a period of hours. The *Z*:*E* ratios measured as peak areas were 2.90 ± 0.02 for 2-buten-2-yl acetates (**20**), 6.16 ± 0.13 for 2-penten-3-yl acetates (**21**), and 20.5 ± 0.7 for 4-methyl-2-penten-3-yl acetates (**22**).

Product Studies. Products of **5** and the isomers of **8** and **16** in aqueous solvents were determined by glc on columns G and H using authentic samples for calibration. The solutions were ~0.1 *M* in substrate and 2,6-lutidine buffer. Product determination at different times indicated that products were stable to reaction conditions. Products from **5** and the isomers of **16** were isolated (see below). Products from (*Z*)-**8** and (*E*)-**8** had retention times identical with authentic samples on columns G and H.

Products of **11** were determined by nmr in 80% CH₃OD–D₂O, 50% pyridine–D₂O, and CD₃CO₂D. Triflate **11** (17 μl), pyridine (15 μl), and 0.3 ml of the solvent were sealed in an nmr tube and heated at 100° until starting material disappeared. In methanol or aqueous pyridine the nmr signals of the dimethyl doublet of 3-methyl-2-butene and the dimethyl triplet of 3-methyl-1,2-butadiene were integrated. In CD₃CO₂D the allenic proton absorptions were compared to the total upfield methyl absorptions of the allene and 3-methyl-2-buten-2-yl acetate.⁵⁴

The products of reaction of **4** and **11** in anhydrous trifluoroethanol were estimated from uncalibrated peak areas. All products from **11** had retention times identical with authentic samples. The preparation of authentic 1,2-dimethylpropenyl trifluoroethyl ether is described below. 2-Bromo-3-methyl-2-butene was prepared by the method of Braude and Evans.⁵⁵

Isolation of Products from 1-Hexen-2-yl Triflate (5) in Aqueous Ethanol. Triflate **5** (1.0 g) and pyridine (0.5 g) were sealed in an ampoule with 10 ml of 50% aqueous ethanol. This solution was heated at 100° for 10 hr, cooled, and poured into a 50-ml volumetric flask containing 40 ml of saturated sodium chloride solution. This mixture was shaken and the organic layer removed with a transfer pipet and dried (K₂CO₃). The products separated from this mixture on glc column A at 75°, 1,2-hexadine (25%), 1-hexyne (65%), and 2-hexanone (10%), had nmr spectra identical with authentic samples.

Isolation of Products from 3-Hexen-3-yl Triflates (16) in Aqueous Ethanol. An unseparated mixture of (*Z*)-**16** and (*E*)-**16** (1.0 g) and pyridine (0.5 g) were sealed in an ampoule with 10 ml of 50% aqueous ethanol. This solution was heated in a 100° bath for 6 hr, cooled, and poured into 40 ml of water in a 50-ml volumetric flask.

(54) An authentic sample of the acetate was prepared as described by the following authors: W. B. Smith and T. K. Chen, *J. Org. Chem.*, **30**, 3095 (1965).

(55) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3324 (1955).

The organic layer was removed with a transfer pipet and dried (CaCl₂). This mixture was separated on glc column A at 75° into 2,3-hexadiene [nmr (CCl₄) δ 0.95 (t, *J* = 6.8 Hz, 3 H, CH₃CH₂), 1.60 (d of d, *J* = 6.5, 4 Hz, 3 H, vinyl CH₃), 1.88 (m, 2 H, CH₂), 4.95 (m, 2 H, vinyl H's) and 3-hexyne and 3-hexanone (both gave nmr spectra identical with those from authentic samples).

Preparation of 1,2-Dimethylpropenyl Trifluoroethyl Ether. In a 100-ml round-bottomed flask fitted with a gas inlet attached to a 50-ml flask, an outlet attached to mercury bubbler, and a magnetic stirrer were placed HgO (0.5 g), boron trifluoride etherate⁵⁶ (2 ml), and trifluoroethanol (14 g, 0.14 mol). Isopropylacetylene (4.0 g, 0.06 mol) was placed in the 50-ml flask and warmed slightly. Air initially passed out through the bubbler as the acetylene vapor filled the system, then a vigorous reaction ensued and the pressure decreased (mercury rose ~20 cm up the bubbler inlet tube). All the acetylene was absorbed over a 10-min period. The reaction was stirred for an additional 30 min, then poured into a mixture of 50 ml of ice-water and 25 ml of pentane. The organic layer was washed with 50 ml of saturated NaHCO₃ and dried (K₂CO₃). Distillation of this mixture from freshly powdered NaHSO₄⁵⁷ (0.5 g) gave 4.3 g of a liquid mixture, bp 90–110° (760 mm). This mixture was separated on glc column D at 50° into 1-isopropylvinyl trifluoroethyl ether [35%; nmr (CCl₄) δ 1.08 (d, *J* = 6.5 Hz, 6 H, (CH₃)₂C), 2.38 (septet, *J* = 6.5 Hz, 1 H, CH), 3.96 (m, 4 H, CH₂=C and CH₂CF₃); ir (thin film) 1664 (C=C), 1458, 1423, 1275, 1227, 1165, and 1126 cm⁻¹], 3-methyl-2-butanone (35%), and 1,2-dimethylpropenyl trifluoroethyl ether [30%; nmr (CCl₄) δ 1.60 (m, 6 H, β-CH₃'s), 1.79 (m, 3 H, α-CH₃), 3.91 (q, *J* = 9 Hz, 2 H, CH₂CF₃); ir (thin film) 1694 (C=C), 1455, 1430, 1388, 1374, 1235, and 1150 cm⁻¹].

Anal. Calcd for C₇H₁₁F₃O: C, 49.99; H, 6.59. Found for 1-isopropylvinyl trifluoroethyl ether: C, 50.53; H, 6.69. Found for 1,2-dimethylpropenyl trifluoroethyl ether: C, 50.13; H, 6.73.

Isolation of Products from Propen-2-yl Triflate (4) in Trifluoroethanol. Propen-2-yl triflate (**4**) (1.0 g) was sealed in an ampoule with 0.5 g of 2,6-lutidine, 0.5 g of lithium bromide, and 6 ml of anhydrous trifluoroethanol. The ampoule was heated at 90° for 12 hr, cooled, and opened. The solution was injected in 1-ml portions on glc column A at 60°. The gaseous products were collected in a gas phase ir cell, but only propyne was observed in the spectrum. The third peak had an nmr spectrum identical with 2-bromopropene. The fourth peak was identified as acetone from its nmr and ir spectra.

Kinetic Methods. Rates in aqueous solvents were determined conductimetrically with a Wayne-Kerr Model B331 Impedance Bridge capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants of 0.2–0.4, and volumes of approximately 25 ml. In a typical experiment, enough substrate to make a 10⁻³ *M* solution was placed in the conductivity cell and 20 ml of solvent was added. The cell was then sealed and equilibrated with stirring for 5 min in the constant-temperature bath. The usual number of measurements was 20. All solvolyses displayed good first-order kinetics to 90% reaction.

Solvolysis rates of **4** and **11** in anhydrous trifluoroethanol and (*Z*)-**10** and (*E*)-**10** in 50% ethanol were determined by glc on column F. Solutions 0.01–0.02 *M* in substrate were prepared in 1 ml of solvent buffered with 0.04 *M* 2,6-lutidine, and sealed in 0.1-ml portions in ampoules made from 5-mm Pyrex tubing. The ampoules were equilibrated with shaking for 30 sec in the constant-temperature bath. At appropriate times ampoules were removed, cooled in an ice bath, and opened. Substrate peak heights, which were proportional to concentration and reproducible within ±2%, were measured for a constant injection size, usually 2 μl. Good first-order kinetics were observed for 2 half-lives.

Reaction rates in 50% dioxane containing 0.115 *M* NaOH were determined by glc on column F. Substrate and an internal standard (acetone for (*Z*)-**8** and (*E*)-**8** and *tert*-butylbenzene for **25** and **26**) 0.02 *M* in 1 ml of dioxane were mixed with 1 ml of a stock solution of 0.2 *M* aqueous NaOH. The procedure was identical with that given above except that the ampoules were opened immediately after quenching and the contents shaken with 30 mg of Rexyn 300 ion exchange resin to remove all salts. Glc analysis involved determining the relative peak heights of substrate and internal standard. These reactions gave reasonable first order kinetics to 2 half-lives.

(56) G. F. Hennion, D. B. Killian, T. H. Vaughn, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **56**, 1130 (1934).

(57) Hoffmann-La Roche Inc., British Patent 897,685 (1962); *Chem. Abstr.*, **57**, 12323 (1962).

All kinetic data were fitted to the first-order rate equation using a modified version of the LSKIN⁵⁸ computer program.

Acknowledgment. We are grateful to the National Science Foundation, the donors of the Petroleum Re-

(58) D. F. DeTar in "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, pp 126-173.

search Fund, administered by the American Chemical Society, the National Institutes of Health (Grants AI-0766 and GM-19134) and Hoffmann-La Roche, Inc., Nutley, N. J., for their support of this work. We also wish to thank Mr. W. J. Sliwinski for a sample of phenyl triflate, and Professor Z. Rappoport for constructive comments.

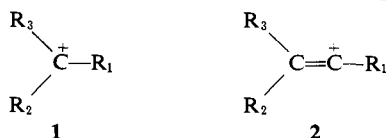
Stereochemistry of Vinyl Cations and Vinylic Substitutions¹

R. H. Summerville² and P. v. R. Schleyer*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. Received May 21, 1973

Abstract: Vinyl cation intermediates are formed in the protonation of allenes and acetylenes in trifluoroacetic acid. The 2-buten-2-yl cation produced by protonation of 1,2-butadiene or 2-butyne captures solvent to give *Z* in preference to *E* product in ratios of 3.3:1 at 75.3°, 4.2:1 at 49.8°, and 5.1:1 at 35°. An attractive effect between the β-methyl group, rendered electron deficient by hyperconjugation, and the attacking nucleophile is postulated to explain the preference for *Z* product. Trifluoroacetolyses of (*Z*)- and (*E*)-2-buten-2-yl triflate give >90% 2-butyne plus trifluoroacetates with *Z/E* ratios of 4.4 and 8.0, respectively. The difference in solvolysis product ratios can be explained by an ion pair mechanism giving rise to only 7.4% net inversion. Acetolysis products of vinyl triflates are found with a larger fraction of inversion. In general, it appears that vinyl triflates solvolyze through an ion pair mechanism in spite of the high energy of the cations involved, rather than by direct solvent displacement (S_N2).

Vinyl cation intermediates, although less stable than the corresponding aliphatic carbenium ions,³ are clearly accessible in both solvolysis and addition reactions.⁴ While reactions involving vinyl cations have direct analogies in aliphatic systems, interesting contrasts in behavior are to be expected. Planar aliphatic carbenium ions (1),⁵ with R₁ ≠ R₂ ≠ R₃ (point group



C_s), present equivalent faces to nucleophilic attack. Thus, the stereochemistry of substitution reactions of chiral substrates, R₁R₂R₃CX, is directly interpretable mechanistically because enantiomeric reactants, transition states, and products are of equal energy.⁶

Although vinyl cations, 2, with R₂ = R₃, are expected from theoretical calculations to prefer linearity (point group C_{2v}),^{3, 4a, 4g, 7} situations when the β substituents are different presents another picture. Vinyl cations 2,

with R₂ ≠ R₃, cannot be exactly linear (∠C=C—R₁ ≠ 180°; point group C_s ~ C₁) and possess diastereotopic⁵ sides that must capture nucleophiles or solvent at different rates even though the deviations of the cations from linearity are small. Furthermore, substitution reactions are complicated by the nonequivalence of transition states and intermediates generated from each isomer of an *E-Z*⁸ pair of vinylic reactants, R₃R₂C=CR₁—X.

In practice, substitution reactions at saturated carbon rarely involve free cations. Simple secondary substrates react by pathways involving considerable solvent assistance⁹ and complete or nearly complete inversion.^{9, 10} Even tertiary and phenyl-substituted secondary substrates which solvolyze with little, if any, kinetic solvent assistance frequently give product with net inversion.^{11, 12} These observations are accommodated by the assumption of ion-pair intermediates.⁹⁻¹² On the other hand, several solvolyses apparently involving free¹³ vinyl cations stabilized by cyclopropyl or aryl

(1) For a preliminary account of part of this work, see R. H. Summerville and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 3629 (1972).

(2) National Science Foundation Predoctoral Fellow, 1969-1972.

(3) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(4) For reviews, see (a) P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 205 (1972); (b) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971); (c) Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, **92**, 4985 (1970); (d) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1972); (e) H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 899.

(5) D. Bethel and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 4.

(6) For a discussion of stereoisomeric relationships, see K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(7) (a) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971); (b) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972), and earlier references cited in these papers.

(8) For the definition of the *E-Z* nomenclature, see J. E. Blackwood, C. F. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(9) See recent reviews emphasizing work at Princeton: D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972); P. v. R. Schleyer in "Reaction Transition States," J. E. Dubois, Ed., Gordon and Breach, New York, N. Y., 1973, p 197.

(10) (a) A. Streitwieser, Jr., and T. D. Walsh, *J. Amer. Chem. Soc.*, **87**, 3686 (1965); (b) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965); (c) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965).

(11) Reference 5, p 174.

(12) J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," American Chemical Society Monograph, 167, C. J. Collins and N. S. Bowman, Ed., Van Nostrand Reinhold, New York, N. Y., 1970, p 90.

(13) Obviously a cation formed by ionization or protonation in solution is in some way associated with an anion. We use "free" here only to imply that the interaction with the counterion is not stereospecific (perhaps due to rapid equilibration) so that the behavior of the ion is independent of the method of generation.