All kinetic data were fitted to the first-order rate equation using a modified version of the LSKIN[58] computer program.

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

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(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.

Stereochemistry of Vinyl Cations and Vinylic Substitutions[1]

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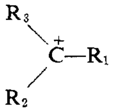
Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received May 21, 1973*

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 (SN2).

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 $R_1 \neq R_2 \neq R_3$ (point group C_s), present equivalent faces to nucleophilic attack. Thus, the stereochemistry of substitution reactions of chiral substrates, $R_1R_2R_3CX$, is directly interpretable mechanistically because enantomeric reactants, transition states, and products are of equal energy.[6]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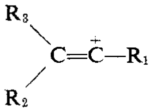
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Although vinyl cations, **2**, with $R_2 = R_3$, are expected from theoretical calculations to prefer linearity (point group C_{2v}),[3,4a,4g,7] situations when the β substituents are different presents another picture. Vinyl cations **2**, with $R_2 \neq R_3$, cannot be exactly linear ($\angle C{=}C{-}R_1 \neq 180°$; point group $C_s \sim C_1$) and possess diastereotopic[5] 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, $R_3R_2C{=}CR_1{-}X$.

In practice, substitution reactions at saturated carbon rarely involve free cations. Simple secondary substrates react by pathways involving considerable solvent assistance[9] 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 free[13] vinyl cations stabilized by cyclopropyl or aryl

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(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.

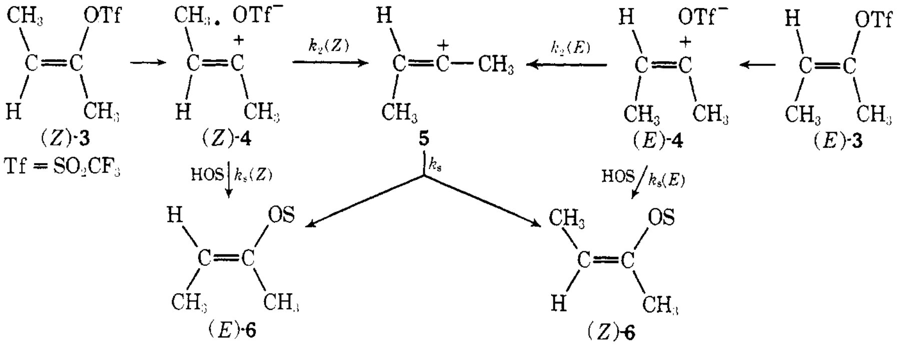
(10) (a) A. Streitwieser, Jr., and T. D. Walsh, *J. Amer. Chem. Soc.*, **87**, 3686 (1965); (b) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965); (c) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965).

(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.

Scheme I

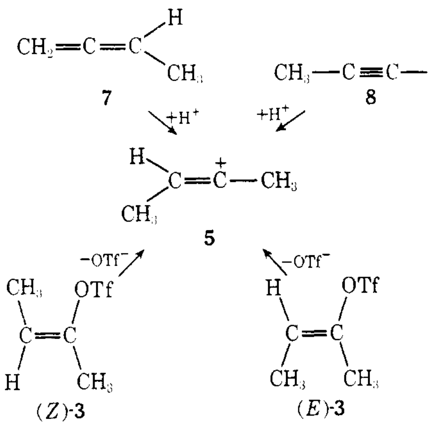


substituents (**2**, R_1 = cyclopropyl or aryl; $R_2 \neq R_3$) have been reported to proceed with little or no inversion to give identical or nearly identical *E–Z* product mixtures.[14,15] Nearly equal amounts of *E* and *Z* product isomers are formed in some of these solvolyses[14a–c,15a,b] showing that differences expected on the basis of symmetry can, in fact, be small. The cationic intermediate in the addition of trifluoroacetic acid to 3-hexyne also gives essentially equal amounts of *E* and *Z* products.[16] Some addition reactions to acetylenes giving unequal amounts of *E* and *Z* products have been shown to involve synchronous approach of the proton and the nucleophile.[17] However, it has been observed recently that the 3,3-dimethyl-1-phenylbutenyl cation formed *via* both protonation and alkylation captures chloride ion trans to the *tert*-butyl group completely within experimental error.[18] In this case, the difference in R_2 and R_3 groups in **2** is large. The solvolysis of simple alkyl-substituted vinyl substrates also seems to involve less backside solvent assistance than the reactions of aliphatic secondary systems, in spite of the lower stability of vinyl over comparably substituted aliphatic cations.[1,4,14] Nevertheless, recent communications indicate that inversion is an important but not exclusive pathway in the substitution product from solvolysis of simple alkyl vinyl triflates.[1,19] The presence of an inversion component in these solvolyses can obscure information about the exact substitution preferences of a "free"[15] vinyl cation. This is illustrated by the simplified ion pair mechanism (ignoring elimination and internal return) for the 2-buten-2-yl system shown Scheme I. Since the product ratio of (*Z*)-**6** to (*E*)-**6** was not the same from both (*Z*)-**3** and (*E*)-**3**, the formation of free[13] cation **5** cannot be the only pathway followed. Because the extent of inversion in diastereomeric ion pairs, $k_s(Z)/k_2(Z)$ *vs.* $k_s(E)/k_2(E)$, is not necessarily equal, the ratio of products from free vinyl cation **5** cannot be determined precisely from product data even when inversion is only partial.

In order to study the stereochemistry of the reactions of simple vinyl cations, it is desirable to produce them in their free[13] state from as many different starting materials as possible. The high acidity, low nucleophilicity, and high ionizing power of trifluoroacetic acid make it a useful solvent for this purpose. Vinyl cations have been generated in trifluoroacetic acid by protonation of 3-hexyne[16] and by solvolysis of a vinyl tosylate[20] (competition by an addition–elimination mechanism can occur in less acidic, less ionizing solvents).[21] Terminal allenes are also indicated to be useful sources of vinyl cations.[4]

Cation **5** is thus potentially available from four starting materials in trifluoroacetic acid (Scheme II).

Scheme II



Cation **5** is the only vinyl cation which can be generated uniquely from both a terminal allene and a symmetrical acetylene by proton addition. We present here a detailed study of the stereochemistry of reactions of alkyl-substituted vinyl cations generated by protonation of allenes and acetylenes in trifluoroacetic acid and the stereochemistry of substitution reactions of alkylvinyl triflates in acetic acid and trifluoroacetic acids.

Synthesis of Vinyl Triflates. Vinyl triflates, (*Z*)-**3** and (*E*)-**3**, were prepared by addition of CF_3SO_3H to 2-butyne (**8**) followed by glc separation of isomers.[22] In the similar addition of CF_3SO_3H to 1-hexyne (**9**) it was necessary to use an excess of the acetylene and to neutralize the crude product carefully before distilla-

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(14) (a) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92** 228 (1970); (b) *ibid.*, **93**, 1941 (1971); (c) *ibid.*, **93**, 1953 (1971); (d) *J. Chem. Soc., Chem. Commun.*, 589 (1973).

(15) (a) Z. Rappoport and Y. Apeloig, *Proc. Isr. J. Chem.*, **7**, 34 (1969); (b) *J. Amer. Chem. Soc.*, **91**, 6734 (1969); (c) however, Z. Rappoport, A. Pross, and Y. Apeloig, *Tetrahedron Lett.*, 2015 (1973), have shown that the β-*tert*-butyl-α-anisylvinyl cation gives *E* product.

(16) (a) P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); (b) *ibid.*, **88**, 4990 (1966).

(17) For reviews, see R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968), and ref 4.

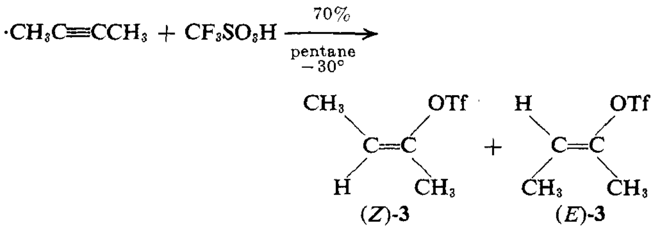
(18) R. Maroni, G. Melloni, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 857 (1972). A. Pross and Z. Rappoport (private communication) have observed the same results for HBr addition to *tert*-butylanisylacetylene.

(19) (a) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 3626 (1972); (b) T. C. Clarke and R. G. Bergman, *ibid.*, **94**, 3627 (1972).

(20) Z. Rappoport and J. Kaspi, *Tetrahedron Lett.*, 4039 (1971).

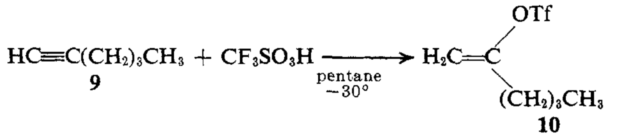
(21) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

(22) P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969).

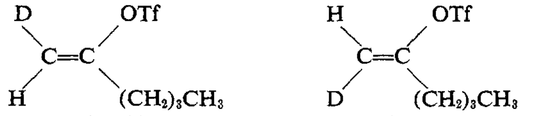


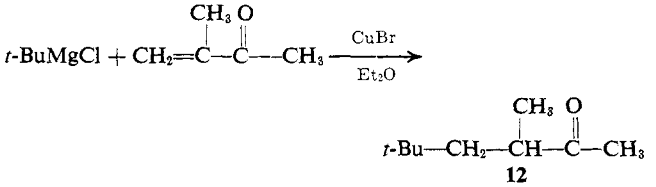
(Z)-3 (E)-3

tion to prevent acid-catalyzed double bond migration. Addition of CF_3SO_3D to **9** gave a product with 74 ± 3% (nmr) of the deuterium cis to the triflate group [(*Z*)-**11** = 74 ± 3%]. Similarly, addition of CF_3SO_3H to 1-hexyne-*1-d* gave predominantly (*E*)-**11** with 77 ± 3% of the deuterium trans to the triflate group [(*E*)-**11** = 77 ± 3%]. Thus, under these conditions cis addition predominates. *tert*-Butylmagnesium chloride added 1, 4 to 3-methyl-3-buten-2-one in the presence of cuprous bromide[23] to give ketone **12**; reaction of **12** with triflic anhydride in pentane in the presence of sodium carbonate[24] gave a mixture of (*Z*)-**13** and (*E*)-**13**. The isomers were isolated by glc. The assignment of stereochemistry, on the basis of nmr and ir analyses, is discussed in the appendix.

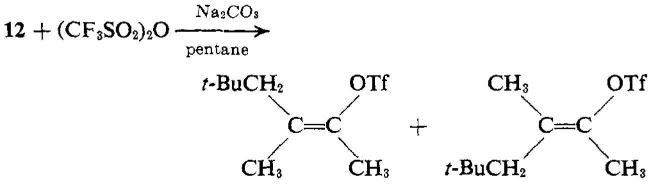


9 10


(Z)-11 (E)-11

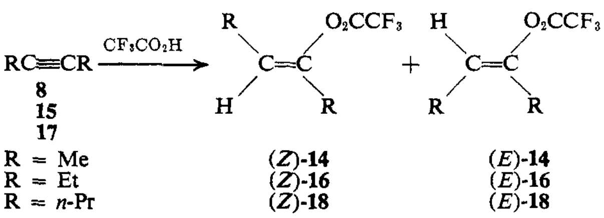


12

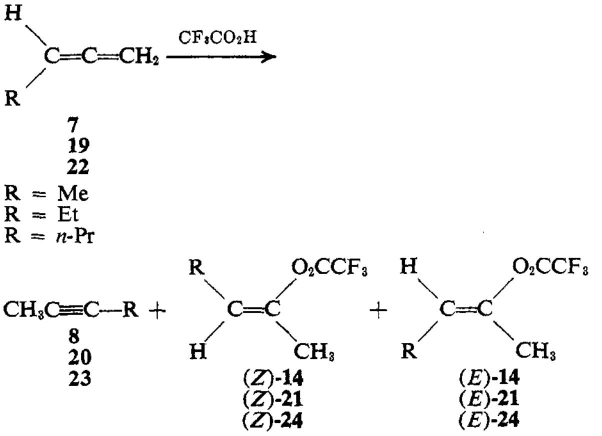


(Z)-13 (E)-13

Reactions in Trifluoroacetic Acid. Kinetics and Products. Trifluoroacetolysis rate constants and product analyses were determined by glc. The kinetic procedure was similar to that used by Peterson and Duddey to investigate the addition of trifluoroacetic acid to acetylenes.[16b] Our pseudo-first-order rate constant for the reaction of 3-hexyne with trifluoroacetic acid at 60° (5.30×10^{-4} sec^{-1}) is in good agreement with the literature value (5.65×10^{-4} sec^{-1}). The K_2CO_3, previously used in a basic forecolumn[25] to remove acid solvent, hydrolyzed trifluoroacetates and partially decomposed triflates. It was found, however, that replacement of the K_2CO_3 with crystal violet, a weakly basic, nonvolatile tertiary amine, gave a forecolumn that removed trifluoroacetic acid without affecting reactants or products. Thus, it was possible to analyze product mixtures directly without work-up. The detector response was calibrated with authentic samples in trifluoroacetic acid at concentrations similar to those in the actual product mixtures.



(1)



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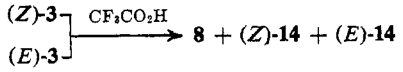
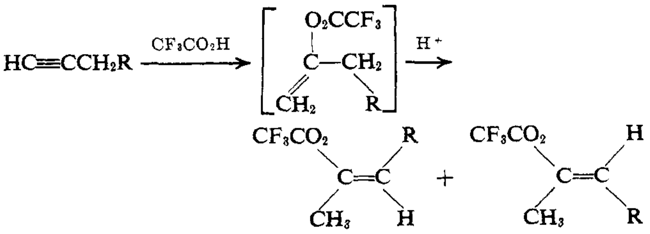


(3)

Reactions 1–3 were investigated in trifluoroacetic acid. Rate constants, activation parameters, and solvent isotope effects are summarized in Table I and product compositions in Table II. Reaction products from symmetrical acetylenes were isolated from preparative scale reactions. Allenes, **19** and **22**, gave unsymmetrical acetylenes, **20** and **23**, respectively, as primary products in TFA. Since **20** and **23** rapidly give vinyl trifluoroacetate mixtures as secondary products, these primary reaction products were identified by glc comparison with authentic samples prepared from terminal acetylenes as described by Peterson and Duddey.[16b]



The identification of trifluoroacetate stereoisomers is discussed in the Appendix.

Ester (*Z*)-**14** isolated from the addition of CF_3CO_2D to **7** and **8** contained only a small amount of dideuterated material (1.7% in each case) as determined by mass spectroscopy. This observation rules out preliminary interconversion of **7** and **8** as an important process in the formation of ester product in these addi-

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(23) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 165.

(24) General procedure: 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).

(25) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

Table I. Rate Constants, Activation Parameters, and Solvent Isotope Effects for Solvolyses and Additions in Trifluoroacetic Acid (0.125 *M* in NaO_2CCF_3)

Compd	Solvent	Temp, °C	k,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{CF_3CO_2H}/k_{CF_3CO_2D}$
7	CF_3CO_2H	75.4	$3.24 \pm 0.08 \times 10^{-3}$	13.3	−32	
		49.8	$6.54 \pm 0.08 \times 10^{-4}$			
8	CF_3CO_2H	75.4	$2.14 \pm 0.07 \times 10^{-4}$			
	CF_3CO_2D	75.4	$8.80 \pm 0.15 \times 10^{-5}$	14.2	−37	2.43 ± 0.13
		102.5	$4.16 \pm 0.20 \times 10^{-4}$			
15	CF_3CO_2H	75.4	$1.48 \pm 0.01 \times 10^{-3}$	16.0	−26	
		60.1	$5.3 \pm 0.15 \times 10^{-4}$			
		60.0[b]	5.65×10^{-4}			
		49.8	$2.16 \pm 0.01 \times 10^{-4}$			
	CF_3CO_2D	75.4	$6.1 \pm 0.6 \times 10^{-4}$			2.45 ± 0.25
(*Z*)-**3**	CF_3CO_2H	75.4	$1.29 \pm 0.04 \times 10^{-4}$			
	CF_3CO_2D	75.4	$1.40 \pm 0.03 \times 10^{-4}$	24.9	−5.1	0.92 ± 0.05
		103.25	$2.16 \pm 0.05 \times 10^{-3}$			
(*E*)-**3**	CF_3CO_2H	75.4	$1.06 \pm 0.01 \times 10^{-4}$			
	CF_3CO_2D	75.4	$9.62 \pm 0.32 \times 10^{-5}$	26.7	−0.5	1.09 ± 0.04
		102.5	$1.68 \pm 0.13 \times 10^{-3}$			

[a] Determined by glc. Error limits are average deviations of duplicate runs. [b] Reference 16b.

Table II. Products of Reaction of Substrates in Trifluoroacetic Acid (0.0125 *M* in NaO_2CCF_3)

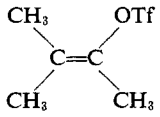
			Normalized product composition, %[a]					
Compd	Solvent[a]	Temp, °C	No. of determinations	Acetylene	Trifluoroacetate, *Z* isomer	Trifluoroacetate, *E* isomer	*Z*/*E*[b] from solvolysis	*Z*/*E*,[c] equilibrium
7	CF_3CO_2H	75.4	4	63.2 ± 1.8	28.4 ± 1.0	8.4 ± 0.8	3.34 ± 0.15	2.36 ± 0.03
		49.8	2	64.8 ± 1.2	28.4 ± 0.9	6.8 ± 0.4	4.21 ± 0.11	
		35.0	2	64.3 ± 0.7	29.8 ± 0.7	5.9 ± 0.1	5.08 ± 0.11	
	CF_3CO_2D	75.4	5	64.2 ± 3.4	27.2 ± 2.6	8.6 ± 0.8	3.18 ± 0.04	
19	CF_3CO_2H	75.4	2	60.7 ± 1.3	23.3 ± 1.1	16.0 ± 0.5	1.46 ± 0.07	2.34 ± 0.05
22		75.4	2	62.0 ± 3.0	24.6 ± 0.8	17.7 ± 0.6	1.38 ± 0.01	2.36 ± 0.01
8		75.4	3		76.9 ± 0.5	23.1 ± 0.5	3.33 ± 0.10	
		49.8	2		80.5 ± 0.6	19.5 ± 0.6	4.13 ± 0.17	
		35.0	2		83.6 ± 0.3	16.4 ± 0.3	5.11 ± 0.09	
	CF_3CO_2D	75.4	4		71.9 ± 0.4	28.1 ± 0.4	2.57 ± 0.05	
15	CF_3CO_2H	75.4	2		47.7 ± 0.03	52.3 ± 0.03	0.91 ± 0.01	>4
		60.1	2		49.8 ± 1.0	50.2 ± 1.0	0.99 ± 0.01	
		60.0[d]			50 ± 2	50 ± 2	1.0	
17		75.4	3		43.6 ± 0.08	56.4 ± 0.08	0.77 ± 0.03	
(*Z*)-**3**	CF_2CO_2D	75.4	3	89.3 ± 0.8	8.5 ± 0.5	2.2 ± 0.3	3.90 ± 0.25	
(*E*)-**3**		75.4	4	91.3 ± 0.6	7.1 ± 0.5	1.6 ± 0.1	4.55 ± 0.04	

[a] Glc areas corrected for experimentally determined response factors. Product error limits are average deviations for the number of runs shown. [b] *Z*/*E* ratios are calculated *for each run*. The error limits shown are average deviations for the number of runs shown. [c] Each isomer was equilibrated for 48 hr with 3–5% CF_3SO_3H. Error limits are the average deviation between two runs, one for each isomer. [d] Reference 16b.

tions. Because of the large amount of elimination observed from (*Z*)-**3** and (*E*)-**3**, the substitution product (*Z*)-**14** from the solvolysis of these substrates in CF_3CO_2D was checked for deuterium incorporation to evaluate the extent to which it was formed by solvent addition to the acetylene, **8**. Trifluoroacetate (*Z*)-**14** isolated from refluxing CF_3CO_2D (~75°) was 17.8% monodeuterated from (*Z*)-**3** and 38.0% monodeuterated from (*E*)-**3** after 12 and 18 min, respectively (these times corresponding to 10% reaction in each case). This showed that addition to **8** is important but direct substitution is the major process.

In order to determine the relationship of the thermodynamic stability of the trifluoroacetate products to the *Z*/*E* product ratios, separate isomers of four *E*-*Z* pairs of trifluoroacetates were equilibrated at 75° with 3–5% of CF_3SO_3H. The resulting mixtures were analyzed by glc to give the equilibrium *Z*/*E* ratios summarized in the last column of Table II.

Acetolysis of Vinyl Triflates. Kinetics and Products. Rate constants in acetic acid buffered with excess sodium acetate were determined by a standard titrimetric method.[26] Acetolysis rate constants and activation parameters for (*Z*)-**3**, (*E*)-**3**, (*Z*)-**13**, (*E*)-**13**, **10**, and **25** are summarized in Table III. Product compositions



25

were determined by glc for the reactions (eq 4–6 and 8). The ratio of (*Z*)-**29** to (*E*)-**29** (eq 7) was determined by nmr. Normalized product compositions are listed in Table IV.

Initially, product compositions were determined for reaction in acetic acid buffered with 0.11 *M* NaOAc at 100°. Under these conditions, vinyl acetates (*Z*)-**26**,

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(26) S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 812 (1948).

Table III. Rate Constants for the Acetolysis of Vinyl Triflates[a]

Compd	Temp, °C	k, sec^{-1} [b] × 10^5	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
(*Z*)-**3**	125.10	95.1 ± 5.0	28.3	−1.8
	102.5	10.38 ± 0.05		
	100.0[c]	7.99		
(*E*)-**3**	125.4	27.2 ± 0.1	30.3	+0.7
	101.13	2.130 ± 0.005		
	100.0[c]	1.88		
10	125.4	43.3 ± 0.2	27.7	−5.1
	103.1	5.17 ± 0.10		
	100.0[c]	3.77		
(*Z*)-**13**	103.1	20.0 ± 0.07	29.2	+1.6
	75.3	0.823 ± 0.015		
	100.0[c]	14.1		
(*E*)-**13**	103.1	18.6 ± 0.1	30.2	+4.2
	75.3	0.687 ± 0.031		
	100.0[c]	13.4		
25	125.4	2.799 ± 0.001	29.7	−0.9
	103.1	2.74 ± 0.01		
	100.0[c]	2.00		

[a] Substrate 0.0025 *M* in acetic acid, 0.0034 *M* in NaOAc, and 1% in Ac_2O. [b] Average deviations of duplicate runs. [c] Calculated from data at other temperatures.

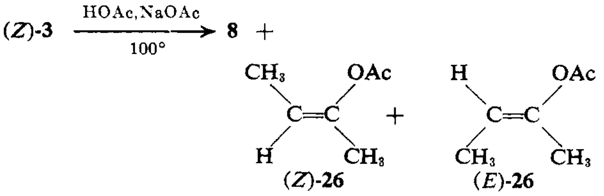
Table IV. Solvolysis Products in NaOAc-Buffered Acetic Acid at 100°

	Normalized product composition, %[a]						
Triflate	Acetylene	Allene	Ketone	Acetate, *Z* isomer	Acetate, *E* isomer	Acetate, % inversion	(*Z*)-OAc/(*E*)-OAc
(*Z*)-**3**[b]	95.3 ± 0.2			1.95 ± 0.2	2.7 ± 0.2	58.2 ± 0.2	0.72 ± 0.02
(*E*)-**3**[b]	77.5 ± 0.5	4.7 ± 0.2		16.8 ± 0.1	1.0 ± 0.1	94.4 ± 0.5	16.8 ± 2.0
10[b]	56.7 ± 0.2	22.9 ± 0.3	20.4 ± 0.1				
(*Z*)-**11** (74 ± 3%)[b,e]	49.0 ± 1.0	27.4 ± 0.4	24.0 ± 1.1				
(*E*)-**11** (77 ± 3%)[b,e]	48.8 ± 0.4	26.0 ± 0.2	25.1 ± 0.1				
10[d]	61.7 ± 0.1	18.5 ± 0.4	2.3 ± 0.1	18.0 ± 0.5			
(*Z*)-**11** (74 ± 3%)[d,e]	62.4 ± 0.1	20.7 ± 0.1	1.0 ± 0.0	16.0 ± 0.2 (68 ± 3% (*E*)-**29**)[c,e]		92 ± 8	~0.09
(*E*)-**11** (77 ± 3%)[d,e]	57.3 ± 0.2	22.5 ± 0.5	3.0 ± 0.1	17.6 ± 0.2 (68 ± 3% (*Z*)-**29**)[c,e]		88 ± 8	~7.4
(*Z*)-**13**[b,f]		39.2 ± 3.0		6.5 ± 0.5	54.4 ± 2.0	89.3 ± 0.4	0.12 ± 0.01
(*E*)-**13**[b,f]		52.3 ± 3.0		20.0 ± 2.0	27.0 ± 3.0	42.5 ± 0.9	0.74 ± 0.03

[a] Glc areas corrected for experimentally determined response factors except where noted. Product error limits are average deviations between duplicate runs except with (*Z*)-**3** which was determined in triplicate. [b] Triflate 0.06–0.1 *M*, NaOAc 0.11 *M*. [c] Inversion percentages were calculated *for each run*. The error limits quoted are average deviations between values for different runs. [d] Triflates 0.5 *M* in CH_3COOD, 1.3 *M* in NaOAc. [e] % of isomer shown in mixture of both *Z* and *E* isomers determined by nmr. Nmr error limits assumed; actual multiple integration gave reproducibilities of ±1%. [f] Uncorrected glc peak areas.

(*E*)-**26**, (*Z*)-**31**, and (*E*)-**31** were stable toward stereomutation and only slowly converted to the corresponding ketones. The elimination products did not react nor did the starting materials isomerize. However, **27** was rapidly converted to **28** ($t_{1/2}$ ~ 2 hr or approximately twice as fast as it was formed from the solvolysis of **10** under these conditions). Trial experiments indicated that the use of deuterated acetic acid slowed the conversion of **27** to **28** by a factor of 3 due to the isotope effect in the rate-limiting vinyl acetate protonation. Saturation of the solvent with NaOAc at 25° (~ 1.3 *M*) reduced the rate of destruction of **27** by a further factor of about 2. The deuterated triflates (*Z*)-**11** and (*E*)-**11** as a 1 *M* solution in CH_3CO_2D 1.3 *M* in NaOAc solvolyzed approximately 1.5 times as fast as **10** reacted in CH_3CO_2H containing 0.11 *M* NaOAc. The total effect of using CH_3CO_2D saturated with NaOAc (*vs.* using 0.11 *M* NaOAc in CH_3COOH) was to increase the formation/destruction rate ratio of **27** from 0.5 to 4.5. The acetolysis products of **10**, (*Z*)-**11**, and (*E*)-**11** were determined under both conditions (Table IV).

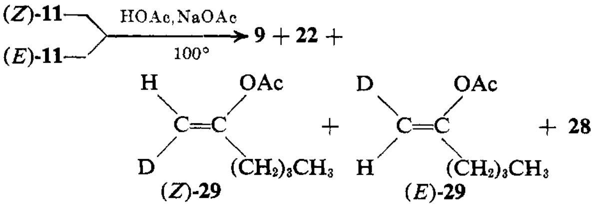
Acetolysis products (*Z*)- and (*E*)-**26**,[27] **27**,[28] and (*Z*)- and (*E*)-**31**[29] were identified by comparison with authentic samples; the nmr and ir spectra of **30** were straightforward. Equilibration at 75° gave an (*E*)-**31**/(*Z*)-**31** ratio of 1.4. Product compositions (Table IV) were determined by a combination of nmr and glc methods.



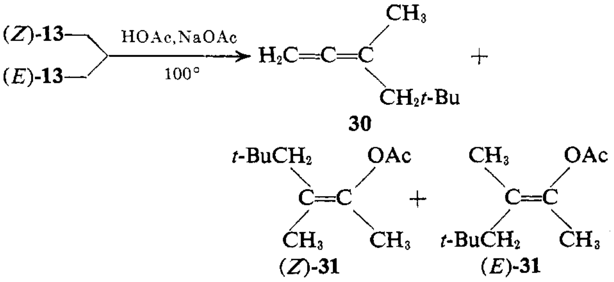
(4)

$$(E)\text{-}\mathbf{3} \xrightarrow[100^\circ]{\text{HOAc,NaOAc}} \mathbf{7} + \mathbf{8} + (Z)\text{-}\mathbf{26} + (E)\text{-}\mathbf{26} \qquad (5)$$

$$\mathbf{10} \xrightarrow[100^\circ]{\text{HOAc,NaOAc}} \mathbf{9} + \mathbf{22} + \underset{\mathbf{27}}{CH_2{=}C(OAc)(CH_2)_3CH_3} + \underset{\mathbf{28}}{CH_3CO(CH_2)_3CH_3} \qquad (6)$$



(7)



(8)

Discussion

Peterson and his coworkers[16,30] have concluded that,

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(27) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(28) G. F. Hennion and J. A. Niewland, *J. Amer. Chem. Soc.*, **56**, 1802 (1934).

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

(30) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970), and references cited therein.

in contrast to the synchronous addition of other protonic acids, trifluoroacetic acid adds to alkylacetylenes *via* stepwise processes involving vinyl cation intermediates. Substituent effects and the formation of nearly equal amounts of (*Z*)-**16** and (*E*)-**16** from **15** provided the chief bases for this conclusion. We have now corroborated the formation of free[13] vinyl cations in trifluoroacetic acid by more extensive investigation.

According to Scheme II, it would be expected that protonation of allene **7** and acetylene **8** should give cation **5**. Our data (Table II) show clearly that a common intermediate is involved in the trifluoroacetic acid addition to these substrates. The *Z*/*E* trifluoroacetate ratios from **7** and **8** are essentially identical at the three temperatures studied (Table II). Even though **7** gives 64% elimination to **8**, significant equilibration of **7** and **8** by CF_3CO_2H is ruled out by the small amount (<2%) of dideuterated ester formed from these substrates in CF_3CO_2D. The common intermediate, presumably cation **5**, collapses to ester product in which (*Z*)-**14** predominates over (*E*)-**14** strongly, in contrast to Peterson's results with 3-hexyne (**15**).[16]

The relationships of **7**, **8**, and **5** can be illustrated in a simple free energy diagram (Figure 1). Although **8** is more stable than **7** by 3.5 kcal/mol (ΔG),[31] its rate of protonation by trifluoroacetic acid is slower by only a factor of 5.4 at 75° (1.2 kcal/mol). (While the observed rate of disappearance of **8** is 15.1 times slower than of **7**, 64% of **5** returns to **8** by elimination and this decreases the difference by a factor of 0.36.)

Even if the symmetry-dictated deviation from linearity in cation **5** is of insignificant magnitude, the two sides of **5** are nonequivalent. Therefore, the *Z*/*E* product ratio is not necessarily an indication of the degree of bending in the cation but rather reflects the differences in transition-state free energies for the reactions leading to *Z* and *E* products. The preponderance of (*Z*)-**14** ester from **5**, although finding precedent in other additions to **7**[32a] and **8**,[32b] is surprising. On steric grounds, *E* product would be expected to predominate since solvent attack cis to the smaller hydrogen rather than cis to the larger methyl would appear to be more favorable.

The most obvious explanation (thermodynamic instead of kinetic control) was quickly ruled out. Although the (*Z*)-**14**/(*E*)-**14** equilibrium ratio was 2.36 ± 0.03 at 75.4°, the product ratio from **7** or **8** (3.34 ± 0.15) exceeded this value significantly. Furthermore, the stereochemical product ratios from allenes **19** and **22**, and especially from acetylene **15**, also differed substantially from their experimentally determined equilibrium ratios (Table II).

Steric effects *are* playing a role in determining the product ratios from vinyl cations. This is shown by the data involving the progression of alkyl groups, methyl, ethyl, and *n*-propyl, summarized in Table II. Additions to the terminal allenes **7**, **19**, and **22** give *Z*/*E* ratios of 3.34, 1.46, and 1.38, respectively, at 75.4°. The trifluoroacetic acid product ratios from the symmetrical alkynes **8**, **15**, and **17** are respectively 3.31, 0.91, and 0.77, at the same temperature.[33a] In both series, the greater change is found in going from methyl to ethyl, as the effective difference in bulk of ethyl and *n*-propyl groups is small. However, the steric effects on the *Z*/*E* trifluoroacetate equilibrium ratios are quite different (Table II). For **14**, **21**, and **24** the value is constant at 75.4°, 2.36 ± 0.05, but for **16** the *Z* isomer predominates by more than a factor of 4. These ratios correspond to the trends exhibited by trans/cis energies of corresponding dialkyl and trialkyl olefin models.[33b]

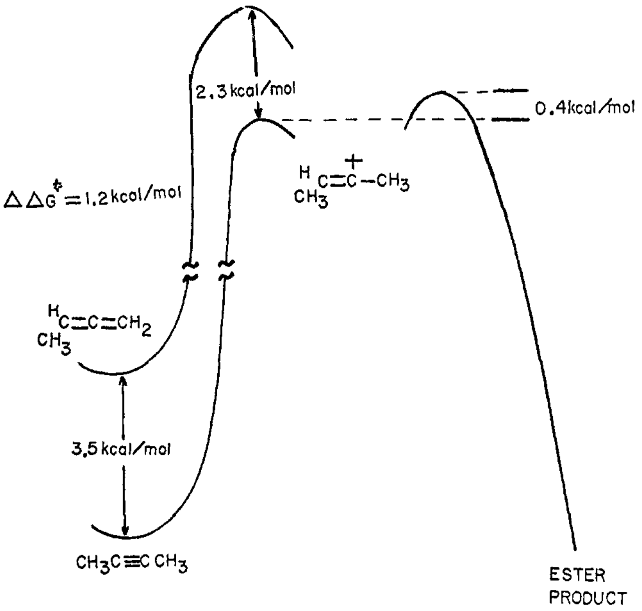

Figure 1. Free energy–reaction coordinate diagram for 1,2-butadiene (**7**), 2-butyne (**8**), and the 2-buten-2-yl cation (**5**) in trifluoroacetic acid at 75°.

An alternative explanation for the preference of trans solvent capture (hydrogen bridging) is ruled out by the absence of significant rearrangement in the acid addition to terminal allenes **19** and **22**. The most sophisticated molecular orbital calculations available also indicate that bridged structures for vinyl cations are unfavorable.[3,7]

Another explanation seems reasonable only on first examination. A nucleophile attacking cis to hydrogen may be diverted by preferred elimination to acetylene and thus the amount of *E* product would be lowered. This possibility is supported by the decrease in the (*Z*)-**14**/(*E*)-**14** ratio from **8** in going from CF_3COOH to CF_3COOD, but is contradicted by the change in elimination/*E* ester ratios for the following series: 7.5 for **7**, 3.8 for **19**, and 3.5 for **17**. Also, a very high *Z*/*E* ratio is observed for reaction of **5** in superacid with CO,[32b] a process in which acetylene formation is not competitive.

A conclusion opposite to that we find experimentally has emerged from EHT molecular orbital calculations on the 1-cyclopropylpropenyl cation, **32**.[14c]

Although **32** is indicated to be most stable in the

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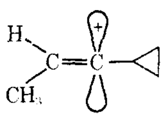
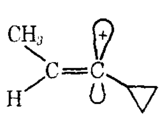
(31) P. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

(32) (a) T. J. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); (b) H. Hogeveen and C. F. Roobeek, *Tetrahedron Lett.*, 3343 (1971).

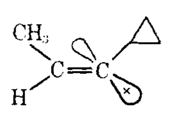
(33) (a) This progression also shows that the nearly equal amounts of (*Z*)-**16** and (*E*)-**16** obtained by trifluoroacetic acid addition to 3-hexyne (**15**)[16] is only a fortuitous result and is not general behavior. (b) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). (c) The same trans effect, CH_3 > H, has been found in tetrahedrally distorted alkyl cations: R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971); L. Radom and J. A. Pople, private communication.



32



33



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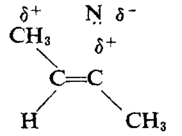
essentially linear form, bending to give **34**, despite the closer approach of the two alkyl groups, is found to be energetically less costly than to give **33**. The vacant orbitals in the bent cations interact more strongly with the β trans than with the β cis groups, and methyl groups stabilize the cation to a greater extent than hydrogen.[33c] Kelsey and Bergman[14] infer that the product should arise from predominant attack on the cis cation **34**, and, in fact, a slight excess is found. Extension of this argument to the less highly stabilized alkyl-substituted vinyl cations such as **5** would lead one to expect an even greater preference for the cis-bent over the trans-bent conformations, and an even larger preponderance of the product with alkyl groups cis. In fact, it is the *Z* isomers (alkyl groups trans) which predominate (Table II), unless the alkyl groups are large.

Evidently an electronic transition state effect is involved. It could be that the electron deficiency on the side *opposite* the 2-methyl group in **35** is less due to the operation of the β-trans methyl effect described by Kelsey and Bergman.[14c] The electron-rich nucleophile would then prefer to attack on the same side as the methyl. Perhaps also the positive polarization of the methyl group (**35**) provides an attractive interaction



35

with the approaching nucleophile. This would also favor attack cis to the 2-methyl group. Hoffmann, *et al.*, have suggested that such steric attractions might be important in the collapse of reactive intermediates.[34]

The behavior of cation **5** generated in the addition reactions of **7** and **8** provides a standard with which to compare the behavior of intermediate(s) in the solvolysis of (*Z*)-**3** and (*E*)-**3** (Scheme I). The mechanism of reaction of these triflates was first investigated to rule out the possibility of an addition–elimination process similar to that observed by Peterson and Indelicato[21] for vinyl tosylates in formic acid. Addition reactions are expected to have large negative entropies of activation, similar to those observed for addition of trifluoroacetic acid to alkenes,[35] and kinetic solvent isotope effects greater than 2 are expected for bimolecular reactions involving rate-determining proton transfer.[36] Table I provides illustrative data gathered in the present study on **7**, **8**, and **15**. Ionization reactions, in contrast, should have entropies of activation near zero and solvent isotope effects near unity, as illustrated by vinyl tosylate trifluoroacetolyses.[20] The activation parameters observed for (*Z*)-**3** and (*E*)-**3** (Table I) indicate an ionization rather than addition process.

The large amount of acetylene found in this reaction suggests that substitution products might be formed by solvent addition to this intermediate. However, the deuterium incorporation in (*Z*)-**14** from (*Z*)-**3**, 17.8%, and from (*E*)-**3**, 38.0%, indicates that most of the ester product is formed without prior elimination. If the deuterated ester is formed from solvent addition to **8** with a *Z*/*E* ratio of 2.57 as it was under the conditions in Table II, then we can calculate the products prior to any solvent addition. Using these product percentages and the rate constants from Table I, we calculate the percentage of deuterium that should be incorporated in (*Z*)-**14** if the deuterated ester is formed by solvent addition to **8** to be 17.3% from (*Z*)-**3** and 40.7% from (*E*)-**3**.[37] These numbers are in reasonable agreement with experiment. Aliphatic tosylates[38] also form more elimination product in solvolysis than olefin protonation reactions[38a] in trifluoroacetic acid. The extra elimination can be explained in both cases as proton transfer to the leaving group in an ion pair.[39] Supporting this conclusion is the fact that in trifluoroacetic acid there is more elimination product from (*E*)-**3**, with its proton cis to the leaving group, than from (*Z*)-**3**, in contrast to the case in acetic acid (Table IV) and aqueous ethanol.[22] The trifluoroacetolysis of these triflates obviously does not proceed through the same "free"[13] cation as the addition reactions. The intermediates are, we feel, best conceived as ion pairs.

The *Z*/*E* product ratios calculated for the two triflates (Table V) are not equal; the direction of the difference means that part of each reaction proceeds with inversion. The counterion also has the interesting effect of increasing the predominance of *Z* product in both substitution reactions beyond that observed in the protonations (Table II).

Table V. Calculated Product Percentages Prior to Their Reaction with Solvent for Reactions in CF_3CO_2D at 75.3°

Compd	**8**	(*Z*)-**14**	(*E*)-**14**	*Z*/*E*
(*Z*)-**3**	91.3	7.1	1.6	4.4
(*E*)-**3**	95.0	4.4	0.55	8.0

The *Z*/*E* product ratios in trifluoroacetic acid, 4.4, from (*Z*)-**3** and 8.0 from (*E*)-**3**, do not show as large a difference as the corresponding values, 0.72 and 16.8, in acetic acid (Table IV). This is consistent with expectations based on the lower nucleophilicity and higher ionizing power of the fluorinated solvent.

These data can be fitted, *e.g.*, to an ion pair mechanism (Scheme I) in which the starting isomers both give some

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(34) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, **95**, 629 (1973).

(35) P. E. Peterson and G. Allen, *ibid.*, **85**, 3608 (1963).

(36) The large fraction of elimination from **5** suggests that protonation of **8** and **15** is occurring reversibly and, hence, proton transfer is *not completely* rate determining. Thus, the solvent isotope effects in trifluoroacetic acid (~2.4 for both **8** and **15**) are larger than those for detritiation of 4-tritio-*m*-xylene and smaller than those for desilylation of chlorophenyltrimethylsilane (6.2) [C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc. B*, 613 (1966)]. They are also smaller than the solvent isotope effects (3–5) observed for protonation with participation (irreversible) of terminal acetylenes; see ref 30. See also Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).

(37) For a discussion of the kinetics of sequential reactions, see K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 321.

(38) (a) P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 5834 (1960); (b) P. E. Peterson and C. Casey, *J. Org. Chem.*, **29**, 2325 (1964); (c) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972).

(39) Although CF_3SO_3H is the strongest simple protonic acid, it is still not highly dissociated in acetic acid (K = 1.26 × 10^{-5}) and should be less so in trifluoroacetic acid. That is, $CF_3SO_3^-$ is a stronger base than RCO_2H, and CF_3SO_3H is a weaker acid than $RCO_2H_2^+$. See T. Gramstad, *Tidsskr. Kjemi, Bergv. Met.*, **19**, 62 (1959).

product through an intermediate "free" cation.[13] This intermediate should give products in the same ratio regardless of the substrate isomer (eq 9), where

$$(Z)^{z}/(E)^{z} = (Z)^{e}/(E)^{e} = (Z)/(E) \qquad (9)$$

Z and E are product isomers and the superscripts z and e refer to Z and E substrate isomers, respectively. In addition, some inversion product may be formed ($(Z)^{e}_{inv}$ from E triflate and $(E)^{e}_{inv}$ from Z triflate) in the fractions I_e and I_z from E and Z substrate, respectively (eq 10 and 11). The observed Z/E ratios are given by eq 12 and 13.

$$I_z = \frac{(E)^{z}_{inv}}{(Z)^{z}_{inv} + (E)^{z} + (E)^{z}_{inv}} \qquad (10)$$

$$I_e = \frac{(Z)^{e}_{inv}}{(Z)^{e} + (E)^{e} + (Z)^{e}_{inv}} \qquad (11)$$

$$\left(\frac{(Z)}{(E)}\right)^{z}_{obsd} = \frac{(Z)^{z}}{(E)^{z} + (E)^{z}_{inv}} \qquad (12)$$

$$\left(\frac{(Z)}{(E)}\right)^{e}_{obsd} = \frac{(Z)^{e} + (Z)^{e}_{inv}}{(E)^{e}} \qquad (13)$$

The Z/E ratio from the "free" cation and the fractions of inversion can be calculated if assumptions are made about the relative magnitudes of I_z and I_e. Two treatments serve to illustrate the possibilities.

First, it can be assumed that the fraction of inversion product is the same for each substrate isomer ($I_z = I_e$). If this is the case with (*Z*)-**3** and (*E*)-**3** in trifluoroacetic acid at 75°, then Z/E is 7.3 and there is 7.4% inversion from each starting isomer. Acetolysis of these substrates at 100° would give Z/E of 7.4 and 53% inversion from each isomeric substrate.

A second possibility is that inversion occurs only with one of the epimers; the other gives only a "free" cation.[13] The same equations apply but $(Z)^{e}_{inv}$ (or $(E)^{z}_{inv}$) = 0. At one extreme, if (*Z*)-**3** reacts with trifluoroacetic acid at 75° with no net inversion ($(E)^{z}_{inv} = 0$), then Z/E will be 4.4 and (*E*)-**3** solvolyzes with 40% inversion. At the other extreme ($(Z)^{e}_{inv} = 0$), Z/E will be 8.0 and (*Z*)-**3** solvolyzes with 8.4% inversion.

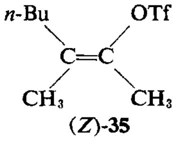
While we have no basis to decide among these alternatives, two conclusions can be drawn immediately from these calculations. (1) Seemingly large differences in Z/E product ratios are consistent with relatively small amounts of inversion especially if each triflate gives product with an equal fraction of inversion. (2) Unless (*E*)-**3** reacts with much more inversion than (*Z*)-**3**, the Z/E ratio for triflate solvolysis is significantly larger than the ratio of 3.3 observed for the addition reactions. The fraction of product which is formed by inversion from an ion pair depends upon the rate of solvent capture by the ion pair (k_s in Scheme I) relative to the rate of dissociation (k_2 in Scheme I). Because the cation in the protonation reactions captures solvent predominantly cis to the methyl group, it seems unreasonable to expect steric hindrance by the β-methyl group in (*E*)-**4** to lower the rate of solvent capture with inversion.

The acetolyses of the isomers of **11** and **13** are more straightforward. In each case both β substituents are of the same type: H and D in **11** and two alkyl groups in **13**. Applying the equal fraction of inversion approximation to (*Z*)-**11** and (*E*)-**11** in acetic acid, we calculated Z/E to be 0.7 and net inversion in both isomers to be ~80%.[40] We attribute this larger fraction of inversion (compared to (*Z*)-**3** and (*E*)-**3**) not so much to the small size of the β H and D in (*Z*)-**11** and (*E*)-**11** but to stabilization of the cation (**5**) by the β-methyl group.

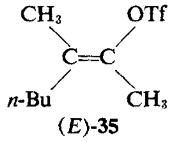
It is interesting that in acetic acid with 0.11 *M* NaOAc there is no preference for trans elimination. Triflate (*E*)-**11** with deuterium trans to the leaving group gives as much acetylene **9** as (*Z*)-**11**, even though deuteration decreases the amount of acetylene formed (Table IV). However, in acetic acid saturated with sodium acetate, a more basic, more nucleophilic, and more ionizing solvent, a preference for trans elimination does appear.

In the solvolysis of (*Z*)-**13** and (*E*)-**13**, the process appears simply to be a preference for attack by solvent on the least hindered side of an ion or ion pair. If an equal amount of the product from each isomer arises from an inversion pathway, the Z/E is 0.19 and there is 32% inversion. In this case, it is reasonable on steric grounds to expect more inversion from a (*Z*)-**13** ion pair than from an ion pair derived from (*E*)-**13**, so the Z/E ratio might be larger (closer to one).

In another example of a vinylic system with two β-alkyl substituents, Clarke, Kelsey, and Bergman[19a] studied the trifluoroethanolysis of (*Z*)-**35** and (*E*)-**35**.



(*Z*)-**35**



(*E*)-**35**

Net inversion in the substitution reaction was found in agreement with our results. Application of the equal fraction of inversion assumption gives a Z/E ratio for the "free" cation of 0.26 and 11% of an inversion component.

Conclusion

Vinyl cations are formed in the protonation of acetylenes and terminal allenes in trifluoroacetic acid. Such "free"[13] vinyl cations show a tendency to capture solvent trans to a β hydrogen. This tendency is reduced and may even be reversed by stabilizing substituents on the cationic center. Solvolyses of vinyl triflates in acetic and trifluoroacetic acids are complicated by ion pair formation and an inversion component is observed in the ester product. However, the amount of inversion necessary to explain most product ratios is closer to that observed in tertiary than secondary aliphatic substitutions, indicating that in spite of the higher energies of vinyl cations, solvolyses of vinyl substrates are SN1 processes.

Experimental Section

All boiling points are uncorrected. Nmr spectra were taken on a Varian Model A60-A spectrometer using tetramethylsilane as internal standard. Infrared spectra were taken on a Perkin-Elmer Model 237 B grating spectrophotometer. Mass spectra were obtained with an AEI-MS-9 spectrometer. Preparative and analytical glc was performed on a Varian Aerograph Model 90-P gas chromatograph equipped with a thermal conductivity detector or a Varian Aerograph Model 1520 equipped with flame ionization detectors fitted with the following columns: A, 0.375 in. × 13 ft 30% SE-30 on 45–60 Chromosorb W; B, 0.375 in. × 15 ft 20%

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[40] Because of the relatively large error in the stereochemical data on (*Z*)-**11** and (*E*)-**11**, this Z/E ratio is indistinguishable from unity.

Carbowax 20M on 45–60 Chromosorb W; D, 0.125 in. × 17 ft 10% Carbowax 20M on 80–100 Chromosorb W; E, 0.125 in. × 15 ft 10% SE-30 on 80–100 Chromosorb W; F, 0.25 in. × 6 ft 20% Carbowax 20M on 45–60 Chromosorb W; G, 0.25 in. × 6 ft 20% SE-30 on 45–60 Chromosorb W; H, 0.25 in. × 3 ft Carbowax 20M on 45–60 Chromosorb W with the first 4 in. packed with crystal violet forecolumn packing (see below). Microanalyses were performed by Hoffmann-La Roche Inc., Nutley, N. J.

Compounds. Alkynes and 1-alkyn-3-ols were purchased from Farchan Research Laboratories. 1,2-Butadiene,[32a] 1,2-pentadiene,[41] and 1,2-hexadiene[42] were prepared from the corresponding 1-alkyn-3-ols by reported methods. Trifluoromethanesulfonic (triflic) acid was generously provided by Dr. R. F. Hansen of 3M Co. Triflic anhydride was prepared from the acid and P_2O_5.[43]

Triflic Acid-*d*. Triflic anhydride was distilled from P_2O_5 and 2.9-g portions were sealed in ampoules with 0.2 g of D_2O. The ampoules were shaken daily until the mixture became homogeneous (3–5 days) and were left an additional week at room temperature before use.

1-Hexyne-*1-d*. Methylmagnesium bromide (Alfa) (0.3 mol) in 100 ml of ether was transferred under nitrogen to a 250-ml flask fitted with a reflux condenser, a dropping funnel, and a magnetic stirrer. 1-Hexyne (15 g, 0.18 mol) was added. The mixture was stirred for 20 hr and then hydrolyzed with D_2O (10 g, 0.5 mol). The reflux condenser was replaced by a 10-cm column packed with glass helices topped by a distillation head. The fraction boiling at 68–71° was collected, dried, and redistilled to give 6.0 g of 1-hexyne-*1-d*, bp 70–71°. The acetylenic proton absorption in the nmr spectrum at δ 1.70 was no longer present.

Synthesis of Vinyl Triflates. (*Z*)-2-Buten-2-yl Triflate [(*Z*)-3] and (*E*)-2-Buten-2-yl Triflate [(*E*)-3]. 2-Butyne (3.0 g, 0.055 mol) was dissolved in 25 ml of pentane and stirred magnetically while cooling to −20°. Triflic acid (10.5 g, 0.069 mol) was added dropwise over 15 min with vigorous stirring. After addition was complete the reaction was allowed to warm to room temperature. The pentane was distilled at 1 atm and the residue distilled at reduced pressure to give 7.6 g (68%) of a mixture of triflates, bp 35–37° (15 mm). The elution order on preparative glc column B at 50° was: (*Z*)-**3** [65% of the mixture; nmr (CCl_4) δ 1.74 (d of q, $J_d = 7.0$ Hz, $J_q = 1.4$ Hz, 3 H, β-CH_3), 2.07 (m, 3 H, CH_3), 5.33 (q of q, $J = 7.0$ and 1.2 Hz, 1 H, vinyl H); ir (thin film) 1706 (C═C), 1409, 1240, 1201, 1151, 1130, 1021, 933, and 872 cm^{-1}] and then (*E*)-**3** [35% of the mixture; nmr (CCl_4) δ 1.72 (d of q, $J_d = 7.0$ Hz, $J_q = 0.9$ Hz, 3 H, β-CH_3), 2.03 (m, 3 H, α-CH_3), 5.56 (q of q, $J = 7.0$ and ≤ 1 Hz, 1 H, vinyl H); ir (thin film) 1696 (C═C), 1416, 1244, 1201, 1149, 1127, 1074, 1004, and 953 cm^{-1}].

Anal. Calcd for $C_5H_7F_3O_3S$: C, 29.41; H, 3.46. Found for (*Z*)-**3**: C, 29.38; H, 3.42. Found for (*E*)-**3**: C, 29.43; H, 3.73.

1-Hexen-2-yl Triflate (10). 1-Hexyne (6.0 g, 0.073 mol) was dissolved in 25 ml of pentane in a 50-ml flask fitted with a magnetic stirrer and cooled to −20°. Triflic acid (6.0 g, 0.040 mol) was added dropwise over 15 min. The cooling bath was removed and as the reaction warmed to 0°, saturated $NaHCO_3$ (15 ml) was added. After this mixture stirred for 5 min, the aqueous layer was removed with a transfer pipet. The organic layer was washed twice more 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 6.5 g (70%) of **10**: bp 67–69° (15 mm); nmr (CCl_4) δ 0.98 (m, 3 H, CH_3), 1.50 (m, 4 H, CH_2CH_2), 2.37 (m, 2 H, allylic CH_2), 4.92 (d, $J = 4$ Hz, 1 H, vinyl H trans to the triflate group), 5.06 (d, $J = 4$ Hz, 1 H, vinyl H cis to the triflate group); ir (thin film) 1672 (C═C), 1420, 1249, 1206, 1170, 1139, 1085, 945, and 890 cm^{-1}. The product was separated from ~5% of other isomers by preparative glc on column B at 70°.

Anal. Calcd for $C_7H_{11}F_3O_3S$: C, 36.20; H, 4.77 Found: C, 36.36; H, 4.64.

(*Z*)-1-Hexen-2-yl-*1-d* Triflate [(*Z*)-11]. 1-Hexyne (3.0 g, 0.37 mol) and CF_3SO_3D (3.0 g, 0.020 mol) gave by the procedure described above 2.7 g (58%) of (*Z*)-**11**; nmr of vinylic region (CCl_4) δ 4.92 (m, H trans to triflate group, 0.74 ± 0.03) and 5.06 (m, H cis to triflate group, 0.26 ± 0.03).

(*E*)-1-Hexen-2-yl-*1-d* Triflate [(*E*)-11]. 1-Hexyne-*1-d* (3.0 g, 0.036 mol) and CF_3SO_3H (3.0 g, 0.20 mol) have by the same procedure 2.3 g (50%) of (*E*)-**11**; nmr of vinyl region (CCl_4) δ 4.92 (m, H trans to triflate, 0.23 ± 0.03) and 5.06 (m, H cis to triflate, 0.77 ± 0.03).

3,5,5-Trimethyl-2-hexanone (12). Grignard reagent[44] prepared from (12.5 g, 0.50 ml) magnesium turnings and 2-methyl-2-propyl chloride (50 g, 0.54 mol) in 500 ml of ethyl ether was filtered under nitrogen into a 1-l. flask equipped with magnetic stirrer, dropping funnel, and reflux condenser. Cuprous bromide (0.5 g) was added. Freshly distilled 3-methyl-3-buten-2-one (28 g, 0.30 mol) in 50 ml of ether was added dropwise with vigorous stirring. The resulting mixture was hydrolyzed with saturated NH_4Cl solution until both layers were clear. The ether layer was separated, washed with 100 ml of saturated NaCl, and dried over K_2CO_3. Distillation gave 19 g (45%) of **12**; bp 121–125° (220 mm); nmr (CCl_4) δ 0.88 (s, 9 H, *t*-Bu), 1.07 (d, $J = 7.0$ Hz, 3 H, CH_3CH), 1.10 (m, 1 H, diastereotopic methylene H), 1.80 (m, 1 H, diastereotopic methylene H), 2.09 (s, 3 H, CH_3CO), 2.95 (m, 1 H, methine H); ir (thin film) 1715 (C═O), 1471, 1393, 1313, 1245, 1178, 1158, 1061, and 948 cm^{-1}.

Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.54; H, 12.61.

(*Z*)-3,5,5-Trimethyl-2-hexen-2-yl Triflate [(*Z*)-13] and (*E*)-3,5,5-Trimethyl-2-hexen-2-yl Triflate [(*E*)-13]. Triflic anhydride (6.0 g, 0.021 mol), Na_2CO_3 (1.5 g, 0.014 mol), and 15 ml of pentane were placed in a 50-ml round-bottomed flask fitted with magnetic stirring. Ketone **12** (4.0 g, 0.028 mol) was added in small portions over 30 min and the reaction mixture was stirred for 20 hr. Water, 20 ml, was added to the mixture and the organic layer separated, washed once with saturated $NaHCO_3$, and dried over K_2CO_3. The solvent was removed under reduced pressure and the residue chromatographed on silica gel with pentane. The first fraction, eluting almost with the solvent front, contained 2.0 g (34%) of (*Z*)-**13** and (*E*)-**13**. In order of elution on preparative glc column B at 75°, the individual isomers were (*Z*)-**13** [45% of the mixture; nmr (CCl_4) δ 0.93 (s, 9 H, *t*-Bu), 1.80 (q, $J = 1.0 \pm 0.1$ Hz, 3 H, β-CH_3), 2.08 and 2.13 (multiplets, 5 H, α-CH_3 and β-CH_2); ir (thin film) 1687 (C═C), 1417, 1259, 1205, 1147, 1087, 935, 916, and 886 cm^{-1}] and (*E*)-**13** [55% of the mixture, nmr (CCl_4) δ 0.98 (s, 9 H, *t*-Bu), 1.85 (q, $J = 1.4 \pm 0.1$ Hz, 3 H, β-CH_3) and 2.03 (m, 5 H, α-CH_3 and β-CH_2); ir (thin film) 1680 (C═C), 1417, 1254, 1208, 1175, 1148, 1120, 1081, 946, 927, and 898 cm^{-1}].

Anal. Calcd for $C_9H_{17}F_3O_3S$: C, 43.78; H, 6.25. Found for (*Z*)-**13**: C, 43.78; H, 6.28. Found for (*E*)-**13**: C, 43.63; H, 6.08.

Preparation of Enol Trifluoroacetates. (*Z*)-2-Buten-2-yl Trifluoroacetate [(*Z*)-14] and (*E*)-2-Buten-2-yl Trifluoroacetate [(*E*)-14]. 2-Butyne (4.0 g, 0.074 mol) was sealed in an ampoule with 50 ml of CF_3CO_2H and the mixture allowed to react at 75.3° for 30 hr. The ampoule was cooled in an ice bath and opened, and the contents poured into a mixture of 50 ml of pentane and 100 ml of ice–water. The organic layer was separated and washed quickly with 50 ml of ice–water and 30 ml of saturated $NaHCO_3$ solution and dried over $CaCl_2$. Distillation at atmospheric pressure gave 4.6 g (37%) of a mixture of enol trifluoroacetates, bp 88–93°. The individual isomers, isolated from a preparative glc column B at 70°, were, in order of elution, (*Z*)-**14** [75% of the mixture, nmr (CCl_4) δ 1.55 (d of q, $J_d = 7.0$ Hz, $J_q = 1.6$ Hz, 3 H, β-CH_3), 1.95 (m, 3 H, α-CH_3), 5.20 (q of q, $J = 7.0$ and 1.2 Hz, 1 H, vinyl H); ir (thin film) 1800 (C═O), 1709 (C═C), 1365, 1290, 1235, 1140, 1029, 932, 878, and 790 cm^{-1}] and (*E*)-**14** [25% of the mixture; nmr (CCl_4) 1.70 (d of q, $J_d = 7.0$ Hz, $J_q \simeq 1$ Hz, 3 H, β-CH_3), 1.93 (m, 3 H, α-CH_3), 5.43 (q of q, $J = 7.0$ and 1.1 Hz, 1 H, vinyl H); ir (thin film) 1795 (C═O), 1702 (C═C), 1442, 1388, 1360, 1225, 1160, 1008, and 883 cm^{-1}].

Anal. Calcd for $C_6H_7F_3O_2$: C, 42.82; H, 4.19. Found for (*Z*)-**14**: C, 42.92; H, 4.21. Found for (*E*)-**14**: C, 42.81; H, 4.23.

(*Z*)-3-Hexen-3-yl Trifluoroacetate [(*Z*)-16] and (*E*)-3-Hexen-3-yl Trifluoroacetate [(*E*)-16]. 3-Hexyne (6.0 g, 0.073 mol) and 50 ml of CF_3CO_2H gave by the method of Peterson and Duddey[16b] 3.5 g (24%) of a 1:1 mixture of trifluoroacetates, (*Z*)-**16** and (*E*)-**16**. The individual isomers, separated on glc column B at 75°, were, in order of elution, (*Z*)-**16** [nmr (CCl_4) 0.98 (t, $J = 7.5$ Hz, 3 H, CH_3), 1.09 (t, $J = 7.5$ Hz, 3 H, CH_3), 1.97 (m, 2 H, β-CH_2), 2.28 (m, 2 H, α-CH_2), 5.08 (t, $J = 7.0$ Hz, 1 H, vinyl H); ir (thin film) 1798 (C═O), 1705 (C═C), 1462, 1365, 1222, 1138, 888, and 837 cm^{-1}] and (*E*)-**16** [nmr (CCl_4) δ 1.05 (t, $J = 7$ Hz, 6 H, both CH_3's), 2.30 (m, 4 H, both CH_2's), 5.25 (t, $J = 8.0$ Hz, 1 H, vinyl H); ir (thin film) 1795 (C═O), 1692 (C═C), 1462, 1352, 1221, 1163, 1135, and 892 cm^{-1}].

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(*Z*)-4-Octyn-4-yl Trifluoroacetate [(*Z*)-18] and (*E*)-4-Octyn-4-yl Trifluoroacetate [(*E*)-18]. 4-Octyne (**17**) (4.0 g, 0.036 mol) was added dropwise over 4 hr to refluxing CF_3CO_2H. The CF_3CO_2H was then distilled at 35° (150 mm) and the residue distilled to give 4.1 g (62%) of a mixture of trifluoroacetates, bp 83–85° (15 mm). The pure isomers, separated by glc on column A at 70°, were (*Z*)-**18** [45% of the mixture; nmr (CCl_4) δ 0.96 and 0.92 (overlapping t, J = 6 and 6.5 Hz, 6 H, CH_3's), 1.35 (m, 4 H, CH_2CH_2's), 1.95 (q, J = 7.0 Hz, 2 H, β vinyl CH_2), 2.28 (q, J = 7.0 Hz, 2 H, α-CH_2), 5.13 (t, J = 7.0, 1 H, vinyl H); ir 1800 (C=O), 1705 (C=C), 1470, 1362, 1225, 1137, 890, and 770 cm^{-1}] and (*E*)-**18** [55% of the mixture; nmr (CCl_4) δ 0.95 (t, J = 6.5 Hz, 6 H, both CH_3's), 1.40 (m, 4 H, CH_2CH_2), 2.09 (q, J = 7 Hz, 2 H, β vinyl CH_2), 2.33 (m, 2 H, α-vinyl CH_2), 5.34 (5, J = 7.5 Hz, 1 H, vinyl H); ir (thin film) 1797 (C=O), 1695 (C=C), 1465, 1362, 1225, 1163, 1137, and 905 cm^{-1}].

Anal. Calcd for $C_{10}H_{15}O_2F_3$: C, 53.57; H, 6.74. Found for (*Z*)-**18**: C, 53.28; H, 6.74. Found for (*E*)-**18**: C, 53.72; H, 6.90.

(*Z*)-2-Hexen-2-yl Trifluoroacetate [(*Z*)-24] and (*E*)-2-Hexen-2-yl Trifluoroacetate [(*E*)-24]. In a method similar to that of Peterson and Duddey,[16b] 1-hexyne (5.0 g, 0.061 mol) and 50 ml of CF_3CO_2H were refluxed for 6 hr. The CF_3CO_2H was distilled (bp 35° (150 mm)) and the residue distilled to give 5.3 g (31%) of a mixture of trifluoroacetates, bp 62–66° (15 mm), containing a little 2-hexanone. The mixture was separated by glc on column A at 70° into (*Z*)-**24** [62% of the mixture; nmr (CCl_4) δ 0.96 (t, J = 6.5 Hz, 3 H, CH_2CH_3), 1.40 (m, 2 H, CH_2CH_3), 1.91 (broad s, 3 H, vinyl CH_3), 2.00 (m, 2 H, vinyl CH_2), 5.05 (t, J = 7.5 Hz, 1 H, vinyl H); ir (thin film) 1797 (C=O), 1707 (C=C), 1364, 1223, 1165, 1137 cm^{-1}], 2-hexanone (**28**), 8% of the mixture, and (*E*)-**24** [30% of the mixture; nmr (CCl_4) δ 0.97 (t, J = 7.0 Hz, 3 H, CH_3CH_2), 1.20 (m, 2 H, CH_2CH_3), 1.97 (broad s, 3 H, vinyl CH_3), 2.10 (m, 2 H, vinyl CH_2), 5.30 (t, J = 7.5 Hz, 1 H, vinyl H); ir (CCl_4) 1795 (C=O), 1698 (C=C), 1460, 1389, 1362, 1225, 1162, 1140, and 900 cm^{-1}.

(*Z*)-2-Penten-2-yl Trifluoroacetate [(*Z*)-21] and [(*E*)-2]Penten-2-yl Trifluoroacetate [(*E*)-21]. 1-Pentyne (5.2 g, 0.077 mol) and CF_3CO_2H were refluxed for 12 hr. The reaction mixture was cooled and poured into 100 ml of ice–water and 50 ml of pentane. The organic layer was separated and washed quickly with 50 ml of cold water and 30 ml of $NaHCO_3$ and dried over $CaCl_2$. The pentane was distilled at atmospheric pressure and the residue distilled at reduced pressure to give 4.6 g of a liquid mixture, bp 52–54° (15 mm), of (*Z*)-**21**, 2 pentanone, and (*E*)-**21** in a ratio of 2:1:1 by glc. The trifluoroacetate isomers collected from glc column B at 65° were, in order of elution, (*Z*)-**21** [nmr (CCl_4) δ 0.98 (t, J = 7.0 Hz, 3 H, CH_3CH_2), 1.97 (m, 5 H, vinyl CH_3 and CH_2), 5.08 (q of t, J_q = 7.0 Hz, $J_t \simeq$ 1.2 Hz, 1 H, vinyl H); ir (thin film) 1800 (C=O), 1708 (C=C), 1465, 1364, 1227, 1165, 1140, 1042, 886, and 824 cm^{-1}] and (*E*)-**21** [nmr (CCl_4) δ 1.05 (t, J = 6.5 Hz, 3 H, CH_3CH_2), 1.95 (broad s, 3 H, α-CH_3), 2.13 (m, 2 H, vinyl CH_2), 5.35 (t, J = 7.0 Hz, 1 H, vinyl H); ir (thin film) 1798 (C=O), 1696 (C=C), 1362, 1232, 1170, 1140, and 896 cm^{-1}].

Anal. Calcd for $C_7H_9O_2F_3$: C, 46.16; H, 4.98. Found for (*Z*)-**21**: C, 46.17; H, 5.25. Found for (*E*)-**21**: C, 46.25; H, 5.40.

Preparation of Enol Acetates. 2-Hexen-2-yl Acetate (27).[28] 1-Hexyne (7.3 g, 0.089 mol) was added dropwise to a solution of 1 g of HgO and 1 ml of BF_3Et_2O in 7 ml of acetic acid to give **27**, 4.3 g (33%), bp 70–73° (35 mm) (lit. bp 74–75° (39 mm)). Pure **27** [nmr (CCl_4) δ 0.91 (t, J = 6.5 Hz, 3 H, CH_3), 1.40 (m, 4 H, CH_2CH_2), 2.05 (s, 3 H, CH_3C=O), 2.20 (t J = 6.0 Hz, 2 H, vinyl CH_2), 4.63 (m, 2 H, vinyl H's)] was collected from preparative glc column C at 85°. In benzene-d_6 the vinyl proton resonances in the nmr spectrum of **27** were clearly separated into two peaks of equal intensity at δ 4.34 (trans to the OAc group) and 4.56 (cis to the OAc group).

(*Z*)-2-Buten-2-yl Acetate [(*Z*)-26] and (*E*)-2-Buten-2-yl Acetate [(*E*)-26]. 2-Butanone (20 g, 0.28 mol) and acetic anhydride (60 g, 0.54 mol) following the procedure of House, *et al.*,[29] gave 17.1 g (54%) of a mixture of acetates boiling at 115–130° (lit.[29] bp 118–124°). The pure isomers were separated on glc column B at 85°.

(*Z*)-3,5,5-Trimethyl-2-hexen-2-yl Acetate [(*Z*)-31] and (*E*)-3,5,5-Trimethyl-2-hexen-2-yl Acetate [(*E*)-31]. Using the method of House, *et al.*,[27] **12** (6.0 g, 0.042 mol) and acetic anhydride (8.0 g, 0.078 mol) gave 6.0 g (78%) of a mixture of acetates, bp 80–90° (20 mm). The pure isomers, collected from glc column B at 120°, were (*Z*)-**31** [nmr (CCl_4) δ 0.88 (s, 9 H, *t*-Bu), 1.71 (broad s, 3 H, β-CH_3), 1.86 (broad s, 5 H, β-CH_2 and α-CH_3), 2.01 (s, 3 H, CH_3-CO; ir (thin film) 1763 (C=O), 1686 (C=C), 1478, 1362, 1236, 1214, 1140, 1090, and 1010 cm^{-1}] and (*E*)-**31** [nmr (CCl_4) δ 1.11 (s, 9 H, *t*-Bu), 1.53 (q, J = 1.5 Hz, 3 H, β-CH_3), 1.78 (m, 3 H, α-CH_3), 1.97 (broad s, 2 H, α-CH_2), 2.03 (s, 3 H, CH_3CO); ir (thin film) 1760 (C=O), 1678 (C=C), 1470, 1362, 1212, 1130, 1090, 1010, and 850 cm^{-1}].

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.95. Found for (*Z*)-**31**: C, 71.78; H, 10.81. Found for (*E*)-**31**: C, 72.00; H, 10.96.

Kinetic Procedures. Solvolysis acetic acid was Baker Analyzed Reagent to which acetic anhydride (1% by volume) and sodium acetate (0.0034 *M*) had been added. Solutions of substrate (0.002–0.003 *M*) in this solvent, sealed in 2-ml ampoules, were introduced simultaneously into a constant-temperature bath. Ampoules were removed from the bath at appropriate times and cooled in an ice bath. The excess NaOAc was titrated potentiometrically with $HClO_4$ in acetic acid on a Beckman Automatic Recording Titrator No. 106302 in the derivative mode.

Trifluoroacetic Acid. Commercial (Eastman) trifluoroacetic acid was distilled from trifluoroacetic anhydride (5%) and a solution was prepared containing 2% by volume of the anhydride and 0.125 *M* NaO_2CCF_3.

Trifluoroacetic Acid-*d*. Trifluoroacetic anhydride (250 g) was distilled from P_2O_5 (10 g). After a forerun of 15 ml, 170 g of anhydride was collected, bp 39–40°. The receiver was then disconnected, fitted with a dropping funnel, a drying tube, and a magnetic stirrer, and cooled to −15°. D_2O (Diaprep, 99.8% D, 16.0 g) was added dropwise with vigorous stirring over a 1-hr period. The deuterated solvent was distilled under a nitrogen atmosphere. After ~10 ml forerun rich in anhydride, 163 g of trifluoroacetic acid-*d* was collected, bp 69–70°. A solution of 2% by volume anhydride and 0.125 *M* NaO_2CCF_3 was prepared in this solvent. The nmr spectrum of a solution of $CHCl_3$ (1.1% by wt) in this solvent indicated that it was 99% deuterated.

Kinetics in trifluoroacetic acid were determined by glc by a modification of the method described previously.[16b] Solutions ~0.1 *M* in substrate were prepared in 1 ml of solvent in an ampoule fitted with a serum cap. A syringe was used to dispense equal portions of this solution into ten ampoules made from 5-mm Pyrex tubing. These ampoules were sealed and immersed simultaneously in a constant-temperature bath. At appropriate times, ampoules were removed from the bath, cooled in an ice–acetone bath, and opened at room temperature, and 5-μl protions of the contents were analyzed on a Varian Aerograph 90-P gas chromatograph equipped with thermal conductivity detector and a forecolumn (see below) to remove trifluoroacetic acid. For kinetic runs, the injector was kept at 60° and fitted with a glass insert. The oven was allowed to equilibrate for 2 hr before an analysis. Solvolyses of **7** and **8** were followed on column F at 65°. Reaction of the other acetylenes were followed on column G. Triflate mixtures were analyzed on column H. Concentration was measured by peak height which was reproducible with a maximum deviation of 2%. This method gave rates within 7% of those reported previously.[16b]

Preparation of the Forecolumn. Crystal violet (2.5 g) and Carbowax 20M (1.0 g) were dissolved in CH_2Cl_2 (50 ml). Chromosorb W (7.0 g, Varian, acid washed and treated with dimethyldichlorosilane) was added to this solution and the solvent was removed on a rotary evaporator. A 15-cm section of 0.25-in. aluminum tubing packed with this material was baked in a glc oven at 200° for 2 hr. This forecolumn removed CF_3CO_2H completely without affecting substrates or products.

Solvolysis Products. Trifluoroacetolysis. Products of solvolysis and addition reactions were determined by glc analysis on columns D and E by procedures identical with those used in kinetic measurements. Peak areas were determined by multiplying peak height and width at half-height. All peak areas were corrected for the relative detector response of authentic samples of the reaction products in trifluoroacetic acid at concentrations similar to those actually found in the reactions.

Acetolysis. Duplicate reaction mixtures from (*Z*)-**3**, (*E*)-**3**, (*Z*)-**13**, and (*E*)-**13** (0.06–0.1 *M*) in acetic acid buffered with 0.11 *M* NaOAc were analyzed by glc after approximately 2 and 4 half-lives. Allenes and acetylenes exposed to these conditions were unchanged after 20 half-lives. Enol acetates with internal double bonds did not isomerize but were converted to ketones with half-lives ~20 times longer than those for their formation. Since enol acetate **27** was converted rapidly to ketone (see below), the products of reaction of **10**, (*Z*)-**11**, and (*E*)-**11** under these conditions were determined after 10–15 half-lives. The products of **10**, (*Z*)-**11**, and (*E*)-**11** were also determined for reaction in CH_3CO_2D (1.3 *M* in NaOAc) after 1–2 half-lives.

Observation of Acetolysis Products of (*Z*)-3 and (*E*)-3 by Nmr. Triflates (*Z*)-**3** and (*E*)-**3**, as 0.3 *M* solutions in CD_3CO_2D buffered with 0.5 *M* pyridine, were sealed in nmr tubes. These solutions were placed in an oil bath at 100°. The spectra of the reaction mixtures were recorded periodically. Triflate (*Z*)-**3**, completely reacted after 3 hr, gave **8** as the only product clearly discernible by nmr. After 14 hr (*E*)-**3** gave a product mixture consistent with a 3:1 mixture of **8** and (*Z*)-**26**.

Reaction of 27 with Acetic Acid. A mixture of **27** and benzene (2:1 by volume) was introduced in 30-μl portions to three nmr tubes containing 300 μl of (1) CH_3CO_2H, (2) CH_3CO_2H saturated with NaOAc, and (3) CD_3CO_2D saturated with NaOAc. The tubes were sealed and placed in a bath at 101.1°. After 4 hr, the tubes were cooled in an ice bath and the amount of **4**-OAc remaining in each was measured by integrating the vinyl proton signal in the nmr relative to the benzene internal standard. In the tube containing CH_3CO_2H, $\sim$25% of **27** remained. In CH_3CO_2H saturated with NaOAc, 55% remained and in CD_3CO_2D saturated with NaOAc, 80% remained. Thus, the rate of destruction was decreased by approximately one-half in the saturated salt solution and by another two-thirds in the deuterated solvent.

Equilibration of Vinyl Trifluoroacetates. To 30-ml portions of the separate isomers of each *E*–*Z* pair of trifluoroacetates 1 μl of triflic acid was added; the solution was sealed in ampoules made of 3-mm Pyrex tubing and these were then placed in an oil bath at 75.3°. At various intervals an ampoule was removed from the bath and opened. A 10-μl portion of the contents was transferred to a 1-ml ampoule fitted with a serum cap and containing 1 ml of pentane and 20 mg of NaOAc. The pentane solution was then analyzed by glc in the same manner as the solvolysis products. This process was repeated until the analyses of mixtures from both *E* and *Z* isomers coincided, 24–48 hr.

Preparative Solvolysis of 10, (*Z*)-11, and (*E*)-11. Vinyl triflate (0.5 g) was sealed in an ampoule with 4 ml of CH_3CO_2D saturated with NaOAc and heated to 100° in an oil bath for 4 hr. The ampoule was cooled in an ice bath and opened, and the contents poured into a mixture of 10 ml of water and 1 ml of pentane. The pentane layer was separated, dried over K_2CO_3, and injected into preparative glc column C at 80°. Products (in order of elution, **22**, **9**, **28**, unreacted **10**, and **27**) were collected and identified by comparison with authentic samples (nmr).

Preparative Solvolysis of (*Z*)-13 and (*E*)-13. A mixture of (*Z*)-**13** and (*E*)-**13** (1 g), sealed in an ampoule with acetic acid (5 ml) and NaOAc (1.0 g), was heated to 100° for 10 hr. The ampoule then was cooled and the reaction mixture partitioned between water (10 ml) and pentane (1 ml). The pentane solution was dried over K_2CO_3 and injected into preparative glc column B. The products, in order of elution at 85°, were: 3,5,5-trimethyl-1,2-hexadiene (**30**) [nmr (CCl_4) δ 0.95 (s, 9 H, *t*-Bu), 1.70 (t, J = 3.0 Hz, 3 H, CH_3C), 1.85 (t, J = 2.0 Hz, 2 H, CH_2), 4.47 (m, 2 H, vinyl H s); ir (thin film) 1956 (C=C=C), 1464, 1388, 1361, 1262, 1234, 1188, and 992 cm^{-1}], **12**, (*Z*)-**31**, and (*E*)-**31**. The last two compounds gave nmr spectra identical with authentic samples prepared from **12**.

Deuterium Incorporation in (*Z*)-14 from (*Z*)-3 in CF_3CO_2D. In a 25-ml flask fitted with a reflux condenser and magnetic stirrer, 7 ml of CF_3CO_2D (0.125 *M* in NaO_2CCF_3) was brought to reflux. Triflate (*Z*)-**3** (1.0 g) was then injected through the condenser into the refluxing solution using a 1-ml syringe fitted with an 18-in. needle. The solution was allowed to reflux for 12 min (10% reaction under the conditions in Table II) and then cooled quickly in an ice bath. Pentane, 1 ml, was added, folllowed by sufficient cold water to raise the organic layer into the neck of the flask, where it was drawn off by pipet and dried over $MgSO_4$. This solution was then injected into glc column A at 60° and (*Z*)-**3** collected as it eluted. The mass spectrum of this sample indicated that it contained 17.8 ± 0.5% of monodeuterated material.

Deuterium Incorporation in (*Z*)-14 from (*E*)-3 in CF_3CO_2D. In an identical procedure (*Z*)-**14** was isolated from the reaction of (*E*)-**3** in 7 ml of refluxing CF_3CO_2D after 18 min (10% reaction for the conditions in Table II). The mass spectrum of this sample indicated that it contained 38.0 ± 0.6% of monodeuterated material.

Deuterium Incorporation in (*Z*)-14 from the Addition of CF_3CO_2D to 8. 2-Butyne (**8**) (0.3 g) was sealed in an ampoule with 5 ml of CF_3CO_2D and heated to 75.3° for 4 hr. The ampoule was cooled in an ice bath and its contents poured into a mixture of pentane (2 ml) and ice–water (15 ml). The organic layer was separated and dried over $MgSO_4$. This solution (0.5 ml) was injected into glc column A and (*Z*)-**14** collected. The mass spectrum of this sample showed the presence of only 1.72 ± 0.05% of dideuterated material.

Deuterium Incorporation in (*Z*)-14 from Addition of CF_3CO_2D to 7. In a procedure identical with that for **8**, (*Z*)-**14** was isolated from the reaction of **7** with CF_3CO_2D after 8 min at 75°. The mass spectrum of this sample indicated that it contained 1.7 ± 0.1% of dideuterated ester.

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Appendix

Stereochemical Assignments. The assignment of stereochemistry to trisubstituted olefins is a subtle problem which we have solved, in general, by recourse in each instance to three independent lines of spectral argument: the relative nmr chemical shifts of the vinyl protons, the relative position of the ir carbon–carbon double bond absorption, and the magnitude of long range coupling between methyl groups on the double bond.

Vinyl protons cis to an ether or ester group are shifted to lower nmr fields than the corresponding trans protons.[45] This chemical shift difference applies to enol acetates,[29,46] to enol trimethylsilyl ethers,[27] and to enol tosylates.[21,47] In particular, the chemical shift of the vinyl proton in (*Z*)-**3** is δ 5.33, while in (*E*)-**3** it is 5.56. Similar differences were shown by all trisubstituted enol esters studied here. In triflate **10**, the two vinyl proton absorptions were clearly separated at δ 4.92 (trans to the triflate group) and 5.06 (cis to the triflate group). Integration of these peaks in the monodeuterated triflates, (*Z*)-**11** and (*E*)-**11**, gave the estimated stereoisomeric isotropic content. The vinyl proton absorptions in the corresponding enol acetate, **27**, were not cleanly separated in CCl_4 solution. It was necessary to measure the spectrum of **27** (and the isomers of **29**) in benzene, a solvent which enhances the vinyl proton chemical shift differences.[27]

The infrared carbon–carbon double bonds in *Z* isomers of dialkylvinyl esters absorb at $\sim$10 cm^{-1} higher frequency than that found in the corresponding *E* isomers. This relationship, pointed out by Kelsey and Bergman[14b] for enol acetates, appears to be quite general for enol ethers[27] and esters;[29] it was observed for all *E*–*Z* pairs of dialkylvinyl esters reported here.

The trans long range coupling between vicinal methyl groups on a double bond is larger than cis coupling.[48] This difference is general in enol ethers and esters[14,27] and was observed for the *E*–*Z* isomers of **3**, **14**, and **26**. The structure of the isomers of **13** and **31** was assigned primarily on the basis of this difference in long range coupling ($J_{CH_3 \ldots CH_3}$ = 1.4 Hz in (*E*)-**13** but 1.0 Hz in (*Z*)-**13**; 1.5 Hz in (*E*)-**31** but <1 Hz in (*Z*)-**31**).

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(47) In our experience the same general difference in vinyl proton chemical shifts is found for the (*E*)- and (*Z*)-2-buten-2-yl triflates as for the tosylates, despite an implication to the contrary (footnote 7 of P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **91**, 6194 (1969)).

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