Mechanism of Reaction of *cis*- and *trans*-3-Phenyl-2-buten-2-yl Triflates. Evidence for Vinylidene Phenonium Ions[1,2]

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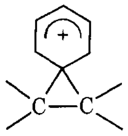
Abstract: The solvolyses of a series of ring substituted *cis*- and *trans*-3-phenyl-2-buten-2-yl triflates were investigated in CF_3CH_2OH. The vinyl triflates were prepared from the corresponding 3-aryl-2-butanones. The ρ value for reaction of the *E* triflates was found to be $\rho = -3.76$ and for the corresponding *Z* isomers $\rho = -1.96$ in 97% aqueous TFE at 100 °C. A Taft σ^* correlation gave a $\rho^* = -6.4$ with the rates for the *Z* isomers falling on the same line as the rates of a series of simple alkylvinyl triflates but the *E* rates falling off the line. The anchimeric assistance by the neighboring aryl group in the geometrically favorable *E* triflates ranged from 599 for the *p*-CH_3O isomer through 68 for the parent compound to 6 for the *p*-NO_2 substituent. The products in all cases were the corresponding *E* and *Z* vinyl ethers and the corresponding allenes. Product stereoselectivity ranged from 99.8% retained "configuration" for the *E*-*p*-CH_3 isomer through 93.5% retained for the *E*-*p*-NO_2 isomer to 98.2% inverted configuration for the *Z*-*p*-CH_3 and 79.4% inverted for the *Z*-*p*-NO_2 compound. These results are interpreted by means of vinylidene phenonium ion involvement in the solvolysis of the (*E*)-3-aryl-2-buten-2-yl triflates.

Neighboring group participation has been and remains one of the keystones of physical-organic chemistry.[3] Such participation occurs in a wide range of reactions through a variety of intermediates, but nowhere is it more prevalent than in solvolytic displacement reactions and carbonium ion chemistry.[4] One of the most widely and thoroughly investigated and intriguing systems has been neighboring aryl participation and the σ-bridged phenonium ion,[5] **1**, first proposed by Cram[6] almost three decades ago.



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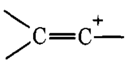

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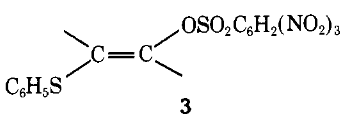
In the last decade or so, besides normal trisubstituted carbonium ions, there has been a great deal of interest and work done pertaining to disubstituted or vinyl cations,[7] **2**, initially through electrophilic additions to alkynes (and allenes) and participation of C≡C and C=C=C bonds in solvolysis and most recently via bond heterolysis and solvolysis of suitable precursors. Such solvolytic generation of vinyl cations opened up the possibility of detailed mechanistic investigations of these intermediates, including the question of rearrangement and neighboring group participation in vinyl cations. Rearrangements involving vinyl cations may be classified into two broad categories: (a) migration of a group to the double bond and (b) rearrangement across the double bond.[7b] Examples of both have been reported.[7] Rearrangements across the double bond and the question of neighboring group participation in vinyl cations was first investigated by Modena and co-workers[8] by means of solvolysis of 2-arylmercaptovinyl trinitrobenzenesulfonates **3**. In a series of elegant studies, they have shown the involvement of thiirenium ions **4** and hence participation by neighboring sulfur in a great many of these solvolyses.[8] Therefore, the possibility of neighboring phenyl participation in vinyl cations and the involvement of vinylidene phenonium ions, analogous to Cram's species **1**, became of interest. In order to examine this problem, we undertook and report in this paper a detailed investigation of the solvolytic behavior of a series of substituted (*E*)-, **5**, and (*Z*)-3-phenyl-2-buten-2-yl triflates, **6**.[9]



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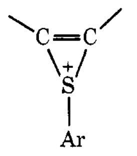

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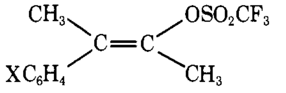
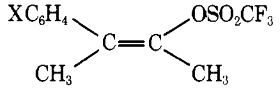
Results and Discussion

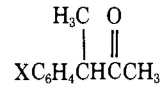
Preparation of Vinyl Triflates 5 and 6. Vinyl triflates **5** and **6** were prepared from the appropriate 3-phenyl-2-butanones **7** by reaction with triflic anhydride according to the procedure of Dueber et al.,[10] separated into *E*, **5**, and *Z*, **6**, isomers by preparative gas chromatography, and identified by spectral means (see Experimental Section).



5a, X = *p*-CH_3O
b, X = *p*-CH_3
c, X = H
d, X = *p*-Cl
e, X = *m*-Cl
f, X = *p*-CF_3
g, X = *p*-NO_2



6a, X = *p*-CH_3O
b, X = *p*-CH_3
c, X = H
d, X = *p*-Cl
e, X = *m*-Cl
f, X = *p*-CF_3
g, X = *p*-NO_2



$$XC_6H_4\overset{H_3C}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_3$$

7a, X = *p*-CH_3O
b, X = *p*-CH_3
c, X = H
d, X = *p*-Cl
e, X = *m*-Cl
f, X = *p*-CF_3
g, X = *p*-NO_2

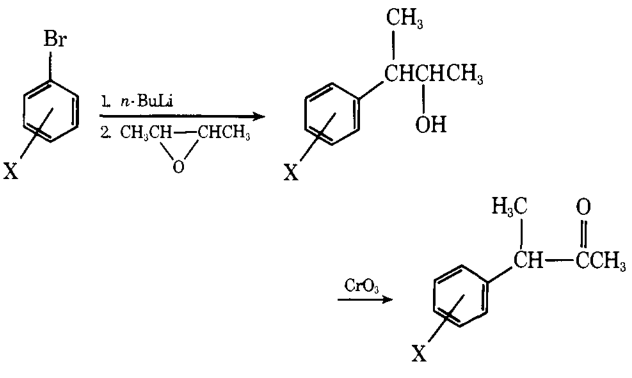
Ketones **7a**, **7c**, and **7d** were prepared by alkylation of the corresponding commercially available phenylacetones with methyl iodide. Ketones **7b**, **7e**, and **7f** were prepared as shown in Scheme I. The appropriate aryl bromides were treated with either Li or *n*-BuLi, followed by reaction with 2,3-butylene oxide, and the resulting crude alcohols were oxidized to the corresponding 3-aryl-2-butanones. Ketone **7g** was prepared as shown in Scheme II starting from *p*-nitrophenylacetic acid. The acid was converted to the acid chloride with thionyl chloride, then reacted with the magnesium salt of diethyl malonate. Saponification and decarboxylation yielded *p*-ni-

Table I. Rates of Solvolyses of Triflates **5** and **6** in 97% TFE

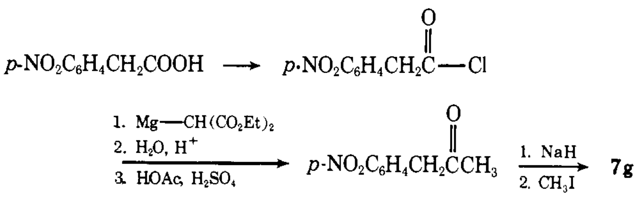
Compd	Temp, °C[a]	k, s^{-1} [b]	$\Delta H^{\ddagger}$,[c] kcal/mol	$\Delta S^{\ddagger}$,[c] eu
5a	25.0[d]	1.97×10^{-5}	21.7	−7.4
	50.02	$(3.59 \pm 0.03) \times 10^{-4}$		
	59.98	$(1.03 \pm 0.06) \times 10^{-3}$		
	69.80	$(2.65 \pm 0.13) \times 10^{-3}$		
	75.0[d]	4.34×10^{-3}		
	100.0[d]	3.75×10^{-2}		
5b	25.0[d]	6.56×10^{-6}	22.0	−8.4
	60.0	$(3.59 \pm 0.06) \times 10^{-4}$		
	75.0[d]	1.57×10^{-3}		
	75.06	$(1.59 \pm 0.2) \times 10^{-3}$		
	85.12	$(3.92 \pm 0.05) \times 10^{-3}$		
	100.0[d]	1.39×10^{-2}		
5c	25.0[d]	1.06×10^{-6}	22.7	−9.6
	74.96	$(3.04 \pm 0.01) \times 10^{-4}$		
	90.52	$(1.27 \pm 0.02) \times 10^{-3}$		
	99.88	$(2.90 \pm 0.09) \times 10^{-3}$		
	100.0[d]	2.91×10^{-3}		
5d	25.0[d]	7.07×10^{-8}	25.9	−4.2
	75.04	$(4.35 \pm 0.16) \times 10^{-5}$		
	84.92	$(1.32 \pm 0.1) \times 10^{-4}$		
	100.0	$(5.70 \pm 0.05) \times 10^{-4}$		
5e	25.0[d]	3.75×10^{-9}	29.7	2.7
	75.0[d]	5.89×10^{-6}		
	100.0	$(1.13 \pm 0.05) \times 10^{-4}$		
	110.03	$(3.17 \pm 0.15) \times 10^{-4}$		
	120.08	$(9.15 \pm 0.73) \times 10^{-4}$		
5f	25.0[d]	5.81×10^{-10}	30.4	1.0
	75.0[d]	1.05×10^{-6}		
	100.0[d]	2.11×10^{-5}		
	109.0	$(6.17 \pm 0.02) \times 10^{-5}$		
	119.95	$(1.77 \pm 0.12) \times 10^{-4}$		
	129.97	$(4.67 \pm 0.32) \times 10^{-4}$		
5g	25.0[d]	1.62×10^{-9}	23.2	−21
	75.0[d]	5.15×10^{-7}		
	100.0[d]	5.15×10^{-6}		
	120.04	$(2.59 \pm 0.02) \times 10^{-5}$		
	130.16	$(5.89 \pm 0.02) \times 10^{-5}$		
	140.55	$(1.17 \pm 0.05) \times 10^{-4}$		
6a	25.0[d]	3.64×10^{-8}	22.7	−16.4
	75.0[d]	1.04×10^{-5}		
	100.0[d]	9.90×10^{-5}		
	100.08	$(1.00 \pm 0.06) \times 10^{-4}$		
	110.09	$(2.25 \pm 0.15) \times 10^{-4}$		
	119.98	$(4.91 \pm 0.20) \times 10^{-4}$		
6b	25.0[d]	3.26×10^{-8}	22.6	−16.9
	75.0[d]	9.06×10^{-6}		
	99.34	$(7.99 \pm 0.04) \times 10^{-5}$		
	100.0[d]	8.57×10^{-5}		
	110.03	$(2.01 \pm 0.02) \times 10^{-4}$		
	120.02	$(4.15 \pm 0.2) \times 10^{-4}$		
6c	25.0[d]	1.11×10^{-8}	24.3	−13.6
	75.0[d]	4.60×10^{-6}		
	85.02	$(1.29 \pm 0.03) \times 10^{-5}$		
	99.97	$(4.86 \pm 0.26) \times 10^{-5}$		
	100.0[d]	5.11×10^{-5}		
	120.0	$(2.87 \pm 0.06) \times 10^{-4}$		
6d	25.0[d]	3.35×10^{-9}	24.6	−14.8
	75.0[d]	1.50×10^{-6}		
	100.0	$(1.73 \pm 0.09) \times 10^{-5}$		
	120.0	$(9.42 \pm 0.63) \times 10^{-5}$		
	129.97	$(2.18 \pm 0.03) \times 10^{-4}$		
6e	25.0[d]	8.84×10^{-10}	26.3	−11.8
	75.0[d]	5.94×10^{-7}		
	100.0[d]	8.01×10^{-6}		
	110.05	$(2.10 \pm 0.02) \times 10^{-5}$		
	120.0	$(4.92 \pm 0.05) \times 10^{-5}$		
	129.96	$(1.20 \pm 0.04) \times 10^{-4}$		
6f	25.0[d]	4.25×10^{-10}	27.2	−9.9
	75.0[d]	3.63×10^{-7}		
	100.0[d]	5.59×10^{-6}		
	120.03	$(3.64 \pm 0.10) \times 10^{-5}$		
	130.07	$(8.95 \pm 0.09) \times 10^{-5}$		
	139.95	$(2.03 \pm 0.11) \times 10^{-5}$		
6g	25.0[d]	7.57×10^{-11}	27.7	−11.8
	75.0[d]	7.28×10^{-8}		
	100.0[d]	1.13×10^{-6}		
	119.69	$(7.69 \pm 0.18) \times 10^{-6}$		
	130.37	$(2.01 \pm 0.03) \times 10^{-5}$		

[a] ±0.05. [b] Average of errors. [c] Activation parameters were all calculated at 25 °C. [d] Extrapolated from other temperatures.

Scheme I



Scheme II



$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{COOH} \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—Cl}$$

$$\xrightarrow[\text{3. HOAc, H}_2\text{SO}_4]{\text{1. Mg—CH(CO}_2\text{Et)}_2\ \text{2. H}_2\text{O, H}^+} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{CH}_3 \xrightarrow[\text{2. CH}_3\text{I}]{\text{1. NaH}} \mathbf{7g}$$

trophenylacetone which was alkylated with CH_3I to give **7g.**

Kinetic Determinations. Rates of reactions of triflates **5** and **6** were measured conductometrically, in pyridine buffered 97% trifluoroethanol (TFE), chosen for its high polarity and low nucleophilicity.[11] Rate measurements are averages of two to six determinations, and in all cases, excellent first-order rates were observed for more than 95% reaction. The computer calculated rate constants as well as activation parameters are given in Table I.

Product Studies. It was not deemed necessary to do product determinations on all the substituted triflates in both series **5** and **6**. Therefore, **5b, 5c,** and **5g** along with **6b, 6c,** and **6g** were selected as representative models and a careful, detailed product study carried out on these six compounds. Product studies were carried out in rigorously anhydrous TFE, buffered with 1.1–2.2 equiv of pyridine at 85 °C. Reaction products were analyzed by VPC with a flame ionization detector, on a freshly prepared analytical column, *free of acid,* by direct on-column injection of small, dilute (0.5 μL, 1% solution) samples in order to avoid isomerization of the product vinyl ethers. Products were identified by coinjection of authentic samples obtained by preparative GC from large scale solvolyses and identified by spectral means. In all cases the products consisted of the respective *E*, **8**, and *Z*, **9**, vinyl ethers and the appropriately substituted allenes, **10**. The results are summarized in Table II.

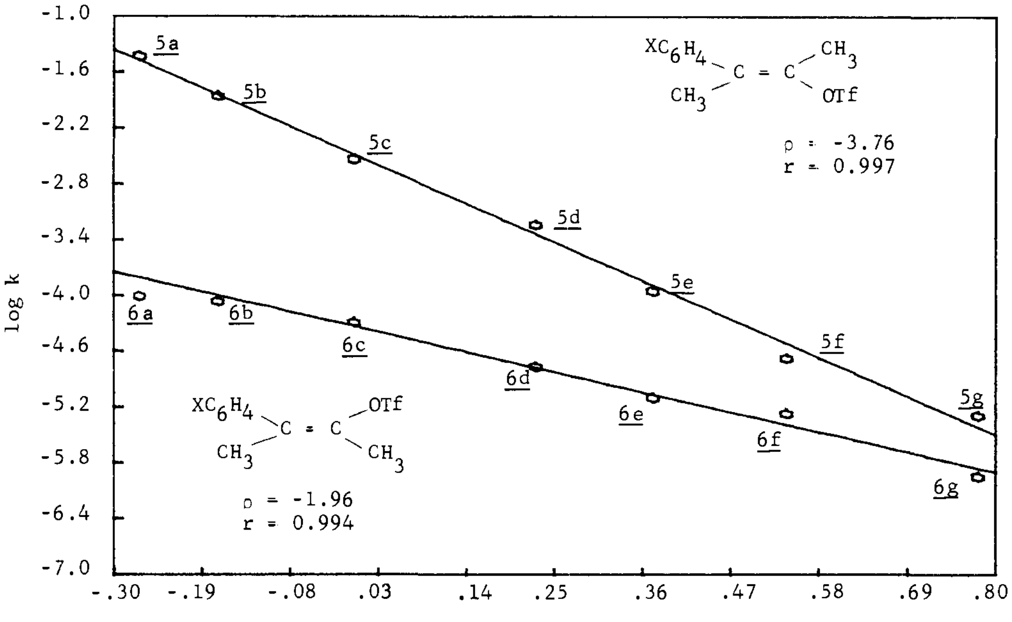
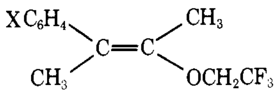


Figure 1. Plot of log k vs. σ for arylvinyl triflates **5** and **6**.

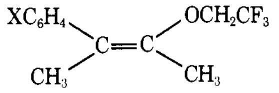
Table II. Products of Reaction of Triflates **5** and **6** in Anhydrous TFE at 85 °C

Vinyl triflate	% of vinyl ethers[a,b]	% of **10**[a,b]	Stereochemistry of vinyl ethers	
			% of **8**[b]	% of **9**[b]
5b	98.2 ± 0.3	1.8 ± 0.3	99.85 ± 0.07	0.15 ± 0.07
5c	93.3 ± 1.0	6.7 ± 1.0	99.47 ± 0.05	0.53 ± 0.05
5g	56.0 ± 3.0	44.0 ± 3.0	93.5 ± 1.0	6.5 ± 1.0
6b	89.1 ± 0.4	10.9 ± 0.4	98.2 ± 0.1	1.80 ± 0.1
6c	76.7 ± 2.0	23.3 ± 2.0	96.4 ± 0.2	3.6 ± 0.2
6g	40.1 ± 2.5	59.9 ± 2.5	79.4 ± 1.0	20.6 ± 1.0

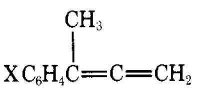
[a] Product determinations were carried out in duplicate and analyzed with the aid of inert standards. [b] Control experiments demonstrated that the products were stable to the reaction and analysis conditions employed.



8b, X = p-CH_3
c, X = H
g, X = NO_2



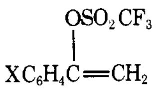
9b, X = p-CH_3
c, X = H
g, X = NO_2



$$XC_6H_4C(CH_3){=}C{=}CH_2$$

10b, X = p-CH_3
c, X = H
g, X = NO_2

Rate Analysis. Examination of the data in Table I reveals a number of interesting facts. In all cases triflates in the E series, **5**, reacted considerably faster than the corresponding compounds in the Z series, **6**, with a rate ratio that varied from **5g**/**6g** = 7 for the p-NO_2 compounds to **5a**/**6a** = 417 for the p-CH_3O compounds at 75 °C. Furthermore the effect of substituents was much larger with **5a**/**5g** = 8.4×10^3 for the E series than for the corresponding Z series with **6a**/**6g** = 1.4×10^2 at 75 °C. These rate effects are best expressed as Hammett σ–ρ plots. Figure 1 shows a computer-drawn least-squares plot of log k vs. σ for the solvolyses of both **5** and **6** in 97% TFE at 100 °C. A study of these data shows that the ρ value of $\rho = -3.76$ for **5** is very much larger than the ρ of -1.96 for **6**, indicating that there is much more charge delocalization into the phenyl ring in the E series **5** than in the Z series **6**. In fact, the ρ of -3.8 for **5** is comparable to the ρ of -4.1[12] for the solvolysis of **11** where the aryl group is α rather than β to the carbon bearing the triflate leaving group. Such a large ρ value for **5**, and in particular, the significant difference in ρ values and rates of solvolyses between **5** and **6**, clearly speaks for aryl participation in **5**.



$$XC_6H_4C(OSO_2CF_3){=}CH_2$$

11

An even better illustration of the difference in behavior between **5** and **6** can be obtained by examination of inductive effects with the aid of Taft σ^* values.[13] If one takes as a model a series of simple alkylvinyl triflates, **12–17**, where, of course, there can be no participation, their rates of solvolysis should correlate with σ^*. Rates of reactions of model compounds **12–17**, all of which have been shown to react via vinyl cations, can be obtained from the literature,[14] and, where necessary, extrapolated to a common temperature of 75 °C and to 97% TFE from aqueous ethanol data. Extrapolations from aqueous ethanol to 97% TFE were made by means of the Winstein–Grunwald[15] relationship and a solvent m value of 0.57 obtained for cis-2-buten-2-yl triflate and 3-methyl-2-buten-2-yl triflate.[14] σ^* values were calculated[13,16] from ionization constants

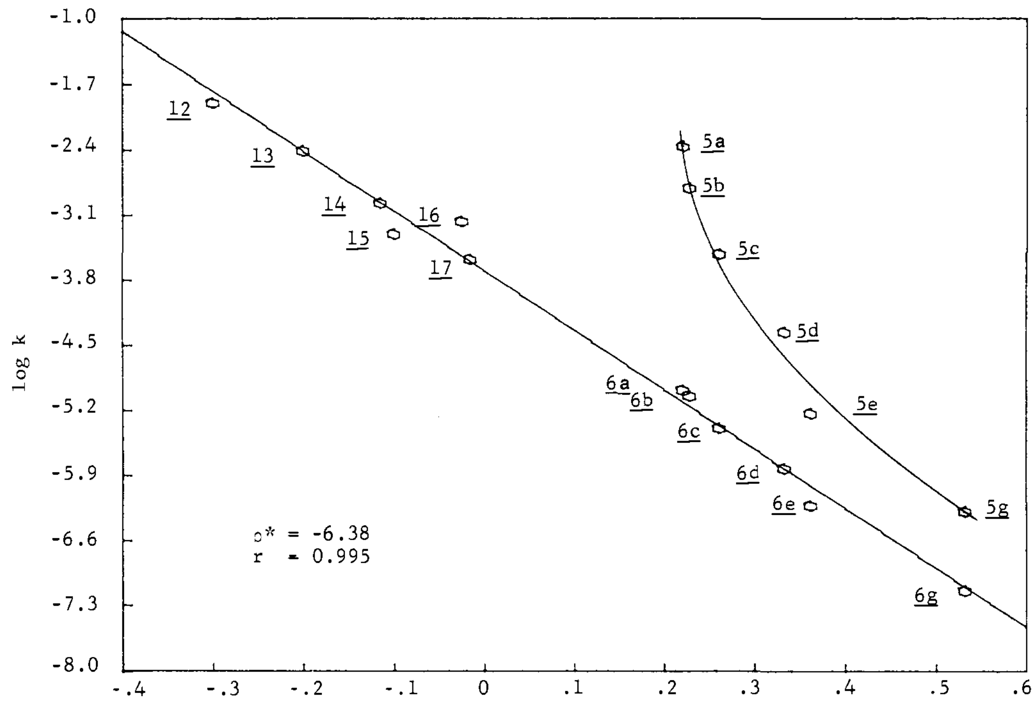


Figure 2. Plot of log k vs. σ^* for arylvinyl triflates **5** and **6** and alkylvinyl triflates **12–17**.

of arylacetic acids[17] with a value of $\sigma^* = 0.0$ for the *cis*-2-buten-2-yl triflate. These data are summarized in Table III.

A computer-drawn least-squares plot of log k vs. σ^* for the data in Table III is shown in Figure 2. Perusal of this figure shows that a good correlation, with $r = 0.995$, is obtained with the rate data for the Z series **6** all falling on the same line as the simple alkylvinyl triflate data but with the data for the (E)-3-phenyl-2-butene-2-yl triflates **5** badly off the correlation. This is exactly what one would expect on the assumption that the Z isomers, which are geometrically less favored for participation, react via normal vinyl cations analogous to the simple alkyl vinyl systems **12–17** with all of the substituent effects satisfactorily accounted for by inductive factors. On the other hand, the deviation of the E isomers, **5**, from the correlation line indicates that they must be solvolyzing under influences other than purely inductive ones. Such a deviation is best accounted for by aryl participation in the solvolysis of the geometrically favorable trans coplanar (E)-3-aryl-2-buten-2-yl triflates **5**. In fact, if the anchimerically unassisted Taft ρ^* line is taken as a measure of the unassisted rates, k_s, then by the well-known Winstein relationship,[18] the deviation is a direct measure of the assisted Fk_Δ rate constants (vide infra).

The large value of $\rho^* = -6.4$ deserves comment. Values of ρ^* for secondary alkyl solvolysis rates generally range from −2.5 to −3.5.[19] The considerably larger value of ρ^* in the present system is most likely due to the greater demand for stabilization of a vinyl cation as compared to a normal secondary carbonium ion.[7]

Correlation of Rate and Product Data. A number of salient features emerge from the data in Table II. In all cases there is more vinyl ether **8** and **9** and less allene, **10**, formed in the solvolysis of the E isomers **5** than in the reaction of the corresponding Z isomers **6**. The degree of stereospecificity is much higher for the product vinyl ethers in the E series, **5**, than for the corresponding Z series **6**. Within a series, the stereospecificity decreases as a function of substituent going from the p-CH_3 to the p-NO_2 group in both **5** and **6**. Moreover, the stereochemistry of the product vinyl ethers **8** is the same (retained) as the starting triflate **5**, but inverted (i.e, mostly **8** instead of **9**) in the case of **6**.

Table III. Rates of Reactions[a] of Vinyl Triflates at 75 °C in 97% TFE and Their σ^* Values

Vinyl triflate	k, s^{-1}	σ^*
$(CH_3)_2C{=}C(OTf)CH(CH_3)_2$ **12**	1.26×10^{-2}	−0.30
(E)-$CH_3CH{=}C(OTf)CH(CH_3)_2$ **13**	3.91×10^{-3}	−0.20
(E)-$CH_3CH_2CH{=}C(OTf)CH_2CH_3$ **14**	1.08×10^{-3}	−0.115
(E)-$CH_3CH{=}C(OTf)CH_2CH_3$ **15**	5.01×10^{-4}	−0.10
(E)-$(CH_3)_2CHCH{=}C(OTf)CH_3$ **16**	6.90×10^{-4}	−0.025
(E)-$CH_3CH_2CH{=}C(OTf)CH_3$ **17**	2.67×10^{-4}	−0.015
6a	1.04×10^{-5}	0.221
6b	9.06×10^{-6}	0.228
6c	4.60×10^{-6}	0.261
6d	1.50×10^{-6}	0.333
6e	5.94×10^{-6}	0.362
6g	7.28×10^{-8}	0.532
5a	4.34×10^{-3}	0.221
5b	1.57×10^{-3}	0.228
5c	3.04×10^{-4}	0.261
5d	4.41×10^{-5}	0.333
5e	5.89×10^{-6}	0.362
5g	5.15×10^{-7}	0.532

[a] Extrapolated where necessary from literature values; see text.

Table IV. Partitioning of Products and Reaction Rates of **5** in 97% TFE at 75 °C

Compd	k_s, s^{-1}	Rate enhanc. k_t/k_s	Fk_Δ, s^{-1}	% assist. path $\frac{Fk_\Delta}{k_t} \times 100$	% yield of ether **8** (retained confign)[a]
5a	7.24×10^{-6}	599	4.33×10^{-3}	99.8	
5b	6.69×10^{-6}	235	1.56×10^{-3}	99.4	98.0
5c	4.50×10^{-6}	68	3.00×10^{-4}	98.7	93.0
5d	1.52×10^{-6}	29	4.26×10^{-5}	96.6	
5e	1.00×10^{-6}	6	4.89×10^{-6}	83.0	
5g	8.19×10^{-8}	6	4.33×10^{-7}	84.1	52.4

[a] Product studies in anhydrous TFE at 85 °C, from Table II.

Finally using the Schleyer-Lancelot[20] method there is a good correlation between the percent of anchimerically assisted solvolysis as determined by kinetics and as measured by product stereospecificity, as shown in Table IV.

Mechanistic Considerations. We have previously shown[9] by means of deuterium labeling that there is extensive rearrangement in the solvolysis of **5c** in aqueous ethanol and some rearrangement in **6c**. In the present study, we have demonstrated by three different criteria that there is neighboring aryl participation in the solvolysis of the geometrically favorable trans coplanar *E* triflates **5**. The Hammett correlation of Figure 1 clearly demonstrates anchimeric assistance for **5** and neglecting[21] ground state differences, and differences in solvation of the resulting ions between **5** and **6**, the rate ratios of **5**/**6** give a semiquantitative measure of rate enhancements. At 75 °C this rate enhancement ranges from 7 for the p-NO_2 compound **5g** to 417 for the p-CH_3O isomer **5a**. The Taft σ^* correlation of Figure 2 demonstrates anchimeric assistance even more dramatically and also provides a quantitative measure of the rate enhancements in the solvolysis of the (*E*)-3-aryl-2-buten-2-yl triflates **5** that range from 6 for the p-NO_2 isomer **5g** to 599 for the p-CH_3O compound **5a**. In fact, these two independent measures of participation are in good agreement. The magnitudes of these rate enhancements are comparable to those observed for the 3-aryl-2-butyl system, in the most favorable and polar solvents.[5a,22]

Product studies provide further evidence for participation in **5**. Not only are there consistently more vinyl ether products **8** and **9** formed in the case of **5** than **6**, but the vinyl ether products are highly stereospecific. In all cases the vinyl ethers (**8** and **9**) resulting from **5** have retained "configuration", that is, **5** gives **8**, with a very high degree of stereoselectivity that ranges from 93.5% for the highly deactivated p-NO_2 isomer **5g** to 99.8% for the activated p-CH_3 isomer **5b**. Such high degree of stereoselectivity and retention of "configuration" can most readily be rationalized by neighboring aryl participation and formation of a vinylidene phenonium ion, **18**, in the solvolysis of **5**. Moreover, as seen in Table IV there is a good correlation between rate enhancement and product stereospecificity.

On the other hand, solvolysis of the (*Z*)-3-aryl-2-buten-2-yl triflates **6** results in much more allene, **10**, formation as well as "inverted" vinyl ether products with much lower stereoselectivity. Such "inverted" products are unlikely to result from the highly unfavorable[23] direct S_N2 displacement and are best explained[24] by formation of an open ion pair, **19**, that is partially protected from solvent capture by the departing triflate counterion. Similar inversion has been observed[27] in the solvolysis of other stereoisomeric triflates.

These results are best summarized and rationalized by the mechanism outlined in Scheme III. Control experiments have demonstrated that neither the starting pure isomeric vinyl triflates nor the pure isomeric vinyl ether products interconvert. Hence, in order to account for the large anchimeric assistance, as well as the high degree of product stereoselectivity (and rearranged products[9]) solvolysis of the geometrically favorable *E* triflates **5** must proceed predominantly, if not exclusively, by a vinylidene phenonium ion. The observed internal return[9] requires formation of an ion pair **18** which converts to **20** and hence into products. On the other hand, triflates **6** must ionize to an open linear vinyl cation pair **19** that can either lose a proton to give allene **10** or be preferentially captured by solvent on the side opposite the leaving group resulting in **8** and **9**. Ion **19**, as the triflate gegenion moves away and the initial unfavorable geometry is lost, may also convert to ion **20** accounting for the rearranged products observed[9] as well as perhaps for some of the stereoselectivity of the ether products.

Rate and product data, vide supra, predict that a minimum of 52.4% of the p-NO_2 isomer **5g**, a minimum of 93% of the parent compound **5c**, and a minimum of 98% of the p-CH_3 triflate **5b** must proceed through vinylidene phenonium ions. Participation by the p-nitrophenyl group is virtually unprec-

Scheme III. Mechanism of Reaction of (*E*)-3-Aryl-2-buten-2-yl, **5**, and (*Z*)-3-Aryl-2-buten-2-yl, **6**, Triflates

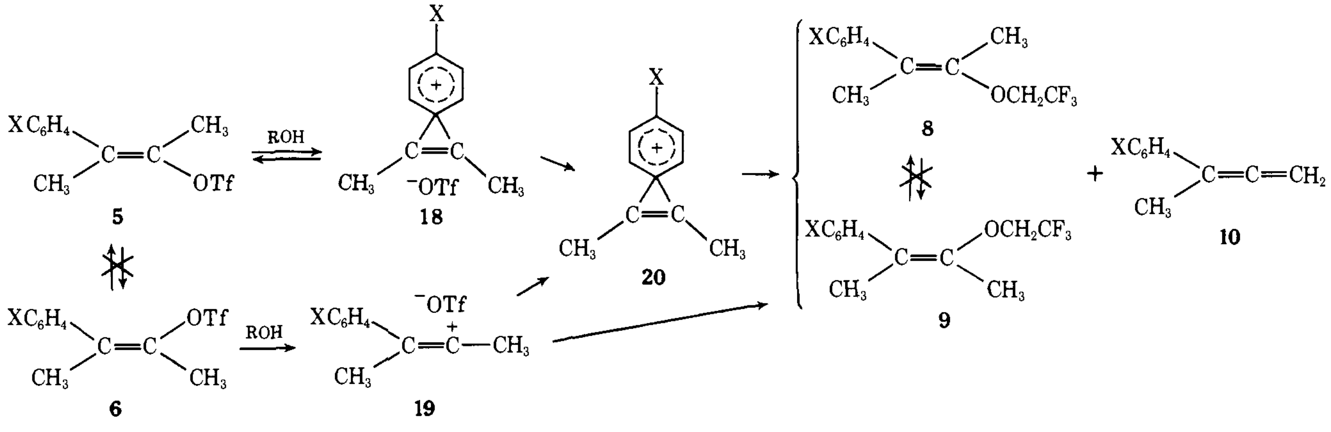


Table V. Comparison of Activation Entropies for the Solvolysis of **5** and **6**

$XC_6H_4(CH_3)C{=}C(OTf)CH_3$	$\Delta S^{\ddagger}$, eu[a] E/Z
X = p-CH_3O	−7.4/−16.9
p-CH_3	−8.4/−16.9
H	−9.6/−13.6
p-Cl	−4.2/−14.8
m-Cl	2.7/−11.8
p-CF_3	1.0/−9.9
p-NO_2	−21/−11.8

[a] At 25 °C in 97% TFE.

edented and once again reflects the greater need of stabilization of a vinyl cation as compared to a normal carbonium ion.

Further evidence for these mechanisms, at least in the case of the parent triflates **5c** and **6c**, is provided by the previously reported[9] kinetic deuterium isotope effects. Moreover, as shown in Table V, in accord with previous suggestions and observations[28] the activation entropies are more negative for the anchimerically unassisted solvolysis **6** than for their assisted counterparts, **5**. The only deviation is the p-NO_2 isomer, probably due to the large experimental error involved in the rate determination at the high temperatures required for reaction of these deactivated isomers.

It is instructive to compare the solvolytic behavior of the 3-aryl-2-buten-2-yl substrates with the triaryl vinyl systems, **21**, with various combinations of phenyl and p-anisyl groups,

$$(Ar)_2C{=}C(Ar)X \qquad (CH_3)_2C{=}C(OTf)CD_3$$

21, X = Br or Cl   **22**

extensively investigated by Rappoport and co-workers[29] and Lee and co-workers.[30] Very little, or no, aryl migration (~10%) was observed in any of the cases in acetic acid or aqueous ethanol, and the experimental results can all be accounted for by open unbridged ions or ion pairs. However, more recent results in TFE indicate substantial rearrangement and possible involvement of vinylidene phenonium ions.[31] Interestingly, no rearrangement was observed as well in the solvolysis of the simple trialkyl vinyl triflate, **22**, investigated[32] by means of deuterium labeling. This is as it should be, for the 2-aryl substituted vinyl cation is sufficiently stable and gains or needs no further stabilization from aryl participation and possible vinylidene phenonium ion involvement. Neither would the ion derived from **22** gain any stabilization from rearrangement as such methyl migration is degenerate in this case, and alkyl groups are not the best migrating groups in any event.

Hence, to date the only unambiguous examples of anchimeric assistance in vinyl cations are the work of Modena and co-workers[8] in the case of thiirenium ions **4** and the present work on 3-aryl-2-buten-2-yl triflates involving vinylidene phenonium ions **20**. Finally, Hoffmann and co-workers[33] have shown by means of molecular orbital arguments that spiroarenes or bridged ions of the type **20** are stable.

Experimental Section

General. All boiling and melting points are uncorrected. Melting points were taken in capillary tubes with a Thomas-Hoover melting point apparatus. Infrared spectra were taken with a Beckman IR5A and are reported in wavenumbers (cm^{-1}) calibrated to the 1602-cm^{-1} line of polystyrene. NMR were taken on a Varian A-60 or A-56/60 spectrometer and are reported in parts per million (δ) downfield from internal Me_4Si. Mass spectra was recorded on a Perkin-Elmer Model 270 analytical mass spectrometer. Preparative GC was carried out on a Varian-Aerograph 90P chromatograph and analytical GC on a Varian-Aerograph series 1200 chromatograph with flame ionization detector and equipped with an Autolab 6300 digital integrator. The following aluminum columns were used: A, 15 ft × 0.375 in., 15% SF-96 on 45/60 Chromosorb W; B, 10 ft × 0.25 in., 10% SF-96 on 60/80 Chromosorb W; C, 5 ft × 0.25 in., 10% SF-96 on 60/80 Chromosorb W; D, 12 ft × 0.125 in., 5% SF-96 on 90/100 Chromosorb W; E, 20 ft × 0.125 in., 5% SF-96 on 90/100 Chromosorb W; F, 10 ft × 0.125 in., 10% QF-1 on 60/80 Chromosorb G; G, 10 ft × 0.125 in., 10% Carbowax 20M on 60/80 Chromosorb G; H, 25 ft × 0.375 in., 20% FFAP on 30/60 Chromosorb W; T, 15 ft × 0.375 in., 15% QF-1 on 45/60 Chromosorb W. Weighings were carried out on Mettler balances H18, H20T, and M5SA. Microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of Ketones 7a, 7c, and 7d. The following general procedure was employed. To a round-bottom flask equipped with a magnetic stirring bar and a reflux condenser with a drying tube were added 6.0 g (0.045 mol) of phenylacetone (Aldrich) and 30 mL of 50:50 dry benzene and ether. To the stirred solution was added 2.22 g (0.05 mol) of a 54.3% oil dispersion of NaH over a period of 1 h. The mixture was refluxed for 4 h, then cooled to 0 °C and 6.4 g (0.045 mol) of CH_3I in 25 mL of dry ether added over a period of 10 min. The reaction mixture was stirred at room temperature for 8 h, then filtered and the filtrate washed with 20 mL of ether. The organic layer was shaken with 25 mL of water, separated, dried over $MgSO_4$, and filtered, and the solvent was removed with a rotary evaporator. The yellow residue was vacuum distilled to give 5.53 g (86%) of **7c**, bp 40-43 °C (0.3 mm). VPC analysis (column A) showed 97.5% of **7c** and 2.5% of 3-methyl-3-phenyl-2-butanone. Spectra for all ketones are reported in Table VI. Ketone **7a**: 0.12 mol of p-methoxyphenylacetone (Research Organic/Inorganic Chemical Corp.) gave 90% yield of **7b**, bp 74-78 °C (0.2 mm), 97% pure by GC. Ketone **7d**: p-chlorophenylacetone (Sapon Labs) gave **7d** in 60% yield, bp 70-71 °C (0.15 mm), 97% pure by GC.

Preparation of Ketones 7b, 7e, and 7f. In a three-neck round-bottom flask mounted with condenser, addition funnel, drying tube, and N_2 inlet were placed 100 mL of anhydrous ether and 3.2 g (0.46 mol) of 1 cm long ether-washed Li wire. The mixture was stirred as a solution of 35.6 g (0.208 mol) of p-bromotoluene in 100 mL of anhydrous ether was added dropwise over a period of 1 h maintaining a steady reflux. After stirring and refluxing for 2 h a solution of 15 g (0.208 mol) of 2,3-butylene oxide (Columbia Organic Chemicals) in 100 mL of anhydrous ether was added over a 45-min period with a resultant slow reflux. The reaction mixture was stirred for 8 h, followed by reaction of the excess Li with 10 mL of ethanol. Addition of a saturated NH_4Cl solution resulted in a clear ether layer that was separated, washed with 10% $NaHCO_3$ and H_2O, then dried over anhydrous $MgSO_4$ and filtered, and the solvent was evaporated on a rotary evaporator. The residual 25 g of light yellow oil showed by GC 10% of starting material and 90% alcohol. This oil was reacted without further purification with chromic acid.[34] To the stirred solution of the alcohol in 60 mL of ether

Table VI. Spectral Properties of 3-Aryl-2-butanones, **7**, $XC_6H_4CH(CH_3{}^{\beta})COCH_3{}^{\alpha}$

	NMR (CCl_4, δ, internal Me_4Si, 0.0)					IR, cm^{-1}		
Compd	α-CH_3	β-CH_3 (^5J, Hz)	CH (^5J, Hz)	ArH	Other	C=O	C=C	Other
7a	1.26	1.88 (7.0)	3.53 (7.0)	6.63, 6.95	3.65 (OCH_3)	1700	1605	1242, 1034 (C-O)
7b	1.30	1.93 (7.0)	3.63 (7.0)	7.12 (m)	2.30 (CH_3)	1706		
7c	1.29	1.90 (7.0)	3.57 (7.0)	7.08 (m)		1709	1597	
7d	1.30	1.93 (7.0)	3.55 (7.0)	7.03, 7.22		1709	1600	835 (C-Cl)
7e	1.33	1.97 (7.0)	3.65 (7.0)	7.17 (m)		1709	1592	846 (C-Cl)
7f	1.37	2.02 (7.0)	3.82 (7.0)	7.37, 7.57		1724	1621	1329, 1128 (CF_3)
7g	1.40	2.05 (7.0)	3.95 (7.0)	7.45, 8.15		1712	1603	1515, 1348 (NO_2)

Table VII. Spectral Properties of 3-Aryl-2-buten-2-yl Triflates **5** and **6**, $XC_6H_4(CH_3^{\beta})C{=}C(OSO_2CF_3)CH_3^{\alpha}$

	NMR (CCl_4, δ, internal Me_4Si, 0.0)					IR, cm^{-1}			
Compd	α-CH_3	β-CH_3	^5J, Hz, ±0.1	ArH	Other	C=C	C=C(Ar)	OSO_2CF_3	Other
5a	2.11	2.05	1.50	7.05, 7.38	3.83 (OCH_3)	1681	1610	958, 894	1181, 1035 (OCH_3)
5b	2.08	2.02	1.42	7.17 (s)	2.33 (CH_3)	1681	1608	956, 897	
5c	2.08	1.97	1.43	7.38 (m)		1686	1605	956, 896	
5d	2.10	2.02	1.42	7.13, 7.43		1669	1603	959, 895	833 (CCl)
5e	2.12	2.02	1.47	7.23 (m)		1686	1600	964, 907	815 (CCl)
5f	2.17	2.06	1.35	7.50, 7.84		1681	1610	958, 897	1116 (CF)
5g	2.15	2.02	1.40	7.73, 8.08		1684	1603	961, 902	1519, 1351 (NO_2)
6a	2.11	2.24	1.1	7.03, 7.37	3.83 (OCH_3)	1680	1610	973, 883	1181, 1035 (OCH_3)
6b[a]	2.04	2.19	0.95	7.07 (s)	2.33 (CH_3)	1684	1605	972, 881	
6c	2.08	2.22	1.0	7.32 (m)		1686	1602	974, 883	
6d	2.05	2.25	0.95	7.17, 7.38		1686	1595	973, 879	833 (CCl)
6e	2.07	2.22	0.90	7.32 (m)		1680	1595	975, 983	815 (CCl)
6f	2.13	2.28	0.95	7.48, 7.81		1686	1618	975, 882	1116 (CF_3)
6g	2.13	2.25	0.95	7.43, 8.23		1684	1602	975, 883	1519, 1351 (NO_2)

[a] NMR spectrum taken neat.

was added 75 mL of a solution of 20 g of $Na_2Cr_2O_7{\cdot}2H_2O$ and 27.2 g of 97% H_2SO_4 diluted to 100 mL over a 15-min period. The mixture was stirred for 1.5 h, then 200 mL of ether added, the organic layer separated, and the aqueous layer extracted three times with 50 mL of ether. The combined ether layer was washed twice with saturated NaCl solution, dried over anhydrous $MgSO_4$, and filtered and the solvent was removed with a rotary evaporator. The residue was vacuum distilled giving 48% of **7b,** bp 51–56 °C (0.075 mm). Ketone **7e** was prepared in a similar manner from 0.135 mol of *m*-chlorobromobenzene (Matheson Coleman and Bell) giving a 30% yield of product, bp 60–64 °C (0.15 mm). Ketone **7f** was prepared in a similar manner from 0.114 mol of *p*-trifluoromethylbromobenzene (PCR Inc.) to give 39% of product, bp 64–70 °C (0.2 mm).

Preparation of Ketone 7g. To a 3-L three-neck flask, equipped with an addition funnel, condenser with drying tube, and a fast mechanical stirrer, were added 13.1 g (0.54 mol) of dry Mg prewashed in acetone, 0.5 mL of CCl_4, and 12.5 mL of absolute ethanol, resulting in a vigorous reaction. Anhydrous ether (188 mL) was slowly added to the reaction mixture over 5 min. To this solution were added 86.3 g (0.54 mol) of diethyl malonate in 63 mL of anhydrous ether and 50 mL of absolute ethanol over a period of 30 min with resultant refluxing. The mixture was stirred and refluxed for an additional 3 h, then freshly prepared *p*-$NO_2C_6H_4CH_2COCl$ (from 96 g, 0.53 mol, of *p*-$NO_2C_6H_4CH_2COOH$ and 200 g, 2.0 mol, of $SOCl_2$) in 400 mL of anhydrous ether was added over 45 min, then the entire reaction mixture was refluxed for an additional 2 h. To the cooled mixture was added 250 mL of 5% H_2SO_4, the layers were separated, and the ether layer was washed with H_2O, concentrated, and mixed with 150 mL of glacial acetic acid, 19 mL of 97% H_2SO_4, and 100 mL of distilled H_2O in a 500-mL round-bottom flask with condenser. This reaction mixture was refluxed for 6 h at 90 °C and at 110 °C for 4 h until the evolution of CO_2 dropped off. The reaction mixture was cooled in an ice-water bath, the crystallized product was filtered, washed with H_2O, and recrystallized from EtOH-H_2O, and the residue was vacuum distilled, bp 130–131 °C (0.2 mm), giving a total of 65 g (68%) of *p*-nitrophenylacetone: mp 59.5–61.5 °C (lit.[35] mp 62 °C); IR (Nujol) 1718 (C=O), 1608 (C=C), 1513 and 1346 cm^{-1} (NO_2). Some of this *p*-nitrophenylacetone (10 g, 0.056 mol) was alkylated with difficulty with CH_3I and 0.14 mol of NaH as above, but the solvent was 125 mL of anhydrous DMF and 30 mL of anhydrous ether, giving 5.6 (52%) of **7g.**

No attempt was made in any of the above preparations to either maximize yields or to completely purify the product ketones as final purification was achieved by preparative GC of the desired vinyl triflates **5** and **6.** The spectral properties of ketones **7** are listed in Table VI.

General Procedure for the Preparation of Vinyl Triflates 5 and 6.[10] **Pyridine Method, A.** 3-Phenyl-2-butanone (**7c**, 1.48 g, 10 mmol) and 0.87 g (11 mmol) of dry pyridine were mixed in an Erlenmeyer flask with a wired-on serum cap. The mixture was cooled to −70 °C in a dry ice-2-propanol bath and 2.82 g (10 mmol) of triflic anhydride [from CF_3SO_3H (3M Co.) + P_2O_5] was injected with a syringe over ~1 min while the mixture was vigorously shaken. The reaction mixture was shaken and gradually warmed to room temperature and 5 mL of CCl_4 was added. The mixture was allowed to stand at room temperature (2–3 days) until it became dark red-brown and free flowing (in no case were products observed prior to a dark color formation and a tarry looking reaction mixture). The mixture was shaken after the addition of 15 mL of CCl_4 and filtered, and the solid was dissolved in ice-cold H_2O and extracted twice with 20 mL of CCl_4. The combined CCl_4 layer was washed with ice-cold H_2O, dried over anhydrous $MgSO_4$, and filtered and the solvent evaporated on a rotary evaporator. The residue was vacuum distilled, yielding 1.6 g (53%) of product, bp 52–58 °C (0.3 mm). GC analysis (column A, 160 °C) showed 8.3% starting ketone, 28.6% 3-phenyl-1-buten-2-yl triflate, 46.7% **5c,** and 16.3% **6c.** The pure triflates **5c** and **6c** were collected by preparative GC on column A, 160 °C. For **6c:** Anal. Calcd for $C_{11}H_{11}SO_3F_3$: C, 47.14; H, 3.95; S, 11.44. Found: C, 48.25; H, 4.22; S, 11.09. Spectral properties of all vinyl triflates are reported in Table VII.

P_2O_5 Method, B. 3-Phenyl-2-butanone (**7c**, 1.48 g, 10 mmol), 3 mL of dry CCl_4, and 1.56 g (11 mol) of P_2O_5 were placed in an Erlenmeyer flask which was wired with a serum cap. The mixture was cooled to −70 °C and 2.82 g (10 mmol) of triflic anhydride added with a syringe while the mixture was shaken. The reaction mixture was kept at 10 °C for 12 h and at room temperature for an additional 12 h until intensely dark in color. The mixture was dissolved in 20 mL of CCl_4 and filtered, the CCl_4 layer was washed with ice-cold H_2O and saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered, and the solvent was evaporated on a rotary evaporator. The residue was vacuum distilled giving 0.92 g of product which upon GC analysis (column A, 160 °C) showed 24% starting ketone, 15% of **6c**, and 61% of **5c** but no 3-phenyl-1-buten-2-yl triflate. The desired vinyl triflates, **5c** and **6c**, were collected by preparative GC as in method A.

Vinyl Triflates 5a and 6a. Prepared by method A from ketone **7a** in 26% yield, bp 79–81 °C (0.15–0.2 mm), isomers **5a** and **6a** were collected together on column C at 130 °C with on-column injections of a 30% CCl_4 solution. Pure **6a** was obtained by kinetic separation of 1.0 g of the mixture in 100 mL of 80% EtOH and 1.1 equiv of pyridine (2 h, 75 °C), extraction of the products with CCl_4, concentration, and preparative GC on column C at 140 °C.

Vinyl triflates 5b and 6b were prepared by method A from ketone **7b** in 57% yield, bp 52–55 °C (0.075 mm). GC on column C at 140 °C indicated 60% **5b,** 20% **6b,** and 20% 3-*p*-tolyl-1-buten-2-yl triflate. Purification was by preparative GC with on-column injections of 30% CCl_4 solutions on column C at 140 °C.

Vinyl Triflates 5d and 6d. Ketone **7d** (15 mmol) gave 2.4 g (52%) of triflates, bp 72–74 °C (0.05 mm), by method A. GC on column A at 180 °C indicated 50% of **5d,** 20% of **6d,** and 30% of 3-(*p*-chlorophenyl)-1-buten-2-yl triflate. Isomers were separated by preparative GC on column A at 180 °C.

Vinyl Triflates 5e and 6e. Ketone **7e** (9.3 mmol) gave 1.5 g (63%) of triflates by method A after 15 days at room temperature, bp 62–66 °C (0.1 mm). GC analysis on column A at 190 °C indicated 60% of

Table VIII. Spectral Properties of the Product Vinyl Ethers **8** and **9**, $XC_6H_4(CH_3{}^{\beta})C{=}C(OCH_2CF_3)CH_3{}^{\alpha'}$

	NMR (CCl_4, δ, internal Me_4Si, 0.0							IR, cm^{-1}		
Compd	α-CH_3	^5J, Hz	β-CH_3	CH_2CF_3	^{HF}J, Hz	ArH	Other	C=C	ArC=C	Other
8b	1.75	1.5	1.93	4.05	8.4	7.02 (m)	2.30 ($ArCH_3$)	1667		1282, 1205, 1163, 971
8c	1.73	1.43	1.91	3.95	8.4	6.97 (m)		1672	1608	1282, 1206 1163, 971
8g	1.83	1.35	2.00	4.1.7	8.5	7.39, 8.23		1667		1520, 1351, 1285, 1166, 973
9b	1.93		1.93	3.70	8.5	7.02 (m)	2.30 ($ArCH_3$)	1671	1604	1282, 1205, 1161, 969
9c	1.90		1.90	3.53	8.2	7.07 (m)		1669	1602	1283, 1208, 1166, 974
9c[a]	1.65	0.9	1.72	3.39	8.5					
9g	2.03		2.03	3.80	8.6	7.35, 8.20		1668	1603	1521, 1352, 1286, 1167, 972
9g[a]	1.50	0.96	1.56	3.37	8.6					

[a] NMR taken in C_6H_6.

Table IX. Spectral Properties of the Product Allenes **10**, $XC_6H_4C(CH_3){=}C{=}CH_2$

	NMR (CCl_4, δ, internal Me_4Si, 0.0)					IR, cm^{-1}	
Compd	CH_3	CH_2	^5J, Hz	ArH	Other	C=C=C	Other
10b	2.06	4.97	3.0	7.02, 7.21	2.31 ($ArCH_3$)	1934	1066, 1020, 864, 852
10c	2.03	4.88	3.0	6.97		1934	1067, 1028, 879, 852
10g	2.06	5.18	3.0	7.48, 8.22		1942	1493, 1348, 1069, 1017, 858

5e, 15% of **6e**, and 25% of 3-(*m*-chlorophenyl)-1-buten-2-yl triflate that were separated by preparative GC.

Vinyl Triflates 5f and 6f. Ketone **7f** (7.6 mmol) gave after 7 days at room temperature by method B 39% of product, bp 65-75 °C (0.25 mm). GC indicated (column A, 170 °C) 90% of **5f** and 10% of **6f**; the isomers were separated by preparative GC with these VPC conditions.

Vinyl Triflates 5g and 6g. Ketone **7g** (17.5 mmol) gave by method A after 2 days at room temperature 55% of product, bp 85-95 °C (0.03-0.04 mm), or 45% yield by method B after 24 h at room temperature. GC on column A at 200 °C with on-column injection of 30% CCl_4 solution indicated 80% of **5g** and 20% of **6g** that were collected by preparative GC.

In all of the above cases, vinyl triflates **5** and **6** were characterized by NMR and IR of GC-pure samples as given in Table VII. *E* and *Z* isomers were assigned on the basis of the long-range coupling between the two methyl groups which as expected[36,37] were in all cases larger for the *E* isomers **5**, ^5J = 1.43 ± 0.07 Hz, than for the corresponding *Z* isomers **6**, ^5J = 0.97 ± 0.05 Hz.

Kinetic Methods. Commercial (Specialty Chemical Corp.) 2,2,2-trifluoroethanol was distilled from P_2O_5 through a Vigreux and stored in a glass-stoppered flask in a P_2O_5-dried desiccator. The solvent for kinetics was diluted to 97% by weight TFE with distilled H_2O and stored in a separatory funnel with a three-way stopcock connected to a drying tube. Solvolysis rates were determined conductometrically with a Heath Servo-recorder Model EU-20B modified with a homebuilt self-balancing Wheatstone bridge. Conductance cells were made of platinum plates sealed in potash lead glass. The platinum plates were treated prior to each set of runs as follows: cleaned with a 5% H_2SO_4 solution with a 300-mA current applied from a Hewlett-Packard 6216A power supply and the polarity reversed every 15 min for 2 h; plated with a 3% solution of chloroplatinic acid with a platinum wire at 300 mA, then recleaned as above. After treatment, the cells were not exposed to air or the platinum plates allowed to dry. Rates were done in a Neslab Instruments constant temperature bath capable of holding the temperature to ±0.02 °C. Beckmann thermometers, which were calibrated by NBS standard thermometers, were used to determine the temperatures. Kinetic measurements were done on a stock solution containing 0.6 μL of triflate and 1.0 μL of pyridine in 10 mL of solvent with the conductance cells sealed and totally immersed in the temperature bath. The rates reported in Table I are averages of two to six determinations. In all cases, good first-order rates were observed for more than 95% reaction. Rate constants were calculated using a nonlinear least-squares computer program LSKIN-1.[38] Data in Figures 1 and 2 were plotted using a Hewlett-Packard 9810A calculator equipped with a Hewlett-Packard 9862A plotter.

Isolation and Characterization of Solvolysis Products. Generally 1.0-1.5 mmol of the appropriate mixture of *E* and *Z* triflates was solvolyzed in 10 mL of anhydrous TFE buffered with 1.1-2.0 equiv of pyridine for 5-8 half-lives. After reaction, the solvent was distilled off at atmospheric pressure, the residue washed with several 2-mL portions of CCl_4, the solvent evaporated, and the products collected by preparative GC: for ethers **8b** and **9b**, column A at 160 °C; for ethers **8c** and **9c**, column A at 160 °C; for **8g** and **9g** the two isomers could not be completely separated, so they were collected and analyzed together on column C at 140-150 °C. Allenes **10b** and **10c** were prepared by reacting ~0.5 mmol of the triflates with 1.0 mmol of Et_3N in 1.0 mL of THF at 100 °C for 10-24 h and the allenes collected by preparative GC. Allene **10g** was isolated from the above solvolysis mixture itself. In all cases the products were characterized by spectral means with the results given in Table VIII for the vinyl ether products and Table IX for the allene products. As in the case of the starting triflates, geometrical isomers of the vinyl ether products were assigned on the basis of long-range coupling[36,37] which in all cases was larger for the *E* isomers **8**, $^5J \simeq$ 1.4 Hz, than the corresponding *Z* isomers **9**, $^5J \simeq$ 0.9 Hz. In all cases the vinyl ether products were found to be sensitive to moisture, so care was taken to keep them dry.

Product Studies. The weighed appropriate triflates were dissolved in enough anhydrous TFE, together with 1.1-2.0 equiv of pyridine and an appropriate internal standard (n-C_{10}-n-C_{14}), to make a 0.01-0.02 M solution and placed in a flame-dried ampule. The ampules were stoppered, then sealed at 25 °C (in order not to condense and pick up H_2O by cooling) and immersed in the constant temperature bath. After reaction, the ampules were cooled to room temperature, cracked open, and immediately stoppered with a serum cap and wrapped with Parafilm. The samples were analyzed immediately by direct on-column injection on columns D and E. Runs were carried out in duplicate and each analyzed four to five times. Standards were made up from authentic samples (previously isolated by preparative GC and identified by spectral means) and analyzed (four to five times) side by side with the product runs. The results are given in Table II.

Control Studies. Proper controls were carried out to show that all of the products were stable to both the reaction and analyses conditions employed, as well as to ascertain that there was no interconversion of the starting pure isomeric vinyl triflates.

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References and Notes

(1) Part 12 in a series on vinyl cations. Part 11: P. J. Stang and R. J. Hargrove, *Tetrahedron*, **32**, 37 (1976).

(2) (a) Abstracted in part from the Ph.D. Thesis of T. E. Dueber, The University of Utah, 1974; (b) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26–31, 1973, Abstracts, No. ORGN-65.

(3) Inter alia: T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper & Row, New York, N.Y., 1976; J. M. Harris and C. C. Wamser, "Fundamentals of Organic Reaction Mechanisms", Wiley, New York, N.Y., 1976; C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969; J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968.

(4) Inter alia: A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962; E. R. Thornton, "Solvolysis Mechanisms", Ronald Press, New York, N.Y., 1964; D. Bethell and V. Gold, "Carbonium Ions", Academic Press, New York, N.Y., 1967.

(5) For reviews and leading references see (a) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", Vol III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972; (b) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965; (c) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964).

(6) D. J. Cram, *J. Am. Chem. Soc.*, **70**, 4244 (1948); **71**, 3863, 3875 (1949); **74**, 2129, 2137, 2149 (1952).

(7) For reviews and leading references see (a) L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975); (b) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); (c) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971).

(8) G. Modena et al., *Chem. Commun.*, 1363, 1676 (1968); 1520 (1969); 1325 (1971); *Tetrahedron Lett.*, 4039 (1968); *J. Chem. Soc. C*, 2617, 2621, 2625 (1970); 374, 381, 1569, 1700 (1971).

(9) A preliminary report on the parent system **5c** and **6c** has appeared: P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2683, 2686 (1973).

(10) T. E. Dueber et al., *Angew. Chem., Int. Ed. Engl.*, **9**, 302 (1970); P. J. Stang and T. E. Dueber, *Org. Synth.*, **54**, 79 (1974).

(11) (a) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (b) W. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Malakofsky, and M. N. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969).

(12) P. J. Stang, R. J. Hargrove, and T. E. Dueber, *J. Chem. Soc., Perkin Trans. 2*, in press; R. J. Hargrove, Ph.D. Thesis, The University of Utah, 1974.

(13) R. W. Taft, Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956.

(14) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *J. Am. Chem. Soc.*, **96**, 1100 (1974).

(15) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(16) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4294 (1969).

(17) G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworth, London, 1961.

(18) A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968); E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

(19) W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962); P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. H. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965).

(20) P. v. R. Schleyer and C. J. Lancelot, *J. Am. Chem. Soc.*, **91**, 4297 (1969).

(21) We have to date been unable to find conditions under which any of the isomeric vinyl triflates **5** and **6** could be equilibrated. However, it is unlikely that such an equilibrium would be far from unity. Furthermore, the preponderance of the *E* isomer over the corresponding *Z* isomer in the formation of these triflates, presumably under thermodynamic conditions,[10] would indicate that the trans isomers **5** may, in fact, be more stable. It is even more difficult to assess transition state differences between **5** and **6** due to hindrance to leaving group departure or differential solvation. However, these effects should remain relatively constant as one moves down a series of substituents and, hence, it is extremely unlikely that they alone could account for the large rate ratios observed.

(22) H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, **91**, 4289 (1969); **93**, 5765 (1971); H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970).

(23) D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, **93**, 1953 (1971); R. H. Summerville and P. v. R. Schleyer, *ibid.*, **94**, 3629 (1972).

(24) Linear vinyl cations with two different β substituents possess diastereotopic faces[25] and ipso facto must be captured by solvent at different rates, resulting in unequal amounts of isomeric products (in the present case differing ratios of **8** and **9**). However, a priori it is difficult to predict which isomer would be favored and by how much. Steric arguments buttressed by the use of *A* values ($C_6H_5 = 3.0$, $CH_3 = 1.7$, $CH_3CH_2O \simeq CF_3CH_2O = 0.9$)[26] would predict a preference for cis solvent capture and the dominance of **9**, contrary to the observed experimental results in Table II.

(25) For a discussion of stereoisomeric relationships, see K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967); K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, New York, N.Y., 1965.

(26) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(27) T. C. Klarke, D. R. Kelsey, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 3626 (1972); R. H. Summerville and P. v. R. Schleyer, *ibid.*, **96**, 1110 (1974); T. C. Clarke and R. G. Bergman, *ibid.*, **96**, 7934 (1974).

(28) C. J. Lancelot and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291 (1969); J. E. Nordlander and W. E. Deadman, *ibid.*, **90**, 1590 (1968); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(29) For a review and leading references, see Z. Rappoport, *Acc. Chem. Res.*, **9**, 265 (1976); Z. Rappoport, E. Noy, and Y. Houminer, *J. Am. Chem. Soc.*, **98**, 2238 (1976).

(30) C. C. Lee et al., *Can. J. Chem.*, **54**, 604 (1976); **53**, 314, 320 (1975); **52**, 2679 (1974).

(31) Y. Houminer, E. Noy, and Z. Rappoport, *J. Am. Chem. Soc.*, **98**, 5632 (1976).

(32) M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Am. Chem. Soc.*, **92**, 3802 (1970).

(33) R. Hoffmann, A. Inamura, and G. D. Zeiss, *J. Am. Chem. Soc.*, **89**, 5215 (1967).

(34) H. C. Brown, C. P. Garg, and K. T. Liu, *J. Org. Chem.*, **36**, 387 (1971).

(35) C. G. Overberger and H. Biletch, *J. Am. Chem. Soc.*, **73**, 4880 (1951).

(36) P. Laszlo and P. J. Stang, "Organic Spectroscopy; Principles and Application", Harper & Row, New York, N.Y., 1971.

(37) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); G. P. Newsroff and S. Sternhell, *Tetrahedron Lett.*, 6117 (1968).

(38) D. F. DeTar and C. E. DeTar, "Computer Programs for Chemistry", Vol. I, W. A. Benjamin, New York, N.Y., 1969.