

Stability–Reactivity Relation on the Reaction of β,β -Disubstituted Vinyl Cations with Ethanol

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A family of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations has been generated by the laser flash photolysis of the corresponding vinyl bromides, and the rates of reactions of the cations with ethanol in acetonitrile have been measured at 25 °C. The observed rate constants differ greatly depending on the substituents, ranging from $3.05 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ to $8.18 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. The thermodynamic stabilities of the vinyl cations have been estimated by means of ab initio MO calculations for model compounds, which reveals that their stability is almost unaffected by β,β -dialkyl substituents. In the present system, therefore, the stability–reactivity relation, in which a less stable cation is expected to show higher reactivity, breaks down. Several model transition structures have been considered in the MO calculations, and the results indicate that the β substituents can move away from the incoming nucleophile to avoid steric congestion but that there still exists a large steric repulsion in the transition state. The calculations indicate that the reactivity of the vinyl cations is primarily controlled by this steric effect, which is the reason for the breakdown of the stability–reactivity relationship.

The relationship between reactivity and selectivity is a well-known concept in organic chemistry. In relation to this concept, Ritchie reported 20 years ago that the relative rates of reactions of stable carbocations with a series of nucleophiles were independent of the reactivity of the cations.^{1,2} Thus, the reactivity differences of stable cations such as crystal violet and *p*-nitrobenzenediazonium ion in reactions with a large variety of nucleophiles ranging from the very reactive MeO^- to the less reactive H_2O were independent of the cation stabilities. These findings have cast serious doubt on the generality of the reactivity–selectivity relationship. Recent reports by Mayr support this conclusion.³ It should be noted, however, that there is an apparently similar but different concept of organic reactivities, the stability–reactivity relationship, in which a more stable cation is considered to react more slowly. In the above examples, the reactivity–selectivity principle breaks down, but the stability–reactivity relationship always holds.

Carbocations generated via solvolytic reactions are normally highly unstable, and the reactions of the cation intermediates with solvent or other nucleophiles are not well elucidated since they are too fast to follow by conventional methods. Reactivities of such unstable cations remain to be determined. Laser flash photolysis is one of the techniques that can be used to generate unstable cationic species in solution and thus allows the study of such reactions of the cations with nucleophiles.^{4–7}

In the case of benzylic cations, laser flash photolysis has shown that a more stable cation reacts with a

nucleophile more slowly.^{4,5} Thus, the stability–reactivity relation holds. For example, the bis(methoxyphenyl)-methyl cation decomposes in acetonitrile/water (1:2 v/v) with a rate constant of 10^5 s^{-1} , which is considerably faster than the corresponding rate for the tris(methoxyphenyl)methyl cation (10^1 s^{-1}).⁴ Similarly, the α -phenylethyl cation, which is 4.9 kcal/mol less stable than the cumyl cation,⁸ reacts with MeOH 10 times faster in HFIP (4.3×10^7 vs $4.1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$).⁵

Stabilities of α -phenylvinyl and benzylic cations are known to differ only slightly in the gas phase.^{8,9} On the basis of heats of formation data compiled in the literature,¹⁰ the intrinsic stability of the vinyl cation is calculated (eq 1, in kcal/mol) to be between those of



methyl and ethyl cations, i.e., 313 (R = CH_3), 287 ($\text{H}_2\text{C}=\text{CH}$), 271 (CH_3CH_2), 251 ($(\text{CH}_3)_2\text{CH}$), and 234 ($(\text{CH}_3)_3\text{C}$). This is true not only for these unstable aliphatic carbocations but also for the relatively stable benzylic cations. The relative stabilities (in kcal/mol) of α -phenyl-substituted carbocations determined by ion cyclotron resonance mass spectrometry have been reported to decrease in the order $\text{PhC}(\text{CH}_3)_2^+$ (0) > $\text{PhCH}(\text{CH}_3)^+$ (6) > $\text{PhC}(\text{=CH}_2)^+$ (8) > PhCH_2^+ (13).^{8,9} Thus, the stability of α -arylvinyl cations is similar to that of benzylic cations. In the present study, we have generated a family of β,β -disubstituted vinyl cations from the corresponding bromides by the laser flash technique and have measured the rates of the reactions of the cations with ethanol (eq 2). Ab initio molecular orbital calculations were also carried out for the cations, protonated

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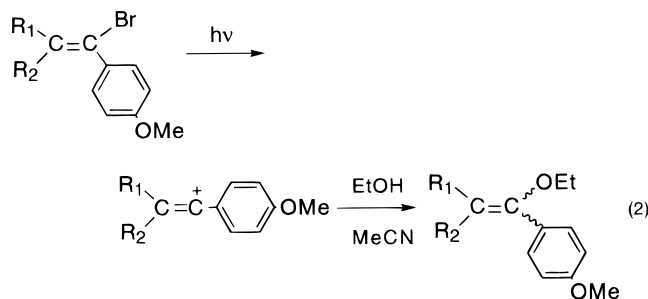
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alcohols, and model transition structures in order to obtain insight into factors controlling reactivity in the vinylic system.

Experimental Results and Calculations

Acetonitrile solutions containing β,β -disubstituted α -(*p*-methoxyphenyl)vinyl bromides and EtOH at varying concentrations were irradiated in a rectangular quartz cell with a 5 ns laser flash of 266 nm light. Concentrations of the bromides were $(0.65\text{--}1.7) \times 10^{-5}$ mol/L. The photolysis of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl bromides resulted in the formation of transient optical absorption spectra characteristic of substituted vinyl cations having absorption maxima around 350 nm.^{11,12} The decay of this transient optical absorption was measured at $\lambda = 340$ nm in the presence of excess EtOH in acetonitrile, and in all cases the decay conformed to pseudo-first-order kinetics as shown in Figure 1. Second-order rate constants were calculated according to eq 3, where k_0 is the decay rate constant obtained in the absence of EtOH. The kinetic plots are illustrated in Figure 2, and rate constants are listed in Table 1.

$$k_{\text{obsd}} = k_0 + k_2[\text{EtOH}] \quad (3)$$

Ab initio MO calculations were carried out to clarify the origin of the effect of β -substituents on the reactivity of the vinyl cations with EtOH. In the model chosen for the calculation, the EtOH nucleophile and the methoxyphenyl group of the cations were replaced by H_2O and by H or Ph, respectively, for simplicity. Vinyl cations have the special conformational characteristic that the vacant p orbital of the cation center lies in the same plane as the β substituents. Therefore, in the model transition states OH_2 was located in the plane of the vinyl moiety and the $\text{C}_\alpha\text{--O}$ bond lengths were fixed at different values. Thus, the calculations were carried out with three coordinates fixed (the $\text{C}_\beta\text{--C}_\alpha\text{--O}$ angle at 90.0° , the $\text{O--C}_\alpha\text{--C}_\beta\text{--R}_1$ dihedral angle at 0.0° , and the $\text{C}_\alpha\text{--O}$ bond length at $R_{\text{C--O}}$ Å) and other coordinates optimized. Three sets of model transition states (TS1, TS2, and TS3) in which $R_{\text{C--O}}$ was 2.0, 2.5, and 2.7 Å, respectively, were considered. All structures were optimized without any symmetry constraint at the HF/3-21G level of theory by using the Gaussian 92 program.¹³ In Table 2 are shown the structures of the model transition states, cations, and

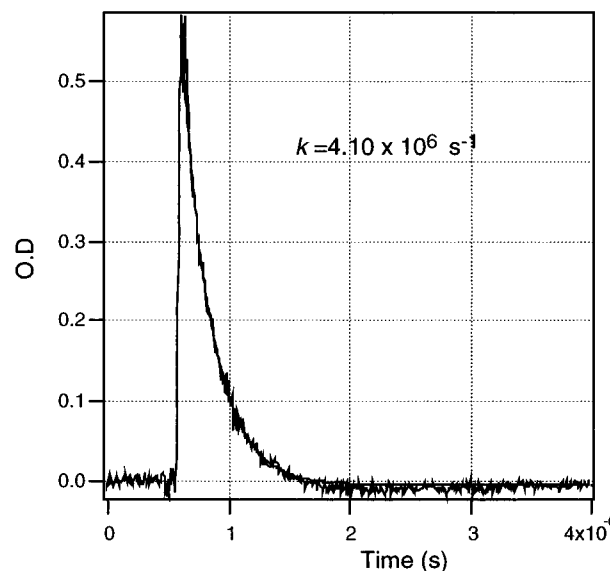


Figure 1. Decay of β,β -dimethyl- α -(*p*-methoxyphenyl)vinyl cation at 340 nm at 25°C .

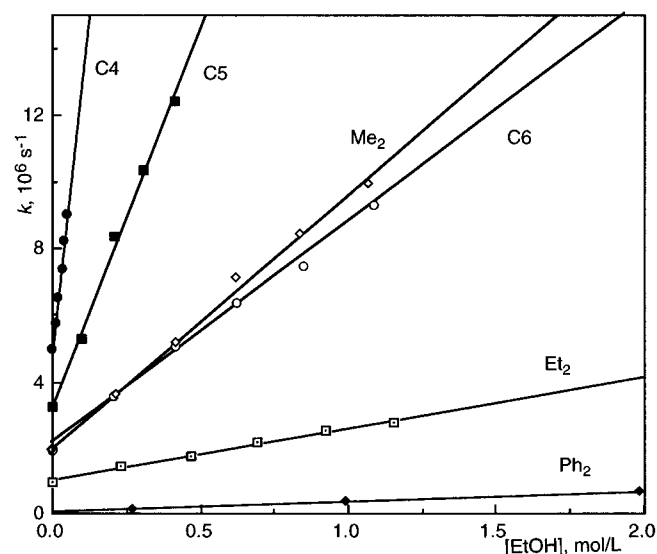


Figure 2. First-order rate constants (s^{-1} , 25°C) for the decay of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations as a function of ethanol concentration in acetonitrile.

Table 1. Second-Order Rate Constants of the Reaction of β,β -Disubstituted α -(*p*-Methoxyphenyl)vinyl Cations with Ethanol in Acetonitrile at 25°C

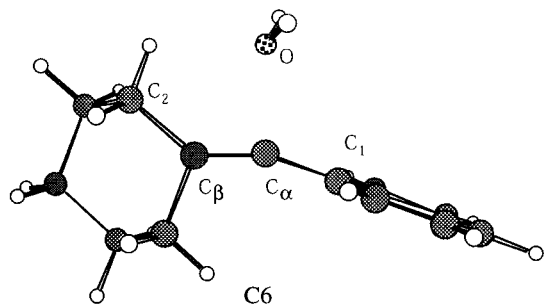
substituent		rate constants	
abbrev	R_1, R_2	k_0 (s^{-1})	k_2 ($\text{L mol}^{-1} \text{s}^{-1}$)
C4	$-(\text{CH}_2)_4-$	4.98×10^6	8.18×10^7
C5	$-(\text{CH}_2)_5-$	3.23×10^6	2.27×10^7
C6	$-(\text{CH}_2)_6-$	1.91×10^6	7.62×10^6
Me ₂	Me, Me	1.90×10^6	9.35×10^6
Et ₂	Et, Et	9.57×10^5	1.67×10^6
Ph ₂	Ph, Ph	5.65×10^4	3.05×10^5

protonated vinyl alcohols. The calculated energies are summarized in Table 3. The level of calculations is rather low because the study required calculations for vinyl cations that had one phenyl group at the α and two phenyl groups at the β position, which made calculations at a higher level impractical. However, the study compares only the variation of energies of vinyl cations, model transition structures, and the protonated vinyl alcohol products for a series of substituted substrates.

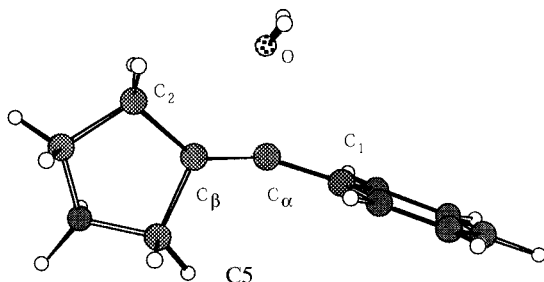
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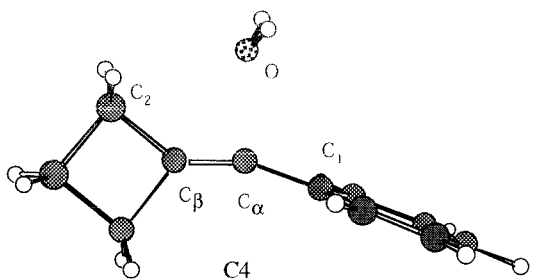
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Table 2. Geometrical Parameters of Cations, Model Transition Structures, and Protonated Vinyl Alcohols^a

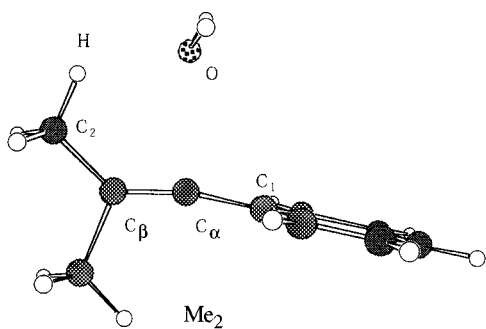
	OC _α	C _α C _β	C _β C ₂	C _α C ₁	OC _α C _β	C _α C _β C ₂	C _β C _α C ₁
cation		1.274	1.535	1.364		122.2	180.0
TS3	2.7	1.276	1.519	1.380	90.0	134.7	171.4
TS2	2.5	1.278	1.516	1.385	90.0	136.7	169.0
TS1	2.0	1.297	1.512	1.413	90.0	138.6	160.3
ROH ₂	1.571	1.310	1.511	1.469	114.4	126.3	136.0



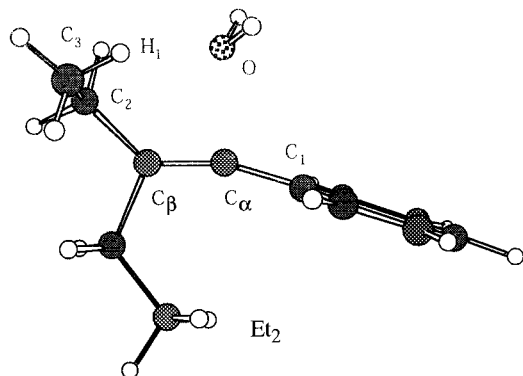
	OC _α	C _α C _β	C _β C ₂	C _α C ₁	OC _α C _β	C _α C _β C ₂	C _β C _α C ₁
cation		1.271	1.549	1.364		125.3	180.0
TS3	2.7	1.273	1.534	1.377	90.0	132.6	172.2
TS2	2.5	1.275	1.531	1.382	90.0	134.3	169.4
TS1	2.0	1.294	1.524	1.410	90.0	136.0	159.9
ROH ₂	1.569	1.306	1.523	1.466	113.3	127.6	136.0



	OC _α	C _α C _β	C _β C ₂	C _α C ₁	OC _α C _β	C _α C _β C ₂	C _β C _α C ₁
cation		1.264	1.559	1.363		134.4	180.0
TS3	2.7	1.265	1.544	1.374	90.0	136.7	173.0
TS2	2.5	1.267	1.538	1.380	90.0	138.3	170.2
TS1	2.0	1.286	1.525	1.408	90.0	140.5	160.0
ROH ₂	1.548	1.300	1.534	1.463	114.5	135.4	136.3

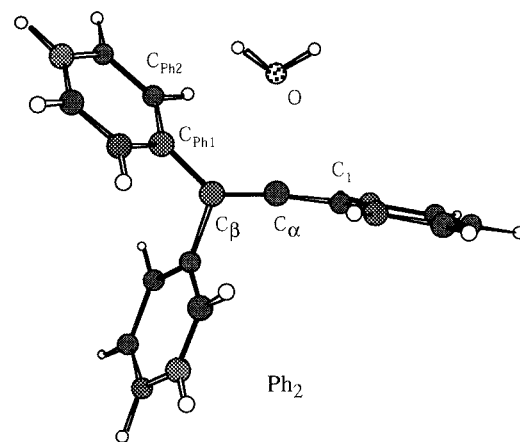


	O-C _α	C _α -C _β	C _β -C _{R1}	C _α -C ₁	O-C _α -C _β	C _α -C _β -C _{R1}	C _β -C _α -C ₁	C _α C _β C ₂ H ₁
cation		1.277	1.530	1.360		121.0	180.0	0.0
TS3	2.7	1.279	1.513	1.376	90.0	133.7	171.4	0.0
TS2	2.5	1.281	1.511	1.382	90.0	135.7	168.9	0.0
TS1	2.0	1.300	1.510	1.410	90.0	133.9	159.8	60.2
ROH ₂	1.566	1.311	1.510	1.469	114.4	125.6	135.9	0.0



	OC _α	C _α C _β	C _β C ₂	C _α C ₁	OC _α C _β	C _α C _β C ₂	C _β C _α C ₁	C _β C ₂ C ₃ H ₁
cation		1.276	1.539	1.363		120.4	180.0	62.6
TS3	2.7	1.279	1.523	1.377	90.0	131.2	173.3	61.9
TS2	2.5	1.281	1.521	1.383	90.0	133.2	170.8	61.7
TS1	2.0	1.300	1.519	1.412	90.0	134.8	162.3	65.3
ROH ₂	1.571	1.311	1.514	1.469	114.0	136.3	124.6	63.2

Table 2 (Continued)



	OC $_{\alpha}$	C $_{\alpha}$ C $_{\beta}$	C $_{\beta}$ C $_{Ph1}$	C $_{\alpha}$ C $_{1}$	OC $_{\alpha}$ C $_{\beta}$	C $_{\alpha}$ C $_{\beta}$ C $_{Ph1}$	C $_{\beta}$ C $_{\alpha}$ C $_{1}$	C $_{\alpha}$ C $_{\beta}$ C $_{Ph1}$ C $_{Ph2}$
cation		1.287	1.500	1.362		119.4	180.0	46.2
TS3	2.7	1.282	1.489	1.375	90.0	133.0	172.2	66.4
TS2	2.5	1.283	1.487	1.381	90.0	134.3	170.2	66.8
TS1	2.0	1.302	1.488	1.409	90.0	134.9	161.5	68.3
ROH $_2$	1.529	1.317	1.498	1.465	114.3	120.6	137.4	63.7

^a ROH $_2$ denotes protonated vinyl alcohol. All distances in Å and all angles in degrees.

Table 3. Calculated Energies of Vinyl Cations, Model Transition Structures, and Protonated Vinyl Alcohols for R $_3$ = H and Ph Series

R $_1$, R $_2$	vinyl cation	TS1	TS2	TS3	protonated alcohol
C4	-420.287 104 (-191.955 390)	-495.890 814	-495.892 072	-495.891 475	-495.908 621 (-267.629 134)
C5	-459.149 583 (-230.817 957)	-534.748 967	-534.751 846	-534.751 980	-534.771 030 (-306.492 422)
C6	-497.976 657 (-269.644 658)	-573.570 139	-573.575 606	-573.576 732	-573.597 365 (-345.319 957)
Me $_2$	-382.667 417 (-154.329 850)	-458.264 353	-458.266 732	-458.267 865	-458.290 417 (-230.012 201)
Et $_2$	-460.30 8846 (-231.975 932)	-535.900 819	-535.905 848	-535.907 127	-535.929 876 (-307.650 990)
Ph $_2$	-761.560 493 <i>b</i>	-837.155 916	-837.156 912	-837.155 944	-837.190 847 (-608.909 867)

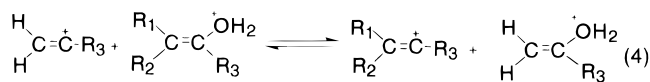
^a Energies in hartrees. Numbers in parentheses are energies (in kcal/mol) for R $_3$ = H. ^b β,β -Diphenylvinyl cation could not be localized because it became a phenyl-bridged cation.

As shown below, the calculated relative stabilities of β -substituted vinyl cations are in good agreement with the corresponding gas phase experimental values, and the use of this level of theory is justified for the present purpose.

Discussion

Table 1 shows observed second-order rate constants for reactions of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations with EtOH for β -substituents Me $_2$, Et $_2$, Ph $_2$, cyclobutyl, cyclopentyl, and cyclohexyl. It can be seen that the reactivity differences arising from the effects of substituents at the β position are surprisingly large. In the conventional interpretation, the reactivity of cations is expected to correlate with their stability in such a manner that a more stable cation shows less reactivity, as has been observed for benzylic cations.⁴ However, it appears that the stability–reactivity relation does not hold for these vinylic cations.

The relative stabilities of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations were evaluated by means of ab initio MO calculations for model compounds. They were obtained on the basis of the isodesmic reaction of eq 4 in which the carbocation is formed from a protonated alcohol. The energies of these cationic species are listed



in Table 3 and the derived relative vinyl cation stabilities

Table 4. Relative Cation Stability on the Bases of Isodesmic Reaction 4^a

R $_1$, R $_2$	R $_3$ = Ph	R $_3$ = H
C4	-4.03	-14.9
C5	-4.08	-14.5
C6	-4.54	-13.9
Me $_2$	-3.10	-9.5
Et $_2$	-4.34	-14.1
Ph $_2$	+1.50	

^a Energies (in hartrees) of H $_2$ O, H $_2$ C=C $^+$ H, H $_2$ C=C(H)OH $_2^+$, H $_2$ C=C $^+$ Ph, and H $_2$ C=C(Ph)OH $_2^+$ are -75.585 960, -76.655 774, -152.353 291, -305.008 928, and -380.636 878, respectively.

in Table 4. For the series with R $_3$ = H in eq 4, the β,β -Me $_2$ cation and the β,β -Et $_2$ cation are seen to be more stable than the parent vinyl cation by 9.5 and 14.1 kcal/mol, respectively. A similar, though less pronounced, trend is found for the R $_3$ = Ph series. These values are comparable to the experimental gas phase stabilities of β -substituted vinyl cations, where the stabilities of the mono- β -substituted phenylvinyl cations have been determined by ICR from the competitive protonation of differently substituted phenylacetylenes. The β -Me- or β -Et-substituted α -(*p*-methoxyphenyl)vinyl cations were thus determined to be more stable than the parent cation by 1.8 and 3.7 kcal/mol, respectively. However, as shown in Figure 3, the reactivity differences for a series of β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations do not show a good correlation with cation stabilities. Thus, the reactivity order does not arise from the relative cation stabilities. However, it is interesting to note that apparently the bulkier the R group the slower the rate.

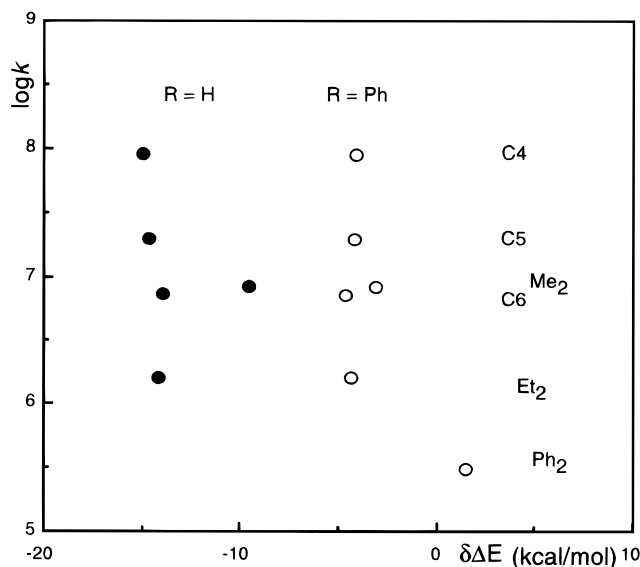


Figure 3. Correlation between $\log k_2$ for β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations with ethanol in acetonitrile and the cation stability.

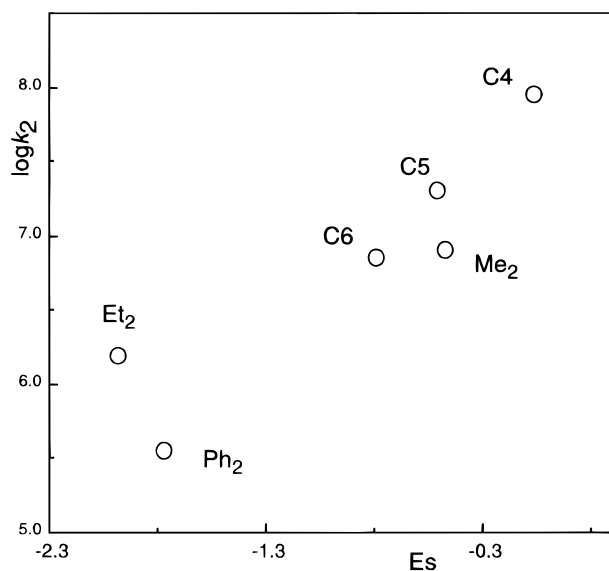


Figure 4. Plots of $\log k_2$ vs Taft's E_s constants.

One way to estimate the degree of steric hindrance for the approach of a nucleophile at the transition state is to examine a correlation between $\log k_2$ and the Taft E_s values of the R_1R_2C groups. Such a correlation is shown in Figure 4. However, although it has some success it is not consistently satisfactory. This is not unexpected because the steric requirement at the TS of the present reaction may not be the same as that of the reference reaction (acid hydrolysis of esters), and this is an unavoidable limitation in the use of steric parameters.¹⁴

In order to see whether the observed reactivity differences can be rationalized in terms of the steric effect of the β substituents, we have considered three families of model transition structures. In the language of physical organic chemistry there are two factors that affect the relative stability of the model transition structures, namely electronic and steric effects. The electronic

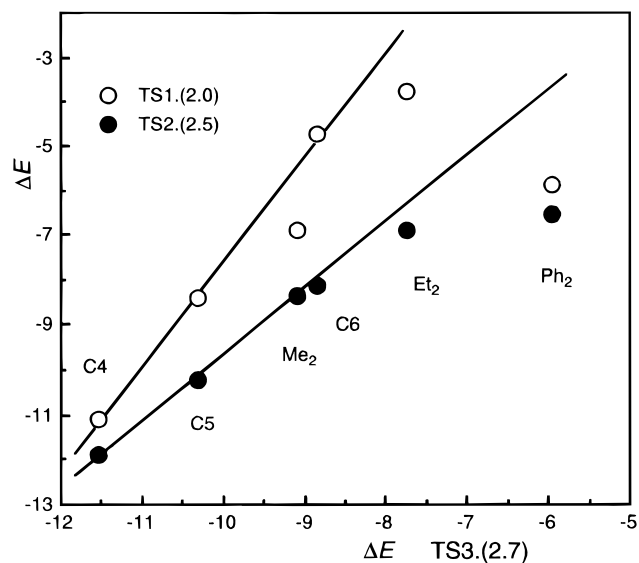


Figure 5. Plots of relative stabilities of TS1 and TS2 vs those of TS3.

substituent effect on the transition state is expected to be negligible in the present system since the effect on the stabilities of the cations (eq 4) is small. It is therefore reasonable to assume that the difference in stability of the model transition structures primarily arises from the steric effect between the β substituents and the OH_2 molecule (nucleophile) that is located closer to the R group in the transition state than in the product state. Hence, calculations were carried out for three different transition states with increasing $C_\alpha\text{--O}$ bond lengths (TS1, TS2, and TS3 in Table 2).

As in the case of $\log k_2$, there is only a crude correlation between the relative stabilities of the model transition structures and E_s . However, correlations among the model transition structures are more informative. Figure 5 shows plots for TS1 (top) and TS2 (bottom) against TS3. The plotted numbers are the relative energies of each model structure given by $\Delta E = E(\text{TS}) - E(R_1R_2C=C^+Ph + H_2O)$. A less negative number means that the model structure suffers more steric repulsion and is less stable. In both cases, the cycloalkyl derivatives for 4-, 5-, and 6-membered rings in Table 3 gave excellent linear correlations with the slopes of 2.4 and 1.4; thus, the cycloalkyl derivatives are well-behaved substituents. The magnitudes of the slopes indicate that the sensitivity to steric bulkiness is larger for a more congested structure. In contrast, Et_2 - and Ph_2 -substituted derivatives deviate downward from the correlation line in the bottom plots in Figure 5. This indicates that Et_2 and Ph_2 in particular exhibit smaller steric destabilization than expected from the correlation line for TS2. A similar trend was found in the upper plots; here, even the Me_2 derivative deviates downward, and the deviation of Ph_2 is very large. These findings indicate that a set of steric parameters that is applicable to one reaction system may not be applied to other systems. The results can be rationalized by assuming that the Me_2 , Et_2 , and Ph_2 substituents are more flexible than the cyclic substituents and can partially accommodate steric repulsion by changing the local conformation when the nucleophile comes very close to them. This assumption is consistent with the optimized geometries shown in Table 2 as described below.

One way for the transition structures to accommodate the steric congestion is to increase the $C_\alpha C_\beta C_2$ angle (here

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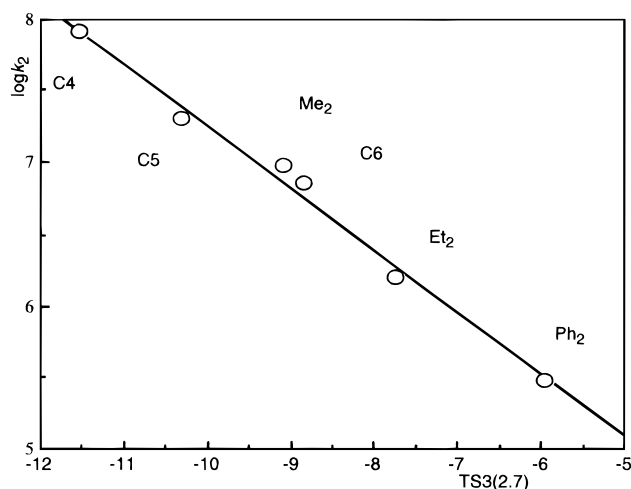


Figure 6. Correlations between $\log k_2$ and the relative stability of TS3.

C_2 is the carbon atom of the substituent attached to C_β in a syn manner); this occurs for all substituents. Additional mechanisms to evade steric congestion operate for the transition structure of the Ph_2 -, Et_2 -, and Me_2 -substituted derivatives. For Ph_2 , twisting of the C_β -Ph bond provides an effective mechanism. The two phenyl groups in the cation tend toward planarity in order to achieve effective π -electron overlap with the double bond. The optimal $C_\alpha C_\beta C_{\text{Ph}1} C_{\text{Ph}2}$ dihedral angle in the cation is 46.2° . However, this dihedral angle becomes larger in going from TS3 (66.4°) to TS2 (66.8°) to TS1 (68.3°) as a result of twisting of the C_β -Ph bond to avoid steric repulsion from the incoming nucleophile. Because of this, the change of the $C_\alpha C_\beta C_R$ angle can be relatively small for the Ph_2 substrate; it varies from 133.0° (TS3) to 134.9° (TS1) in contrast to the larger change for the C6 cycloalkyl substrate, from 134.8° (TS3) to 138.6° (TS1). For the Me_2 and Et_2 derivatives, conformational change at the C-C bond is the mechanism adopted to avoid steric congestion. For Me_2 , the two Me groups at the β position in the cation have the conformation shown in Table 2. The conformation in TS2 and TS3 is the same as in the cation. However, TS1, in which OH_2 comes close to the Me group, takes up a different conformation by rotating 60° around the C_β - C_2 bond. For Et_2 , rotation of the CH_3 - CH_2 bond is the preferred mechanism for absorbing steric repulsion; the C-C bond rotates to move CH_2 -H away from the nucleophile in more congested transition structures.

Figure 6 shows plots of $\log k_2$ against the relative stabilities of the model TS3. The reasonably good straight line obtained indicates that the reactivity of the β,β -disubstituted α -(*p*-methoxyphenyl)vinyl cations is controlled by the steric effect. It can be concluded that the reactivities of β,β -disubstituted vinyl cations with a nucleophile depend only slightly on their stabilities and are primarily controlled by the steric effect. This control by steric effects is the reason for the breakdown of the stability- $\log k_2$ relation in the vinylic system. It should also be emphasized that steric parameters that are applicable to one system may not be applied successfully to another system because the effect of steric congestion is different from system to system and substituents behave differently where steric requirements differ.

Experimental Section

Acetonitrile and ethanol were purified according to standard procedures.¹⁵ β,β -Dialkyl- α -(*p*-methoxyphenyl)vinyl bromides were prepared by refluxing dichloromethane solutions of the corresponding ketone (60 mmol) and Vilsmeier reagent (DMF (15 mL)- PBr_3 (30 mL)) for 3 days. Laser flash photolysis was carried out as reported previously.⁷

1-(*p*-Methoxyphenyl)-1-bromo-2-ethyl-1-butene: colorless liquid; bp $140^\circ\text{C}/2.5$ mmHg; $^1\text{H-NMR}$ (CDCl_3) δ 0.95 (t, 3H, $J = 7.5$ Hz), 1.1 (t, 3H, $J = 7.5$ Hz), 2.04 (q, 2H, $J = 7.5$ Hz), 2.40 (q, 2H, $J = 7.5$ Hz), 3.80 (s, 3H), 6.85 (d, 2H, $J = 8.7$ Hz), 7.20 (d, 2H, $J = 8.7$ Hz); mass spectrum m/z (relative intensity) 268 (M^+ , 157.2), 269 ($\text{M} + 1$, 30.3), 270 ($\text{M} + 2$, 160.9)

[(*p*-Methoxyphenyl)bromomethylene]cyclobutane: colorless liquid; bp $100^\circ\text{C}/2.5$ mmHg; $^1\text{H-NMR}$ (CDCl_3) δ 2.00 (q, 2H, $J = 7.8$ Hz), 2.79–2.88 (m, 4H), 3.80 (s, 3H), 6.84 (d, 2H, $J = 8.7$ Hz), 7.38 (d, 2H, $J = 8.7$ Hz).

[(*p*-Methoxyphenyl)bromomethylene]cyclopentane: colorless crystal; mp 36.5 – 37.5°C (EtOH); $^1\text{H-NMR}$ (CDCl_3) δ 1.70–1.78 (m, 4H), 2.27 (m, 2H), 2.47–2.2.52 (m, 2H), 3.81 (s, 3H), 6.84 (d, 2H, $J = 8.7$ Hz), 7.32 (d, 2H, $J = 8.7$ Hz)

[(*p*-Methoxyphenyl)bromomethylene]cyclohexane: colorless crystal; mp 57 – 59°C (EtOH); $^1\text{H-NMR}$ (CDCl_3) δ 1.44–1.68 (m, 6H), 2.13 (t, 2H), 2.53 (t, 2H), 3.81 (s, 3H), 6.84 (d, 2H, $J = 8.7$ Hz), 7.21 (d, 2H, $J = 8.7$ Hz); mass spectrum m/z (relative intensity) 280 (M^+ , 170.5), 282 ($\text{M} + 2$, 171.0)

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