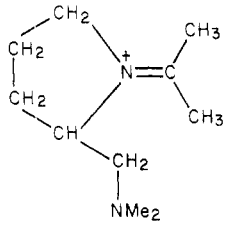
is probably largely due to the pyrrolidine nitrogen atom. A plot of log k_{im} vs. pK_a for primary amines in which steric effects are reasonably constant has a slope of 0.59.[3] Assuming that a similar relationship would hold for equally hindered pyrrolidines, we estimate that polar effects decrease k_{im} by about fivefold. We then take the remaining 20-fold decrease to be a steric effect. Much of the particularly great reactivity of pyrrolidine was attributed to the decreased steric repulsions in the iminium ion formed from the pyrrolidine relative to those present in an iminium ion formed from a secondary amine in which the two R groups attached to nitrogen are not held together in a five-membered ring. However, in **2**, the iminium ion



2

formed from **1** and acetone, there should be strong repulsions between the (dimethylamino)methyl group from **1** and a methyl group from acetone.

The rate constant for imination by **1**-H^+ (k_{imh}) is about twice as large as that for **1** (k_{im}) in spite of the fact **1** is far more basic than **1**-H^+. Hence the reaction of **1**-H^+ is being speeded by the internal acid catalysis of dehydration of the intermediate carbinolamine. However, the rate constant for monoprotonated *N,N*-dimethylethylenediamine (0.30)[3,11] is more than four times as large as the value for **1**-H^+. One reason for this is the hindrance present in the iminium ion **2**. Another reason is based on the fact that the reactive form of monoprotonated diamines of the type we are considering must have the tertiary amino group protonated and the primary or secondary amino group free. Since pyrrolidine is considerably more basic than a primary amine, a significantly smaller fraction of the tertiary amino groups is probably protonated in **1**-H^+ than in monoprotonated *N,N*-dimethylethylenediamine.

Experimental Section

2-[(Dimethylamino)methyl]pyrrolidine. *N,N*-Dimethyl-5-oxo-2-pyrrolidinecarboxamide[13] (47 g) was reduced with 14.3 g of lithium aluminum hydride in 700 mL of refluxing tetrahydrofuran for 18 h. To the cooled solution was added 16 mL of 15% aqueous sodium hydroxide, 35 mL of water, and 240 mL of tetrahydrofuran and the mixture was refluxed for 30 min. Then the mixture was filtered and the filtrate was dried over potassium carbonate and distilled. The major fraction (9.6 g), bp 100–105 °C (80 mm), was redistilled to give 8.2 g of colorless liquid, bp 105–110 °C (80 mm) [lit.[5] bp 133–135 °C (760 mm)], which was 99.9% pure by GLC on a Carbowax–KOH column, containing two impurities with shorter retention times: 300-MHz ^1H NMR[14] (D_2O, shifts upfield from HOD) δ 1.73 (quintet, 1, J = 7 Hz, $CHCH_2NMe_2$), 2.01 (d of t, 1, J = 10, J' = 7 Hz, CHHNH), 2.13 (d of t, 1, J = 10, J' = 7 Hz, CHHNH), 2.50 (m, 2, CH_2NMe_2), 2.66 (s, 6, CH_3), 2.95 (m, 1, $CHHCH_2NH$), 3.15 (m, 2, $CHHCH_2NH$ and $CHHCHCH_2NMe_2$), 3.58 (d of q, 1, J = 13, J' = 8 Hz, $CHHCHCH_2NMe_2$); IR (neat) 3250 (NH), 2750–2950 (CH), 1420 cm^{-1} (CNH); mass spectrum (70 eV), m/z (relative intensity) 128 (1), 84 (2), 83 (3), 82 (2), 72 (2), 71 (6), 70 (100), 69 (2), 68 (4), 59 (38), 58 (62).

Both the dihydrochloride and dihydrobromide of **1** were prepared and found to be too hygroscopic to be handled conveniently.

Kinetics. The kinetics was followed by spectrophotometric measurements at 275 nm, near the absorption maximum of acetone, as described previously.[2-4] The results obtained are listed in Table I.

Registry No. **1**, 70754-93-7; **2**, 74420-39-6; hydroxylamine, 7803-49-8; *N,N*-dimethyl-5-oxo-2-pyrrolidinecarboxamide, 74420-40-9; acetone, 67-64-1.

(11) This is the value for total monoprotonated diamine. It is obtained by multiplying the value for tertiary-protonated diamine[3] by the fraction of monoprotonated diamine that is protonated at the tertiary amino group (0.38).[12]

(12) Hine, J.; Via, F. A.; Jensen, J. H. *J. Org. Chem.* **1971**, *36*, 2926–9.

(13) Angier, R. B.; Smith, V. K. *J. Org. Chem.* **1956**, *21*, 1540–3.

(14) The NMR assignments are based in part on decoupling experiments.

Vinyl Cation Intermediates in Solvolytic and Electrophilic Reactions. 1. Solvolysis of α-Arylvinyl Derivatives

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The solvolysis of 16 α-arylvinyl tosylates, bromides, and chlorides has been investigated in various alcohol–water mixtures and in acetic acid at several temperatures. All substrates were substituted with either 2-methyl or 2,6-dimethyl groups to accelerate the rates of reaction. The major or exclusive product isolated in most cases was the acetophenone arising from hydrolysis of the expected enol ethers or acetates during workup. The kinetics were simple first order in the vast majority of cases, with excess base added to prevent side reactions. Leaving group effects, Winstein–Grunwald m values, Schleyer Q values, and effects of solvent nucleophilicity all point to a limiting S_N1 ionization generating a vinyl cation intermediate, in which there is little rear-side nucleophilic assistance by solvent. Substituent effects led to ρ values in the range −3.9 to −5.3 vs. σ^+. Activation parameters are typical for an S_N1 process, and $\Delta S^\ddagger$ is insensitive to the presence of zero, one, or two *o*-methyl groups, as are the effects of solvent polarity on the rates. The results should therefore be directly comparable with other solvolytic or electrophilic reactions generating formally similar vinyl cation intermediates.

Vinyl cations are now well established as organic reaction intermediates, due to considerable activity in this area over the past 10 years.[1] Probably the two most common ways these intermediates are generated are by solvolytic or

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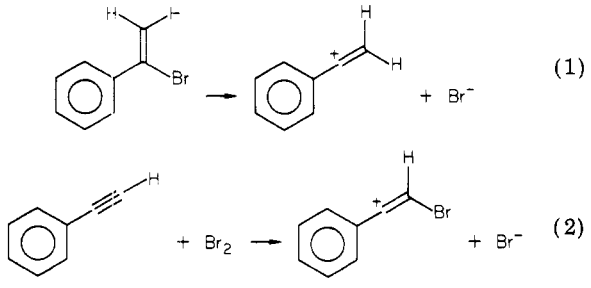
nucleophilic displacement from arylvinyl derivatives and by electrophilic addition to the triple bonds of acetylenic derivatives. For example, the cationic intermediates formed in the solvolysis of α-phenylvinyl bromide and in the addition of molecular bromine to phenylacetylene are formally very similar, as shown in eq 1 and 2.

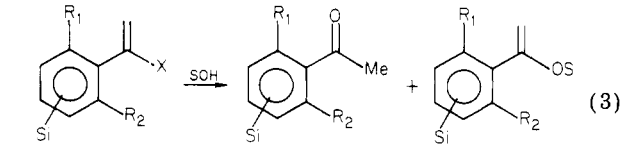


(1)

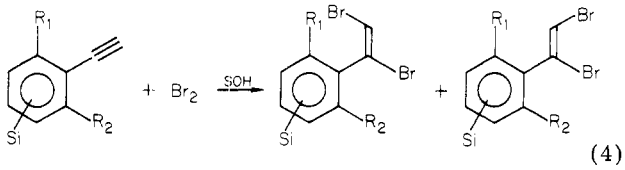
(2)

Although these two types of cationic intermediates are generated by different processes, and at very different rates, there should nonetheless be significant similarities in their response to such factors as structural change and solvent polarity, especially if discrete vinyl cations are actually present on the reaction coordinate, and perhaps some interesting differences. Clearly the presence of an α-halo substituent in eq 2 may have some effect on a comparison of the two systems. Unfortunately it is not easy to remove this difference by studying the solvolysis of α,β-dibromovinyl derivatives.[2] Indeed, the solvolyses of α-arylvinyl systems containing such typical leaving groups as bromide and tosylate are normally so sluggish that special structural factors or high reaction temperatures must be used in order to study the reactions on a convenient time scale. We have previously shown in a preliminary study[3] that *o*-methyl groups are effective in accelerating arylvinyl solvolysis by destabilizing the ground state through loss of conjugation between the aryl and vinyl π systems. This enables vinyl solvolysis rates to be measured conveniently and compared with analogous saturated systems, without the need to use unusual or "super" leaving groups such as triflate and nonaflate.

It was therefore of interest to investigate and compare the behavior of the cationic intermediates (and the preceding transition states) expected in the systems shown in eq 3 and 4. These systems should be directly compa-



(3)

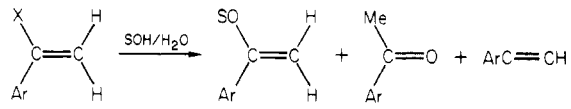


(4)

R_1 = Me, R_2 = H or Me, X = OTs, Br, or Cl

R_1 = Me, R_2 = H or Me,
X = OTs, Br, or Cl

Scheme I[a]



[a] X = OTs, Br, and Cl

rable, providing it can be shown that the steric effects of the *o*-methyl groups do not introduce any significant differences between the two types of reaction, such as, for example, important inhibition of solvation in one and not in the other. The present paper deals with the solvolysis reactions. The accompanying paper[4] describes the analogous electrophilic additions.

We have extended our previous preliminary work on the solvolysis of hindered arylvinyl systems partly to provide a broader basis for comparison with the electrophilic reactions and partly to investigate standard linear free-energy relationships in the two types of system.

Results and Discussion

Typical products of solvolysis of some of the α-arylvinyl systems which were studied kinetically in various alcohol–water systems and in acetic acid are shown in Table I. These are the expected enol ethers, enol acetates, arylacetylenes, and the ketones arising from hydrolysis of enolic derivatives, either directly or during workup (see Scheme I). It can be seen from Table I that in most cases the major or even exclusive product is the acetophenone derivative. Although the products are generally consistent with an S_N1 type of solvolysis, little else can be deduced from the product distributions, due to the variable product ratios obtained as a function of the leaving group and solvent composition.

The compounds studied all gave simple first-order kinetics in the presence of added base,[5] except for three compounds which all involve bromide as the leaving group. These were 1-(4-methoxy-2-methylphenyl)vinyl bromide and (*E*)- and (*Z*)-1-bromo-1-(2,4-dimethylphenyl)propene. In these cases the first-order plots showed some curvature, and the values of the observed solvolytic rate constants were found to be dependent on the concentration of added base. Presumably a second mechanism in addition to the S_N1 mechanism is also operating in these cases. However, in the vast majority of cases the kinetics were cleanly first-order, and the rate constants were independent of the concentration of added base.

The effect of the leaving group on the rate can be used as a good criterion for characterizing S_N1 and S_N2 processes, especially if unusual steric effects are not operative.[6] In Table II are given the rate ratios for some of the vinyl chlorides, bromides, and tosylates. The chloride to bromide rate ratios of about 60 and the tosylate to bromide ratios of 100–400 are similar to values obtained for the S_N1 solvolyses of analogous alkyl compounds.[7] In particular, the element effect (k_{Br}/k_{Cl}) is comparable with the ratios of 42, 58, and 19 obtained for the solvolyses of *tert*-butyl,[8] adamantyl,[9] and α-phenylethyl[10] halides, respectively.

(1) (a) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); (b) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); (c) Z. Rappoport, *Acc. Chem. Res.*, **9**, 265 (1976); (d) P. J. Stang, Z. Rappoport, M. Hanack, and M. L. Subramanian, "Vinyl Cations", Academic Press, New York, 1979.

(2) See, however: P. Bassi and U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 1283 (1974); Z. Rappoport and M. Atidia, *ibid.*, 2316 (1972).

(3) J. J. Périé and K. Yates, *J. Org. Chem.*, **39**, 1902 (1974).

(4) K. Yates and G. Mandrapilias, *J. Org. Chem.*, following paper in this issue.

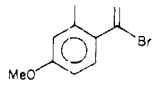
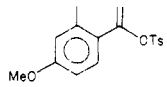
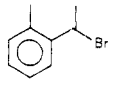
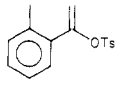
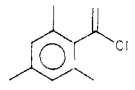
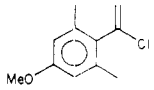
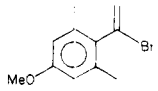
(5) All kinetic runs were carried out in the presence of a five- to tenfold excess of sodium acetate or triethylamine to suppress side reactions caused by the formation of HCl, HBr, or HOTs during solvolysis.

(6) C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960); Z. Rappoport, J. Kaspi, and Y. Apeloig, *ibid.*, **96**, 2616 (1974).

(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, Chapter 4.

(8) K. A. Copper and E. D. Hughes, *J. Chem. Soc., Chem. Commun.*, 1183 (1973).

Table I. Distribution of Solvolysis[a] Products

substrate	T, °C	solvent[c]	products,[b] % ketone	acetylene	enol acetate	enol ether
	36.5	50:50 M-W	100			
		80:20 E-W	100			
	36.5	50:50 M-W	100			
	88.0	50:50 M-W	97	3		
	88.0	50:50 M-W	100			
	88.0	50:50 M-W	60	15		25
	69.6	50:50 M-W		51	6	44
		80:20 E-W	5	40	8	47
		HOAc	trace	trace	100	
	69.6	50:50 M-W	56		trace	44
		80:20 E-W	100		trace	

[a] Solvolysis carried out in presence of 10 molar equiv of added NaOAc. [b] See Scheme I for identification of individual products. [c] M-W = methanol-water, and E-W = ethanol-water.

Since the difference in C–X bond dissociation energy for vinyl chloride and bromide is very similar to the difference in bond dissociation energy between ethyl chloride and bromide,[11] similar element effects would be expected for the vinyl and saturated systems. The high rate ratios in Table II also appear to exclude the possibility of an Ad_E2-E type process, since if the reaction were acid-catalyzed, the rate-determining step would be protonation of the vinyl group, and such large ratios would not be expected.[12]

The solvent dependence of the reaction rate was also investigated by using a variety of approaches. The complete Winstein–Grunwald equation (eq 5)[14] is obtained from eq 6 if the partial derivatives are constant and equal

$$\log k/k_0 = mY + lN \quad (5)$$

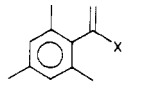
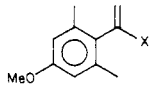
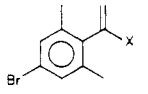
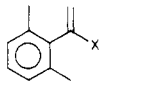
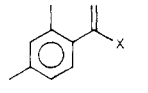
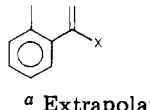
$$\mathrm{d} \log k = \left(\frac{\partial \log k}{\partial Y}\right)_N \mathrm{d}Y + \left(\frac{\partial \log k}{\partial N}\right)_Y \mathrm{d}N \quad (6)$$

to m and l, respectively. The more commonly used simple form (eq 7) is based on the assumption that the term lN

$$\log k/k_0 = mY \quad (7)$$

is zero or shows negligible variation. This is justified if solvents of similar nucleophilicity are used (i.e., $\partial N \simeq 0$)

Table II. Leaving Group Effects in Arylvinyl Solvolysis

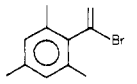
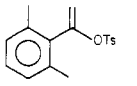
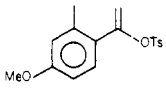
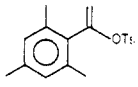
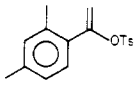
substrate	X	k_{obsd}, s^{-1}	reaction conditions[d]	ratio
	Cl	2.73×10^{-4}	50:50 M-W, 88 °C	1
	Br	1.52×10^{-2} [a]		56
	OTs	1.0[b]		3700
	Br	5.60×10^{-5}	50:50 M-W, 36.5 °C	1
	OTs	7.95×10^{-3} [c]		140
	Br	1.80×10^{-5} [c]	80:20 E-W, 67.6 °C	1
	OTs	6.03×10^{-3} [c]		335
	Cl	5.49×10^{-6} [a]	80:20 E-W, 36.5 °C	1
	Br	3.13×10^{-4}		57
	Br	1.09×10^{-5}	50:50 M-W, 71.8 °C	1
	OTs	3.41×10^{-3}		311
	Br	1.84×10^{-4}	50:50 M-W, 81.0 °C	1
	OTs	3.01×10^{-2} [a]		164
	Br	2.60×10^{-6} [c]	80:20 E-W, 88.0 °C	1
	OTs	1.05×10^{-3} [c]		400
	Br	1.97×10^{-4}	50:50 M-W, 88.0 °C	1
	OTs	2.31×10^{-2} [b]		120
	Br	9.01×10^{-6}	50:50 M-W, 88.0 °C	1
	OTs	1.43×10^{-3} [a]		160

[a] Extrapolated values from data at other temperatures. [b] Extrapolated values from data in ref 3. [c] Values from ref 3. [d] M = methanol, E = ethanol, and W = water.

or if the effect of solvent nucleophilicity on the rate is negligible[15] [i.e., $(\partial \log k/\partial N)_Y \simeq 0$]. One or both of these

(9) P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).
(10) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1602 (1957).
(11) A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 519 (1960); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(12) Although rate ratios in the range 10–100 have been observed[1d] for solvolysis of α-anisylvinyl bromides and chlorides in a similar range of solvents to the one studied here, low values of k_{Br}/k_{Cl} have been associated with competing Ad_E2-E-type reactions.[13]
(13) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).
(14) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

Table III. Rate Dependence on Solvent Nucleophilicity at Constant Ionizing Power

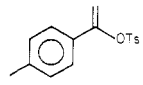
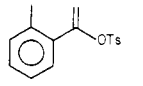
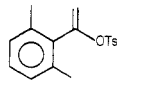
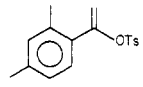
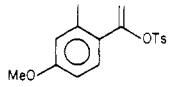
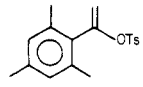
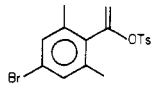
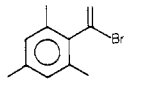
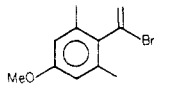
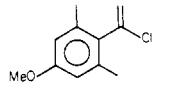
substrate	10^5k_1,[b] s^{-1}	10^5k_1, s^{-1}	T, °C	k_{HOAc}/k_{E-W}
	1.19	1.07	88.0	1.11
	3.54	3.98	68.0	0.89
	6.24	7.05	36.5	0.89
	2.76	2.20	36.5	1.25[a]
	1.57	1.38	67.6	1.14[a]

[a] Taken from ref 3. [b] In HOAc. [c] In 98:2 ethanol-water.

conditions may hold true for limiting S_N1 solvolysis. In order to test the possibility that in vinyl solvolysis the solvent does not play a significant role as a nucleophile, we studied the variation of the rate constant at a constant ionizing power (Y) and a different N. The rate ratios for several substrates measured in 98:2 ethanol–water and in acetic acid are given in Table III. These two solvents each have $Y \simeq -1.68$ but quite different nucleophilicities ($N_{HOAC} = -2.35$; $N_{98:2,E-W} \simeq 0$).[17] The results in Table III show that the rate ratios are close to unity for the five substrates listed and demonstrate clearly that there is very little rear-side nucleophilic assistance by solvent in S_N1 solvolysis of vinyl bromides and tosylates.

This also means that the simple form (eq 7) of the Winstein–Grunwald equation can be used to test the overall dependence of the reaction on solvent ionizing power (presumably mainly electrophilic solvation of the incipient anionic leaving group). The m values obtained for a typical series of vinyl tosylates, bromides, and chlorides are listed in Table IV. A typical plot of log k/k_0 vs. Y is shown in Figure 1. As can be seen from the dashed line, an excellent correlation is obtained if only the data for the binary ethanol–water system are considered. However, the correlations using all the data points are still reasonably good ($r \simeq 0.99$), and these were used to obtain the m values given in Table IV. When these m values are corrected[18] to a common temperature of 25 °C, the values are in the range 0.75–0.86 for the vinyl tosylates and 0.85–0.96 for the bromides, and the value is 0.77 for the chloride. The m values for the bromides are generally higher than those for the tosylates. A similar trend has been noted for the solvolysis of alkyl derivatives and has been attributed to variations in solvent hydrogen bonding

Table IV. Winstein m Values and Schleyer Q Values for Solvolysis of Arylvinyl Derivatives

substrate	m[a]	m_{exptl}[e]	Q[b]	solvents[c]
	0.84	0.69 (88)	0.71	3-7
	0.86	0.71 (88)	0.73	3-7
	0.75	0.66 (68)	0.76	1-3, 5-8
	0.65[d]		0.76[d]	
	0.53	0.51 (37)	0.66	1-8
	0.62[d]		0.67[d]	
	0.75	0.66 (68)	0.71	2-7
	0.96	0.81 (88)		1-5, 7-8
	0.85	0.82 (37)		2-6
	0.77	0.67 (70)		3-7

[a] Values obtained from plots of log k/k_0 vs. Y values, where k_0 refers to the reference solvent mixture (80:20 E-W). Values converted from the experimental temperature to 25 °C by $m_1/m_2 = T_2/T_1$.[18] [b] See ref 19. [c] Solvents: (1) 98:2 E-W; (2) 90:10 E-W; (3) 80:20 E-W; (4) 70:30 E-W; (5) 60:40 E-W; (6) 50:50 E-W; (7) 50:50 M-W; (8) acetic acid. [d] Values taken from ref 3. [e] Experimental m values with temperatures (°C) in parentheses.

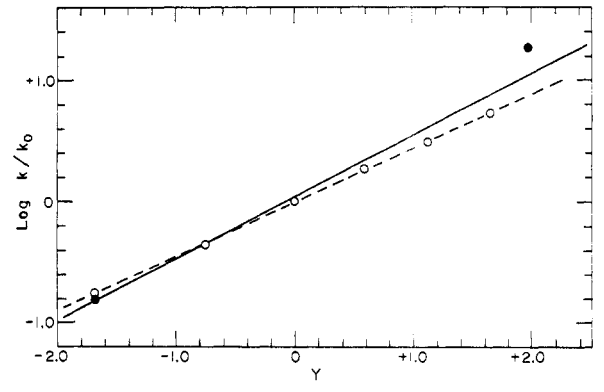


Figure 1. Plot of log k/k_0 for solvolysis of 1-(4-methoxy-2-methylphenyl)vinyl tosylate in various solvents at 36.5 °C vs. Winstein's Y values: reference solvent (log k_0) 80:20 ethanol–water; open circles refer to ethanol–water mixtures.

capacity toward the different leaving groups.

Although some of the m values in Table IV are somewhat low for typical S_N1 solvolysis,[21] they are in most cases

(15) As pointed out by a referee, the other possibility is that Y and N are linearly related, as has been shown to be the case for some binary solvent mixtures.[16] This can hardly be the case for the present comparisons of 98:2 ethanol–water and acetic acid.

(16) J. Kaspi and Z. Rappoport, *Tetrahedron Lett.*, 2035 (1977).

(17) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).

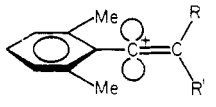
(18) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5397 (1957).

(19) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972).

(20) P. R. Wells, "Linear Free Energy Relationships", Academic Press, London, 1968, Chapter 3.

(21) They are, however, not too different from the m-value results reported[22] for the solvolysis of a hindered anthryl system, also presumed to react via an S_N1 process.

not too far from the expected limiting value of unity. The important feature of these results is that the presence of zero, one, or two *o*-methyl substituents in the molecule does not seem to have any significant effect on the magnitude of *m*; nor were the results in Table III significantly different for compounds with either one or two *o*-methyl groups. This argues strongly that the methyl groups cannot be causing significant steric inhibition to solvation from either side of the developing vinyl cationic center. Presumably solvent molecules could easily approach from above or below in the plane of the developing empty p orbital at C_α in structure I, where R and R′ are hydrogens.



I

As pointed out by Rappoport,[1c] very low *m* values (0.36–0.48) are to be expected when more bulky groups are attached to the β-carbon, since these lie in the plane of the p orbital at C_α.[23]

To avoid difficulties inherent in the Winsten–Grunwald treatment, Schleyer[19] has proposed a three-parameter equation which relates the solvolytic rate constant of a given substrate to those of two reference standards: 2-adamantyl tosylate, which solvolyses by a limiting S_N1 mechanism, and methyl tosylate, which reacts by a limiting S_N2 mechanism. This treatment results in a parameter *Q* which lies between the two extremes; *Q* = 1 for 2-AdOTs and *Q* = 0 for MeOTs. Unfortunately, only limited data exist for the bromide and chloride reference compounds, and *Q* values could only be obtained for the present vinyl tosylates.[24] The values given in Table IV are in the range 0.66–0.76, which are again somewhat low for an S_N1 process, as were some of the *m* values.[25] Nonetheless, these *Q* values are much closer to those of the limiting adamantyl tosylate case than to those of the methyl tosylate case. They are also in the same range as *Q* values for moderately hindered secondary alkyl tosylates such as 2-pentyl (0.69), cyclopentyl (0.67), and cyclohexyl (0.75).[19]

Again, the important point to note from Table IV is that the magnitude of *Q* is clearly not dependent on the number of methyl groups at the ortho position. This supports the previously stated conclusion that these groups do not seriously hinder any necessary solvation of the developing vinyl cation or its leaving group.

Although the effect of substituents on the rate has been used extensively to support and compare reaction mechanisms,[26] it is generally the case with aryl systems that the ring substituents are introduced exclusively at positions meta or para to the reaction center. For systems such as the present α-arylvinyl tosylates, bromides, and chlorides,

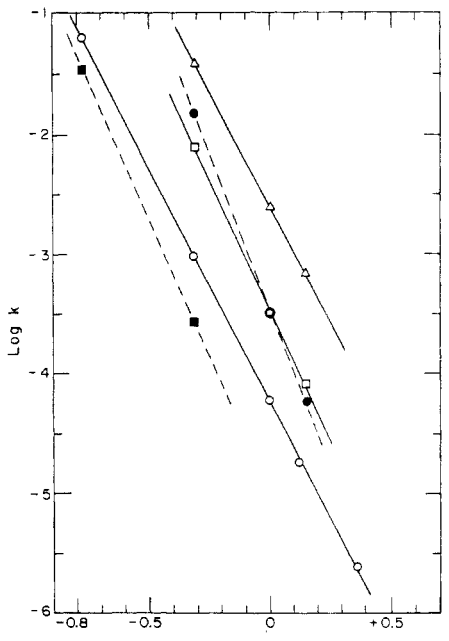
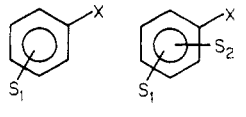


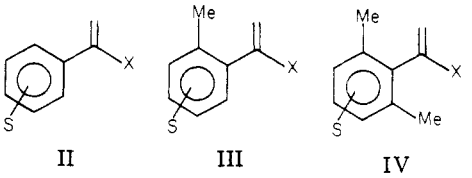
Figure 2. Plots of log *k* vs. σ^+ for solvolyses of α-arylvinyl systems: open circles, 1-(2-methylphenyl)vinyl tosylates in 50:50 methanol–water at 58 °C; open squares, 1-(2,6-dimethylphenyl)vinyl tosylates in 50:50 methanol–water at 36.5 °C; open triangles, 1-(2,6-dimethylphenyl)vinyl tosylates in 80:20 ethanol–water at 88 °C; solid circles, 1-(2,6-dimethylphenyl)vinyl bromides in 50:50 methanol–water at 88 °C; solid squares, 1-(2,6-dimethylphenyl)vinyl chlorides in 50:50 methanol–water at 88 °C.

there are one or two *o*-methyl substituents in each case. However, it has long been known that if substituent effects are approximately additive for multiply substituted phenyl groups, it should be possible to compare the A and B types



A B

of systems, independently of whether the group S_2 is substituted ortho, meta, or para to the reaction center X. This is true provided the groups S_2 do not change the mechanism and that no special buttressing effects of two adjacent groups occur.[27] Both of these requirements should be reasonably satisfied for the systems under investigation, and it should be possible to establish and compare Hammett-type linear free-energy relationships for the systems II–IV with none, one, or two *o*-methyl substituents.



II III IV

The solvolytic rate constants for a number of the (2-methylphenyl)- and (2,6-dimethylphenyl)vinyl tosylates, bromides, and chlorides studied are listed in Table V.

An attempt to correlate the rates of solvolysis of the series of ring-substituted (2-methylphenyl)vinyl tosylates (in 50:50 methanol–water at 58 °C) vs. σ substituent constants gave a very poor fit (*r* = 0.943). Correlation of the same data with Brown's σ^+ constants,[28] however, gave an

(22) Z. Rappoport, P. Schulman, and M. Thuval, *J. Am. Chem. Soc.*, **100**, 7041 (1978).

(23) In such cases common-ion rate depression is also frequently observed, and this has been attributed partly to steric hindrance to solvent approach.[1c] In the present investigation, no common-ion rate depression was ever observed, either during normal runs or with addition of lithium bromide. The absence of external ion return supports the conclusion that the *o*-methyl groups do not strongly shield the cationic center at Cα from solvent approach.

(24) Even for the *Q* values of the tosylates, it was necessary to measure the rates of solvolysis of methyl tosylate in the solvents of interest. The necessary rate constants for this compound are given as supplementary material.

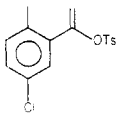
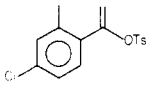
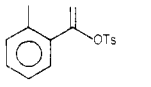
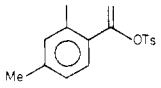
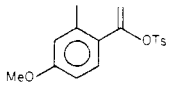
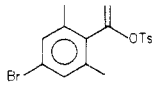
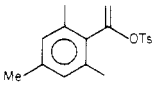
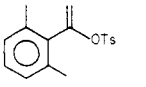
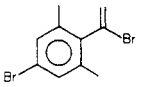
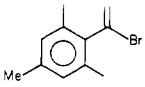
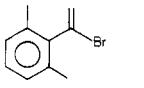
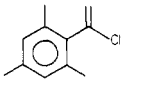
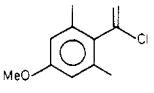
(25) A referee has suggested that the problem may be that *m* and *Q* values for vinylic systems could have different limiting values from those of the saturated systems used to set up these scales because of the different geometries involved.

(26) N. B. Chapman and J. Shorter, Eds., "Advances in Linear Free Energy Relationships", Plenum Press, London, 1972.

(27) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

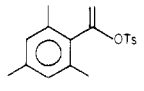
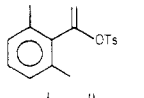
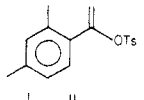
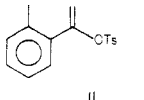
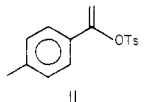
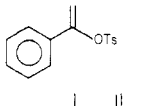
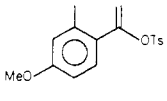
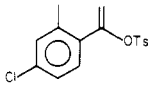
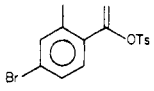
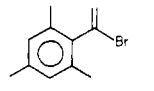
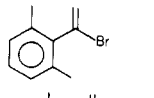
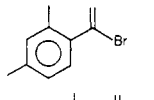
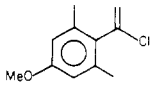
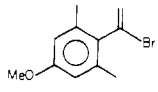
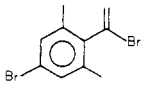
(28) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

Table V. Rate Constants for the Solvolysis of Ring-Substituted Arylvinyl Derivatives in Alcohol-Water Mixtures

substrates	k, s^{-1}	log k	σ^{+a}	reaction conditions[d]
	2.42×10^{-6}	−5.616	0.373	50:50 M-W, 58 °C
	1.82×10^{-5}	−4.740	0.114	50:50 M-W, 58 °C
	6.07×10^{-5}	−4.217	0	50:50 M-W, 58 °C
	9.23×10^{-4} [b]	−3.035	−0.311	50:50 M-W, 58 °C
	6.25×10^{-2}	−1.204	−0.778	50:50 M-W, 58 °C
	8.12×10^{-5}	−4.090	0.15	50:50 M-W, 36.5 °C
	6.88×10^{-4}	−3.163		80:20 E-W, 88 °C
	7.95×10^{-3}	−2.100	−0.311	50:50 M-W, 36.5 °C
	3.91×10^{-2}	−1.408		80:20 E-W, 88 °C
	3.21×10^{-4}	−3.493	0	50:50 M-W, 36.5 °C
	2.47×10^{-3}	−2.607		80:20 E-W 88 °C
	5.80×10^{-5}	−4.237	0.15	50:50 M-W 88 °C
	1.52×10^{-2}	−1.818	−0.311	50:50 M-W, 88 °C
	3.19×10^{-4}	−3.496	0	50:50 M-W, 88 °C
	2.73×10^{-4}	−3.560	−0.311	50:50 M-W, 88 °C
	3.80×10^{-2} [c]	−1.42	−0.778	50:50 M-W, 88 °C

[a] Taken from ref 28. [b] Taken from ref 3. [c] Value extrapolated from values at lower temperatures (see table of supplementary material). [d] M = methanol, E = ethanol, and W = water.

Table VI. Activation Parameters for the Solvolysis of α-Arylvinyl Tosylates, Bromides, and Chlorides

substrate	solvent[d]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu mol^{-1}
	50:50 M-W	18.4[a]	−8[a]
	80:20 E-W	21.8[a]	−5[a]
	50:50 M-W	21.6 ± 0.2	−4.9 ± 0.5
	80:20 E-W	24.7 ± 1.0	−2.0 ± 2.0
	50:50 M-W	21.4[a]	−10[a]
	80:20 E-W	23.4[a]	−1[a]
	50:50 M-W	24.1 ± 0.7	−5.3 ± 1.9
	50:50 M-W	24.5[a]	−8[a]
	50:50 M-W	24.2[b]	−18[b]
	50:50 M-W	19.0 ± 0.2	−6.9 ± 0.5
	80:20 E-W	21.1 ± 0.2	−5.9 ± 0.8
	50:50 M-W	23.9 ± 0.6	−8.1 ± 1.6
	50:50 M-W	22.4 ± 1.0	−5.2 ± 2.0
	80:20 E-W	23.9 ± 2.0	−7.2 ± 1.9
	50:50 M-W	23.5 ± 1.0	−2 ± 3.7
	80:20	25.2[a]	−7[a]
	50:50 M-W	24.7 ± 2.4	−6.5 ± 1.9
	50:50 M-W	24.7 ± 1.0	−7.5 ± 2.0
	50:50 M-W	19.8 ± 0.3	−10.4 ± 0.8
	80:20 E-W	23.1 ± 0.9	−8.0 ± 2.1
	80:20 E-W	21.7 ± 0.8	−4.6 ± 2.0
	50:50 M-W	25.0 ± 0.4	−9.1 ± 1.1

[a] Data obtained from ref 3. [b] Data obtained from ref 34. [c] M = methanol, E = ethanol, and W = water.

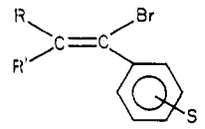
excellent fit (r = 0.9996) with a ρ value of −3.86. Data for the 2,6-dimethylphenyl series are much more limited, because these compounds are not as readily synthesized. However, correlation of log k for the three tosylates (S_1 = p-Me, H, and p-Br) vs. σ^+ gave a good linear plot, as shown in Figure 2, with ρ values of −4.3 and −4.4 in 50:50 methanol–water at 36.5 °C and in 80:20 ethanol–water at 88 °C, respectively.

Although less data are available for the corresponding bromides, values of log k for four (2,6-dimethylphenyl)vinyl compounds (S_1 = p-OMe, p-Me, and p-Br) also gave a good correlation (r = 0.9995) against σ^+, with a ρ of −5.1 for

solvolysis in 50:50 methanol–water at 88 °C.

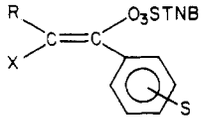
The correlations shown in Figure 2, albeit based on limited data in some cases, show that the ρ values for the solvolysis of the various α-arylvinyl systems are not very strongly dependent on (a) the nature of the leaving group (b) the number of *o*-methyl groups, or (c) the solvent composition. The ρ values are generally in the range −3.9 to −5.3, which is similar to the typical range of ρ values for solvolysis of analogous saturated systems. For example, the solvolysis of $ArC(Me)_2Cl$ in 90:10 acetone–water gives $\rho = -4.54$ at 25 °C.[29]

More importantly, these ρ values compare reasonably closely with values for similar unsaturated systems.[1d] Miller[30] has studied the solvolysis of triaryliodoethylenes in DMF at 184 °C and obtained $\rho = -3.6$. The solvolysis of V yields a ρ value of −4.1 against σ^+.[31] Tonellato has



V, R = R′ = *o*-anisyl; S = H, *p*-Me, *p*-OMe

obtained ρ values in the range −4.1 to −5.1 for the solvolysis of the series VI, depending on the nature of the β-halogen.[2]



VI, R = Ph; X = I, Cl, Br; TNB = 2,4,6-trinitrobenzenesulfonate

This last series is very interesting in the sense that β-halo substitution does not have a very profound effect on the magnitude of the substituent dependence, although it has a marked effect on the absolute rates. This suggests that the behavior of the vinyl cation intermediates (or transition states) obtained in Ad_E reactions of bromine and arylacetylenes (to be described in the following paper[4]) can be compared directly with that of the intermediates (or transition states) being described in the present paper.

It would be very interesting also to compare the substituent dependence of the parent series (II) with no *o*-methyl groups present. These reactions, however, are very slow, since no special structural factors such as ortho or β steric effects are present to accelerate the solvolyses. In their pioneering work on vinyl solvolysis, Grob and Cseh[32] did nevertheless study five systems of this type (II; X = Br; S = *p*-NH_2, *p*-$NHCOCH_3$, *p*-OMe, H, *p*-NO_2), at elevated temperatures in most cases. The values of log k_2 for three of these compounds,[33] extrapolated to a common temperature of 100 °C, do correlate well with σ^+ with an approximate ρ of −5.3, which reinforces the idea that the number of *o*-methyl substituents is not critical in determining the overall substituent dependence.

The activation parameters for the solvolysis of the vinyl compounds studied are presented in Table VI. The enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) of activation in the range of 20 to 25 kcal/mol and 0 to −10 eu, respectively, are in the range of values expected for an S_N1 mechanism, particularly the values for $\Delta S^\ddagger$. For example, values reported[9,35] for solvolyses of *tert*-butyl and 2-adamantyl derivatives in alcohol–water mixtures and in acetic acid are in the range 22–26 kcal for $\Delta H^\ddagger$ and −2 to −3 eu for $\Delta S^\ddagger$, whereas corresponding values for S_N2 solvolysis of methyl and ethyl derivatives are in the range 20–22 kcal and −15 to −18 eu, respectively.[36]

In 50:50 methanol–water, the (2,4,6-trimethylphenyl)-, (2,4-dimethylphenyl)-, and (4-methylphenyl)vinyl tosylates show essentially constant $\Delta S^\ddagger$ values with methyl substitution, and the observed rate enhancements of 18000:320:1, respectively, are caused by a lowering of $\Delta H^\ddagger$ by about 3 kcal/mol for each methyl group; that is, $\Delta H^\ddagger$ increases from 18.4 to 21.4 to 24.5 kcal/mol. This type of increase is also observed for the (2,6-dimethylphenyl)- and (2-methylphenyl)vinyl tosylates. The change in solvent from 50:50 methanol–water to 80:20 ethanol–water produces a higher $\Delta H^\ddagger$ and a somewhat less negative $\Delta S^\ddagger$. These changes are reasonable for an increase in solvent polarity, leading to a modest rate enhancement.

The activation parameters for the less reactive vinyl bromides and one vinyl chloride are also presented in Table VI. The data are limited in this series, but similar trends are observed. The major difference between the vinyl tosylates, bromides, and chloride is the lowering of $\Delta H^\ddagger$ for the better leaving group, with only minor changes in $\Delta S^\ddagger$.

The activation parameters show that there are no anomalous changes in $\Delta S^\ddagger$ with the introduction of one or two methyl groups at the ortho position(s). As has been pointed out, steric crowding around the vacant p orbital can cause a lowering of the *m* values due to less effective solvation[1c] of the transition state; this hindrance to solvation would be reflected in a lowering of the $\Delta S^\ddagger$ term. Hyne[37] has compared the solvolysis of *o*-, *m*-, and *p*-methylbenzyl chlorides and has explained the smaller $\Delta S^\ddagger$ obtained for the *o*-methyl compound in terms of steric hinderance to solvation at the reaction center. Barclay[38] has compared the solvolyses of 2,4,6-trimethyl- and 2,4,6-tri-*tert*-butylbenzyl chlorides, which show $\Delta S^\ddagger$ values of −11.0 and +0.3 eu, respectively, and has drawn a similar conclusion. However, a comparison of the $\Delta S^\ddagger$ values in 50:50 methanol–water for the solvolysis of the (4-methylphenyl)- and the (2-methylphenyl)vinyl tosylates or the (2,4-dimethylphenyl)- and the (2,6-dimethylphenyl)vinyl tosylates (cf. Table VI) shows only minor variations. Thus, little if any steric hinderance to solvation is caused by the *o*-methyl groups.[23]

In conclusion, the present results point to a solvolysis mechanism for these α-arylvinyl tosylates, bromides, and chlorides which closely approaches a limiting S_N1 process to give a discrete α-arylvinyl cation as the intermediate. This is supported by the product studies, kinetics, *m* values, *Q* values, linear free-energy relationships (magnitude and sign of ρ, dependence on σ^+), and activation

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(30) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968).
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(32) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).
(33) The rate of solvolysis of the *p*-nitro derivative could not be measured, even at the highest temperature used (190 °C). The value of log k_2 for the *p*-amino compound at 100 °C, which involved a long extrapolation from data at or below 25 °C, does not fall anywhere near a line through the other points and was omitted in calculating the ρ value quoted here.
(34) P. E. Peterson and J. M. Indelicato, *J. Am. Chem. Soc.*, **91**, 6194 (1969).
(35) E. R. Thornton, "Solvolysis Mechanisms", Ronald Press, New York, 1964, Chapter 5; J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).
(36) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953); E. Tommila, and J. Jutila, *Acta Chem. Scand.*, **6**, 844 (1952).
(37) J. B. Hyne and R. Wills, *J. Am. Chem. Soc.*, **79**, 1913 (1957).
(38) L. R. C. Barclay, H. R. Sonawane, and J. C. Hunson, *Can. J. Chem.*, **50**, 2318 (1972).

parameters. It also appears from the lack of rate dependence on solvent nucleophilicity that there is very little rear-side assistance by solvent in the ionization process.

In addition, and most importantly, there appear to be no unusual steric effects arising from the presence of the *o*-methyl groups which were introduced simply to accelerate the solvolyses to a conveniently measurable rate range. It therefore should be possible to make direct comparisons of these vinyl cation intermediates and their preceding transition states with the analogous species thought to be formed during the Ad_E2 reactions of acetylenes (as is presented in the following paper in this series[4]).

Experimental Section

General Methods. Melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin–Elmer 237B or 337 spectrophotometer. Unless otherwise stated, liquid sample spectra were obtained neat on sodium chloride plates and solid sample spectra in carbon tetrachloride. Routine ultraviolet spectra were obtained on a Unicam SP800A. Mass spectra were determined on a CEC 21-490 at 70 eV, and the *m/e* values of the significant ions are reported with the intensities relative to that of the base peak (100%) in parentheses.

Nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian T-60 or T-60A instrument. Unless otherwise indicated, carbon tetrachloride solutions with tetramethylsilane as an internal standard were used. Chemical shifts are reported on the δ scale.

Analytical gas–liquid chromatography (GLC) was performed on a Carlo Erba Fractovap GI gas chromatograph equipped with a flame-ionization detector. Preparative GLC was carried out on a Wilkins Aerograph Model 705 equipped with a flame-ionization detector.

Microanalyses were performed by A. Gygli Co.

Kinetic Measurements. All kinetic runs were followed spectrophotometrically by using the change in absorbance at the most suitable wavelength in the range 230–260 nm. All runs were carried out at least in duplicate and agreed in most cases to within 2%. Temperatures were measured in the UV cell to within ±0.05 °C by using a thermometer which was standardized against a National Bureau of Standards thermometer. Either a Unicam 800 or SP1800, both equipped with an automatic cell changer and recorder, was used. Reactions were followed for 3 half-lives, and infinity values were taken after 10 half-lives. All infinity values were found to be stable. For runs above 80 °C, Grob's sealed-ampule technique was used.[32] Stock solutions were approximately 1×10^{-4} M in substrate and $(5–10) \times 10^{-4}$ M in base (sodium acetate or triethylamine). Calculations of the first-order rate constant were performed by means of linear least-squares correlation in $\ln (A - A_\infty)$ vs. time. Rate constants for all compounds studied are listed in the table in supplementary material.

Activation parameters were obtained from the least-squares plots of $\log (k/T)$ vs. $1/T$.

Materials. Ethanol was purified by refluxing absolute ethanol with magnesium turnings and crystals of iodine until all the magnesium was converted to the ethoxide. After further addition of absolute ethanol, the solution was refluxed overnight and distilled through a 30-cm Vigreux column. Methanol (ACS) was dried by the formation of the magnesium methoxide as in the case of ethanol and distilled.

Glacial acetic acid was purified by being refluxed with chromium oxide and acetic anhydride for 1 day. After a prerun was taken, the acid was distilled through a 30 × 1 in. column packed with glass beads, collected, and stored under nitrogen. Singly distilled water was used without further purification.

The (2-methylphenyl)vinyl substrates were prepared from the corresponding 2-methylacetophenones, which were either commercially available or were prepared essentially by the method described by Coleman[39] for the synthesis of 9-acetylphenanthrene from 9-cyanophenanthrene. This method gave 4-chloro-2-methylacetophenone, bp 108–111 °C (10 mm) [lit.[40] bp 240–242 °C (730 mm)]. 5-Chloro-2-methylacetophenone was prepared in the same way from the corresponding nitrile; bp 57 °C (0.3 mm) [lit.[41] bp 121–122 °C (7 mm)]. The ^{1}H NMR and IR spectra were fully consistent with the assigned structures.

The (2,6-dimethylphenyl)vinyl substrates were prepared from the corresponding 2,6-dimethylacetophenones, which were synthesized as follows. 2,6-Dimethylacetophenone itself was prepared by diazotizing 2,6-dimethylaniline by the method of Vogel,[42] followed by carbonation of the Grignard reagent using standard procedures. The resulting 2,6-dimethylbenzoic acid [mp 115–116 °C (lit.[43] mp 115 °C)] was then reacted with thionyl chloride, followed by distillation, to give the acid chloride, bp 40–41 °C (0.3 mm) [lit.[44] bp 90–91 °C (5 mm)]. This was then completely reacted with methyllithium in dry ether under nitrogen, followed by addition of water. The organic layer was washed successively with saturated $NaHCO_3$ solution, water, and brine solution, followed by drying ($MgSO_4$) and vacuum distillation. The resulting 2,6-dimethylacetophenone, bp 49.5–50.5 °C (0.5 mm) [lit.[45] bp 114–116 °C (21 mm)], had ^{1}H NMR and IR spectral characteristics consistent with the assigned structure. For the 4-bromo-2,6-dimethylacetophenone, the corresponding bromoaniline was prepared from the 2,6-dimethylaniline by the method of Noelting.[46] The aniline was converted to the nitrile by reaction of the diazonium salt with cuprous cyanide according to the method described by Marvel.[47] The product, 4-bromo-2,6-dimethylbenzonitrile had a melting point of 67–71 °C (lit.[48] mp 71–72 °C). Hydrolysis of the nitrile with 60% aqueous sulfuric acid at 150 °C for 3 h gave the acid [mp 198–199 °C (lit.[48] mp 197–198 °C)], which was then converted to the acid chloride as described previously, mp 55–58 °C (lit.[46] mp 56–57 °C). The acetophenone was then prepared by the method of Gilman.[49] The final product, 4-bromo-2,6-dimethylacetophenone [bp 60–61 °C (0.5 mm)] was characterized by its carbonyl band in the IR region at 5.92 μm and by its ^{1}H NMR spectrum: 2.22 (s, 6 H), 2.37 (s, 3 H), 7.15 (s, 2 H). For the preparation of 2,6-dimethyl-4-methoxyacetophenone, 3,5-xylenol was first brominated by the method of Auwers and Borsche[50] to yield crude 4-bromo-3,5-dimethylphenol, mp 109–112 °C [lit.[50] mp (114–115 °C)], followed by methylation by the method of Icke[51] to give 4-bromo-3,5-dimethylanisole, bp 108–112 °C (10 mm) [lit.[47] bp 131–134 °C (14–15 mm)].

The method outlined above for the synthesis of 2,6-dimethylbenzoic acid was used to give 2,6-dimethyl-4-methoxybenzoic acid. The crude acid melted at 128–143 °C (lit.[52] mp 144–146 °C). The acid chloride was synthesized by the method outlined for 2,6-dimethylbenzoyl chloride; bp 75–78 °C (0.6 mm) [lit.[44] bp 105–107 °C (5–6 mm)]. The acid chloride hydrolyzed rapidly when exposed to air and was kept under a nitrogen atmosphere. The corresponding acetophenone was synthesized by the method outlined above for the 4-bromo-2,6-dimethylacetophenone using dimethylcadmium. The desired 2,6-dimethyl-4-methoxyacetophenone was obtained (mp 46–48 °C) and characterized by the carbonyl band in its IR spectrum at 5.89 μm and by its ^{1}H NMR spectrum: 2.18 (s, 6 H), 2.32 (s, 3 H), 3.70 (s, 3 H), 6.42 (br s, 2 H).

A general synthesis for the phenylacetylenes and vinyl com-

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pounds required for kinetic studies, starting from commercially available or the above-synthesized acetophenones, is described for o-methylacetophenone. The scheme is similar to the one outlined by Périé and Yates.[3]

In a typical procedure, 51.3 g (0.246 mol) of phosphorus pentachloride was weighed into a two-necked flask equipped with a drying tube, pressure-equalizing dropping funnel, and magnetic stirrer. Through the dropping funnel was added slowly at room temperature 32 g (0.24 mol) of o-methylacetophenone over a 0.5-h period. The solution was stirred for an additional hour, and the phosphorus oxychloride produced was removed by vacuum distillation. Fractional distillation yielded two fractions: first, 11.5 g, bp 75 °C (α-chlorostyrene); second, 23.9 g, bp 105 °C (12 mm) [1,1-dichloro-1-(2-methylphenyl)ethane]; 85% total yield. The assigned structures of both compounds were consistent with their IR and ^{1}H NMR spectra. The mixture of the monochloro and dichloro compounds was then dehydrochlorinated. Into a dry, three-necked flask equipped with a dry ice condenser, a dropping funnel, and an ammonia inlet was condensed 600 mL of ammonia in which was dissolved 10 g (0.26 mol) of sodium amide. To this solution was added slowly over 1 h 20 g of the mixture of the above aryl chlorides. After the mixture was stirred for several hours, 200 mL of sodium-dried ether was added, and the ammonia was allowed to evaporate overnight. To the reaction mixture was added 200 mL of a 10% ammonium chloride solution, and the aqueous layer was thoroughly extracted with ether. The ether layer was washed twice with 50 mL of a 5% $NaHCO_3$ solution, 50 mL of water, and finally 50 mL of brine and then was dried over magnesium sulfate. The ether was removed under reduced pressure, and the yellow residue was distilled to give 17 g (61% yield) of o-methylphenylacetylene, bp 47–49 °C (12 mm) [lit.[53] bp 42–44 °C (6 mm)].

1-(2-Methylphenyl)vinyl Bromide. Gaseous anhydrous hydrogen bromide was bubbled through a solution of 11.6 g (0.10 mol) of the acetylene in 120 mL of dry ethanol-free chloroform. The reaction was followed by the disappearance of the ^{1}H NMR signal of the acetylene proton. The solution was then washed twice with 50 mL of a 10% Na_2CO_3 solution, with 50 mL of water, and finally with 50 mL of brine. After the solution was dried ($MgSO_4$) and the solvent evaporated, the resulting yellow liquid was distilled to give 16.7 g of 1-(2-methylphenyl)vinyl bromide: 85% yield; bp 85 °C (12 mm); purity shown to be greater than 99.5%; IR 6.15 μm; ^{1}H NMR 2.40 (s, 3 H), 5.67 (d, J = 1.2 Hz, 1 H), 5.82 (d, J = 1.2 Hz, 1 H), 7.00–7.27 (m, 4 H); mass spectrum, 198 (25), 196 (25), 117 (100), 116 (15), 115 (40), 91 (15).

Anal. Calcd for C_9H_9Br: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.96; H, 4.73; Br, 40.34.

1-(2-Methylphenyl)vinyl Tosylate. To a solution of 4.23 g of the α-bromostyrene in 35 mL of dry acetonitrile was added a solution of silver tosylate[54] (6.2 g, 0.022 mol) in 35 mL of acetonitrile. The reaction mixture was sealed in a thick-walled ampule and heated at 100 °C for 5 h. After the mixture cooled, the silver bromide was filtered off and the solvent evaporated. The solid residue was washed three times with cold pentane to remove any unreacted starting material or acetophenone which was formed. The residue was dissolved in carbon tetrachloride and filtered again to remove any unreacted silver tosylate. After the filtrate was dried ($MgSO_4$), the solvent was removed. The resulting solid was recrystallized from chloroform–pentane (1:9) to give 3.68 g of the vinyl tosylate in 60% yield. After three recrystallizations, the tosylate was used for kinetics: mp 47 °C; IR 6.08, 8.35, 8.50 μm; ^{1}H NMR 2.28 (s, 3 H), 2.40 (s, 3 H), 4.92 (d, J = 2 Hz, 1 H), 5.25 (d, J = 2 Hz, 1 H), 7.07 (m, 4 H), 7.13 (d, J = 8 Hz, 2 H), 7.58 (d, J = 8 Hz, 2 H); mass spectrum, 288 (<1), 155 (30), 133 (50), 132 (23), 119 (90), 116 (36), 115 (23), 92 (12), 91 (100), 77 (10).

Anal. Calcd for $C_{16}H_{16}SO_3$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.61; H, 5.45; S, 11.36.

1-(4-Methylphenyl)vinyl Tosylate. The tosylate was prepared from the corresponding α-bromostyrene by the method of Périé and Yates;[3] mp 58–59 °C (lit.[3] mp 59 °C).

1-(4-Methoxy-2-methylphenyl)acetylene. Methylation of 4-hydroxy-2-methylacetophenone was carried out by the method outlined for the synthesis of 4-bromo-3,5-dimethylanisole; bp 72–74 °C (0.10 mm) [lit.[55] bp 145–146 °C (18 mm)].

Reaction of the acetophenone with phosphorus pentachloride at 15 °C yielded the α-chlorostyrene derivative, bp 112 °C (100 mm). The product was characterized by its spectra: IR 6.13 μm; ^{1}H NMR 2.38 (s, 3 H), 3.77 (s, 3 H), 5.25 (br s, 1 H), 5.55 (br s, 1 H), 6.15–6.67 (complex, 2 H), 7.10–7.23 (complex, 1 H).

Dehydrochlorination followed by recrystallization of the crude product from ethanol–water yielded the acetylene, mp 30–31 °C. A sample was sublimed for use in kinetics: IR 3.04, 4.77 μm; ^{1}H NMR 2.42 (s, 3 H), 3.30 (s, 1 H), 3.77 (s, 3 H), 6.48–6.68 (m, 2 H), 7.10–7.42 (m, 1 H); mass spectrum, 146 (100), 131 (21), 115 (12), 103 (24), 77 (21).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.06; H, 6.85.

1-(4-Methoxy-2-methylphenyl)vinyl Bromide. Addition of hydrogen bromide to the above acetylene gave the α-bromostyrene, bp 62 °C (100 mm). The α-bromostyrene was distilled three times to give the bromide in greater than 99% purity by GLC: IR 6.15 μm; ^{1}H NMR 2.35 (s, 3 H), 3.77 (s, 3 H), 5.65 (d, J = 1.5 Hz, 1 H), 5.78 (d, J = 1.5 Hz, 1 H), 6.50–6.67 (m, 2 H), 7.07–7.22 (m, 1 H); mass spectrum, 228 (11), 226 (11), 147 (100), 115 (17), 131 (12).

Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.89; H, 4.88; Br, 35.19. Found: C, 52.99; H, 4.86; Br, 35.42.

1-(4-Methoxy-2-methylphenyl)vinyl Tosylate. The corresponding α-bromostyrene was reacted with silver tosylate in the presence of triethylamine to give, after three recrystallizations from chloroform–pentane, the required tosylate, mp 82–84 °C. The tosylate turned pink on standing but could be stored at 5 °C under nitrogen for several weeks: IR 6.07, 8.38, 8.47 μm; ^{1}H NMR 2.33 (s, 3 H), 2.40 (s, 3 H), 3.75 (s, 3 H), 4.83 (d, J = 2 Hz, 1 H), 5.17 (d, J = 2 Hz, 1 H), 6.37–6.58 (m, 2 H), 6.93–7.20 (m, 3 H), 7.57 (d, J = 8 Hz, 2 H); mass spectrum, 318 (1), 164 (21), 146 (100), 149 (48), 131 (13).

Anal. Calcd for $C_{17}H_{18}SO_4$: C, 64.13; H, 5.70; S, 10.07. Found: C, 64.23; H, 5.91; S, 10.16.

1-(4-Chloro-2-methylphenyl)acetylene. Reaction of 4-chloro-2-methylacetophenone with phosphorus pentachloride yielded on distillation the corresponding α-chlorostyrene and the 1,1-dichloro-1-arylethane, bp 100 and 125 °C (12 mm), respectively. The assigned structures of the two compounds were consistent with the ^{1}H NMR and IR data.

Reaction of the chloro compounds with sodium amide in liquid ammonia gave the acetylene in poor yield. The elimination could be carried out in good yield if potassium hydroxide in ethanol was used, according to the method of Dufraisse and Dequesnes.[56] After workup of the mixture, the acetylene was distilled, bp 82 °C (12 mm). The acetylene used for kinetics was distilled three times and showed greater than 99.5% purity by GLC: IR 303, 4.74 μm; ^{1}H NMR 243 (s, 3 H), 3.18 (s, 1 H), 6.97–7.43 (complex, 3 H).

Anal. Calcd for C_9H_7Cl: C, 71.77; H, 4.69; Cl, 23.54. Found: C, 71.86; H, 4.87; Cl, 23.60.

1-(4-Chloro-2-methylphenyl)vinyl Bromide. Initial attempts to make the α-bromostyrene produced substantial amounts of the undesired β-bromostyrene (this could be hydrobrominated to give the starting acetylene with potassium hydroxide in ethanol). Pure α-bromostyrene was obtained if the chloroform was saturated with oxygen and the reaction carried out in an ice bath in the absence of light. After workup of the mixture, the α-bromostyrene was distilled at 65 °C (75 μm) in 80% yield. The purity was checked by GLC: IR 6.15 μm; ^{1}H NMR 2.33 (s, 3 H), 5.65 (d, J = 2 Hz, 1 H), 5.08 (d, J = 2 Hz, 1 H), 7.00–7.13 (m, 3 H); mass spectrum, 234 (4), 232 (23), 230 (14), 153 (32), 152 (10), 151 (100), 116 (66), 115 (65).

Anal. Calcd for C_9H_8BrCl: C, 46.69; H, 3.48; Cl, 15.15; Br, 34.52. Found: C, 46.56; H, 3.48; Cl, 15.31; Br, 34.13.

1-(4-Chloro-2-methylphenyl)vinyl Tosylate. Reaction of the bromide with silver tosylate in a sealed ampule at 107 °C for

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10 h yielded the required tosylate, which was recrystallized from chloroform–pentane: mp 83 °C; IR 6.06, 9.35, 8.44 μm; ^{1}H NMR 2.30 (s, 3 H), 2.40 (s, 3 H), 4.92 (d, J = 2 Hz, 1 H), 5.22 (d, J = 2 Hz, 1 H), 7.03 (s, 3 H), 7.15 (d, J = 8 Hz, 2 H), 7.57 (d, J = 8 Hz, 2 H); mass spectrum, 324 (0.3), 322 (0.1), 167 (16), 155 (50), 153 (53), 91 (100).

Anal. Calcd for $C_{16}H_{15}SO_3Cl$: C, 59.53; H, 4.70; S, 9.93; Cl, 10.98. Found: C, 59.45; H, 4.82; S, 9.93; Cl, 10.87.

1-(5-Chloro-2-methylphenyl)acetylene. The starting acetophenone was reacted with phosphorus pentachloride at 80 °C for 10 h. Distillation yielded two fractions: the α-chlorostyrene and the 1-aryl-1,1-dichloroethane, bp 54 and 70 °C (150 mm), respectively. The structures of the two chlorides were consistent with ^{1}H NMR and IR data. The mixture was dehydrochlorinated with potassium hydroxide in ethanol to give the required acetylene, bp 82–83 °C (12 mm). The acetylene was redistilled until it was better than 99.3% pure on GLC: IR 3.04, 4.75 μm; ^{1}H NMR 2.38 (s, 3 H), 3.18 (s, 1 H), 6.95–7.38 (complex, 3 H); mass spectrum, 152 (7), 150 (66), 115 (100), 89 (6), 63 (10).

Anal. Calcd for C_9H_7Cl: C, 71.77; H, 4.69; Cl, 23.54. Found: C, 71.96; H, 4.58; Cl, 23.66.

1-(5-Chloro-2-methylphenyl)vinyl Tosylate. Reaction of the acetylene with hydrogen bromide gave 1-(5-chloro-2-methylphenyl)vinyl bromide: 85% yield; bp 67 °C (100 torr). The assigned structure of the vinyl bromide was consistent with the IR and ^{1}H NMR spectra.

Reaction of the vinyl bromide with silver tosylate was carried out at 140 °C for 1 day to yield the required tosylate. After three recrystallizations from chloroform–pentane, the tosylate showed a constant melting point of 87 °C and was used for kinetics: IR 6.08, 8.35, 8.45 μm; ^{1}H NMR 2.25 (s, 3 H), 2.37 (s, 3 H), 4.95 (d, J = 2 Hz, 1 H), 5.30 (d, J = 2 Hz, 1 H), 6.93–7.35 (complex, 3 H), 7.12 (d, J = 9 Hz, 2 H), 7.57 (d, J = 8 Hz, 2 H); mass spectrum, 324 (<0.5), 322 (1.5), 169 (15), 155 (50), 153 (48), 91 (100).

Anal. Calcd for $C_{16}H_{15}SO_3Cl$: C, 59.53; H, 4.68; S, 9.93; Cl, 10.98. Found: C, 59.49; H, 4.60; S, 9.94; Cl, 10.85.

1-(2,4-Dimethylphenyl)acetylene. The acetylene was synthesized by the method of Périé and Yates[3] with the following modification. After reacting 2,4-dimethylacetophenone with phosphorus pentachloride, the α-chlorostyrene was obtained; bp 99.5–100 °C (12 mm). The structure was consistent with the ^{1}H NMR and IR spectra. The resulting chlorostyrene was dehydrochlorinated almost quantitatively by using potassium *tert*-butoxide in dry dimethyl sulfoxide. Water was then added to the mixture and the aqueous layer thoroughly extracted with pentane. The pentane layer was washed three times with water and then with a brine solution. After the pentane layer was dried ($MgSO_4$), the pentane was removed under vacuum and the residue distilled at 74.5 °C (12 mm) [lit.[53] bp 69–71 °C (9 mm)]. The structure of the acetylene was consistent with the ^{1}H NMR and IR spectra.

1-(2,4-Dimethylphenyl)vinyl Bromide. The vinyl bromide was prepared from the acetylene; bp 75 °C (12 mm) [lit.[3] bp 42 °C (50 mm)]. The compound was purified by GLC, followed by molecular distillation, and was found to be greater than 99.5% pure by GLC. The ^{1}H NMR and IR spectra are in agreement with the published spectra.[3]

1-(2,6-Dimethylphenyl)acetylene. The corresponding acetophenone was reacted with phosphorus pentachloride to yield the α-chlorostyrene and 1-aryl-1,1-dichloroethane, bp 80 and 115 °C (12 mm), respectively. The ^{1}H NMR and IR spectral data were consistent with the structures of these chloro compounds. The mixture was dehydrochlorinated with potassium *tert*-butoxide in dry Me_2SO in almost quantitative yield; bp 64 °C (12 mm). The acetylene showed greater than 99% purity by GLC after three distillations: IR (CCl_4) 3.02, 4.74 μm; ^{1}H NMR 2.38 (s, 6 H), 3.33 (s, 1 H), 6.83–6.97 (m, 3 H).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.87.

1-(2,6-Dimethylphenyl)vinyl Bromide. Addition of hydrogen bromide to the above acetylene gave the required bromide, bp 44–45 °C (150 mm). The bromide was purified by GLC and found to be greater than 99% pure: IR 6.12 μm; ^{1}H NMR 2.35 (s, 6 H), 5.60 (d, J = 1.6 Hz, 1 H), 5.88 (d, J = 1.6 Hz, 1 H), 6.87–7.03 (m, 3 H); mass spectrum, 212 (15), 210 (16), 131 (100), 116 (25), 115 (25), 91 (25).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.85. Found: C, 57.01; H, 5.42; Br, 37.57.

1-(2,6-Dimethylphenyl)vinyl Tosylate. The tosylate was synthesized by refluxing the vinyl bromide and silver tosylate for 1 h in dry acetonitrile. Recrystallization from chloroform–pentane yielded the tosylate. The tosylate was recrystallized three times for kinetics: mp 71–72 °C; IR 6.04, 8.38, 8.45 μm; ^{1}H NMR 2.22 (s, 6 H), 2.38 (s, 3 H), 4.78 (d, J = 2 Hz, 1 H), 5.43 (d, J = 2 Hz, 1 H), 6.72–6.97 (m, 3 H), 7.12 (d, J = 8 Hz, 2 H), 7.53 (d, J = 9 Hz, 2 H); mass spectrum, 302 (1), 155 (10), 147 (35), 130 (100), 115 (35), 91 (35).

Anal. Calcd for $C_{17}H_{18}SO_3$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.60; H, 6.09; S, 10.49.

(4-Bromo-2,6-dimethylphenyl)acetylene. The corresponding acetophenone was reacted with phosphorus pentachloride by refluxing in carbon tetrachloride for 33 h to yield the α-chlorostyrene, bp 63–65 °C (350 mm). The structure of the chlorostyrene was consistent with ^{1}H NMR and IR spectral data. Dehydrochlorination with potassium *tert*-butoxide in Me_2SO yielded the acetylene, bp 60–62 °C (300 mm). After two more distillations the acetylene was shown to be greater than 99.5% pure by GLC: IR 3.04, 4.77 μm; ^{1}H NMR 2.40 (s, 6 H), 3.40 (s, 1 H), 6.93 (s, 2 H); mass spectrum, 210 (95), 208 (94), 129 (66), 128 (100), 127 (45).

Anal. Calcd for $C_{10}H_9Br$: C, 57.44; H, 4.34; Br, 38.22. Found: C, 57.56; H, 4.34; Br, 38.09.

1-(4-Bromo-2,6-dimethylphenyl)vinyl Bromide. Hydrogen bromide was bubbled through a solution of the corresponding acetylene in oxygenated methylene chloride to yield the vinyl bromide, bp 78 °C (100 mm). The bromide was distilled to give a compound which was shown to be greater than 99% pure by GLC: IR 6.14 μm; ^{1}H NMR 2.32 (s, 6 H), 5.63 (d, J = 2 Hz, 1 H), 5.92 (d, J = 2 Hz, 1 H), 7.13 (s, 2 H); mass spectrum, 292 (13), 290 (24), 288 (13), 211 (80), 209 (82), 130 (100), 129 (48), 128 (34), 127 (15), 115 (48).

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48; Br, 55.11. Found: C, 41.55; H, 3.64; Br, 54.94.

1-(4-Bromo-2,6-dimethylphenyl)vinyl Tosylate. The tosylate was prepared from the bromide and silver tosylate by refluxing in acetonitrile for 8 h. Recrystallization yielded the required tosylate: mp 126–127.5 °C; IR 6.06, 8.42, 8.51 μm; ^{1}H NMR ($CDCl_3$) 2.23 (s, 6 H), 2.40 (s, 3 H), 4.82 (d, J = 2.2 Hz, 1 H), 5.45 (d, J = 2.2 Hz, 1 H), 7.03 (s, 2 H), 7.13 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H); mass spectrum, 382 (<1), 380 (<1), 210 (94), 208 (100), 129 (68), 128 (94), 127 (45), 91 (23).

Anal. Calcd for $C_{17}H_{17}BrSO_3$: C, 53.56; H, 4.49; S, 8.41; Br, 20.96. Found: C, 53.30; H, 4.33; S, 8.36; Br, 20.78.

1-(2,6-Dimethyl-4-methoxyphenyl)vinyl Chloride. The starting ketone was refluxed with phosphorus pentachloride for 30 h. Distillation gave the required α-chlorostyrene, bp 61–63 °C (0.2 mm). The distilled chloride was found to be greater than 99.5% pure by GLC: IR 6.13 μm; ^{1}H NMR 2.30 (s, 6 H), 3.70 (s, 3 H), 5.15 (s, 1 H), 5.62 (s, 1 H), 6.45 s, 2 H); mass spectrum, 198 (11), 196 (33), 161 (100), 160 (87), 146 (15), 145 (17), 115 (27).

Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.18; H, 6.66; Cl, 18.02. Found: C, 67.04; H, 6.83; Cl, 17.88.

1-(2,6-Dimethyl-4-methoxyphenyl)vinyl Bromide. The arylacetylene was prepared from the α-chlorostyrene, recrystallized from ethanol–water, and sublimed for kinetics, mp 50–52 °C. The structure of the acetylene was consistent with the ^{1}H NMR and IR spectral data.

The addition of hydrogen bromide gave the α-bromostyrene, bp 68 °C (100 mm). The bromide was redistilled and was shown to be greater than 99% pure by GLC: ^{1}H NMR 2.32 (s, 6 H), 3.73 s, 3 H), 5.57 (d, J = 1 Hz, 1 H), 5.85 (d, J = 1 Hz, 1 H), 6.45 (s, 2 H); mass spectrum, 242 (<1), 240 (<1), 161 (13), 160 (100), 115 (8).

Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 55.01; H. 5.54; Br, 32.98.

The products of the solvolytic reactions were studied to show that they are consistent with a unimolecular mechanism. Product analyses were carried out by GLC and ^{1}H NMR spectroscopy. The ketones and acetylenic products were compared with authentic samples on two GLC columns. Quantitative data were obtained by using an internal standard and agreed with the ^{1}H NMR results to within ±5%. The enol acetate products could

be obtained from solvolysis in acetic acid. The enol ether products were identified by ^1H NMR spectroscopy and GLC.

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Registry No. 4-Chloro-2-methylacetophenone, 37074-38-7; 5-chloro-2-methylacetophenone, 58966-35-1; 2,6-dimethylbenzoic acid, 632-46-2; 2,6-dimethylbenzoyl chloride, 21900-37-8; 2,6-dimethylacetophenone, 2142-76-9; 4-bromo-2,6-dimethylbenzonitrile, 5757-66-4; 4-bromo-2,6-dimethylbenzoic acid, 74346-19-3; 4-bromo-2,6-dimethylbenzoyl chloride, 74346-20-6; 4-bromo-3,5-dimethylphenol, 7463-51-6; 4-bromo-3,5-dimethylanisole, 6267-34-1; 2,6-dimethyl-4-methoxyacetophenone, 60999-76-0; 2,6-dimethyl-4-methoxybenzoic acid, 37934-89-7; 2,6-dimethyl-4-methoxybenzoyl chloride, 31247-59-3; 1-(2-methylphenyl)vinyl chloride, 38379-19-0; 1,1-dichloro-1-(2-methylphenyl)ethane, 74346-21-7; *o*-methylphenylacetylene, 766-47-2; 1-(2-methylphenyl)vinyl bromide, 74346-22-8; 1-(2-methylphenyl)vinyl tosylate, 74331-76-3; 1-(4-methylphenyl)vinyl bromide, 51270-89-4; 1-(4-methoxy-2-methylphenyl)acetylene, 74331-69-4; 4-hydroxy-2-methylacetophenone, 875-59-2; 1-(4-methoxy-2-methylphenyl)vinyl chloride, 74346-23-9; 1-(4-methoxy-2-methylphenyl)-vinyl bromide, 74346-24-0; 1-(4-methoxy-2-methylphenyl)vinyl tosylate, 74331-92-3; 1,1-dichloro-1-(4-chloro-2-methylphenyl)ethane, 74346-25-1; 1-(4-chloro-2-methylphenyl)vinyl bromide, 74346-26-2; 1-(4-chloro-2-methylphenyl)vinyl tosylate, 74346-27-3; 1-(5-chloro-2-methylphenyl)acetylene, 74331-72-9; 1-(5-chloro-2-methylphenyl)vinyl tosylate, 74346-28-4; 1-(5-chloro-2-methylphenyl)vinyl bromide, 74346-29-5; 1-(2,4-dimethylphenyl)acetylene, 16017-30-4; 2,4-dimethylacetophenone, 89-74-7; 1-(2,4-dimethylphenyl)vinyl chloride, 74346-30-8; 1-(2,4-dimethylphenyl)vinyl bromide, 51270-86-1; 1-(2,6-dimethylphenyl)acetylene, 74331-74-1; 1-(2,6-dimethylphenyl)vinyl chloride, 74331-79-6; 1,1-dichloro-1-(2,6-dimethylphenyl)ethane, 74346-31-9; 1-(2,6-dimethylphenyl)vinyl bromide, 74331-78-5; 1-(2,6-dimethylphenyl)vinyl tosylate, 74331-77-4; (4-bromo-2,6-dimethylphenyl)acetylene, 74331-75-2; 4-bromo-2,6-dimethylacetophenone, 53379-63-8; 1-(4-bromo-2,6-dimethylphenyl)-vinyl chloride, 74346-32-0; 1-(4-bromo-2,6-dimethylphenyl)vinyl bromide, 74346-33-1; 1-(4-bromo-2,6-dimethylphenyl)vinyl tosylate, 74346-34-2; 1-(2,6-dimethyl-4-methoxyphenyl)vinyl chloride, 74331-91-2; 1-(2,6-dimethyl-4-methoxyphenyl)vinyl bromide, 74346-35-3; 1-(2,6-dimethyl-4-methoxyphenyl)acetylene, 74331-73-0; 1-(2,4-dimethylphenyl)vinyl tosylate, 51270-87-2; 1-(4-bromo-2-methylphenyl)vinyl tosylate, 74346-36-4; 2,6-dimethylaniline, 87-62-7; *o*-methylacetophenone, 577-16-2; 1-(4-methylphenyl)vinyl tosylate, 51270-88-3; 1-(4-chloro-2-methylphenyl)acetylene, 74331-71-8.

Supplementary Material Available: Listing of rate constants for all compounds studied (6 pages). Ordering information is given on any current masthead page.

Vinyl Cation Intermediates in Solvolytic and Electrophilic Reactions. 2. Bromination of Arylacetylenes

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The kinetics of bromination of a series of ten ring-substituted phenylacetylenes were investigated in anhydrous acetic acid at 25 °C. All substrates were substituted with one or two methyl groups at the ortho position(s) for comparison with the behavior of analogously substituted α-arylvinyl tosylates, bromides, and chlorides, which generate formally very similar vinyl cation intermediates. The phenylacetylenes show wide variations in bromination rate, with second-order rate constants in the range 10^{-3}–10^4 M^{-1} s^{-1}. Activation parameters were also measured, with $\Delta S^{\ddagger}$ showing little variation with the number of ortho substituents. The rates of bromination correlate much better with σ^+ than with σ, yielding ρ values of −6.9 and −6.7 for the 2-methyl and 2,6-dimethyl series, respectively. The magnitudes of these ρ values are compared with those for the parent phenylacetylene series and with the corresponding values for α-arylvinyl–X solvolysis. The product distributions and stereochemistry are very similar to those found for phenylacetylenes with no *o*-methyl substituents.

As mentioned in the preceding paper,[1] vinyl cations are now well established as organic reaction intermediates. The present paper describes the generation of this type of intermediate by electrophilic addition of bromine to substituted phenylacetylenes for comparison with the behavior of structurally similar cationic intermediates formed during the solvolysis of α-arylvinyl derivatives. Although bromination of some substituted phenylacetylenes has already been investigated,[2] the present study deals exclusively with *o*-methyl and 2,6-dimethyl substituted phenylacetylenes for direct comparison with the solvolysis of similarly substituted α-arylvinyl systems, described in the preceding paper. In the latter systems, *o*-methyl groups were necessary to accelerate the solvolytic reactions to a conveniently measurable rate range with typical leaving groups.

Results and Discussion

Although it is well-known[3] that the kinetics of bromine addition to acetylenes generally follows the three-term expression of eq 1, the experimental conditions were adjusted in the present case so that eq 1 would reduce to a simpler pseudo-first-order rate equation (eq 2), where k_{obsd} = k_1[acetylene]. This was done by using low initial bro-

$$V = -d[Br_2]/dt = [\text{acetylene}](k_1[Br_2] + k_2[Br_2]^2 + k_3[Br_2][Br^-]) \quad (1)$$

$$-d[Br_2]/dt = k_{obsd}[Br_2] \quad (2)$$

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