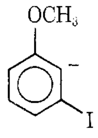
trast, amide ion **3** would be expected to attack the ortho hydrogen atom to a greater extent than the iodine atom in *m*-anisole since the former yields a more stable iodoanisole anion, **10**, than the carbanion, **11**, produced by the latter.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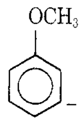
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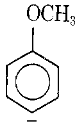
The decreased acidity of the hydrogen atom in *p*-iodoanisole as compared to that of *m*-iodoanisole apparently allows amide ion attack on iodine to compete with aryne formation. However, that the yield of anisole is less for *p*-iodoanisole (28%) than for *o*-iodoanisole (76%) is a result of the lower stability of carbanion **12** as compared to carbanion **8**.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Experimental Section

Glpc analyses were performed on a Beckman GC-5 chromatograph using nitrogen as carrier gas at a flow rate of 60 ml/min, inlet temperature of 150°, detection temperature of 200°, and column temperature of 100°. A 10 ft × 0.125 in. i.d. column packed with 10% SE-30 (silicone rubber) on Chromosorb W, acid-washed, 80–100 mesh, was used to analyze anisole. Nmr spectra were obtained using a Perkin-Elmer R-12B nmr spectrophotometer.

Materials. Di-*n*-propylamine was obtained from Eastman Kodak Co. and was dried, distilled, and then stored over anhydrous potassium carbonate. *n*-Butyllithium, 1.9–2.2 *M* in hexane, was obtained from Alfa Inorganics Inc., and was manipulated in a nitrogen-atmosphere glove bag. *m*- and *p*-fluoroanisoles were procured from Pierce Chemical Co.

m- and *p*-iodoanisoles,[11] *m*-bromoanisole,[12] and *m*- and *p*-chloroanisoles[13] were synthesized according to literature procedures.

General Procedure. The reactions were carried out using oven-dried glassware and under a nitrogen atmosphere. In a typical reaction, 0.05 mol of *n*-butyllithium was added dropwise to a stirred solution containing 25 ml of anhydrous ether and the appropriate amount of di-*n*-propylamine, and the solution was refluxed for 10 min to ensure complete amide formation. After 0.025 mol of haloanisole followed by 25 ml of anhydrous ether was added, the solution was refluxed (overnight) for at least 18 hr. The reaction was then quenched by the dropwise addition of water until the brightly colored solution changed to cloudy white. The ether solution was washed with water, extracted three times with 10% hydrochloric acid (25 ml each) to remove the basic aryne products, dried ($CaCl_2$), and concentrated by careful evaporation of ether to yield anisole. Anisole was quantitatively analyzed by vpc using phenetole as internal standard. The acidic aqueous extracts were combined, made basic with 10% sodium hydroxide, and extracted with three 25-ml portions of ether. After the basic ether extracts were combined, dried ($MgSO_4$), and concentrated, an oily residue was obtained which yielded the appropriate aryne amine product(s) upon vacuum distillation. *m*-haloanisoles yielded *N,N*-di-*n*-propyl-*m*-anisidine in these reactions, whereas the para isomeric anisoles gave a mixture of the corresponding meta and para isomeric anisidines. Infrared and nmr spectra were consistent with proposed structures. Nmr spectrum of the meta anisidine showed a singlet at τ 6.35 corresponding to the methoxy hydrogen atoms, whereas in the spectrum of the meta–para mixture two singlet peaks were observed in this region.

A higher boiling by-product, which was present in reactions with no excess amine solvent as a residue after vacuum distillation of the normal anisidine product, was pooled from a number of reactions and vacuum distilled, bp 153–154 (0.3 mm). The nmr spectrum was not clearly resolved, indicating a mixture, but showed aromatic hydrogens (τ 2.5–3.7), methoxy group (τ 6.3–6.4), and aliphatic hydrogens (τ 6.6–9.3). Mass spectrographic analysis was difficult to interpret due to polymerization. Infrared spectrum contained no N–H bands.

References and Notes

(1) (a) Sponsored in part by Grant N-118 of the Robert A. Welch Foundation, Houston, Texas; (b) Robert A. Welch Predoctoral Fellow.

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Solvolysis of Arylvinyl Bromides and Tosylates

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The bromides and tosylates of the 1-(4-methylphenyl)vinyl, 1-(2,4-dimethylphenyl)vinyl, and 1-(2,4,6-trimethylphenyl)vinyl systems have been prepared and their rates of solvolysis measured in alcohol-water mixtures and in acetic acid in the temperature range 35–88°. Rate enhancements of up to 4×10^5 over the parent 1-phenylvinyl systems have been obtained, with ortho-methyl substitution leading to significant steric acceleration of these normally slow solvolytic reactions. The kinetics, medium effects, and leaving-group effects are all in accord with a simple S_N1 type solvolysis mechanism leading to vinyl cation intermediates. However, the Winstein-Grunwald *m* values, Schleyer *Q* values, and insensitivity to solvent nucleophilicity all point to a weak nucleophilic assistance component in these vinyl solvolyses. Solvent effects in these solvolytic reactions are compared with those in electrophilic additions leading to analogous cationic intermediates.

In connection with some previous work of one of us,[1] concerning the relative ease of formation of carbonium ions and vinyl cations, as well as solvation effects on these species in electrophilic additions, we have been interested in investigating the rates and solvent effects of related solvolytic reactions leading to similar vinyl cationic intermediates. A second objective was to obtain more quantitative information about the reactivity of vinylic substrates,

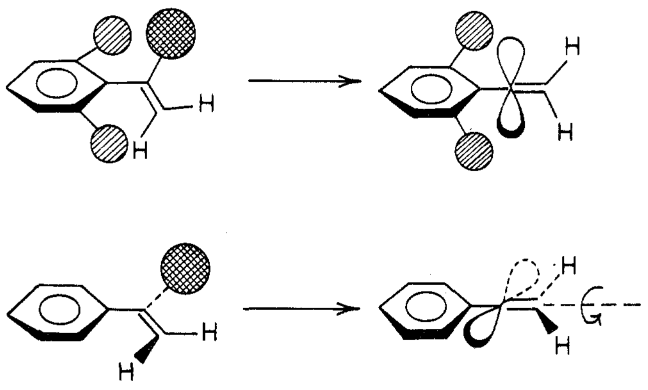
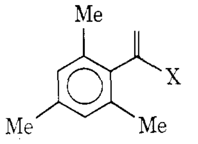


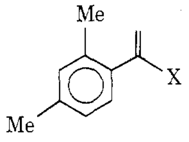
Figure 1.

since it is well known that such compounds generally show very sluggish solvolytic behavior. This has been ascribed to reactant stabilization, since a $C(sp^2)$–X bond is of lower energy than a corresponding $C(sp^3)$–X bond. However, other factors which could be important in producing this low reactivity are less effective backside solvation of the developing vinyl cation intermediate and the high energy of such a cation[2] compared with that of an analogous trisubstituted or "normal" carbonium ion.

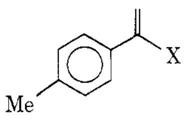
We have therefore investigated these two points in the solvolysis and acetolysis of several arylvinyl bromides and tosylates by comparing the relative reactivities of differently substituted compounds, as well as solvation effects on these reactions. The compounds investigated were the following.



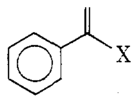
Ia,b



IIa,b



IIIa,b



IVa,b

a, X = Br
b, X = OTs

If we consider the model compound I and compare this with the parent system IV it can be predicted from an examination of molecular models that substitution in the neighborhood of the leaving group would produce two effects, as shown in Figure 1.

(1) Steric hindrance to coplanarity produced by the two ortho substituents should essentially destroy the conjugation between the phenyl and vinyl π systems and thus increase the initial state energy of I relative to IV. (This difference can be estimated to be of the order of 4–5 kcal based on enthalpies of hydrogenation.)

Examination of molecular models for Ib indicates that, because of the bulk of the tosylate group, the two π systems are probably very nearly orthogonal. Even for the less bulky bromide the interplanar angle between phenyl and vinyl in Ia is probably around 60–70°.

(2) As the system approaches the transition state during solvolysis, the vacant p orbital which develops at the π carbon as the leaving group departs can be directly conjugated with the phenyl ring in system I with little necessity for rotation about the C_α–phenyl bond. In the case of system IV, where the two π systems are initially coplanar, this conjugation could not be achieved until after the transition state had been reached.

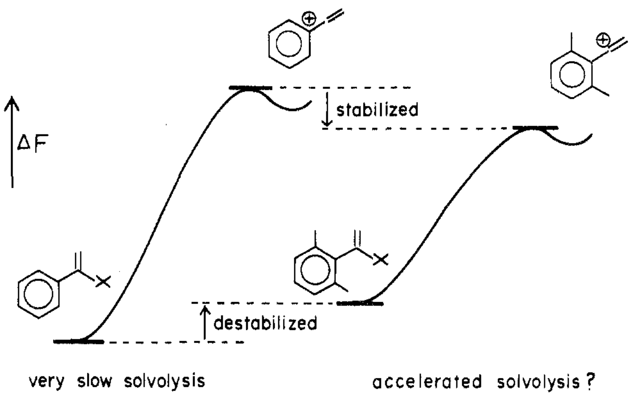


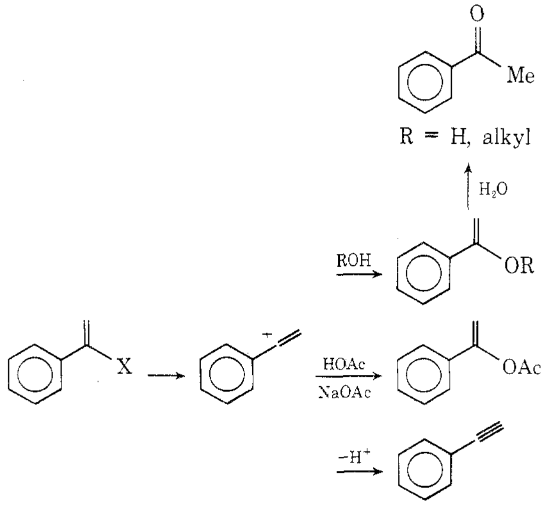
Figure 2.

Thus it would be expected that the total activation energy in the first case should be significantly lowered relative to that of the parent phenylvinyl system, as shown in Figure 2. Therefore, systems like I should solvolyze at reasonable rates at moderate temperatures, even with normal leaving groups, without requiring the use of highly polar leaving groups such as triflate, which have been used recently to obtain conveniently measurable solvolysis rates in vinyl systems.[3] In this way the solvolytic reactivity of arylvinyl bromides and tosylates can be more directly compared with the wealth of information available on the solvolysis of analogous saturated substrates,[4] and also with electrophilic additions to arylacetylenes.[1]

Results and Discussion

Although the S_N1 mechanism has been observed in most previous studies of vinyl solvolysis, other possible solvolytic processes cannot automatically be excluded. Other observed processes have been nucleophilic addition followed by elimination,[5] electrophilic addition and elimination in acidic solution,[6] and E2-type elimination.[7] The S_N2 mechanism is another possibility, although theoretical calculations suggest that it is energetically unfavorable for vinyl systems.[8] Therefore it is important to establish that the arylvinyl substrates studied here do in fact follow simple S_N1 type processes.

Evidence for an S_N1 Mechanism. This mechanism can be established from product analysis and kinetic measurements in the following way. Firstly, product analysis based on either solvolysis in alcohol-water mixtures or acetolysis in acetic acid–sodium acetate shows in all cases



that the ketone (or acetate) is the major product. The minor product (10–30%) in all cases is the corresponding arylacetylene, presumably formed by proton loss from the vinyl cation intermediate. (The proportions of product formed from each substrate are given in the Experimental Section.)

The kinetics in each case are simple first order in substrate, and the rate constants obtained are independent of the concentration of added nucleophile or base, as illustrated in Table I. Even when sodium hydroxide is used in tenfold excess of the concentration of the starting tosylate, there is a negligible change in the observed rate constant. This is consistent only with an SN1 process.

It is well known that the effect of a change in leaving group on solvolytic rate is a good criterion for distinguishing between SN1 and SN2 processes.[4] For example, if the ratio k_{OTs}/k_{Br} for ROTs and RBr solvolysis is close to unity, this indicates an SN2 type process, whereas, if the ratio is of the order of 200 or greater, this indicates an SN1 mechanism. The results in Table II for the solvolysis of Ia,b and IIa,b clearly indicate an SN1 mechanism for these vinyl substrates. We will show later, when discussing solvation effects, that the rates of these arylvinyl-X solvolyses are significantly increased (by more than 10^2) by increasing the ionizing ability of the solvent (as from acetic acid to water). This is also much more consistent with an SN1 process, since SN2 processes are known to be relatively insensitive to changes in solvent polarity.

Table I
Effect of Added Base on the Solvolysis of Ib in 80:20 Ethanol–Water at 36.5°

$[ROTs]_0$	Base (M)	[Base]/[ROTs]	$10^4 k_{obsd}$, sec^{-1}
10^{-4}	NaOAc (1.5×10^{-4})	1.5	2.08
10^{-4}	NaOAc (5×10^{-4})	5	2.02
10^{-4}	NaOAc (10^{-3})	10	2.01
10^{-4}	NaOH (10^{-3})	10	2.20

Table II
Leaving-Group Effects on Arylvinyl Solvolysis

Substrate	k, sec^{-1}	Reaction conditions	k_{OTs}/k_{Br}
Ia	$1.80 \pm 0.02 \times 10^{-5}$	E/W 80:20[a]	335
Ib	$6.03 \pm 0.01 \times 10^{-3}$	$T = 67.8°$	
IIa	$2.60 \pm 0.04 \times 10^{-6}$	E/W 80:20[a]	400
IIb	$1.05 \pm 0.01 \times 10^{-3}$	$T = 88.0°$	

[a] Ethanol–water.

Table III
Rates of Solvolysis of Arylvinyl Tosylates in $MeOH–H_2O$ (50:50) at 36.5.

System	Ib	IIb	IIIb	IVb
k,[a] sec^{-1}	7.95×10^{-3}	1.39×10^{-4}	4.36×10^{-7}	1.90×10^{-8} [b]
k_{rel}	4.2×10^5 (1.8×10^4)	7.3×10^3 (320)	23 (1)	1

[a] $[ROTs]_0 = 10^{-4}\ M$; $[NaOAc] = 5 \times 10^{-4}\ M$. [b] Value extrapolated to 36.5° from data in ref 7 using activation parameters.

Table IV
Rates of Solvolysis of Arylvinyl Bromides in $EtOH–H_2O$ (80:20) at 88.0.

System	Ia	IIa	IIIa	IVa
k,[a] sec^{-1}	1.54×10^{-4}	2.60×10^{-6}	3.5×10^{-8}	8.7×10^{-10} [b]
k_{rel}	$(1.8 \times 10^5$ (4.5×10^3)	3×10^3 (75)	40 (1)	1

[a] $[RBr]_0 = 10^{-4}\ M$; $[NaOAc] = 5 \times 10^{-4}\ M$. [b] Value extrapolated to 88.0° from data in ref 9 using activation parameters and $\rho\sigma^+$ relationships.

Effects of Substitution. The solvolysis rate enhancements which result from methyl substitution in the phenyl ring are shown by the two sets of data in Tables III and IV for the phenylvinyl tosylates and bromides, respectively.

From these two sets of data, and particularly from the tosylate data, it can be seen that the effect of methyl substitution in the para position, which gives only polar effects, is significantly less than that of ortho substitution. Substitution at the ortho position, and particularly at both, produces rate enhancements larger than would be expected from the additive polar effects of several methyl substituents. Thus, even though the measured rate enhancements are the sum of polar and steric accelerations, the results show that the latter contributes a large proportion of the observed enhancement of the vinyl solvolysis rate.

These results are in good agreement with the predictions based on the energy profile diagram of Figure 2 and show that the reactivity of vinyl substrates can be greatly enhanced by this type of substitution, without the need for highly polar leaving groups such as triflate. It is interesting to compare the effects of similar substitution on the rates of SN1 solvolysis of corresponding saturated compounds, such as the 1-phenylethyl chlorides studied by Charlton and Hughes.[10] These effects are shown in Table V.

In comparing the rate effects of methyl substitution in Tables III–V, the polar effect of a 4-methyl is expected to be roughly similar whether a carbonium ion or vinyl cation type of transition state is being produced, and in fact this is found to be the case. However, further substitution in the ortho positions produces rate accelerations which are less than cumulative[11] for the saturated series, but more than cumulative for the vinyl series. Thus steric effects in the saturated series are retarding, since they prevent carbonium ion delocalization into the phenyl group, but in the corresponding vinyl substrates they are accelerating, since they permit or even enforce vinyl cation delocalization. This comparison between the saturated and unsaturated series of solvolysis reactions supports the description given earlier of steric effects in the arylvinyl systems.

Solvent Effects. It is of interest to obtain more information about solvent participation in the solvolysis of vinyl compounds, partly to determine whether the low reactivity of such compounds is related to less effective solvation of vinyl cation intermediates and transition states,

Table V
Relative Rates of Solvolysis of Substituted 1-Phenylethyl Chlorides in EtOH at 34.8.

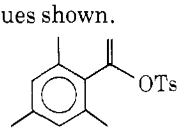
Substituent (registry no.)	2,4,6-Trimethyl (51270-90-7)	2,4-Dimethyl (51270-91-8)	4-Methyl (2362-36-9)	
k_{rel}	1440 (36)	560 (14)	40 (1)	1

and partly to compare solvent effects on the rates of solvolytic reactions with those observed for electrophilic additions generating analogous cationic intermediates. Two methods used to assess solvent effects were the Winstein-Grunwald treatment[12] and the more recent approach of Schleyer.[13]

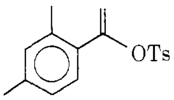
Determination of the effect of changing the solvent on the solvolytic rates of Ia and IIa gives the results shown in Table VI. These values can be used to calculate the parameter *m*, which is a measure of the sensitivity of the reaction to changes in solvent polarity (*Y*) according to the relation below.

$$\log k/k_0 = mY$$

Good linear plots were obtained in each case, yielding values of *m* at the reaction temperatures involved. The empirical relationship $m_1/m_2 = T_2/T_1$[14] can then be used to correct these values to the standard temperature of 25°, for direct comparison with other available *m* values. This yields the values shown.



$m^{25°} = 0.62$



$m^{25°} = 0.65$

Compared with *m* values previously obtained for typical SN1 reactions,[12] these values are low, although they are comparable in magnitude to those found for the trianisylvinyl system.[15] To assess whether these low *m* values could be due to a less effective nucleophilic assistance component of the solvent participation, the complete Winstein-Grunwald equation

$$\log k/k_0 = mY + lN$$

was used to try to determine the extent of partial S_N2 character in these vinyl solvolyses. Unfortunately, the range of solvent nucleophilicity parameters (*N*) available is not large, but the contribution of the term *lN* can be determined[4] by using this equation in differential form

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

and by measuring the ratio of rate constants obtained in two solvents of the same *Y* value ($\partial Y = 0$) but with considerably different nucleophilicities ($\partial N \neq 0$). Two such solvents are ethanol-water (98:2) and acetic acid, for which $Y = -1.68$ in each case. The results obtained in these two solvents are shown in Table VII. From the rate ratios $k_{KOAc}/k_{E/W}$ it is clear that a significant change in nucleophilicity of the solvent[13] produces no significant change in rate (*i.e.*, $d \log k/\partial N \cong 0$) compared with the changes obtained for typical S_N2-type reactions (which show rate enhancements of 3×10^2 to 1.3×10^4 in changing from acetic acid to ethanol[16]). These results point to a very important aspect of the solvolysis of vinyl compounds, the absence of any significant rear-side nucleophilic assistance by solvent molecules or external nucleophiles. It is probable that the low values of *m* obtained using the simple Winstein-Grunwald equation result partly from the fact that these systems are poorly solvated from the rear side as they approach the transition state, compared with the solvation in typical S_N1 processes of saturated systems.

Table VI
Rates of Solvolysis in Ethanol–Water Mixtures

System EtOH-H$_2$O	98:2	90:10	80:20	70:30	60:40	50:50
Ib	2.20×10^{-5} [a]	7.03×10^{-5}	2.02×10^{-4}	3.71×10^{-4}	9.81×10^{-4}	2.32×10^{-1}
IIb	1.38×10^{-5} [b]	3.96×10^{-5}	1.04×10^{-4}	2.65×10^{-4}	4.38×10^{-4}	1.13×10^{-3}

[a] Measured at 36.5°. [b] Measured at 67.6°.

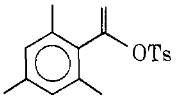
Table VII

System	*k*, sec^{-1}, in HOAc	*k*, sec^{-1} in E/W (98:2)	$k_{HOAc}/k_{E/W}$
Ib	2.76×10^{-5} [a]	2.20×10^{-5} [a]	1.25
IIb	1.57×10^{-5} [b]	1.38×10^{-5} [b]	1.13

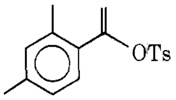
[a] At 36.5°. [b] At 67.6°.

Relative Ease of Solvolytic Formation of Vinyl Cations and Carbonium Ions. From the *m* value of 0.62 obtained for Ia and Charlton and Hughes' results[10] for the corresponding 1-arylethyl chloride, an estimate can be made of the relative solvolytic reactivity of vinyl and saturated systems. For the vinyl system I k_{EtOH} (Ia) = 1.90×10^{-5} sec^{-1} at 36.5° and using the ratio $k_{OTs}/k_{Br} = 335$ determined in this work, with the ratio $k_{Br}/k_{Cl} = 60$ obtained for other vinylic substrates,[15] it can be estimated that k_{RCl} (vinyl, 36.5°) = 9.5×10^{-10} sec^{-1}. From previous results[10] k_{RCl} (satd, 36.5°) for the 1-(2,4-6-trimethylphenyl)ethyl chloride is 1.35×10^{-3} sec^{-1}. Thus $(k_{RCl})_{satd}/(k_{RCl})_{vinyl} \cong 1.4 \times 10^6$. Previous estimates in the literature of saturated *vs.* vinyl solvolytic reactivity are of the same order of magnitude, although more approximations were required. It is worth pointing out that the above rate factor of ~10^6 is a lower limit, since steric effects on the saturated compound are unfavorable to solvolysis, as shown earlier. It seems very likely that 1-phenylethyl chloride itself would solvolyze at least 10^8 times as fast as 1-phenylvinyl chloride.

Determination of the Schleyer *Q* Parameter. The importance of rear-side nucleophilic assistance can also be assessed using the recently developed treatment of Schleyer,[13] which seems to have received little application so far despite its potential utility. The treatment is based on a comparison of solvent effects on the reaction of a tosylate of interest with the corresponding solvent effects in two extreme cases, that of methyl tosylate solvolysis, which is taken as a good model for strong nucleophilic assistance ($Q = 0$), and the case of 2-adamantyl tosylate, which is an excellent model for no rear-side nucleophilic assistance ($Q = 1.0$). Values of *Q* were determined using the solvent pair ethanol-water (80:20) as standard solvent, and methanol-water (50:50). The *Q* values obtained are



$Q = 0.67 \quad (T = 36.5°)$

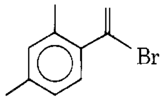


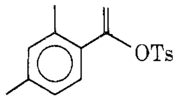
$Q = 0.76 \quad (T = 67.6°)$

These values show that arylvinyl systems are much more adamantyl-like in terms of nucleophilic assistance to solvolysis than methyl-like; in other words, that solvent participation from the rear side of the developing vinyl cation is weak. This is in good accord with the results obtained from the extended Winstein-Grunwald equation. The above Q values can be compared with the values obtained by Schleyer[13] for saturated substrates, and are in the range of those determined for systems like cyclohexyl and 3-octyl tosylate, where rear-side nucleophilic assistance to solvolysis is expected to be weak because of steric hindrance to rear-side attack.[14]

Another advantage of the Q parameters is that they can be used to calculate rate constants in other solvents, which are used to estimate rates in solvents where data are not experimentally accessible. For example using Q = 0.67 for Ia, the calculated rate constant for this substrate in acetic acid at 36.5° is $k_{\text{calcd}} = 1.12 \times 10^{-5}\ \text{sec}^{-1}$, which compares reasonably with the experimental value of $1.57 \times 10^{-5}\ \text{sec}^{-1}$.

In this way we are able to estimate rate constants in pure water, and so obtain the ratio $k_{H_{2}O}/kAcOH$, which cannot be experimentally determined for solubility reasons. Examples are given below.

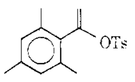
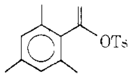
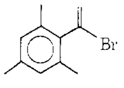
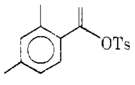
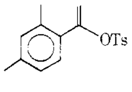
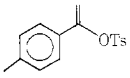
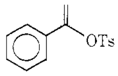

$k_{H_2O}/k_{AcOH} = 384$ (at 36.5°)


$k_{H_2O}/k_{AcOH} = 1.15 \times 10^3$ (at 67.7°)

These solvent effects will be compared later with those for other systems.

Activation Parameters. Rate measurements were made at several temperatures for some of the substrates, in an attempt to rationalize the observed rate enhancements in terms of changes in ΔH^* and ΔS^* values produced both by substitution and by solvent polarity changes. The activation parameters obtained are listed in Table VIII.

Table VIII
Activation Parameters for Vinyl Solvolysis

Solvent	Compd		ΔH^*	ΔS^*
E/W 80:20		(Ib)	21.8	−5
M/W 50:50		(Ib)	18.4	−8
E/W 80:20		(Ia)	25.2	−7
E/W 80:20		(IIb)	23.4	−1
M/W 50:50		(IIb)	21.4	−10
M/W 50:50		(IIIb)	24.5	−8
M/W 50:50		(IVb)	24.2[a]	−18[a]

[a] From ref 7.

Comparing the values for Ib, IIb, and IIIb (all in 50:50 methanol-water) it can be seen that ΔS^* remains essentially constant with methyl substitution, and that the observed rate enhancements (1.8×10^4:320:1) are mainly due to a lowering of ΔH^* by about 3 kcal for each ortho methyl group. A similar trend is found by comparing the values for Ib and IIb in 80:20 ethanol-water. A change in solvent from 80:20 ethanol-water to 50:50 methanol-water produces a lower ΔH^* (by about 2-3 kcal) and a somewhat more negative (and compensating) value of ΔS^*. This can be seen by comparing the values for Ib or IIb in the two solvents. These changes are not unreasonable for an increase in solvent polarity leading to a modest rate enhancement of the magnitude observed. The major difference between the tosylate (Ib) and the bromide (Ia) is a significantly lower ΔH^* for the better leaving group, with the ΔS^* values being almost the same. The above results are interesting mainly in that they show there are no striking or anomalous changes in ΔS^* with the introduction of either one or two ortho methyl substituents. Thus the transition states in the rate-enhanced systems appear to be no more restricted compared with their initial states than are the unsubstituted systems. Thus the enhancements observed are mainly due to enthalpy changes produced by more favorable electronic stabilization in the nonplanar arylvinyl systems.

Solvent Stabilization of Vinyl Cation *vs.* Normal Carbonium Ion Intermediates. The values previously estimated for the rate ratios k_{H_2O}/k_{HOAc} for arylvinyl solvolysis are of the order of 10^3. These ratios are of the same order as, or less than, would be expected for the solvolysis rates of the corresponding saturated substrates in the same two solvents (since the m values for arylvinyl solvolysis appear to be somewhat low for S_N1-type reactions). Thus the large rate ratios of the order of 10^6–10^8 which can be estimated for $k_{\text{satd}}/k_{\text{vinyl}}$ in solvolytic reactions involving the same leaving groups would not be expected to decrease significantly with an increase in solvent polarity (such as from acetic acid to water), and would if anything be expected to increase. This is in marked contrast to the relative rates of electrophilic addition to typical olefins and acetylenes, which show a dramatic decrease with such a change in solvent. For example, it has been shown[1] that $k_{\text{styrene}}/k_{\text{phenylacetylene}}$ changes from 2.6×10^3 to 0.6 for brominations in acetic acid and water, respectively. Thus, despite the fact that the cationic intermediates being generated in the two types of reaction are formally very similar in structure (as shown), the solvent stabilization of the vinyl cation intermediates in solvolysis must be much less effective than vinyl cation stabilization in electrophilic

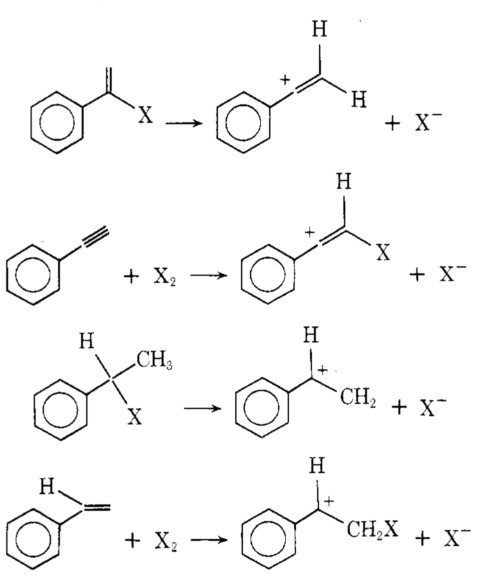


Table IX

Bromide	Ia	IIa	IIIa
Bp, °C (0.05 mm)	44	42	49
Ir ($\nu_{C=C}$), μ	6.13	6.13	6.20
Nmr (CCl_3, TMS), δ	2.21 s (3 H)	2.28 s (3 H)	2.33 s (3 H)
	2.25 s (6 H)	2.34 s (3 H)	5.62 d (1 H) J = 2 Hz
	5.50 d (1 H) J = 2 Hz	5.58 d (1 H) J = 2 Hz	5.97 d (1 H) J = 2 Hz
	5.78 d (1 H) J = 2 Hz	5.74 d (1 H) J = 2 Hz	6.95–7.50
	6.68] (2 H)	6.8–7.2 m (3 H)	
Analysis, %			
Calcd C	58.69	56.89	54.85
Found C	59.88	57.25	54.23
Calcd H	5.78	5.21	4.57
Found H	5.95	5.80	4.95
Calcd Br	35.52	37.88	40.53
Found Br	33.79	37.20	39.72
Mass spectra, *m/e*	226, M (^{81}Br)	212, M (^{81}Br)	198, M (^{81}Br)
	224, M (^{79}Br)	210, M (^{79}Br)	196, M (^{79}Br)
	145[a] (M − Br)	131[a] (M − Br)	117[a] (M − Br)

[a] Relative intensity 100.

Table X

Tosylate	Ib[a]	IIb[a]	IIIb[a]
Mp, °C	88	65	59
Ir ($\nu_{C=C}$), μ	5.98	6.08	6.12
(ν_{OTs}), μ	8.35, 8.45	8.40, 8.50	8.35, 8.45
Nmr (CCl_3, TMS), δ	2.16 s (9 H)	2.18 s (3 H)	2.25 s (3 H)
	2.35 s (3 H)	2.22 s (3 H)	2.42 s (3 H)
	4.72 d (1 H) J = 2 Hz	2.38 s (3 H) J = 2 Hz	4.96 d (1 H) J = 2 Hz
	5.40 d (1 H) J = 2 Hz	4.83 d (1 H) J = 2 Hz	5.22 d (1 H) J = 2 Hz
	6.73 s (2 H)	5.18 d (1 H)	6.90–7.80 m (8 H)
	7.03–7.60 m (4 H)	6.8–7.8 m (7 H)	
Mass spectra, *m/e*	316 (M)	302 (M)	288 (M)
	144[b] (M − OTs)	130[b] (M − OTs)	116[b] (M − OTs)

[a] Satisfactory combustion analytical data for C, H, and S (±0.7%) were reported for these compounds. [b] Relative intensity 100.

addition, relative to that of the corresponding trisubstituted or "normal" carbonium ion intermediates in each case. The reason for this difference in effectiveness of solvent stabilization of vinyl cations in solvolytic and addition reactions is difficult to understand, but it must be connected with the less effective nucleophilic participation in vinyl solvolysis, as evidenced by the low *m* and high *Q* values for these reactions, and their insensitivity to solvent or solute nucleophilicity, as shown earlier. It remains a striking fact that although typical vinyl systems must ionize to give cationic intermediates which are among the least stable carbonium species known in solvolysis reactions, they appear to do so by SN1-like processes in all solvents.

Experimental Section

Melting points are corrected; boiling points are not. Solvents were purified using standard procedures. Nmr spectra were recorded on a Varian T-60 spectrometer and chemical shifts are given in δ units relative to TMS. Infrared and ultraviolet spectra were obtained using Perkin-Elmer 337 and Cary 16 instruments, respectively. Kinetic measurements were made using either a Unicam SP-800 or Cary 16 spectrophotometer, using constant wavelength and scale expansion. Gc analyses were performed on a Carlo-Erba Model 61 chromatograph.

Preparation of Arylvinyl Bromides. Compounds Ia, IIa, and IIIa were prepared from the corresponding acetophenones, which are commercially available. These were first converted into the vinyl chlorides using a reported procedure.[18,19] The chlorides were dehydrochlorinated using sodium amide in liquid ammonia[19] and the resulting arylacetylenes were converted into the desired bromides using the following typical procedure. Through a solution of 10.0 g (0.074 mol) of 2,4-dimethylphenylacetylene in 120 ml of ethanol-free $CHCl_3$, gaseous, anhydrous HBr was bubbled for 30 min. (The course of the reaction was followed by the disappearance of the nmr signal of the acetylenic proton.) The solution was then washed ($NaHCO_3$, then H_2O) and dried over $MgSO_4$. Evaporation of solvent gave 14.5 g (94% yield) of a yellow material, whose nmr spectrum showed the presence of little impurity. Further purification was achieved by vacuum distillation. The results for all three bromides are summarized in Table IX.

Preparation of Arylvinyl Tosylates. The tosylates (Ib, IIb, and IIIb) were obtained by reaction of the above bromides with silver tosylate in acetonitrile using the following procedure, as for compound Ib. To a solution of 7.5 g (0.033 mol) of Ia in 50 ml of dry acetonitrile was added 11 g (0.04 mol) of silver tosylate in 120 ml of acetonitrile. (The commercial silver salt had been recrystallized from 1:1 acetonitrile–ether and dried under vacuum for 2 hr at 80°.) The mixture was kept at 80° for 30 min. After cooling, the silver bromide was filtered off and the solvent was evaporated. The solid residue was washed with pentane, and then CCl_4 was added. The resulting solution was dried ($MgSO_4$) and the solvent was evaporated. The remaining solid (7.6 g, 73% yield) was recrystallized from pentane–chloroform (9:1), giving crystals melting at 88°. The same procedure was used for IIb but the reaction was slower (reaction time 5 hr, yield 52%). The bromide IIIa does not react under the above conditions, and it was necessary to heat the acetonitrile solution at 120° for 3 hr in a sealed ampoule (yield 38%). The results for all three tosylates are summarized in Table X.

Product Analysis. Solvolysis. A 300-mg portion of the compound (bromide or tosylate) was dissolved in the appropriate alcohol–water mixture, with the corresponding amount of sodium acetate as base, and kept at the selected temperature for 10 half-lives in a sealed ampoule. The solvent was then removed by evaporation, and the product was extracted with ether and dried with magnesium sulfate. After removal of the solvent the products (Table XI) were analyzed by gas chromatography; quantitative analysis was achieved by integration after standardization with authentic samples, and by nmr.

Acetolysis. The same procedure was used, with acetic acid as solvent. The solvent was removed by evaporation and the solid residue was extracted with carbon tetrachloride, washed with an aqueous solution of sodium bicarbonate, then with water, and dried over magnesium sulfate. The product analysis was achieved by gas chromatography and nmr as previously. The acetates

Table XI
Solvolysis Products

Compd	Products, %		
	Ketone	Acetylenic	Acetate
Ia or Ib (EtOH–H_2O, NaOAc)	65	35	
Ib (HOAc, NaOAc)		30	70
In (HOAc, without NaOAc)	100		
IIa or IIb (EtOH–H_2O, NaOAc)	70	30	
IIb (HOAc, NaOAc)		20	80
IIIa or IIIb (EtOH–H_2O, NaOAc)	90	10	

Table XII

Compd	Ia	IIa	IIIa	Ib	IIb	IIIb
λ, nm (solvolysis)	235	231	256	233	234	233
(acetolysis)				256	253	

formed were identified by comparison of their nmr and ir spectra with those of authentic samples obtained by reaction of silver acetate in glacial acetic acid on the corresponding bromide following the procedure of Rappoport.[20]

Kinetic Measurements. All kinetic runs were followed spectrophotometrically, using the change in absorbance at the most suitable wavelength (Table XII).

All runs were made at least in duplicate. For those up to 85°, the cell was thermostated with a water bath, with continuous recording of the absorbance for fast reactions, or by periodical recording for the slower runs. For the runs above 85°, Grob's technique of sealed ampoules in an oil bath was used.[9] The ampoules were filled with a syringe to avoid any evaporation and thus avoid changes in concentration leading to irreproducibility in the uv measurements. The samples were sealed after cooling in acetone–Dry Ice bath. First-order rate coefficients, *m* values, and activation parameters were calculated by least-squares treatment of the experimental data. In most cases an infinity absorbance value was used, except for acetolysis, for which the Guggenheim method was applied.

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Registry No.—Ia, 51270-84-9; Ib, 51270-85-0; IIa, 51270-86-1; IIb, 51270-87-2; IIIa, 51270-89-4; IIIb, 51270-88-3; IVa, 98-81-7; IVb, 26190-67-0.

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