Vinylic Cations from Solvolysis. XXI.[1,2] Solvent Effects on the External Ion Return and the Internal Return in Several Vinylic Solvolyses

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Abstract: The solvolyses of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides (**5**-Br and **6**-Br), the cis chloride (**5**-Cl), and the cis and trans mesylates (**5**-OMs and **6**-OMs) in 80% EtOH gave the ethers **5**-OEt and **6**-OEt and the ketone **25.** Solvolysis of **5**-Br and **6**-Br in 1:1 AcOH-HCOOH gave the acetates **5**-OAc and **6**-OAc and the vinyl formates which decomposed to **25,** while solvolysis of **5**-Br in 1:1 AcOH-Ac_2O gave **5**-OAc and **6**-OAc. Cis-trans isomerization of the vinyl halides was observed in all the solvents, and strong common ion rate depression was observed in the RCOOH media. Both phenomena were used to show the appearance of both the free ion **7** and the ion pair **8** during the solvolysis-isomerization, to calculate the ionization rate constant (k_{ion}) and to evaluate the extent of the external ion return and the internal return. The solvent effects on k_{ion} (1:1 AcOH-HCOOH > 80% EtOH > AcOH > 1:1 AcOH-Ac_2O), on the internal return (AcOH ~ 1:1 AcOH-HCOOH > 80% EtOH ~ 1:1 AcOH-Ac_2O), and on the external ion return (1:1 AcOH-Ac_2O > AcOH > 1:1 AcOH-HCOOH > 80% EtOH) are discussed in terms of the ionizing power, dissociating power, and nucleophilicity of the solvents. The use of the titrimetric rate constant (k_t) as a model for k_{ion} is discussed in relation to several kinetic parameters.

The intermediacy of ion pairs in the solvolysis of saturated compounds was extensively studied.[3] In vinylic solvolysis,[4] ion pairs were suggested as intermediates on the basis of stereochemical evidence,[5a-d] substituent effects,[5b] the effect of added base,[5b] the cis-trans interconversion of the unreacted substrate,[1,2,5e,f] and other kinetic evidence.[5g,h] Previous to our work,[1] kinetic evidence for ion pairs was obtained only in the acetolysis of 2-phenylthio-1,2-ditolylvinyl 2,4,6-trinitrobenzenesulfonate[6] which showed a $LiClO_4$ "special salt effect."[7] However, free ("dissociated") cations,[8a] which were observed only in a limited number of saturated solvolyses,[6,8,9] are intermediates in a relatively large number of vinylic and related solvolyses.[10]

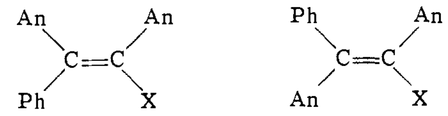
In the simplified mechanistic Scheme I,[11] where R^+X^- is a tight ion pair, and R^+ is a free ion, our knowledge regarding the solvent effect on the "selectivity" of the free ion as measured by $\alpha = k_{-2}/k_4$ is meager. In aqueous-organic media, α decreases on increasing the water content,[9b,c,10j] but data are absent for pure organic media. Increasing the dissociating power of the solvent, *e.g.*, by the change AcOH → Ac_2O,[12] increases the importance of R^+ as a product-forming intermediate, but comparisons are difficult since the ROAc is almost entirely derived from R^+X^- in AcOH, while 97% of it is formed from R^+ in Ac_2O.[12]

Scheme I

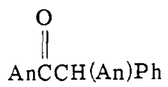
$$\begin{tikzcd} RX \arrow[r, shift left, "k_1"] & R^+X^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[d, "k_3", "SOH"'] & R^+ + X^- \arrow[l, shift left, "k_{-2}"] \arrow[d, "k_4", "SOH"'] \\ & ROS & ROS \end{tikzcd}$$

The solvent effect on the extent of internal return, as measured by $1 - F = k_{-1}/(k_{-1} + k_2 + k_3)$ where F is the fraction of R^+X^- which gives products, was studied in several systems. The ion-pair return as measured by internal return with isomerization is more important for AcOH and trifluoroacetic acid (TFA) than for HCOOH and for alcohols,[13,14] while oxygen equilibration in an arenesulfonate leaving group gave the following order for $1 - F$: TFA > AcOH ≃ HCOOH > MeOH.[15] In aqueous acetone, $1 - F$ decreases on increasing the water content,[16] confirming that dissociation becomes more important as the ionizing power of the solvent increases.[7b]

The preceding paper[1] has shown that in the acetolysis of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides (**5**-Br and **6**-Br),[17] methanesulfonates (mesylates, **5**-OMs and **6**-OMs),[1] and the cis chloride (**5**-Cl),[17] almost all the products are derived from free R^+'s. The study of the concurrent cis-trans isomerization showed the importance of internal return and enabled comparison of the effects of the leaving group on both the internal return and the external ion return. Using the same substrates, we evaluate now the solvent effect on $1 - F$ and α, using solvents which differ from AcOH in their nucleophilicities and dielectric constants.[18]



X = Br:	**5**-Br	**6**-Br
X = Cl:	**5**-Cl	**6**-Cl
X = OMs:	**5**-OMs	**6**-OMs
X = OTs:	**5**-OTs	**6**-OTs
X = OEt:	**5**-OEt	**6**-OEt
X = SCH_2Ph:	**5**-SR	**6**-SR
X = OAc:	**5**-OAc	**6**-OAc
X = OCHO:	**5**-OCHO	**6**-OCHO
X = H:	**5**-H	**6**-H


$AnC(=O)CH(An)Ph$

25

Results

Reactions in 80% EtOH. (a) 5-Br, 6-Br, and 5-Cl. Solvolyses of the vinyl halides in the presence of excess NaOH gave 20–25% of the ethers **5**-OEt and **6**-OEt and 75–80% of the ketone **25**, but only **25** was observed in the presence of 2,6-lutidine. The titrimetric rate coefficient k_t (eq 1) was

$$k_t = (2.3/t)\log[a/(a - x)] \qquad (1)$$

constant throughout the run, although k_t was sometimes 10% lower than the average value after 2 half-lives. Simultaneous isomerization of unreacted halide accompanied the solvolysis. The first-order isomerization rate coefficient, k_{isom} (eq 2),[1] was calculated by assuming that at equilibri-

$$k^{5\text{-Br}}_{\text{isom}} = (2.3/t)\log\{\%(6\text{-Br})_\infty/[(\%6\text{-Br})_\infty - (\%6\text{-Br})_t]\} \qquad (2)$$

Table I. Solvolysis–Isomerization in 80% EtOH

Compd	Base	Concn, $10^2\,M$	T, °C	10^6k_t, sec^{-1}	Relative k_t	10^6k_{isom},[a] sec^{-1}	10^6k_{ion},[b] sec^{-1}	% of ion pairs **8** which give RX[c]	Products[d]
5-Br	2,6-Lutidine	8.7	120.3	189 ± 4		120 ± 6	309 ± 10	39.0	61.0
5-Br	NaOH	39	120.3	253 ± 7	1.32	115 ± 6	368 ± 13	31.5	68.5
5-Br	NaOH	39	130.2	504 ± 15		285 ± 14	789 ± 29	36.3	63.7
5-Br	NaOH	39	60.0	1.52[e]			1.34[e]		
6-Br	NaOH	39	120.3	292 ± 9	1.52	155 ± 8	447 ± 17	34.6	65.4
6-Br	NaOH	39	130.2	558 ± 7		302 ± 15	860 ± 22	35.0	65.0
6-Br	NaOH	39	60.0	2.32[e]			3.10[e]		
5-Cl	NaOH	39	120.3	3.05 ± 0.17		0.90 ± 0.04	3.95 ± 0.57	23.0	77.0
$An_2C{=}C(Br)An$[f]	NaOH	18–52	120.0	408 ± 27	2.12				
$An_2C{=}C(Cl)An$[f]	NaOH	29	120.0	7.1 ± 0.5					
$Ph_2C{=}C(Br)An$[f]	NaOH	30–50	120.0	192 ± 4	1.00				
$AnC(Br){=}CH_2$[g]	NaOAc	18	120.0	248 ± 1	1.29				

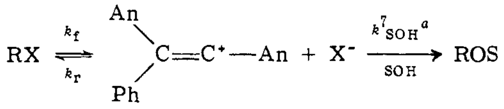
[a] The error is estimated as ±5%. The k_{isom} value was calculated by using 1 as the [**5**-Br]–[**6**-Br] equilibrium ratio. [b] Calculated by eq 3. The error is the combined error in the two terms. [c] RX refers to a cis–trans mixture of the vinyl halides. [d] Products are formed from either **7** or **8** (see text). [e] Extrapolated value. [f] From ref 26. [g] From ref 10b.

um the **5**-Br–**6**-Br ratio is 1[19] since a cis–trans vinyl halide equilibrium is not achieved during the run. The ionization rate constant, k_{ion}, was calculated from eq 3 (see below) and is given in Table I together with the other k's and those for related compounds.

$$k_{\text{ion}} = k_t + k_{\text{isom}} \qquad (3)$$

Reaction of 0.044 M **1**-Br with 0.087 M 2,6-lutidine and 0.087 M Et_4NBr gave a depressed rate constant,[8a] $10^4k_t^{\text{d}} = 1.50 \pm 0.02$ sec^{-1} at 120.3°. By applying mechanistic Scheme **II** which involves the free cation **7** as the only cationic intermediate and eq 4,[8a] an apparent selectivity constant α_{app} $(=k_r/k^7_{\text{SOH}})$ of 3 l. mol^{-1} [20] was calculated.

Scheme II



7

[a] k^7_{RCOO} in RCOOH media.

$$k_t^{\text{d}} = k_t^0/(1 + \alpha_{\text{app}}[\text{Br}^-]) \qquad (4)$$

Solvolysis of **5**-Br with excess of benzylthiolate ion at 120.5° gave a mixture containing 20% of **5**-OEt + **6**-OEt and 80% of an approximately 1:1 mixture of the thiolates **5**-SR and **6**-SR.[17] The isomerization was only moderately affected: 12% of **6**-Br was observed in the RBr fraction as compared with 17% in the absence of the benzylthiolate ion.

(b) 5-OMs, 6-OMs, and 5-OTs + 6-OTs. Solvolysis of **5**-OMs, **6**-OMs, or a 56:44 mixture of **5**-OTs to **6**-OTs[1] was followed conductometrically in the presence of 2,6-lutidine and was of a first order. The data are in Table II. The products are **5**-OEt + **6**-OEt (*ca.* 1:1)[21] and the ethanone **25**, while the vinyl bromides **5**-Br and **6**-Br are also formed in the presence of Et_4NBr (Table III). A lower limit of α_{app} of 0.9 l. mol^{-1} [20] for the capture of R^+ by Br^- was calculated from these values.[22] In all cases, <3% of the isomeric mesylate was observed by nmr after 2 half-lives.

Table II. Solvolysis of the Vinyl Sulfonates in 80% EtOH

Compd[a]	T, °C	10^5k_t, sec^{-1} [b]
5-OMs	60.0	2.80 ± 0.004
6-OMs	60.0	2.53 ± 0.0008
5-OTs + **6**-OTs[c]	45.1	0.623 ± 0.0006
	60.0	3.62 ± 0.01
	120.3	1150[d]

[a] [Substrate] = 0.004 M; [2,6-lutidine] = 0.045 M. [b] The error quoted is the standard deviation. [c] A 56:44 mixture of **5**-OTs to **6**-OTs was used. [d] Extrapolated value.

Reactions in AcOH–HCOOH and AcOH–Ac$_2$O Mixtures. One-point runs with 0.044 M **5**-Br and 0.087 M RCOONa at 99.7° gave $10^4k_t = 6.34$ sec^{-1} after 45 min in 2:1 HCOOH–AcOH, while $10^4k_t = 8.65$ sec^{-1} after 30 min in 72% HCOOH–28% AcOH.

In a 1:1 AcOH–HCOOH (v/v) mixture containing the sodium carboxylates, the products at early reaction times were mainly the vinyl formates (**5**-OCHO and **6**-OCHO) (recognized by a band at 1740 cm^{-1} but were not isolated) and some of the acetates **5**-OAc and **6**-OAc (band at 1770 cm^{-1}). The vinyl formates decomposed rapidly, and the acetates are converted slowly to **25**; after 340 min, the products are **25** (59%), **5**-OAc + **6**-OAc (21%), and **5**-OCHO + **6**-OCHO (21%), and after 45 hrs. they are **25** (97%) and the vinyl acetates (3%). Only **25** was formed in the slower solvolysis of **5**-Cl.

Due to common ion rate depression, the titrimetric rate coefficient k_t decreased strongly during the reaction, and k_t for **5**-Br at 82% reaction was half of the initial extrapolated value k_t^0. A concurrent cis halide $\rightleftharpoons$ trans halide isomerization took place, establishing an equilibrium of 54% of **5**-Br and 46% of **6**-Br during the reaction. The k_{isom} of eq 2 which is based on this ratio increased during the run.

In AcOH, the AcO$^-$ is the capturing nucleophile,[1] but in 1:1 AcOH–HCOOH **7** is captured by both the AcO$^-$ and the HCOO$^-$ ions, giving eq 5 where the subscripts designate the capturing nucleophile. Since AcOH and HCOOH have similar nucleophilicities,[23] we assumed that $k_{\text{HCOO}} = k_{\text{AcO}}$, thus obtaining the right-hand side of eq 5 where $[\text{RCOO}^-] = [\text{AcO}^-] + [\text{HCOO}^-]$.

rate of capture of **7** =

$$k_{\text{HCOO}}[\text{HCOO}^-] + k_{\text{AcO}}[\text{AcO}^-] = k_{\text{RCOO}}[\text{RCOO}^-] \qquad (5)$$

We calculated k_t^0 and α_{app} $(=k_r/k^7_{\text{RCOO}})$ from eq 6

$$1/k_t = 1/k_t^0 + \alpha_{\text{app}}/k_t^0(1 - n)[n \ln[na/(na - x)]/\ln[a/(a - x)] - 1] \qquad (6)$$

(where $n = [\text{RCOO}^-]_0/[\text{RX}]_0$) which is derived from the steady-state treatment of Scheme II.[1] The values obtained are given in Table II. As in AcOH,[1] computer simulation of Scheme II gave α_{app} values similar to those derived from eq 6, a fit of the experimental concentration *vs.* time profiles for the decay of the starting bromide and the product formation but more isomerization than predicted from return from **7** alone.

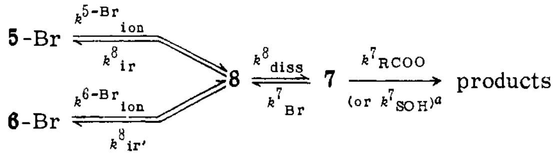
Scheme III, which involves both the ion pair **8** which gives internal return to original RX (k^8_{ir}) and isomeric RX′

Table III. Solvolysis Products of the Vinyl Sulfonates in 80% EtOH

Substrate[a]	[2,6-Lutidine], *M*	[Et$_4$NBr], *M*	Time, hr	Products, %: **25**	Products, %: **5**-OEt + **6**-OEt[b]	Products, %: **5**-Br + **6**-Br[c]
5-OMs	0.087		24	20	80	
			170	25	75	
6-OMs	0.087		170	30	70	
5-OMs	0.17	0.26	17	25 ± 4	63 ± 4	12
6-OMs	0.17	0.87	17	5	52 ± 2	43 ± 2

[a] [Substrate] = 0.043 *M*; reaction at 60°. [b] A mixture of *ca.* 1:1 of **5**-OEt to **6**-OEt. [c] A mixture of 48% of **5**-Br and 52% of **6**-Br was formed.

Scheme III



[a]In 80% EtOH.

($k^8_{ir'}$) and dissociation to **7** (k^8_{diss}), and **7** which gives external ion return (k^7_{Br}) and products (k^7_{RCOO}), was therefore applied.[1] The "total cis content" method in the form of eq 3 was used for calculating k_{ion},[1] assuming that the unknown **5**-OCHO-**6**-OCHO equilibrium ratio is 54:46, as found with the bromides and the acetates.[24] Indeed, eq 3 gave constant k_{ion} values (Table IV). Scheme III was simulated as described earlier,[1] until a fit was obtained between the experimental and calculated profiles for all the species. The resulting best α's, the distribution of **7** among the return and product-forming routes (when [Br$^-$] = [RCOO$^-$]), the distribution of **8** between the return and dissociation routes, and related data in AcOH are given in Table IV.

Designating the fraction of ion pairs which give dissociation by *F*, the return *vs.* dissociation ratio is given by eq 7, and $\alpha = \alpha_{app}/(1 - F)$.

$$(k^8_{ir} + k^8_{ir'})/k^8_{diss} = (k^{5\text{-Br}}_{ion}/k_t^0) - 1 = (1 - F)/F \quad (7)$$

Solvolysis at 99.3° of **5**-Br in the presence of (i) 0.076 *M* Bu$_4$NBr and 0.011 *M* NaOAc and of (ii) 0.14 *M* Bu$_4$NBr and 0.087 *M* NaOAc gave respectively $10^5k_t^d = 7.15$ sec^{-1} at 59% reaction and $10^5k_t^d = 4.7$ sec^{-1} at 70% reaction; *i.e.*, k_t^d/k_t^0 are 0.25 and 0.10. From eq 8, by using an average

$$k_t^d = k_t^0/(1 + \alpha_{app}[\text{Br}^-]/[\text{RCOO}^-]) \quad (8)$$

[RCOO$^-$] of 0.061 *M*, $\alpha_{app} > 4.3$ from experiment (ii). From k_t^d/k_t^0, >90% of the products is formed from **7**.

Isomerization in the solvolysis of **5**-Cl is apparent by ir, but the evaluation of k_{isom} is associated with high error and was not attempted.

In 1:1 AcOH-Ac$_2$O (v/v), the products from **5**-Br are 54% of **5**-OAc and 46% of **6**-OAc, and the common ion rate depression within a run was the strongest yet found for compound **5**-Br. This is exemplified in Table V, which also shows the constancy of k_{ion} as calculated by eq 3. Other data are in Table IV.

Reaction in Trifluoroacetic Acid. A solution of **6**-Br in TFA at room temperature turns immediately pink, then brown, and finally black within 1 hr. When a mixture of **5**-Br and **6**-Br is trifluoroacetolyzed in the presence of 0.087 *M* NaOOCCF$_3$ at 65.5°, $10^4k_t = 4.2$ sec^{-1} after 30 min, and the ir show the presence of **25** and of a vinyl trifluoroacetate (band at 1790 cm^{-1}).

Isomerization of 1,2-Dianisyl-2-phenylethylenes. No mutual isomerization of the ethylenes **5**-H and **6**-H takes place in 80% EtOH-NaOH after 64 hr at 120°, *i.e.*, $10^6k_{isom} < 0.45$ sec^{-1}. In 1:1 AcOH-HCOOH-0.087 *M* RCOONa, an equilibrium mixture containing 51.5% of **5**-H and 48.5% of **6**-H was obtained starting from **5**-H, and the first-order k_{isom} is $1.52 \pm 0.01 \times 10^{-4}$ sec^{-1} at 99.7°.

Discussion

Exclusion of Addition-Elimination Routes. For using the isomerization as a mechanistic tool, it is essential to exclude addition-elimination isomerization routes where a nucleophile or an electrophile adds to the double bond and departs after a free rotation around the C_α-C_β bond in the intermediate.

Nucleophilic addition-elimination (Ad$_N$-E)[25] is excluded in 80% EtOH by comparing our solvolysis rates with those for related systems,[25b,26] by the stereochemistry in the presence of PhCH$_2$S$^-$ ion,[17] and by the k_{Br}/k_{Cl} and the k_{Cl}/k_{OMs} ratios (Table VI) which are close to unity in the Ad$_N$-E route.[25a,27] The isomerization rate ratios (k_{isom}(RBr)/k_{isom}(RH) > 250-340) argue strongly for isomerization *via* C-Br bond heterolysis. Electrophilic addition-elimination (Ad$_E$-E)[10b,28] in AcOH-HCOOH and AcOH-Ac$_2$O is excluded by the nature of the products,[1,28b] by the k_{Br}/k_{Cl} ratio[10b,29] and the k_{OMs}/k_{Br} ratio, and by analogy with the S$_N$1 solvolysis of 1-anisyl-2-methylpropen-1-yl tosylate in TFA[30a] and in AcOH-HCOOH mixtures.[30b]

In 1:1 AcOH-HCOOH at 99.7°, k_{isom}(**5**-H)/k_{isom}^0 (**5**-Br) = 0.6, but it can still be argued that contribution from the Ad$_E$-E route for the isomerization of **5**-Br is small. However, the isomerization of **5**-Cl is qualitatively much slower than that of **5**-H, and contribution from the Ad$_E$-E route cannot be excluded.

Intermediates in 80% EtOH. The absence of common ion rate depression during a run in 80% EtOH is consistent with product formation either (a) *via* free ions **7** when capture is faster than return (k^7_{SOH}[SOH] ≫ k^7_{Br}[Br$^-$]), or (b) *via* ion pairs **8** when $k^8_{diss} \ll k^8_{SOH}$ (capture of **8** by the solvent), or *via* both a and b.[8a] From the k_t^d/k_t^0 ratio we calculate that >21% of the products is derived from **7**. This is a lower limit since the salt effect on k_t^0 was neglected, and higher [Br$^-$] concentrations were not used.[31] The lower α_{app} than that for **5**-Br in AcOH[1] is due to the higher nucleophilicity of 80% EtOH.

In spite of some product formation from **7**, the bulk of the product can still be derived from **8**, and it may be argued that the formation of 80% of **5**-SR and **6**-SR is due to capture of both **7** and **8** by the strong thio-nucleophile, PhCH$_2$S$^-$. However, since k_{isom} is only moderately reduced, we believe that isomerization occurs mainly *via* a tight ("intimate") uncapturable ion pair **8**.[32] This is the justification for calculating k_{ion} by eq 3 from the sum of k_{isom} (*via* the uncapturable **8**) and k_t (*via* **7** which does not return within a run). From the k_t/k_{isom} ratios, 31.5-39% of the ion pairs from **5**-Br and **6**-Br returns to covalent bromide with isomerization (Table I).

Table IV. Kinetic Data for Solvolyses in Carboxylic Acid Media

Compd[a] RX	Solvent	T, °C	10^5k_{ion},[b] sec^{-1}	$10^5k_t^0$,[c] sec^{-1}	α_{app}[c]	α[d]	% of the ion pairs **8**[d] which give Original RX	Isomeric RX	Free ion **7**	% of the free ions **7**[e] which give Ion pair **8**	Products
5-Br	1:1 AcOH-HCOOH (v/v)	99.7	55.0 ± 0.1	30.6 ± 0.9	2.57 ± 0.20	5.45	23.4	23.0	53.6	84.5	15.5
6-Br	1:1 AcOH-HCOOH (v/v)	99.7	64.7 ± 0.5	33.5 ± 0.1	2.67 ± 0.22	5.93	22.7	22.3	55.0		
5-Cl	1:1 AcOH-HCOOH (v/v)	99.7		2.03 ± 0.12	2.64 ± 0.50						
6-Br	1:1 AcOH-Ac$_2$O (v/v)	120.3	4.00 ± 0.10	2.77 ± 0.36	26.6 ± 4.7	87.0	31.0[f]		69.0	98.9	1.1
5-Br[g]	AcOH	120.3	7.52 ± 0.05	4.02 ± 0.11	21.3	45.0	25.4	22.0	52.6	97.8	2.2
6-Br[g]	AcOH	120.3	7.73 ± 0.11	4.04 ± 0.10	21.3	45.0	25.4	22.0	52.6		
5-Br[h]	AcOH	99.7	1.00	0.418							
6-Br[h]	AcOH	99.7	0.99	0.392							
5-Cl[g]	AcOH	120.3	0.306 ± 0.018	0.168 ± 0.018	5.7	15.0	20.3	17.7	62.0	93.7	6.3

[a] [Substrate] = 0.044 M; [RCOONa] = 0.087 M. [b] From the "total *cis*-content" method. [c] From eq 6. [d] Calculated by the simulation method. [e] Calculated from α for the case, [RCOO$^-$] = [X$^-$]. [f] % Return to **5**-Br + **6**-Br. [g] From ref 1. [h] Extrapolated from data of ref 1.

The lower nucleophilicity of the OMs$^-$ anion resulted in the absence of both ion and ion-pair return with isomerization. The formation of 43% of a 1:1 mixture of **5**-Br and **6**-Br in the solvolysis of **5**-OMs with excess Br$^-$ suggests that >43% of the products is derived from the sp-hybridized **7**.[33] The lower α_{app} (0.9) in this capture experiment,[22] as compared with $\alpha_{app} = 3$ from the common ion rate depression in the reaction of **5**-Br, may be due to the different reaction conditions.

That the ethers are the main products from **5**-OMs at 60° but the minor products from **5**-Br at 120.3° is due to the increased ROEt → **25** decomposition at the higher temperature. This enol ether hydrolysis in 80% EtOH is dependent on the bulk of the β substituents since α-bromo-p-methoxystyrene gives no ether,[10b,34] and 1-bromo-1-p-methoxyphenylpropene gives the ether as a minor product.[5f,35] The higher decomposition in the presence of 2,6-lutidine as compared with NaOH has precedent,[10g] while the higher k_{ion} in the presence of NaOH compared with 2,6-lutidine is ascribed to a positive salt effect on the heterolysis rate.

Intermediates in Carboxylic Acids Media. Solvent Effect on the Ionization, Internal Return, and External Ion Return. In the less nucleophilic carboxylic acids media, the increased life-time of the cationoid intermediates leads to an extensive external ion return. Tables I and IV enable comparisons of the ionization, internal return, and external ion return as a function of four solvent properties: (a) ionizing power, measured by Y values;[36] (b) dissociating power, measured by the dielectric constant ϵ; (c) nucleophilicity of the solvent, measured by the N_{PW}[23a] or the N_{BS}[23b] parameters,[37] and (d) anion solvation. Table VII shows that 80% EtOH is a good ionizing solvent and the most dissociating and nucleophilic among our solvents. Among the carboxylic acids which have similar nucleophilicities,[23] AcOH-HCOOH is the most ionizing and dissociating, AcOH is moderately ionizing and poorly dissociating, and AcOH-Ac$_2$O is moderately dissociating and poorly ionizing.

The ionization rate is mainly determined by the ionization power, and the relative k_{ion} at 120.3° [1:1 AcOH-Ac$_2$O (0.53) < AcOH (1.0) < 80% EtOH (4.9) < 1:1 AcOH-HCOOH (52 at 99.7°)] indeed follows the Y values. An mY plot[36] for the four solvents should be curved as shown by the "m" values[38] for the 80% EtOH-AcOH, AcOH-1:1 AcOH-HCOOH, and AcOH-Ac$_2$O pairs (Table VI). The low m values (excluding that in AcOH-HCOOH) which are common in vinylic solvolysis[5b,10g,i,25b,26,39] are not due to solvent assisted k_s route[40] which is sterically hindered in triarylvinyl halides.[2,10a,h,i,39b]

The similarity of the reactivity ratios with those for p-methoxyneophyl tosylate, a model for the k_Δ route[41] [1:1 AcOH-Ac$_2$O (0.52 at 25°) < AcOH (1.0) < 80% EtOH (1.85 at 75°) < 1:1 AcOH-HCOOH (32 at 25°)][42] may indicate β-anisyl participation in the ionization. This is excluded by both the similar rates and product distributions from both **5**-Br and **6**-Br. We believe that in both cases the low solvent sensitivities arise from an extensive dispersal of the positive charge over the anisyl group and from a local dielectric constant near the reaction center which is relatively insensitive to that of the bulk of the solvent, due to crowding of the bulky substituents around the cationic orbital. The specific solvation *via* hydrogen bonding to the incipient halide ion is much less sensitive to the steric hindrance, and m in AcOH-HCOOH is in the region characteristic of the k_c route.[43]

A remarkable feature of the behavior of the ion pair is that dissociation takes over completely (in RCOOH) or mainly (in 80% EtOH) over capture by the solvent. The inherent electronic stability of the α-anisylvinyl cation, com-

Table V. Solvolysis of 0.043 *M* **5**-Br in 1:1 AcOH–Ac_2O (v/v) Containing 0.087 *M* NaOAc at 120.3°

Time, min	0	70	115	282	580	900	2250	2680	6600
% reaction		8.4	10.25	18.0	26.2	33.1	48.9	53.8	72.2
$10^6 k_t$, sec^{-1}	27.7[a]	20.8	15.7	11.7	8.73	7.44	4.97	4.80	3.23
% **6**-Br[b]		3.7	7.1	17.2	31.4	37.2	46.0	46.0	46.0
% isomerization[c]		8.0	15.5	37.4	68.4	80.9	100	100	100
$10^6 k_{isom}$, sec^{-1}	12.3[a]	19.8	24.5	27.6	33.1	30.7			
$10^6 k_{ion}$, sec^{-1}		40.6	40.2	39.3	41.8	38.1		40.0 ± 1.0[d]	

[a] Extrapolated value. [b] In the RBr fraction. [c] Based on the observed infinity value of 46% **6**-Br. [d] Average value.

Table VI. Comparison of Kinetic and Activation Parameters Based on k_t^0 (or k_t)[a] and k_{ion}, Respectively

			Based on					Based on	
Parameter	Solvent[b]	*T*, °C	k_t^0	k_{ion}	Parameter	Compd	*T*, °C	k_t^0	k_{ion}
k(**5**-Br)/*k*(**6**-Br)	80% EtOH	120.3	0.86	0.82	$(k_{80\%\,EtOH}/k_{RCOOH})_{Y=0}$	**5**-Br	99.7	0.61	0.46
		130.2	0.90	0.92	$(k_{80\%\,EtOH}/k_{RCOOH})_{Y=0}$	**6**-Br	99.7	0.74	0.61
	1:1 AcOH–HCOOH	99.7	0.91	0.85	*m* (AcOH–80% EtOH)	**5**-Br	120.3	0.57	0.44
k(**5**-OMs)/*k*(**6**-OMs)	80% EtOH[c]	60.0	1.11	1.11		**6**-Br	120.3	0.51	0.47
k(**5**-Br)/*k*(**5**-Cl)	80% EtOH	120.3	83	93		**5**-Cl	120.3	0.14	*d*
	1:1 AcOH–HCOOH	99.7	15.1	*d*	*m* (AcOH–HCOOH)	**5**-Br	99.7	0.72	0.78
k(**5**-OMs)/*k*(**5**-Br)	80% EtOH	60.0	18.4	20.8		**6**-Br	99.7	0.75	0.80
k(**6**-OMs)/*k*(**6**-Br)	80% EtOH	60.0	10.8	8.2		**5**-Cl	99.7	0.84	*d*
k(OTs)/*k*(Br)[e]	80% EtOH	60.0	18.8	16.3	*m* (AcOH–Ac_2O)	**5**-Br	120.3	0.33	0.19
		120.3	42.2	28.2	ΔH^* (80% EtOH)[g]	**5**-Br	120.3–130.2	21.3	23.6
k(OTs)/*k*(OMs)[f]	80% EtOH	60.0	1.36	1.36	ΔS^* (80% EtOH)[h]	**5**-Br	120.3	−20	−12
					ΔH^* (80% EtOH)	**6**-Br	120.3–130.2	20.0	20.3
					ΔS^* (80% EtOH)	**6**-Br	120.3	−23	−21
					ΔH^* (80% EtOH)[c,i]	**5**-OTs + **6**-OTs	45.0–60.0	24.2	24.2
					ΔS^* (80% EtOH)[j]	**5**-OTs + **6**-OTs	60.0	−5	−5

[a] Based on k_t^0 in the RCOOH media and on k_t in 80% EtOH. [b] 80% EtOH contains NaOH unless otherwise stated; RCOOH media contain RCOONa. [c] Containing 2,6-lutidine. [d] k_{ion} for **5**-Cl was not calculated due to the high error in k_{isom}. [e] Ratio of *k*(**5**-OTs + **6**-OTs) to the average *k* for **5**-Br and **6**-Br. [f] Ratio of *k*(**5**-OTs + **6**-OTs) to the average *k* of **5**-OMs and **6**-OMs. [g] Estimated error, ±2 kcal mol^{-1}. [h] Estimated error, ±6 eu. [i] Estimated error, ±1.5 kcal mol^{-1}. [j] Estimated error, ±5 eu.

Table VII. Ionizing Power (*Y*), Dissociating Power (ϵ), and Nucleophilicity (N_{PW} and N_{BS}) of Several Solvents

Solvent	*Y*[a]	ϵ[b]	N_{PW}[c]	N_{BS}[d]
80% EtOH	0.00	35.80[f]	0.00	0.00
AcOH	−1.64	6.2[g]	−1.52	−2.05
1:1 AcOH–HCOOH (v/v)	0.76	32.3[h]	−1.66	−2.05
1:1 AcOH–Ac_2O (v/v)	−2.47[e]	15.0[i]		

[a] From ref 36c. [b] At 20 or at 25°. [c] From ref 23a. [d] From ref 23b. [e] Average of *Y* values for AcOH and Ac_2O. [f] D. Decroocq, *Bull. Soc. Chim. Fr.*, 127 (1964). [g] O. W. Kolling and W. L. Cooper, *Anal. Chem.*, **42**, 758 (1970). [h] Average of ϵ values for AcOH and HCOOH. [i] Interpolated from data in ref g, this table. Interpolation of the data of R. T. Myers [*J. Phys. Chem.*, **69**, 700 (1965)] gives ϵ = 13.5.

bined with the relatively large distance between the solvation shell and the shielded cationic orbital, reduces the collapse rate with SOH and increases the dissociation rate.

The extent of internal return is expected to decrease on increasing the dissociating power, but the order and the magnitude of the 1 − *F* values [AcOH (0.47) ~ 1:1 AcOH–HCOOH (0.46) > 80% EtOH (0.32) ~ 1:1 AcOH–Ac_2O (0.31)] do not follow this prediction. While our 1 − *F* values cover a smaller range than those in saturated systems,[13,15] the identical internal return in AcOH and in 1:1 AcOH–HCOOH is in contrast with those for several saturated systems where 1 − *F* (AcOH) > 1-*F* (HCOOH),[13] although 1 − *F* values from ^{18}O-equilibration studies behave similarly.[13] It is tempting to ascribe the insensitivity of the 1 − *F* values to a high degree of tightness in the ion pair, and this is supported by the absence of $LiClO_4$ "special salt effect" in the solvolysis of **5**-Br in AcOH.[1]

The external ion return, as measured by α, can rarely be compared for several solvents either since products are formed from ion pairs, or only α_{app} is measured. The α values should be mainly determined by the nucleophilicity of the anions toward **7**, and their increase for Br^- in the series AcOH–Ac_2O > AcOH > AcOH–HCOOH parallels the decreased solvation by hydrogen bonding to Br^- throughout the series Ac_2O < AcOH < HCOOH. Apparently, the parallel change in the solvation of $RCOO^-$ is lower. Solvation arguments also suggest that Cl^- is less nucleophilic than Br^- in protic solvents,[44] and consequently that $\alpha(Br^-) > \alpha(Cl^-)$. Surprisingly, while this holds in AcOH,[1] in 1:1 AcOH–HCOOH, a solvent where the inequality should be more pronounced, $\alpha_{app}(Br^-) = \alpha_{app}(Cl^-)$. Since $\alpha(1 - F) = \alpha_{app}$, $\alpha(Br^-)$ can be higher than $\alpha(CL^-)$ only when (1 − *F*) for Cl^- > (1 − *F*) for Br^-. This inequality could hold for an unsolvated halide ion in the ion pair, but it contradicts the higher 1 − *F* for Br^- as compared with Cl^- in AcOH.[1] At present we are unable to explain the apparent similar external ion returns of Br^- and Cl^-.

A lower α (80% EtOH) is expected but comparison with α(RCOOH) is impossible since the extent of capture by the different nucleophiles (H_2O, EtOH, OH^-, EtO^-) is unknown.

The combination of the high stability of **7** due to steric crowding and α-anisyl stabilization[1] with the low solvent nucleophilicity leads to the high α(AcOH–Ac_2O).

k_t as a Measure of k_{ion}. k_t is the parameter usually measured in solvolysis, while k_{ion} is the appropriate parameter for reactivity comparison. Various kinetic parameters which are based on k_t and k_{ion} were compared in the preceding paper in AcOH, and they are compared now in the other solvents (Table VI).

(a) Cis–Trans Reactivity Ratio. The *k* (**5**-Br)/*k* (**6**-Br) ratios are close to unity in all the solvents, and the difference between using k_t and k_{ion} is within the combined experimental errors. The effect of substituents on k_t in 80% EtOH is mainly additive, but the change of a β-phenyl to a β-anisyl group is lower than that observed for the $Ar_2C{=}C(Br)Ph$ system in 60% EtOH.[10f] Apparently, the lower ability of the α-aryl to support a positive charge results in a greater response to the electronic effect of the β substituents.

(b) Leaving Groups Reactivity Ratios. The k_{Br}/k_{Cl} ratio differs only slightly when based on k_t or k_{ion}, and is characteristic of SN1 reactions.[25b,26,45] The order of the ratios, 80% EtOH > AcOH > AcOH–HCOOH, reflects a more efficient solvation of the incipient chloride ion in the more acidic solvents.[45d]

The low k_{OMs}/k_{Br} and k_{OTs}/k_{Br} ratios are of interest in connection with Hoffmann's view of the mechanistic importance of these ratios,[46] and they were discussed earlier.[47] We argued[1] that since $1 - F$ (ROMs) < $1 - F$ (RBr), the k_{OMs}/k_{Br} and k_{OTs}/k_{Br} ratios which are based on k_t would be ***higher*** than those based on k_{ion}. Table VI shows that this is generally the case except for the k(**5**-OMs)/k(**5**-Br) in 80% EtOH.[48]

(c) Activation Parameters. The activation parameters in 80% EtOH resemble those for related systems.[10i,26] We believe that the difference in the values based on k_t or on k_{ion} for **5**-Br results from a relative large error due to the small temperature interval studied.[49]

(d) Solvent Effects. Due to the relative solvent insensitivity of the F values, the use of k_t instead of k_{ion} has little effect on classifying the "m" values[38] as "high" or "low." The ratios $k_{80\%\ EtOH}/k_{RCOOH}$ at constant Y (=0) value, which were obtained by extrapolation to 99.7°, and assuming a linear mY behavior for AcOH–HCOOH mixtures, are given in Table VI. These ratios were recently suggested by Bentley and Schleyer[50] as new tools for recognizing internal return. For a k_c process, they are *ca.* 0.5–1.0, and it was argued that they would be greater in solvolyses where internal return is absent. For our compounds, the ratios based on k_t are 0.61–0.74 and those based on k_{ion} are lower, strengthening Bentley and Schleyer's argumentation[50] and indicating the absence of solvent participation in our solvolyses.

Experimental Section

Materials and Solvents. The preparation and isolation of **5**-Br, **6**-Br, **5**-Cl, **5**-H, **6**-H, **5**-OMs, **6**-OMs, **5**-OTs + **6**-OTs, **5**-OAc and **6**-OAc, and **25** were described earlier.[1,17] Formic acid was purified according to Winstein and Marshall[51] and 80% EtOH according to Grob,[34] and acetic anhydride was distilled twice, and the fraction boiling at 139° was used. Tetra-*n*-butylammonium bromide (Eastman), mp 107–108°, was crystallized from ethyl acetate.

1,2-Di(*p*-methoxyphenyl)-2-phenylvinyl Ethyl Ethers (5-OEt + 6-OEt). A mixture of **5**-Br and **6**-Br (2 g, 5 mmol) and silver carbonate (1.4 g, 5 mmol) was refluxed in absolute EtOH (30 ml) in the dark for 15 hr. The hot mixture was filtered, the solvent was evaporated, and nmr on the remaining oil is consistent with the presence of 70% of **5**-OEt + **6**-OEt and 30% of the ketone **25.** Two crystallizations (MeOH, 25°) gave pale yellow crystals of an approximately 1:1 cis–trans mixture of 1,2-di(*p*-methoxyphenyl)-2-phenylvinyl ethyl ethers, mp 141–145° (1.4 g, 80%): δ ($CDCl_3$) 1.17 (3 H, 2 merging t, Me), 3.62 (2 H, 2 merging q, CH_2), 3.65, 3.68, 3.70 (6 H, 3 s in a 1:2:1 ratio, MeO), 6.43–7.20 (13 H, m, Ar); λ_{max} (C_6H_{12}) 236 nm (ϵ 16,900), 301 (17,800); ν_{max} (CS_2) 3050–2870 (s), 2830 (s), 1295 (s), 1248 (v), 1172 (v), 1040 (v); *m/e* 360 (M, 99%), 331 (M-Et, 77%), 316 ($AnC(Ph){=}C^+HAn$, 3%), 315 ($AnC(Ph){=}C^+An$, 2.2%), 303 (An_2CPh^+, B), 195 (*p*-methoxyfluorenyl$^+$, 23%) 135 ($AnCO^+$, 22%).

Isomerization of 1,2-Dianisyl-2-phenylethylenes. The cis–trans ratio of the ethylenes was determined from the intensities of the methoxy signals (**5**-H:δ 3.69; **6**-H: δ 3.73 in $CDCl_3$). **5**-H or **6**-H (96 mg) in 0.49 *M* NaOH–80% EtOH (7 ml) were kept for 64 hr at 120°. The mixture was poured into chloroform–water, separated, washed with dilute HCl, dried, and concentrated. No isomerization (limit of detection 5%) was observed. In 1:1 AcOH–HCOOH, the work-up was as above except for wash with dilute $NaHCO_3$ solution instead of HCl. The equilibrium mixture of the ethylenes was obtained from either isomer after 18 hr at 99.7°.

Kinetic Procedure. (a) With the Vinyl Halides. Ampoules were prepared and cleaned according to Grob and Cseh.[34] Because of the low solubility in 80% EtOH, material for each ampoule was weighed independently, 7 ml of the solvent-base mixture was added, and the sealed ampoules were kept at the reaction temperature for a few minutes and shaken for a few seconds to ensure complete dissolution. The ampoules were opened, and 5-ml aliquots were titrated (Volhard) with $AgNO_3$ using eosin indicator for the bromides and dichlorofluorescein for **5**-Cl. The remaining 2 ml was evaporated, the residue was dissolved in CCl_4, washed with water, dried, evaporated, and dissolved in CS_2, and the cis-trans halide distribution was determined by using the ir calibration curves which were described earlier.[1] Absorption of **25** does not interfere at the wavelength of interest. The acetates and the ether–ketone ratios were determined by nmr.

For reaction with sodium benzylthiolate, 0.1 *M* NaOH and 0.1 *M* benzyl mercaptan were used. The mixture was poured into chloroform, washed with 5% NaOH until the complete removal of the thiol, and dried. The cis-trans ratio was determined by ir since **5**-SR + **6**-SR has only a weak absorption at 575 cm^{-1}.

The reaction in the carboxylic acid media was followed as described earlier.[1]

(b) With the Vinyl Sulfonates. The organic mesylate (16.4 mg) was kept in a conductivity cell for 15 min at 60° until a complete dissolution. Conductivity water (2 ml) and 2,6-lutidine were added, the mixture was shaken, and the reaction was followed conductometrically. Infinity readings which were taken after 30 hr remained steady for several days. At our concentration range, the concentration-conductivity plot for 2,6-lutidinium mesylate is linear. Rate constants were calculated with the aid of the KINDAT program,[52] using at least 30 experimental points.

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(19) The error involved in this assumption is small since (i) starting from **5**-Br (or **6**-Br) *ca.* 35% of the isomeric bromide was observed at the end of the reaction, and (ii) the **5**-Br–**6**-Br, **5**-Cl–**6**-Cl, **5**-OAc–**6**-OAc, and **5**-OMs–**6**-OMs equilibrium ratios are 54:46 in AcOH[1] or in acetonitrile and should be only slightly solvent dependent.

(20) Following Ingold[8b] we define α_{app} for competition between X^- and the solvent SOH as the ratio between the second- and the pseudo-first-order constants for capture of R^+ by X^-. Its dimensions are reciprocal concentrations.

(21) The nmr of the mixture shows the methyl groups as two merging triplets with similar intensities.

(22) When $[\mathrm{Br}^-] \gg [\mathrm{substrate}]$, ([**5**-Br] + [**6**-Br])/([**5**-OEt] + [**6**-OEt] + [**25**]) = $k_r[\mathrm{Br}^-]/k^7{}_{\mathrm{SOH}}[\mathrm{SOH}] = \alpha_{\mathrm{app}}[\mathrm{Br}^-]$. The α_{app} calculated by this method will be a lower limit since the $[\mathrm{Br}^-]$ decreases slightly during the experiment.

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(24) Similar ratios were also observed for the **5**-H–**6**-H and the **5**-OMs–**6**-OMs equilibria.

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(31) At very high external Br^- concentration, the change in $[\mathrm{Br}^-]$ due to the reaction is small, and the corresponding error in k_t is large.

(32) Isomerization *via* ion pairs in aqueous EtOH was previously suggested for (*E*)-1-*p*-methoxyphenyl-1-bromopropene.[1f]

(33) The slight preference for formation of **6**-Br in this experiment contradicts the slight preference for formation of **5**-Br when **7** is captured in AcOH. This may be due to a required small correction of the calibration curves due to the absorption of the ethers and suggested the use of 1 as the **5**-Br–**6**-Br ratio.

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