Vinylic Cations from Solvolysis. XX.[1,2] Ion Pairs and Free Ions in the Solvolysis and Isomerization of 1,2-Dianisyl-2-phenylvinyl Halides and Mesylates. Use of Cis–Trans Isomerization as a Mechanistic Tool

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Abstract: The acetolysis of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides (**5**-Br and **6**-Br) and the cis chloride (**5**-Cl) in unbuffered and buffered AcOH shows strong common ion rate depression within a run, or by added halide ion; >93% of the products arises from the "dissociated" ion **7**. The products are 54% of the cis and 46% of the trans acetates (**5**-OAc and **6**-OAc). Methods for evaluating the extrapolated titrimetric rate constants k_t^0 and the apparent selectivity constant α_{app} of **7** are discussed. Capture of **7** by Cl^- gives a 1:1 mixture of **5**-Cl and **6**-Cl. These reactions are accompanied by extensive cis–trans isomerization of the unreacted halide, which is the main process in the presence of external halide ion. A mechanism involving the ion pair **8** which gives internal return with isomerization and **7** which gives either external ion return with isomerization or solvolysis products fits the data and is verified by a simulation method: **8** from **5**-Br gives 25.4% of **5**-Br, 22% of **6**-Br, and 52.6% of **7**. The ionization rate constant k_{ion} and the true selectivity constant α of **7** were evaluated by several methods. Both solvolysis and isomerization are accelerated by AgOAc, but only the isomerization is appreciably accelerated by $LiClO_4$. Acetolysis of the corresponding mesylates **5**-OMs and **6**-OMs shows external ion return by OMs^-, and the ion pair **16** gives 13.6% of **5**-OMs, 10.4% of **6**-OMs, and 76% of **7**. Nonheterolytic isomerization routes were excluded by using several criteria. Reasons for the high selectivity of the cationic species *vs.* the sluggish reactivity of their precursors and the similar reactivity order of the anions $Br^- > Cl^- > OMs^-$ in both internal and external ion return are discussed. The use of k_t (or k_t^0) as a measure of k_{ion} in vinylic systems was evaluated.

An important development in the study of solvolysis reactions is the recognition that more than one cationic species is involved in many of these reactions.[3] Winstein's extended mechanistic scheme involves the covalent RX, an intimate ion pair R^+X^-, a solvent-separated ion pair $R^+\|X^-$, and the "dissociated" cation R^+, all or some of which may give solvolysis products.[3,4] Methods for estimating the extent of ion pairing include the "special salt effect"[4b,5] and the comparison of the rate of product formation (k_t) with those of other processes presumably connected with the ionization. These include the loss of optical activity (k_α or k_{rac}),[3,6] the concurrent rearrangement in either R[3,7a] or X,[3,7b] and the oxygen equilibration in a leaving group which carries several oxygen atoms.[3,8] Dissociated (free) carbonium ions are recognized by the appearance of common ion rate depression by the common ion X^- or by exchange of X in RX by labeled X^-.[4a,c]

Information regarding the nature of cationic intermediates in vinylic solvolysis[9] is scarce. Product formation from dissociated ions is evident from common ion rate depression in the solvolysis of several α-arylvinyl systems where X = Cl,[10,11] Br,[9,10c,12-14] I,[15] 2,4,6-$(O_2N)_3C_6H_2OSO_2$,[16] and OTs[14b,17] in solvents such as AcOH,[2,10a,c,12] AcOH–HCOOH mixtures,[2c] aqueous EtOH,[10b,11] acetone,[16b] aqueous acetone,[11,17] aqueous DMF,[15] and 2,2,2-trifluoroethanol (TFE).[14]

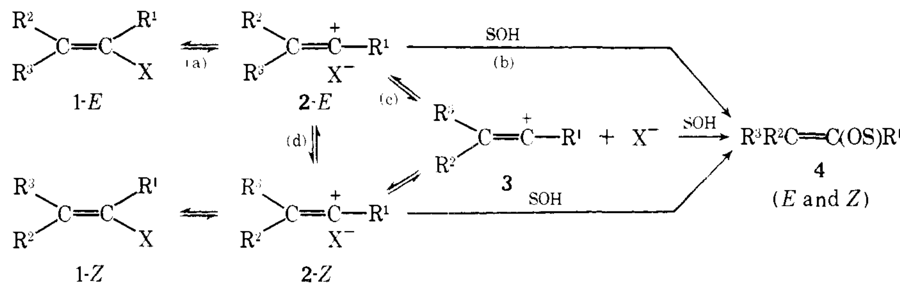
Ion pairs were invoked to explain the predominant inversion in the solvolysis of several vinyl triflates,[18,19] the faster elimination from *trans*-1,2-dimethylvinyl triflate with NaOH than in neutral solution,[18c] the smaller substituent effects in the solvolysis of acyclic vinyl triflates compared with 1-cyclohexenyl triflate,[18c] the small amount of cis–trans interconversion of 1-cyclopropyl-1-iodopropenes with AgOAc in AcOH[20] and of *cis*-α-bromoanethole in 80% EtOH,[21] the products in the photochemical decomposition of β-acyloxydiazoalkenes,[22] and the increase in k during a run in the acetolysis of 2-methyl-3,4-pentadien-1-yl tosylate.[23] The acetolysis of 2-phenylthio-1,2-ditolyl 2,4,6-trinitrobenzenesulfonate showed a $LiClO_4$ "special salt effect" suggesting the presence of solvent-separated ion pair.[16]

Except for the latter example and an attempt to use the stereochemistry of the solvolysis as a tool for estimating the extent of ion pairing,[18c] no quantitative data on the distribution of the various cationic species are available. Estimation of the internal return from the k_α/k_t ratios is possible in principle with optically active vinylic systems,[24] but this method was not yet reported and is not generally applicable.

We suggested[2] that a cis–trans isomerization concurrent with the solvolysis could be used as a general tool[25] for investigating vinyl cation formation and the intervention of ion pairs. The essence of this method is the following. The first intermediate in the heterolysis of the vinyl halide **1-*E*** is the ion pair **2-*E***[26] which can enter into four reaction sequences (Scheme I): (a) a hidden return to covalent **1-*E***; (b) product (**4**) formation; (c) dissociation to the free ion **3**, which may return to **2-*E*** or **2-*Z***, give the product **4**, or be recaptured by the leaving group giving both **1-*E*** and **1-*Z***; (d) internal rotation to give the isomeric ion pair **2-*Z*** which on recombination gives **1-*Z***. By following the concurrent **1-*E*** ⇌ **1-*Z*** isomerization and product formation from both isomers, ion pairs could be detected, and the distribution of the intermediates among the various routes could be determined. For example, the stereochemical evidence for ion pairing is explained in terms of a faster solvent capture of either **2-*E*** or **2-*Z*** from the rear, as compared with their mutual interconversion.

There are considerable differences between the $d \rightarrow l$ racemization used with saturated substrates and the cis → trans isomerization as mechanistic tools. The solvolysis rates of d-RX and l-RX are identical, and capture of the symmetrical trigonal free ion by a nucleophile will always lead to racemized products. On the other hand, the solvolysis rates of **1-*E*** and **1-*Z*** may differ greatly,[12,21,27] and when $R^2 \neq R^3$, the ion **3** is unsymmetrical from the direction of approach of the nucleophile and is captured preferentially from its less hindered side. Since **3** is formed from both **1-*E*** and **1-*Z***, excess retention will be found for one isomer and excess inversion for the other. Moreover, nonsol-

Scheme I

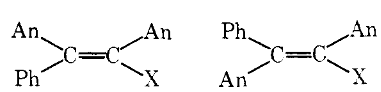


volytic addition–elimination isomerization routes are available for the vinylic but not for the saturated substrates.

A relatively simple case will be when **1-*E*** and **1-*Z*** react with similar rates, and where capture from both sides of the cationic orbital has similar probability. The study of one such system, (*E*)- and (*Z*)-α-bromo-β-deuterio-*p*-methoxystyrenes, is discussed elsewhere.[28] In the present paper, we discuss the 1,2-dianisyl-2-phenylvinyl system,[29] where the intermediate is known to be captured by different nucleophiles,[29] and the two β substituents are sufficiently similar to ensure similar solvolysis rates for both isomers and similar capture rates from both sides of the cation. Moreover, the common ion rate depression, which was observed with structurally related compounds,[11-17] suggests that isomerization by capture of the free cation should be mandatory in this system.

Results and Discussion

Synthesis. The preparation and separation of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides (**5-Br** and **6-Br**), chlorides (**5-Cl** and **6-Cl**), and acetates (**5-OAc** and **6-OAc**) were described previously.[29] Careful determination of the cis–trans equilibrium distribution in AcOH at 120° gave the same **5**:**6** composition of 54:46 for the bromides, acetates, and chlorides.[30] These results modify somewhat earlier reported values.[29,31] Reaction of an equilibrium mixture of **5-Br** and **6-Br** with 1.1 equiv of silver tosylate or silver mesylate in acetonitrile gave products indicated both to be 54:46 cis–trans mixtures by nmr integration. **5-OMs** and **6-OMs** could be separated by recrystallization. Stereochemical assignment was made in analogy with the corresponding bromides and acetates,[29] by assuming that the isomer with the lower field methoxyl and methyl and the higher field phenyl signals was *trans*-**6-OMs**. This assignment was consistent with the general observation that cis isomers predominate at equilibrium.



X = H	5-H	6-H
X = Br	5-Br	6-Br
X = Cl	5-Cl	6-Cl
X = OMs	5-OMs	6-OMs
X = OTs	5-OTs	6-OTs

Acetolysis of 5-Br and 6-Br in Unbuffered AcOH. Vinylic solvolysis of RX in a buffered solvent avoids substitution *via* addition–elimination of the liberated HX to the double bond of RX.[10b,32] However, in connection with the question whether the vinyl cation is captured by AcO^- or AcOH, we acetolyzed 0.044 *M* **5-Br** at 120.3° in unbuffered AcOH and found that the initial reaction is slower than that with NaOAc: $10^6\ k_t$ = 3.47 and 3.07 sec^{-1} after 530 and 1200 min. After 9 and 12 hr, the residual RBr is 92.5 and 100% isomerized, respectively. However, the reaction mixture blackens after longer reaction times, and only 7% of Br^- was titrated after 48 hr, when the ir showed signals at 1762 (AcO, s) and 1705 (C=O, w) cm^{-1}.[33]

Common ion rate depression was demonstrated by the $10^5\ k_t$ values of 5.0 and 1.63 sec^{-1} at 120.3°, in the solvolysis of 0.087 *M* **5-Br** after 20 hr with and without 0.087 *M* Et_4NBr, which gives a selectivity value α (= k_{Br}/k_{AcOH}) = 24.

Exactly the same behavior was observed in the acetolysis of **5-Br** when 0.087 *M* urea was used as the nonnucleophilic buffer.[34]

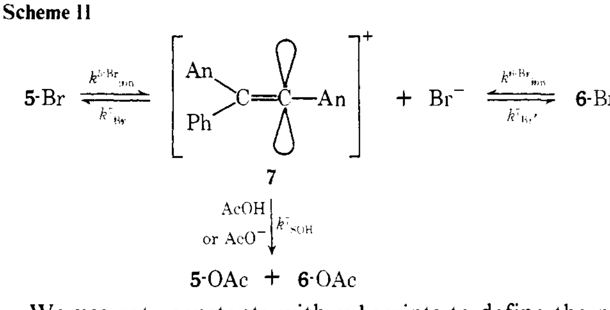
Acetolysis of 5-Br, 6-Br, and 5-Cl in Buffered AcOH. Dissociated Cations. Acetolysis of **5-Br**, **6-Br**, and **5-Cl** in the presence of NaOAc gives 100% of the acetates **5-OAc** and **6-OAc** in a 54:46 ratio. We did not acetolyze **6-Cl** which was difficult to obtain in a pure form. The titrimetric rate constant k_t (eq 1) decreases strongly with the progress

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

of the reaction due to common ion rate depression by the formed halide ion; k_t at 75% reaction is 12–20% of the initial value (k_t^0) (Table I). The concurrent cis–trans isomerization which was monitored by ir gave the equilibrium mixture of 54% **5-Br** (or **5-Cl**) to 46% of **6-Br** (or **6-Cl**) during the acetolysis, starting from either halide.

Appearance of common ion rate depression[35] is the operative definition for the occurrence of "dissociated" ("free") cations.[4a] The common ion rate depression and the isomerization can be explained by the simple mechanistic Scheme II, where both **5-Br** and **6-Br** give the same linear "free" cation **7**.[36] As shown in a stereochemical study,[29] the approaches of Br^- to both lobes of the cationic orbital of **7** have similar probabilities since the steric and electronic environments at these both sides are similar. Hence, the external Br^- return will lead to a cis–trans isomerization of the recovered bromide.

Scheme II



We use rate constants with subscripts to define the process measured (ion, ionization; Br, capture by Br^-; SOH, capture by the solvent or its conjugate base; OAc, capture by OAc^-, etc.,) and with superscripts to designate the reacting species. The formation of **5-OAc** and **6-OAc** was presented as irreversible since no RBr was formed from **5-OAc** and Bu_4NBr after 150 hr at 120°.[29]

Scheme II requires that (a) almost all the products arise from free cations, and that (b) the extent of isomerization by capture of **7** should match that predicted from the com-

Table I. Solvolysis and Isomerization of **5**-Br and **6**-Br in AcOH–NaOAc at 120.3°[a]

Time, min	0	40	70	110	200	280	410	900	2155	4200	16,800
					5-Br						
% solvolysis[b]	0	6.7	9.9	13.3		23.6	29.4	41.3	60.8	75.6	97.2
$10^6 k_t$, sec^{-1}	40.6[c]	28.9	24.8	21.6		16.0	14.2	9.9	7.3	5.6	
% cis bromide[d]	100	95.2	91.3	86.7		70.5	63.6	56.3	54	54	
% isomerization[e]	0	10.4	18.9	28.9		64.1	79.1	94.9	100	100	
$10^6 k_{isom}$, sec^{-1}		45.8	49.9	51.7		61.2	63.8	95.0			
$10^6 k_{ion}$, sec^{-1} [f]		74.7	74.7	73.3		77.2	78.0				
					6-Br						
% solvolysis[b]	0	6.8	10.1	13.7	19.4	24.0		42.1	61.3	75.8	97
$10^6 k_t$, sec^{-1}	40.8[c]	29.3	25.3	22.3	18.0	16.3		10.1	7.3	5.6	
% cis bromide[d]	0	6.0	10.5	17.0	26.7	34.9		54	54	54	
% isomerization[e]	0	11.1	19.4	31.4	49.4	64.6		100	100	100	
$10^6 k_{isom}$, sec^{-1}		49.0	51.5	57.1	56.8	61.8					
$10^6 k_{ion}$, sec^{-1} [f]		78.3	76.8	79.4	74.8	78.1					

[a] [RBr] = 0.044 *M*, [NaOAc] = 0.087 *M*. [b] From titration. [c] Extrapolated value. [d] In the unreacted vinyl halide fraction. [e] Based on the equilibrium ratio of 54 (**5**-Br):46 (**6**-Br). [f] Calculated by using eq 17.

mon ion rate depression. Common ion rate depression as extensive as ours is rare in saturated systems, and since we found no precedent for calculations, we will first discuss in some detail our method to obtain the required kinetic parameters.

For applying the steady-state approximation to Scheme II, it is essential to know whether AcOH or AcO^- captures **7**. We believe that most of the capture is by AcO^- for the following reasons. (i) The initial k_t's in AcOH are 8–12 times lower than those in the presence of 0.087 *M* NaOAc. The faster isomerization shows that ion return is more important in the unbuffered AcOH.[37] (ii) The solvolysis is slower at lower [NaOAc] than at higher concentrations. (iii) Common ion rate depression is more extensive in unbuffered compared with buffered AcOH. (iv) The simulation method, discussed below, gives a better fit for OAc^- as the capturing nucleophile.

When the second-order k_{OAc} replaces k_{SOH} in Scheme II, the rate of formation of **5**-OAc and **6**-OAc (d[ROAc]/d*t*) from either **5**-Br or **6**-Br is given by eq 2, where the apparent selectivity factor for capture of **7** by Br^- *vs.* capture by OAc^-, α_{app}, is defined by eq 3 (the term "apparent" is justified below). While the two k_{ion} values could in principle be obtained from reaction at very low [RX] when $[Br^-] \sim 0$ and $k_t = k_{ion}$, this was not possible at our conditions (see below). Fortunately, the similarity of the [ROAc] *vs.* time profiles for **5**-Br and **6**-Br suggested that $k^{5\text{-Br}}_{ion} \sim k^{6\text{-Br}}_{ion}$, and therefore eq 4 for **5**-Br and a similar one for **6**-Br are good approximations for eq 2.

$$\frac{d[\mathrm{ROAc}]}{dt} = \frac{k^{5\text{-Br}}_{ion}[\mathbf{5}\text{-Br}] + k^{6\text{-Br}}_{ion}[\mathbf{6}\text{-Br}]}{1 + \alpha_{app}[\mathrm{Br}^-]/[\mathrm{OAc}^-]} \quad (2)$$

$$\alpha_{app} = (k^7_{Br} + k^7_{Br'})/k^7_{OAc} \quad (3)$$

$$d[\mathrm{ROAc}]/dt = k_{ion}([\mathbf{5}\text{-Br}] + [\mathbf{6}\text{-Br}])/(1 + \alpha_{app}[\mathrm{Br}^-]/[\mathrm{OAc}^-]) \quad (4)$$

We first tried to evaluate k_{ion} and α_{app} from the instantaneous rate constant k_{ins} (eq 5) since combination of eq 4

$$(d[\mathrm{ROAc}]/dt)/([\mathbf{5}\text{-Br}] + [\mathbf{6}\text{-Br}]) = k_{ins} \quad (5)$$

$$1/k_{ins} = 1/k_{ion} + (\alpha_{app}/k_{ion})[\mathrm{Br}^-]/[\mathrm{OAc}^-] \quad (6)$$

and 5 give eq 6. Winstein and coworkers[4a,38] calculated k_{ins} from the tangent d[ROAc]/d*t* at each [RX] from large-scale plots of [product] *vs.* time. However, in our system the curvatures of the "per cent reaction" *vs.* time plots were much higher than those of Winstein, *et al.*,[38] and the estimation of the tangents was unreliable up to >50% reaction. We then evaluated $k_t{}^0$ by three other methods, two of which also gave α_{app}.

(a) The smooth curve of the integrated k_t *vs.* time plot was graphically extrapolated to $t = 0$ (Figure 1) giving $k_t{}^0$ when $[Br^-] = 0$. Attempts to use a nonlinear least-squares program (NONLSQ) for extrapolation failed since k_{ion} and α_{app} are correlated.

(b) We found for several solvolyses of α-arylvinyl halides which show common ion rate depression[10c] that insertion of the integrated "constant" k_t of eq 1 instead of k_{ins} in eq 6 resulted in a linear $1/k_t$ *vs.* $[Br^-]/[OAc^-]$ plot (Figure 2). k_{ion} and α_{app} were calculated from the intercept and the slope, respectively (see note 46).

(c) Integration of eq 4 by assuming that $k^{5\text{-Br}}_{ion} = k^{6\text{-Br}}_{ion}$ gave eq 7, where $a_0 = [RX]_0 = ([\mathbf{5}\text{-Br}] + [\mathbf{6}\text{-Br}])_0$, $x = [X^-]_t$, and $n = [OAc^-]_0/[RX]_0$. Combination of eq 1 and 7 gave eq 8, where the second term on the right describes the change of k_t due to common ion rate depression.

$$k_{ion}t = \ln[a/(a-x)] - [\alpha_{app}/(1-n)] \times \ln[a/(a-x)] + [n\alpha_{app}/(1-n)]\ln[na/(na-x)] \quad (7)$$

$$1/k_t = 1/k_{ion} + [\alpha_{app}/k_{ion}(1-n)] \times [(n \ln\{na/(na-x)\})/\ln(a/(a-x)) - 1] \quad (8)$$

A plot of $1/k_t$ *vs.* the expression in the parentheses should be linear with intercept of $1/k_{ion}$ and a slope of α_{app}/k_{ion}, and we applied a computer program (SHAI) which searches the best k_{ion} and α_{app}, and these are given in Table II. Since $\alpha_{app} = k_{ion}$(slope), the error in α_{app} includes both the error in the slope and in k_{ion}.[39]

Table II shows that methods a–c give very close $k_t{}^0$ values, while the α_{app}'s of method c are higher than those of method b.[40] Since the α_{app}'s of method c are in good agreement with those of the simulation method (see below), they are used in the discussion.

Salt effects on k_{ion} or k_t were so far neglected. The constant "ionic strength," when NaBr replaces NaOAc during the reaction, is meaningless at our salt concentrations in the low-dielectric AcOH, and specific salt effects[41] may be important. However, our comparisons are valid; since the extrapolated $k_t{}^0$ should not be affected, most of our reactions were conducted at identical total salt concentrations, and the isomerization and solvolysis rates were compared in the same medium.

Table III gives data on the solvolysis in the presence of added salts. According to the theory of common ion rate depression,[4a] the percentage of products from dissociated cat-

Table II. $k_t{}^0$ and α_{app} Values for the Acetolysis of **5**-Br, **6**-Br, and **5**-Cl, as Obtained by Various Procedures

Compd[a]	Solvent	T, °C	$10^5k_t{}^0$, sec^{-1}, from procedure a	b	c	α_{app} from procedure b	c	Simulation
5-Br	AcOH	120.3	4.10	4.06 ± 0.12	4.02 ± 0.11	11.9 ± 0.6	23.3 ± 1.0	21.3
5-Br	AcOH	140.2	28.0	30.0 ± 2.9	29.4 ± 3.0	12.1 ± 2.1	23.2 ± 4.5	20.4
5-Br[b]	AcOH	120.3	5.45	5.13 ± 0.07	4.79 ± 0.09	27.2 ± 0.9	40.4 ± 2.1	41.2
5-Br	AcOD	120.3	3.55	2.99 ± 0.07	2.99 ± 0.07	9.84 ± 0.52	19.6 ± 1.1	21.6
6-Br	AcOH	120.3	4.22	4.08 ± 0.11	4.04 ± 0.10	11.4 ± 0.50	22.2 ± 0.9	21.3
6-Br	AcOH	140.2	30.0	33.7 ± 3.2	32.8 ± 3.2	12.7 ± 2.1	24.2 ± 4.3	21.3
5-Cl	AcOH	120.3	0.191	0.173 ± 0.018	0.168 ± 0.018	3.0 ± 0.5	5.5 ± 1.1	5.7
5-Cl	AcOH	140.2	1.19	1.25 ± 0.12	1.16 ± 0.12	2.6 ± 0.5	4.2 ± 1.0	4.9
5-Cl	AcOH	158.5	5.35	5.52 ± 0.12	5.40 ± 0.17	2.6 ± 0.1	4.8 ± 0.3	5.0
5-Cl	AcOD	158.5	4.95	4.90 ± 0.21	4.78 ± 0.24	2.4 ± 0.2	4.3 ± 0.5	4.9

[a] [RX] = 0.044 M; [NaOAc] = 0.087 M unless otherwise stated. [b] [RX] = 0.0044 M.

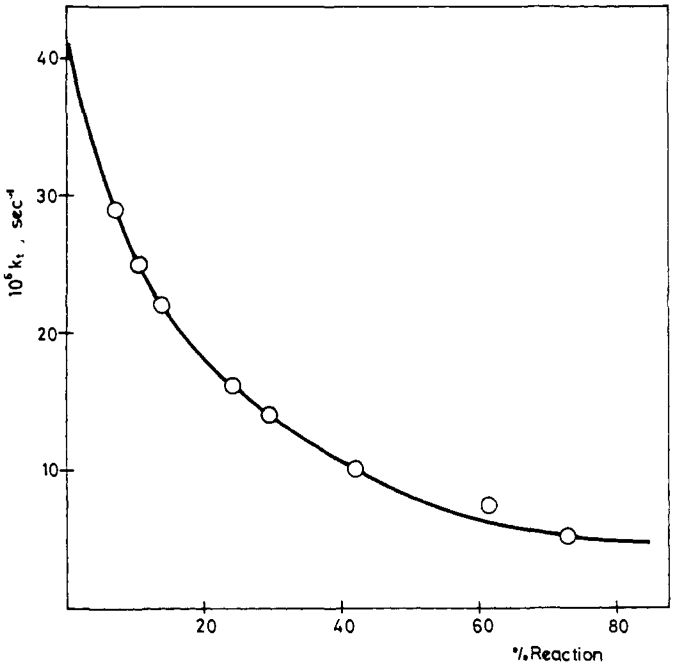


Figure 1. Plot of k_t of eq 1 *vs.* the percentage of the acetolysis reaction of 0.044 M **5**-Br in the presence of 0.087 M NaOAc in AcOH at 120.3°. Extrapolation gives $k_t{}^0 = 4.1 \times 10^{-5}$ sec^{-1}.

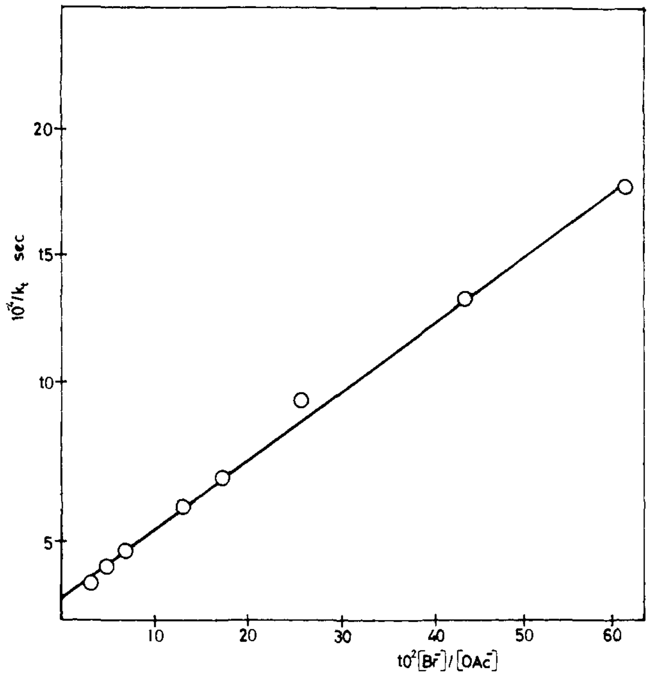


Figure 2. Plot of $1/k_t$ *vs.* [Br$^-$]/[OAc$^-$] in the acetolysis of 0.044 M **5**-Br in the presence of 0.087 M NaOAc in AcOH at 120.3°.

ions is given by 100 $[1 - (k_d/k_t{}^0)]$ where k_d is the depressed rate constant in the presence of added X$^-$. From the data of Table III for solvolysis for 48 hr in the presence of Bu_4NBr, $10^6\ k_d = 3.1$ sec^{-1} at 120.3°. Hence >93% of the ROAc arises from **7**, and correction for salt effect on $k_t{}^0$ by using a "normal" salt effect[4,41] constant $b = 3.5$ (see below) raises the value to >94%. Similar behavior was found with other α-anisyl-β,β-disubstituted vinyl cations in AcOH,[10a,c] TFE,[14] and aqueous acetone.[17]

As a measure of the isomerization of the unreacted vinyl halide, we define an "isomerization rate coefficient k_{isom}" as exemplified by eq 9 for **5**-Br, where (% **6**-Br)$_t$ and (% **6**-Br)$_\infty$ refer to the *percentages* of **6**-Br in the RBr fraction at

$$k^{5\text{-Br}}_{isom} = (2.3/t)\log(\%\mathbf{6}\text{-Br})_\infty/[(\%\mathbf{6}\text{-Br})_\infty - (\%\mathbf{6}\text{-Br})_t] \quad (9)$$

the time t and at infinity, respectively. Under solvolytic conditions k_{isom} is usually not constant since the bimolecular isomerization rate increases with the increase in [Br$^-$] as the reaction progresses.

Table II demonstrates that the α_{app} values for **5**-Br are 4.2–5.5 times higher than those for **5**-Cl. The solvent isotope effects (SIE) $k_t{}^0$(AcOH)/$k_t{}^0$(AcOD) are 1.34 ± 0.07 for **5**-Br and 1.13 ± 0.09 for **5**-Cl, and the isomerization of the unreacted **5**-Br was also 15% faster in AcOH than in AcOD.

Ion Pairs. According to Scheme II, any cation **7** is captured either by Br$^-$ or by OAc$^-$. If *only* **7** gives isomerization, the solvolysis should be completely suppressed by addition of external Br$^-$, and only a first-order isomerization with a constant k_{isom} $(=k_t{}^0)$ should be observed. Capture of **7** by another nucleophile would be of a first order with the same $k_t{}^0$, and isomerization should be suppressed.

A suitable nucleophile is Cl$^-$ which captures the ion **7**,[29] giving products which survive in AcOH. Capture of the cation ($k^7{}_{Cl}$) with sufficiently high LiCl concentration (Table III) exclude >90% of the ROAc formation, giving **5**-Br to **6**-Br and **5**-Cl to **6**-Cl ratios close to the equilibrium values. It is highly significant that the **5**-Br ⇌ **6**-Br isomerization still continues even when **7** was almost completely captured. To determine $k^7{}_{Cl}$ $(=k_{ion}$ of Scheme II), we studied the incorporation of labeled Cl$^-$ into the RCl at low conversion to ROAc, using the isotopic dilution method, with a 1:1 mixture of **5**-Cl to **6**-Cl as "diluents." Three runs at 120.3°, with 0.044 M **5**-Br, 0.087 M NaOAc, and 0.071 $Et_4N^{36}Cl$, at 2–15% reaction, gave an average $10^5\ k^7{}_{Cl}$ of 5.2 sec^{-1}. When the salt effect was accounted for by taking $b = 4.5$ (see below) for Et_4NCl, $10^5\ k^7{}_{Cl} = 3.95$ sec^{-1} with 0.087 M NaOAc as the only salt. Since this value is almost iden-

Table III. Solvolysis and Isomerization of 0.044 M **5**-Br or **6**-Br in the Presence of Added Salts in AcOH at 120.3°

Compd	NaOAc, 10^2 M	Added salt	Concn, 10^2 M	Reaction time, min	% ROAc	% **6**-Br[a]	% isomerization
6-Br[b,c]	8.7			110	22.8	82.8	37.4
				280	42.0	64.0	78.0
5-Br	5.7	$LiClO_4$	3.0	40	8.0	31.2	67.8
				110	13.6	41.1	89.4
5-Br	8.7	$LiClO_4$	3.0	40	10.3	23.7	51.5
				110	17.0	36.3	79.5
				280	28.9	46.0	100.0
6-Br	3.0	$LiClO_4$	3.0	280	31.0	46.0	100.0
5-Br	1.1	Bu_4NBr	7.6	110	*ca.* 1	20.5	44.7
				280	*ca.* 2	36.3	79.0
				2880	41.5	46.0	100.0
5-Br	1.1	Bu_4NBr	15.2	280	*ca.* 2	38.8	84.5
5-Br	3.5	Bu_4NBr	9.0	2880	41.5	46.0	100.0
6-Br	1.1	Bu_4NBr	7.6	110	*ca.* 1	77.4	41.9
				280	*ca.* 2	59.0	76.0
5-Br	1.1	LiCl	7.6	290	4[d]	22.6	49.1
5-Br	8.7	Et_4NCl	7.1	110	29.0[e]	8.4	18.3
				280	58.2[e]	19.6	42.6
5-Br	8.7	Bu_4NBr	15.2	110	*ca.* 1	24.4	53.0
5-Br[f]		AgOAc	4.4	25	55.0	35.4	77.0
5-Br		AgOAc	2.2	75	50.0	41.5	90.5
6-Br		AgOAc	2.2	75	50.0	50.0	92.5

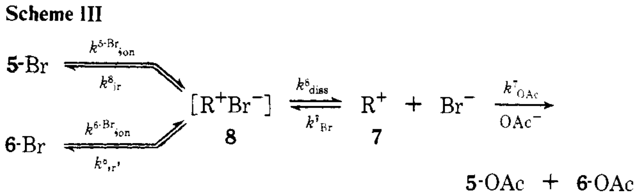
[a] In the vinyl bromide fraction. [b] [RBr] = 0.0044 M. [c] After 24 hr, $k_t = 2.5 \times 10^{-5}$ sec^{-1} and [**5**-Br]/[6-Br] = 54/46. [d] 50% of RCl were formed. [e] The products are the vinyl chlorides. [f] At 75°.

tical with k_{ion} of Table II, >90% of the cations **7** is captured by Cl^-. One-point titration and nmr analysis gave 10^5 k_t = 0.46 sec^{-1} for the ROAc formation (or 0.35 sec^{-1} with only 0.087 M NaOAc). The isomerization of **5**-Br to **6**-Br under these conditions was studied up to 55% Cl^- incorporation and was a first-order process with 10^5 k_{isom} = 3.3 (or 2.52 after correction for the salt effect of Et_4NCl) sec^{-1}.

It is apparent that in spite of the complete capture of **7** by Cl^-, there is an additional isomerization which is not accounted for by Scheme II. This was verified by using a simulation program (see Appendix) for calculating the concentrations *vs.* time profiles of ROAc, **5**-Br, and **6**-Br, and comparing them with the experimental profiles. Starting from either bromide and using k_t^0 of Table II, the [ROAc] *vs.* time profiles were reproduced accurately, but the development of the isomeric bromide was always slower than that found experimentally, even when α_{app} was allowed to change (Figure 3).

We exclude below cis-trans isomerizations which do not involve primary ionization, and we account for the extra isomerization by extending Scheme II to include the ion pairs **8** in the solvolysis-isomerization mechanism (Scheme III).[42] These ion pairs may further dissociate (k^8_{diss}) or give internal return (ir) to either **5**-Br (k^8_{ir}) or **6**-Br ($k^8_{ir'}$). Since the products are formed from **7** only, we added no capture process k^8_{SOH}.

Scheme III



According to Scheme III, k_{ion} is given by eq 10 where k^8_{isom} is the first-order isomerization constant *via* the ion pair, and k_t^0 is known from Table II or from k^7_{Cl}. We used

$$k_{ion} = k_t^0 + k^8_{isom} \quad (10)$$

three methods for estimating either k^8_{isom} or k_{ion} directly. (a) In the chloride capture experiment $k_{isom} = k^8_{isom}$, and

Table IV. Cis-Trans Isomerization of 0.044 M **5**-Br and 6-Br in the Presence of 0.011 M NaOAc at 120.3° in AcOH

Compd	Bu_4NBr, M	$10^5 k_{isom}$, sec^{-1} [a]	$10^5 k_{ion}$, sec^{-1} [a]
5-Br	0.076	8.92 ± 0.19	9.32 ± 0.19
5-Br	0.152	11.30 ± 0.2	11.70 ± 0.2
6-Br	0.076	8.48 ± 0.08	8.88 ± 0.08

[a] Corrected for the formation of ROAc during the isomerization.

$k_t^0 = k^7_{Cl} + k_t$, where k_t measures the minor concurrent ROAc formation. This yields 10^5 k_{ion} = 6.83 at 120.3° when [NaOAc] = 0.087 M.

(b) Since >94% of ROAc is derived from **7**, a first-order isomerization from both **7** and **8** ($k^7_{isom} + k^8_{isom}$) is the main process in the presence of large excess of Br^-, and it differs from k_{ion} only in k_t for the minor formation of ROAc (eq 11).

$$k_{ion} - k_t = k_{isom} = k^7_{isom} + k^8_{isom} \quad (11)$$

Table IV summarizes three first-order isomerization runs, where k_{isom} values are based on the observed ("equilibrium") infinities. At these high Br^- concentrations 10^6 k_t = 4 sec^{-1}, and k_{ion} values were calculated by eq 11. The salt effect of Bu_4NBr on $k^{5\text{-Br}}_{ion}$ was calculated according to eq 12 for the normal salt effect,[41a] where k_0 is the rate

$$k_t = k_0(1 + b[\text{salt}]) \quad (12)$$

constant in the absence of salt. The b value is 4.4,[43] giving 10^5 k_0 = 6.96 sec^{-1} in the presence of 0.011 M NaOAc. Since b values for NaOAc are low,[3,10b,41a] we used b = 0.5,[41a] obtaining 10^5 k_{ion} = 7.23 sec^{-1} at 120.3°.

(c) Neither a nor b is applicable in the absence of added salt. In analogy with saturated systems where k_α measures the change in the "d isomer content" from pure d-RX to the infinity combination of d-RX + d-ROS, we developed a general treatment which we call "the total *cis* content," and which is exemplified for a reaction starting from **6**-Br.

Let x be the per cent reaction by titration and y the per cent of **6**-Br in the RBr fraction at the time t. The per cent of trans products (**6**-OAc + **6**-Br) in the RX + ROAc mixture, Z, is given by eq 13, where 46 is the equilibrium per-

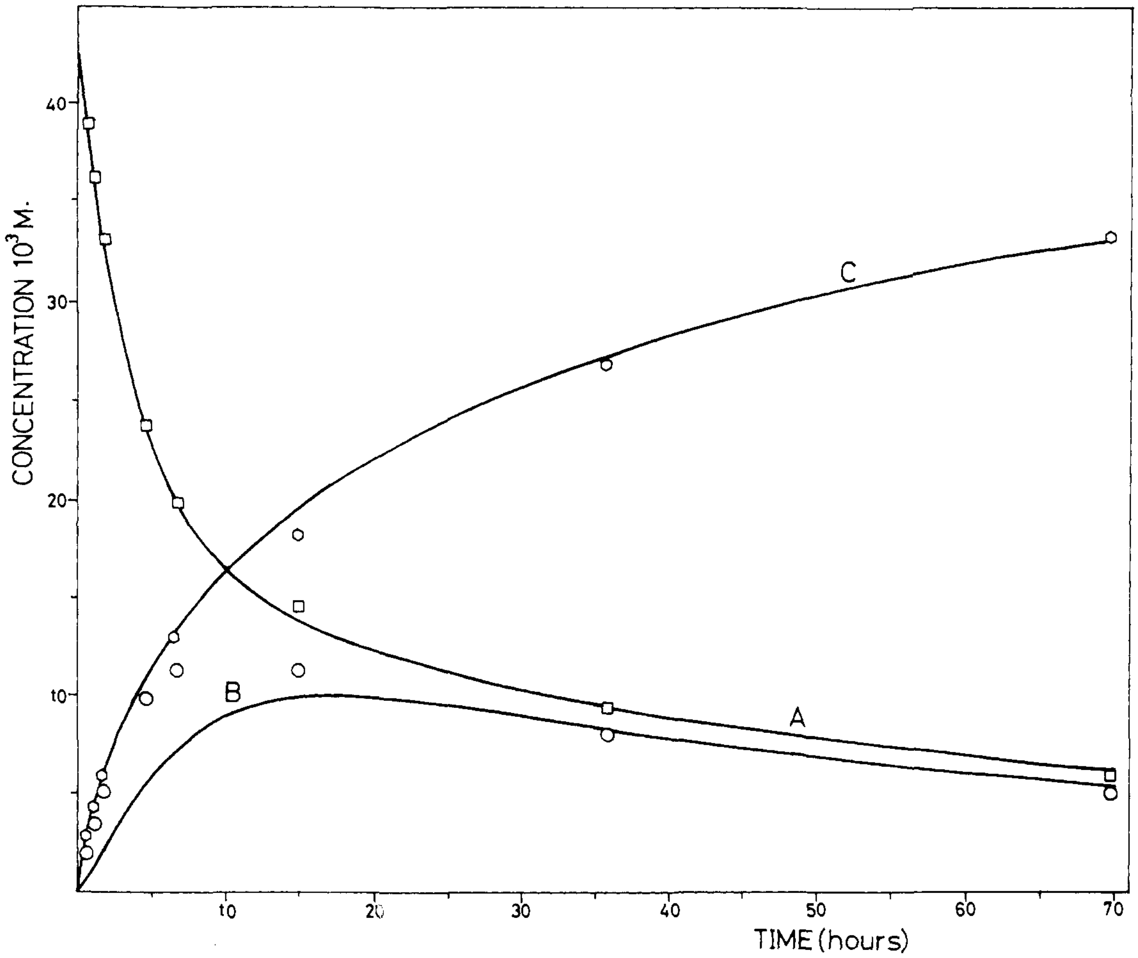


Figure 3. Concentration *vs.* time profiles for the solvolysis–isomerization of 0.044 *M* **6**-Br with 0.087 *M* NaOAc in AcOH at 120.3°. The points are experimental [(O) **5**-Br; (□) **6**-Br; (○) **5**-OAc + **6**-OAc], and the lines [(A) for **6**-Br; (B) for **5**-Br; and (C) for **5**-OAc + **6**-OAc] are theoretical and calculated by simulation of Scheme II.

$$Z = (46/100)x + [(100 - x)/100]y \qquad (13)$$

centage of **6**-OAc in the ROAc fraction. In our system, the percentages of **6**-OAc in the ROAc fraction and of **6**-Br in the RBr fraction are identical, and the "*cis* content" (**5**-Br + **5**-OAc) will reach the "*cis* equilibrium content" in a first-order reaction, with rate constant k_{ion} (eq 14) since capture of **7** or **8** by either Br^- or AcO^- contributes to the achievement of the "*cis* equilibrium content." Combination of eq 13 and 14 gives eq 15 for k_{ion}, and combination of eq 1 and 9 gives the same expression (eq 16), resulting in eq 17

$$k_{ion} = \ln[46/(46 - Z)]/t \qquad (14)$$

$$k_{ion} = \left[\ln\frac{100}{(100 - x)(1 - y/46)}\right]/t = \ln[100/(100 - x)]/t + \ln[1/(1 - y/46)]/t \qquad (15)$$

$$k_t + k_{isom} = \ln[100/(100 - x)]/t + \ln[46/(46 - y)]/t = \ln[100/(100 - x)]/t + \ln[1/(1 - y/46)]/t \qquad (16)$$

$$k_{ion} = k_t + k_{isom} \qquad (17)$$

where k_{ion} which is the sum of k_t and k_{isom} (which are not constant during a run) can be calculated from the titrimetric and the isomer distribution data in each kinetic run.[44] The basis of eq 17 is that the return of **7** to RX which decreases k_t within a run gives a parallel increase in k^7_{isom}. The validity of eq 17 is demonstrated in Table I, and k_{ion} values of method c are in Table V. Table VI compares the k_{ion} values from the three methods. Their agreement seems satisfactory considering the fact that at least two k's were measured in each method, and that small errors may result from the assumptions that $b[Et_4NCl] = b[Bu_4NBr]$ and that $b[NaOAc] = 0.5$.

We used a computer simulation of Scheme III, using as an input the k_{ion} values and Winstein's k's for internal return and cation–anion recombination.[45] The program searches the $(k^7_{Br} + k^7_{Br'})/k^7_{OAc}$ and $(k^8_{ir} + k^8_{ir'})/k^8_{diss}$ ratios which would give the best fit for the experimental [concentration] *vs.* time profiles for the various species (see Appendix). The good fit observed in all our cases is demonstrated in Figure 4, where the points are experimental, and the lines are calculated.[46] Scheme III accounts therefore quantitatively for both the solvolysis and the isomerization, and we believe that it represents the solvolysis mechanism of the vinyl halides studied.

We define in eq 18 "true" α values which measure return from **7** to **8** even if it does not terminate in the covalent RX, and we denote by F the fraction of ion pairs which dissociates further[47] (eq 19). The relationship between the α_{app}

$$\alpha = (k^7_{Br} + k^7_{Br'})/k^7_{OAc} \qquad (18)$$

$$F = k^8_{diss}/(k^8_{diss} + k^8_{ir} + k^8_{ir'}) \qquad (19)$$

values which account only for return which terminates in RX, and α of eq 18 is given by eq 20. The return to disso-

$$\alpha_{app} = \alpha(k^8_{ir} + k^8_{ir'})/(k^8_{ir} + k^8_{ir'} + k^8_{diss}) = \alpha(1 - F) \qquad (20)$$

Table V. k_{ion}, α, and $(1 - F)/F$ Values for the Acetolysis of **5**-Br, **6**-Br, and **5**-Cl

Compd[a]	Solvent	T, °C	10^5k_{ion},[b] sec^{-1}	α[c]	$(1 - F)/F$	% return from **8**
5-Br	AcOH	120.3	7.52 ± 0.05	45.0	0.905	47.5
5-Br	AcOH	140.2	44.0 ± 2.3	54.0	0.613	38.0
5-Br[d]	AcOH	120.3	11.0 ± 0.3	78.0	1.250	55.5
5-Br	AcOD	120.3	6.78 ± 0.04	45.0	0.923	48.0
6-Br	AcOH	120.3	7.73 ± 0.11	45.0	0.896	47.3
6-Br	AcOH	140.2	47.0 ± 2.5	54.0	0.654	39.5
5-Cl	AcOH	120.3	0.306 ± 0.018	15.0	0.613	38.0
5-Cl	AcOH	140.2	2.00 ± 0.12	12.2	0.667	40.0
5-Cl	AcOH	158.5	9.20 ± 0.20	12.0	0.710	41.5
5-Cl	AcOD	158.5	8.40 ± 0.21	12.1	0.680	40.5

[a] [RX] = 0.044 M; [NaOAc] = 0.087 M unless otherwise stated. [b] From the "total *cis* content." [c] From the simulation program. [d] [**5**-Br] = 0.0044 M.

Table VI. k_{ion} Values, Obtained by Various Methods, for the Acetolysis of **5**-Br in the Presence of NaOAc[a]

Method	10^5k_{ion}, sec^{-1}, at 120.3°	From[b]
(a) Chloride ion capture	6.83[c]	$k^7_{Cl} + k^8_{isom} + (k_t)$
(b) Bromide ion capture	7.23[c]	$k^7_{isom} + k^8_{isom} + (k_t)$
(c) Total cis content	7.52	$k_t + k_{isom}$

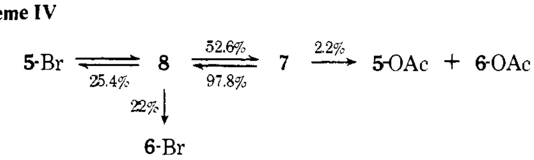
[a] [**5**-Br] = 0.044 M; [NaOAc] = 0.087 M. [b] In parentheses, contribution from the minor concurrent solvolysis. [c] Based on extrapolation involving salt effects.

ciation ratio $(k^8_{ir} + k^8_{ir'})/k^8_{diss}$ is then $(1 - F)/F$. The α, $(1 - F)/F$, and percentage of ion return from **7** to RX values are summarized in Table V.

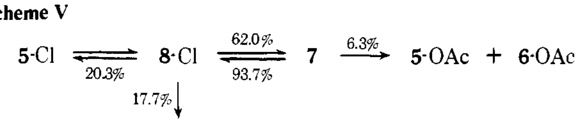
The best α and $(1 - F)/F$ ratios for **5**-Br from Table V were applied together with the simulation program for the following processes: (a) reproducing the experimental data starting from **6**-Br; (b) for the runs of **5**-Br and **6**-Br in the presence of external Br$^-$, taking the salt effect into account; (c) for the capture experiment with Cl$^-$. For a and b, an excellent fit with the experimental results was found for all the runs, while for c the best fit gave 39% of return from **8** as compared with the 47.5% calculated from the solvolysis runs of **5**-Br.[48] The success of all three methods supports the assumption that **7** and **8** are common intermediates in the solvolyses of **5**-Br and **6**-Br, and that **7** is also common for the solvolysis of **5**-Cl. All the methods gave a $k^8_{ir}/k^8_{ir'}$ ratio of 1.15, which is reflected in the **5**-Br/**6**-Br and the **5**-OAc/**6**-OAc ratios of 1.17 at equilibrium.

The distributions of the cationoid species among the various reaction routes when $[RX]_0$ = 0.044 M and [NaOAc] = 0.087 M are summarized in Scheme IV for **5**-Br and in Scheme V for **5**-Cl, where **8**-Cl is the ion pair [R$^+$Cl$^-$]. Since the reactions of **7** depend on the nucleophile concentration, the values were calculated for the case when [Br$^-$] = [OAc$^-$]. In the absence of data for the solvolysis of **6**-Cl, we used the same $k^8_{ir}/k^8_{ir'}$ ratio as found for **6**-Br.

Scheme IV



Scheme V



Reaction in the Presence of AgOAc. Strong electrophilic catalysis is shown by AgOAc, which on an equimolar scale

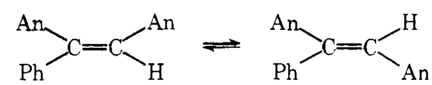
Table VII. Isomerization of 1,2-Dianisyl-2-phenylethylenes at 120.3°

Substrate	Solvent	Added salt	10^6k_{isom},[a] sec^{-1}	% **5**-H at equilibrium[b]
5-H[c]	AcOH		9.47 ± 0.66	54
5-H[c]	AcOD		3.72 ± 0.29	54
6-H[c]	AcOH		9.5 ± 1.3[d]	
5-H[e]	AcOH	0.025 M AgOAc	11.0[f]	
5-H[e]	AcOH	0.025 M AgOAc .	15.0[f]	

[a] Based on the infinity distribution of **5**-H and **6**-H. [b] In the **5**-H + **6**-H mixture. [c] [Substrate] = [NaOAc] = 0.087 M. [d] Based on two points. [e] [Substrate] = [NaOAc] = 0.025 M. [f] One-point experiment.

gives 2–3 orders of magnitude faster solvolysis than with NaOAc (Table III). It is remarkable that the recovered RBr from the solvolysis of excess **5**-Br or **6**-Br is partially isomerized. The isomerization is faster with AgOAc (k_{isom} = 5.2 × 10^{-4} sec^{-1}) than with NaOAc (k_{isom} = 5.0 × 10^{-5} sec^{-1}).

Isomerization *via* electrophilic addition–elimination (Ad_E-E) of Ag$^+$ to the double bond is excluded by the study of the first-order isomerization of *cis*- and *trans*-1,2-dianisyl-2-phenylethylenes (**5**-H and **6**-H) (eq 21) with and

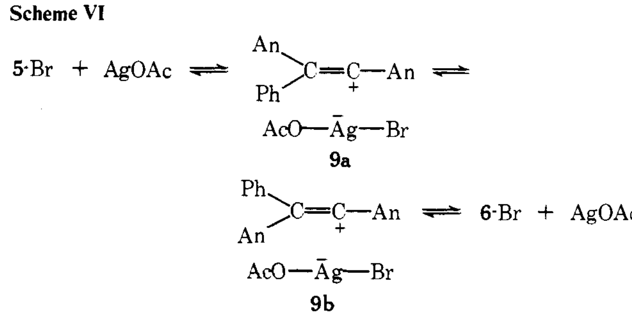


5-H 6-H (21)

without AgOAc. The isomerizations of **5**-H and **6**-H are 15 and 55% accelerated in the presence of AgOAc (Table VII), and since electrophilic addition to the ethylenes is easier than to the bromides, this route is negligible in the isomerization of the bromides.

We suggest Scheme VI, where the AgOAc molecule is

Scheme VI



the electrophile, as the AgOAc-catalyzed route, since the dissociation of AgOAc in AcOH is probably low. The first

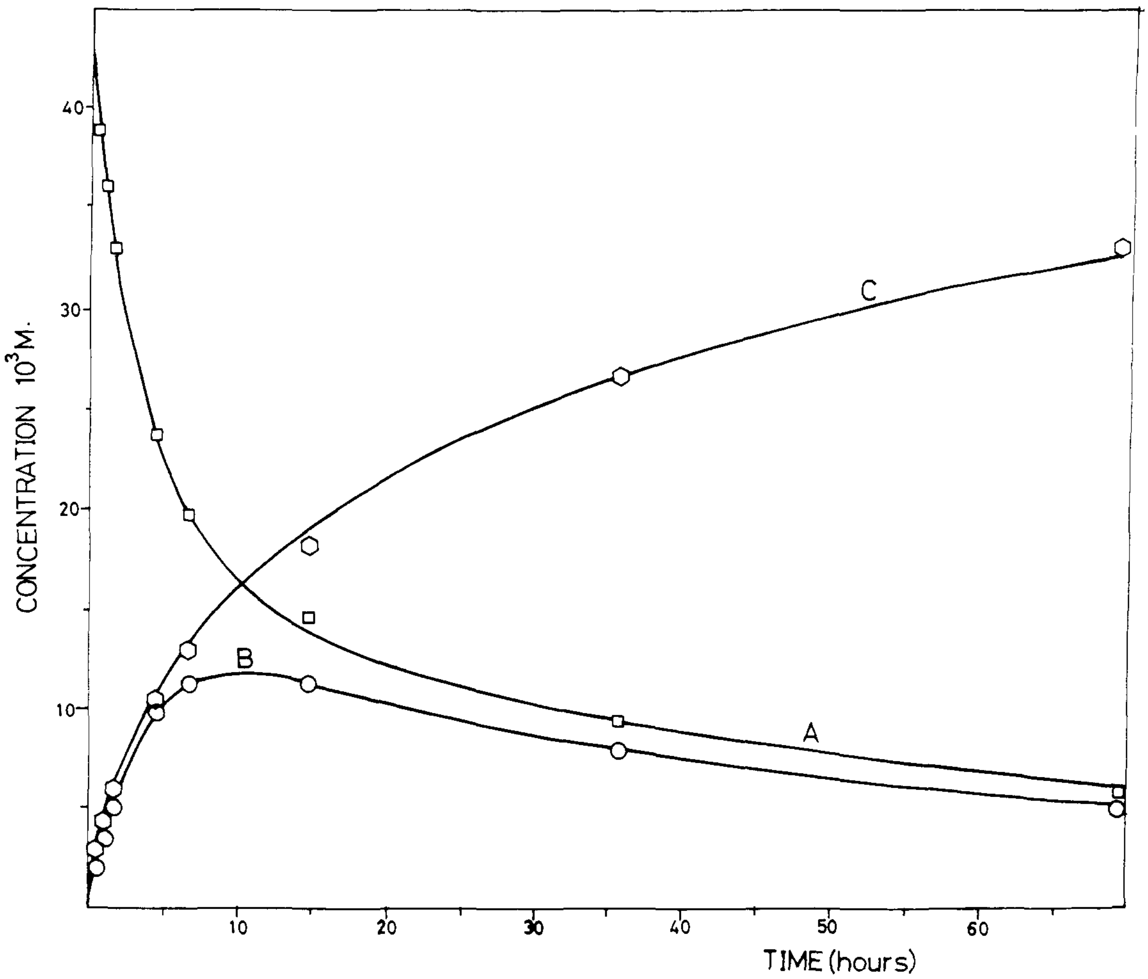
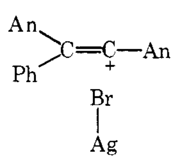


Figure 4. Concentration *vs.* time profiles for the solvolysis-isomerization of 0.044 *M* **6**-Br with 0.087 *M* NaOAc in AcOH at 120.3°. The points are experimental [(○) **5**-Br; (□) **6**-Br; (○) **5**-OAc + **6**-OAc] and the lines [(A) for **6**-Br; (B) for **5**-Br; and (C) for **5**-OAc + **6**-OAc] are theoretical and calculated by simulation of Scheme III.

formed intermediate is the ion pair **9a** rather than the ion-molecule pair **10**, and isomerization occurs *via* **9b** and in-



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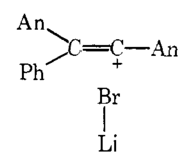
ternal return. A similar scheme was suggested by Kelsey and Bergman for the isomerization observed in the acetolysis of 1-cyclopropyl-1-iodopropenes.[20b]

Reaction in the Presence of $LiClO_4$. The correspondence of k_t^0 values of Table VI and k^7_{Cl} suggests that **8** is not captured by Cl^-. Table III shows that the rate of ROAc formation at $LiClO_4$ concentrations sufficient for complete capture of any "solvent separated" ion pair present[4b,5] is only slightly accelerated, arguing strongly that **8** is not a solvent-separated ion pair but probably an intimate ion pair. However, the isomerization rate increases *ca.* 4.5-fold, and k_{ion} with 0.03 *M* $LiClO_4$ is 4.5-fold higher than in its absence. Precedents for Li-salt promoted ionization in saturated solvolyses are known,[41c,49] but if the effect is more pronounced in our sluggish vinylic system,[50] almost all the ion pairs formed in the promoted reaction return to RBr. This may result from a favorable transfer of the bromide ion from the solvated Li^+ of the ion-molecule pair **11** or the ion pair **12** to the sterically crowded poorly solvated R^+, but more work is needed to clarify this behavior.



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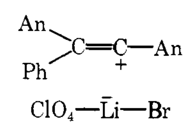

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Reaction at Low Concentration of RBr. We expected a first-order solvolysis and isomerization only *via* the ion pair **8** when $k^7_{OAc} \gg k^7_{Br}[Br^-]$. Surprisingly, when the **5**-Br concentrations were reduced tenfold to 0.0044 *M*, k_t^0, k_{isom}, and α increased 1.26-, 1.46-, and 1.73 times, respectively (Tables II and V), and k_t and k_{isom} also increased for **6**-Br (Table III).

Our treatment implies that [NaOAc] = $[OAc^-]$ and [NaBr] = $[Br^-]$. However, for salts which are not completely dissociated, *e.g.*, NaBr, both free Br^- ions (f) and ion pairs Na^+Br^- (p) should be considered, and $k^7_{Br}[Br^-]$ should be replaced by the sum in eq 22. Since ion pairs are

$$k^7_{Br}[Br^-] = k^7_{Br,f}[Br^-]_f + k^7_{Br,p}[Br^-]_p \quad (22)$$

less reactive than free ions,[51] and the $[Br^-]_f/([Br^-]_f + [Br^-]_p)$ ratio increases on dilution, the rate of the **7** → RBr reaction would decrease on dilution less than predicted for reaction with only one species (when $k^7_{Br,f} \gg k^7_{Br,p}$) and α and k_{isom} will increase. The increase of return at the expense of dissociation at low salt concentration could be due to increased dissociation in the presence of NaBr as compared with NaOAc. Comparison of α and k_{ion} values for

Table VIII. Acetolysis of **5**-OMs, **6**-OMs, and **5**-OTs + **6**-OTs[a]

Compd	T, °C	Added salt	Concn, 10^2 M	10^5k_t,[b] sec^{-1}	10^5k_{isom}, sec^{-1}	10^5k_{ion}, sec^{-1}
5-OMs	75.1			10.0 ± 0.18	3.6 ± 0.5	13.6 ± 0.68
6-OMs	75.1			8.62 ± 0.07	2.8 ± 0.2	11.42 ± 0.27
6-OMs	75.1	Et_4NOMs	32.6	6.18 ± 0.34	7.1 ± 1.1	13.28 ± 1.44
6-OMs	75.1	Et_4NBr	4.3	8.55 ± 0.03[c]	*d*	
ROTs[e]	75.1			11.5 ± 0.2[f]		
ROTs[e]	89.8			57.9 ± 0.2		
ROTs[e]	120.3			1130[g]		

[a] [ROMs] = 0.0435 M; [NaOAc] = 0.087 M. [b] Values and standard deviations of runs of 5–6 points. [c] Sum of k's for formation of RBr and of ROAc; *e.g.*, at 38.2% reaction 10^5k for bromide capture is 8.0 and for the formation of the 2% ROAc, $10^5 k = 0.5$; at 65.4% RBr formation, 10^5k is 7.4 for the bromide capture and 1.2 for the ROAc formation. [d] The percentage of **5**-OMs in the ROMs fraction is *ca.* 5% during the reaction. [e] A 56:44 mixture of **5**-OTs and **6**-OTs was used. [f] $\Delta H^* = 26.7$ kcal/mol; $\Delta S^* = 0$ eu. [g] Extrapolated value.

different substrates should be therefore made at the same substrate and salt concentrations.

The Possibility of Induced Common Ion Rate Depression. An alternative to Scheme III could be Scheme VII, where only "intimate" (**13**) and "solvent separated" (**14**) ion pairs are formed, NaOAc is a "special" salt, and the kinetics are due to "induced common ion rate depression" (ICRD)[5h] where NaX and NaOAc compete for **14**. Cristol, *et al.*,[52] applied a similar scheme for the acetolysis of *syn*-7-chlorobenzonorbornadiene with KOAc as a "special" salt, and KOAc,[53] LiOAc,[5e,h] and $NaOOCCF_3$[38d] were suggested as "special" salts in other solvolyses.

Scheme VII

$$\mathrm{RBr} \rightleftharpoons \underset{\mathbf{13}}{\mathrm{R^+Br^-}} \rightleftharpoons \underset{\mathbf{14}}{\mathrm{R^+||Br^-}} \underset{\mathrm{Na^+Br^-\ or\ R_4N^+Br^-}}{\overset{\mathrm{Na^+OAc^-}}{\rightleftharpoons}} \underset{\mathbf{15}}{\mathrm{R^+||OAc^-}} \rightleftharpoons \mathrm{ROAc}$$

Scheme VII is disproved by the following reasoning. (a) The best "special" salt, $LiClO_4$,[5] did not show special salt effect. If **14** is captured completely by NaOAc, exchange of **15** with $LiClO_4$ would give $Li^+\|ClO_4^-$ ion pairs and lower extent of ICRD than with NaOAc alone. However, Table III shows a similar common ion rate depression with and without $LiClO_4$. (b) The strong common ion rate depression in unbuffered AcOH and the similarity of k_{ion} in unbuffered[37] and in buffered AcOH does not fit Scheme VII. (c) The "fully depressed" rate for ICRD reflects the ROAc formation from **14**, *i.e.*, it should be k_t^0 in the unbuffered AcOH or in AcOH buffered by urea. However, k_t at high Br^- concentrations is lower than k_t^0 in unbuffered AcOH. (d) The salt effect of NaOAc, which should be substantial for Scheme VII, is closer to the "normal" effect observed in the acetolysis of α-bromo-*p*-methoxystyrene, where common ion rate depression is absent.[10b] (e) Analogy with the common ion rate depression observed for α-arylvinyl halides in the absence of added salts in several solvents[10a,b,11,13-15,17] substantiates Scheme III.

Acetolysis of 5-OMs, 6-OMs, and 5-OTs + 6-OTs in Buffered AcOH. Dissociated Ions and Ion Pairs. Acetolysis of either **5**-OMs or **6**-OMs or a 56:44 mixture of **5**-OTs and **6**-OTs gave a 54:46 mixture of **5**-OAc and **6**-OAc at 19–100% reaction, and nmr and ir showed that only solvolysis and isomerization take place. The rate constants did not decrease during a run and were calculated by the KINDAT program.[54] They were identical either when the appearance of ROAc or the disappearance of ROMs was followed.

The acetolysis of the mesylates was accompanied by a **5**-OMs ⇌ **6**-OMs isomerization which was less extensive than that of **5**-Br and **6**-Br. After 50% acetolysis, only *ca.* 10% of the isomeric mesylate was present in the ROMs fraction. Equilibration of **5**-OMs and **6**-OMs was not achieved during the acetolysis and a first-order k_{isom} was calculated by using an "infinity" distribution of 54% **5**-OMs to 46% **6**-OMs (Table VIII).

Scheme VIII describes the solvolysis–isomerization of the

Scheme VIII

$$\mathbf{5}\text{-OMs} \underset{k^{16}_{ir}}{\overset{k^{5\text{-OMs}}_{ion}}{\rightleftharpoons}} \underset{\mathbf{16}}{[\mathrm{R^+OMs^-}]} \underset{k^{7}_{OMs}}{\overset{k^{16}_{diss}}{\rightleftharpoons}} \underset{\mathbf{7}}{\mathrm{R^+}} + \mathrm{OMs^-} \xrightarrow{k^{7}_{OAc}} \mathrm{ROAc}$$

$$\mathbf{6}\text{-OMs} \underset{k^{16}_{ir'}}{\overset{k^{6\text{-OMs}}_{ion}}{\rightleftharpoons}} \underset{\mathbf{16}}{[\mathrm{R^+OMs^-}]}$$

mesylates. The constancy of k_t within a run indicates that k_{isom} measures return with isomerization only from the ion pair **16**, and that k_{ion} is the sum of the first-order constants of eq 23. The ROAc can still be formed from **7** whose cap-

$$k_{ion} = k_t + k_{isom} = k_t + k^{16}_{isom} \tag{23}$$

ture by OAc^- is faster than return, and reaction of **6**-OMs in the presence of Et_4NOMs indeed gave k_t^d which was only 72% of k_t in the absence of Et_4NOMs, *i.e.*, >28% of the ROAc arises from **7**.[55] The derived selectivity factor k_{OMs}/k_{OAc} is 0.104, and correcting for normal salt effect, by using $b = 0.5$ for Et_4NOMs, as calculated from the two points for **6**-OMs in Table VIII, gives $\alpha = k_{OMs}/k_{OAc} = 0.16$. Simultaneously, k_{isom} increases significantly, but although the unreacted mesylate was 65% isomerized after 2 solvolytic half-lives, the **5**-OMs ⇌ **6**-OMs equilibrium was not achieved during a run.

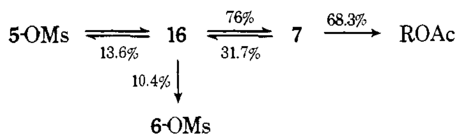
A more complete capture of **7** formed from **6**-OMs takes place with Br^-. Reaction of **6**-OMs in the presence of 0.043 M NaOAc and 0.043 M Et_4NBr gave >94.5% **5**-Br and **6**-Br (in a 52.2:47.8 ratio), indicating that the incomplete capture of **7** from **5**-Br is due to the increase of $k^{5\text{-Br}}_{ion}$ at high salt concentrations. After formation of 65% of RBr, nmr and AcO^- titration showed the presence of 5.5% of 54:46 of **5**-OAc and **6**-OAc, and this value was increased to 18% ROAc after 5 half-lives. The α_{app} of **17** which was obtained from the [RBr]/[ROAc] ratio is close to the α_{app}'s of Table II.[56] The sum of the rate constants for ROAc formation and the Br^- disappearance is identical with k_t in the acetolysis of **6**-OMs.

If Br^- captures only **7**, the isomerization of **6**-OMs should be similar with and without Et_4NBr. Nmr showed that *ca.* 5% of **5**-OMs accompanies the unreacted **6**-OMs, but its concentration changes only slightly during the reaction. Whether this is an experimental error, or some **16** is captured by the Br^- is unknown.

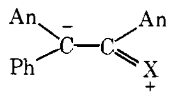
Scheme IX summarizes the distribution of the intermediates from ROMs among the various routes.

Exclusion of Nonheterolytic Isomerization Routes. Whenever cis–trans isomerization is used as a mechanistic tool in vinylic solvolysis, other isomerization routes should be explicitly excluded. An isomerization *via* rotation

Scheme IX



around the central bond in the contributing structure **17** contradicts the slower isomerization with added Cl^- and



17

the pronounced solvent and substituent effects on the isomerization. A nucleophilic addition-elimination isomerization (eq 24)[57] is highly unlikely for our nucleophilic sub-

$$\mathbf{5}\text{-Br} + \mathrm{OAc}^- \rightleftharpoons \begin{matrix}\mathrm{AnC^-(Ph)C(Br)(OAc)An} \\ \text{or } \mathrm{AnC(Ph)(OAc)C^-(Br)An}\end{matrix} \rightleftharpoons \mathbf{6}\text{-Br} + \mathrm{OAc}^- \quad (24)$$

strates and the weak OAc^- nucleophile, as judged by the behavior of the 9-(α-haloarylidene)fluorenes.[58]

The electrophilic addition-elimination route (Ad_E-E)[10b,32] (Scheme X) is known to operate both for substitution and for acid-catalyzed isomerization of vinylic compounds.[59] The following distinguishing criteria[10b,32c] favor the SN1 and discard the Ad_E-E route in our system.

(a) **Products.** An α-phenyl group stabilizes a neighboring positive charge better than α-bromine or chlorine, and addition would give the 1,2-diacetate **21** *via* the cation **19**. The non-Markovnikov addition may give some of the 1,1-diacetate **23** *via* **18** and **22**. None of these were observed.

(b) **The Solvent Effect.** The electrophilic addition should be faster in AcOH than in 80% EtOH.[32a,60] For compound **24**-Br which reacts *via* SN1, k_t(80% EtOH)/k_t(AcOH) = 15, while for **24**-Cl, which reacts by both SN1 and Ad_E-E, the ratio is 0.13.[10b] Our k_t(80% EtOH)/k_t(AcOH) ratios of 6.3, 7.0, and 3.2 for **5**-Br, **6**-Br and **5**-Cl, respectively, fit the SN1 route.

(c) **The Solvent Isotope Effect.** Literature data[10b] give sol-

AnC(X)=CH_2
X = Cl: **24**-Cl
X = Br: **24**-Br
X = H: **24**-H

vent isotope effects (SIE) k_{AcOH}/k_{AcOD} of $\leq$1.2 for the vinylic SN1 solvolysis and much higher values for the Ad_E process, *e.g.*, 3.4 for addition of AcOH to **24**-H. The SIE based on k_{ion} of 1.11 for **5**-Br and 1.10 for **5**-Cl are within the SN1 range.[61]

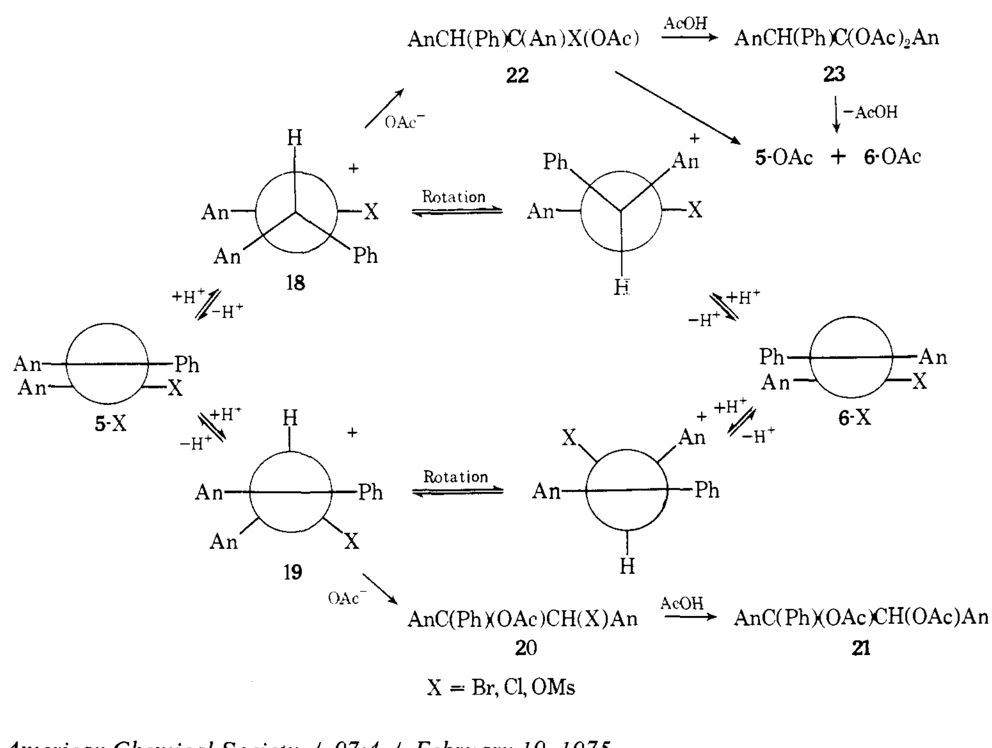
As a closer model, we determined a SIE of 2.55 for the cis-trans isomerization of the ethylenes **5**-H and **6**-H in AcOH-NaOAc, assuming that it involves a rate-determining addition of a proton to the double bond (Table VII). According to the Hammond's principle[62] as applied to the SIE in the Ad_E reactions,[63] this should be a good approximation to the SIE in the addition of proton to **5**-Br and **5**-Cl since the k_{Br}/k_H ratio of Table IX suggests that the degree of proton transfer from AcOH to the double bond in the transition state is similar for the additions to both **5**-H and **5**-Br.

(d) **The Effect of the Leaving Group.** The Ad_E rate to **5**-X should decrease on increasing the electron-withdrawing ability of X, *i.e.*, with σ_I and σ_R.[64] When X = H, the SN1 process is unfeasible, and when X = OAc, it will be very slow. The relative reactivities of good leaving groups would be determined by the C–X bond strength, by the polarizability and the charge dispersal on the group X, and by solvation effects.

Our data for the solvolysis and isomerization of **5**-X for X = Cl, Br, OMs, OTs, H, OAc, and σ_I and σ_R values of the six groups,[65,66] and literature data on observed reactivity ratios for various X groups for both routes,[10b,67-69] are given in Table IX. $\sigma(OSO_2Ph)$ was approximated for σ(OTs) since σ(OTs) $\sim$ σ(OMs).

We found only two studies on the Ad_E process to vinyl X when X = H, Br, and Cl.[67,68,70] The addition of CF_3COOH to 2-X-propenes is a closer model to our case,[67] but data on bromination of CH_2=C(X)CH_2Cl[68] were also included. The effect of an α-OAc group on the Ad_E rate in AcOH is highly dependent on the other α substituents: k(MeC(OAc)=CH_2)/k(MeCH=CH_2) = 1300,[71] while k(An-

Scheme X



X = Br, Cl, OMs

Table IX. Relative Reactivities for the Ad_E and the SN1 Reactions

Group X	$\sigma_I(X)$	$\sigma_R(X)$	Relative k for Ad_E A[d]	B[e]	C[f]	Relative k_t,[g] literature	Relative k_t,[h] experimental	Relative k^0_{isom},[h] experimental
H	0[a]	0[a]	12	5000	11.4			0.27
Cl	0.51[a]	−0.35[a]	4.3	0.8	(2.1)	0.03	0.04	0.04
Br	0.50[a]	−0.34[a]	1.0	1.0	(1.0)	1.0	1.0	1.0
OAc	0.40[a,b]	−0.32[a,b]			314	$<1.5 \times 10^{-5}$	<0.002	<0.01
OMs	0.43[c]	−0.14[c]				85	244[i]	100[i]
OSO_2Ph	0.40[c]	−0.13[c]				100	281	

[a] Reference 65. [b] W. A. Sheppard and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **94**, 1919 (1972), reported $\sigma_I(OAc) = 0.27$, $\sigma_R^0(OAc) = -0.20$. [c] Calculated from the relationship $\sigma_I = 1.6\sigma_m - 0.55\sigma_p$; $\sigma_R = -1.83\sigma_m + 1.6\sigma_p$ which is based on the equations derived by O. Exner [*Collect. Czech. Chem. Commun.*, **31**, 65 (1966)] for substituents with at lone electron pair at the α-position. The σ_m and the σ_p values are from ref 66. [d] Addition of CF_3COOH to 2-X-propenes (ref 67). [e] Bromination of $CH_2{=}C(X)CH_2Cl$ in 50% MeOH (ref 68). [f] Solvolysis and isomerization of **24** in AcOH (ref 10b). The values in the parentheses are upper limits since the solvolysis of **24**-Br is SN1 and that of **24**-Cl is *via* a combination of the SN1 and the Ad_E routes. [g] See text for evaluation of the relative rates. [h] At 120.3°. [i] Assuming identical activation energies for ROMs and ROTs.

$C(OAc){=}CH_2)/k(AnCH{=}CH_2) = 28.$[10b]

The predicted k_t are based on the k_{Br}/k_{Cl} ratios for vinylic[10a,c,72] and saturated systems,[73] the k_{OMs}/k_{OTs} ratios for the trianisylvinyl[17] and saturated systems,[74] and on a k_{OTs}/k_{Br} ratio of 100 which is close to that for the trianisylvinyl system in AcOH,[17] although ratios of 5.15–765 were found for vinylic systems[1] and higher ones for saturated compounds.[75] The k_{Cl}/k_{OAc} ratios are for the *tert*-butyl system.[69]

Table IX and these considerations suggest for X the following reactivity order: for the Ad_E route, OAc > H > Br < Cl > OMs ~ OTs; and in the SN1 route, OTs > OMs > Br > Cl ≫ OAc. The actual order of k_t (OTs ≥ OMs > Br > Cl ≫ OAc)[76] and k^0_{isom} (OMs > Br > Cl < H) indicates an SN1 route, except probably for the k^0_{isom}(**5**-H)/k^0_{isom}(**5**-Cl) ratio.

(e) The Effect of Catalyst. The much stronger AgOAc catalysis for the solvolysis and isomerization of **5**-Br than for the isomerization of **5**-H indicates a C–Br bond heterolysis.

(f) Comparison with Other Systems. 24-Br acetolyzes *via* the SN1 route. We argued that since β-phenyl substituents retard the Ad_E reactions on styrenes,[77] and they usually accelerate the SN1 reaction, the AnCX=C(Ar)Ar′ compounds would acetolyze *via* SN1.[10b] This applies for our compounds since k_t(**5**-Br)/k_t(**24**-Br) and k_t(**6**-Br)/k_t(**24**-Br) ratios are 2.72 in AcOH at 120.3°.

Selectivity and Reactivity of the Cationoid Species. The almost exclusive formation of products from free ions is rare in solvolysis reactions.[78] Winstein implied that as the relative stability of R^+ increases, the solvent attack shifts to a more dissociated species,[4a] and accordingly, the ion **7** is more stable than most of the R^+'s studied in AcOH.

The selectivity constant α for saturated cations increases with the increased stability of R^+ (which is measured by k_t for RX).[35a,79] While we found no α value for comparison between halide and acetate ions in AcOH, our values are higher than the α's ($=k_{Br}/k_{AcOH}$, k_{Cl}/k_{AcOH}) for the stable Ph_2CH^+ cation since Ph_2CHCl and Ph_2CHBr show no common ion rate depression in AcOH.[80] This raises the question why the sluggishly formed vinyl cation is so much more stable than anticipated from the reactivity-selectivity principle.

When the products are derived mainly or exclusively from ion pairs, the fraction $(1 - F)$ of ion pair return in AcOH (0.62–0.96 for $ArCH_2CH_2OTs$,[45,81a] norbornyl bromide, chloride, and brosylate,[4c,7a,81b] and 2-anisylcyclopentyl tosylate[81c]) is usually higher than in our system. The appreciable internal return suggests a tight proximity of R^+ and X^- in **8**, while the absence of products from **8** (and probably from **16**) suggests that proximity of R^+ and OAc^- is excluded at the ion pair stage. Models show that the cis β-Ar and α-An and the cis β-Ar and α-Br groups in the covalent substrates are within bonding distance and on ionization to a tight ion pair, the front-side remains shielded by the leaving group. While some of the cis α-An and β-Ar interaction is relieved in the sp-hybridized R^+, approach of the solvent is still retarded. Indeed, **24**-Br with two β hydrogens does not show common ion rate depression and give products from the ion pairs.[10a,28] Furthermore, the electron-donating *p*-methoxyphenyl group stabilizes the various cationic species and leads to dissociation of the ion pairs.

Similar factors are responsible for the selectivity (*i.e.*, the "stability") of the cation **7**. Approach to the α carbon is severly hindered, and its electrophilicity is reduced since the charge resides partly on the anisyl group. The failure of the reactivity-selectivity principle, applied to saturated and vinyl cations together, is due to these effects and to the stabilized ground state of the vinylic compound (*cf.* structure **17**).

Ritchie[82] found that the reactivity of nucleophiles toward several highly stable cations is expressed by eq 25, where k_n

$$\log (k_n/k_{H_2O}) = N_+ \quad (25)$$

and k_{H_2O} are the rate constants for the reaction of a cation with a nucleophile and with water, respectively, and N_+ is a parameter which characterizes the nucleophile and is independent of the cation. The failure of the reactivity-selectivity principle for solvolytically formed ions[35a,79] was partially explained as due to product formation from ion pairs.[82b,83] However, a correct application of the reactivity-selectivity principle requires comparison of k_{ion} and α, while the actual comparison was made between k_t and α_{app}.[35a,79,80] The relationship between k_t and k_{ion} and α and α_{app} (eq 20 and 26) suggests that such comparison can lead to erroneous re-

$$k_t^0 = Fk_{ion} \quad (26)$$

sults. The exclusive product formation from **7** gives a unique opportunity to study the reactions of nonisolable free carbonium ions with nucleophiles. In Table X, we compare the relative reactivities of several X^- toward **7** (as calculated from the α values) at the same salt concentration, assuming that the ion pair dissociation constants and the k_f/k_p ratios of the different salts are independent of the salt.

We found no data in AcOH for comparison with Table X. Swain and Scott's n values[84] show that our selectivity values for the Br^-, Cl^-, and OMs^- ions are only slightly lower than those toward MeBr in water, but that of the OAc^- ion is higher. The $k(AcO^-)/k(AcOH)$ ratio toward **7** differs slightly from the $k(OH^-)/k(H_2O)$ ratio toward MeBr but is much higher than the $N_+(OH^-)/N_+(H_2O)$ or

Table X. Relative Reactivity of Nucleophiles Toward the Cation 7[a]

Nucleophile	Rel reactivity
OMs^-	1.0
OAc^-	6.2
Cl^-	94
Br^-	282
(AcOH)	(0.015)[b]

[a] At 120.3°; [RX] = 0.044 *M*; [total salts] = 0.087 *M*. [b] Based on several one-point experiments in unbuffered AcOH or in the presence of urea.

the $N_+(MeO^-)/N_+(MeOH)$ ratios.[82] The differences between Br^-, Cl^-, and OMs^- ions are due to solvation; the less nucleophilic anion is more solvated.

External ion return (Table X) and internal return (Schemes IV, V and IX) show the same reactivity order, indicating the same contributing factors to both returns, except that solvation of X^- in the tight ion pair is much lower than that of the free X^- ion.

The order of $1 - F$ values [Br (0.47) > Cl (0.38) > OMs (0.24)] resembles those for the norbornyl [$1 - F$ = 0.96(Br),[4c] 0.91(Cl),[81b] 0.71(OBs)[6a]] and the cyclobutyl systems [$1 - F$ = 0.43(Cl), 0.20(OMs), 0.08(OTs)[85]] in AcOH where products arise from ion pairs. Roberts[85] noted a correspondence between the size of X^- and the extent of return, which calls for less return than that observed for our bromide. However, more data are required to decide between the solvation and steric explanations.

The slight preference for capturing **7** from one side and the independence of the cis/trans capture ratio of the nucleophile are in contrast to the large differences observed when the bulk of the β substituents in R^+ is changed.[12,27] The insensitivity to the electronic nature of the β substituents and the steric bulk of the nucleophile suggest a reactant-like transition state for the recombination reaction.

k_t as a Measure of k_{ion}. Ionization rates should be correlated in terms of k_{ion}, and discrepancies in correlations involving k_t are often attributed to ion pair return.[80] Up to now, structural and solvent effects in vinylic systems were discussed in terms of k_t since data on k_{ion} were absent. Such treatment implies that in comparison of k_t^0 values, the F's would be similar (eq 26). Table XI compares several reactivity ratios, SIE, and activation parameters, which are now available for both k_t^0 and k_{ion}, and leads to the following conclusions for our systems.

(i) The similarity of the F values for each pair of isomers justifies the discussion of the k_{cis}/k_{trans} ratios in terms of k_t^0. The ratios of *ca.* 1 both when X = OMs and Br argue against β-anisyl participation since β-anisyl and β-phenyl groups are trans to the leaving group in **5** and in **6**, respectively.[86] This is supported by the identical **5**-OAc/**6**-OAc mixtures which are formed from the different precursors under kinetic control.

(ii) Qualitative discussion of the k_{Br}/k_{Cl} ratios in terms of k_t^0 is justified. The ratios resemble those found in the acetolyses of vinylic[10a,b,72] or saturated[73] systems.

(iii) SIE which are based on k_t^0 may replace those based on k_{ion}, but k_{ion} values are more reliable since errors in k_t are compensated in k_{isom}.

(iv) The k_{OMs}/k_{Br} ratios which are based on k_{ion} are appreciably lower than those based on k_t^0 since F(ROMs) > F(RBr). Our actual ratios and the k_{OTs}/k_{Br} ratio of 281 at 120.3° resemble the k_{OTs}/k_{Br} value of 231, which was suggested as typical for a secondary substrate,[87] but the values are lower than those for many aliphatic and bicyclic compounds.[75,88] Our results show that the low k_{OTs}/k_{Br} ratios observed for k_t in some vinylic solvolyses[1,17] are not due to internal return since the ratios which are based on k_{ion} would be even lower.

(v) While it is difficult to estimate the errors in the activation parameters (because of the extrapolations used), the high activation energies which are based on k_{ion} seem to behave more regularly than those based on k_t^0.

(vi) The reactivity ratio k(**5**-Br)/k(**24**-Br) which is based on k_{ion} differs slightly from that based on k_t^0, because of small differences in the F's. This is encouraging regarding the comparison of k_t values of structurally different compounds since **5**-Br and **24**-Br differ greatly in the steric and electronic effects of the β substituents and in the product-forming cationoid intermediate.[89]

Experimental Section

Melting points are uncorrected. Uv spectra were recorded with a Perkin-Elmer 450 spectrophotometer, ir spectra with a Perkin-Elmer 337 spectrophotometer, mass spectra with a MAT 311 instrument, and nmr spectra with Varian T-60 and HA-100 instruments.The signal positions are given in δ units downfield from tetramethylsilane. Radioactivity was counted with a Packard 3320 scintillation counter.

Materials and Solvents. The preparation of **5**-Br, **6**-Br, **5**-Cl, **6**-Cl, **5**-H, **6**-H, and dry AcOH and the isolation of **5**-OAc and **6**-OAc were described earlier.[29] Bu_4NBr (Eastman), mp 107–108°, was crystallized from ethyl acetate, and Et_4NOMs[90] was dried at 120° before use. $Et_4N^{36}Cl$ was prepared by equilibration of Et_4NCl (Aldrich) with $H^{36}Cl$ (The Radiochemical Center, Amersham) in water for 24 hr, evaporating the water, crystallizing the salt from acetone, and drying it *in vacuo* for 48 hr. AcOD (containing ≤2% AcOH) was prepared by refluxing an equilibrium mixture of D_2O and acetic anhydride for several hours, distillation, and collection of the middle fraction, bp 117°.

***cis*- and *trans*-1,2-Di(*p*-methoxyphenyl)-2-phenylvinyl Methanesulfonates (5-OMs and 6-OMs).** A 1:1 mixture of **5**-Br and **6**-Br (6.3 g, 16 mmol) and silver methanesulfonate (3.6 g, 17.5 mmol) was refluxed in dry acetonitrile (100 ml) in the dark for 6 hr, filtered, and evaporated, and the remaining oil (*ca.* 1:1 **5**-OMs to **6**-OMs) was recrystallized from MeOH (100 ml). The first fraction contained 90% of **5**-OMs and 10% of **6**-OMs, and the second fraction contained 90% **5**-OMs + 10% **6**-OMs. The overall yield was 5.6 g (85%).

Recrystallization of the first fraction (MeOH) gave white pyramids of *trans*-1,2-di(*p*-methoxyphenyl)-2-phenylvinyl methanesulfonate (**6**-OMs), mp 140–141°; δ ($CDCl_3$) 2.53 (3 H, s, OSO_2Me), 3.77, 3.83 (2 × 3 H, 2 s, MeO), 7.15 (5 H, s, Ph), 6.68–7.47 (8 H, 2 merging q, 2 An); *m/e* 410 (M, 12%), 331 (M − SO_2Me, 76%), 316 (M − SO_2Me − Me, 7%), 315 (PhC(An)=CAn$^+$, 4%), 303 (An_2CPh^+, B), 195 (*p*-methoxyfluorenyl$^+$, 14%), 165 (fluorenol$^+$, 10%), 153 (10%), 152 (18%), 135 ($AnCO^+$, 17%), and 77 (Ph, 16%)

$$[410 \xrightarrow{m^*\ 224} 303;\ 410 \xrightarrow{m^*\ 244} 316;\ 410 \xrightarrow{m^*\ 268} 331;\ 316 \xrightarrow{m^*\ 290} 303;\ 331 \xrightarrow{m^*\ 302} 316]$$

λ_{max} (C_6H_{12}) 236 nm (ϵ 21,000), 297 (15,300); ν_{max} (CCl_4) 2900–3060 (C–H), 2835 (C–H or MeO), 1600 (b, C=C), 922 (d, differs from **5**-OMs), 605, and 562 cm^{-1}.

Recrystallization (MeOH) of the second fraction gave white crystals of *cis*-1,2-di(*p*-methoxyphenyl)-2-phenylvinyl methanesulfonate (**5**-OMs), mp 145–146°: δ ($CDCl_3$) 2.45 (3 H, s, OSO_2Me), 3.73, 3.78 (2 × 3 H, 2 s, MeO), 7.38 (5 H, m, Ph), 6.60–7.48 (8 H, 2 q, 2 An); *m/e* 410 (M, 9%), 331 (M − SO_2Me, 59%), 316 (M − SO_2Me − Me, 6%), 315 (AnC(Ph)=CAn$^+$, 4%), 303 (An_2CPh^+, B), 195 (*p*-methoxyfluorenol$^+$, 18%), 165 (fluorenol$^+$, 15%), 153 (18%), 152 (27%), 135 ($AnCO^+$, 26%), 77 (Ph, 26%), and the same metastable peaks as for **6**-OMs; λ_{max} (C_6H_{12}) 241 nm (ϵ 21,500), 300.5 (14,800); ν_{max} (CCl_4) 2900–3060 (C–H), 2835 (C–H of MeO), 1600 (b, C=C), 940, 912, 585 (differs from **6**-OMs), and 570 cm^{-1}.

Anal. Calcd for $C_{23}H_{22}O_5S$: C, 67.30; H, 5.40; S, 7.81. Found (trans isomer): C, 67.46; H, 5.32; S, 8.33. Found (cis isomer): C, 67.60; H, 5.25; S, 7.88.

1,2-Di(*p*-methoxyphenyl)-2-phenylvinyl *p*-Toluenesulfonates (5-

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

Parameter	T, °C	Based on k_{ion}	Based on k_t^0	Parameter	T, °C	Based on k_{ion}	Based on k_t^0
k(**5**-Br)/k(**6**-Br)	120.3	0.97	1.00	k(**5**-Br)/k(**24**-Br)	120.3	1.93	2.72
	140.2	0.94	0.90	ΔH^*(**5**-Br), kcal/mol	120.3	27.6	31.1
k(**5**-OMs)/k(**6**-OMs)	75.1	1.19	1.16	ΔS^*(**5**-Br), eu	120.3	−7.0	0.6
k(**5**-Br)/k(**5**-Cl)	120.3	24.6	23.9	ΔH^*(**6**-Br), kcal/mol	120.3	28.2	32.8
	140.2	22.0	25.3	ΔS^*(**6**-Br), eu	120.3	−5.4	4.9
k(**5**-OMs)/k(**5**-Br)	75.1	200[b]	492[b]	ΔH^*(**5**-Cl), kcal/mol	120.3	29.0	28.4
k_{AcOH}/k_{AcOD} (**5**-Br)	120.3	1.11	1.34 ± 0.07	ΔS^*(6-Cl), eu	120.3	−9.8	−12.4
k_{AcOH}/k_{AcOD} (**5**-Cl)	158.5	1.10	1.13 ± 0.09				

[a] All the data are for [RX] = 0.044 M and [NaOAc] = 0.087 M. [b] Based on the extrapolated values: 10^7k_{ion} = 6.85 sec^{-1} and $10^7k_t^0$ = 2.03 sec^{-1} for **5**-Br at 75.1°.

OTs and 6-OTs). A 1:1 mixture of **5**-Br and **6**-Br (25.2 g, 64 mmol) and silver p-toluenesulfonate (18 g, 64 mmol) was refluxed for 24 hr in dry acetonitrile (100 ml) in the dark. Treatment similar to that for the mesylates gave an oil (18.5 g, 60%) which was crystallized (MeOH, 25°), giving a mixture of *cis*- and *trans*-1,2-di(p-methoxyphenyl)-2-phenylvinyl p-toluenesulfonates (**5**-OTs and **6**-OTs), mp 115–120°: δ ($CDCl_3$) 2.35 (3 H, s, Me), 3.70, 3.78 (6 H, 2 s (in 56:44 ratio), 2 MeO), 6.43–7.42 (17 H, m, Ar); λ_{max} (EtOH) 228.7 nm (ϵ 28,800), 292 (15,850); ν_{max} (CS_2) 1360 (s), 1300 (s), 1260 (vs), 1180 (vs), and 1150 (s) cm^{-1}; m/e 486 (M, 2.5%), 332 (AnCHPhCOAn$^+$, 27%), 331 (M − $O_2SC_6H_4Me$, 99%), 316 (M − $O_2SC_6H_4Me$ − Me, 55%), 315 (AnC(Ph)=CAn$^+$, 51%), 303 (An_2CPh^+, B), 197 (AnCHPh$^+$, 17%), 195 (p-methoxyfluorenyl$^+$, 20%), 165 (fluorenyl$^+$, 15%), 152 (10%), 135 (AnCO$^+$, 56%).

Anal. Calcd for $C_{29}H_{26}O_5S$: C, 71.58; H, 5.39; S, 6.59. Found: C, 71.54; H, 5.48; S, 6.81.

Kinetic Procedure. (a) With the Vinyl Halides. Stock solutions of the vinyl halides in AcOH–NaOAc were used. The sealed ampoules technique was followed. The Br$^-$ formation was followed titrimetrically or potentiometrically, while the vinyl chloride solvolysis was followed by titration of the NaOAc with $HClO_4$–AcOH, using crystal violet indicator.

The isomerization was followed by ir in CS_2, using calibration curves which were prepared from the pure halide isomers and the two acetates. The intensity ratios at 575 (**5**-Br) and 615 (**6**-Br) and 575 (**5**-Cl) and 635 cm^{-1} (**6**-Cl) were used for the bromides and the chlorides, respectively. These strong peaks do not overlap any strong peak of the isomeric halide, but a relatively weak absorption of the ROAc introduces an error at high reaction percentages. The estimated accuracy of the **5**-Br/**6**-Br and the **5**-Cl/**6**-Cl ratios is ±1%, when the ratios are 0.2–4.0.

Samples (2 ml) for the isomerization were taken from the ampoules before titration, evaporated, dissolved in CCl_4, filtered, washed with water, dried, evaporated, dissolved in CS_2, and analyzed.

(b) With the Vinyl Sulfonates. Reaction mixtures in AcOH–NaOAc were kept in a volumetric flask, and samples were withdrawn and cooled immediately in ice-water. The unreacted NaOAc was titrated with $HClO_4$–AcOH using crystal violet indicator. A mixture of concentrated $NaHCO_3$ and CCl_4 was added immediately, the organic layer was rapidly separated, the indicator was extracted with dilute HCl, and the mixture was washed with water, dried, and evaporated. Nmr and ir determinations were carried on the remaining oil. Nmr showed that the appearance of ROAc and the disappearance of ROMs have similar rates.

The extent of isomerization was determined by nmr from the ratio of the methyl singlets of **5**-OMs and **6**-OMs. The extent of reaction of **6**-OMs in the presence of Et_4NBr was determined by titration of both the unreacted Br$^-$ and OAc$^-$ ions. For most points, the amount of ROAc formed was also determined by nmr.

Reaction of 5-Br with Radioactive $^{36}Cl^-$. Ampoules containing a mixture of **5**-Br (43.5 mmol/l.), NaOAc (87 mmol/l.), and $Et_4N^{36}Cl$ (71 mmol/l., 5000 cpm/mg) in AcOH (3 ml) were kept at 120°. At the appropriate times, samples were transferred completely into CCl_4 (30 ml) containing 500 ml of a 1:1 mixture of **5**-Cl and **6**-Cl. This ratio resembles that obtained in the reaction with excess Cl$^-$. The use of a different composition of "diluents" results in an error in the calculation of k. The mixture was washed with water, dried ($MgSO_4$), evaporated, and dissolved in MeOH (20 ml). Ethanolic $AgNO_3$ (5 ml) was added, the AgBr formed was filtered, most of the solvent was evaporated, CCl_4 was added, the mixture was washed with water, and the organic layer was dried and evaporated. The remaining oil was crystallized from MeOH (15 ml), half of the precipitate was dried to a constant weight, and its radioactivity was counted twice, and the other half was recrystallized and was also counted twice. The difference in count was ±1.5%, and the average value was used for the kinetic calculations. Ir showed that the sample contained <5% of **5**-Br and **6**-Br.

The very strong quenching by our compounds required the use of internal $Na^{36}Cl$ standard, but even this method gave positive deviations when the quenching was higher than 40%. Moreover, toluene scintillation solution or toluene Triton-X solution cannot be used due to a different efficiency in the counting of the organic and the inorganic chloride under identical conditions. These difficulties were avoided by using a Bray solution (60 g of naphthalene, 4 g of POP, 200 g of POPOP, 100 ml of MeOH, 20 ml of ethylene glycol, completed to 1 l. with dioxane) and a sample of 50 mg/10 ml or less.

The isomerization rate was studied under identical conditions as described above. Since both **5**-Cl and **5**-Br absorb at 575 cm^{-1}, calibration curves for different ratios of 1:1 **5**-Cl and **6**-Cl to **5**-Br and **6**-Br were used for evaluating the **5**-Br/**6**-Br ratio.

For calculation, we used the equation $k^7{}_{Cl} = (2.3/t)\log[n_\infty/(n_\infty - n_t)]$ where $n_\infty = 4.35m/7.1$ (m is the activity of the whole solution at $t = 0$) is the expected count of RCl at infinity, and n_t is the count of the sample at the time t. This was calculated from the relationship $n_t = r(500 + p)/q$ where r is the average count at the time t, q is the weight (in milligrams) of the sample, and p is the weight of the RCl formed by the reaction at the time t.

Isomerization of 1,2-Di(p-methoxyphenyl)-2-phenylethylenes (5-H and 6-H). The cis/trans ratio of the ethylenes **5**-H and **6**-H and the isomerization rates were determined from the intensity ratio of the δ 3.69 to the δ 3.74 signal. An equilibrium mixture of 54% **5**-H to 46% **6**-H was obtained after 192 hr at 120° or after 18 hr at 150°.

Solvolysis and Isomerization in the Presence of AgOAc. (a) Equimolar amounts of the RBr and AgOAc (25 mmol) were refluxed in AcOH in a light-protected flask for 45–60 min. The AgBr was filtered off, and analysis of the organic fraction showed the quantitative formation of a 54:46 mixture of **5**-OAc to **6**-OAc.

(b) **5**-Br or **6**-Br (95 mg, 0.24 mmol) and AgOAc (20 mg, 0.12 mmol) were refluxed in AcOH (10 ml) for 45 min. After the usual work-up, 50% of vinyl acetates was observed. The recovered RBr from **5**-Br was 58.5% **5**-Br, and that from **6**-Br contained 50% **5**-Br. When equimolar amounts of **5**-Br and AgOAc (44 mmol) were kept at 75° for 25 min, the mixture contained 55% of ROAc in a ratio of 53% **5**-OAc to 47% **6**-OAc, and the remaining bromides were 64.6% **5**-Br and 35.4% **6**-Br.

Acknowledgments. We are indebted to the Volkswagen Foundation for partial support of the work, to Professor A. Lifshitz and Mr. M. Frenklach for the use of their computer simulation method, to Professor P. v. R. Schleyer for preprints, and to Professor S. Patai for discussions.

Appendix

Scheme III was simulated by using a computer program which applies the Runge–Kutta procedure for numerical integration. We used the following procedure: (a) $k^{5\text{-Br}}_{ion}$ and $k^{6\text{-Br}}_{ion}$ were obtained from the "total *cis* content" method. (b) Steady-state treatment gives eq 27 when $k^{5\text{-Br}}_{ion} = k^{6\text{-Br}}_{ion}$.

$$(k^8_{ir} + k^8_{ir'})/k^8_{diss} = (k^{5\text{-Br}}_{ion}/k_t^0) - 1 = (1 - F)/F \tag{27}$$

Using the known k_t^0, a first approximation for $(1 - F)/F$ is obtained. (c) From the equilibrium constant K for the **5**-Br $\rightleftharpoons$ **6**-Br isomerization (eq 28), and the $k^{5\text{-Br}}_{ion}$

$$K = [\text{cis}]/[\text{trans}] = k^8_{ir}k^{6\text{-Br}}_{ion}/k^8_{ir'}k^{5\text{-Br}}_{ion} \tag{28}$$

and $k^{6\text{-Br}}_{ion}$ values, the $k^8_{ir}/k^8_{ir'}$ ratio is obtained. (d) An estimate of α was obtained by measuring and estimating the other terms of eq 20. (e) All the rate constants and their ratios were introduced as a first guess into the program, together with k^8_{ir} and $k^8_{ir'}$ of 10^2–10^3 sec^{-1} and k^7_{Br} and k^7_{OAc} values of 10^8–10^9 l. mol^{-1} sec^{-1}.[45] Change of these constants did not affect the results, as far as they exceed much k_{ion}, but increased the computation time. (f) Using the above data, α and $(1 - F)/F$ values were changed until the best fit between experimental and calculated points was obtained.

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(31) The 54:46 ratio of **5**-OAc to **6**-OAc was obtained starting from either **5**-Br or **6**-Br (or **6**-Cl). This is in contrast to the small inversion selectivity which was observed for α-substituted cyclopropylvinyl iodides.[20]

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(40) This is due to the fact that the values on the $[Br^-]/[OAc^-]$ axis are *ca.* two times higher than the correct values of method c; see also note 46.

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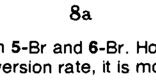
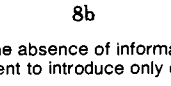


8a



8b

istry from **5**-Br and **6**-Br. However, in the absence of information on the interconversion rate, it is more convenient to introduce only one ion pair **8**.

(43) Using the two points for **5**-Br from Table IV and the point from method *c* (Table V) gives $b = 3.6$ for Bu_4NBr.

(44) The situation is much more complicated when the equilibrium percentages of **5**-OAc and **5**-Br differ. In this case, the corresponding logarithmic expression for k_{ion} of eq 15 cannot be separated into two terms.

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(47) F is usually defined as the fraction of ionization which gives products (see ref 49a and eq 26 below). However, in most systems,[3] F relates to product formation *via* ion pairs, while in our case it relates to formation of free ions which both give products and return.
(48) This is probably due to a small error in the concentration of **6**-Cl. A 5% error in the **5**-Cl/**6**-Cl ratio of the last experimental points is sufficient to change the return from **8** from 45 to 39%.
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(55) The upper limit for ROAc formation from **7** is unknown since higher Et_4NOMs concentrations could not be used for solubility reasons.
(56) When $[OAc^-]$, $[Br^-] \gg [ROMs]$, $\alpha_{app} = [RBr]/[ROAc]$. This is not the case here, and since the $[Br^-]$ decreased during the run more than the $[OAc^-]$, and RBr also yields some ROAc, the α_{app} calculated from product analysis should be lower than that based on common ion rate depression.
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