Vinylic Cations from Solvolysis. 25.[1] Ion Pairs in the Solvolysis, Isomerization, and Rearrangement of α-Arylvinyl Halides in Pivalic Acid

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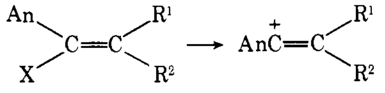
Abstract: The pivalolysis of α-anisyl-β,β-disubstituted vinyl bromides (AnC(Br)=CR^{1}R^2) is a first-order reaction when R^1 = R^2 = Me or An, but the first-order titrimetric constant (k_t) decreases during a run or by added Br$^-$ for **7-Br**, when R^{1}R^{2}C= = anthronylidene. The pivalolysis of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides (**3-Br** and **4-Br**) is accompanied by a >100-fold faster **3-Br** $\rightleftharpoons$ **4-Br** isomerization and gives a 1:1 mixture of the *cis*- and *trans*-pivalates (**3-OPiv** and **4-OPiv**). A special salt effect with LiClO$_4$ decreases the gap between k_t and k_{isom}. The solvolysis of 2,2-dianisyl-1-phenylvinyl bromide (**8-Br**) in pivalic acid-silver pivalate gives only the rearranged pivalates **3-OPiv** and **4-OPiv** in a 43:57 ratio. It is suggested that all these reactions involve ion pairs which participate in three processes: return to covalent bromide, which is the most favored; dissociation to a product-forming free ion, which is not observed until the bulk of the β substituents is large, as in **7-Br**; and capture by the solvent to give products. Solvent separated ion pairs are involved in the reactions of **3-Br** and **4-Br** and a tighter ion pair in the reaction of **8-Br**. The ionization power parameter Y of pivalic acid is −3.6.

Preceding work on the solvolysis of α-anisylvinyl halides (**1**, X = Cl, Br)[2] demonstrated that free vinyl cations **2** are often the product-forming intermediates.[3,4] This was deduced from the appearance of common ion rate depression, either during a kinetic run by the formed halide ion or by added halide ion. The extent of the common ion rate depression is measured by the "mass law constant" α[5,6] (or α_{app}),[6] which is the selectivity constant for the competitive capture of the free ion by X$^-$ and the solvent or its conjugate base. For α-anisylvinyl halides α increases with the increase in the bulk of the β substituents.[2g,3,7] For example, in the solvolysis of **1**, X = Br in AcOH, where α_{app} measures competition between Br$^-$ and AcO$^-$ for **2**, $\alpha_{\text{app}} = 0$ when R^1 = R^2 = H,[3b] $\alpha_{\text{app}} = 4.3$ when R^1 = R^2 = Me,[3c] α_{app} = 10–21 when R^1 = R^2 = Ar,[3a,c,4a,b] and $\alpha_{\text{app}} > 32$ when R^{1}R^{2}C= = anthronylidene.[2g,7] Products arise in all these systems (excluding R^1 = R^2 = H) from free vinyl cations.[2g,3,4,7] This was ascribed to increased shielding of the cationic orbital of **2** by R^1 and R^2 and consequently to greater selectivity.[2g,3,4,7]

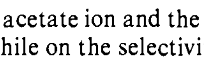


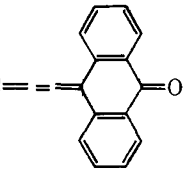
1 **2**

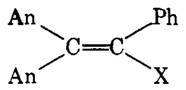
Ion pairs are intermediates in solvolyses of several α-alkylvinyl systems[8] and are also involved as intermediates in the solvolysis and isomerization of several α-arylvinyl systems.[4,9,10] Both product formation and cis–trans isomerization in the solvolysis of α-bromo-*p*-methoxystyrene (**1**, R^1 = H; R^2 = H or D; X = Br) involve ion pairs.[10] In the solvolysis of 1,2-dianisyl-2-phenylvinyl bromides **3-Br** and **4-Br** in AcOH, AcOH-HCOOH, and AcOH-Ac$_2$O,[4] the products are derived exclusively from the free ions, while both free ions and ion pairs are involved in the simultaneous **3-Br** $\rightleftharpoons$ **4-Br** isomerization. The distribution of the cationic intermediates between the dissociation, capture, and return processes was delineated.[4b,c]

β-Aryl rearrangements across the double bond in triarylvinyl cations were also observed.[1,11,12] It was established that the degenerate β-anisyl rearrangements of trianisylvinyl bromide (**6-Br**)[1] or *cis*- and *trans*-2-anisyl-1,2-diphenylvinyl bromides in TFE,[11c] as well as the nondegenerate rearrangement of 2,2-dianisyl-1-phenylvinyl bromide[11a,b] proceeds via free triarylvinyl cations.[1,11] However, there is evidence that with other systems, e.g., triphenylvinyl trifluoromethanesulfonate,[12a] the rearrangement proceeds via ion pairs.

Since free ions are important intermediates in the reactions in the low dielectric acetic acid,[3a,c,d,4] it was of interest to see if a significant shift to less dissociated intermediates would take place in a lower dielectric solvent. Pivalic acid (trimethylacetic acid) was chosen as such a solvent for several reasons. It resembles acetic acid in acidity (at 25 °C, pK_a(AcOH) = 4.76, pK_a(Me$_3$CCOOH) = 5.03)[13] and probably in its nucleophilicity,[14] but has a very low dielectric constant.[15] The pivalate ion is bulkier than the acetate ion and the effect of the size of the capturing nucleophile on the selectivity could be investigated. Finally, we had already showed that degenerate rearrangements (e.g., of the trianisylvinyl cation), which take place in AcOH via free ions, do not occur in pivalic acid.[1] We therefore studied the solvolysis of compounds **3-Br**–**7-Br**, the **3-Br** $\rightleftharpoons$ **4-Br** isomerization, and the solvolysis–rearrangement of **8-Br** in pivalic acid.



	X = Br	X = OCOCMe$_3$	X = OAc	X = Cl
R^1 = An; R^2 = Ph	**3-Br**	**3-OPiv**	**3-OAc**	
R^1 = Ph; R^2 = An	**4-Br**	**4-OPiv**	**4-OAc**	
R^1 = R^2 = Me	**5-Br**	**5-OPiv**		
R^1 = R^2 = An	**6-Br**	**6-OPiv**	**6-OAc**	**6-Cl**
R^{1}R^{2}C=  (anthronylidene)	**7-Br**	**7-OPiv**	**7-OAc**	



8-Br, X = Br
8-OPiv, X = OCOCMe$_3$

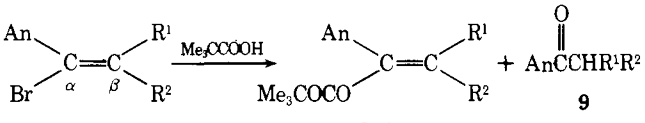
Results

Solvolysis Products. The pivalolysis of α-anisylvinyl bromides (**3-Br**–**7-Br**) and the chloride **6-Cl** in pivalic acid-sodium

Table I. Solvolysis Products of Several α-Anisylvinyl Bromides

				Signals used for the analysis, δ			
				For **9**		For ROCOCMe$_3$	
Compd	% reaction	% ROCOCMe$_3$	% **9**	o-H	CH	CH$_3$	t-Bu
3-Br	73	80	20	7.94, 8.02	5.94		0.90
5-Br	85	72	28	7.85, 8.00		2.04	
6-Br	85	87	13	7.95, 8.08	5.91	0.90	
	88	75	25				

pivalate is slow and hence requires high reaction temperature. Most of the reactions were followed at 185.4 °C. Under these conditions the main solvolysis products were the vinyl pivalates (**3-OPiv–7-OPiv**), which were accompanied by the corresponding hydrolysis products, the α,α-disubstituted 4-methoxyacetophenones **9** (eq 1). The percentage of **9** increases with the reaction time and the decreased bulk of the β substituent, as shown in Table I. The percentages of the ketone were usually determined from the NMR of the crude reaction mixture. Compounds **9** show half of the quartet of the ortho hydrogens adjacent to the carbonyl group at low field. Comparison of the intensity of this signal or that of the benzhydrylic proton of **9** with the singlet of the pivalate group gave the relative amounts of **9** and the vinyl pivalate. The ir of the reaction mixture showed carbonyl stretching absorptions for both the ketone and the vinyl pivalate.



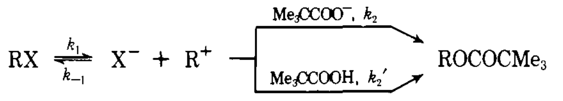
1-Br **1-OPiv** **9** (1)

7-OPiv did not isomerize to 9-anisoyl-10-pivaloyloxyanthracene, in contrast to the isomerization of **7-OAc** to 10-acetoxy-9-anisoylanthracene.[7]

Solvolysis Kinetics. The pivalolysis of all the compounds in Me$_3$CCOOH-Me$_3$CCOONa, except for **7-Br**, showed first-order kinetics with no evidence for common ion rate depression during the kinetic run. The absence of this phenomenon for **3-Br–6-Br** and **6-Cl** is manifested by the ca. 50% rate increase in the solvolysis rate of trianisylvinyl bromide (**6-Br**) in the presence of 0.1 M tetra-n-butylammonium bromide.

In contrast, in the pivalolysis of 10-(α-bromoanisylidene) anthrone (**7-Br**), the first-order *integrated* titrimetric rate constant (k_t) decreased moderately during the kinetic run, being almost half of the initial value at one half-life. The extrapolated k_t at zero reaction time ($k_t^0 = k_1$) and the selectivity constant at 0.035 M of **7-Br** and 0.0453 M of sodium pivalate were calculated according to Scheme I.

Scheme I



Since it is unknown whether the cation is captured by pivalic acid or its conjugate base, we calculated with the aid of eq 2 and 3, which were derived earlier,[3f,4b] both k_1 and two selectivity constants: $\alpha_{app} = k_{-1}/k_2$ for capture by Me$_3$CCOO$^-$, and $\alpha_{app}' = k_{-1}/k_2'$ for capture by Me$_3$CCOOH alone[6] (n = [Me$_3$CCOO$^-$]$_0$/[**7-Br**]$_0$; x = [Br$^-$]$_t$). When the plots of $1/k_t$ vs. the term in the second parentheses were analyzed, both regressions gave similar fit, with $k_t^0 = (1.02 \pm 0.04) \times 10^{-5}$ s^{-1} and $\alpha_{app} = 2.36 \pm 0.30$ (r = 0.9930), and $k_t^0 = (1.10 \pm 0.05) \times 10^{-5}$ s^{-1} and $\alpha_{app}' = 88 \pm 11$ M^{-1}, which leads to the dimensionless α_{app}'/[Me$_3$CCOOH] value of 1109 (r = 0.9940).

$$1/k_t = 1/k_1 + [\alpha_{app}/k_1(1-n)] \times [(n \ln (na/(na-x))/\ln (a/(a-x)) - 1] \quad (2)$$

$$1/k_t = 1/k_1 + (\alpha_{app}'/k_1)[(a-x)/\ln (a/(a-x))] \quad (3)$$

That the rate decrease is due to common ion rate depression was verified by the fact that in the presence of 0.0354 M Bu$_4$NBr and 0.01 M Me$_3$CCOONa, the initial rate constant was 20% of k_t^0 and it decreased slightly during the run. The points for this run were on the line of the k_t vs. percent reaction plot for the reaction in the absence of added bromide ion. Calculation of α_{app} and α_{app}' values from Winstein's modified equations,[5b,c]

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

$$k_t^d = k_t^0/(1 + \alpha_{app}'[\text{Br}^-]) \quad (5)$$

where k_t^d is the depressed rate constant extrapolated to zero reaction time, gave $\alpha_{app} = 1.3$ and $\alpha_{app}' = 113$ M^{-1}. Comparison with the values obtained from eq 2 and 3 cannot assist in deciding whether pivalic acid or pivalate anion is the capturing nucleophile, and by analogy with the behavior in AcOH we assume that the capturing nucleophile is the pivalate anion. The solvent isotope effect was studied in pivalic acid containing 10% (v/v) of either H$_2$O or D$_2$O. Table II shows that this amount of water has a negligible effect on the value of the rate constant, although the amount of D$_2$O is sufficient to convert 90% of the solvent to Me$_3$CCOOD. The solvent isotope effect k(Me$_3$CCOOH)/k(Me$_3$CCOOD) is 1.05 ± 0.07. The kinetic data for all the compounds except for **3-Br** and **4-Br** are summarized in Table II.

Table II. Pivalolysis of α-Anisylvinyl Halides

Compd	Concn, 10^2 M	[NaOCOCMe$_3$], 10^2 M	T, °C	$10^6 k_1$, s^{-1}
5-Br	5.8	20.0	185.4	5.86 ± 0.17
6-Br[a]	3.54	8.34	186	4.75 ± 0.14
	3.54	4.53	185.4	3.75 ± 0.03
	3.54	2.66	185.4	3.75 ± 0.08
	3.54[b]	4.53	185.4	5.80 ± 0.23
	4.42	5.28	185.4	3.94 ± 0.07[c]
	4.42	5.28	185.4	3.68 ± 0.10[d]
	3.54	4.53	163.2	0.379 ± 0.010
	3.54	4.53	120.3	2.14×10^{-3} [e]
6-Cl	3.54	4.53	185.4	0.404 ± 0.029
7-Br	3.54	4.53	185.4	10.2 ± 0.44[f]
	3.54[g]	1.00	185.4	2.2[e]

[a] $\Delta H^{\ddagger} = 40$ kcal mol^{-1}; $\Delta S^{\ddagger}$ (185.4 °C) = 3.3 eu. [b] In the presence of added 0.1 M Bu$_4$NBr. [c] In 90% Me$_3$CCOOH–10% H$_2$O (v/v). [d] In 90% Me$_3$CCOOH–10% D$_2$O (v/v). [e] Extrapolated value. [f] Extrapolated value (see text). [g] In the presence of 0.0354 M Bu$_4$NBr.

Solvolysis and Isomerization of 3-Br and 4-Br. Pivalolysis

Table III. Solvolysis and Isomerization of **3-Br** and **4-Br** in Pivalic Acid[a]

Compd	T, °C	Added salt	10^6k_t, s^{-1}	10^6k_{isom}, s^{-1}	10^6k_{ion}, s^{-1}
3-Br	160			24 ± 2	ca. 24 ± 2
3-Br	160	0.01 M $LiClO_4$	4.8 ± 0.7	37 ± 3	41.8 ± 3.7
3-Br	172			293 ± 9	295 ± 11
3-Br	172			290 ± 20[b]	293 ± 23
3-Br[c]	185.5		4.9 ± 0.3		
4-Br	160			22 ± 8	22 ± 8

[a] [RBr] = 0.044 M; [$NaOCOCMe_3$] = 0.083 M. [b] In Me_3CCOOD. [c] [$NaOCOCMe_3$] = 0.147 M.

Table IV. Comparative Data for the Cis and Trans Isomers of AnC(Ph)═C(An)OCOR

Property	R = CH_3[a]		R = $C(CH_3)_3$	
	Cis	Trans	Cis	Trans
Mp, °C	117-118	140-141	127-129	135-137
δ (R),[b] ppm	1.85	1.90	1.03	1.08
δ (MeO),[b] ppm	3.66, 3.67	3.70, 3.75	3.74, 3.75	3.73, 3.78
δ (Ph),[b] ppm	7.19	7.05	7.23	7.09

[a] From ref 17. [b] In $CDCl_3$.

Table V. Pivalolysis of *tert*-Butyl Chloride[a]

T, °C	10^7k_1, s^{-1}
110 ± 0.5	272 ± 23[b]
125 ± 0.5	932 ± 58
25	0.0245[c]

[a] [t-BuCl] = 0.044 M; [Me_3CCO_2H] = 0.088 M. [b] $\Delta H^{\ddagger}$ = 24.0 kcal mol^{-1}; $\Delta S^{\ddagger}$(125 °C) = −17 eu. [c] Extrapolated value from the above data.

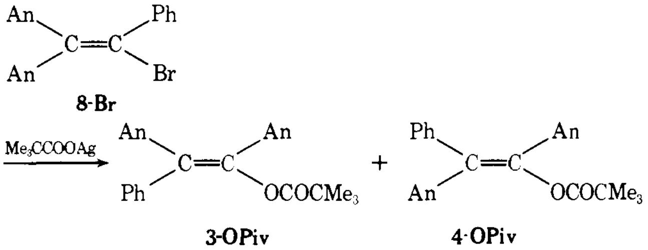
of either pure *cis*- or pure *trans*-1,2-dianisyl-2-phenylvinyl bromide (**3-Br** and **4-Br**, respectively) in the presence of silver pivalate gave a mixture of the *cis*- and *trans*-pivalates (**3-OPiv** and **4-OPiv**). In duplicate experiments, the NMR of the crude reaction mixture showed two *tert*-butyl singlets of equal intensity within the experimental error, i.e., the **3-OPiv** to **4-OPiv** ratio is 1:1. **4-OPiv** was found to be stable to isomerization under the reaction conditions.

The solvolysis in pivalic acid buffered by sodium pivalate was much slower, but formation of a 1:1 mixture of the cis and trans vinyl pivalates was indicated again by the NMR. However, a very extensive **3-Br** $\rightleftharpoons$ **4-Br** isomerization accompanies the solvolysis and may be the main reason for the observed product distribution. The isomerization was much faster than the solvolysis and concurrent monitoring of the solvolysis and isomerization was not feasible. Hence, the solvolysis at high temperature was followed by Br^- titration, while the isomerization rate was determined at a lower temperature from the intensities of two characteristic peaks in the ir with the use of a calibration curve as described previously.[4b]

Both the solvolysis and the isomerization reactions were of first order. Addition of 0.01 M $LiClO_4$ caused a 1.5-fold increase in the isomerization rate and a much higher increase in the solvolysis rate, enabling the determination of both rates at the same temperature. The rate constants are summarized in Table III. The solvent isotope effect for the isomerization, $k(Me_3CCOOH)/k(Me_3CCOOD)$, was calculated from a pair of three point runs and is 1.01 ± 0.05.

The structural assignments of the isolated **3-OPiv** and **4-OPiv** were based on analogies with several parameters used for the assignments of the structures of the acetates **3-OAc** and **4-OAc** (Table IV).[17] The isomer with the higher melting point shows the higher chemical shift difference between the methoxyl signals, a *tert*-butyl signal at lower field, and a phenyl signal at higher field. It was therefore assigned the trans configuration (**4-OPiv**).

Solvolysis–Rearrangement of 8-Br. Pivalolysis of 2,2-dianisyl-1-phenylvinyl bromide (**8-Br**) is very slow. Complete solvolysis was achieved after long reaction times only in the presence of silver pivalate. The products were the rearranged pivalates **3-OPiv** and **4-OPiv**, which were isolated and identified. The unrearranged pivalate (**8-OPiv**) was not observed, even in the NMR of the crude product. In three different determinations of the **4-OPiv**/**3-OPiv** ratios they were 55.5:44.5, 56.4:43.6, and 59.2:40.8, respectively, giving an average distribution of 57 ± 1.5 of **4-OPiv** to 43 ± 1.5 of **3-OPiv**.



Ionization Power of Pivalic Acid. The low dielectric constant of pivalic acid and the lower reactivity of *p*-methoxyneophyl tosylate in octanoic acid compared with AcOH[16c] suggests a low value for the ionizing power parameter Y. We therefore solvolyzed *tert*-butyl chloride in pivalic acid (Table V). From the extrapolated ionization rate to 25 °C and by using k_0(25 °C) = 9.26×10^{-6} s^{-1} for the solvolysis of *tert*-butyl chloride in 80% EtOH,[18] the Y(25 °C) value for pivalic acid is −3.6.

Discussion

Three phenomena, solvolysis, isomerization, and rearrangement, which are intimately connected with the ionization, were studied in pivalic acid. The kinetic behavior and the nature of the products for the same reactions in acetic acid are compared in Table VI. The unifying explanation for the differences in the behavior in the two solvents is that ion pairs play an important role in the ionization–dissociation–return scheme in pivalic acid.

Pivalic acid has not been hitherto studied as a medium for

Table VI. Comparison of Acetolysis and Pivalolysis of α-Arylvinyl Systems

Phenomena studied	Pivalolysis	Acetolysis
$k(\mathrm{RCOOH})/k(\mathrm{RCOOD})$	1.05 for **6-Br**	1.11 for **3-Br**;[a] 1.2 for **5-Br**;[b] 0.85 for **6-OTs**;[c] 1.05 for **6-OBs**;[c]
k(**6-Br**)/k(**6-Cl**)	9.5	10.8[d]
Common ion rate depression	Not observed for **3-Br–6-Br** $\alpha_{\mathrm{app}} = 2.4$ for **7-Br**	Observed for **3-Br–6-Br**[b,d,e] $\alpha_{\mathrm{app}} > 32$ for **7-Br**[f]
3-Br $\rightleftharpoons$ **4-Br** isomerization during the solvolysis	Very extensive: $k_{\mathrm{isom}} \gg k_t$	Appreciable: $k_{\mathrm{isom}} \sim k_t$[e]
Percent of ion pairs returning to RBr	>99%	47.5%[e]
Effect of $\mathrm{LiClO_4}$ in the **3-Br–4-Br** system	Special salt effect; rate constants increase with 0.01 M $\mathrm{LiClO_4}$ k_t greatly; k_{isom} 1.5-fold	Salt promoted ionization;[e] rate constants increase with 0.03 M $\mathrm{LiClO_4}$ k_t slightly; k_{isom} 4.5-fold
Intermediates in the **3-Br–4-Br** system	Solvent separated ion pair	Intimate ion pair and free ion[e]
Relative reactivity for **6-Br** based on k_t	3.23×10^{-5} at 120.3 °C	1[b,d]
Relative reactivity for **3-Br** based on k_{ion}	3.57×10^{-4} at 185.5 °C	1[b]
Products from **3-Br** and **4-Br**	50% of **3-OPiv** and 50% of **4-OPiv**	54% of **3-OAc** and 46% of **4-OAc**[e,g]
Products from **8-Br**	43% of **3-OPiv** and 57% of **4-OPiv**	50% of **3-OAc** and 50% of **4-OAc**[h]
Degenerate β-anisyl rearrangement during the reaction of **6-Br**	Not observed	Extensive[i]

[a] From ref 4b and based on k_{ion}. [b] From ref 3c. [c] From ref 21. [d] From ref 3a. [e] From ref 4b. [f] From ref 2g and 7. [g] From ref 17. [h] From ref 11a. [i] From ref 1 and 12c.

vinylic solvolysis and an electrophilic addition–elimination mechanism,[19] rather than S_N1 reaction, may be an alternative route to the solvolysis products. This route was excluded previously for the reaction in AcOH and is excluded for the reaction of the trianisylvinyl derivatives in pivalic acid for the following reasons: (i) The solvent isotope effect is close to unity and, as discussed elsewhere[3b,4b] and demonstrated in Table VI for related compounds which solvolyze via a rate determining C–X bond cleavage, the value fits an S_N1 process, in contrast to the values expected for a rate determining protonation; (ii) the "element effect", $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$, which resembles that in AcOH, is much higher than unity, and therefore cannot be due to a rate determining electrophilic addition.[3b,4b]

Solvolysis. The low dielectric constants of acids similar in structure to pivalic acid,[15] as well as the Y value[20] of -3.6 calculated for pivalic acid (Table V) suggest decreased ionization and solvolysis rates, as indeed was observed. The Winstein-Grunwald "m" values,[20] derived from the two k_t values for AcOH and $\mathrm{Me_3CCOOH}$, are 2.28 for **6-Br** at 120.3 °C and 1.75 for **3-Br** at 185.5 °C. These are extremely high values and the reason for this is discussed below.

The first-order kinetics for compounds **3-Br–6-Br** deserves comment. The integrated rate constants in the solvolyses of α-anisyl-β,β-disubstituted vinyl halides in solvents such as AcOH or TFE usually decrease extensively during the kinetic run or with added halide ion,[2g,3,4,7,9,11b] due to a common ion rate depression. Hence, the products in these solvents are derived from the free vinyl cations, indicating that dissociation of the ion pairs is preferred over their capture by the solvent even in the low dielectric acetic acid. Steric hindrance to capture by the nucleophile, due to the double bond substituents, both at the ion pair and free ion stages, were suggested to account for both the preferred dissociation and the selectivity of the free cations.[3,4,21]

The absence of common ion rate depression (except for **7-Br**) in pivalic acid may be due to several reasons: (a) product formation from unstable free ions which are captured faster by the solvent than by bromide ion;[5b,c] (b) a masking of the common ion rate depression by a rate increase due to a "normal" salt effect;[5b,c,22] (c) formation of products from ion pairs.[5b,c]

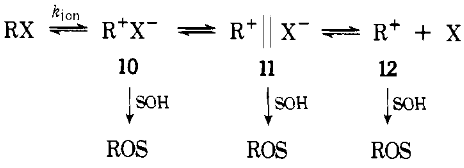
Solvation of the halide ion would be similar or inferior in pivalic acid compared with acetic acid. Capture by pivalic acid (or by $\mathrm{Me_3CCOO^-}$) probably has a similar rate to that by AcOH (or by $\mathrm{AcO^-}$),[14] although the reaction with the bulkier nucleophile may be slower for steric reasons. Combination of these factors exclude possibility a. Possibility b is excluded for the following reasons. The normal salt effect constant b

$$k_t = k_t^0(1 + b[\mathrm{salt}]) \qquad (6)$$

(eq 6) was calculated to be ca. 4 for $\mathrm{NaOCOCMe_3}$ from the data at several $\mathrm{NaOCOCMe_3}$ concentrations at constant [**6-Br**] and a b value of 5.5 for $\mathrm{Bu_4NBr}$ was obtained from the experiment with excess $\mathrm{Bu_4NBr}$. Since $\mathrm{NaOCOCMe_3}$ is converted to NaBr during the reaction, the rate increase during a run should be small if $b(\mathrm{NaBr}) \sim b(\mathrm{Bu_4NBr})$. Moreover, b is usually insensitive to the nature of the substrate, while α_{app} increases with the increased bulk of the β substituents (e.g., $\alpha_{\mathrm{app}} = 4.3$ for **5-Br** and 18 for **6-Br** in AcOH).[3c] Hence, exact balance between the rate decrease via α_{app} and the rate increase by salt effect for both **5-Br** and **6-Br** seems highly unlikely. Formation of the products from ion pairs (possibility c) seems therefore the most plausible explanation.

The intimate ion pair **10** formed in the initial heterolysis of the C–X bond can participate according to Winstein's solvolysis scheme[5b] (Scheme II) in three different processes. It can

Scheme II



dissociate to the solvent separated ion pair **11**, which can further dissociate to the free ("dissociated") ion **12**, it can be captured by the solvent to give products, and it may return to covalent RX. These processes respond differently to changes in the substrate and the solvent. Increased steric interactions between the α and β substituents will increase both the ionization rate by steric acceleration and the **10** → **11** dissociation by reducing the steric interactions between $\mathrm{R^+}$ and $\mathrm{X^-}$ in **10**. Increased steric interaction also reduces the capture rates: that of **12** only by increased shielding of the empty p orbital[3a,4b,21] and that of **10** and **11** also by shielding of the cationic part by $\mathrm{X^-}$. Return processes will show the same sensitivity to structural variations, but with two important differences. The leaving group is usually more polarizable than the solvent, and hence return will be less sensitive to steric effects than capture by the solvent. Moreover, the return will become easier with increased "tightness" of the ion pair due to a lower loss of entropy.

For solvents of similar bulk and solvation type the increase in the dielectric constant will tend to increase both the ionization and the dissociation rates and will tend to reduce both the return and the capture rates. The capture will be slower for a bulkier solvent, provided that steric interactions for the substrate are severe. These effects are demonstrated schematically in Scheme III. Apparently, combination of these effects in AcOH results in a capture of the ion pair when the β substituents are small (**1**, $R^1 = R^2 = H$),[10] but when $R^1 = R^2 = Me$ or a larger group, dissociation is so effective that products are formed only from the free ion **12**.[3,4,11b] On lowering the dielectric constant, products are formed from **11** even when R^1 and R^2 are appreciable in size. Only when they become very bulky is the product formed from **12**. This is achieved in pivalic acid with the anthronylidene derivative **7-Br**, where it was calculated from the common ion rate depression that ≥80% of the products are derived from the free vinyl cation. The derived free ion (**2**, $R^1R^2C{=} =$ anthronylidene) shows some of the highest α_{app} values in AcOH and TFE,[7] and models show a severe hindrance for its capture by nucleophiles.

Scheme III

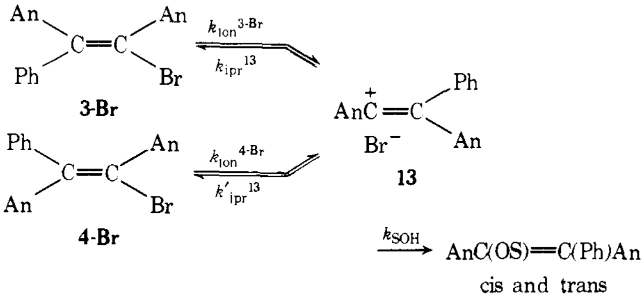
For a bulkier R or a higher dielectric constant

Ionization and dissociation $\uparrow$ Return and capture $\downarrow$

The selectivity constant α_{app} in pivalic acid is 13 times lower than in AcOH, contrary to what is expected. Since pivalate ion is bulkier than acetate ion, α_{app}' should be lower in AcOH if steric effects on the capture rate are dominant. Moreover, bromide ion will be less solvated, and hence more nucleophilic in pivalic acid. This is supported by the increase in the α_{app} values for **3-Br** in the solvents Ac_2O-AcOH > AcOH > AcOH-HCOOH,[4b,c] which probably reflects solvation of the Br^-. The dielectric constant effect will be canceled on comparing the ratios of the rates of the cation–anion recombination reactions in the two solvents. We believe that the lower α_{app} value in pivalic acid is therefore due to a smaller dissociation of NaBr or Bu_4NBr compared with that in AcOH. The concentration of the free Br^- in pivalic acid will be lower than in AcOH, and this effect will more than compensate for the higher nucleophilicity of the free Br^-. There are ample precedents for this phenomenon in nucleophilic reactions.[23]

Isomerization. The **3-Br** ⇌ **4-Br** isomerization which accompanies the solvolysis was previously used as a tool for investigating the intervention of ion pairs during the solvolysis and to estimate the extent of ion pair return.[4,10] Since the electrophilic addition–elimination route was excluded for the solvolysis of the closely related **6-Br** and the solvent isotope effect on the isomerization is 1.01, the isomerization is also not due to electrophilic addition–elimination. Common ion rate depression was not observed for compounds **3-Br** and **4-Br** and isomerization, therefore, takes place at the ion pair stage.[4b] Product formation (via $k_{ion} \rightarrow k_{SOH}$) and isomerization (via $k_{ion}^{3\text{-}Br} \rightarrow k'_{ipr}{}^{13}$ or via $k_{ion}^{4\text{-}Br} \rightarrow k_{ipr}{}^{13}$; ipr = ion pair return) are, therefore, competing processes of the same intermediate (Scheme IV).

Scheme IV



Under these conditions, the ionization rate constant (k_{ion}) is given by

$$k_{ion} = k_t + k_{isom} \tag{7}$$

where k_t is the pseudo-first-order titrimetric rate constant and k_{isom} is the first-order isomerization rate constant. The k_{ion} values are given in Table III. The fraction of the ion pairs which give products (F) and the fraction which returns to covalent RBr ($1 - F$), are given by

$$F = k_t/(k_t + k_{isom})$$
$$1 - F = k_{isom}/(k_t + k_{isom}) \tag{8}$$

As the isomerization rate greatly exceeds the solvolysis rate (Table III), k_t and k_{isom} could not be determined at the same temperature. Since k_{isom} for **3-Br** at 172 °C is 59 times higher than k_t, $1 - F = >0.99$ according to eq 8, i.e., >99% of the ion pairs return to **3-Br** and **4-Br**, while <1% end up as solvolysis products.

This ion pair return is much more extensive than the ion pair return in AcOH, AcOH-HCOOH, and Ac_2O-AcOH.[4b,c] For example, in AcOH, 47% of the ion pairs return to RBr, while 53% dissociate further to the product-forming free ion.[4b] The unprecedented high extent of ion pair return in vinylic systems is understood, since the other reaction routes open to the ion pair (Scheme II) are difficult: dissociation due to the low dielectric constant of the solvent, and capture due to steric hindrance both by X^- and the substituents in R^+. The ion pair return is favored both due to the low dielectric constant and since the two reacting entities are already favorably oriented in the ion pair. The preference for return over capture may be as high in acetic acid as in pivalic acid, but this cannot be estimated, since the dissociation in AcOH becomes so important that the products are formed exclusively from the free ion, so that any capture of the ion pair is masked.

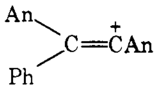
In both solvents the titrimetric rate constants are very poor guides to k_{ion}, but for different reasons. Only 2% of the initially formed cationoid species in AcOH and <1% of those formed in pivalic acid give products. In AcOH it is mainly due to external ion return[4b] and in pivalic acid to ion pair return. The Winstein-Grunwald m values, which are based on k_t, will therefore be much higher than those based on k_{ion}, which are the appropriate values for mechanistic comparisons. Indeed, the use of the k_{ion} values determined for the two solvents AcOH and Me_3CCOOH give lower m values: 0.63 for **3-Br** at 172 °C and 1.25 for **6-Br** at 120.3 °C. The value for **3-Br** is in the range found for solvolyses in carboxylic acid media.[3d,4c,24,25] The difference between the m values which are based on k_t and k_{ion} demonstrates dramatically how the solvent effect may be misinterpreted if ion pair return is not taken into account. It also suggests that when extremely high m values are obtained an extensive ion pair return should be considered.[26]

The nature of the ion pairs is inferred from the effect of $LiClO_4$ and the structure of the products. Addition of 0.01 M $LiClO_4$ increases k_t by >tenfold, while the concurrent k_{isom} increases only 1.5-fold. This cannot be due to a normal salt effect (eq 6), which will require a b value of 1000. We interpret it as a "special" salt effect,[27] where $LiClO_4$ captures a solvent separated ion pair by forming $R^+ClO_4^-$, thus reducing the return and shifting the reaction to the direction of the product. The increase in k_{isom} amounts to $b = 54$, a value higher than usually found for $LiClO_4$.[27i] However, part of the increase in

k_{isom} may be due to a salt-promoted ionization, as found for several solvolyses in the presence of lithium salts.[22c,28]

Although the gap between k_{ion} and k_t is appreciably reduced at 0.01 M LiClO$_4$ it is still large; only 11.5% of the ion pairs give products, while 88.5% return to covalent bromide.

The solvolysis of **3-Br** and **4-Br** and the corresponding mesylates in several solvents and in the presence of several nucleophiles gave ca. 1:1 cis–trans mixtures of the capture products.[4b,c,17] An in-plane attack on the linear free vinyl cation **14** has, therefore, nearly equal probabilities from both sides of the cationic orbital. Since appreciable inversion was observed for several solvolyses of vinylic systems, where the products are formed from ion pairs,[8] the 1:1 cis–trans pivalolysis products suggest that shielding by X$^-$ in the product-forming intermediate is relatively insignificant. Since the intermediacy of a free carbonium ion was excluded, the product-forming intermediate should be an ion pair where R$^+$ and X$^-$ are remote, i.e., a solvent separated ion pair.



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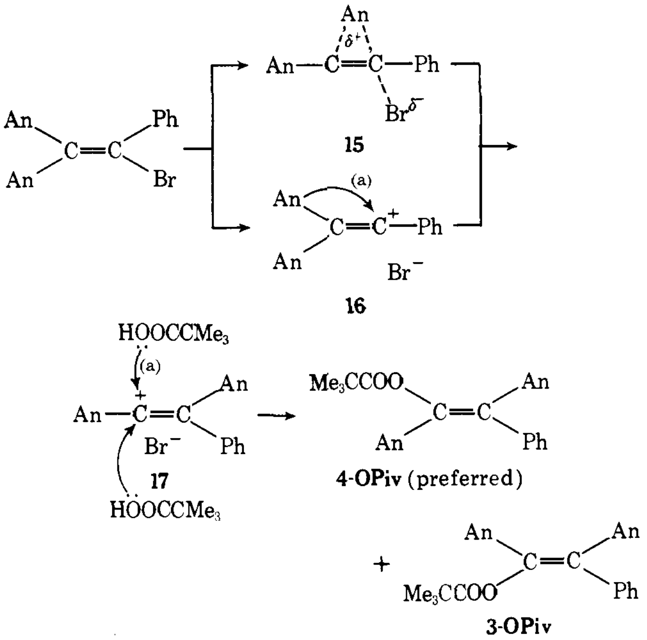
These results differ from those in AcOH, where addition of 0.03 M LiClO$_4$ changes k_t only slightly, while k_{isom} increases 4.5-fold, indicating that the intermediate involved in the isomerization and the ion pair return is the intimate ion pair.[4b] The difference in the ion pair in two solvents is not easily understood, since a more advanced ion pair is expected in the more dissociating solvent. We note, however, that the present data do not exclude the possibility that the majority of the ion pairs in Me$_3$CCOOH (e.g., 88%) are still the intimate ion pairs. More data are required to answer this question.

Rearrangement. The AgOCOCMe$_3$-assisted pivalolysis gave only the rearranged pivalates **3-OPiv** and **4-OPiv**. The absence of the unrearranged **8-OPiv** is consistent with the formation of only the rearranged products from **8-Br** in AcOH,[11a] TFE,[11b] and 60% EtOH.[11b] Apparently, the driving force for the formation of the rearranged α-anisylvinyl cation from the α-phenylvinyl cation is sufficient to make the rearrangement faster than the reaction with the solvent.

The product distribution from the reactions leading to the vinyl esters depends on the starting material and the solvent. The acetolysis of **3-Br** or **4-Br** gives a 54:46 mixture of **3-OAc** to **4-OAc**, while the rearrangement-solvolysis of **8-Br** gives a 50:50 mixture of the two acetates.[29] The pivalolysis of **8-Br** gives a 43:57 mixture of **3-OPiv** to **4-OPiv**, while those of **3-Br** and **4-Br** gives a 50:50 mixture of these pivalates. The product-forming intermediate should differ, at least in part, in the two types of reactions.

A much longer reaction time and higher temperatures were required for the pivalolysis of **8-Br**, and if the distribution in the reaction of **3-Br** is kinetically controlled and the equilibrium mixture is richer in **4-OPiv**, the observed distribution in the pivalolysis of **8-Br** may be due to post isomerization. This is unlikely, since the cis isomers (**3**) are slightly preferred in the equilibrium mixtures of the corresponding bromides, chlorides, and acetates,[4b,c] and since **4-OPiv** is stable to isomerization to **3-OPiv** in the presence of silver pivalate.

Scheme V



A more likely possibility is a different type of ion pair as the product-forming intermediate in each reaction. Either β-anisyl participation in the ionization (via transition state **15**) or preferential migration of the anisyl group on the opposite side of the shielding Br$^-$ in the initially formed ion pair (transition state **16**)[30] will give the intimate ion pair **17**.[31] Preferential capture of **17** by pivalic acid or pivalate ion from its least hindered side[27f] (Scheme V, route a) will give more of **4-OPiv**. This process competes with the dissociation to the solvent separated ion pair **13**, which will give a 50:50 product distribution. The observed inversion argues strongly that the ion pair **17** is tighter than those formed in the solvolysis of **3-Br** and **4-Br**, and is therefore an intimate ion pair.[31] However, it is not clear whether the moderate preference for inversion reflects the reaction of **17** alone or whether it is due to capture of both **13** and **17**, where **13** is formed either from **17** or from **3-Br** and **4-Br**, which are obtained, in turn, from internal return of **17**.

It is interesting that while a degenerate β-anisyl rearrangement during the solvolysis of **6-Br** was observed in AcOH,[1,11c] none was observed in pivalic acid.[1] It was shown that the rearrangement in AcOH proceeds exclusively via the free ion.[1] In view of the above results it is possible that the lack of rearrangement in pivalic acid is due to the fact that the free ion is not formed in pivalic acid.

Conclusions

The initial ionization of α-anisylvinyl bromides in Me$_3$CCOOH–Me$_3$CCOONa gives ion pairs. In competition between their capture by the solvent to give products, their dissociation to free ions which also give products, and their return to covalent vinyl bromides, return is the dominant process. Dissociation to the free vinyl cation becomes important when the β-aryl substituents become very bulky. At least part of the ion pairs involved in the solvolysis and isomerization of **3-Br** are solvent separated ion pairs, as shown by the special salt effect of LiClO$_4$. Tighter ion pairs are involved in the solvolysis-rearrangement of **8-Br** in Me$_3$CCOOH–Me$_3$CCOOAg.

Experimental Section

Melting points were determined with a Fisher-Johns apparatus and are uncorrected. NMR spectra were recorded with a Varian HA-100 or a T-60 spectrometer and the signal positions are given in δ units downfield from internal Me$_4$Si. Mass spectra were recorded with a MAT 311 instrument and uv spectra with a Unicam SP 800 spectrophotometer. Ir spectra for the kinetic measurements were recorded on a Perkin-Elmer 337 spectrophotometer. The potentiometric titrations were performed with a Radiometer TTT 1c instrument with a silver cathode and calomel reference.

Solvents and Materials. Pivalic acid, mp 35.5 °C (Fluka, purum, δ 1.22), was distilled and a middle fraction, bp 161 °C, was used for the kinetics. Pivalic acid-d_1 was prepared by stirring pivalic acid with two successive portions of 2.5 mol equiv of D$_2$O, separating, drying (MgSO$_4$), and distilling. The acid, bp 161 °C, was >99% deuterated by NMR. Its ir spectra showed strong O–D stretching at 2040 and

2220 cm^{-1}. Silver pivalate was prepared in 43% yield by reacting silver carbonate with pivalic acid and a purer sample was obtained by adding silver nitrate to pivalic acid in ammonia solution.[32] Silver nitrate solutions (0.01 M) were prepared from ampule concentrates (BDH). *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl bromides,[17] trianisylvinyl bromide[33] and chloride,[34] 1-anisyl-2,2-dimethylvinyl bromide,[3b] and 10-(α-bromoanisylidene)anthrone[7] were prepared as described previously.

***cis*- and *trans*-1,2-Dianisyl-2-phenylvinyl Pivalates (3-OPiv and 4-OPiv).** (a) A 4:6 mixture of **3-Br** to **4-Br** (2.96 g, 7.5 mM) was stirred at 130 °C with silver pivalate (1.55 g, 7.5 mM) in pivalic acid for 105 min. The warm reaction mixture was decanted and poured slowly with stirring into a saturated sodium bicarbonate solution. The organic precipitate was recrystallized thrice from hot methanol, giving the pure high mp isomer **4-OPiv**, mp 135–137 °C (1.25 g, 40%). Evaporation of the mother liquor gave a solid, mp 90–95 °C, which on repeated crystallization from methanol gave white crystals of the pure second isomer **3-OPiv**, mp 127–129 °C (1.25 g, 40%).

Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found for **4-OPiv**: C, 77.70; H, 6.68. Found for **3-OPiv**: C, 78.16; H, 6.80.

The ir spectra (KBr) resemble those of the corresponding ethylenes and acetates with stretching frequencies at 2840 (MeO), 1735 (C=O), and 1610 (C=C) cm^{-1}. The fingerprint region of the two isomers is distinguished by peaks at 530 cm^{-1} for **4-OPiv** and 550 and 790 cm^{-1} for **3-OPiv**; for **4-OPiv**, λ_{max} (EtOH) 239 (ϵ 20 400), 300 nm (ϵ 17 500); NMR δ ($CDCl_3$) 1.03 (9 H, s, CMe_3), 3.74, 3.75 (6 H, 2 s, 2 MeO), 6.64–7.23 (8 H, m, Ar), 7.23 (5 H, s, Ph); for **3-OPiv**, λ_{max} (EtOH) 246 (ϵ 22 600), 303 nm (ϵ 16 100); NMR δ ($CDCl_3$) 1.08 (9 H, s, CMe_3), 3.73, 3.78 (6 H, 2 s, 2 MeO), 6.62–7.22 (8 H, m, An), 7.09 (5 H, s, Ph). The mass spectra of the two isomers are identical: *m/e* 416 (79%, M), 322 (90%, MH − $COCMe_3$), 331 (100%, M − $COCMe_3$), 303 (75%, An_2C^+Ph), 197 (10%, AnC^+HPh), 135 (38%, $AnCO^+$), 57 (57%, CMe_3^+).

(b) When equimolar amounts of pure **3-Br** or pure **4-Br** and silver pivalate (0.4 g, 1 mM) were heated in pivalic acid at 130–140 °C for 2 h, the NMR spectrum of the oil obtained showed the two *tert*-butyl singlets in equal intensities within the experimental accuracy of ±3%. NMR spectra of each of the aliquots from the kinetic run for the solvolysis of **3-Br** or **4-Br** gave the two isomeric pivalates in equal amounts.

Stability of 4-OPiv. When a pure sample of **4-OPiv** was refluxed in pivalic acid for 8 days or when equimolar amounts of **4-OPiv** and silver pivalate were refluxed in pivalic acid for 5 h, the NMR spectrum (after treatment with $NaHCO_3$ and extraction with ether) showed the presence of only **4-OPiv**.

Trianisylvinyl Pivalate (6-OPiv). A mixture of trianisylvinyl bromide (1.28 g, 3 mM) and silver pivalate (0.69 g, 3.3 mM) in pivalic acid (20 ml) was heated for 135 min at 140 °C. The warm solution was decanted into a stirred $NaHCO_3$ solution and the solid formed (0.94 g, 70%) was recrystallized twice from methanol, giving white crystals of trianisylvinyl pivalate, mp 115–117 °C: λ_{max} (EtOH) 249 (ϵ 24 000), 304.5 nm (ϵ 19 700); ν_{max} (KBr) 2820 (MeO), 1740 (C=O), 1605 (C=C) cm^{-1}; NMR δ ($CDCl_3$) 1.07 (9 H, s, CMe_3), 3.73, 3.74, 3.78 (3 × 3 H, 3 s, MeO), 6.63–7.25 (12 H, m, Ar); MS *m/e* 446 (30%, M), 361 (100%, M − $COCMe_3$), 334 (73%, An_3CH), 135 (62%, $AnCO^+$), 57 (29%, Me_3C^+).

Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.31; H, 6.77. Found: C, 75.38; H, 6.85.

1-Anisyl-2,2-dimethylvinyl Pivalate, (5-OPiv). A mixture of 1-anisyl-2-methylpropen-1-yl bromide (**5-Br**) (0.72 g, 3 mM) and silver pivalate (6.9 g, 3.3 mM) in acetonitrile (20 ml) was stirred for 3.5 h at 130 °C. After workup as above, a yellow oil was obtained (0.62 g, 80%). This could not be induced to crystallize from methanol, even after purification by TLC, but was identified by NMR and mass spectrum as 1-anisyl-2,2-dimethylvinyl pivalate: NMR δ ($CDCl_3$) 1.24 (9 H, s, CMe_3), 1.51, 1.59 (2 × 3 H, 2 s, Me), 3.76 (3 H, s, MeO), 6.80, 6.89, 7.23, 7.32 (4 H, AA′BB′ q, An); MS *m/e* 262 (67%, M), 178 (100%, MH − $COCMe_3$), 177 (38%, M − $COCMe_3$), 163 (61%, $AnCOC^+HMe$), 135 (95%, $AnCO^+$), 85 (30%, Me_3CCO^+), 77 (46%, Ph^+), 57 (99%, Me_3C^+).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.48; H, 8.31.

10-(Anisylideneanthrone-α-ol) Pivalate (7-OPiv). A mixture of 10-(α-bromoanisylidene)anthrone (**7-Br**) (2 g, 5 mM) and silver pivalate (1.1 g, 5 mM) in acetonitrile (50 ml) was refluxed for 20 h. The warm solution was filtered, giving a yellow precipitate, which was separated from residual silver salts by dissolving in chloroform and filtering. Recrystallization from acetonitrile gave yellow crystals of **7-OPiv**, mp 221–224 °C (1.52 g, 75%): λ_{max} (EtOH) 236 (ϵ 42 800), 375 nm (ϵ 10 300); ν_{max} (KBr) 1745 (C=O), 1660 (C=C) cm^{-1}; NMR δ ($CDCl_3$) 1.22 (9 H, s, Me_3C), 3.78 (3 H, s, MeO), 6.70–8.28 (12 H, m, Ar); MS *m/e* 412 (11%, M), 328 (100%, MH − $COCMe_3$), 327 (7%, M − $COCMe_3$), 135 (36%, $AnCO^+$), 85 (13%, Me_3CCO^+), 57 (90%, Me_3C^+).

Stability of 7-OPiv. Pure **7-OPiv** was refluxed for 7 days. After workup, the uv and the NMR spectra of the product indicated that only **7-OPiv** was recovered.

Solvolysis–Rearrangement of 2,2-Dianisyl-1-phenylvinyl Bromide (8-Br). Equimolar amounts (3 mM) of 2,2-dianisyl-1-phenylvinyl bromide and silver pivalate were refluxed in pivalic acid (25 ml) for 63 h. After workup as above, the crude solid (1 g, 80%) was analyzed by NMR. The two signals of the *tert*-butyl group at δ 1.03 and 1.08 were used for the analysis, by integration and weighing cut out traces of the peaks. The δ 1.08/δ 1.03 ratio was found to be 1.25.

Three fractional crystallizations from methanol gave compound A, mp 138–139 °C (Anal: C, 77.99; H, 6.69; NMR δ ($CDCl_3$) 1.08 (s), 3.73, 3.78 (2 s), 6.62–7.22 (m, An), 7.10 (s, Ph)), and compound B (Anal: C, 77.93; H, 6.55; NMR δ ($CDCl_3$) 1.03 (s), 3.74, 3.75 (2 s), 6.62–7.24 (m, An), 7.24 (s, Ph)). These were identical (mixed mp, ir, NMR), respectively, with the *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl pivalates (**3-OPiv** and **4-OPiv**) described above.

When the reaction was repeated with reflux times of 69 and 80 h, the respective δ 1.08/δ 1.03 signal ratios were 1.3 and 1.45, respectively.

Kinetic Runs. Due to the low solubility of the triarylvinyl bromides a sample for each kinetic point was weighed and added to the pivalic acid–Na_2CO_3 mixture (and dissolution was achieved after warming to 70 °C). The mixtures were sealed in separate ampules, which were treated according to Grob,[35] and kept at the appropriate reaction temperature. Due to the high temperature and the long reaction times, temperature fluctuations were up to ±0.7 °C. The reactions were stopped by withdrawing the ampules to room temperature. The organic material was extracted with carbon tetrachloride, neutralized with a large excess of sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. The oil or solid obtained was analyzed by NMR in $CDCl_3$ in the solvolysis experiments or by ir after dissolution in CS_2 for the isomerization experiments.

The total aqueous phase, which contained all the halide ion, was titrated potentiometrically with 0.01 M silver nitrate. Control experiments that were carried out confirmed that pivalic acid does not retain any of the released halide ion and that none of the halide ion is lost during the extraction.

The **3-Br** $\rightleftharpoons$ **4-Br** isomerization was followed by monitoring the change in the intensities of the peaks at 575 and 515 cm^{-1} and using an appropriate calibration curve[4b] to convert relative peak heights to isomer ratio. Control experiments showed that the absorptions of a 1:1 mixture of **3-OPiv** to **4-OPiv** do not interfere with accurate determination of the ratio of the vinyl bromides when the vinyl pivalates make up ≤20% of the mixture.

Acknowledgment. We are indebted to the Volkswagen Foundation for partial support of this work.

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(31) While the same products are formed from **3-Br** and **4-Br** in pivalic acid, this cannot be used for deducing the nature of the intermediate, since the **3-Br** $\rightleftharpoons$ **4-Br** isomerization is much faster than the solvolysis reaction.
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Formation of Trianions of 2,4,6-Triketones. Synthesis of 3,5,7-Triketo Acids Using Lithium Diisopropylamide

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Abstract: Ionization of the methyl group of 1-phenyl-1,3-butanedione (**1**) and of 1-phenyl-1,3,5-hexanetrione (**2**) by KNH$_2$, NaNH$_2$, and LiNH$_2$ in liquid NH$_3$ has been studied by measurement of deuterium loss from the methyl-deuterated species. KNH$_2$ and NaNH$_2$ brought about rapid and complete formation of the dianion of **1**; formation of trianion with **2** was slow and failed to go to completion. Reversibility led to loss of >1.0 D/methyl group from **2** after long reaction periods. Using LiNH$_2$, dianion formation was slow with **1**, and **2** failed to form the trianion. Lithium diisopropylamide (LDA) in tetrahydrofuran brought about rapid and complete ionization of the methyl group of **2**, 3 equiv of the base being required. The use of LDA for synthesis of 3,5,7-triketo acids from triketones was found to be a substantial improvement over the alkali amides. An improved yield of triketo acid **9** was obtained using LDA with **2**. Four small aliphatic triketones (**5–8**) also gave satisfactory yields of carboxylation products; alkali amides in liquid NH$_3$ had previously failed to give useful quantities of trianions with these compounds. Carboxylation of an unsymmetrical triketone, 3-methyl-2,4,6-heptanetrione, did not show regiospecificity; equal amounts of isomeric resorcylic acids (**24** and **25**) were obtained after aldol cyclization of the carboxylation products. The chemistry of the biologically important triketo acid, 3,5,7-trioxooctanoic acid (**13**), was explored. Acid **13** was converted to orsellinic acid (**15a**) by pH 5 acetate buffer, to tetraacetic lactone (**22**) by Ac$_2$O, to 4-pyrone ester **19** by H$_2$SO$_4$/MeOH, and to methyl ester **18** by CH$_2$N$_2$. Ester **18** was cyclized to methyl orsellinate (**15b**) by pH 5 acetate buffer and to a mixture of **15a**, **15b**, and 2,4,6-trihydroxyacetophenone (**21**) by aqueous KOH.

The chemistry of 3,5,7-triketo acids has attracted much attention due to the apparent involvement of some of these compounds in the biosynthesis of phenolic natural products.[1] Much of the effort has been concentrated on derivatives of the triketo acids, i.e., pyrones and ketals, because of the inaccessibility and instability of the polycarbonyl compounds themselves, but in this laboratory the emphasis has been on unprotected compounds, following the discovery that triketo