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VINYLIC CATIONS FROM SOLVOLYSIS. IV. ABSENCE OF β-ARYL PARTICIPATION IN THE SOLVOLYSIS OF TRIARYLVINYL HALIDES

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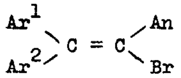
In the solvolysis of triarylvinyl halides[1] and sulfonates[2] the Grunwald-Winstein m values[3] are low for an S_N1 reaction ($m \sim 0.4$). The derived triarylvinyl cations have long life-time as judged from the observation of a common ion rate depression in acetolysis.[4] Both phenomena are ascribed to steric hindrance in the approach of the solvent or the nucleophile to the cationic orbital in the transition state or the ion. Alternate explanation involving β-aryl participation and formation of phenonium ions is rejected on the basis of the formation of the same 1:1-cis-trans acetate mixture from the acetolysis of either cis or trans-1,2-dianisyl-2-phenylvinyl halides.[5] Moreover, the solvolysis rate of the triarylvinyl bromide and the corresponding α-bromostyrene in aqueous ethanol[1] or DMF[6] are very similar. However, since the monoarylvinyl and the triarylvinyl systems differ in m-values,[4] in Hammett's ρ values[7,8] in the selectivity of the ion,[4] and in the activation energies[1] the reactivity ratios are solvent-, substituent-, concentration- and temperature-dependent. In view of the difficulties in estimation of the inductive effects of β-aryl groups[9] and since small rate accelerations may accompany extensive participation,[9,10] comparison of the two systems may be misleading. Since the degree of β-phenylthio participation in a vinylic system was calculated assuming no β-aryl participation[11] a comparison of more similar compounds in a wider solvent range seems desired.

Titrimetric rate coefficients k_1 for the solvolysis of trianisyl- , cis- and trans-1,2-dianisyl-2-phenyl- and 1-anisyl-2,2-diphenylvinyl bromides (1)-(4) in 80% EtOH, AcOH and 50% AcOH - 50% HCOOH are collected in the Table. In 80% EtOH k_1 is stable during a run, although a concurrent *cis-trans* isomerization[12] which is about as fast as the solvolysis takes place and the average k_1 is given. In AcOH and AcOH-HCOOH mixtures the value of k_1 change during a run due to both *cis-trans* isomerization and common ion rate depression. In both solvents the observed rate coefficient (k_{obs}) obeys the equation $k_{obs} = k_1 / (1 + k_{-1}[Br^-]/k_2[OAc^-])$ where k_1 is the rate coefficient for formation of the cation, and k_{-1} and k_2 are the rate coefficients for its capture by bromide and acetate ions,respectively. The values given in the Table are k_1 values extrapolated to zero reaction time (k_1^{o}) from which ion return is eliminated.[12] Additional evidence against a competing addition-elimination process in acetic acid is the low solvent isotope effect $k_{CH_3COOH}/k_{CH_3COOD} \sim 1.1$.



$\mathrm{Ar^1(Ar^2)C{=}C(An)Br}$

An. = *p*-$CH_3OC_6H_4$-

1. $Ar^1 = Ar^2 = An$. 2. $Ar^1 = An$; $Ar^2 = Ph$.
3. $Ar^1 = Ph$; $Ar^2 = An$. 4. $Ar^1 = Ar^2 = Ph$.

The solvolysis rates of 2 and 3 are almost the same in the three solvents studied. This is in line with the indirect evidence that *cis*- and *trans*-2-anisyl-1,2-diphenylvinyl iodides solvolyze in similar rates, which are 1.38-times faster than that of triphenylvinyl iodide in aqueous DMF.[6] Since inductive effects are very similar for 2 and 3 and since in 2 the much better participating anisyl group is *trans* to the leaving group while in 3 a much less participating phenyl group is in the *trans* position we conclude that *no β-aryl participation in the solvolysis of triarylvinyl halides is evident*[13] in agreement with the stereochemical data.[5] Since the importance of participation increases in the solvent order: 80% EtOH < AcOH < 50% AcOH-50% HCOOH [14] it can be assumed that in other solvents of higher nucleophilicities than 50% AcOH - 50% HCOOH (e.g., aqueous DMF,[6] nitromethane-methanol[11]) β-aryl participation will be negligible.

The changes in k_1 for 1 - 4 are additive as expected for inductive effects. In 80% EtOH replacement of *trans* and *cis* (to the leaving group) phenyl by anisyl enhances the rate by 31% and 52% respectively, from which k_1 value for 1 is calculated to be 38.2×10^{-5} sec^{-1}. Similar results are obtained in AcOH if β-anisyl/β-phenyl enhancement of 1.9 is used. The higher rate of 3 compared to 2 is probably due to the

Table. Solvolysis of Triarylvinyl Bromides.

Compound	$10^5 k_1$, sec^{-1}		
	80% EtOH^{a}	AcOH^{a,b}	50%AcOH-50%HCOOH ^{c}
1	40.8^{d}	6.7^{e}	
2	25.2	4.0	29.3
3	29.2	4.2	32.0
4	19.2	2.0^{e}	

^{a} At 120.3° . ^{b} [RX] = 0.043M , [NaOAc] = 0.087M . ^{c} At 99.7°.

^{d} From ref. 1 . ^{e} From ref. 4 .

shorter distance between the electropositive *cis* substituent and the C-Br bond. An analogous explanation was used for the differences between the ionization constants of *cis* and *trans* cinnamic acids.[15]

For 2 and 3 Grunwald-Winstein's m is 0.72 at 100° in AcOH - 50%AcOH-50%HCOOH. This value should be compared to m ~0.4 for 1 (leaving group bromide or tosylate) in aqueous ethanol[1] or acetone.[2] We suggest that this is due to the fact that in these solvents the transition state is stabilized mainly by electrophilic solvation of the leaving group[16] and is not very sensitive to hindrance by the aryl groups, while solvation in the nucleophilic solvents is mainly from the rear and is highly hindered by these groups.

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8. ρ values (based on σ^+) are > -4.5 and -3.6 for α-bromo-*p*-substituted styrenes in 80% EtOH[6,8] and for 2,2-diphenyl-1-arylvinyl iodides in 70.4% DMF,[6] respectively.
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10. E.g., using data for 1 and α-bromo-*p*-methoxystyrene[1,4,7] calculations without any

correction for the effects of the β-aryl groups give 75% and 40% anisyl participation in AcOH and 80% EtOH, respectively.

11. G. Modena and U. Tonellato, in press. We thank these authors for communicating their unpublished results to us.
12. Z. Rappoport and Y. Apeloig, to be published. While the accurate k_1^o value depends somewhat on the extrapolation, the decrease of k_1 during the reaction is almost the same for both 2 and 3 .
13. Comparison should be made between the unknown ionization rather than the solvolysis rate coefficients. Since the isomerizations of 2 and 3 (which may partly involve ionization which does not liberate bromide ions) have almost identical rates, the ratio of the titrimetric values is probably similar to the ratio of the ionization values.
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