m/e 198 (M^+). It was assigned the structure 2,5-dimethylnaphthol[1,2-*b*]2,3-dihydrofuran.

(C) Thermal Rearrangement at 145°. A solution of naphthalenone **18** (0.20 g) in 5 ml of *N,N*-dimethylaniline was heated at 145° in a sealed tube for 2 h and worked up as usual to give 0.15 g of 2-allyl-4-methyl-1-naphthol as a brown oil. Its ir spectrum had a hydroxy peak at 3550 cm^{-1}. Its NMR spectrum had peaks at τ 1.78–2.00 (m, 1 H), 2.12–2.38 (m, 1 H), 2.55–2.82 (m, 2 H), 3.13 (s, 1 H), 3.67–5.25 (m, 4 H), 6.60 (d, J = 6 Hz, 2 H), and 7.52 (s, 3 H).

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Vinylic Cations from Solvolysis. XXIII.[1] Degenerate β-Anisyl Rearrangement during the Solvolysis of 2-Anisyl-1,2-diphenylvinyl Bromides. Free Ions as Intermediates

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Abstract: The solvolysis of *trans*-2-anisyl-2-pentadeuteriophenyl-1-phenylvinyl bromide (**6***-Br) in 60% EtOH, 80% EtOH, and TFE buffered by 2,6-lutidine and in AcOH–AgOAc is accompanied by an extensive (>85%) degenerate β-anisyl rearrangement. A 7:3 mixture of the cis and trans isomers and pure **6***-Br give the same extent of rearrangement in 60% EtOH, suggesting that the rearrangement proceeds via the free vinyl cation **13***. The migratory aptitudes of anisyl and phenyl groups in the vinylic system are normal, and rearrangement ratios $k_{r(\mathrm{An})}/k_{r(\mathrm{Ph})}$ of 76–120 were obtained from the internal competition in the ion **13*** or by comparison with the migration in the triphenylvinyl cation. The migration origin, the migration terminus, and the bridged transition state for the migration are stabilized better by anisyl than by phenyl group. The degenerate migration is not an important contributor to the selectivity of the ion **13***. The use of mass spectral and NMR analyses for determining the extent of the degenerate rearrangement is discussed.

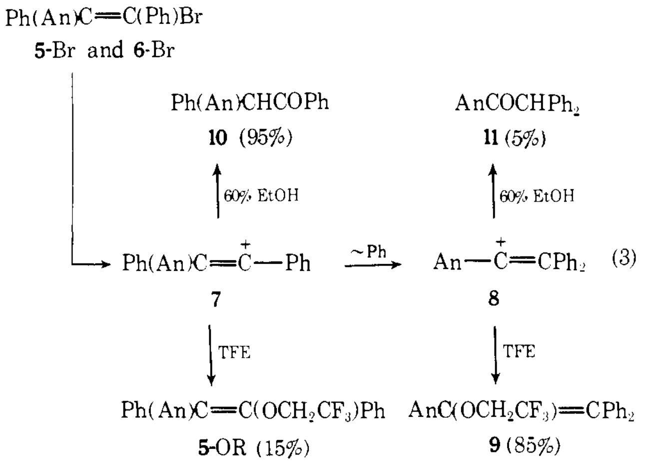
Several processes which accompany the heterolytic ionization of triarylvinyl halides were recently studied. These include external ion return and ion pair return with isomerization to the geometrical isomer,[2] capture of the ion by the solvent or by other nucleophiles,[2,3] and β-aryl rearrangement across the double bond of the intermediate cation to form a more stable triarylvinyl cation.[4] When we began our work we were interested as to whether degenerate rearrangements also occur in these systems. Meanwhile, degenerate β-anisyl and β-phenyl rearrangement in triarylvinyl cations were observed.[5,6]

Eight β-aryl rearrangements are possible in the ion **1**, when Ar^1, Ar^2, and Ar^3 are all possible combinations of phenyl and anisyl groups (eq 1). Two of these, phenyl rearrangement when Ar^1 = An, Ar^2 = Ar^3 = Ph and the anisyl rearrangement when Ar^1 = Ar^2 = An, Ar^3 = Ph, were not observed since they lead to a less stable α-arylvinyl cation than the precursor ion. Two rearrangements which lead from an α-phenyl to an α-anisylvinyl cation were observed. In the solvolysis of the bromide **2** via ion **3**, both the product ion **4** and the transition state for the rearrangement are stabilized by anisyl groups and only rearranged products were formed[4] (eq 2). β-Phenyl rearrangement during the solvolysis of *cis*- and *trans*-2-anisyl-1,2-diphenylvinyl bromides

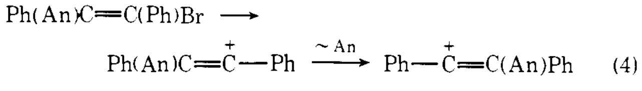
$$\underset{\mathbf{1}}{\mathrm{Ar^3Ar^2C{=}\overset{+}{C}{-}Ar^1}} \longrightarrow \mathrm{Ar^2{-}\overset{+}{C}{=}CAr^3Ar^1}\ \text{or}\ \mathrm{Ar^3{-}\overset{+}{C}{=}CAr^2Ar^1} \qquad (1)$$

$$\underset{\mathbf{2}}{\mathrm{An_2C{=}C(Br)Ph}} \longrightarrow \underset{\mathbf{3}}{\mathrm{An_2C{=}\overset{+}{C}{-}Ph}} \longrightarrow \underset{\mathbf{4}}{\mathrm{An{-}\overset{+}{C}{=}C(Ph)An}} \qquad (2)$$

(**5**-Br and **6**-Br, respectively) gives 85% of the rearranged product in trifluoroethanol, but only 5% of the rearranged product are formed in the more nucleophilic 60% EtOH[4b] (eq 3). Of the four degenerate rearrangements which may take place in **1** (phenyl rearrangement when (a) Ar^1 = Ar^2 = Ar^3 = Ph[5a,e] and (b) Ar^1 = Ar^2 = An,[5b,d,6] Ar^3 = Ph, or anisyl rearrangement when (c) Ar^1 = Ar^2 = Ar^3 = An[5c,6] or (d) Ar^1 = Ar^2 = Ph, Ar^3 = An), which were studied by Lee,[5a-d] Collins,[5e] and by us,[6] only the β-anisyl rearrangement in the 2-anisyl-1,2-diphenylvinyl cation **7** (eq 4) was not yet reported. This system is suitable to give an answer to some of the following questions.



(a) What is the nature of the cationic intermediates in the degenerate rearrangements of triarylvinyl cations? The solvolysis and β-aryl rearrangements in the (*E*)-3-phenyl-2-buten-2-yl system proceed with extensive β-aryl bridging,[7] while open ions are dominant in the reactions of the *Z* isomer.[7] Degenerate β-aryl rearrangement which accompany the solvolysis and the deamination of several 1,2,2-triarylethyl derivatives proceed via open carbonium ions.[8] This was not established for the analogous 1,2,2-triarylvinyl derivatives, although the evidence for open carbonium ions in the solvolysis and the isomerization of the triarylvinyl system is abundant.[2-4] For example, the similar solvolysis rates and extents of β-phenyl rearrangements of both **5**-Br and **6**-Br[4b] argue for the intermediacy of free ions. However, the negligible lyate ion effect on the extent of the degenerate phenyl rearrangement in the triphenylvinyl cation is consistent with the intermediacy of ion pairs.[5a]



$$\mathrm{Ph(An)C{=}C(Ph)Br} \longrightarrow \underset{\mathbf{7}}{\mathrm{Ph(An)C{=}\overset{+}{C}{-}Ph}} \xrightarrow{\sim\mathrm{An}} \underset{\mathbf{7a}}{\mathrm{Ph{-}\overset{+}{C}{=}C(An)Ph}} \quad (4)$$

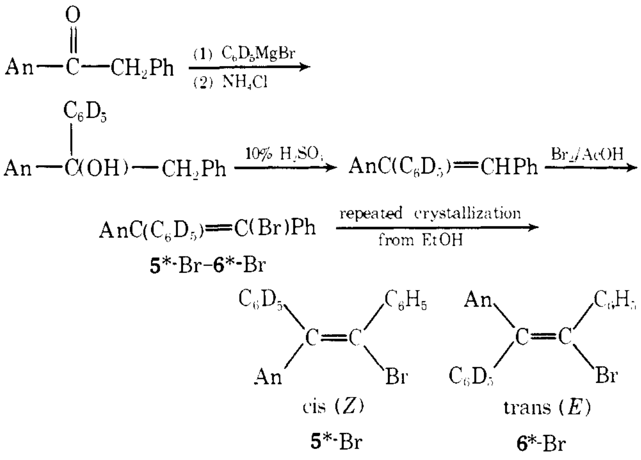
(b) The migratory aptitude of an anisyl group usually exceeds that of a phenyl group in β-aryl rearrangements in saturated systems,[9] but it is not clear whether this is true for vinylic systems. The formation of 85% of **9** in the solvolysis of **5**-Br and **6**-Br in TFE raised the possibility that phenyl migration may be preferred over anisyl migration in vinylic systems due to a lower loss of a stabilizing ground-state migrating-β-Ar-π(C=C) conjugation. Moreover, the lower extent of β-anisyl rearrangement in the deamination of 1,2,2-trianisylethylamine[10] compared with the β-phenyl rearrangement in 1,2,2-triphenylethylamine[8] may be interpreted in terms of a preferred phenyl migration in nonbridged cationoid species. Comparison of the extents of β-phenyl and β-anisyl rearrangements in **7** could establish the order of migratory aptitude in a vinylic system. These relative rearrangement rates could be compared with the rates of capture of **7** by the solvent and the leaving group.

(c) The selectivity of triarylvinyl cations was ascribed to steric shielding to the approach of the nucleophile and the solvent to the cationic orbital, by the bulky β substituents.[2] A possible alternative explanation is that a rapid degenerate β-aryl rearrangement increases the selectivity by driving off both the solvent and the leaving group from the vicinity of the cationic orbital (a "windshield wiper effect"). The importance of this factor may be assessed by studying the degenerate rearrangement under conditions where the vinyl cations exhibit their selectivity.

Results

In order to study the degenerate rearrangement of compounds **5**-Br and **6**-Br, the β-phenyl group of these compounds was labeled by replacing it by a pentadeuteriophenyl (Ph*) group. The labeled bromides, *cis*- and *trans*-2-anisyl-2-pentadeuteriophenyl-1-phenylvinyl bromides (**5***-Br and **6***-Br), were prepared as a mixture by the sequence of reactions outlined in Scheme I. Repeated crystallization of the mixture at our preparative scale gave the pure trans isomer, but only a 70%-30% mixture of **5***-Br to **6***-Br, which was used as such in the solvolysis experiments.

Scheme I



Solvolysis in 60% EtOH (v/v). Solvolysis of **6***-Br for 233 h at 160 °C in 60% aqueous ethanol buffered by 2,6-lutidine gave a mixture of unrearranged **10*** and β-anisyl-rearranged α-anisyl-α-pentadeuteriophenylacetophenone (**10a***) and β-phenyl-rearranged α-phenyl-α-pentadeuteriophenyl-*p*-methoxyacetophenone (**11***) (eq 5). The extent of the degenerate β-anisyl rearrangement was first determined by NMR in CDCl$_3$ from the intensity ratio of the two *o*-benzoyl protons of **10*** (which are absent in **10a***) at δ 8.06 to the benzhydryl protons of both **10*** and **10a*** at δ 5.84. This ratio, which should be 2 in the absence of rearrangement and 1 at complete β-anisyl rearrangement, was found to be 1.14 ± 0.04. The ratio should be corrected for the presence of the ketone **11*** whose *o*-anisoyl and benzhydryl protons resonate at positions similar to those of **10***. By using the intensities of the methine protons of **10*** and **11***, which give separate signals in C$_6$D$_6$, the **11*** to **10*** + **10a***

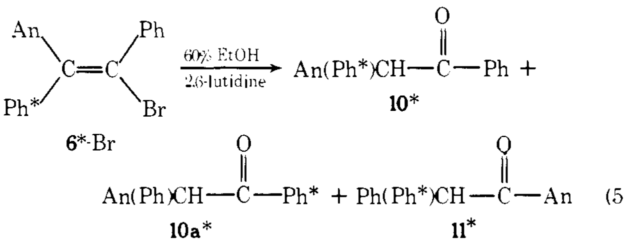


Table I. Relative Peak Intensities[a] and Percent Rearrangement in the Mass Spectral Fragmentation of the Solvolysis Products

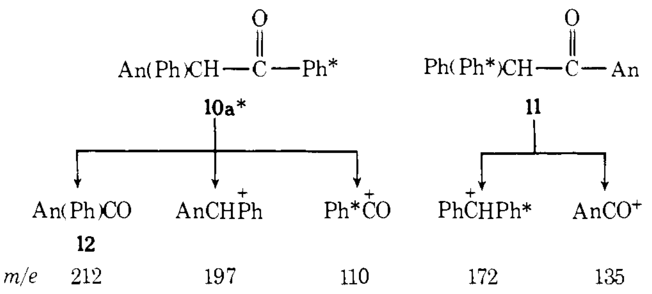
Reactant	Solvent	Analyzed product	Temp, °C[b]	m/e 110/ m/e 105	% rearrangement	m/e 202/ m/e 197	% rearrangement	m/e 217/ m/e 212	% rearrangement
6*-Br	60% EtOH	**10***–**10a***	50	44.7/55.3	89.5	55.7/44.3	88.6	55/45	90
			60[c]	44.7/55.3	89.5	55.9/44.1	88.2		
			170[c]			57/43	86		
			80	44/56	88	55/45	90	54.1/45.9	88.2
			120	43.5/56.3	87	55.6/44.4	88.8	54/46	92
30% **6***-Br + 70% **5***-Br	60% EtOH	**5***-Br + **10***–**10a***	95	45.6/54.4	91.2	54.8/45.2	90.2	56.5/43.5	87
6*-Br	AcOH	**5***-OAc + **5a***-OAc + **6***-OAc + **6a***-OAc	50			55/45	90.0		
			80	43.3/56.7	86.6	52.7/47.3	94.6		
			120	44/56	88	53.2/46.8	93.6		

[a] From the mass spectra of the crude material. [b] Temperature of the mass spectral fragmentation. [c] From the mass spectrum of the crystallized ketone.

ratio was previously determined to be 0.05%,[4b] and this was verified now. Correction for this value gave 89 ± 2% β-anisyl rearrangement. The extensive rearrangement is qualitatively evident by the appearance of the singlet of the β-phenyl group at δ 7.25, a signal which appears in the spectra of **10** and **10a*** but is absent in the spectrum of **10***. NMR of a crystallized sample of the ketone (**10*** + **10a***) showed 55.8 ± 0.4% of **10*** and 44.2 ± 0.4% of **10a***, i.e., the ketone is 88.4 ± 0.8% rearranged.

Determination of the extent of rearrangement by mass spectral analysis is an attractive method due to its simplicity and the possibility for providing a double check by internal consistency, provided that isotope effects on the mass spectral cleavage are negligible. Each ketone should give rise to highly abundant substituted benzoyl and benzhydryl ions. The five signals at m/e 105, 110, 135, 197, and 202 were indeed abundant, but the cleavage of **11*** gave almost exclusively the more stable p-methoxybenzoyl ion (Scheme II) and only a very small signal at m/e 172. Less abundant fragments at m/e 212 and 217 were also observed and were ascribed to the formation of p-methoxybenzophenone (**12**) and its pentadeuterio derivative (**12***) from the cleavage of **10a*** and **10***, respectively, in the basic media used for the solvolysis. Cleavage of β,β-dianisyl-p-methoxyacetophenone to p,p′-dimethoxybenzophenone in basic aqueous ethanol was previously observed.[3a]

Scheme II



Comparison of the intensities of the labeled and unlabeled pairs of benzoyl, p-methoxybenzhydryl and p-methoxybenzophenone fragments, gives an internal consistency test. A priori, the highest significance should be attributed to the values based on the p-methoxybenzhydryl signals since the relative intensities of the m/e 212 and 217 signals suggest that they are formed from the benzhydryl moieties and may further cleave to give a substituted benzoyl fragment with an opposite labeling pattern to that formed directly from the triarylethanone (Scheme II). Table I gives the data and the percentage of rearrangement at different fragmentation temperatures, calculated on the assumption that the rearrangement proceeds via two degenerate isomeric open ions and that the ratio of **10*** and **10a*** at 100% rearrangement is 1:1.

Table I shows that the peak intensities are practically independent of the temperature of the fragmentation and that all three pairs of signals give essentially the same extent of rearrangement. Contribution from a ArAr′CO → ArCO+ fragmentation is therefore small, if any. The average value of 88.6 ± 1.4% rearrangement obtained from the benzhydryl fragments is in excellent agreement with the NMR data.

Solvolysis of a 7:3 mixture of **5***-Br to **6***-Br at 160 °C for 240 h in 60% EtOH buffered by 2,6-lutidine showed 42.6 ± 1% of **10*** by NMR, which after correction for the presence of **11*** gave 86.9 ± 1.0% rearrangement, while the mass spectra which was nearly identical with that obtained from **6***-Br gave 90.7 ± 0.5% rearrangement (Table I).

In an attempt to capture the unrearranged carbonium ion, **6***-Br was solvolyzed in the presence of 0.5 M NaOH. However, the NMR showed that only 15% of **10*** and **10a*** were formed, and from the positions of the methoxy signals it is tentative that the main products (ca. 55%) are **12** and **12*** and the vinyl ethers **5***-OEt, **5a***-OEt, **6**-OEt, and **6a***-OEt. Hence, the NMR could not be used for analyzing the extent of rearrangement. The mass spectrum suggested an extensive rearrangement (e.g., (m/e 110)/(m/e 105) = 1.08), but the appearance of peaks with >50% abundance at m/e 278 (AnC^+PhPh^*), 217 (AnCOPh*), 212 (AnCOPh), and 135 (AnCO*) suggest that a large portion of the benzoyl and the benzhydryl peaks are derived from secondary fragmentations, and they cannot indicate the extent of the rearrangement.

Solvolysis in 80% EtOH. The solvolysis of **6***-Br in 80% EtOH (v/v) at 160 °C for 336 h gave by NMR in C_6D_6 a 6 ± 1% of **11*** and 94 ± 1% of **10*–10a*** mixture which showed 73% β-anisyl rearrangement. The mass spectrum of the crude product was temperature independent at 50–120 °C and did not show the signals of **12** and **12***. The extent of rearrangement is 83 ± 3% based on the *m/e* 110, 105 pair, while it is 87 ± 2% when based on the *m/e* 197, 202 pair.

Solvolysis in AcOH–AgOAc. Reflux of **6***-Br with two molar excess of silver acetate for 48 h gave exclusively (by NMR) a 55:45 mixture of the vinyl acetates **5***-OAc–**5a***-OAc to **6***-OAc–**6a***-OAc. (The index a represents the anisyl-rearranged species.) The mass spectral fragmentation showed that a loss of the acetoxy group leads to a base peak at *m/e* 307, which is the molecular peak of the ketones **10*–10a***. Further cleavage resembled that of the ketone and gave a temperature-independent mass spectra (Table I). The average extents of rearrangement, based on both the benzoyl and the benzhydryl signals, are 87.3 ± 0.7 and 92.7 ± 1.8%, respectively.

Basic hydrolysis of the vinyl acetates gave (by NMR) a mixture of 55.5 ± 2% of **10*** to 44.5 ± 2% of **10a*** and some of the benzophenones, **12** and **12***. The mass spectra showed >95% rearrangement due to further cleavage of **12** and **12*** and could not be used for analysis of the extent of rearrangement.

Solvolysis in TFE. The β-phenyl-rearranged trifluorethyl ether **9** is the main solvolysis product of **6**-Br in TFE–2,6-lutidine.[4b] Since **6**-Br shows common ion rate depression in this solvent,[4b] we attempted to suppress the solvolysis–rearrangement by conducting the reaction in TFE–2,6-lutidine containing 0.15 M of Bu_4NBr. The products after 240 h at 140 °C were 72% of **9**, 10% of **5***-OR, **5a***-OR, **6***-OR, and **6***-OR, and 18% of a **5***-Br–**6***-Br mixture. Determination of the extent of the degenerate rearrangement by NMR is difficult owing to the high amount of the phenyl-rearranged product. Separation of **5***-OR, **5a***-OR, **6***-OR, and **6a***-OR from the mixture was unsuccessful. The mass spectrum shows the molecular peaks of the ethers at *m/e* 389, a small anisoyl signal at *m/e* 135, and several signals similar to those obtained in the fragmentation of the ketones and suggests a complete rearrangement, since the signals at *m/e* 105 and 110 are of equal intensities.

Discussion

Comments on the Mass Spectral and NMR Methods. A priori, the mass spectral method should be very convenient to follow the rearrangements. The triarylethanones formed as products in aqueous solvents or by the hydrolysis of the vinyl acetates will give abundant substituted benzoyl and benzhydryl cations. The five mass units difference between chemically identical but isotopically different fragments ensure negligible contribution from P + 1 and P + 2 peaks.

The advantages of the method, i.e., no need for degradation, rapid analysis, accuracy, and internal consistency, are demonstrated in Table I for our reactions. However, while the ratio of the labeled and unlabeled signals is temperature independent for **10*–10a***, *it is* temperature dependent and fragment dependent for related ketones, e.g., 1,2-dianisyl-2-phenylethanone. Two reasons which are responsible for this behavior should be also considered in the present case.

(a) Mass spectral fragmentation of the solvolysis products may give one of the fragments used in the analysis by two different routes. For example, the sequence

$$\mathrm{ArCOCHArAr'} \xrightarrow{-\mathrm{CO}} \mathrm{Ar_2CHAr'^+} \longrightarrow \mathrm{Ar_2CH^+} + \mathrm{ArCHAr'^+}$$

which was observed when Ar = An,[6] will change the amount of the labeled benzhydryl fragment. Fortunately, the Ph_2CHAn fragment is of low abundance in the spectrum of **10***, and cleavage to the benzoyl and the benzhydryl signals is apparently preferred over expulsion of CO.

Table II. Extent of β-Anisyl Rearrangement during the Solvolysis of **5***-Br and **6***-Br

Substrate	Solvent	% rearrangement
6*-Br	60% EtOH	88.6 ± 1.4
6*-Br–**5***-Br (3:7)	60% EtOH	90.7 ± 0.5
6*-Br	80% EtOH	73 ± 3
6*-Br	AcOH	92.7 ± 1.8

(b) Side products which are capable to give one of the fragments used in the analysis may be formed in the reaction. An example is the formation of substituted benzophenone during the solvolysis of the vinyl bromide in basic media probably by oxidation of the benzhydryl fragment. The $\mathrm{ArAr'CO} \rightarrow \mathrm{ArCO^+}$ cleavage will change the proportion of the rearranged fragment. The extent of the $\mathrm{Ar_2CHCOAr'} \rightarrow \mathrm{Ar_2CO}$ reaction increases with the number of the anisyl groups in the triarylethanone.[3a,11] As mentioned, the extent of formation of the *p*-methoxybenzophenone from **10*** is small, and contribution from the $\mathrm{An(Ph)CO} \rightarrow \mathrm{AnCO^+}$ fragmentation is negligible.

Vinyl ethyl ethers could be formed in addition to the triarylethanones in aqueous ethanol.[2b,3a] A main fragment in the spectra of the ethers is triarylmethane,[4b,6] and cleavage to the benzhydryl fragment may complicate the mass spectral analysis. The amount of ether is very low in 60% EtOH, but the difference between the mass spectral and NMR analysis in 80% EtOH may be due to higher proportion of ethers in this solvent. In conclusion, the mass spectral analysis is suitable and reliable for our system, but caution should be exercised in generalizing this conclusion to systems substituted with more anisyl groups.

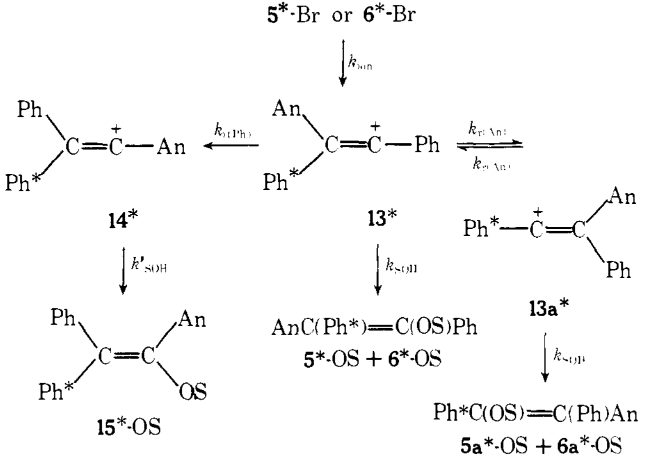
The NMR analysis is complementary to the mass spectral analysis by being able to detect side products and by avoiding undesirable fragmentations. Its limitation lies in its low accuracy with small samples, since the signal of a one methine hydrogen is used for analysis. Nevertheless, there is a close agreement between the results of the two methods. The best data are summarized in Table II.

The Nature of the Cationic Intermediate. Evidence on the nature of the intermediate cationoid species comes from the identical extents of β-anisyl rearrangement of **5***-Br and **6***-Br. If the rearrangement proceeds via initial formation of a bridged ion, **6***-Br (with the potentially participating β-anisyl at trans position to the bromine) would give a higher extent of β-anisyl rearrangement than **5***-Br, contrary to what was observed. If the rearrangement occurs at the ion pair stage, it is plausible that, similarly to the extra inversion which was found for vinylic solvolysis via ion pairs,[12] shielding by the leaving group in an ion pair would reduce the rearrangement from its side, giving higher extent of β-anisyl rearrangement from **6***-Br. Hence, the identical extents of rearrangement from **5***-Br and **6***-Br and the formation of ca. 1:1 mixture of **5**-OAc and **6**-OAc in AcOH or 5-OR and 6-OR in TFE[4b] are consistent with product formation from the free linear 2-anisyl-1,2-diphenylvinyl cation **13*–13a***. A similar argument suggests that the β-phenyl rearrangement occurs via the same free ion.[4b]

Migratory Aptitudes of β-Anisyl and β-Phenyl Groups in Vinylic Systems. In β-aryl rearrangement to a cationic terminus in saturated systems, β-*p*-anisyl shows, generally, a superior migratory aptitude compared with β-phenyl.[9] The β-anisyl/β-phenyl migratory ratios are ca. 6–500 for solvolysis[9a-c] and related reactions, e.g., the Schmidt rearrangement,[9d] and much lower (ca. 1.2–2.0) in the deamination reaction.[9e] The differences may be ascribed to different extents of assistance by the β-aryl group during the heterolysis.[9e] However, a migration ratio >1 should not necessarily be the same in vinylic rearrangements. First, some of the literature values may reflect conformational or participation effects and may not be applicable for migration in free ions. Indeed, Bonner and Putkey found a lower extent of β-anisyl rearrangement in the deamination of 1,2,2-trianisylethylamine[10] than of β-phenyl migration in the deamination of 1,2,2-triphenylethylamine,[8d] which proceeds via open ions. This difference may be due to a different charge distribution in the migration terminus in both systems.[10] Second, the gain in the bridging by charge dispersal over the migrating group may be overcome by an opposing effect of the loss of ground-state conjugation stabilization of the migrating group and the double bond. If the latter effect is more important than the former for anisyl compared with phenyl, a migration ratio <1 may be obtained. Our study enables us to determine the ratios both by internal and by external comparisons.

We suggested above that free ions are the cationoid species involved in the degenerate migrations of **5***-Br and **6***-Br. Scheme III shows the two degenerate ions **13*** and **13a***, the phenyl-rearranged α-anisylvinyl cation **14***, and the products derived from them. The rate constants are k_{ion} for the ionization, $k_{\text{r(Ph)}}$ for the phenyl rearrangement, $k_{\text{r(An)}}$ for the anisyl rearrangement, and k_{SOH} and k'_{SOH} for the capture processes by the solvents. Isotope effects on these constants, which should be very small, were neglected. Since solvolysis of 1-anisyl-2,2-diphenylvinyl bromide gives only unrearranged products,[3a] the **13*** → **14*** process was regarded as irreversible. A steady-state treatment of the cationoid intermediates in Scheme III or an analogous treatment by Collins[8d] gave the following connections between the product distribution and the rate coefficients (eq 6 and 7).

Scheme III



SOH = AcOH, TFE, and H_2O (in aqueous EtOH)

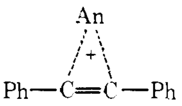
$$[\mathbf{15^*}\text{-OS}]/([\mathbf{5^*}\text{-OS}] + [\mathbf{5a^*}\text{-OS}] + [\mathbf{6^*}\text{-OS}] + [\mathbf{6a^*}\text{-OS}]) = k_{\text{r(Ph)}}/k_{\text{SOH}} \qquad (6)$$

$$([\mathbf{5^*}\text{-OS}] + [\mathbf{6^*}\text{-OS}])/([\mathbf{5a^*}\text{-OS}] + [\mathbf{6a^*}\text{-OS}]) = 1 + (k_{\text{SOH}}/k_{\text{r(An)}}) \qquad (7)$$

The data of Table II and previous data on the extent of β-phenyl rearrangement[4b] gave $k_{\text{r(An)}}/k_{\text{SOH}} = 4.0$ and $k_{\text{SOH}}/k_{\text{r(Ph)}} = 19$, leading to the combined reactivity order: $k_{\text{r(An)}}:k_{\text{SOH}}:k_{\text{r(Ph)}}$ of 76:19:1 in 60% EtOH. By using the value of 92.7 ± 1.8% as the extent of the rearrangement in AcOH, a $k_{\text{r(An)}}/k_{\text{SOH}}$ ratio of 6.35 is obtained. The β-phenyl-rearranged ester, **15***-OAc, is not observable in the NMR and by assuming that 5% is the limit of its detection, then $k_{\text{r(An)}}:k_{\text{SOH}}:k_{\text{r(Ph)}} = 120:19:1$ in AcOH. It should be emphasized that a relatively small error in the extent of the rearrangement results in a very high relative error in these ratios: As the percentage of rearrangement approaches 100%, the ratio on the left-hand side of eq 7 approaches unity, making the $k_{\text{SOH}}/k_{\text{r(An)}}$ ratio extremely sensitive to the first and second decimal digits in the unrearranged/rearranged ester ratio. For example, the experimental value of 92.7 ± 1.8% rearrangement in AcOH, which reflects 2.3% difference between the highest and the lowest values in the percentages of the rearranged ester, lead to $k_{\text{r(An)}}/k_{\text{SOH}}$ ratios which differ by 70% (5.0 and 8.6 in the two extremes). The low extent of the phenyl rearrangement results in a high error in the $k_{\text{r(Ph)}}/k_{\text{SOH}}$ ratio according to eq 6. A difference of 1% in [**15***-OAc] changes the $k_{\text{SOH}}/k_{\text{r(Ph)}}$ ratio from 19 to 25. Hence, the combined error in the $k_{\text{r(An)}}/k_{\text{r(Ph)}}$ ratio is rather high.[13]

Although these errors are important when discussing the actual reactivity ratios, it is clear that the $k_{\text{r(An)}}/k_{\text{r(Ph)}}$ ratios are rather high in the three solvents investigated. The same conclusion probably also holds for TFE, where in spite of the experimental difficulties, the mass spectra suggest a complete β-anisyl rearrangement. Moreover, complete β-anisyl rearrangement of labeled trianisylvinyl bromide and an extensive β-phenyl rearrangement of labeled 1,2-dianisyl-2-phenylvinyl bromide were found in TFE.[6] Comparison with data for other solvents show that the extent of the degenerate rearrangements in TFE is much higher, supporting a tentative value of >99.5% β-anisyl rearrangement for **6***-Br in TFE. Comparison of this value and the observed value of 85% β-phenyl rearrangement[4b] gave $k_{\text{r(An)}}:k_{\text{r(Ph)}}:k_{\text{SOH}}$ ratios of >100:5.7:1, i.e., $k_{\text{r(An)}}/k_{\text{r(Ph)}}$ ratio of ≥18.

The $k_{\text{r(An)}}/k_{\text{r(Ph)}}$ ratios, which are based on competing migrations in the ion **13***, reflect differences in the transition state energies of the two rearrangements since the ground state is identical. In terms of the transition states **16** and **17** for anisyl and phenyl migration in the open ions,



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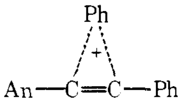

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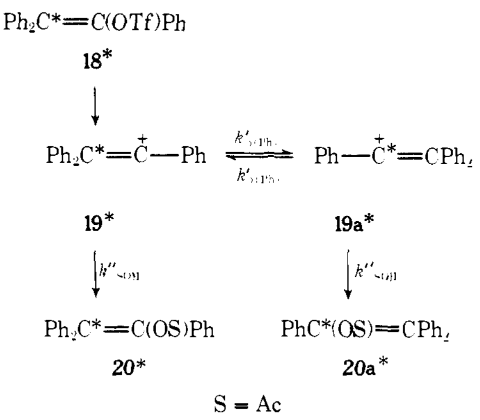
these differences arise from combination of three terms: (a) a better bridging by anisyl compared with phenyl; (b) a higher loss of π(migrating Ar)-π(C=C) conjugation when Ar = An compared with Ph; (c) a difference in the charge stabilizing ability of the bridged species by the nonmigrating aryl group.

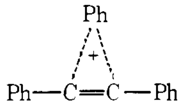
The similarity of the ratios for vinylic and saturated systems suggest that factor b is of little importance. The same conclusion is obtained by comparing systems where both the ground-state and the transition-state effects may be important. Lee[5a,b] found recently that the acetolysis of labeled triphenylvinyl triflate **18*** in AcOH-AgOAc with or without NaOAc shows 13.4 ± 0.2% of degenerate β-phenyl rearrangement. By assuming that Scheme IV describes the rearrangement[14] and application of equation similar to eq 7, together with the experimental [**20***]/[**20a***] ratio of 13.9, we obtained $k''_{\text{SOH}}/k'_{\text{r(Ph)}} = 12.9$. A reasonable assumption is that the capture rates of the cations **19***, **19a***, **13***, and **13a*** are identical in AcOH since replacing a β-anisyl by a β-phenyl substituent should not affect much the

Scheme IV



capture rate, and according to this assumption k_{SOH} = k''_{SOH}.

Comparison of the **13*** ⇌ **13a*** with the **19*** ⇌ **19a*** rearrangements, which proceed, respectively, via the transition states **16** and **21**, should give $k_{r(An)}/k_{r(Ph)}$ ratios which will reflect a combination of factors a and b above, since factor c is identical in both reactions. Comparison of the rearrangement ratios gives $k_{r(An)}/k_{r(Ph)}$ of 82 in AcOH. The similarity of the ratio obtained by external comparison of



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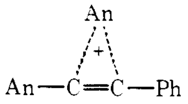
two different substrates with that obtained by internal comparison of two rearrangements of one substrate (**6***-Br) supports the conclusion that a differential ground-state $\pi(\beta\text{-Ar})$-π(C═C) conjugation between β-phenyl and β-anisyl groups has little influence on the extent of β-aryl rearrangement. This is not surprising since much of the moderate expected π(Ar)-π(C═C) conjugation is lost in **13***, since interaction between the two β-aryl groups twist both of them from the plane of the double bond.

Solvent Effect. The extent of the β-anisyl rearrangement is high in all the solvents studied, but the analysis above suggests that the small differences reflect high difference in the rearrangement vs. capture ratios. It is not surprising that the solvent effect on the $k_{r(An)}/k_{SOH}$ ratios follows the order TFE < AcOH < 60% EtOH < 80% EtOH, which is the order of increasing nucleophilicity[15] (i.e., of increasing k_{SOH}) of these solvents.

β-Anisyl Rearrangement as a Function of the Migration Origin and Terminus. The β-anisyl rearrangement in **13*** fills a gap in the sequence of migrations of this group between phenyl- and anisyl-substituted migration origin and terminus. Thus, in AcOH, the rearrangement of the ion **3** via the transition state **22** is complete, while recent data on the degenerate rearrangement in the trianisylvinyl cation **23**[5c,6] via the transition state **24** shows ca. 40% rearrangement. The corresponding rate ratios of rearrangement vs. capture by AcOH/AcO⁻, $k_{r(An)}/k_{AcOH}$, are given in Table III.



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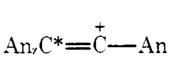

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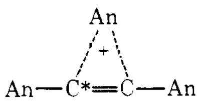

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Since transition states **16** and **22** differ only in the nonmigrating aryl group, the higher extent of migration in **3** reflects the higher charge stabilization by this substituent in the bridged ion.[16] A more important effect is the nature of the α-aryl group. Since capture of the less selective α-phenylvinyl cation will be faster than that of an α-anisylvinyl cation, the difference in the $k_{r(An)}/k_{AcOH}$ ratio for **3** and **23** reflects a lower limit for the rearranging ability to a phenyl vs. anisyl-substituted terminus. This value should be, therefore, much higher than 60 (Table III) and is accounted for by the much higher electrophilicity of the α carbon in the α-phenylvinyl cation as compared with the α-anisylvinyl cation, where the positive charge is effectively spread over the anisyl group. A similar trend was observed in the deamination of the 1,2,2-triarylethylamines,[17] which proceeds via saturated transition states analogous to **22** and **24**.

Table III. $k_{r(An)}/k_{AcOH}$ Ratios for β-Anisyl Migrations in AcOH

Precursor ion	Transition state	$k_{r(An)}/k_{AcOH}$
3	**22**	>20
13*	**16**	6.35
23	**24**	0.33

In summary, the higher charge stabilizing ability of an anisyl compared with a phenyl group is manifested whether these groups are at the migration origin, at the migration terminus, or are the migrating groups themselves.

β-Aryl Rearrangement as a Factor in the Selectivity of Triarylvinyl Cations. The high selectivity of triarylvinyl cations, judged by the occurrence of common ion rate depression in the solvolysis of triarylvinyl bromides, such as **6**-Br,[2,3d,e,4b] was attributed to increased lifetime of the cation due to steric shielding of the cationic orbital by the α- and β-aryl substituents.[2,3d,e] However, it could be argued that for ion **13*** very rapid β-aryl rearrangements contribute to the selectivity of the ion by effectively excluding the solvent and the leaving group from the side of the orbital where the migration takes place.

The degenerate rearrangement should reduce the capture of the ion from the side where it takes place, and the extent of this effect will be determined by the relative rates of aryl rearrangement vs. capture. Hence, it will be of different importance at the two sides of the cationic orbital, being less important for **13*** from the side of the slower rearranging phenyl group. Consequently, capture from this side should be dominant if the effect is important. Experimentally it was found that either in TFE, where both β-phenyl[4b] and β-anisyl rearrangements are important, or in AcOH, where only the β-anisyl rearrangement is important,[4a] the product composition is close to 1:1 of the cis-trans mixture of the products. We conclude that windshield wiper effect cannot be an important contributor to the selectivity of the ion **13***.

Experimental Section

Melting points were determined with a Fisher-Johns apparatus. Ir spectra were recorded with a Perkin-Elmer 257 instrument. NMR spectra were recorded with a Varian T-60 or HA-100 instruments, and the chemical shifts are given in δ units downfield from internal tetramethylsilane. Mass spectra were recorded on a MAT 311 spectrometer. TLC was carried out on silica gel G plates with light petroleum (bp 60–80 °C) containing 10–20% acetone as the eluent. Solvolysis (in sealed ampules) and work-up procedures were previously described.[4b]

Solvents and Materials. Ethanol was purified according to Lund and Bjerrum.[18] EtOH (60 or 80%, v/v) was prpared with conductivity water. 2,6-Lutidine was distilled from solid KOH. Acetic acid was purified as previously described.[4b]

2-Anisyl-2-pentadeuteriophenyl-1-phenylvinyl Bromides (5*-Br and 6*-Br). (a) **2-Anisyl-2-pentadeuteriophenyl-1-phenylethanol.** A solution of 1-*p*-methoxyphenyl-2-phenylethanone (10.3 g, 45 mmol) in dry ether (100 ml) was added slowly to a solution of pentadeuteriophenylmagnesium bromide, prepared from pentadeuteriobromobenzene (10 g, 62.5 mmol) and magnesium (1.5 g, 62.5 mg-atoms) in dry ether (50 ml). The solution was refluxed for 1 h; the mixture was poured into 3 M aqueous ammonium chloride solution (200 ml) and extracted twice with ether (250 ml). The organic layer was washed with water, dried ($MgSO_4$), and evaporated, giving 13.5 g (95%) of 2-*p*-methoxyphenyl-2-pentadeuteriophenyl-1-phenylethanol, which was crystallized to a solid, mp 112 °C (lit.[19] 112 °C) from ethanol.

(b) **2-Anisyl-2-pentadeuteriophenyl-1-phenylethylenes.** The triarylethanol (13 g, 42 mmol), which was obtained in the preceding section, was refluxed with 10% H_2SO_4 (150 ml) for an hour. After cooling, the mixture was extracted with chloroform, the organic layer was washed with water, sodium bicarbonate, and water, dried ($MgSO_4$), and the solvent was evaporated, giving an oil (11.7 g, 96%) which by NMR is a 1:1 mixture of cis and trans ethylenes: δ (CCl_4) 3.70, 3.73 (3 H, 2 s of equal intensity, MeO), 7.00 (4 H, center of AA′BB′ q, An), 6.95, 7.00 (5 H + 1 H, 2 s, Ph + CH).

(c) **5*-Br and 6*-Br.** To a cooled solution of the above ethylene (11 g, 38 mmol) in acetic acid (70 ml), bromine (7 g, 43 mmol) was added dropwise, and the temperature was kept below 40 °C. The solution was refluxed for 2.5 h, water was added to turbidity, and the solution was cooled. The oil so obtained was decanted, and the isomers were purified by repeated crystallization from ethanol. The pure trans isomer (**6***-Br) had mp 117–119 °C (lit.[19] 118–120 °C for **6**-Br): ν_{max} 1296, 1240, 1175, 1148, 1107, 1040, 959, 690, 610, and 555 cm^{-1}; δ (CCl_4) 3.74 (3 H, s, MeO), 6.73–7.39 (9 H, m, An + Ph); *m/e* 372, 370 (20%, 20%, M), 290 (100%, M − Br), 275 (19.5%, M − Br − Me), 258 (22%, M − Br − MeOH), 257 (21%), 246 (16%), 244 (13%), 243 (13%), 170 (6%), and 165 (8%).

Anal. Calcd for $C_{21}H_{12}D_5BrO$: C 68.18; H, 4.74. Found: C 68.36; H, 4.69. Also isolated was a *cis*-(**5***-Br) and *trans*-(**6***-Br) mixture (70:30), mp 90–110 °C (lit.[19] mp of pure **5**-Br 97–98 °C). The mass spectrum of the mixture was identical with that of **6***-Br. The ir spectrum was similar to that of an authentic 70:30 cis–trans mixture.

2-Anisyl-2-pentadeuteriophenyl-1-phenylethanone (**10***). A solution of 4-methoxybenzoin (0.6 g, 2.5 mM) in THF (10 ml) was added dropwise to a solution of pentadeuteriophenylmagnesium bromide, prepared from pentadeuteriobromobenzene (2.5 g, 15 mmol) and magnesium (0.4 g, 16 mg-atoms) in THF (13 ml). The solution was refluxed for 4 h. Ice-cooled 2% sulfuric acid was added and the product extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated under vacuum. The oil so obtained was refluxed in 10% sulfuric acid (15 ml) for 2 h. The solution was poured into ice-water, extracted with carbon tetrachloride, washed with aqueous sodium carbonate and water, dried ($MgSO_4$), and evaporated under reduced pressure. Purification by TLC afforded pure **10***, mp 85–86 °C from ethanol (lit.[4b] 85–89 °C for unlabeled **10**): δ ($CDCl_3$) 3.73 (3 H, s, OMe), 5.84 (1 H, s, CH) 6.75, 7.10 (4 H, AA′BB′ q, J = 9 Hz, An), 7.54 (3 H, m, meta and para protons of Ph), and 8.06 (2 H, m, ortho protons of Ph); *m/e* 307 (4.5%, M), 202 (100, An(C_6D_5)CH^+), 135 (38, AnCO), 105 (28, $PhCO^+$).

Stability of 10* in 60% Ethanol. A sealed ampule of **10*** (71 mg, 23.2 mmol) in 0.08 M solution of 2,6-lutidine in 60% ethanol (5 ml) was left at 160 °C for 240 h. The solvent was removed under reduced pressure. The NMR and mass spectrum of the residue were identical with those of the starting material, indicating the absence of anisyl rearrangement in **10*** at our analytical conditions.

Basic Hydrolysis of 6*-OAc + 6a*-OAc. The product (100 mg) from the solvolysis of **6***-Br in acetic acid was refluxed in ethanol-water 1:1 (50 ml) containing potassium carbonate (0.5 g) for 2 h. The solution was poured into water and the product extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. TLC of the residue indicated a quantitative transformation of the acetates into the ketones **10*–10a***.

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