in the tertiary system due to the conformation of the aryl ring [for example, see N. L. Allinger and M. T. Tribble, *Tetrahedron Lett.*, 3259 (1971)], or some other factor.

(13) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970); J. K. Fry, C. L. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970); J. M. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2542 (1970).

(14) (a) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 132 (1975); (b) A. Miotti and A. Fava, *ibid.*, **88**, 4274 (1966).

(15) S. Winstein, B. K. Morse, E. Grunwald, K. C. Shreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

(16) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

(17) For a review, see P. R. Story and B. C. Clark in "Carbonium Ions" (ref 5c), Chapter 23.

(18) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 7454 (1975).

(19) (a) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963); (b) B. A. Hess, Jr., *J. Am. Chem. Soc.*, **93**, 1000 (1971).

(20) S. Winstein, H. Walborsky, and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

(21) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 7920 (1972).

(22) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2398 (1973).

(23) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 7442 (1975).

(24) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 5899 (1972).

(25) (a) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 2900 (1975); (b) R. A. Sneen, *ibid.*, **80**, 3982 (1958); (c) P. G. Gassman and D. S. Patton, *ibid.*, **91**, 2160 (1969).

(26) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 7449 (1975).

(27) H. C. Brown, S. Ikegami, and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5909 (1969).

(28) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5911 (1969).

(29) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95**, 2400 (1973).

(30) For recent reviews, see (a) H. G. Richey, Jr., in "Carbonium Ions" (ref 5c), Chapter 25; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, *ibid.*, Chapter 26.

(31) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).

(32) (a) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968); (b) E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973).

(33) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951); R. H. Mazur et al., *ibid.*, **81**, 4390 (1959).

(34) Data for **6** taken from H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956), and corrected for difference in solvent and leaving group (i.e., $7.42 \times 10^{-13}\ \mathrm{s^{-1}}$).

(35) For example, ^{1}H NMR data are consistent with classicial 1-phenylcyclobutyl cation; see G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Am. Chem. Soc.*, **94**, 146 (1972).

(36) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); (b) H. C. Brown and E. N. Peters, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 132 (1974).

(37) H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).

(38) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).

(39) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*,, **87**, 376 (1965).

(40) (a) H. L. Goering and J. V. Clevenger, *J. Am. Chem. Soc.*, **94**, 1010 (1972); (b) H. L. Goering and K. Humski, *ibid.*, **90**, 6213 (1968). (c) For benzhydryl *p*-nitrobenzoates, see H. L. Goering and H. Hopf, *ibid.*, **93**, 1224 (1971).

(41) A. Fentiman, Jr., Ph.D. Thesis, The Ohio State University, 1969.

Vinylic Cations from Solvolysis. 24.[1] Degenerate β-Aryl Rearrangements during the Solvolysis of 1,2-Dianisyl-2-phenylvinyl Bromides and Trianisylvinyl Bromide. Free Vinyl Cations as Intermediates

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Abstract: The degenerate β-phenyl rearrangement in the 1,2-dianisyl-2-phenylvinyl cation (**8**) and the β-anisyl rearrangement in the trianisylvinyl cation (**13**) were studied by using the precursor bromides labeled by β-$\mathrm{CD_3OC_6H_4}$ groups. In AcOH, $\mathrm{Me_3CCOOH}$, or aqueous EtOH, **8** does not rearrange at all or only to a small extent, while 53 ± 6% of β-phenyl rearrangement was found in TFE. Ion **13** shows 11.5, 35, 0, and 100% β-anisyl rearrangement in 60% EtOH, AcOH, $\mathrm{Me_3CCOOH}$, and TFE, respectively, and it can be captured by $\mathrm{Br^-}$ before rearrangement in AcOH and TFE. It is suggested that the rearrangement proceeds via free open vinyl cations, whose selectivity is not due to a rapid migration of the β-aryl group between a pair of degenerate vinyl cations. The direction and extent of rearrangement in phenyl- and anisyl-substituted triarylvinyl cations are determined by the better charge dispersal ability of the anisyl group, either in the ground or transition state. Low nucleophilicity and high dissociation power of the solvent favor the rearrangement, making TFE the best medium for these reactions. Relative rate constants for reactions of triarylvinyl cations (capture by $\mathrm{Br^-}$ (k_{Br}), capture by the solvent (k_{SOH}), β-phenyl migration ($k_{\mathrm{r(Ph)}}$), and β-anisyl migration ($k_{\mathrm{r(An)}}$)) were evaluated. E.g., k_{Br} (1 M $[\mathrm{Br^-}]$)$:k_{\mathrm{r(An)}}:k_{\mathrm{SOH}} = 78{:}25{:}1$ for **13** in TFE, and k_{Br} (1 M $[\mathrm{Br^-}]$)$:k_{\mathrm{SOH}}:k_{\mathrm{r(Ph)}} = 21{:}1{:}{<}0.01$ for **8** in AcOH. The possible use of degenerate rearrangements for obtaining the heterolysis rate in nonsolvolytic media and the effect of the α substituent on the nature of the cationic intermediate are discussed. The limitations of the mass spectral and the NMR analyses in studying the degenerate rearrangements are scrutinized.

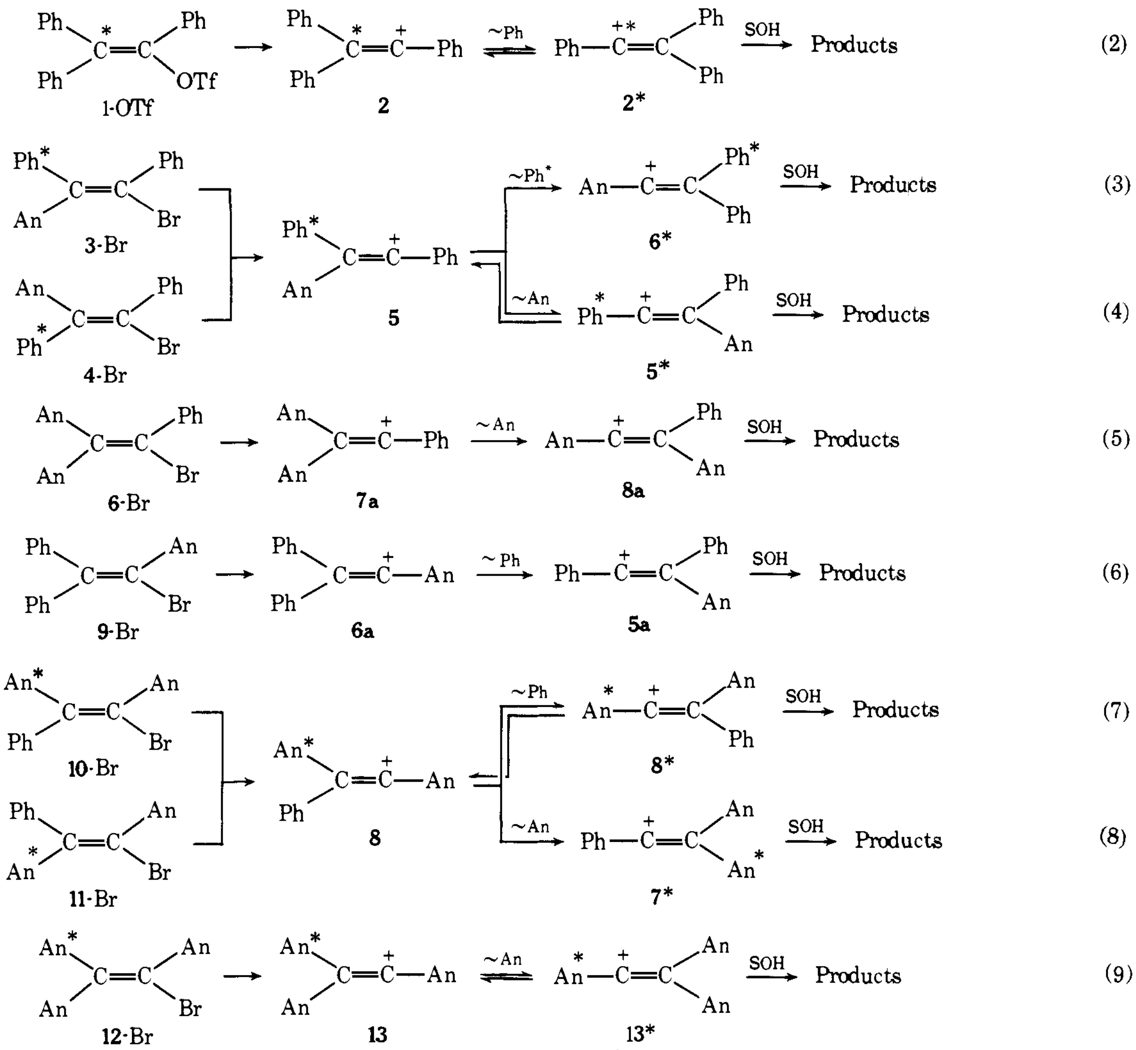
The cationoid intermediates formed in the solvolysis of triarylvinyl halides or sulfonates participate in a variety of processes, such as capture by the leaving group,[2,3] the solvent,[2,3] or other nucleophiles,[2,3,4] and rearrangement of a β-aryl group across the double bond.[5]

$$\mathrm{Ar^3Ar^2C{=}C(X)Ar^1} \xrightarrow{-\mathrm{X^-}} \mathrm{Ar^3Ar^2C{=}C^+{-}Ar^1}$$
$$\rightleftharpoons \mathrm{Ar^3{-}{}^+C{=}CAr^1Ar^2} + \mathrm{Ar^2{-}{}^+C{=}CAr^1Ar^3} \quad (1)$$

The extent of the rearrangement and the stereochemistry of its products depend on several factors: the relative stability and the capture vs. rearrangement rates of the rearranged and unrearranged ions; and the nature of the cationoid intermediate, whether it is bridged[6] or open.[5]

Substituent and solvent effects on the β-aryl rearrangement across the double bond will be better understood if a series of closely related reactions are compared. Triarylvinyl systems substituted by all the possible combinations of phenyl and anisyl groups provide such a series as shown in Scheme I (eq 2-9).[7] The precursors are four α-phenyl- and four α-anisyl-substituted systems, where each subseries includes a pair of geometrical isomers. Two compounds are di-β-phenyl and two compounds are di-β-anisyl substituted, and the other four are

Scheme I



$OTf = OSO_2CF_3$

SOH = Solvent

β-anisyl-β-phenyl derivatives. There are four possible β-anisyl rearrangements and four β-phenyl rearrangements, and two of each type are degenerate rearrangements. A study of the extents of these reactions in different solvents will be useful in elucidating the nature of the rearrangement reaction.

All the reactions of Scheme I were investigated either by Lee et al.[8] or by us.[1,5] However, while systems **1**, **3**, **4**, and **6** were studied extensively, the degenerate rearrangements of the 1,2-dianisyl-2-phenylvinyl (**10**-Br, **11**-Br) and the trianisylvinyl (**12**-Br) bromides were studied by Oka and Lee only in carboxylic acid media,[8c,d] and additional evidence concerning the nature of the intermediates is required. We then used a different labeling pattern and studied these two systems in a variety of solvents in an attempt to answer five questions:

(a) What is the nature of the cationoid intermediates in these reactions, and is there a correlation between the nature of the α substituent and the type of the cationoid intermediate in rearrangement across the double bond?

(b) Is the selectivity of triarylvinyl cations[2,3] due to a combination of steric and electronic effects which operate in "static" vinyl cations, or is there a "dynamic" equilibrium between two degenerate cations that accounts for this selectivity?

(c) What are the effects of the α- and β-aryl groups, the migrating group, and the solvent on the extent of the rearrangement?

(d) What are the relative reactivities of these vinyl cations in rearrangement, capture by the solvent, and external ion-return processes?

(e) Can the heterolysis rate in nonsolvolytic media be evaluated from the extent of the degenerate rearrangement in these media?

In addition, we wanted to evaluate the usefulness of the mass spectral and the proton NMR analytic methods for the study of degenerate rearrangements in the triarylvinyl systems.

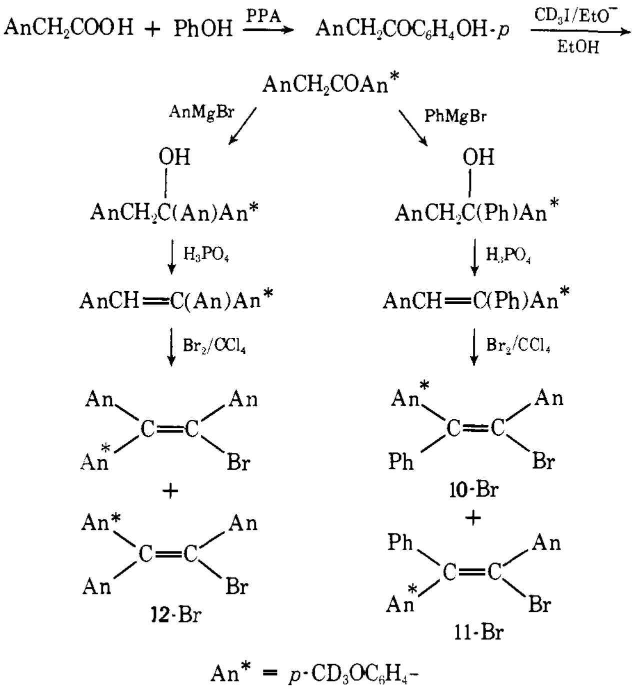
Results

For the degenerate rearrangements we used compounds **10**-Br, **11**-Br, and **12**-Br labeled by a β-*p*-(trideuteriomethoxy)phenyl group. The synthetic pathways are given in Scheme II. *p*-Hydroxy-α-*p*-methoxyphenylacetophenone was obtained by condensation of *p*-methoxyphenylacetic acid with phenol in polyphosphoric acid. This method gives only a 7% yield, but it has an advantage over the demethylation of deoxyanisoin,[9] which produces and requires separation from the isomeric α-*p*-hydroxyphenyl-*p*-methoxyacetophenone. The other reactions follow the usual pattern of preparation of triarylvinyl bromides.[4] Stereospecific labeling is not expected in the formation of labeled trianisylvinyl bromide. Its NMR showed three methoxy signals in a 1:2:1 ratio, indicating the formation of a 1:1 mixture of the two isomeric bromides, where the larger signal corresponds to the α-anisyl group; and the mixture was designated **12**-Br.

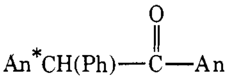
A mixture of **10**-Br and **11**-Br was obtained, and complete separation by repeated crystallization could not be achieved on our preparative scale. A 5:1 mixture of **10**-Br–**11**-Br was mostly used.

Solvolysis and Rearrangement of 2-*p*-(Trideuteriom-

Scheme II

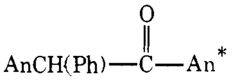


ethoxy)phenyl-1-*p*-methoxyphenyl-2-phenylvinyl Bromides (10-Br and 11-Br). (**a**) **In 60% EtOH.** A 5:1 mixture of **10**-Br-**11**-Br was kept in 60% EtOH buffered by 2,6-lutidine for 17 h at 125 °C. The only products obtained were the ketones **14** and **14***. From the 96:4 ratio of the methoxy signals at δ 3.70 (for **14**) to that at δ 3.67 (for **14***) in CDCl$_3$ a value of 8 ± 2% was calculated for the β-phenyl rearrangement via the open free ion.[10] This is an upper limit, since the position of the δ 3.67 signal was slightly concentration dependent, and its presence might be attributed either completely or partially to the methoxy signal of a small amount of *p*-methoxybenzophenones **15** and **15a** which may be formed during the solvolysis.



$$An^{*}CH(Ph)-\overset{O}{\overset{\|}{C}}-An$$

14



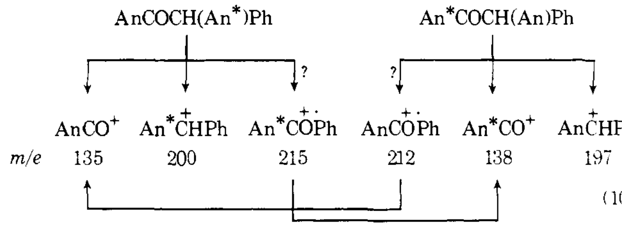
$$AnCH(Ph)-\overset{O}{\overset{\|}{C}}-An^{*}$$

14*

An*COPh
15

AnCOPh
15a

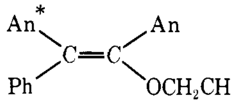
Mass spectral analysis was conducted on the crude reaction mixture. Metastable peak analysis on the precursor ion corresponding to **14-14*** showed that the daughter peaks are the anisoyl and the *p*-methoxybenzhydryl signals. We expected to get the same extent of rearrangement from the pairs of ions at *m/e* 135, 138 and 197, 200 (eq 10). However, different results were obtained from each of these pairs, as well as from the signals at *m/e* 212 and 215, which correspond to the ions derived from **15** and **15a**. Moreover, the signal ratio in each pair was strongly dependent on the fragmentation temperature (cf. Table VI in the Experimental Section).



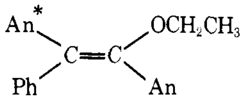
(10)

We attribute this discrepancy to two reasons. The small peaks observed for **15** and **15a** may be formed either from the cleavage of **14-14*** during the reaction or the mass spectral cleavage of **14-14***. A metastable ion spectra of the precursor ion at *m/e* 212 (**15a**) shows daughter peaks at *m/e* 135 (main peak) and 105. Hence, the ions at *m/e* 135 and 138 may be formed from **15-15a**, thus invalidating any conclusion based on these fragments, as demonstrated in eq 10. The analysis of the benzhydryl signals seems a priori more reliable, but the temperature dependence indicates complications with these peaks too. The mass spectra of **14-14*** show a small fragment at *m/e* 307, formed by a loss of a CO molecule. Metastable ion spectra of this precursor ion showed broad daughter peaks at *m/e* ca. 273 (M − MeO, M − OCD$_3$), 230 (An(An*)CH$^+$), and 197-200 (An(Ph)CH$^+$ and An*(Ph)CH$^+$). The intensity of the fragment at *m/e* 230 greatly exceeds that of *m/e* 197-200 and this cleavage apparently contributes little to the overall formation of the *p*-methoxybenzhydryl peak. Hence, the value based on the benzhydryl fragment should be considered as an upper limit for the extent of the rearrangement.

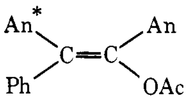
(**b**) **In 80% EtOH.** Solvolysis under the same conditions in 80% EtOH gives the ketones **14-14*** and small quantities of the ethers **10**-OCH$_2$CH$_3$ and **11**-OCH$_2$CH$_3$. The overlap of the signals of the methylene quartet and the methoxy signals of the ethers and ketones resulted in a very approximate value of 14 ± 3% of **14*** in the ketone fraction. The mass spectrum showed the same signals as in 60% EtOH, in addition to the base peak of the ethers at *m/e* 363. From the benzhydryl signals a value of 2.0 ± 0.7% for **14*** in the ketone mixture was evaluated (Table VI). This is an upper limit not only for the reasons stated above, but also because fragmentation of the ethers can also contribute to these signals.



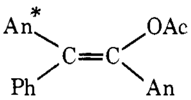
10-OCH$_2$CH$_3$



11-OCH$_2$CH$_3$



10-OAc

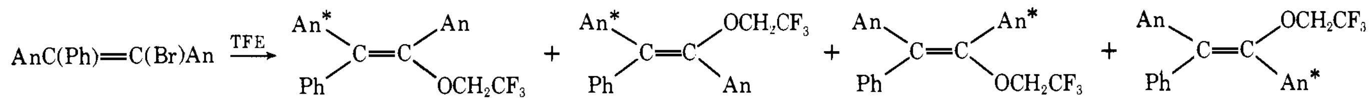


11-OAc

(**c**) **In AcOH.** Reaction of a 5:1 mixture of **10**-Br-**11**-Br with 2 mol equiv of NaOAc in AcOH for 187 h at 120 °C gave 72% of a 1:1 mixture of the acetates **10**-OAc and **11**-OAc, and 28% of **14-14***. In the acetate fraction only two methoxy signals of equal intensities at δ 3.68 and 3.70 appear in the expanded 100-MHz spectrum. Since the unlabeled cis acetate has methoxy signals at δ 3.67 and 3.68 and the unlabeled trans acetate at δ 3.70 and 3.76,[4b] we concluded that no rearrangement took place within the detection limits (±3%).

The mass spectra showed a main signal for triarylethanone at M − 42. The relative intensities of the pairs of aroyl, substituted benzhydryl, and substituted benzophenone fragments which are apparently derived from it were strongly temperature dependent (Table VI). Based on the benzhydryl fragment, the rearranged acetates consist of ≤3.5 ± 1% of the total vinyl acetates. However, most of these fragments may be derived from the ion at *m/e* 307, which is also formed from the vinyl acetates. Indeed, this was verified by a metastable ion spectra of this ion.

When a similar mixture of **10**-Br and **11**-Br was solvolyzed in the presence of 0.077 M Bu$_4$NBr and 0.011 M NaOAc for 6 h (1.2 solvolytic half-lives) at 120 °C, isomerization of the vinyl bromides to their equilibrium mixture (54% **10**-Br:46% **11**-Br)[2a] took place. Only the methoxy signals of the α-anisyl groups were observed at δ (CDCl$_3$) 3.67 (**10**-Br) and 3.80 (**11**-Br), and none of those of the β-anisyl groups at δ 3.70 (**10**-Br) and 3.73 (**11**-Br). The extent of rearrangement is therefore <3%.



10-OCH$_2$CF$_3$ 11-OCH$_2$CF$_3$ 10*-OCH$_2$CF$_3$ 11*-OCH$_2$CF$_3$

δ (CDCl$_3$) 3.62 3.60 3.68 3.57 (11)

(d) In Pivalic Acid. Reaction of a 5:1 mixture of **10**-Br-**11**-Br in pivalic acid/sodium pivalate for 48 h at 160 °C gave only ca. a 1:1 mixture of **10**-Br-**11**-Br. Neither the β-phenyl rearranged product nor the pivalolysis products were observed by NMR.

(e) In TFE. Trifluoroethanolysis of a 5:1 mixture of **10**-Br-**11**-Br in TFE buffered by 2,6-lutidine gave a mixture of the rearranged and unrearranged cis and trans trifluoroethyl vinyl ethers (eq 11). Signals for both the α-methoxy groups (δ (CDCl$_3$) 3.60 and 3.62) and the β-methoxy groups (δ 3.57 and 3.68)[5b] were observed, and 53 ± 6% rearrangement was determined from the ratio of the intensities of the signals at δ 3.68-3.62. The error is rather large due to the proximity of the four signals.

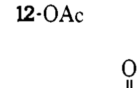
(f) In 1:1 AcOH-HCOOH (v/v). Solvolysis of either a 5:1 or a 3:2 mixture of **10**-Br to **11**-Br in 1:1 AcOH-HCOOH buffered by NaOAc for 21 h at 25 °C gave 75% of the ketones **14**-**14***, and 15% of the vinyl acetates **10**-OAc and **11**-OAc together with the rearranged acetates. The remainder are presumably the vinyl formates, since their molecular peak at *m/e* 353 was observed as a small signal in the mass spectra.

From the NMR of the methoxy signals, **14*** consists of 34 and 28% of the ketones in the two experiments, respectively. The mass spectral method is an unreliable guide to the extent of the rearrangement, due not only to the complications mentioned above, but also to the fact that metastable ion spectra of the ion at *m/e* 353 show daughter ions at *m/e* 308 for triarylmethane, and peaks derived from it at *m/e* 230, 200, 197, and 135.

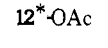
Control experiments showed that **14** forms 17% of **14*** under the reaction conditions. Consequently, neither the NMR method nor the mass spectral method gives the extent of rearrangement via the vinyl cation.

(g) In Acetonitrile. A 0.044 M solution of a mixture of 59% of **10**-Br and 41% of **11**-Br and 0.08 M 2,6-lutidine was kept in acetonitrile at 120 °C for 508 h. After workup, only the two α-methoxy signals at δ 3.70 and 3.73 of the unrearranged bromides were observed. Apparently, no degenerate rearrangement took place. Some small unidentified signals were observed at δ 3.71, 3.75, and 3.79.

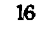
Solvolysis of 1,2-Dianisyl-2-*p*-(trideuteriomethoxy)phenylvinyl Bromide (12-Br). (a) In 60% EtOH. Solvolysis of **12**-Br in 60% EtOH buffered by NaOAc gave (by NMR) 95% of the trianisylethanones **16** and **16*** and 5% of trianisylvinyl acetates (**12**-OAc and **12***-OAc). The intensity ratios of the methoxy signals of **16**-**16*** (δ (CCl$_4$) 3.67 (β-MeO), 3.64 (α-MeO)), which are expected to be unity at no rearrangement and two at complete β-anisyl rearrangement,[10] indicated 11.5 ± 2% rearrangement. This value is an upper limit, since the methoxy signals of **17a**, which was actually isolated from the solvolysis of **12**-Br in 80% EtOH,[4a] appear at δ 3.67. Any formation of **17**-**17a** will increase the extent of rearrangement as calculated from the NMR.



12-OAc



12*-OAc



$$\mathrm{An(An^*)CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}An}$$

16

$$\mathrm{An_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}An^*}$$

16*

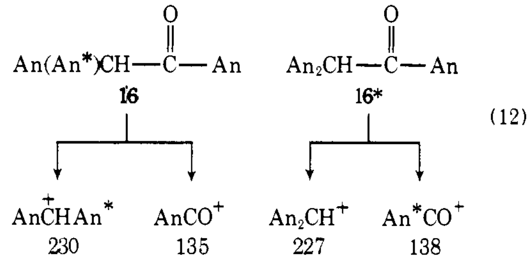
An(An*)CO

17

An$_2$CO

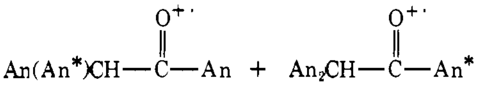
17a

The mass spectra show the molecular peak of **16**-**16*** at *m/e* 365, a small M − CO fragment at *m/e* 337, the *p*-methoxybenzoyl and *p,p'*-dimethoxybenzhydryl signals (eq 12), and



(12)

small peaks for **17** and **17a** at *m/e* 245 and 242. The fragmentations according to eq 12 were only slightly temperature dependent at 50-120 °C for each pair of peaks. However, a different extent of rearrangement is shown by each pair: 13.5 ± 2 and 8.3 ± 0.5% of **16*** are indicated by the *p*-methoxybenzoyl and the *p,p'*-dimethoxybenzhydryl signals, respectively. The mass spectral method is less reliable than the NMR method, since both signals are formed by additional pathways. Cleavage of the *p,p'*-dimethoxybenzophenone fragment will increase the intensity of the anisoyl peak. The cleavage pattern of eq 13 will give two times the *m/e* 230 peak compared with the *m/e* 227 peak, and will therefore exaggerate the extent of the rearrangement. Indeed, metastable ion spectra of the precursor ion at *m/e* 337 (eq 13) indicated the formation of the



$$\mathrm{An(An^*)CH{-}\overset{\overset{\displaystyle O^{+\cdot}}{\|}}{C}{-}An + An_2CH{-}\overset{\overset{\displaystyle O^{+\cdot}}{\|}}{C}{-}An^*}$$

$$\xrightarrow{-CO} \mathrm{An_2\overset{+\cdot}{C}HAn^*} \longrightarrow \mathrm{An_2CH^+ + An(An^*)CH^+} \quad (13)$$

substituted benzhydryl signals at *m/e* 227-230.

An analogous solvolysis in 80% EtOH gave a mixture of 43% of **16**-**16*** (recognized by the CH singlet), 9% of **12**-OAc (+**12***-OAc?) (recognized by the Me singlet), and 48% of the ethers **12**-OCH$_2$CH$_3$ (recognized by the Me triplet). Consequently, the methoxy-methylene region becomes complicated, thus preventing determination of the extent of rearrangement. Mass spectral analysis was worthless due to partially overlapping fragmentation patterns of the various products.

(b) In AcOH. Solvolysis of **12**-Br for 170 h in AcOH/NaOAc at 120 °C gave 95% of the vinyl acetates **12**-OAc-**12***-OAc and 5% of a **16**-**16*** mixture. The two methoxy signals which were observed in CDCl$_3$ were separated to three signals at δ 3.16 (α-An), 3.19 (*cis*-β-An), and 3.29 (*trans*-β-An) in C$_6$D$_6$. By assuming that their ratio will be 2:1:1 at no rearrangement and 1:1:1 at complete scrambling,[10] the percent of rearrangement was calculated as 35 ± 2%, taking into account the presence of **17**.

The base peak in the mass spectra is at *m/e* 365, corresponding to the ketones **16**-**16***, and fragments at *m/e* 337, 245, 242, 138, and 135 were also observed. Metastable ion spectra of the precursor ion at *m/e* 337 (An$_2$CHAn*) shows that it forms the *p,p'*-dimethoxybenzhydryl fragments. The percentage of **16*** was estimated as 17 ± 2% from these fragments.

The reaction of **12**-Br in the presence of 0.076 M Bu$_4$NBr and 0.011 M NaOAc at 120 °C for 6 h (2.5 solvolytic half-lives) gave 88 ± 2% of the recovered vinyl bromide and 12 ± 2% of the vinyl acetates. From the nearly 1:2:1 ratio of the methoxy signals of the vinyl bromides (after correcting for the

Table I. Rearrangement of 12-Br[a] in TFE Buffered by 2,6-Lutidine[a] at 120 °C.

Reaction time, min	$[\mathrm{Bu_4NBr}]$, M	% rearrangement in $\mathrm{An_2C{=}C(X)An}$: X = Br	% rearrangement in $\mathrm{An_2C{=}C(X)An}$: X = $\mathrm{OCH_2CF_3}$
480			100 ± 5
14		⩾80 ± 15	>95
14	0.8	56 ± 3	
14	3.6	0 ± 3	

[a] 0.08 M.

unreacted **12**-Br) the vinyl bromide contains 1.3 ± 0.5% of the rearranged compound, **12***-Br.

$\mathrm{An_2C{=}C(Br)An^*}$ **12***-Br $\quad$ $\mathrm{An(An^*)C{=}C(OCH_2CH_3)An}$ **12**-$\mathrm{OCH_2CH_3}$

$\mathrm{An_2C{=}C(OCH_2CH_3)An^*}$ **12***-$\mathrm{OCH_2CH_3}$

(c) **In Pivalic Acid.** From the reaction of **12**-Br in pivalic acid buffered by sodium pivalate for 48 h at 160 °C, only the unarranged **12**-Br was recovered.

(d) **In 1:1 AcOH–HCOOH.** The main solvolysis products of **12**-Br in 1:1 AcOH-HCOOH (v/v) after 21 h at 95 °C are 62% of the triarylethanones. The remainder are rearranged and unrearranged vinyl formates and acetates. From the partially overlapping methoxy singals it was calculated that the **16–16*** mixture contains 13.2 ± 0.8% of **16***. The mass spectra, which was only slightly temperature dependent, gave 23 ± 2% of **16*** based on the anisoyl signals, and 26 ± 2% based on the *p,p'*-dimethoxybenzhydryl signals.

(e) **In Acetonitrile.** Equimolar mixtures (0.044 M) of **12**-Br and 2,6-lutidine were kept in acetonitrile at 120 °C. NMR spectra showed the presence of **12**-Br-**12***-Br, and a small amount of additional unidentified compound. From the ratio of the methoxy signals, 15 ± 1.2 and 43.2 ± 0.8% rearrangements were observed after 50 and 120 h, respectively. The corresponding 10^7k_t values are 9.1 ± 0.9 and 9.8 ± 0.3 $\mathrm{s^{-1}}$, respectively, assuming rearrangement via an open ion.[10]

$\mathrm{An(An^*)C{=}C(OCH_2CF_3)An}$ **12**-$\mathrm{OCH_2CF_3}$ $\quad$ $\mathrm{An_2C{=}C(OCH_2CF_3)An^*}$ **12***-$\mathrm{OCH_2CF_3}$

(f) **In TFE.** Trifluoroethanolysis of **12**-Br in TFE buffered by 2,6-lutidine for 8 h at 120 °C gave only the trifluoroethyl vinyl ethers **12**-$\mathrm{OCH_2CF_3}$ and **12***-$\mathrm{OCH_2CF_3}$. The methoxy signals of **12**-$\mathrm{OCH_2CF_3}$ are at δ ($\mathrm{CDCl_3}$) 3.71, 3.76, and 3.81 in a 1:2:1 ratio. The observed ratio of 1:1:1 in the trifluoroethanolysis products indicates a complete rearrangement. The error limit of ±3% reflects the integration error and the proximity of a small part of the $\mathrm{CH_2}$ quartet to two of the methoxy signals.

When the same reaction was conducted for 14 min, both the vinyl trifluoroethyl ethers (ca. 60%) and the vinyl bromides (ca. 40%) were formed. Some mutual overlap of the methoxy signals and part of the $\mathrm{CH_2}$ quartet introduces an integration error. Nevertheless, the vinyl ethers were >93% rearranged, and the vinyl bromides were 75 ± 15% rearranged. By using data on the trifluoroethanolysis of **12**-Br at 90 °C[11] and the activation energy for its solvolysis in 80% EtOH,[4a] we estimated that 14 min are four solvolytic half-lives at 120 °C in the absence of common-ion rate depression. Hence, the vinyl bromide which participated in the reaction is >80% rearranged.

Solvolysis for 14 min in the presence of 0.8 M $\mathrm{Bu_4NBr}$ gave only ⩽15% of the ethers. The recovered vinyl bromides were 56 ± 3% rearranged. When the solvolysis was conducted under the same conditions in the presence of 3.6 M $\mathrm{Bu_4NBr}$, only **12**-Br was detected. The data are summarized in Table I.

(g) **In Trifluoroacetic Acid.** Solvolysis of **12**-Br in $\mathrm{CF_3COOH/CF_3COONa}$ at 50 °C gave the triarylethanones **16–16***. Mass spectral analysis according to eq 12 showed 33 ± 4% of **16*** in the mixture. This value corresponds to complete rearrangement via the open ion.[10]

Discussion

Evaluation of the Mass Spectral and the NMR Methods. In a previous work on the degenerate rearrangements of the 2-anisyl-1,2-diphenylvinyl cation,[1] the mass spectral analysis of the solvolysis products was shown to be a rapid, accurate, and reproducible method, and therefore more convenient than methods which require degradation of the products. The analysis was supplemented by NMR analysis. Application of the same analytical methods in the study of the degenerate rearrangements which accompany the solvolysis of **10**-Br–**11**-Br and **12**-Br revealed three types of limitations which severely hinder the use of these methods for accurate determination of the extent of rearrangement: (a) side reactions in the solvolysis; (b) instability of the solvolysis products; and (c) complications due to mass spectral fragmentation patterns.

(a) In basic aqueous ethanol, the triarylethanones can be cleaved during the reaction to substituted benzophenones.

$$\mathrm{Ar^3Ar^2CHCOAr^1} \xrightarrow{\text{base}} \mathrm{Ar^3Ar^2CO} \qquad (14)$$

The propensity for such cleavage increases with the number of anisyl groups in the ethanone. Benzophenone **17a** is the main product of the long-time solvolysis when $\mathrm{Ar^1 = Ar^2 = Ar^3}$ = An,[4a] while **15a** is a minor product when $\mathrm{Ar^2}$ = Ph, $\mathrm{Ar^1 = Ar^3}$ = An,[4b] and it is formed in negligible amounts, if at all, when $\mathrm{Ar^2}$ = An, $\mathrm{Ar^1 = Ar^3}$ = Ph.

This cleavage complicates the NMR analysis of methoxy-labeled compounds by introducing an additional signal into the methoxy region.

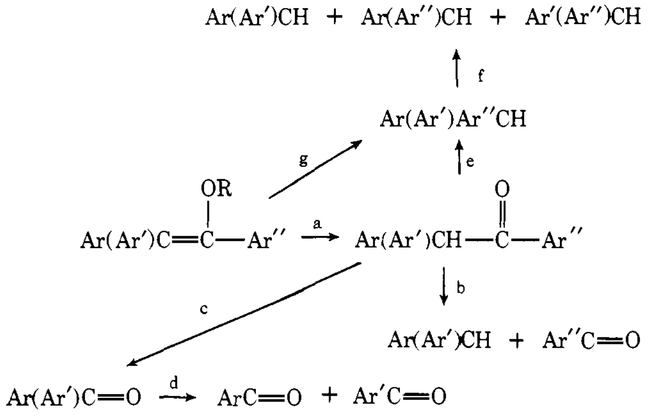
Acetolysis produces mainly the vinyl acetates and some triarylethanone. While the mechanism of formation of the latter is not yet clear,[12] it probably occurs without rearrangement. This complicates the methoxy region of the NMR, but does not affect the mass spectral analysis, since triarylethanone is formed anyway in fragmentation of the vinyl acetates. Formation of the vinyl acetates, vinyl formates, and ketone in AcOH-HCOOH makes accurate analysis even more difficult.

Formation of both the triarylethanone and vinyl ethers in 80% EtOH makes the mass spectral analysis of the mixture useless (see below) and complicates the methoxy region in the NMR analysis.

These complications are not unique to our analytical methods. A radioactive determination[8a] of the extent of rearrangement will not give better results when applied to mixtures of the various products. The ^{13}C NMR method which was applied successfully for systems **10**-Br–**12**-Br in RCOOH[8b–d] will be free of these complications provided that the signals of the various products do not overlap.

(b) Degenerate rearrangement of the solvolysis products in the reaction medium can hinder the determination of the extent of rearrangement via vinyl cations. Ketone **14** rearranges partially in 1:1 AcOH-HCOOH to its isomer **14***. Similar acid-catalyzed ketone-ketone rearrangements are known for analogous ketones, such as labeled 1,2,2-triphenylethanones,[13] and possible mechanisms were discussed.[14] Consequently, neither this solvent nor more acidic solvents such as $\mathrm{CF_3COOH}$ are suitable for studying the extent of the rearrangement. Moreover, similar reservation applies for systems substituted with more anisyl groups, such as the trianisylvinyl system. We found complete scrambling in the trifluoroacetolysis of **12**-Br, which leads to the trianisylethanone, and complete scrambling was previously observed in the same reaction in $\mathrm{CF_3COOH}$/

Scheme III



$AgOOCCF_3$, which leads to trianisylvinyl trifluoroacetate.[8c] Although a high extent of scrambling is reasonable in this low-nucleophilic medium, some of the observed scrambling may take place in the ethanone or in the sp^3-hybridized ion which is formed by initial protonation of trianisylvinyl bromide or trifluoroacetate.[15] Such protonation fits the development of a purple color when **12**-Br is dissolved in CF_3COOH.[8c]

(c) The strength of the mass spectral method is the formation of two pairs of fragments, where the relative abundance of the labeled and unlabeled peaks gives directly both the extent of rearrangement and an internal consistency test for the reliability of the results. In the present work, the temperature dependence of the relative intensities within each pair of peaks and the inconsistency of the results of the two pairs in several occasions (Table VI) makes the mass spectral method only a guide for an upper limit for the extent of the rearrangement. We ascribe this behavior to multiple fragmentation patterns (Scheme III). The mass spectral method is based on fragmentation a → b. While for R = Ac or CHO the fragmentation commenced via a, further fragmentation via c leads to aroyl signals of the opposite labeling pattern than those obtained via b. Moreover, cleavage e leads to scrambling of all the aryl groups prior to formation of the benzhydryl peaks, and when Ar = Ar′ = Ar″ it will exaggerate the extent of rearrangement.

When R = Et or CH_2CF_3, the base peak in the mass spectra is the triarylmethane fragment. Whether it is formed via g or a and e, it renders the mass spectral method useless.

The cleavage patterns of Scheme III were verified by metastable peak analysis on the precursor ions corresponding to the triarylethanone, triarylmethyl, and benzophenone ions which show daughter peaks corresponding to routes b-f. The temperature dependence is therefore due to competition between routes b, c, and e, which apparently have different activation energies.

This complexity requires that the mass spectral method should be evaluated individually for each reaction. For each reaction of the systems studied in this work and related systems, it should be checked in regard to the temperature dependence of the fragmentation and internal consistency. In the present work it was usually found to be inferior to the NMR method. Table II gives the results of the extent of rearrangement based on the two methods. The more reliable value (as justified above) is given in italics.

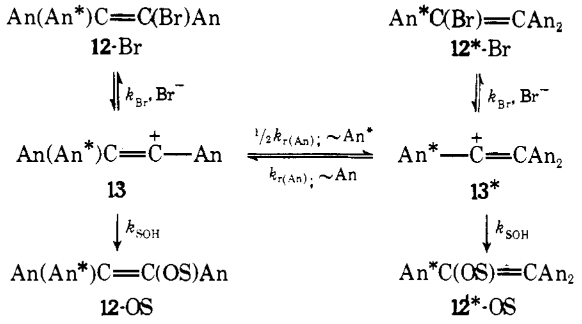
Free Vinyl Cation as a Rearrangement Intermediate. Evidence against Contribution of a Windshield Wiper Effect to the Selectivity of Triarylvinyl Cations. The high selectivities of triarylvinyl cations, manifested by the common-ion rate depression in the solvolysis of the triarylvinyl bromides,[2,3,5b] was attributed to shielding of the cationic orbital by the α- and β-aryl substituents in a "static" vinyl cation.[2,3,5b] An alternative is that a very rapid degenerate β-aryl migration between "degenerate" vinyl cations leads to "dynamic" equilibrium

Table II. Degenerate Rearrangements during the Solvolysis of Triarylvinyl Bromides[a]

Compd	Solvent	Base	Added salt	T, °C	% rearrangement[b] from NMR	% rearrangement[b] from MS	k_{SOH}/k_r or k_{SOH}'/k_r
10-Br–**11**-Br	60% EtOH	2,6-Lutidine		125	8 ± 2	5 ± 1	38 ± 9
(5:1)	80% EtOH	2,6-Lutidine		115	28 ± 6	4 ± 1.5	48 ± 20
	AcOH	NaOAc		120	<3[c]	7 ± 2	⩾65
	AcOH	NaOAc	Bu_4NBr	120	<3[c,d]		
	AcOH		AgOAc	Reflux	0[e]		⩾100[e]
	Me_3CCOOH	$NaOCOCCMe_3$		160	0[d]		
	TFE	2,6-Lutidine		120	53 ± 6		1.77 ± 0.4
	1:1 AcOH–HCOOH	NaOAc		95	68 ± 4		
10-Br–**11**-Br (3:2)	1:1 AcOH–HCOOH	NaOAc		95	56 ± 4		
12-Br	60% EtOH	NaOAc		120	11.5 ± 2	16.5 ± 1	11.5 ± 2.3
	AcOH	NaOAc		120	35 ± 2	51 ± 6	2.8 ± 0.25
	AcOH	NaOAc	Bu_4NBr	120	4 ± 1.5[d]		
	AcOH		AgOAc	Reflux	40 ± 2[f]		
	1:1 AcOH–HCOOH	NaOAc		95	40 ± 2	73 ± 5	
	CF_3COOH	$NaOCOCF_3$		50		100	
	CF_3COOH		$AgOCOCF_3$	Room temp.	100[f]		
	Me_3CCOOH	$NaOCOCMe_3$		160	0[c]		
	TFE	2,6-Lutidine		120	100 ± 3		<0.04
	TFE	2,6-Lutidine	Bu_4NBr[g]	120	0 ± 3[d]		
	MeCN	2,6-Lutidine	(50 h)	120	15 ± 1		
			(160 h)	120	43 ± 1		

[a] The more reliable values are underlined; the error reported either reflects average of data of duplicate experiments or an average of several determinations of the same run. [b] For **10**-Br–**11**-Br, 100% rearrangement corresponds to formation of 50% of the rearranged product. For **12**-Br, 100% rearrangement corresponds to formation of 33.3% of the rearranged product. [c] Within the detection limit of the NMR. [d] In the recovered vinyl bromide. [e] From ref 8d, by ^{13}C analysis. [f] From ref 8c by ^{13}C analysis. [g] At 3.6 M concentration.

Scheme IV



between them, and consequently both the solvent and the leaving group are excluded from the side of the orbital where the migration takes place. This "windshield wiper effect" was excluded in the solvolysis-rearrangement of **3** and **4,** since the extents of both β-phenyl and β-anisyl rearrangements were identical for both compounds,[1,5b] and the solvolysis gave ca. 1:1 mixture of the cis and trans products.[5b] A consideration of the same alternatives is of interest for our α-anisylvinyl systems, which form more selective cations, for two reasons: (i) the 1,2-dianisyl-2-phenylvinyl system holds a key position in our understanding of the involvement of free ions and ion pairs in the solvolysis,[2] and any additional effect should be included in the whole picture; (ii) the pair of isomers cannot be separated in our labeled trianisylvinyl system.[16] Since both β substituents in the cation **13** are identical, equal shielding of both lobes of the cationic orbital[10] is possible.

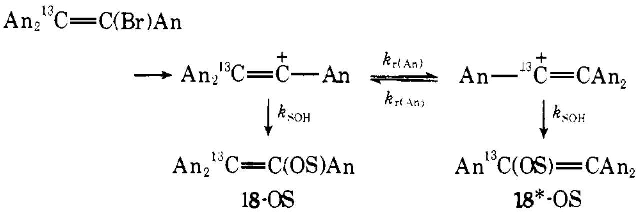
The windshield wiper effect should be considered when there are: (a) an extensive β-aryl migration; (b) equal possibility of migration of the two β-aryl groups which occupy positions at both sides of the cationic orbital; and (c) faster migration compared with capture by the solvent or bromide ion. None of these is fulfilled for the ion **8**, while for the trianisylvinyl cation **13** condition b is always fulfilled and condition a is fulfilled in TFE and partially in AcOH. The test of c is discussed in terms of Scheme IV.

The solvolysis product will be completely rearranged, i.e., a 2:1 mixture of **12-OS** and **12*-OS** when $k_{r(An)} \gg k_{SOH}$. Since complete scrambling requires several forth and back rearrangements, it could be deduced that the windshield wiper effect might contribute to the selectivity only when $k_{r(An)} \gg k_{Br}[Br^-]$ with added high concentration of $[Br^-]$. Under these conditions the products will be a 2:1 mixture of **12-Br–12*-Br** at high $[Br^-]$, since $k_{Br}[Br^-] > k_{SOH}$. If the windshield wiper effect is unimportant, we expect that at low $[Br^-]$ the first-order rearrangement will be faster than the second-order reaction with Br^-, i.e., $k_{r(An)} > k_{Br}[Br^-]$. The products will then be partially rearranged (i.e., **12-OS** + **12*-OS**) and will be accompanied by partially rearranged starting materials (**12-Br** + **12*-Br**). At high $[Br^-]$ the capture by Br^- will be dominant, i.e., $k_{Br}[Br^-] > k_{r(An)} > k_{SOH}$, and only the *unrearranged* starting material **12-Br** will be recovered.

Table I shows that complete and nearly complete rearranged trifluoroethyl ethers were obtained in TFE after 8 h and 14 min, respectively. However, the vinyl bromide is regenerated in the presence of a large excess of $[Br^-]$, as expected from the extensive common-ion rate depression observed for **12**-Br in AcOH[3a,d] and TFE.[11] The extent of rearrangement in the vinyl bromide decreases on increasing $[Br^-]$, until only nonrearranged **12**-Br is regenerated in the presence of 3.6 M $[Br^-]$! The condition $k_{Br}[Br^-] \gg k_{r(An)} > k_{SOH}$ is therefore fulfilled and the selectivity of the ions is not due to a windshield wiper effect. The similar retardation of the rearrangement by Br^- in AcOH leads to a similar conclusion concerning the reaction in AcOH.

The absence or the low extent of anisyl migration in the ion **8** in most solvents, combined with the formation of ca. 1:1 cis-trans products,[2,4b,5b] excludes the windshield wiper effect for **8** in most of these solvents. Such an effect is not unequivocally excluded in TFE, where the rearrangement is considerable, but it is excluded by analogy with the behavior of the ion **13**.

Scheme V



The suppression of the rearrangement by the addition of the common bromide ion is a clear and strong evidence that the reaction proceeds via the *free* triarylvinyl cation in both TFE and AcOH.

Additional strong evidence for the intermediacy of an open ion in the acetolysis of trianisylvinyl bromide arises from comparison of our data with that of Oka and Lee.[8c] Our labeling in the anisyl group leads to scrambling of the three anisyl groups at complete rearrangement via the free ion (Scheme IV). In Oka and Lee's experiment trianisylvinyl-*2*-^{13}C bromide was studied and the two vinylic carbons were scrambled at complete rearrangement (Scheme V). Both experiments together amount to a "double labeling" experiment of the type used by Collins and Bonner[17] to establish the involvement of an "open" cation in the reactions forming the 1,2,2-triphenylethyl cation.

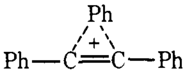
When the steady-state treatment or an analogous treatment of Bonner and Collins[17b] is applied to the cationic intermediates of Schemes IV and V and isotope effects and capture by Br^- (which does not affect the product distribution at infinity) are neglected, the following relationships are obtained.[18]

$$[\mathbf{12\text{-}OS}]/[\mathbf{12^*\text{-}OS}] = 2[1 + (k_{SOH}/k_{r(An)})] \qquad (15)$$

$$[\mathbf{18\text{-}OS}]/[\mathbf{18^*\text{-}OS}] = 1 + (k_{SOH}/k_{r(An)}) \qquad (16)$$

In AcOH/AgOAc, the [**18-OS**]/[**18*-OS**] ratio is 4.0 ± 0.25,[8c] i.e., from Scheme V $k_{SOH}/k_{r(An)} = 3.0 \pm 0.25$. The [**12-OS**]/[**12*-OS**] ratio is 7.6 ± 0.49, i.e., from Scheme IV $k_{SOH}/k_{r(An)} = 2.8 \pm 0.25$. The identity, within the experimental error, of the two values for compounds labeled differently, argues that the assumption on which Schemes IV and V are based, i.e., that free vinyl cation is the intermediate, is correct.[18]

Ease of Migration as a Function of the Solvent, the Migrating Group, the Migration Origin, and the Migration Terminus. Data concerning the different rearrangements across the double bond in phenyl- and anisyl-substituted triarylvinyl cations are now available. We can therefore assess the effect of the solvent, the migrating group, and the groups at the migration origin and terminus on the ease of rearrangement. The transition states for these rearrangements have structures **19–24**, where **19, 21, 23,** and **24** represent those for degenerate rearrangements, and **20** and **22** may be obtained in two ways, either when the migration origin is substituted by a phenyl or an anisyl group.



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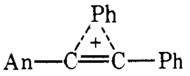

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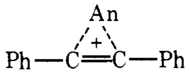

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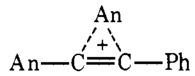

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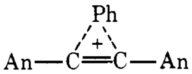

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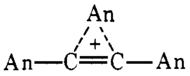

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Table III. Extent of β-Aryl Rearrangements in the Solvolysis of 1,2,2-Triarylvinyl Systems (A) and the Deaminations of 1,2,2-Triarylethylamines (B)[a]

	Transition state (A)						
Solvent	19	20	21	22	23	24	Ref
TFE	>13.4[b]	85 (0)[c]	100[b]	100 (0)[c]	53	100	1, 5, 8a
AcOH	13.4	~0	93	100	<3	35	1, 3a,d, 5a, 8a
60% EtOH		5	89	100	5	11.5	1, 5
Me_3CCOOH		(0)[c]		100	0	0	33
	Transition state (B)						
	25	27		28		26	
H_2O	54	(0.9)[c]		90.8		33.4	19, 20

[a] The migration origin is the carbon drawn on the left in structures 19–28. [b] Estimated value. [c] The migration origin is the carbon drawn on the right in these structures.

Table III gives the relative extents of rearrangements together with data from the work of Bonner and co-workers[19,20] on the extent of rearrangement in the corresponding saturated 1,2,2-triarylethylamines.

The solvents studied differ markedly in the combination of two properties relevant to the rearrangement: their nucleophilicity (N) and their dissociation power. The latter is measured by the dielectric constant ϵ, since we assume that increase in ϵ increases the stability and the lifetime of the cation. TFE has high dissociation power ($\epsilon = 26.67$)[21] and a low nucleophilicity ($N = -2.74$),[22] while 60% EtOH has higher dissociation power ($\epsilon = 44.8$)[23] and higher nucleophilicity (N (50% EtOH) $= -0.20$).[24] AcOH has moderate dissociation power ($\epsilon = 6.15$)[25] and relatively low nucleophilicity ($N = -2.05$),[24] while pivalic acid has both low dissociation power and nucleophilicity.[26]

Trifluoroethanol is the best of our solvents in promoting the rearrangement of all the systems studied (Table III). The value given as a lower limit for the rearrangement of the triphenylvinyl system in TFE was estimated on this basis. The efficiency of TFE as a rearrangement medium has precedents in saturated systems.[27] Its low nucleophilicity (i.e., low k_{SOH}) enables k_r to take over in our systems. This effect is emphasized in the high extents of degenerate rearrangements in the ions **8** and **13**, where the driving force for the reaction is inherently low (see below).

The other extreme is 60% EtOH, where k_{SOH} is relatively high due to its high nucleophilicity. In this solvent the different extents of rearrangements of the various systems are more pronounced, and they reflect different migration aptitudes and different extents of ground-state and transition-state stabilizations. AcOH shows an intermediate behavior between the extremes. The data in pivalic acid should not be compared with those for other solvents, since the intermediate is probably different (see below).

Quantitative comparison of the solvent effect for compounds **10**-Br-**12**-Br are made by recourse to Schemes IV and VI, where $k_{r(Ph)}$, $k_{r(An)}$, k_{SOH}, and k_{SOH}' are the rate constants for rearrangement of phenyl and anisyl groups, and capture by the solvent, respectively.

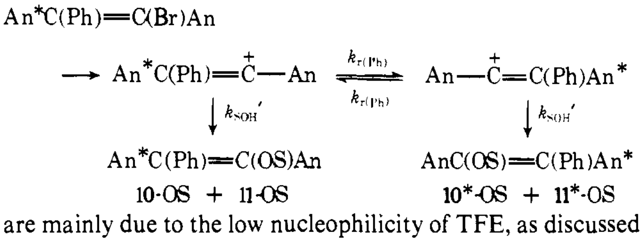
Equations 15 and 17 relate the rate constants and the extents of rearrangements.

$$([\mathbf{10}\text{-OS}] + [\mathbf{11}\text{-OS}])/([\mathbf{10}^*\text{-OS}] + [\mathbf{11}^*\text{-OS}]) = 1 + (k_{SOH}'/k_{r(Ph)}) \quad (17)$$

The $k_{SOH}'/k_{r(Ph)}$ and $k_{SOH}/k_{r(An)}$ ratios calculated from the more reliable data are given in Table II. Typically, a large error is associated with a very small or a very large extent of migration.

The $[k_{SOH}'/k_{r(Ph)}]$ (60% EtOH)/$[k_{SOH}'/k_{r(Ph)}]$ (TFE) ratio is 21 for **10**-Br-**11**-Br, while the $[k_{SOH}/k_{r(An)}]$ (60% EtOH)/$[k_{SOH}/k_{r(An)}]$(TFE) is >144 for **12**-Br. These ratios are mainly due to the low nucleophilicity of TFE, as discussed above.

Scheme VI



$$\begin{tikzcd}
An^*C(Ph){=}C(Br)An \arrow[r] & An^*C(Ph){=}\overset{+}{C}{-}An \arrow[r, shift left, "k_{r(Ph)}"] \arrow[d, "k_{SOH}'"] & An{-}\overset{+}{C}{=}C(Ph)An^* \arrow[l, shift left, "k_{r(Ph)}"] \arrow[d, "k_{SOH}'"] \\
 & \begin{array}{c} An^*C(Ph){=}C(OS)An \\ \mathbf{10}\text{-OS} + \mathbf{11}\text{-OS} \end{array} & \begin{array}{c} AnC(OS){=}C(Ph)An^* \\ \mathbf{10}^*\text{-OS} + \mathbf{11}^*\text{-OS} \end{array}
\end{tikzcd}$$

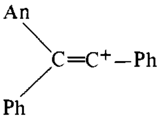
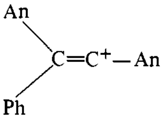
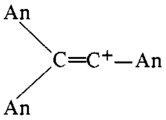
The effects of the migrating group and the groups at the migration origin and terminus are shown in Table III. The anisyl group stabilizes a positive charge better than a phenyl group and for the same combination of migration origin and terminus (either phenyl- or anisyl-substituted) anisyl bridging is favored over phenyl bridging in our systems. A quantitative comparison between the three pairs of transition states **19, 21**; **20, 22**; and **23, 24** is difficult in TFE, since all the anisyl migrations are complete. Nevertheless, relative migration aptitudes, $k_{r(An)}/k_{r(Ph)}$ are >22 in TFE, >23 in AcOH, and 3.3 in 60% EtOH for the **23, 24** pair, while values of 76 (TFE) and 120 (AcOH) were previously obtained for the **19, 21** pair.[1] These values (excluding that in 60% EtOH)[28] are not <1 or abnormally low, as would be the case if the loss of anisyl group double-bond conjugation would be similar or less than the gain by bridging. This question was discussed in detail previously.[1,5b,29]

Substitution at the migration origin and terminus shows similar effects. Migration to an α-phenyl-stabilized cation is favored over the corresponding migration to an α-anisyl-stabilized cation (cf. reactions via **20** vs. **23** and **22** vs. **24**). Migration from an anisyl-substituted migration origin to a phenyl-substituted migration terminus is therefore favored over the corresponding degenerate rearrangement (cf. reactions via **22** vs. **21** and **24**, and **20** vs. **23**). On the other hand, rearrangement from an α-anisyl-substituted vinyl cation to an α-phenyl-substituted cation (**6a** → **5a** (eq 6) and **8** → **7*** (eq 8)) was never observed.[2,4] Although a very low extent of such rearrangement may escape detection, it seems that transition states **20** and **22** are formed almost exclusively in the direction of the phenyl-substituted migration terminus.

Combination of these effects makes the migration of an anisyl group from an anisyl-substituted migration origin to a phenyl-substituted migration terminus the most favored of those studied. On the other hand, phenyl migration between two anisyl-substituted centers is the least favored.

Comparison of β-aryl rearrangements to sp-hybridized cation with those leading to sp^2-hybridized cation is difficult, since the bond lengths, angles, and strengths are different, p-π conjugation is important in the vinyl cation, and conformational effects are important in the sp^2-hybridized cation. Only one pair of data is sufficiently close for a valid comparison.

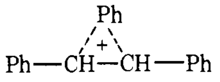
Table IV. Relative Rate Constants for Several Processes Involving Triarylvinyl Cations

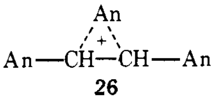
Ion	Solvent	T, °C	Relative rate constant				Ref
			k_{Br}[a]	k_{SOH}	$k_{r(Ph)}$	$k_{r(An)}$	
 **5**	TFE	120	97	1	5.7		5b
	60% EtOH	160		1	0.053	4	1, 5b
	AcOH	117		1	0.053	6.3	1, 5b
 **8**	TFE	120		1	0.56		This work
	80% EtOH	115	3.1	1	0.021		2b, this work
	AcOH	120	21	1	<0.01		2a, this work
 **13**	TFE	120	78	1		25	11, this work
	AcOH	120	27	1		0.36	3d, 11, this work

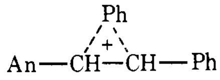
[a] At 1 M [Br^-].

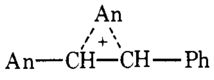
Acetolysis of C-1 labeled 1,2,2-triphenylethyl tosylate gave 39% net phenyl migration from the α to the β position,[17a,32] giving a $k_{SOH}/k_{r(Ph)}$ ratio of 0.56 for migration via **25**. Only 6.7% net phenyl migration took place in the analogous triphenylvinyl cation **2**, i.e., $k_{SOH}/k_{r(Ph)} = 13$. Further comparison of the $k_{r(Ph)}$ values is impossible without information concerning the k_{SOH} values.

Another comparison is with Bonner's data on the deamination-rearrangement of 1,2,2-triarylethylamines in water, which proceed via the triarylethyl cations. The rearrangements, via the transition states **25–28** (Table III), differ from those in the vinylic analogues in several respects: (a) anisyl migration via **26** exceeds the phenyl migration via **25**; (b) phenyl migration to an anisyl-substituted terminus (via **27**) was observed; and (c) anisyl migration via **28** is not complete.


25


26


27


28

Bonner explains fact a by a lower electrophilicity of the migration terminus in the 1,2,2-trianisylethyl cation compared with that in the 1,2,2-triphenylethyl cation, due to a more extensive charge delocalization on the anisyl group. This explanation is rather incomplete, since decrease in the electrophilicity of the charged α-carbon atom would result in lowering of both k_r and k_{SOH}, and the nature of the β-aryl group is also important. The situation found by Bonner will be observed only when k_r will be more affected than k_{SOH} with a change from an α-phenyl- to an α-anisyl-substituted cation. Apparently, the change from **13** to **2** resulted in a lower change in k_r (which leads to the much required charge dispersal) compared with the change in k_{SOH}.

In quantitative terms, $k_{AcOH}/k_{r(An)} = 2.8$ for **13** and $k_{AcOH}/k_{r(Ph)} = 13$ for **2**,[18] while $k_{H_2O}/k_{r(An)} = 4.0$ for the trianisylethyl cation and $k_{H_2O}/k_{r(Ph)} = 1.7$ for the triphenylethyl cation. If we use migratory aptitude ratio $k_{r(An)}/k_{r(Ph)}$ of >20, we find that the capture rate of **13** by AcOH exceeds that of **2** by >4.4-fold, contrary to expectation. This is understood if replacement of a β-phenyl by a β-anisyl group increases the extent of rearrangement in the vinylic system by ≥4.4-fold. From Bonner's data and a $k_{r(An)}/k_{r(Ph)}$ ratio of ca. 2 for the deamination[20] we obtain a similar value of ca. 4.5 for the effect of the β-aryl groups in the 1,2,2-triarylethyl system.

The absence of rearrangement in **6** compared with the small extent of rearrangement via **27** fits the higher requirement for charge dispersal in the vinylic system. Transfer of a positive charge from an α-anisyl-substituted cation to the migrating and the remaining β-phenyl groups is energetically unfavored.

Relative Reactivity in Processes Involving Free Triarylvinyl Cations. Free vinyl cations are intermediates in the solvolysis,[2,3] rearrangement,[1,5] capture,[2,3] and isomerization[2] of triarylvinyl halides. Quantitative comparisons of some of these processes are given in Table IV, relative to k_{SOH}.

Sufficient data are available for the closely related triarylvinyl cations **5**, **8**, and **13**. For them capture by Br^- is the most favored process. β-Anisyl migration is usually faster than capture by the solvent, except when the driving force for it is inherently low, while phenyl migration is slower than capture by the solvent except in a solvent with low nucleophilicity. This conclusion is not necessarily general for other ions. The main conclusion from Table IV is that these cations have long lifetimes and are able to participate in several processes before being quenched by the solvent.

Rearrangement as a Tool for Obtaining Ionization Rates in Nonsolvolytic Media. The rate of ionization of triarylvinyl halides in nonsolvolytic media cannot be followed by bromide ion formation, and it therefore requires a process which initiates in the heterolysis. We found previously that cis-trans isomerization of the vinyl halides is such a process, e.g., **10-Br** isomerizes to **11-Br** in acetonitrile via **8** with a rate constant of ca. $2 \times 10^{-5}\ s^{-1}$.[11] We find now that the degenerate β-phenyl rearrangement in the ion **8** in acetonitrile is much slower and could not be evaluated. The $k_{r(An)}$ value for **12-Br** could be measured in acetonitrile and its value ($9.5 \times 10^{-7}\ s^{-1}$ at 120 °C) was found to be 20-fold lower than k_{isom} of **10-Br**,[11] although **12-Br** solvolyzes somewhat faster than **10-Br** or **11-Br** in AcOH[2a,3a,d] or aqueous ethanol.[2b,4a] This difference suggests that isomerization takes place in a less dissociated intermediate than the rearrangement. Indeed, the **10-Br** $\rightleftharpoons$ **11-Br** isomerization proceeds via both free ions and ion pairs,[2] while the rearrangement of **12-Br** in TFE or AcOH proceeds via the free cation. Moreover, the isomerization of **10-Br** in pivalic acid, which proceeds via ion pairs,[33] is faster than the solvolysis, which in turn is faster than the degenerate β-phenyl

Table V. Intermediates in β-Aryl Rearrangements across the Double Bond

Compd	Solvent	Cationoid intermediate	Evidence	Ref
E-PhC(CD_3)=C(OTf)Me	aq EtOH	Bridged	Stereochemistry, isotope effects, kinetics	6
Ph_2C^*=C(OTf)Ph	RCOOH	Ion pair	No capture by $RCOO^-$	8a
An_2C=C(Br)Ph	Me_3CCOOH	Ion pair	Stereochemistry	33
	AcOH, TFE	Ion pair or free ion	No capture by ArS^-; stereochemistry	5
Ph*(An)C=C(Br)Ph	TFE, aq EtOH	Free ion or some ion pair	Stereochemistry; only *some* capture by ArS^-	5b
Tol_2C=C(N=NNHPh)Ph[a]	AcOH	Free ion	Capture by AcO^-	36
An*C(An)=C(Br)An	AcOH, TFE	Free ion	Capture by Br^-	This work

[a] Tol = *p*-tolyl.

rearrangement, which was too slow to observe.

This conclusion is reasonable, since isomerization requires either rotation of the Br^- around the vinyl cation or rotation of the cation around its C=C axis followed by a cation–anion recombination. Apparently, these processes require a lower activation energy than the degenerate rearrangement of the aryl group which involves bond breaking. Consequently, cis-trans isomerization is superior to the degenerate rearrangement as a method for obtaining a lower limit for the ionization rate constant in an aprotic solvent.

Nature of the Cationoid Intermediates in Rearrangements Across the Double Bond. Generalizations concerning the effect of substituents on the nature of the intermediates in the β-aryl rearrangements across the double bond are summarized in Table V. In solvents with high or medium dielectric constants, a change of the α substituent to a better carbonium-ion stabilizer changes the nature of the intermediate involved in the rearrangement from a bridged ion to an open free ion.

Overwhelming evidence (kinetics, stereochemistry, labeling) indicates a bridged transition state and bridged products-forming ion in the rearrangements of (*E*)-1,2-dimethyl-2-arylvinyl triflates.[6,34] There is conflicting evidence concerning the nature of the intermediates in the rearrangement of various β,β-diaryl-α-phenylvinyl systems. Kinetics, stereochemistry, and the same extent of β-phenyl and β-anisyl rearrangements in the reactions of **3**-Br and **4**-Br suggest the absence of bridging both in the transition state of the heterolysis and in the product-forming intermediate.[1,5b] However, the intermediate in the rearrangement of **1** in RCOOH is not captured by $RCOO^-$ before rearrangement, while *p*-toluenethiolate ion captures some of the intermediates in the solvolyses of **3**-Br and **4**-Br, but none in the solvolysis of **6** in TFE.[5b] These facts can be accomodated either by assuming rearrangement via an ion pair[8a,35] or by a free ion whose rearrangement is faster than capture even by strong nucleophiles, although the possibility of phenyl bridging in the triphenylvinyl system is not yet unequivocally eliminated.[8d] Intermediate ion pairs in the rearrangement of **6** in the low dielectric pivalic acid are suggested by the formation of more of the isomer with trans anisyl groups.[33] With α-anisyl activated systems such as **12**-Br, it was suggested[8d] and it is shown in the present work that the rearrangements proceed *via* the free vinyl cation **13**.

Capture of an α-phenylvinyl cation before rearrangement occurs with nitrogen as the leaving group: the 1-phenyl-2,2-ditolylvinyl cation, which is formed in the decomposition of a triazene precursor in AcOH, was captured completely by acetate ion before rearrangement.[36]

Experimental Section

Melting points were determined with a Fisher-Johns apparatus. Ir spectra were recorded with a Perkin-Elmer 337 spectrophotometer. NMR spectra were taken in deuteriochloroform with a Varian T60 or HA 100 instruments with tetramethylsilane as an internal standard. Mass spectra were recorded on a MAT 311 instrument. TLC was carried out on silica gel G plates and elution was with light petroleum (bp 60–80 °C) containing 10–20% acetone.

Solvents and Materials. Ethanol was purified by the method of Lund and Bjerrum.[37] EtOH (60 or 80% v/v) was prepared with conductivity water. 2,6-Lutidine was distilled from solid KOH. Acetic acid and formic acid were purified as previously described.[2] 2,2,2-Trifluoroethanol was refluxed over a mixture of anhydrous $CaSO_4$ and anhydrous K_2CO_3,[3c] distilled, and the fraction boiling at 73–74 °C was used. Acetonitrile was distilled from P_2O_5 and pivalic acid was distilled before use. Unlabeled materials were available from previous works.[2,3a,4] Trianisylvinyl trifluoroethyl ether was prepared by Apeloig[11] and has the following NMR in $CDCl_3$: δ 3.71, 3.76, and 3.81 (3 × 3 H, MeO), 3.90 (2 H, center of CH_2 q, J = 8.6 Hz), 6.50–7.07 (12 H, *m*, Ar).

2-*p*-Trideuteriomethoxyphenyl-1-*p*-methoxyphenyl-2-phenylvinyl Bromides (10-Br and 11-Br). **(a) *p*-Hydroxy-α-*p*-methoxyphenylacetophenone.** *p*-Methoxyphenylacetic acid (30 g, 180 mM) and phenol (26 g, 270 mM) were stirred in polyphosphoric acid (75 g) at 75–80 °C for 4 days. The solution was poured into ice-water and the red oil which was separated was extracted with chloroform (2 × 250 ml). The organic layer was washed with dilute sodium hydroxide solution, then with water, and dried ($CaCl_2$). The solvent was evaporated under reduced pressure to give a red oil. Two recrystallizations from benzene afforded amorphous solid (3.2 g, 7.4%); mp 179–180 °C (lit.[9] mp 175–178 °C); ir ν_{max} (Nujol) 3350, 2900, 1660, 1580 cm^{-1}; NMR (Me_2SO-d_6) δ 3.64 (3 H, s, MeO), 4.02 (2 H, s, CH_2), 6.57–7.06 (6 H, m, An + *m*-protons of C_6H_4OH), 7.70 (2 H, half of an AA′BB′ q of *o*-protons of C_6H_4OH). About 80% of the products is the corresponding phenyl ester.

(b) *p*-Trideuteriomethoxy-α-*p*-methoxyphenylacetophenone. *p*-Hydroxy-α-*p*-methoxyphenylacetophenone (5 g, 20 mM) was added to a 1 M sodium ethoxide solution in ethanol (20 ml). When all the ketone was dissolved, trideuteriomethyl iodide (3 g, 20 mM) was added, and the solution was refluxed for 3.5 h. The cooled solution was filtered and evaporated. The residue was recrystallized from methanol to give needles (3 g, 57%): mp 111–113 °C (lit.[38] of the unlabeled compound 110.4 °C); NMR ($CDCl_3$) δ 3.77 (3 H, s, MeO), 4.34 (2 H, s, CH_2CO), 7.00–7.34 (6 H, m, An + *m*-protons of COAn), 8.05 (2 H, m, *o*-protons of COAn). The unlabeled compound has the same spectrum with a second methoxy signal at δ 3.82.

(c) 2-*p*-(Trideuteriomethoxy)phenyl-1-*p*-methoxyphenyl-2-phenylethylene. A solution of phenylmagnesium bromide, made from bromobenzene (4.5 g, 28 mM) and magnesium (0.7 g, 28 mM) in ether (10 ml), was added dropwise to a suspension of *p*-trideuteriomethoxy-α-*p*-methoxyphenylacetophenone (2 g, 7.7 mM) in benzene (15 ml) and ether (7 ml). The mixture was refluxed for 4 h, then poured into ice-cooled ammonium chloride solution and extracted with benzene (2 × 50 ml). The organic layer was washed with water, dried ($MgSO_4$), and evaporated to give an oil (2.2 g, 85%)—crude 2-*p*-(trideuteriomethoxy)phenyl-1-*p*-methoxyphenyl-2-phenylethanol: NMR δ 2.25 (1 H, s, OH), 3.55 (2 H, s, CH_2), 3.74 (3 H, s, MeO), 6.56–7.60 (13 H, m, An + Ph).

The oil was heated in 85% phosphoric acid (9 ml) at 100 °C for 3 h. The solution was poured into a mixture of chloroform (50 ml) and cold water (75 ml). The organic layer was washed with aqueous sodium bicarbonate, then with water, and dried ($CaCl_2$). Evaporation of the solvent gave a 1:1 mixture of the cis and trans ethylenes: NMR δ 3.68, 3.70 (3 H, two s of equal intensity, MeO), 6.50–7.35 (14 H, m, 2 An + Ph + CH).

(d) 2-*p*-(Trideuteriomethoxy)phenyl-1-*p*-methoxyphenyl-2-phenylvinyl Bromides. To a solution of the ethylenes (2 g, 6.2 mM) in CCl_4 (15 ml) a solution of bromine (1 g, 6.2 mM) in CCl_4 (3 ml) was added slowly. The solvent was evaporated to give an oil which was purified

Table VI. Percent of Rearranged Fragment in the Solvolysis of a 5:1 Mixture of 10-Br–11-Br in Various Solvents

		% of rearranged fragment from		
		m/e 138	*m/e* 197	*m/e* 212
Solvent	T, °C[a]	*m/e* 135 + *m/e* 138	*m/e* 197 + *m/e* 200	*m/e* 212 + *m/e* 215
60% EtOH	80	31.5	3.0	1.5
60% EtOH	120	14.5	2.0	28
80% EtOH	50	22.5	2.0	2.0
80% EtOH	80	14.0	1.0	4.0
80% EtOH	120	9.0	2.5	
AcOH	60	38.5	5.0	3.0
AcOH	80	18.0	3.0	3.0
AcOH	120	6.0	2.5	6.0
1:1 AcOH–HCOOH	50	24.5	16.0	8.0
1:1 AcOH–HCOOH	80	15.5	5.0	6.0
1:1 AcOH–HCOOH	120	8.0	6.5	6.5

[a] The temperature at which the mass spectral analysis was conducted.

by TLC. Recrystallization from methanol gave two fractions: one, mp 100–116 °C, consisted of a 5:1 mixture of **10**-Br–**11**-Br, and the other, mp 88–94 °C, contained a 59:41 mixture of **10**-Br–**11**-Br. The bromides showed NMR ($CDCl_3$) signals at δ 3.70, 3.73 (3 H, a 1:1 d of the *cis*- and *trans*-MeO, respectively), 6.64–7.30 (13 H, m, 2An + Ph); *m/e* 399, 397 (39, 40%, M), 318 (100%, M − Br), 267 (5%), 252 (4%), 239 (9%), 228 (10%), 226 (10%).

1,2-Dianisyl-2-*p*-(trideuteriomethoxy)phenylvinyl Bromide (12-Br). (a) **1,2-Dianisyl-2-*p*-(trideuteriomethoxy)phenylethylene.** To a suspension of *p*-trideuteriomethoxy-α-*p*-methoxyphenylacetophenone (1 g, 3.8 mM) in benzene (10 ml) and ether (5 ml) a solution of *p*-methoxyphenylmagnesium bromide, made from *p*-bromoanisole (2.88 g, 15 mM) and magnesium (0.375 g, 15 mM) in ether (10 ml), was added slowly and the mixture was refluxed for 4 h. Workup as usual afforded an oil (1.3 g), which was treated with phosphoric acid as above, and after workup gave an oil (1.3 g, 96%) with NMR signals at δ 3.77, 3.82, 3.85 (6 H, 1:2:1 t, 3 MeO), 6.80–7.05 (13 H, m, 3 An + CH).

(b) **Bromination of the Ethylene.** The ethylene (1.3 g) was brominated as discussed above in the preparation of **10**-Br–**11**-Br. Workup, purification by TLC, and recrystallization from cyclohexane gave pure 1,2-dianisyl-2-*p*-(trideuteriomethoxy)phenylvinyl bromide (0.9 g, 57%): mp 118–120 °C (lit.[4a] mp of the unlabeled compound 118–119 °C; NMR ($CDCl_3$) δ 3.68, 3.74, 3.80 (6 H, 1:2:1 t, *cis*-β-OMe; α-OMe, *trans*-β-OMe, respectively); *m/e* 429, 427 (31, 32%, M), 348 (100%, M − Br).

Solvolysis. The solvolysis reactions were conducted in sealed ampules and the workup procedures were identical with those described previously.[1] Typical data for the mass spectral fragmentation of **10**-Br–**11**-Br are given in Table VI.

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References and Notes

(1) Part 23. Z. Rappoport, E. Noy, and Y. Houminer, *J. Am. Chem. Soc.*, **98**, 2238 (1976).

(2) (a) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **97**, 821 (1975); (b) *ibid.*, **97**, 836 (1975).

(3) (a) Z. Rappoport and A. Gal, *Tetrahedron Lett.*, 3233 (1970); (b) Z. Rappoport and J. Kaspi, *J. Chem. Soc., Perkin Trans. 2*, 1102 (1972); (c) *ibid., J. Am. Chem. Soc.*, **96**, 4518 (1974); (d) A. Gal, Ph. D. Thesis, The Hebrew University, 1972.

(4) (a) Z. Rappoport and A. Gal, *J. Am. Chem. Soc.*, **91**, 5246 (1969); (b) Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969).

(5) (a) Z. Rappoport, A. Gal, and Y. Houminer, *Tetrahedron Lett.*, 641 (1973); (b) Z. Rappoport and Y. Houminer, *J. Chem. Soc., Perkin Trans 2*, 1506 (1973).

(6) P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2683, 2686 (1973).

(7) In this paper, numbers, numbers with asteriks, and numbers with the affix a are given to unrearranged labeled compounds, the corresponding rearranged labeled compounds, and the unlabeled compounds, respectively.

(8) (a) C. C. Lee, A. J. Cessna, B. A. Davis, and M. Oka, *Can. J. Chem.*, **52**, 2679 (1974); (b) F. H. A. Rummens, R. D. Green, A. J. Cessna, M. Oka, and C. C. Lee, *ibid.*, **53**, 314 (1975); (c) M. Oka and C. C. Lee, *ibid.*, **53**, 320 (1975); (d) C. C. Lee and M. Oka, *ibid.*, **54**, 604 (1976).

(9) D. Lednicer and M. F. Grostic, *J. Org. Chem.*, **32**, 3251 (1967).

(10) Rearrangement via open ions assumes that at infinity all the anisyl groups of **8** and **13** are completely scrambled. Rearrangement via bridged ions or ion pairs, where the rearrangement from the side of the leaving group is sterically retarded, may lead to a different "infinity" distribution of the anisyl groups.

(11) Z. Rappoport and Y. Apeloig, unpublished results.

(12) For a possible mechanism see S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **93**, 1925 (1971).

(13) T. C. Clark and A. Fry, unpublished results, quoted in ref 14; C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *J. Am. Chem. Soc.*, **81**, 460 (1959).

(14) A. Fry in *Mech. Mol. Migr.*, **4**, 113 (1971).

(15) For discussions of such electrophilic addition–elimination route in the solvolysis of aryl-substituted vinylic systems, see (a) Z. Rappoport, T. Bässler, and M. Hanack, *J. Am. Chem. Soc.*, **92**, 4985 (1970); (b) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).

(16) However, stereospecific labeling of one of the β-anisyl groups or the α-anisyl group may give an additional tool for studying the nature of the cationoid intermediate.

(17) (a) C. J. Collins and W. A. Bonner, *J. Am. Chem. Soc.*, **77**, 92 (1955); (b) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

(18) In this treatment k_{SOH} in AcOH was taken as equivalent to k_{AcOH}, the capture rate constant by AcOH. However, we had shown previously that most of the capture in AcOH/NaOAc is done by the AcO^- ion.[2,3d] The k_{SOH}/k_r ratio should be therefore dependent on the $[AcO^-]$. The similar k_{SOH}/k_r values obtained in AcOH/NaOAc (Scheme IV) and AcOH/AgOAc (Scheme V) calls for further studies to settle the question of the capturing nucleophile.

(19) M. J. McCall, J. M. Townsend, and W. A. Bonner, *J. Am. Chem. Soc.*, **97**, 2743 (1975).

(20) W. A. Bonner and T. A. Putkey, *J. Org. Chem.*, **27**, 2348 (1962).

(21) J. Murto and C. L. Heino, *Suom. Kemistil. B*, **39**, 263 (1966).

(22) J. Kaspi, Ph. D. Thesis, The Hebrew University, 1975.

(23) M. L. Le Huerou and M. C. R. Guerillot, *C. R. Acad. Sci.*, **258**, 2549 (1964).

(24) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972).

(25) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 55th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1974–1975, p E-56.

(26) Judged by the dielectric constants and nucleophilicities of closely related compounds.

(27) E.g., W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); D. D. Roberts, *J. Org. Chem.*, **36**, 1913 (1971); **37**, 1510 (1972); D. S. Noyce, R. L. Castenson, and D. A. Meyers, *ibid.*, **37**, 4222 (1972); D. S. Noyce and R. L. Castenson, *J. Am. Chem. Soc.*, **95**, 1247 (1973); F. L. Schadt and P. v. R. Schleyer, *ibid.*, **95**, 7860 (1973).

(28) That the value in 60tOH differs much from the other values suggests that the actual extent of rearrangement is lower than the upper limit given in Table II.

(29) If the migrating group is regarded as an internal nucleophile, the k_{SOH}/k_r value is a competition ratio of two nucleophiles on a free carbonium ion. Ritchie's "constant selectivity" rule[30,31] predicts then that this ratio will be independent of the nature of the cation, i.e., the extents of migration of an aryl group to different migration termini should be the same. The reason that this is not the case (Table III) is that the substituted β-carbon atom should be considered as a part of the nucleophile, since it carries part of the charge in the transition state, and hence the nucleophiles differ in different systems.

(30) C. D. Ritchie and P. O. I. Virtanen, *J. Am. Chem. Soc.*, **94**, 4966 (1972).

(31) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).

(32) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).

(33) Z. Rappoport, I. Schnabel, and P. Greenzaid, *J. Am. Chem. Soc.*, in press.

(34) T. E. Dueber, Ph. D. Thesis, University of Utah, 1974; *Diss. Abstr. Int., B*, 128 (1974–1975).

(35) However, the constituents of the ion pair should be sufficiently remote in order to account for the nearly similar capture rates from both sides of the cation.[5b]

(36) W. M. Jones and F. W. Miller, *J. Am. Chem. Soc.*, **89**, 1960 (1967).

(37) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(38) J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2163 (1929).