Nature of the Cationoid Intermediates in the Solvolytic Rearrangement of 2,2-Dianisyl-1-arylvinyl Bromides in 2,2,2-Trifluoroethanol and Acetic Acid

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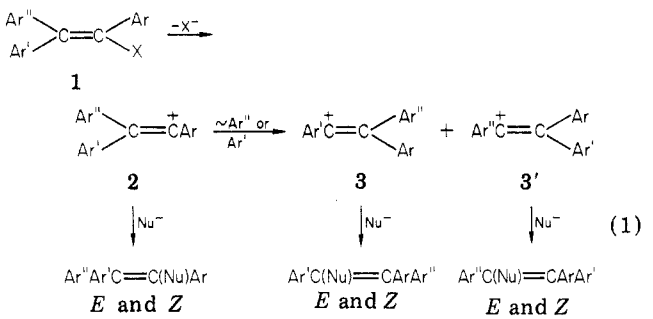
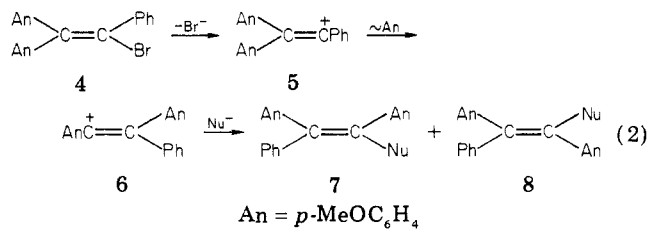
The two isotopomers of 2,2-dianisyl-1-phenylvinyl bromide specifically labeled by a CD_3 group in either methoxy group (**17-E** and **17-Z**) and an α-*p*-tolyl analogue (**18-Z**) were synthesized. Solvolysis of **17-E** in TFE/2,6-lutidine or of **17-E** or **17-Z** in AcOH/AgOAc gave ca. 50:50 mixtures of the rearranged (*E*)- and (*Z*)-1,2-dianisyl-2-phenylvinyl derivatives with very slight preference (53:47 and 51:49, respectively) for migration of the anisyl group trans to bromine. No preference and slight preference were found for the similar migration in the solvolysis of **18-Z** in AcOH/AgOAc and TFE/2,6-lutidine, respectively. The acetolysis of **17-Z** in AcOH/AgOAc is accompanied by an extensive rearrangement to **17-E**. It is suggested that most of the reactions proceed at the free-ion stage with a possible small contribution from reaction at the ion-pair stage. Two possible isomerization routes were discussed. Ionization followed by ion-pair return with isomerization contributes little, if at all, to the isomerization which proceeds mainly, if not exclusively, via electrophilic addition–elimination.

Degenerate and nondegenerate β-aryl rearrangements across the double bond during the solvolysis of triarylvinyl bromides, triazenes, and triflates (eq 1) were studied extensively in recent years.[2-8] The 2,2-dianisyl-1-phenylvinyl



X = Br, OTf, NNNHPh; Nu^- = Br^-, R_3CCOO^-, OH^-, RO^-, RS^-; Ar, Ar′, Ar″ = Ph, *p*-tolyl, *p*-An, *o*-An, 2,5-$(MeO)_2C_6H_3$, *p*-$^-OC_6H_4$

system **4** occupies an important position in the spectrum of the systems studied: the rate of β-anisyl rearrangement in the derived ion **5** to form the rearranged ion **6** (eq 2)[8]



An = *p*-$MeOC_6H_4$

should exceed the rates of almost all the similar migrations reported so far in related systems[9] since the presence of the two β-anisyl groups in **5** supplies a strong driving force for the rearrangement to the α-anisylvinyl cation **6** by stabilizing both the transition state for the rearrangement and the product ion by anisyl groups, whereas **5** is stabilized only by an α-phenyl group. The higher thermodynamic stability of **6** compared with **5** makes the β-anisyl rearrangement faster than in the case of the trianisylvinyl cation,[5b,6c,d,g,k] which also contains two β-anisyl groups, but where the rearrangement is degenerate.

Consequently, whereas both rearranged and unrearranged products are usually obtained in the solvolysis of compounds **1** by capture of both **2** and **3** by the solvent, the solvolysis of **4** in AcOH/NaOAc,[8a] in 60% EtOH,[8b] in 2,2,2-trifluoroethanol (TFE),[8b] in Me_3CCOOH/$Me_3CCOONa$,[8c] and even in the presence of the strong thio nucleophile *p*-$MeC_6H_4S^-$ in TFE[8b] gave products which were exclusively derived from the rearranged ion **6**. Products derived from the ion **5** were never reported under these conditions.

The distributions of the products **7** and **8** from the reactions with the various nucleophiles resemble the *E*/*Z* distribution obtained with the same nucleophiles in the solvolysis of either (*E*)- or (*Z*)-1,2-dianisyl-2-phenylvinyl bromides **9** and **10**.[10] The nearly 50:50 distribution of **7**

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(1) (a) Preliminary communication: Ikeda, T.; Kobayashi, S.; Rappoport, Z.; Taniguchi, H., International Symposium on the Chemistry of Carbocations, University College of North Wales, Bangor, Sept 7–11, 1981. (b) Paper No. 35 in the series "Vinylic Cations from Solvolysis" from Jerusalem.

(2) For a summary, see Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; Chapter 6.

(3) For reviews, see (a) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. (b) Lee, C. C. In "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1980; Vol. 5, Chapter 1.

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

(5) (a) Rappoport, Z.; Noy, E.; Houminer, Y. *J. Am. Chem. Soc.* **1976**, *98*, 2238. (b) Houminer, Y.; Noy, E.; Rappoport, Z. *Ibid.* **1976**, *98*, 5632. (c) Rappoport, Z.; Houminer, Y.; Aviv, M., unpublished results.

(6) (a) Lee, C. C.; Cessna, A. J.; Davis, B. A.; Oka, M. *Can. J. Chem.* **1974**, *52*, 2679. (b) Rummens, F. H. A.; Green, R. D.; Cessna, A. J.; Oka, M.; Lee, C. C. *Ibid.* **1975**, *53*, 314. (c) Oka, M.; Lee, C. C. *Ibid.* **1975**, *53*, 320. (d) Lee, C. C.; Ko, E. C. F. *Ibid.* **1976**, *54*, 3041. (e) Lee, C. C.; Oka, M. *Ibid.* **1976**, *54*, 604. (f) Lee, C. C.; Paine, A. J.; Ko, E. C. F. *J. Am. Chem. Soc.* **1977**, *99*, 7267. (g) Lee, C. C.; Ko, E. C. F. *Can. J. Chem.* **1978**, *56*, 2459. (h) Lee, C. C.; Paine, A. J.; Ko, E. C. F. *Can. J. Chem.* **1977**, *55*, 2310. (i) Lee, C. C.; Weber, U.; Obafemi, C. A. *Ibid.* **1979**, *57*, 1384. (j) Lee, C. C.; Ko, E. C. F.; Rappoport, Z. *Ibid.* **1980**, *58*, 884. (k) *Ibid* **1980**, *58*, 2369. (l) Lee, C. C.; Obafemi, C. A.; Quail, J. W.; Rappoport, Z. *Ibid.* **1981**, *59*, 2342.

(7) (a) Sonoda, T.; Kobayashi, S.; Taniguchi, H. *Bull. Chem. Soc. Jpn*, **1976**, *49*, 2560. (b) Ohba, H.; Ikeda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1980**, 988. (c) Sonoda, T. Ph.D. Thesis, Kyushu University, Fukuoka, Japan, 1977. (d) Ikeda, T. Ph.D. Thesis, Kyushu University, Fukuoka, Japan, 1981. (e) Ikeda, T.; Matsuyama, M.; Kobayashi, S.; Taniguchi, H., unpublished results.

(8) (a) Rappoport, Z.; Gal, A.; Houminer, Y. *Tetrahedron Lett.* **1973**, 641. (b) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506. (c) Rappoport, Z.; Schnabel, I.; Greenzaid, P. *J. Am. Chem. Soc.* **1976**, *98*, 7726. (d) For rearrangements in the gas phase, see Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H.; Stahl, D. *J. Am. Chem. Soc.* **1981**, *103*, 2770.

(9) Migrations of the β-(*p*-oxidophenyl) group (*p*-$^-OC_6H_4$) in triarylvinyl cations are fast and nearly complete in several system.[7b,d,e]

(10) (a) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6734. (b) *Tetrahedron Lett.* **1970**, 1817, 1845. (c) *J. Am. Chem. Soc.* **1975**, *97*, 821. (d) *Ibid.* **1975**, *97*, 836. (e) Unpublished results.

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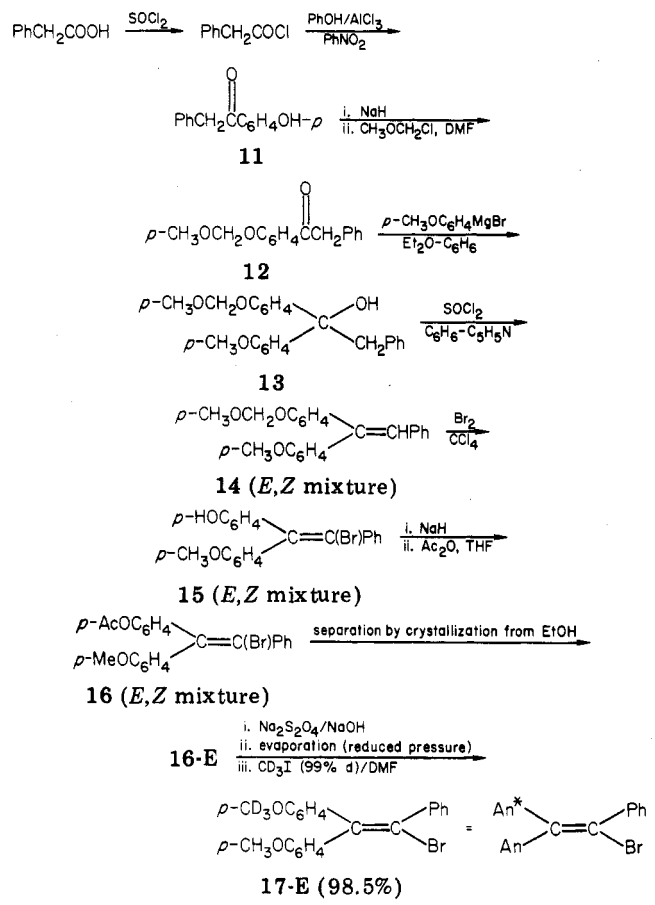
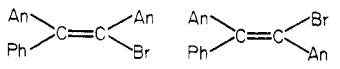
Scheme I[a]



[a] An* = p-$CD_3OC_6H_4$.

to 8 when Nu^- = AcO^-, CF_3CH_2OH, and p-$MeC_6H_4S^-$[8a,b] suggests that the product-forming intermediate 6 in the solvolysis of both 4 and 9 and 10 is a free cation.[2,3a,10] However, there are small differences in the 7/8 ratios between 4 on the one hand and 9 and 10 on the other in AcOH[8a,10c] and more significant differences in pivalic acid,[8c] a solvent with low dielectric constant. It was therefore suggested that ion pairs are involved in the solvolytic rearrangement of 4 in the latter solvent.[8c]



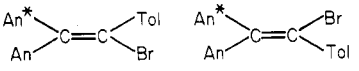
Whereas the product-forming intermediate in the other solvents is a free ion, the migration of the β-anisyl group could take place at the ion-pair stage with preferential migration of the group trans to the leaving bromine, followed by dissociation to the product-forming free ion. Moreover, although 9 and 10 solvolyze with similar rates[8c,10b,c] and the solvolysis rates of triphenylvinyl bromide, (E)- and (Z)-1,2-diphenyl-2-anisylvinyl bromides, and 4 show additivity of the effects of the β-substituents,[8b] 4 reacts 12.5 times faster than triphenylvinyl bromide.[8b] Since even small rate accelerations may be associated with a significant extent of participation,[11] additional evidence concerning the nature of the reaction intermediates is required. We therefore synthesized the pair of the methoxy-labeled E and Z isomers of 4, (E)- and (Z)-2-[p-(trideuteriomethoxy)phenyl]-2-(p-methoxyphenyl)-1-phenylvinyl bromides (17-E and 17-Z), and studied the extent of β-anisyl migration in AcOH and in TFE. The α-p-tolyl analogue 18-Z was also studied for comparison.

(11) Schleyer, P. v. R.; Lancelot, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 4297.

Table I. β-Anisyl Migration from Cis and Trans Positions to the Leaving Group

substrate	solvent	trans An/cis An migration[a]	E/Z product ratio	observation of precursor $E \rightleftharpoons Z$ isomerization
17-E	TFE/2,6-lutidine	53:47	50:50[b]	no
17-Z	AcOH/NaOAc			extensive
17-E	AcOH/AgOAc	51:49		extensive
17-Z	AcOH/AgOAc	51:49	53:47	
18-Z	TFE/2,6-lutidine	51.3:48.7	58:42	?
18-Z	AcOH/AgOAc	50:50	54:46	yes

[a] Migration from the β position. Trans and cis relate to the Br. [b] Reference 8b.



Tol = p-MeC_6H_4

Results

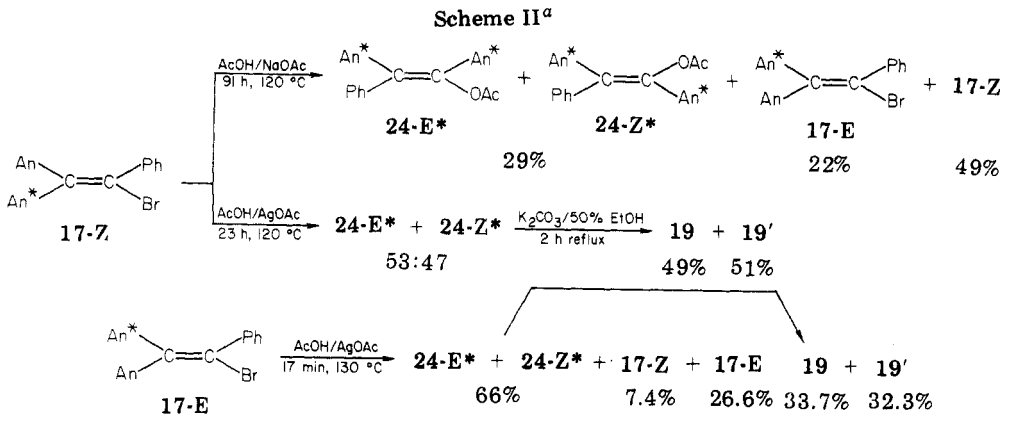
Synthesis. The preparation of 17-E and 17-Z is described in Scheme I. Treatment of p-hydroxydeoxybenzoin (11) with sodium hydride, followed by methoxymethyl chloride in DMF gave the ketone 12. Reaction with (p-methoxyphenyl)magnesium bromide gave the carbinol 13, which on dehydration gave an E,Z mixture of the ethylenes 14. Bromination in carbon tetrachloride resulted both in bromination of the double bond and in hydrolysis of the methoxymethylene group to form an E,Z mixture of 2-anisyl-2-(p-hydroxyphenyl)-1-phenylvinyl bromides 15. The hydrolysis is probably due to the formation of HBr in the bromination step. Acetylation of the phenolic group with NaH/Ac_2O gave a mixture of the acetoxy derivatives 16-E and 16-Z, which was separated by crystallization from ethanol at room temperature. Reaction of pure 16-E with NaOH and sodium hydrosulfite in ethanol, followed by evaporation of the solvent, and further reaction with 99% CD_3I gave 17-E, which by analysis of the methoxy signals in the ^1H NMR spectrum was ≥98.5% isotopically pure. The remainder is the isomer 17-Z or 4 according to the NMR. Hydrolysis of 16-Z with NaOH and sodium hydrosulfite in ethanol for 2 h, followed by treatment with CD_3I, afforded 17-Z, which was ≥98.4% isotopically pure.

The two key points in the synthesis involve the use of the two easily removable groups: the methoxymethylene group in acidic solution and the acetoxy group in basic solution. Direct separation of the vinyl bromides 15-E and 15-Z, followed by etherification, was found to be impractical since the hydroxy derivatives 15-E and 15-Z are sensitive to oxidation and are somewhat configurationally unstable in neutral solution.

The last step of the synthesis is described in the Experimental Section. The other parts[7d] will be described elsewhere.

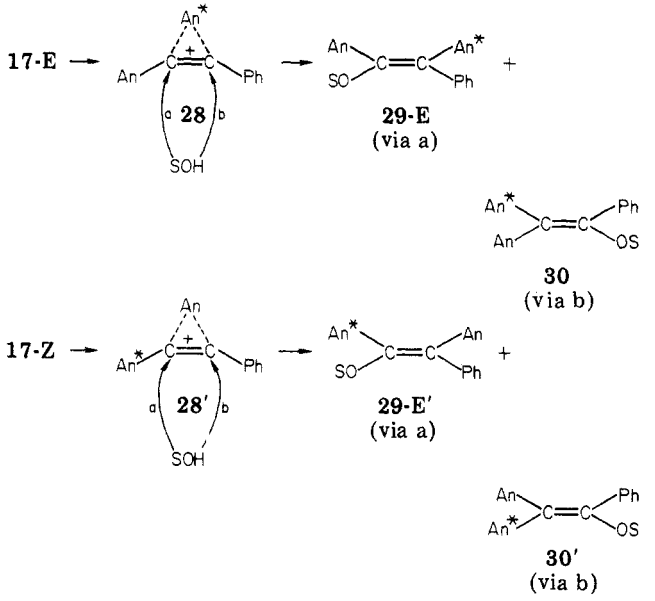
Solvolysis–Rearrangement. (a) Determination of the Extent of Rearrangement. The distribution of the label in the solvolysis products was determined by two

Scheme II[a]



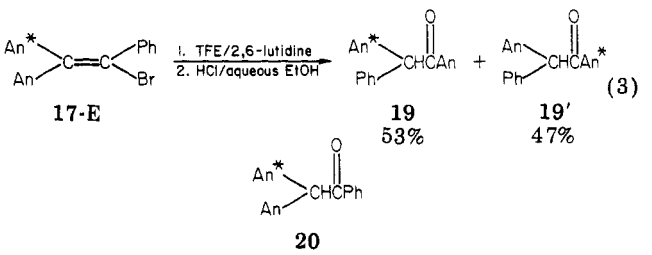
[a] The asterisk indicates that the exact distribution of the label between C-1 and C-2 was not determined.

Scheme III



methods. For simplification of the NMR spectra the crude solvolysis product was usually hydrolyzed before the analysis, and the ketones formed were analyzed by integration of the various methoxy signals in the NMR spectra. The ketones were also subjected to mass spectral analysis and the ratios of two pairs of isotopic peaks were analyzed.

(b) Trifluoroethanolysis. Solvolysis of **17-E** in TFE buffered by 2,6-lutidine for 200 h at 140 °C gave a mixture which showed four methoxy signals and two methylene quartets at positions corresponding to those of the isomeric vinyl trifluoroethyl ethers **7** and **8** (Nu = OCH_2CF_3).[8b] However, due to overlap of the signals, no further analysis was performed and the mixture was hydrolyzed with aqueous ethanolic HCl. The products (according to the NMR spectra) were the ketones **19** and **19'**. No evidence for the formation of the unrearranged ketone **20** was obtained (eq 3). Mass spectral analysis of the mixture of



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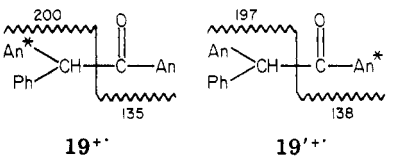
19 and **19'** was concentrated on the anisoyl and the *p*-methoxybenzhydryl peaks (cf. $19^{+\cdot}$ and $19'^{+\cdot}$). The ratio

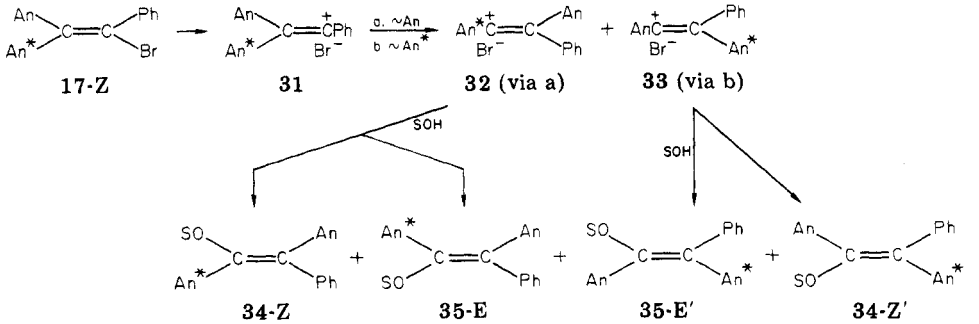


of the base peak at *m/e* 135 to the isotopic peak at 138 ($AnCO^+/An^*CO^+$) is 53:47, while the peaks at *m/e* 200 and 197 (An^*C^+HPh/AnC^+HPh) gave a 55:45 ratio. The integration of the methoxy signals gave a 54:46 ratio of **19** to **19'**. The average of all the determinations is 54:46, but since we believe that the mass spectral analysis of the $AnCO^+$ and the An^*CO^+ peaks is the most accurate, we will use the 53:47 ratio in the subsequent discussion.

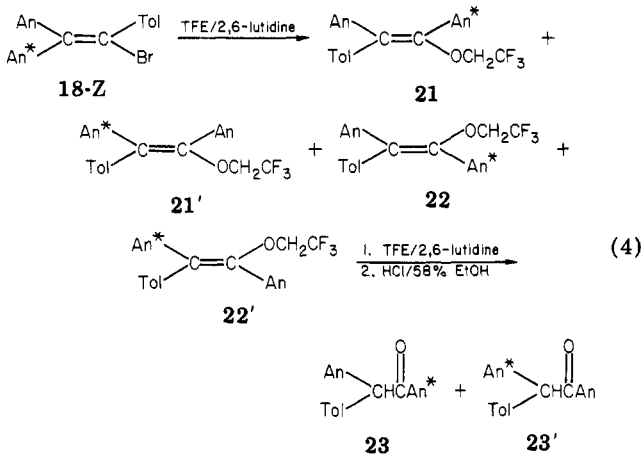
A search for the formation of **17-Z** after 10% or 57% reaction showed that no **17-E** ⇌ **17-Z** isomerization can be detected within the accuracy of the NMR method.

Solvolysis of **18-Z** in TFE buffered by 2,6-lutidine at 140 °C for 24 h gave a mixture of the vinyl trifluoroethyl ethers **21**, **21'**, **22**, and **22'**. By integration of the methyl signals the **21** + **21'** to **22** + **22'** ratio is 58:42. Hydrolysis in

Scheme IV



aqueous ethanolic HCl gave a mixture of the ketones **23** and **23′** (eq 4). NMR in benzene showed a 50.7:49.3 ratio



(4)

of the methoxy signals and mass spectral analysis showed that the ratio of the m/e 135 to 138 signal is 48.7:51.3, i.e., the ketone **23** is formed in slight excess. Isomerization of the starting material during the reaction could not be detected due to overlap of the methoxy signals of **18-E** and the products.

(c) Acetolysis. Reflux of **17-Z** in AcOH/NaOAc for 91 h gave a mixture which by NMR analysis contained 49 ± 2% of **17-Z**, 22 ± 0.3% of **17-E**, and 29 ± 0.7% of a mixture of the vinyl acetates **24-E** and **24-Z**. Reflux of **17-Z** for 23 h in AcOH/AgOAc gave a mixture of **24-E** and **24-Z** in a 53:47 ratio by integration of the acetoxy signals. A previous, less accurate analysis, gave a ca. 50:50 distribution.[8a] Comparison with literature values suggested that the unrearranged acetate, labeled 2,2-dianisyl-1-phenylvinyl acetate, is not formed at all.

Hydrolysis of the mixture of the vinyl acetates by reflux for 2 h with 9 molar equiv of K_2CO_3 in 50% aqueous EtOH gave again a mixture of the ketones **19** and **19′**. NMR analysis of the methoxy signals showed a 47 ± 2:53 ± 2 ratio of **19′** to **19**, whereas a gas chromatographic–mass spectral analysis showed that the m/e 138 to 135 ratio was 1.04 ± 0.02, i.e., the **19′**/**19** ratio is 51:49.

The solvolytic rearrangement of **17-E** in AcOH/AgOAc was studied for a shorter time in order to detect any possible **17-E** ⇌ **17-Z** isomerization during the AgOAc-assisted solvolysis. After 17 min at 130 °C (66% reaction) the product ratio after hydrolysis showed very slight preference for **19** over **19′**. NMR before hydrolysis showed that **17-E** was partially isomerized: the ratio of **17-E** to **17-Z** in the recovered vinyl bromide was 3.6:1. The results are summarized in Scheme II.

The reaction of the unlabeled **4** with AcOH in the presence of 2 molar equiv of silver acetate is relatively rapid. Reaction for 35 min at 130 °C gave 83% of the vinyl acetates.

Solvolysis of **18-Z** in AcOH/AgOAc for 22 h gave a 54:46 mixture of the (*E*)- to the (*Z*)-vinyl acetates **25-E** to **25-Z**. Hydrolysis in K_2CO_3/50% EtOH gave a mixture which showed two methyl signals in the NMR in a 87:13 ratio and two MeO signals in a 57:43 ratio. The mass spectra showed that the m/e 135 to 138 ratio is 1.0. The data can be interpreted as due to the formation of a 1:1 mixture of **23** and **23′** together with 13% of the unrearranged ketone **27**. The 57:43 ratio of the methoxy signals will then reflect overlap of the methoxy signals of **23** and **27** (eq 5; asterisk indicates that the position of the label was not determined). Indeed, a peak at m/e 230, corresponding to the AnAn*CH^+ fragment of **27** appears in the mass spectrum of the hydrolysis mixture. However, no peak at m/e 119 corresponding to $TolCO^+$ was found, which agrees with the higher stability of the benzhydryl fragment.[12]

Reflux of **18-Z** in AcOH with 1.8 molar equiv of AgOAc for 4 min gave 9% of a methoxy signal in the NMR at a position corresponding to **18-E** but no signal for the acetoxy group of either **25-E** or **25-Z**. Isomerization is apparently faster than the solvolysis.

Discussion

The present work revealed two mechanistic phenomena which are relevant to the mechanism of the solvolytic rearrangement. They are the different extent of migration of the β-anisyl groups from cis and trans positions to the leaving group and the occurrence of (*E*)- ⇌ (*Z*)-vinyl bromide isomerization during the reaction. Table I summarizes the results in relation to the two phenomena and give the *E*/*Z* distribution of the solvolysis products.

Mechanistic Consequences of the Different Extent of Migration of the Two β-Anisyl Groups. Table I shows that in most of the systems studied there is a preference, although mostly very slight, for migration of the anisyl group trans to the bromine over that cis to the bromine. Since migration from a trans position to the leaving group is a phenomenological characteristic of neighboring β-aryl participation, the possibility that this route is involved in our reaction will be discussed. However, the problem was previously discussed for system **4**[8] and our discussion will be brief.

β-Anisyl participation in the solvolytic transition state involves the anisyl trans to bromine and ions **28** and **28′** should be formed via the bridged transition states from **17-E** and **17-Z**, respectively. If the ions are the product-forming intermediates, nucleophilic ring opening from the side opposite to the bridge can take place at C_α, giving skeletally and isotopically unrearranged product, or at C_β with the formation of a rearranged product with two cis anisyl groups and anisyl migration. The possibilities when SOH is the solvent are shown in Scheme III.

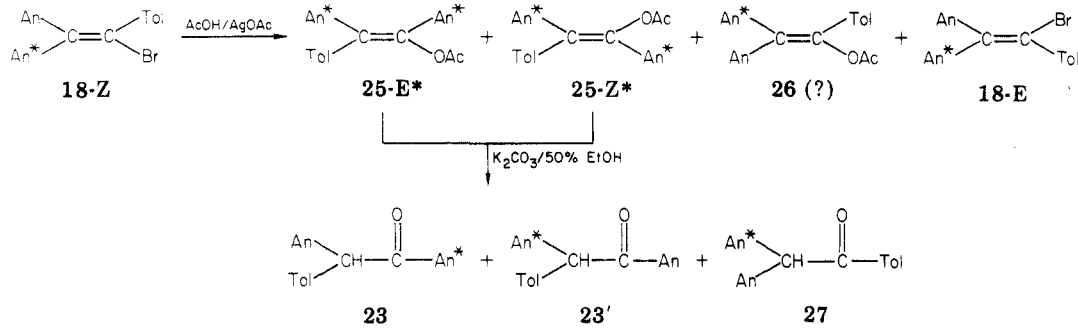
The fact that ring opening of unlabeled **4** gave only rearranged products is consistent with route a above, but since the products with AcOH, TFE, and *p*-$MeC_6H_4S^-$ are nearly 1:1 mixtures of the *E* and *Z* isomers (Table I),[8] this route is excluded. There is still the remote possibility that anchimeric assistance gives **28** or **28′** which rearrange to a more stable open ion before product formation and the latter gives the *E* and the *Z* products. This possibility requires exclusive migration of the anisyl group trans to the Br and is therefore excluded by the present results which show nearly identical migration of the two β-anisyl groups.[13] A large difference between the migration of the two groups is expected in pivalic acid,[8c] but so far we did not find a reliable analytical method to evaluate this difference.[14]

The rearrangement can therefore take place either at the free-ion or at the ion-pair stage. In the former case the unequivalent migration of the two groups can be due to isotope effects. The two transition states for migration

(12) However, it should be noted that this observation may exclude the formation of **26**, since the loss of CO from the molecular ion can give a species which may give various substituted benzhydryl fragments (An*C^+HTol, AnC^+HTol, AnC^+HAn*). This problem is discussed in ref 5b.

(13) A very minor contribution of the k_Δ route cannot be excluded.

(14) Pivalolysis of **17-Z** seems to involve a larger preference for migration of the trans anisyl than in the other solvents. However, due to overlap of signals it is difficult to evaluate accurately this preference. Hydrolysis to **19** and **19′** requires more drastic conditions for the vinyl pivalates than for the acetates or the ethers.



(5)

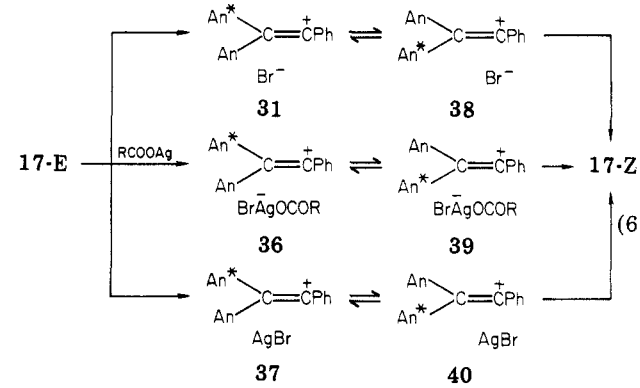
in the free ion are **28** and **28'** where both groups stabilize the positive charge to a different extent. Although some of the small effects are of a magnitude expected for a remote isotope effect,[15] their direction[16] and especially the similar preference for trans β-anisyl migration for both **17-E** and **17-Z** exclude this possibility. We therefore suggest that the differences may reflect the intervention of ion pairs in the rearrangement process. This is shown in Scheme IV which was discussed previously for reactions in pivalic acid.[8c] The main point is that steric hindrance for migration in the ion-pair **31** prefer the formation of **32** by An migration over formation of **33** by An* migration. Steric hindrance to capture will give more **34-Z** than **35-E** from **32** and more **35-E'** than **34-Z'** from **33**.

The preference for trans β-anisyl migration in all the cases is very small. The real value in AcOH/AgOAc should be somewhat different from the value given in Table I since the **17-E** ⇌ **17-Z** isomerization during the reaction will reduce the value. This is not the case in TFE/2,6-lutidine. It is possible that in addition to any small isotope effect which affects the ratio, the values reflect a small contribution of a few percent from migration in ion pairs superimposed on the main migration via the free ion. However, the preference for formation of **34-Z** is too small to be detected. To the extent that the small differences between systems **17** and **18** are meaningful, the lower preference for trans β-anisyl migration in system **18** where the cationic moiety is more stable is consistent with a contribution from an ion-pair route. We expect that the contribution of reactions via ion pairs will increase in a less dissociating solvent such as pivalic acid.[14]

Finally, it was suggested that the β-phenyl rearrangement during the solvolysis of triphenylvinyl derivatives proceeds at the ion-pair stage rather than at the free-ion stage.[6a,c,d,g,k] Since the driving force for this degenerate rearrangement is lower than for the **5** → **6** rearrangement, extrapolation from the present results is not possible. However, a similar labeling technique of one defined β-phenyl group may give an answer to this question.

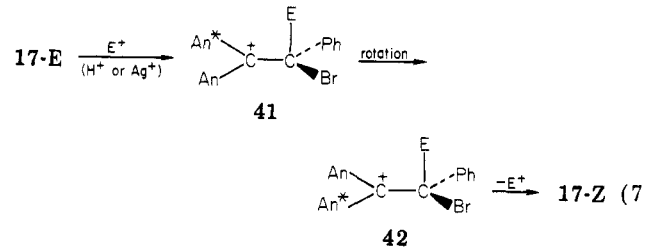
E ⇌ ***Z*** **Isomerization of Systems 17 and 18.** A rather extensive **17-E** ⇌ **17-Z** isomerization accompanies the solvolysis in AcOH in the presence of either NaOAc or AgOAc, but it is not observed in buffered TFE. A **18-E** ⇌ **18-Z** isomerization probably also takes place in AcOH/AgOAc. Regardless of whether the isomerization is relevant (eq 6) or parasitic (eq 7) to the solvolysis reaction, it has interesting mechanistic consequences for the solvolysis of α-arylvinyl derivatives.

Two routes can be envisioned for the isomerization. (i) The initially formed ion pair **31**, or the ion pair **36** (or the ion–molecule **37**) formed in a silver-assisted process[10c] undergo rotation around the long axis of the carbonium ion, or the bromine-containing species migrates from one side of the carbonium ion to the other to form **38**, **39**, or **40**. Recombination of the bromide ion with the carbonium ion gives the isomeric vinyl bromide (eq 6). (ii) An initial



(6)

electrophilic addition of either a proton or a Ag^+ ion (E^+) to the double bond gives the ion **41**, which after internal rotation around the C_α–C_β bond expels the electrophile from **42** to form the isomeric bromide (eq 7).



(7)

Route i raises several difficulties. Although an internal return from a carbonium ion–AgBr ion–molecular pair seems apriori unlikely, there are precedents to this route in the solvolysis–isomerization of vinyl halides.[10c,18] The AgOAc-assisted acetolysis of 1-cyclopropyl-1-iodopropene is accompanied by isomerization,[18] and the **9** ⇌ **10** isomerization which accompanies the solvolysis in AcOH/AgOAc was suggested to take place via an ion pair similar to **39**. Return during silver salt assisted solvolysis of aliphatic halides is also known[19] and is easy to understand if the assistance is by the silver carboxylate and the ion pair resembles **39**. The main difficulty is that rotation followed by return to the unrearranged ion should be competitive with the β-anisyl migration, although the **5** → **6** migration

(15) Melander, L.; Saunders, W. H. "Reaction Rates of Isotopic Molecules"; Wiley: London, 1980.

(16) If hyperconjugative effects are more important than inductive effects and if the charge is more localized on the bridging aryl group than on the nonmigrating aryl group, migration of An in **17-E** will be preferred over migration of An*, contrary to the observation.

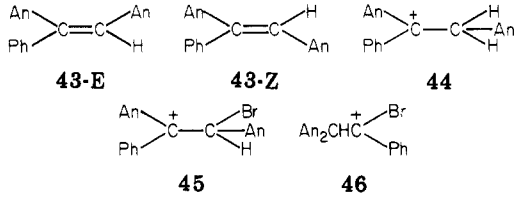
(17) A priori, the positions of the Br^- in **32** and **33** are expected to be different since the bromide may be "pushed" during the **31** → **33** rearrangement.

(18) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1941.

(19) Kevill, D. N. In "The Chemistry of Functional Groups, Supplement D, The Chemistry of Halides, Pseudohalides and Azides"; Patai, S., Rappoport, Z., Eds.; Wiley: London, 1982.

is much faster than the capture of the free-ion **5** by much better nucleophiles than Br^- such as p-$MeC_6H_4S^-$.[8b] However, the anionic moiety in the ion pair may be so much more nucleophilic than, e.g., a free p-$MeC_6H_4S^-$ ion that it can partially intercept the rearrangement. The available data cannot corroborate or exclude this possibility. For example, the rearrangement of the (unlabeled) ion-pair **31** to **32** and the return of **32** with isomerization are both faster than capture by the solvent in $Me_3CCOOH/Me_3CCOONa$ or Me_3CCOOH/Me_3COOAg, respectively,[8c] so that the relative rates of return and migration cannot be compared. While we cannot exclude route i unequivocally, we show below that route ii is the main route. However, in view of the present results, the possibility of internal return to the precursor ion with isomerization before rearrangement should be considered in future studies, especially in degenerate rearrangements in triarylvinyl systems with identical aryl groups, when the return may be hidden.

Electrophilic isomerization (eq 7, $E^+ = H^+$) are well-known. Since isomerization was observed in AcOH but not in the less acidic TFE, it seems to be associated with the acidic nature of the medium. A rough estimate of the expected isomerization rate via this route is obtained by comparison with the isomerization rates of the related olefins **43-E** and **43-Z** which isomerize to one another via cation **44**.[10c] Bromine is deactivating in electrophilic additions to olefins[22] so that isomerization of **9** and **10** via cation **45** will be approximately one order of magnitude slower than the isomerization of **43-E** and **43-Z**.[22a] The



43-E **43-Z** **44**

45 **46**

addition to **17-E** was formulated in eq 7 as giving the cation **41** formed by addition to C_α rather than the isomeric ion **46**, formed by addition to C_β, which seems less stable. Since the positive charge in **41** is more delocalized than in **44** and **45** the isomerization of **17-E** via eq 7 should be faster than those of **9** or **10**.[23] The approximate isomerization rate constant of **17-E** in AcOH at 120 °C is 3×10^{-6} s^{-1}, whereas the values for **43-E** and **43-Z** are 9.5×10^{-6} s^{-1}, i.e., the isomerization rate of **17-E** is higher than that of **9** or **10**. We conclude that isomerization via route ii is dominant but the evaluation of any contribution of route i is difficult since it depends on the relative stabilities of the transition states leading to **41**, **44**, and **45**.

The rate acceleration is higher in the Ag^+-assisted process. The approximate rate constant for the heterogeneous isomerization of **17-E** in AcOH/0.052 M AgOAc at 120 °C is estimated as 2×10^{-4} s^{-1}, 15-fold higher than the value for the isomerization of **43-E** or **43-Z** (1.3×10^{-5} s^{-1}) in AcOH/0.025 M AgOAc,[10c] and the ratio of reactivities of **17-E** to **9** or **10** will be much higher. Consequently, the isomerization presumably proceeds via route ii,[24] either via a Ag-substituted ion **41**, E = Ag, or via a more complex process which involves an initial complexation of the Ag^+ with the double bond.

Experimental Section

Melting points are uncorrected. UV spectra were determined with a Shimadzu 200S spectrometer and NMR with JEOL MH-60, JEOL FT 100-MHz, and Brucker spectrospin 300-MHz instruments, and the data are given in δ units downfield from internal tetramethylsilane. Mass spectra were determined with a JEOL JMS-07 spectrometer.

(*E*)-2-[*p*-(Trideuteriomethoxy)phenyl]-2-(*p*-methoxyphenyl)-1-phenylvinyl Bromide (17-E). To a cooled (5–10 °C) solution of (*E*)-2-(*p*-acetoxyphenyl)-2-(*p*-methoxyphenyl)-1-phenylvinyl bromide (500 mg, 1.2 mmol) in ethanol (70 mL) was added dropwise a 5% aqueous NaOH solution (20 mL) of sodium hydrosulfite (310 mg, 1.8 mmol). The solution turned yellow. After the solution stood for 1 h, the solvent was evaporated under reduced pressure and dimethylformamide (20 mL) was added, followed by commercial CD_3I (99% *d*, 0.23 mL, 3.5 mmol). The reaction mixture was extracted with 1:1 benzene–ether (40 mL). The solvent was evaporated and the remaining solid was crystallized from EtOH–benzene, giving colorless crystals of **17-E** (372 mg, 80%), mp 116.3–118 °C, which according to the NMR contained 1.5% of **17-Z** or of **4**: UV (cyclohexane) λ_{max} 313 nm (ϵ 10200), 243 (21300); NMR ($CDCl_3$) δ 3.62, 3.71 (3 H, 2 s in 1.5:98.5 ratio, MeO), 6.35–7.40 (13 H, m, Ar); mass spectrum, *m/e* 399, 397 (M^+, 85, 85), 318 (M^+ – Br, 100).

(*Z*)-2-[*p*-(Trideuteriomethoxy)phenyl]-2-(*p*-methoxyphenyl)-1-phenylvinyl Bromide (17-Z). To a solution of (*Z*)-2-(*p*-acetoxyphenyl)-2-(*p*-methoxyphenyl)-1-phenylvinyl bromide (490 mg, 1.2 mmol) in ethanol (70 mL) was added a 1.0 N solution of NaOH (5.97 mL) containing sodium hydrosulfite with cooling (5–10 °C). The reaction was continued as discussed above for preparation of the *E* isomer and gave a white solid which was crystallized from EtOH–benzene, giving colorless crystals of **17-Z** (370 mg, 78%): mp 112–114 °C; NMR ($CDCl_3$) δ 3.62, 3.71 (3 H, 2 s in 98.4:1.6 ratio, MeO), 6.35–7.40 (13 H, m, Ar).

(*Z*)-2-[*p*-(Trideuteriomethoxy)phenyl]-2-(*p*-methoxyphenyl)-1-(*p*-tolyl)vinyl Bromide (18-Z). To a solution of (*Z*)-2-(*p*-acetoxyphenyl)-2-(*p*-methoxyphenyl)-1-(*p*-tolyl)vinyl bromide (416 mg, 0.95 mmol) in ethanol (100 mL) was added an aqueous solution of 1.0 N NaOH (20 mL) of $Na_2S_2O_4$ with cooling. The solution stood for additional 1 h and the solvent was evaporated. Dimethylformamide (20 mL) was added, followed by CD_3I (99% *d*, 0.28 mL, 4.3 mmol) with cooling, and the mixture was left for 1 h. Workup as above gave a solid, which was crystallized from EtOH–benzene, giving colorless crystals of **18-Z** (370 mg, 94%), mp 90.5–92.5 °C, contaminated with 1.6% of an impurity which may be either **18-E** or the unlabeled compound: UV (cyclohexane) λ_{max} 313 nm (ϵ 10000), 245 (22300); NMR (CCl_4) δ 2.26 (3 H, s, Me), 3.61, 3.74 (3 H, 2 s in 98.4:1.6 ratio, MeO), 6.35–7.30 (12 H, m, Ar).

Trifluoroethanolysis of 17-E. (a) A mixture of **17-E** (50 mg, 0.12 mmol) and 2,6-lutidine (0.03 mL, 0.24 mmol) in TFE (10 mL) was heated for 3.5 h in a sealed ampule at 140 °C. After workup the NMR of the crude reaction mixture showed the formation of 10% trifluoroethyl vinyl ethers,[8b] but no signal at δ 3.62 due to **17-Z** was observed. When the reaction mixture was refluxed for 20 h at 120 °C under the same conditions, 57% of the trifluoroethyl vinyl ethers was formed, but **17-Z** was not detected.

(b) A mixture of **17-E** (200 mg, 0.49 mmol) and 2,6-lutidine (0.11 mL, 0.97 mmol) in TFE (10 mL) was heated in a sealed ampule for 210 h at 140 °C. After the usual workup the NMR of the crude reaction mixture showed only the presence of the mixture of **7** and **8**, Nu = OCH_2CF_3, in a 1:1 ratio [NMR ($CDCl_3$) δ 3.68, 3.72, 3.73, 3.76 (4 s, MeO), 3.90, 3.92 (center of 2 q, J = 8 Hz, CH_2),

(20) A method to distinguish between the possibilities is to increase the lifetime of the intermediate and thus the ion-pair dissociation constant by increasing the electron-donating ability of the α-aryl substituent. The rate of the electrophilic addition will be only slightly affected. Unfortunately, we did not have enough of **18-Z** to make this comparison.

(21) For example, Noyce, D. S.; Pryor, W. A.; King, P. A. *J. Am. Chem. Soc.* **1959**, *81*, 5423. Noyce, D. S.; Woo, G. L.; Jorgenson, M. J. *Ibid.* **1961**, *83*, 1160. Noyce, D. S.; Hatter, D. R.; Miles, F. B. *Ibid.* **1968**, *90*, 4633. Fahey, R. C.; Schneider, H.-J. *Ibid.* **1970**, *92*, 6885.

(22) (a) Peterson, P. E.; Bopp, R. I. *J. Am. Chem. Soc.* **1967**, *89*, 1283. (b) Rappoport, Z.; Gal, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 301.

(23) The higher rate of electrophilic addition to 1,1-dianisyl-2-substituted ethylenes compared with 1-anisyl-1-phenyl-2-substituted ethylenes can be judged from the ρ of –2.27 for the bromination of 1-anisyl-1-(*p*-substituted phenyl)ethylenes: Hegarty, A. F.; Lomas, J. S.; Wright, W. V.; Bergman, E. D.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 2222.

(24) Since the reaction order in the silver salt is unknown and the reactions are heterogeneous, a quantitative estimation of the contribution of both routes requires much more extensive data.

6.67–7.43 (m, Ar)]. Column chromatography (Al_2O_3, 4 g) gave the mixture of the ethers,[8b] and 170 mg of the mixture was hydrolyzed with 2 N HCl (6 mL) in ethanol (14 mL) at 80 °C for 96 h, giving an oil, which on two recrystallizations from *n*-hexane–ethanol gave white crystals of a mixture of the two ketones **19** and **19′**: mp 75.5–77.5 °C (lit.[8b] mp 73–75 °C); NMR ($CDCl_3$) δ 3.68, 3.73 (2 H, 2 s, MeO), 5.90 (1 H, s, CH), 6.67–8.07 (13 H, m, Ar); mass spectrum, *m/e* 335 (M^+, 2), 200 (M – AnCO, 26), 197 (M – An*CO, 22), 138 (An*CO, 86), 135 (AnCO, 100), (*m/e* 135/*m/e* 138 = 53:47, *m/e* 200/*m/e* 197 = 55:45, δ 3.73/δ 3.68 = 54:46).

Acetolysis of 17-Z. (a) A mixture of **17-Z** (26 mg, 0.065 mmol) and Na_2CO_3 (27 mg, 0.25 mmol) in acetic acid (4 mL) was refluxed for 91 h. Ice and water were poured into the reaction mixture, which was then extracted with a 1:1 mixture of benzene and ether (60 mL). The organic phase was washed with water and then with saturated $NaHCO_3$ solution and dried (Na_2SO_4), the solvent was evaporated under reduced pressure, and the NMR of the remainder was determined in CCl_4. Integration of the methoxy signals at δ 3.62 and 3.71 (**17-E** and **17-Z**) and at δ 3.67, 3.68, 3.73 (**24-E** and **24-Z**) as well as the OAc signals at δ 1.80 and 1.85 gave a product distribution of 49% unreacted **17-Z**, 22% of the isomeric **17-E**, and 29% of the vinyl acetates.

(b) A mixture of **17-Z** (77 mg, 0.19 mmol) and silver acetate (65 mg, 0.39 mmol) was refluxed in AcOH (10 mL) for 23 h. The reaction mixture was poured into water, extracted with 1:1 benzene–ether (40 mL), washed with water and with $NaHCO_3$ solution, and dried (Na_2SO_4), and the solvent was evaporated. The vinyl acetates (NMR spectrum as in a above) were obtained as an oil, and integration of the acetoxy signals showed a 53:47 distribution of **24-E** to **24-Z**. The crude reaction mixture was refluxed for 2 h with K_2CO_3 (400 mg, 1.7 mmol) in 50% aqueous ethanol (10 mL). The mixture gave an NMR spectrum identical with that of a mixture of **19** and **19′**, which according to the methoxy region were present in a 47:53 ratio. The *m/e* 138/*m/e* 135 intensity ratio was 1.04 ± 0.02.

Acetolysis of 17-E. A mixture of **17-E** (40 mg, 0.1 mmol) and AgOAc (35 mg, 0.21 mmol) was refluxed in AcOH (4 mL) for 17 min. NMR analysis showed 66% conversion and **17-E** to **17-Z** ratio of 26.6:7.4. Hydrolysis gave **19** and **19′**, which according to the NMR were formed in a 51:49 ratio.

Acetolysis of 18-Z. A mixture of **18-Z** (58 mg, 0.14 mmol) and silver acetate (50 mg, 0.28 mmol) in AcOH (10 mL) was refluxed for 24 h. Ice water (50 mL) was added, the solution was extracted with a 1:1 mixture of ether and benzene (40 mL), and the organic phase was washed successively with water (50 mL) and with saturated aqueous $NaHCO_3$ solution (50 mL) and dried (Na_2SO_4). The solvent was evaporated and the remaining oil was analyzed by NMR: (CCl_4) δ 1.82, 1.825, 1.84 (3 H, overlapping 3 s, AcO), 2.21, 2.28 (3 H, 2 s in a 55:45 ratio, Me), 3.62, 3.66 (3 H, 2 s in a 69:31 ratio, MeO), 6.40–7.14 (12 H, m, Ar).

The crude product was then refluxed for 2 h with K_2CO_3 (300 mg, 2.2 mmol) in 50% EtOH. Workup was similar to that described above. NMR (CCl_4) δ 2.24, 2.26 (3 H, 2 s in ca. 85:15 ratio, Me), 3.61, 3.66 (3 H, 2 s in a 57:43 ratio, MeO), 5.70 (1 H, s, CH), 6.52–7.95 (13 H, m, Ar). The methyl signals are better separated in C_6H_6, though their positions are inverted: NMR (C_6H_6) δ 1.95, 2.06 (13:87); mass spectrum, *m/e* 349 (M, 3), 321 (An*AnC$^+$Tol, 0), 230 (AnAn*CH$^+$, 50), 214 (An*C$^+$HTol, 100), 211 (AnC$^+$HTol, 100), 138 (An*CO$^+$, 92), 135 (AnCO$^+$, 92), 119 (TolCO$^+$, 6). From the mass spectra the ratio of **23** to **23′** is 1:1.

Isomerization of 18-Z. A mixture of **18-Z** (33 mg, 0.08 mmol) and silver acetate (25 mg, 0.15 mmol) in AcOH (5 mL) was refluxed for 4 min. After workup as above the NMR showed signals at δ (CCl_4) 3.60 and 3.70 in a 91:9 ratio. Comparison with the positions of the MeO signals in the unlabeled compound and in **18-E** and **18-Z** showed that 9% of **18-E** was formed. No acetate signals at δ 1.8–1.9 were observed.

Trifluoroethanolysis of 18-Z. A mixture of **18-Z** (77.2 mg, 0.19 mmol) and 2,6-lutidine (0.04 mL, 0.37 mmol) in TFE (15 mL) was kept in an ampule for 24 h at 140 °C. The solvent was evaporated and the remainder was chromatographed over slightly basic alumina (4 g), using for elution hexane–benzene mixtures with ratios varying from 3 to 1. NMR of the vinyl ethers fraction and comparison with the unlabeled samples[5c] showed that the ratio of the (*E*)-vinyl ethers (**21** + **21′**) to the (*Z*)-vinyl ethers (**22** + **22′**) is 58:42: NMR (CCl_4) δ 2.22, 2.32 (3 H, 2 s in a 58:42 ratio, Me), 3.63, 3.69, 3.73 (3 H, 3 s, MeO), 3.82 (2 H, q, J = 8 Hz, CF_3CH_2O), 6.40–7.25 (12 H, m, Ar).

The crude reaction product was refluxed in aqueous ethanolic HCl (2 N, 10 mL; EtOH, 14 mL) for 65 h. Workup as described above gave an oil, which was analyzed by NMR: (CCl_4) δ 2.25 (3 H, s, Me), 3.63, 3.69 (3 H, 2 s in 50.5:49.5 ratio, MeO), 5.68 (1 H, s, CH), 6.49–7.45 (12 H, 3 AA′BB′ q, Ar); (C_6H_6) δ 2.09 (3 H, s, Me), 3.18, 3.30 (3 H, 2 s in a 50.7:49.3 ratio, MeO), 5.90 (1 H, s, CH), 6.47–8.16 (m, Ar + C_6H_6). Hence **23** is formed in excess over **23′**. This is corroborated by mass spectral analysis of the mixture: *m/e* 214 (An*C$^+$HTol, 98), 211 (AnC$^+$HTol, 100), 138 (An*C$^+$O, 91), 135 (AnC$^+$O, 90) (*m/e* 135/*m/e* 138 = 48.7:51.3). *m/e* 227 was not observed.

Registry No. **7**, 50438-42-1; **8**, 50438-41-0; (*E*)-**16**, 81012-37-5; (*Z*)-**16**, 81012-38-6; (*E*)-**17**, 81012-39-7; (*Z*)-**17**, 81012-40-0; (*Z*)-**18**, 81012-41-1; **19**, 61081-97-8; **19′**, 61081-98-9; **21**, 81012-42-2; **21′**, 81012-43-3; **22**, 81012-44-4; **22′**, 81012-45-5; **23**, 81012-46-6; **23′**, 81012-47-7; (*E*)-**24**, 81012-48-8; (*Z*)-**24**, 81012-49-9; (*Z*)-2-(*p*-acetoxyphenyl)-2-(*p*-methoxyphenyl)-1-(*p*-tolyl)vinyl bromide, 81012-50-2; 2,2,2-trifluoroethanol, 75-89-8; acetic acid, 64-19-7.