Vinylic Cations from Solvolysis. 33.[1] Solvolysis of (*E*)- and (*Z*)-1-Anisyl-2-(*p*-nitrophenyl)propen-1-yl Chlorides

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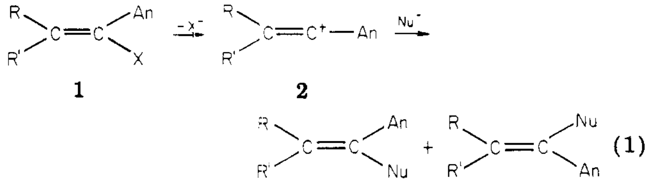
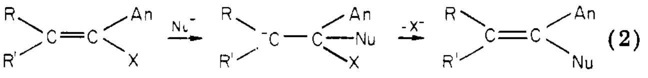
The solvolysis of (*E*)- and (*Z*)-1-anisyl-2-*p*-nitrophenylpropen-1-yl chlorides (**4**-*E* and **4**-*Z*) in buffered aqueous EtOH, TFE, and aqueous TFE was studied. The products in aqueous EtOH are a 6:4 ratio of the ethers **9**-*E* and **9**-*Z* and 1-anisyl-2-(*p*-nitrophenyl)-1-propanone (**6**), and in TFE a 7:3 ratio of the trifluoroethyl ethers **11**-*E* and **11**-*Z* and **6** are formed. The Grunwald–Winstein *m* values at 120 °C in aqueous EtOH are 0.53 (**4**-*E*) and 0.62 (**4**-*Z*) and in aqueous TFE are 0.98 (**4**-*E*) and 0.88 (**4**-*Z*). In aqueous EtOH, common-ion rate depression and a **4**-*E* ⇌ **4**-*Z* isomerization during the solvolysis are negligible, whereas in TFE and less so in aqueous TFE strong common-ion rate depression and an extensive isomerization, which give an equilibrium ratio of 66:34 **4**-*E*/**4**-*Z*, accompany the solvolysis. In 80% EtOH/p-$MeC_6H_4S^-$ the reaction is of second order, the products are a 6:4 ratio of the vinyl thiolates **12**-*E* and **12**-*Z*, and a rapid **4**-*E* ⇌ **4**-*Z* isomerization takes place. In TFE containing $CF_3CH_2O^-$ or p-$MeC_6H_4S^-$ neither isomerization nor common-ion rate depression were observed, and the reactions were several times faster than in TFE/2,6-lutidine. An ionization to a cationoid species is suggested in all cases except in 80% EtOH/RS^-. In aqueous EtOH the reaction probably proceeds via the ion pairs **24a** and **24b**, whose capture by the solvent is slower than their interconversion but faster than internal return. In TFE a long-lived and selective free vinyl cation, **23**, is formed. Preferential capture of the Cl^- over the solvent occurs from the less hindered side of **23**, resulting in common-ion rate depression and isomerization. In the presence of the stronger nucleophiles RO^- and RS^-, the capture occurs at the ion-pair stage. In 80% EtOH/p-$MeC_6H_4S^-$ the mechanism is probably a nucleophilic substitution via a carbanionic intermediate, but the isomerization follows a different route, probably a reversible electron-transfer process.

Previous work on the solvolysis of α-anisyl-β,β-disubstituted vinyl halides **1** (eq 1) indicated a profound effect of electron-donating β substituents (R = R′ = H, alkyl, aryl) on several characteristics of the reaction.[2] An increase in the bulk of R and R′ resulted in a decrease in both the Grunwald–Winstein *m* values[3] and the k_{OTs}/k_{Br}[4] reactivity ratios and in an increase in the selectivities of the ions **2**.[5,6] Steric effects also determine the stereochemical outcome, and the **3a**/**3b** ratio increases when R becomes bulkier compared with R′.[5b,7] The relative reaction rates of compounds **1** reflect a complex balance between steric and electronic effects, although the electronic effect for β,β-diaryl derivatives is small as judged by the low Hammett ρ values.[2a,8]



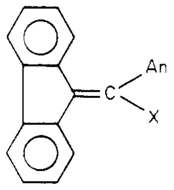
1 **2** **3a** **3b**

When the β substituents are electron withdrawing (e.g., CN, CO_2R), the substitution of X by good nucleophiles usually proceeds with retention of configuration via the nucleophilic addition–elimination (Ad_N-E) route (eq 2).[9,10]



1 **3a**

For mildly electron-withdrawing substituents, competition between the S_N1 and the Ad_N-E routes may be observed. The single system for which this was observed so far is **1a** where R′RC= is the fluorenylidene moiety: in 80% EtOH it undergoes an Ad_N-E reaction when Nu^- = RS^- and an S_N1 reaction when Nu^- = OAc^-.[11]



1a

In continuation of our work on the effect of the β substituents on the characteristic features of vinylic solvolysis and in a search for other systems at the borderline between the S_N1 and the Ad_N-E routes, we prepared the β-(*p*-nitrophenyl)-substituted compounds **4**-*E* and **4**-*Z*. Their solvolysis in the presence of several nucleophiles is presented below.

Results

Starting Materials. A mixture of (*E*)- and (*Z*)-1-anisyl-2-(*p*-nitrophenyl)propen-1-yl chlorides (**4**-*E* and **4**-*Z*)

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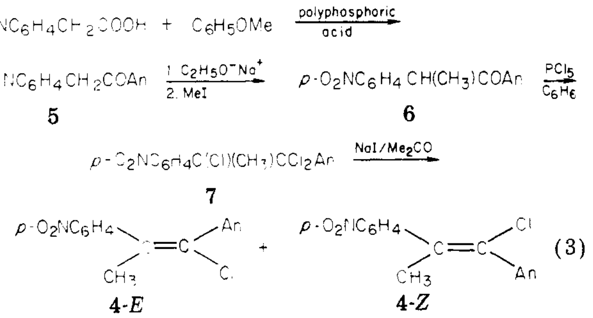
was prepared by the sequence of reactions of eq 3. *p*-



(3)

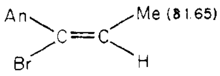
An = p-MeOC$_6$H$_4$

Methoxy-ω-(*p*-nitrophenyl)acetophenone (**5**) was methylated to 1-anisyl-2-(*p*-nitrophenyl)-1-propanone (**6**) which was chlorinated to 1-anisyl-1,1,2-trichloro-2-(*p*-nitrophenyl)propane (**7**). E2 dechlorination with NaI in acetone in the dark gave a mixture of 70% of **4**-*E* and 30% of **4**-*Z*. Since photochemical isomerization changes this composition, **4**-*E* was separated from the mixture by repeated crystallization from ethanol in the dark. When an ethanolic solution of **4**-*E* was kept for several hours in sunlight, the mixture becomes richer in **4**-*Z* which was purified by several crystallizations from EtOH.

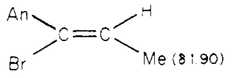
Assignment of the Geometrical Configurations. Several physical properties of **4**-*E* and **4**-*Z* serve as the basis for the assignment of the geometrical configurations. Whereas the higher melting point is consistent with the *trans*-stilbene skeleton of **4**-*Z*,[12] the best criterion for the assignment is the dipole moment. The dipole moments for the two isomers were determined by the Guggenheim method[13] as modified by Smith[14a] and Palit.[14b] The measured values are 3.17 ± 0.10 D for the isomer with a melting point of 100–101 °C and 5.70 ± 0.06 D for the isomer with a melting point of 137–138 °C. Calculation of the dipole moments was based on a vectorial addition of the bond moments[15] without correction for α(Ar)–β(Ar) conjugation and on the assumption that methoxy is electron-donating[16] with a bond moment at an angle of 72° to the C$_4$–C$_1$–O axis and shows a free rotation.[15] The calculated values of 3.23 D for **4**-*E* and 5.65 D for **4**-*Z* are in a very good agreement with the experimental values and corroborate the assignments.

The isomer with the *trans*-stilbene chromophore frequently absorbs at a higher wavelength than the cis isomer,[17–19] but the opposite was found for stilbenes substituted by bulky α substituents such as α,α'-dimethylstilbenes.[19] For α,α'-dihalostilbenes the cis isomer shows the higher λ_{max} values. Suzuki concluded that the effect of the α substituent is due to a lower conjugation in the cis isomer.[19] Consequently, the UV spectra are of little value in structural assignments. Comparison of the spectra of compounds **4** with that of p-O$_2$NC$_6$H$_4$CH=C(Cl)An[20] shows that the α-methyl group lowers the λ_{max}, especially of the *E* isomer. The effect of the α-chlorine is smaller as shown by the comparison of (*E*)-AnCH=CHC$_6$H$_4$NO$_2$-*p* [λ_{max} (methylcyclohexane–isohexane) 358 nm (ϵ 32 000), 365 (32 000)][17] with (*E*)-AnC(Cl)=CHC$_6$H$_4$NO$_2$-*p* [λ_{max} (EtOH) 348 nm (ϵ 19 500)].[20]

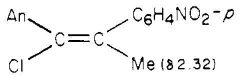
Compounds **8**-*E* and **8**-*Z* are useful references for NMR comparisons.[21] The NMR suggests that in the isomer with a methyl signal at lower field the methyl is cis to the halogen. Similarly, the methyl groups of *cis*-α,α'-dimethylstilbene[19] appear at a lower field than in the trans isomer. The signal for the aromatic protons of trans stilbene and its derivatives, e.g., the *p*-methoxy derivative,[22] are more widely spaced and appear at a lower field than in the cis isomers. This is consistent with our assignments since the aromatic quartets of **4**-*Z* are wider and appear at a lower field than those of **4**-*E*.



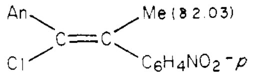
8-*E*



8-*Z*



4-*E*



4-*Z*

4-*E* ⇌ 4-*Z* Isomerization. A **4**-*E* ⇌ **4**-*Z* isomerization takes place under several conditions, and the results together with data on the isomerization which accompanies the solvolysis (see below) are given in Table I.[23] Isomerization to mixtures richer in **4**-*Z* takes place on exposure to sunlight, and a change in the solvent, the temperature, or the nucleophile has a small effect on the composition of 72–80% **4**-*Z* and 20–28% of **4**-*E* obtained in sunlight. Irradiation of **4**-*Z* with light with λ >490 nm in the presence of iodine for 20 h gave a 4:1 mixture of **4**-*Z* to **4**-*E*, whereas similar irradiation of **4**-*E* gave a 1:3 mixture of **4**-*Z* to **4**-*E*.

Isomerization did not take place in the dark in the absence of the solvolysis reaction, but an equilibrium mixture of ca. 66% **4**-*E* and 34% **4**-*Z* is obtained during the solvolysis in the dark. Reflux of either isomer in Me$_2$SO or heating in nitrobenzene at 120 °C for 13 h in the dark gave no isomerization. Heating for 12 h in CH$_2$Cl$_2$ in the presence of H$_2$SO$_4$ resulted in a partial decomposition. When **4**-*Z* was heated in a 1:3 mixture of cyclohexane and CHCl$_3$ containing 0.2 M HCl at 120 °C, 20% of **4**-*E* was formed both after 2 and after 22 h. When **4**-*E* was heated for 18 h under the same conditions, 30% of **4**-*Z* was formed. Apparently equilibrium was not reached under these conditions.

Solvolysis in Aqueous EtOH. The solvolysis of compounds **4** in basic aqueous EtOH gave the ketone **6** and the two vinyl ethers **9**-*E* and **9**-*Z* (eq 4). *p*-Nitroacetophenone (**10**) was also formed in the solvolyses in the presence of NaOAc but was a minor product or was not formed at all in the presence of excess Et$_4$NCl or 2,6-lutidine. Since **6** is stable under the reaction conditions, **10** is probably formed by decomposition of the ethers **9**. The product distributions in various aqueous EtOH mixtures were determined by NMR and are given in Table II.[23] The ethers were prepared (but not separated) in a low yield

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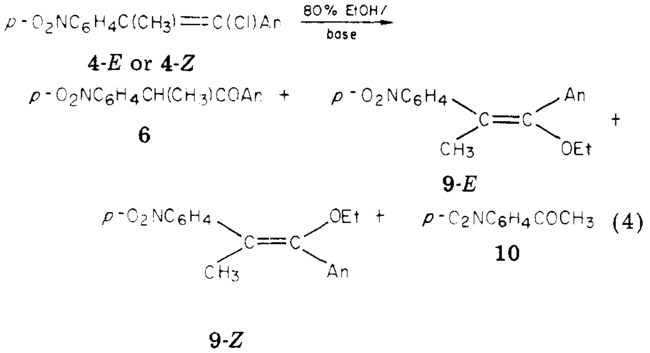
[23] See paragraph at the end of the paper regarding supplementary material.



(4)

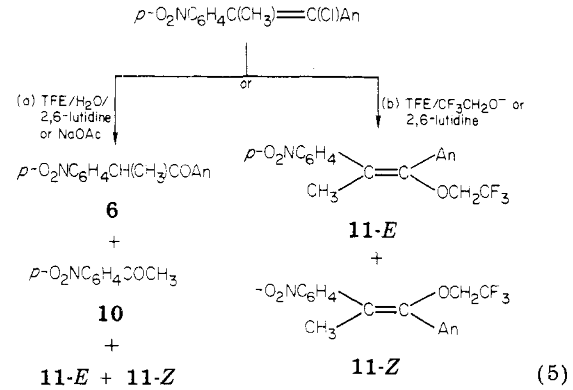
by the reaction of 4-*E* or 4-*Z* with $AgNO_3$ in absolute EtOH.

The ethers were formed in a ca. 60:40 ratio which was nearly independent of the geometry of the precursor, the reaction time, the solvent composition, and the added base (Table II).[23] Comparison of the NMR spectra of **9** with those of 4-*E*, 4-*Z*, and the trifluoroethyl ethers 11-*E* and 11-*Z* (see below) suggests that the isomer formed in excess which has a methyl group at a lower field and a methoxy group at a higher field is 9-*E*.

The solvolysis was followed by titration of the Cl^- and was a first-order reaction. The first-order rate constant k_t (Table III) was independent of the extent of the reaction, of the nature and the concentration of the added base, and of added Et_4NCl. A plot of log k_t for 4-*Z* vs. the ionizing power parameter Y[24] was linear with $m = 0.62$ at 120 °C in 50–80% EtOH. The two points for 4-*E* gave $m = 0.53$ at 120 °C.

Inspection of the NMR of the methyl and methoxy regions during the solvolysis showed that the extent of a concurrent 4-*E* $\rightleftharpoons$ 4-*Z* isomerization was small. After one solvolytic half-life (46 h at 120 °C) of 4-*E* in 80% EtOH, 4-*Z* was not observed. Likewise, in the solvolysis of 4-*Z* in 80% EtOH/NaOAc, ≤7% of 4-*E* was formed. In the presence of 2,6-lutidine, 8 ± 3% and 16 ± 3% of 4-*Z* was observed after 37% (120 h) and 60% (238 h) reaction, respectively.

Solvolysis and Isomerization in TFE and in Aqueous TFE. 4-*E* and 4-*Z* were also solvolyzed in 2,2,2-trifluoroethanol (TFE) and in aqueous TFE mixtures buffered by 2,6-lutidine, NaOAc, or $CF_3CH_2O^-Na^+$. The main product (69–92%) in 60% TFE is the ketone **6**, and the minor products are (*E*)- and (*Z*)-1-anisyl-2-(*p*-nitrophenyl)propen-1-yl trifluoroethyl ethers (11-*E* and 11-*Z*, 5–12%) and *p*-nitroacetophenone (**10**, 3.5–19%) (see eq 5 and Table V).[23] The percentage of the ethers increased



(5)

at the expense of **6** on increasing the TFE content of the medium, and in pure TFE/2,6-lutidine or TFE/$CF_3CH_2O^-$ the ethers are formed exclusively. The mixture of the ethers was isolated from solvolysis of 4-*E* or 4-*Z* in TFE/$CF_3CH_2O^-Na^+$. The ethers **11** are stable for relatively long reaction times at 120 °C in TFE, but they tend to decompose slowly to **10** in aqueous TFE.

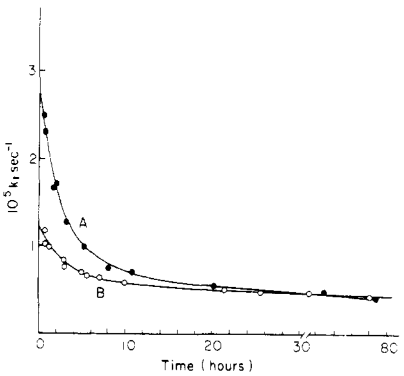


Figure 1. Decrease of k_t with time for the reactions of 0.0167 M of 4-*E* (A) and 4-*Z* (B) in TFE/0.05 M 2,6-lutidine at 120 °C.

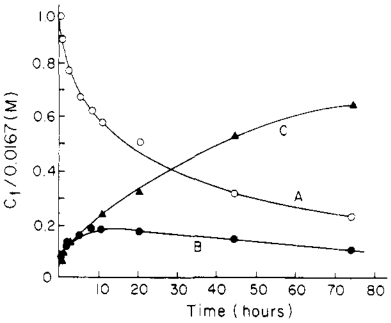


Figure 2. Concentration vs. time profiles for the solvolysis–isomerization of 0.0167 M 4-*E* in the presence of 0.06 M 2,6-lutidine in TFE at 120 °C: A, 4-*E*; B, 4-*Z*; C, products.

Solvolysis of either pure 4-*E* or 4-*Z* in TFE in the presence of 2,6-lutidine or $CF_3CH_2O^-$ or in 60% TFE/NaOAc gave an identical mixture of 70% 11-*E* and 30% 11-*Z* at infinity. The product distribution from either isomer in the presence of $CF_3CH_2O^-$ or 2,6-lutidine up to 60–70% reaction is 16–25% of 11-*Z* to 75–84% of 11-*E*. The assignment of the main isomer as 11-*E* is based on the appearance of a low-field methyl group and a high-field methoxy group compared with the groups of the other isomer, which is in line with the assignments for the 4-*E*/4-*Z* and the 9-*E*/9-*Z* pairs.

In 70–100% TFE/2,6-lutidine the integrated titrimetric first-order rate constants k_t decreased during the reaction, and the decrease was stronger in the less aqueous media. In pure TFE the decrease of k_t is strong for 4-*E* and moderate for 4-*Z* (Figure 1). The initial k_t value in the presence of Et_4NCl is lower than in its absence, and the effect is more pronounced in the less aqueous media.

The rate decrease was ascribed to common-ion rate depression,[25] and several methods were attempted for calculating the initial k_t value (k_t^0) and the selectivity constant $\alpha' = k_{Cl}/k_{SOH}$ (see Discussion) for capture of the intermediate cation by Cl^- and the solvent.[2] Whereas graphical extrapolation of k_t vs. time curves to $t = 0$ is not very accurate, it was used to determine k_t^0 when the rate

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[24] (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846–854. (b) Fainberg, A. H.; Winstein, S. *Ibid.* **1956**, *78*, 2770–2777.

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Table III. Solvolysis of 4 in Aqueous EtOH at 120 °C

substr	10^2[substr], M	[base], M (base)	% EtOH[a]	[Et_4NCl], M	10^8k_t, s^{-1}
4-*Z*	3.0	0.18 (NaOAc)	50		943 ± 15
	3.0	0.18 (NaOAc)	50	0.088	926 ± 70
	1.67	0.10 (NaOAc)	50		1230 ± 7
	1.67	0.10 (NaOAc)	60		554 ± 3
	1.67	0.10 (NaOAc)	60	0.13	580 ± 40
	1.67	0.10 (NaOAc)	70		360 ± 3
	1.67	0.10 (NaOAc)	80		107 ± 2
	1.67	0.10 (NaOAc)	80	0.13	115 ± 10
	1.67	0.25 (NaOAc)	80		99 ± 3
	1.67	0.14 (2,6-lutidine)	80		106 ± 8
	1.67	0.30 (*p*-toluidine)	80		101 ± 1
4-*E*	3.0	0.18 (NaOAc)	50		3220 ± 30
	1.67	0.10 (NaOAc)	80		420 ± 20

[a] In the $EtOH-H_2O$ mixture.

Table V. Solvolysis and Isomerization in Buffered TFE and Aqueous TFE

substr[a]	[base], M (base)	% TFE[b]	10^2[Et_4-NCl], M	$10^6k_t^0$, s^{-1}	α', M^{-1}	10^6k_{isom},[c] s^{-1}
4-*Z*	0.18 (NaOAc)	60		45.9 ± 1.6[d]	5.3[f]	
	0.18 (NaOAc)	60	8.60	31.6 ± 2		
	0.54 (NaOAc)	60		44.8 ± 1.5[d]	4.86[f]	
	0.051 (2,6-lutidine)	70		34 ± 2[e]	11.8[f]	
	0.051 (2,6-lutidine)	70	7.55	18 ± 1		
	0.051 (2,6-lutidine)	80		28 ± 2[e]	23.4[f]	
	0.051 (2,6-lutidine)	80	7.80	9.9 ± 2		
	0.051 (2,6-lutidine)	90		18 ± 2		
	0.051 (2,6-lutidine)	100		9.4 ± 0.1[g] (12 ± 1[e])	200 ± 42[g]	45 ± 2
	0.051 (2,6-lutidine)	100	4.9	3.0 ± 0.2	61.2[f]	
	0.051 (2,6-lutidine)	100	10.1	1.9 ± 0.1	52[f]	57 ± 2
	0.051 (2,6-lutidine)	100	34.0	1.9 ± 0.1	15[f]	59 ± 2
4-*E*	0.18 (NaOAc)	60		120 ± 3[d]		
	0.051 (2,6-lutidine)	100		27 ± 0.4[h]	1029 ± 110[h]	20 ± 3[i]
	0.051 (2,6-lutidine)	100	34.0	1.7 ± 0.1	44[f]	17 ± 3[i]

[a] [4] = 0.03 M in the presence of NaOAc and 0.0167 M in the presence of 2,6-lutidine. [b] Percent TFE in $TFE-H_2O$ (v/v). [c] Obtained by NMR and calculated by eq 8. [d] k_t remains constant during the reaction. [e] Obtained by graphical extrapolation. [f] Determined by eq 6. [g] Determined by eq 7 with points up to 85% reaction ($r = 0.8759$). [h] Determined by eq 7 with points up to 65% reaction ($r = 0.9558$). [i] The error in k_{isom} is larger than for 4-*Z* (see text).

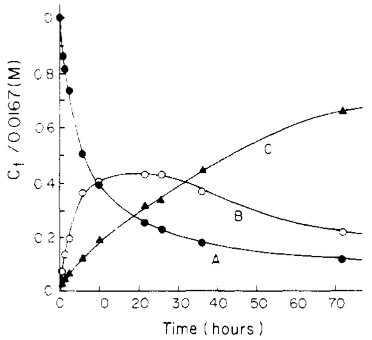

Figure 3. Concentration vs. time profiles for the solvolysis–isomerization of 0.0167 M 4-*Z* in the presence of 0.06 M 2,6-lutidine in TFE at 120 °C: A, 4-*Z*; B, 4-*E*; C, products.

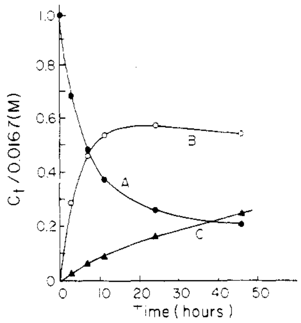

Figure 4. Concentration vs. time profiles for the solvolysis–isomerization of 0.0167 M 4-*Z* in the presence of 0.05 M 2,6-lutidine and 0.34 M Et_4NCl in TFE at 120 °C: A, 4-*Z*; B, 4-*E*; C, products.

decrease was not very severe, i.e., in most of the aqueous TFE mixtures. The α' values were then calculated from eq 6 where k_d and k_t^0 are the rate constants in the presence

$$k_d = k_t^0/(1 + \alpha'[Et_4NCl]) \qquad (6)$$

and the absence of Et_4NCl, respectively. For a more severe rate decrease, as in pure TFE, we calculated k_t^0 and α' from eq 7, where $[4]_0 = a$ and $[Cl^-]_t = x$.[26] The assumptions

$$1/k_t = 1/k_t^0 + (\alpha'/k_t^0)[(a - x)/\ln (a/(a - x))] \qquad (7)$$

involved in the derivation of eq 7 are discussed in the Discussion. The correlation coefficients of the linear regression were higher for 4-*E* than for 4-*Z*, and the correlations were improved when points only up to 65% reaction were used. The k_t^0 and α' values are given in Table V.

In the reactions in 60% TFE/NaOAc k_t did not decrease during a run, and vinylic acetates were not formed. However, for 4-*E* in 100% TFE buffered by 0.05 M 2,6-lutidine, 22% and 37% reaction took place after 9 and 24 h, respectively, whereas with 0.15 M of 2,6-lutidine, the corresponding values were 32% and 45.4% reaction.

Solvolysis of either isomer in TFE/2,6-lutidine is accompanied by a 4-*E* $\rightleftharpoons$ 4-*Z* isomerization (Table VI).[23] The reaction profiles are shown in Figures 2 and 3. Starting

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(26) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518–4530.

Table VII. Solvolysis in TFE in the Presence of Strong Nucleophiles at 120 °C

substr[a]	nucleophile	concn, mol L^{-1}	10^5k_t, s^{-1}
4-*E*	$CF_3CH_2O^-$		8.37 ± 0.16[b]
		0.15	10.20 ± 0.12
		0.29	12.00 ± 0.15
		0.42	13.45 ± 0.16
	p-$MeC_6H_4S^-$[c]	0.097	11.6 ± 0.2
		0.027	11.1 ± 0.3[d]
4-*Z*	$CF_3CH_2O^-$		3.45 ± 0.13[b]
		0.15	4.25 ± 0.04
		0.23	4.60 ± 0.1
		0.31	5.12 ± 0.03
		0.47	6.00 ± 0.1
		0.52	6.04 ± 0.04
	p-$MeC_6H_4S^-$[c]	0.097	3.87 ± 0.03

[a] [4] = 0.0167 M. [b] Extrapolated value at zero salt concentration from a plot of k_t vs. $[CF_3CH_2O^-Na^+]$. [c] Not corrected for the formation of 13. [d] From data up to 30% reaction.

from either isomer, the concentration of the second isomer reaches a maximum during the reaction, and an equilibrium consisting of 66% 4-*E* to 34% 4-*Z* at 120 °C is achieved at high reaction percentages. Similar reaction profiles and a 4-*E* to 4-*Z* equilibrium are observed in the presence of Et_4NCl except that more of the geometrical isomer is accumulated (Figure 4).

An isomerization rate constant k_{isom} for 4-*Z* is defined by eq 8 where X_{eq} is the percentage of 4-*Z* at equilibrium

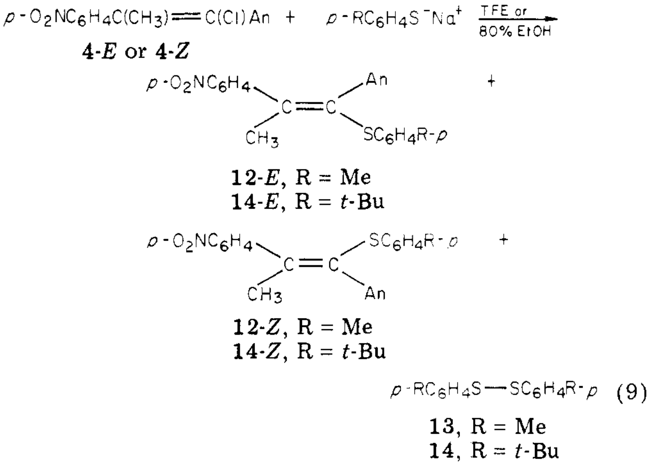
$$k_{isom} = (2.3/t) \log (X_{eq}/(X_{eq} - X_t)) \qquad (8)$$

and X_t is its fraction in the 4-*E*/4-*Z* mixture at the time t. The k_{isom} value for 4-*E* is defined similarly. In the solvolysis without Et_4NCl k_{isom} for 4-*Z* remained nearly constant while k_{isom} for 4-*E* decreased slightly with the progress of the reaction, probably due to a large error since the relative change in [4-*E*] term up to X_{eq} is lower. Whereas k_t decreases strongly in the presence of Et_4NCl, k_{isom} is only slightly affected.

Both the solvolysis and the isomerization of 4-*E* in TFE/0.05 M 2,6-lutidine were accelerated by added 0.01 M $LiClO_4$. For example, after 9 h at 120 °C, $k_t = 1.82 \times 10^{-5}$ s^{-1}, whereas in the absence of $LiClO_4$, $k_t = 0.70 \times 10^{-5}$ s^{-1}.

Reaction in the Presence of Sodium Trifluoroethoxide. The solvolysis of 4-*E* and 4-*Z* in TFE in the presence of $CF_3CH_2O^-Na^+$ is a first-order process: k_t remains constant during the reaction, and a 4-*E* ⇌ 4-*Z* isomerization is not observed. k_t increases linearly on increasing the base concentration, and the normal salt effect[27] parameter b is 1.5 for both 4-*E* and 4-*Z*. The extrapolated k_t values to zero salt concentration are ca. 3 times higher than the k_t^0 values in the presence of 2,6-lutidine (Table VII).

Solvolysis and Isomerization in the Presence of Arylthiolate Ions. The reactions were also conducted in the presence of p-toluenethiolate and p-*tert*-butylbenzenethiolate ions in 80% EtOH or TFE at 120 °C. The reaction products with p-toluenethiolate ion, formed from either isomer in both solvents, were ≥95% of a 60:40 mixture of the thioethers 12-*E* and 12-*Z* and the disulfide 13 (eq 9). The NMR-determined ratio of the two thioethers remained constant during the reaction. The assignment of configurations is again based on the analogy with the vinyl chlorides and ethers, and the isomer which shows a lower Me and a higher MeO signal is assigned as 12-*E*. A vectorial addition of the bond moments suggests a lower dipole moment for 12-*E*, and, indeed, it migrates slightly faster on a TLC plate with 10% acetone–90% petroleum ether.


4-*E* or 4-*Z*

12-*E*, R = Me
14-*E*, R = *t*-Bu

12-*Z*, R = Me
14-*Z*, R = *t*-Bu

(9)

13, R = Me
14, R = *t*-Bu

The products from the reaction in the presence of sodium p-*tert*-butylbenzenethiolate were not isolated. However, the NMR spectrum showed the formation of >90% of a 54:46 mixture of the thioethers 14-*E* and 14-*Z* and the disulfide 15. The assignment of configurations is based on the positions of the Me and the MeO signals.

The reactions of 4-*Z* with the two thiolate anions in 80% EtOH gave good pseudo-first-order rate constants at high concentrations (0.15–0.30 mol L^{-1}) of RS^-. However, at lower concentrations of p-toluenethiolate ion (e.g., 0.05 mol L^{-1}) k_t decreased slightly at high reaction percentages, and k_t^0 is given. The k_t values were dependent on the concentration of the thiolate ion. However, the $[RS^-]$ concentration available for the reaction is lower than the stoichiometric one due to the formation of the disulfides 13 and 15. Correction for this was introduced in the case of p-toluenethiolate ion (Table VIII) by using the concentrations of 13 as determined by NMR. The concentrations of 15 could not be determined similarly due to overlap of the *tert*-butyl signals of 15 and 14-*E*. When the k_t values were divided by $[RS^-]_{cor}$ for p-toluenethiolate ion or by the stoichiometric $[RS^-]$ term for p-*tert*-butylbenzenethiolate ion, nearly constant second-order rate constants (k_2) were obtained (Table VIII). In the reaction of 4-*E* with p-toluenethiolate ion k_t decreased with the progress of the reaction even at high thiolate ion concentrations (Table IX).[23]

A 4-*E* ⇌ 4-*Z* isomerization accompanies the solvolysis of either isomer in the presence of the two arylthiolate anions in 80% EtOH. A control experiment showed that this is not due to the workup procedure. A mixture of 66% of 4-*E* to 34% of 4-*Z* was obtained during the solvolysis.

The isomerization rate was dependent on the concentration of the thiolate ion. At concentrations >0.14 M of RS^- the equilibrium distribution of 4-*E* and 4-*Z* was achieved at a very early stage (i.e., ≤6%) of the solvolysis reaction. At a concentration of 0.05 M of p-toluenethiolate ion the isomerization was slower, but it was still faster than the substitution (Table X).[23] Addition of 0.025 M hydroquinone did not affect the extent of the substitution or the isomerization reaction.

The solvolysis rates of 4-*E* in TFE were determined in the presence of two p-toluenethiolate ion concentrations. The k_t value is constant up to 50% reaction at 0.097 M RS^-. At 0.027 M RS^- k_t decreases slightly after 30% reaction, but the value calculated up to 30% reaction is

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[27] Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763–2767.

Table VIII. Reaction of 4-Z[a] with Arylthioate Ions in 80% EtOH at 120 °C

nucleophile	$[RS^-]$ added, M	$[RS^-]_{cor}$,[b] M	$10^5 k_t$, s^{-1} [c]	$10^4 k_2$, $M^{-1} s^{-1}$ [d]
p-$MeC_6H_4S^-$	0.21	0.07 ± 0.005	2.1 ± 0.05	3.00
p-$MeC_6H_4S^-$	0.14	0.046 ± 0.005	1.49 ± 0.02	3.24
p-$MeC_6H_4S^-$	0.05	0.02 ± 0.005	0.64 ± 0.05[e]	3.20
p-t-$BuC_6H_4S^-$	0.30		3.28 ± 0.02	1.09
p-t-$BuC_6H_4S^-$	0.15		1.81 ± 0.02	1.20

[a] [4-Z] = 0.0167 M. [b] Corrected for the formation of **13**. [c] Pseudo-first-order rate constant. [d] $k_2 = k_t/[RS^-]_{cor}$ for the reactions with p-$MeC_6H_4S^-$. [e] Calculated from data at early reaction times.

similar to that obtained at the higher $[RS^-]$. The k_t value for **4**-Z at low nucleophile concentration could not be determined accurately, and only one concentration of p-$MeC_6H_4S^-$ was studied. The results are given in Table VII. A **4**-E ⇌ **4**-Z isomerization was not observed during the reaction starting from either isomer.

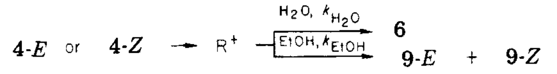
Discussion

Solvolysis in Aqueous EtOH in the Presence of Moderate Nucleophiles. The solvolysis in aqueous EtOH containing moderate nucleophiles such as 2,6-lutidine, p-toluidine, or NaOAc proceeds by the S_N1 mechanism as indicated by the following arguments. (a) The reaction is of first order, and k_t is independent of the nature of the added base. (b) k_t increases on increasing the ionizing power[24] of the solvent. The Grunwald–Winstein m values of 0.62 (**4**-Z) and 0.53 (**4**-E) at 120 °C can be extrapolated to 25 °C by using the approximate relationship $m_1/m_2 = T_2/T_1$,[28] giving $m = 0.70$ for **4**-E and $m = 0.82$ for **4**-Z. These values are in the range expected for the k_c variant[29] of the S_N1 route.[2a] (c) The magnitude of the k_t values is in the region predicted for the S_N1 route. The k_t value for AnC(Cl)=C(Me)Ph in 80% EtOH at 120 °C can be estimated as 2.3×10^{-5} s^{-1} from the average of the k_t values for compounds **16**[30] and **17**. The k_t value for **17** was

AnC(Cl)=CR$_2$	AnC(Br)=C(Ar)Ar′
16, R = Me	**19**, Ar = Ar′ = Ph
17, R = Ph	**20**, Ar = Ar′ = An
18, R = An	**21**, Ar = Ph; Ar′ = An

estimated from the k_t's for compounds **18**–**20**.[8a] By use of a Hammett ρ value of −1.3 for the β-aryl substituent as obtained from the solvolyses of **20** and **21** in 60% EtOH,[8b] $k_t = 2.4 \times 10^{-6}$ s^{-1} for AnC(Cl)=C(Me)$C_6H_4NO_2$-p of unspecified geometry. This is similar to the k_t values of 1.06×10^{-6} s^{-1} for **4**-Z and 4.2×10^{-6} s^{-1} for **4**-E. (d) The formation of an identical 60:40 mixture of **9**-E to **9**-Z starting either from **4**-E or **4**-Z indicates a common intermediate from both precursors. This can be ascribed to the formation of a linear, free vinyl cation,[5b,8b] although a mixture of a rapidly equilibrating pair of bent ions is not excluded.[31] The predicted stereochemistry for the Ad_N-E route is retention of configuration.[9] The constancy of the **9**-E/**9**-Z ratio during the reaction and the absence of a **4**-E ⇌ **4**-Z isomerization excludes postisomerization as the reason for the identical products mixture. (e) The formation of **6**, **9**-E, and **9**-Z is consistent with a competitive capture of an intermediate cation by the solvent components.

The selectivity constant of the product-forming intermediate R^+ toward the solvent components (k_{EtOH}/k_{H_2O}) can be evaluated from eq 10 and 11 which assume that the



$$4\text{-}E \text{ or } 4\text{-}Z \rightarrow R^+ \begin{cases} \xrightarrow{H_2O,\ k_{H_2O}} 6 \\ \xrightarrow{EtOH,\ k_{EtOH}} 9\text{-}E + 9\text{-}Z \end{cases} \quad (10)$$

$$k_{EtOH}/k_{H_2O} = ([9\text{-}E] + [9\text{-}Z])[H_2O]/[6][EtOH] \quad (11)$$

capture processes are first order in the solvent components. The concentration of the formed p-nitroacetophenone (**10**) is included in the ether fraction since **6** is stable under the reaction conditions, whereas in the preparation of **9** in absolute EtOH/$AgNO_3$, **10** was obtained, but **6** was not formed.

9-E and **9**-Z are unstable under mildly basic or neutral conditions and they decompose to **6**. In 80% EtOH the [**9**]/[**6**] ratios are 0.5 and 2.0 in the presence of 2,6-lutidine and NaOAc, respectively. In unbuffered 60% EtOH, **9** is not formed, whereas 36% of **9** is formed in the presence of 0.1 M of NaOAc. Hydrolysis of vinyl ethers under mildly basic conditions to the corresponding ketones was observed previously.[21] Apparently, the protonation of **4** to the stabilized ion **22** can occur under mildly basic conditions in a protic solvent (eq 12).

$$4 \xrightarrow{H^+ \text{ (from solvent)}} \underset{22}{p\text{-}O_2NC_6H_4CHMe\text{—}C^+(An)OEt} \rightarrow$$
$$p\text{-}O_2NC_6H_4CH(Me)\text{—}C^+(OH_2)(An)OEt \rightarrow \rightarrow 6 \quad (12)$$

The [**9**]/[**6**] ratios increase at higher mole fraction of EtOH as observed for the solvolysis of **1a**.[11] The ratios are 0.43, 2.33, and 4.7 for **4**-Z in 50%, 60%, and 80% EtOH buffered by NaOAc and 0.42 and 0.92 for **4**-E in 50% and 80% EtOH, respectively. All the corresponding k_{EtOH}/k_{H_2O} ratios of 1.39, 5, and 3.8 for **4**-Z and 1.35 and 0.76 for **4**-E, except one, are >1 as expected since EtOH is more nucleophilic than water. The inverted selectivity of **4**-E in 80% EtOH where $k_{EtOH}/k_{H_2O} < 1$ may be due to the fact that the percentage of **10** in this case is rather low. It is not known if the fact that the k_{EtOH}/k_{H_2O} values are not constant is due to a failure of the assumption involved in the derivation of eq 11 or to a varying degree of hydrolysis of **9** to **6**.

The absence of common-ion rate depression by the Cl^- which amounts to a selectivity constant $\alpha' = 0$ can be due to three reasons. (a) Products are formed from an unstable free ion **23** which can be captured faster by the solvent SOH than by the Cl^- (Scheme I, $k_{SOH}^{23}[SOH] \gg k_{Cl}[Cl^-]$). (b) Products are formed exclusively from the ion pairs **24a** and **24b** whose capture by the solvent is faster than their dissociation to **23** (i.e., $k_{SOH}^{24a}[SOH] \gg k_{diss}^{24a}$; $k_{SOH}^{24b} \gg k_{diss}^{24b}$). (c) The common-ion rate depression is compensated by a rate increase due to a normal salt effect. This is unlikely since in the acetolysis of **25**-E in AcOH $b = 4.4$ for Bu_4NBr,[5b] and the value for Et_4NCl should be lower

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[28] This was suggested in ref 8a on the basis of the behavior of α-phenylethyl chloride (Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1597–1602, 1602–1608).

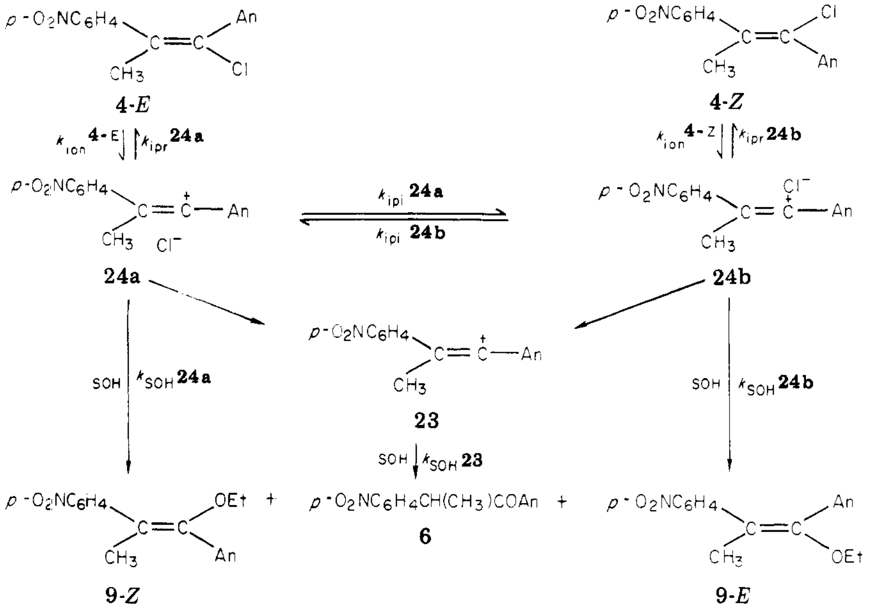
[29] Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 2542–2544.

[30] Rappoport, Z.; Gal, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 301–310.

[31] This possibility is rendered unlikely in view of the identical kinetic energy release value in the formation of the $(M - Br)^+$ ion in the gas-phase cleavage of **21**-E and **21**-Z (Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H.; Stahl, D., submitted for publication).

[32] Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

Scheme I



in the more polar 80% EtOH.[33]

It is not easy to distinguish between the other alternatives. The high nucleophilicity of the solvent should increase the k_{SOH} terms compared with less nucleophilic solvents such as TFE, as was indeed observed. Due to the electron-withdrawing β-*p*-nitrophenyl group the free ion **23** is more reactive than the ions **26** and **27** formed in the solvolysis of **21**-*E* and **25** in aqueous EtOH[34,35] (eq 13).

$$\begin{array}{l} RR'C{=}C(Br)An \\ \textbf{21-}E,\ R = Ph;\ R' = An \\ \textbf{25},\ R = R' = H \end{array} \xrightarrow{-Br^-} \begin{array}{l} RR'C{=}C^+\text{-}An \\ \textbf{26},\ R = Ph;\ R' = An \\ \textbf{27},\ R = R' = H \end{array} \rightarrow \text{products} \quad (13)$$

The solvolysis of **21**-*E* in 80% EtOH shows some common-ion rate depression, and ≥21% of the product is derived from the free ion **26**,[34] whereas the solvolysis of **25** in 50% EtOH shows no common-ion rate depression.[35] The possibility that the product-forming intermediate is mainly or exclusively an ion pair seems likely in both cases. Consequently, the electronic effect and the smaller bulk of the substituents in **23** than in **27** favor an ion-pair intermediate in the solvolysis of **4**-*E* and **4**-*Z*.

However, the formation of an identical **9**-*E*/**9**-*Z* mixture from **4**-*E* and **4**-*Z* is inconsistent with product formation from the different ion pairs **24a** and **24b** formed from the isomeric precursors. Shielding from the front by the Cl^- in the ion pairs will result in formation of a higher extent of an inverted product than from **23**, i.e., in a higher **9**-*E*/**9**-*Z* ratio from **24a** than from **24b**. Such behavior was observed in the solvolysis–rearrangement of **28** in pivalic

$$\begin{array}{c} An_2C{=}C(Br)Ph \\ \textbf{28} \end{array}$$

acid[36] and in the solvolysis of other vinylic systems which proceed via ion pairs.[37] Product formation from the ion pairs is therefore possible only if a mutual isomerization of the ion pairs **24a** and **24b** (k_{ipi}) is much faster than their capture by the solvent; i.e., $k_{ipi}^{24a} \gg k_{SOH}^{24a}[SOH]$ and $k_{ipi}^{24b} \gg k_{SOH}^{24b}$. The appearance of a **4**-*E* ⇌ **4**-*Z* isomerization during the solvolysis indicates the involvement of ion pairs and isomerization via the **4**-*E* ⇌ **24a** ⇌ **24b** ⇌ **4**-*Z* route. The small extent of isomerization suggests that $k_{SOH} > k_{ipi}$ for both **24a** and **24b**. This is consistent with the effect of the β substituents on the isomerization via ion pairs in other α-arylvinyl systems. The ion pair derived from β-deuterio-*p*-methoxystyrene in 50% EtOH is captured without any internal return.[35] A small extent of return accompanies the solvolysis of **8**-*E*,[21] and 31% of internal return was observed in the solvolysis of **21**-*E* in 80% EtOH.[34] We conclude that an increased bulk of the β substituent results in a more hindered nucleophilic approach to the ion pair, and the consequent longer lifetime of the latter results in a higher extent of ion-pair return. The lower extent of internal return for compounds **4**-*E* and **4**-*Z* than for **21**-*E* is due to this effect, coupled with the electronic destabilization of **24a** and **24b** by the β-*p*-nitrophenyl substituent. The ionization rate constant k_{ion} is therefore only slightly higher than the titrimetric rate constant k_t.

Solvolysis in Aqueous EtOH in the Presence of Arylthiolate Ions. Since the ArS^- ions are stronger nucleophiles than AcO^- or 2,6-lutidine, a partial or a complete reduction in the extent of isomerization and a corresponding increase in k_t is expected if the capture rates of **24a** and **24b** by the ArS^- ion are larger than the k_{ipi} or the k_{ipr} terms. Alternatively, the negative charge dispersal ability by the β-*p*-nitrophenyl group may lead to an Ad_N-E process[9,10] where bond formation to the thio anion precedes the C–Cl bond cleavage. This route was observed for the reaction of β-halo-*p*-nitrostyrenes with ArS^- ions,[38] and a change from the S_N1 route in the presence of AcO^- to the

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[33] Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974; Vol. 2, Chapter 3.

[34] Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1975**, *97*, 836–842.

[35] Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1974**, *96*, 6428–6436.

[36] Rappoport, Z.; Schnabel, I.; Greenzaid, P. *J. Am. Chem. Soc.* **1976**, *98*, 7726–7733.

[37] (a) Sherrod, S. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1925–1940. (b) Bergman, R. G.; Kelsey, D. R. *Ibid.* **1971**, *93*, 1941–1952. (c) Summerville, R. H.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 3629–3631; **1974**, *96*, 1110–1121. (d) Clarke, T. C.; Bergman, R. G. *Ibid.* **1974**, *96*, 7934–7944.

[38] (a) Marchese, G.; Modena, G.; Naso, F. *Tetrahedron* **1968**, *24*, 663–674. (b) Marchese, G.; Naso, F.; Modena, G. *J. Chem. Soc. B* **1968**, 958–962.

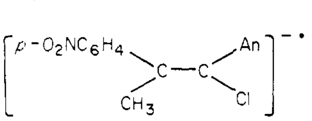
Ad_N-E route in the presence of RS^- ions was observed for **1a**.[11]

The reactions of **4**-*E* and **4**-*Z* with p-$MeC_6H_4S^-$ and p-$Me_3CC_6H_4S^-$ ions are much faster than in the presence of the weaker bases. For **4**-*Z* at ca. 0.14 M of nucleophile $k_t(p\text{-}MeC_6H_4S^-)/k_t(2,6\text{-lutidine}) = 14$ and $k_t(p\text{-}Me_3CC_6H_4S^-)/k_t(2,6\text{-lutidine}) = 18$, and at ca. 0.2 M of nucleophile $k_t(p\text{-}MeC_6H_4S^-)/k_t(NaOAc) = 21$. For **4**-*E* $k_t(p\text{-}MeC_6H_4S^-)/k_t(NaOAc) = 4.8$ at a 0.1 M concentration of nucleophile. Moreover, Table VIII shows that the reactions are of second order and that p-$Me_3CC_6H_4S^-$ is less reactive than p-$MeC_6H_4S^-$.[39] The kinetic behavior is therefore consistent with substitution via the Ad_N-E route involving the intermediacy of the carbanion **29** (eq 14 for **4**-*E*).[40]

$$\textbf{4}\text{-}E \xrightarrow{ArS^-} \underset{\textbf{29}}{p\text{-}O_2NC_6H_4C^-(CH_3)\text{-}C(An)(Cl)SAr} \xrightarrow{-Cl^-} \textbf{13}\text{-}E \quad (14)$$

However, two stereochemical aspects are inconsistent with this route. First, the observed stereochemistry of the Ad_N-E route is complete or preferred retention of configuration when the intermediate is short-lived,[9,10] and this is supported by recent calculations.[41] Only one case, when the intermediate carbanion is much more stable than **29**, leads to stereoconvergence.[42] Whereas a kinetically controlled stereoconvergence via **29** can be definitely excluded, the stereoconvergence is the outcome of the rapid **4**-*E* ⇌ **4**-*Z* isomerization which gives their equilibrium at early reaction percentages. The similarity of the **4**-*E*/**4**-*Z* (66:34) and the **13**-*E*/**13**-*Z* (60:40) ratios indicates a substitution with nearly complete retention.[43,44] Second, the **4**-*E* ⇌ **4**-*Z* isomerization cannot result by this route since expulsion of Cl^- from the intermediate is expected to be much faster than expulsion of the ArS^- ion. No precedent for isomerization of a substituted vinyl chloride during vinylic substitution is known when Nu ≠ Cl^-.

The isomerization can proceed by two alternative routes. The formation of the disulfide **13** indicates the presence of the ArS· radicals in the reaction mixture. Radical-induced cis–trans isomerization of substituted double bonds is known,[12b] and if it occurs by an initial attack on C_β, it will not lead to substitution. The alternative is an initial reversible electron-transfer process from the ArS^- to **4**-*E* or **4**-*Z* to form the radical anion **30**. If internal rotation in **30** is rapid compared with other processes, a **4**-*E* ⇌ **4**-*Z* isomerization will be observed.[45] This route is feasible in view of the substitution of p-nitrobenzyl systems by thiolate ions which proceeds by an initial electron transfer.[46,47] However, since addition of hydroquinone does not affect the extent of the isomerization and the substitution reactions, more work is required.



30

Solvolysis in TFE and in Aqueous TFE Mixtures in the Presence of Moderate Nucleophiles. The higher ionizing power and the lower nucleophilicity of TFE compared with aqueous EtOH[32] suggest that the lifetime of any cationoid intermediate, e.g., **23**, will be longer in TFE than in aqueous EtOH. An S_N1 mechanism for **4**-*E* and **4**-*Z* in TFE and in TFE–H_2O mixtures is supported by the following facts. (a) Since the Ad_N-E route is unimportant in EtOH–H_2O, it is unlikely in the less nucleophilic TFE-containing media. (b) The reaction is overall first order with a small dependence on the concentration of added NaOAc or 2,6-lutidine. (c) Common-ion rate depression accompanies the solvolysis. (d) An identical product distribution is obtained from **4**-*E* and **4**-*Z*. (e) The solvolysis rate increases with the increase in the ionizing power of the medium. With Y values from an interpolation of a graph of Y vs. the weight percent of water in aqueous TFE,[48] the m values are found to be 0.88 for **4**-*Z* (r = 0.9840) from a five-point plot at 60–100% TFE and 0.98 for **4**-*E* on the basis of the points at 60% and 100% TFE. A plot of log k_t(**4**-*Z*) vs. Y values which are based on 1-adamantyl bromide[49] is nonlinear. However, a linear plot with a negative slope was obtained when log k_t was plotted vs. Y values which are based on $E_T(1)$ values.[26,50]

The solvolysis in TFE is accompanied by common-ion rate depression and by a **4**-*E* ⇌ **4**-*Z* isomerization, phenomena which were used previously[2] to probe the details of the solvolysis reaction. Both phenomena and the formation of an identical **11**-*E* to **11**-*Z* mixture from either **4**-*E* or **4**-*Z* are consistent with product formation from an identical, linear, free vinyl cation, **23**. Capture of **23** by the solvent gives the two ethers, and the preference for formation of **11**-*E* reflects a lower steric hindrance to an in-plane nucleophilic approach to **23** from the side of the smaller (Me) substituent. Ion **23** is sufficiently long-lived in TFE to be involved in a competitive capture by the solvent and the Cl^-. The stereochemistry of the capture by Cl^- is similar to that by the solvent; i.e., **4**-*E* is the preferred isomer. However, since **23** is formed from both **4**-*E* and **4**-*Z*, such return necessarily involves a **4**-*E* ⇌ **4**-*Z* isomerization.

In the solvolysis of **21**-*E* and **21**-*Z* the extent of the accompanying isomerization was higher than that calculated on the basis of common-ion rate depression.[5b,34] This was ascribed to the formation of ion pairs which are involved in the isomerization but not in the solvolysis. Since the k_t values decreased during a run, the ionization rate constants, k_{ion}, were calculated by applying a computer program (SHAI) to eq 7, with the assumption (as was indeed

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(39) However, the difference between the k_2 values may disappear if a correction for the formation of **15** is introduced.

(40) The k_2 for the reaction of **1a** with p-$MeC_6H_4S^-$ is 2 orders of magnitude higher, and the p-$O_2NC_6H_4CH{=}CHCl$ + PhS^- reaction is several orders of magnitude faster[38b] than the reaction of **4**-*E* with p-$MeC_6H_4S^-$. This is consistent with the higher negative charge dispersal ability of the fluorenyl compared with the p-nitroethyl moiety and with the reduction of the electrophilic reactivity of C_α of **4**-*E* by $\pi(\alpha\text{-Ar})$–π-(C=C) ground-state conjugation and steric hindrance to nucleophilic approach.

(41) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095–5098. Texier, F.; Henri-Rousseau, O.; Bourgois J. *Bull. Soc. Chim. Fr.* **1979**, 86–94.

(42) Rappoport, Z.; Topol, A. *J. Am. Chem. Soc.* **1980**, *102*, 406–407.

(43) The **13**-*E*/**13**-*Z* ratio should be somewhat different at early reaction times, but since the isomerization is fast compared with the solvolysis (cf. Table IX), this ratio could not be determined accurately at low conversions to the vinyl thiolates.

(44) A **13**-*E* ⇌ **13**-*Z* isomerization by the excess ArS^- is also possible. Product isomerization was previously observed in the reaction of β-chloro-p-nitrostyrene with PhS^- ion.[38b]

(45) For a recent study of the isomerization of the stilbene anion radicals, see: Jensen, B. S.; Lines, R.; Pasberg, P.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1977**, *31*, 707–710.

(46) E.g.: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745. Russell, G. A.; Pecorano, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3331–3334.

(47) The possibility that the substitution may proceed via recombination of **30** with the ArS· moiety to give **29** cannot be excluded.

(48) Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838–4843.

(49) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977–5981.

(50) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1–37.

observed) that the two isomers react at similar rates.[34] In our system $k_{ion}^{4\text{-}E}$ differs from $k_{ion}^{4\text{-}Z}$, as observed for other systems substituted by β-substituents with different bulk.[51] In aqueous EtOH where the isomerization is small or negligible, $k_{ion}^{4\text{-}E}/k_{ion}^{4\text{-}Z}$ = 3.4–3.9, whereas in TFE/$CF_3CH_2O^-$ the ratio is 2.4. Consequently, the reaction scheme (eq 15) is more complicated than that for compounds **21**. For example, when **23** is formed from the faster 4-*E*, return to 4-*E* results in the rate decrease associated with common-ion rate depression. However, a second contribution to the rate decrease is due to the formation of 4-*Z*, whose reionization is slower than that of 4-*E*. Hence, the α' value will be higher than the real selectivity constant. Likewise, the solvolysis of 4-*Z* will give preferential return to the faster 4-*E*, and the rate decrease and the measured α' would be smaller than expected for the common-ion rate depression. The α' values based on 4-*E* and 4-*Z* should therefore be regarded as upper and lower limits to the real α' values, respectively. The k_t^0 (=k_{ion}) values obtained by this method are similar in accuracy to the values obtained by graphical extrapolations. Again, $k_{ion}^{4\text{-}E}$ is 2.5 ± 0.3 times higher than $k_{ion}^{4\text{-}Z}$.

$$\textbf{4}\text{-}E \underset{k_{Cl}^{\mathbf{23}}}{\overset{k_{ion}^{4\text{-}E}}{\rightleftharpoons}} \underset{+\ Cl^-}{\mathbf{23}} \underset{k'_{Cl}^{\mathbf{23}}}{\overset{k_{ion}^{4\text{-}Z}}{\leftrightharpoons}} \textbf{4}\text{-}Z \qquad (15)$$

Figures 2 and 3 show that the rate decrease observed for 4-*E* is indeed higher than that for 4-*Z*. The relative decrease in k_t up to 50% reaction is 5.7 for 4-*E* and 2.7 for 4-*Z*. The isomerization of 4-*Z* to the equilibrium mixture is faster than that of 4-*E* (Table V), and in the absence of Et_4NCl $k_{isom} > k_t^0$ for 4-*Z*, but $k_{isom} < k_t^0$ for 4-*E*. As a consequence of this and the higher percentage of 4-*E* at equilibrium the lines describing the concentrations of the two isomers intersect before reaching equilibrium when starting from 4-*Z* but not from 4-*E*. The concentrations of the two isomers then decrease, reaching the same equilibrium mixture of 66% 4-*E* and 34% 4-*Z*. This was achieved earlier (at 35% reaction) by starting from 4-*Z* rather than from 4-*E* (at 50% reaction). From this point, the solvolysis rates of the mixtures starting from both isomers are identical.

Since the same equilibrium is obtained from both isomers, this is the thermodynamic equilibrium at 120 °C. Equation 16 is obtained from eq 15, and by using the $k_{ion}^{4\text{-}E}/k_{ion}^{4\text{-}Z}$ and the [4-*E*]/[4-*Z*] ratios at equilibrium, k_{Cl}^{23}/k'_{Cl}^{23} = 5.0 ± 0.5. A higher value of k_{Cl}^{23} compared with k'_{Cl}^{23} is indeed expected on steric grounds as discussed above.

$$k_{ion}^{4\text{-}Z}k_{Cl}^{23}/k_{ion}^{4\text{-}E}k'_{Cl}^{23} \qquad (16)$$

Calculation of α' from the k_d values in the presence of Et_4NCl and the use of eq 6 suffer from the same limitations involved in the use of eq 7. The k_d values in the aqueous TFE media are based on a single determination, whereas those in TFE are based on several points, and the difference between the α' values of eq 6 and 7 is not surprising.[52] The α' values so obtained can be used semiquantitatively for three purposes: (a) for approximate evaluation of the percentage of products derived from the free ion **23** and for detection of a possible intervention of ion pairs in the product-forming process; (b) for analyzing the solvent effect on the lifetime of **23**, and (c) for comparison of the selectivity of **23** with those of other α-anisylvinyl cations.

The percentage of products derived from **23** was calculated from eq 17.[25c,d] The error associated with the 4-*E* ⇌ 4-*Z* isomerization was minimized by using in eq 17 the k_t^0 value for an equilibrium mixture of the two isomers, calculated from the weighted average of the k_t^0 values and the concentrations at equilibrium of the two isomers. In pure TFE ≥91% of the products are formed from **23** even without correction for the normal salt effect of Et_4NCl. When such a correction is introduced by using b = 4.4, as found for Bu_4NBr in AcOH,[5b] the value rises to ≥93%. This is a lower limit since a limit to the *actual* rate decrease was not observed. If products are formed at all from the ion pair in TFE, their percentage should be negligible.

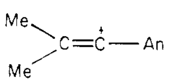
$$\%\ \text{of product from the free ion} = 100(1 - k_d/k_t^0) \qquad (17)$$

Rate depression by added Cl^-, i.e., product formation from the free ion, is appreciable in aqueous TFE mixtures. For 4-*Z* the minimum percentage of products formed from **23** is 31%, 47%, and 65% in 60%, 70%, and 80% TFE, respectively. The regular decrease of α' with the increase in X_{H_2O} (Table V) finds a parallel in the solvolysis of 1-anisyl-2-methylpropen-1-yl bromide in aqueous TFE/2,6-lutidine.[26] This trend was analyzed in terms of the changes in the dielectric constant, the nucleophilicities, the solvation abilities, and the concentrations of the solvent components. Since the change of α' with X_{H_2O} is similar in our case, it is sufficient to note that the higher nucleophilicity of the more aqueous media combined with the lower relative rate of the **23** + Cl^- reaction account for the data.

The shorter lifetime of the cation in the more aqueous media is also reflected in the extent of the 4-*E* ⇌ 4-*Z* isomerization. In 60% TFE the isomerization was not observed, in 70% TFE the isomerization is ca. 10%, and in pure TFE the isomerization is sufficiently rapid to give the equilibrium distribution of 4-*E* and 4-*Z*.

The possibility that both phenomena are due to an increased capture of the ion pairs **24a** and **24b** cannot be excluded on the basis of the present data since only one Et_4NCl concentration was studied at each solvent composition. However, the appreciable rate decrease when [Et_4NCl] < 0.1 M suggests that this is not the case.

There are no $\alpha' = k_{Cl}/k_{TFE}$ values for other α-anisylvinyl systems, but the k_{Br}/k_{TFE} values for the ions **31**[26] and **32**[5c] which are given below together with the k_t^0 values are higher than those for the ion **23**. In AcOH the k_{Cl}/k_{AcO} value for the ion **26** is ca. 4 times smaller than the k_{Br}/k_{AcO} values.[5b] If a similar difference applies also in TFE, the selectivity differences are rather small although the re-



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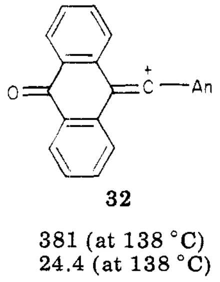
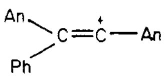


32

	31	**32**
k_{Br}/k_{TFE}	360 (at 35 °C)	381 (at 138 °C)
$10^4k_t^0$, s^{-1}	3.03 (at 35 °C)	24.4 (at 138 °C)



26

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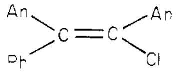
[51] Rappoport, Z.; Pross, A.; Apeloig, Y. *Tetrahedron Lett.* **1973**, 2015–2018.

[52] One difference is based on the fact that the concentrations of the salts (MCl) in the two types of experiments are different. Since the ion-pair dissociation constants when M = 2,6-lutidinium and Et_4N^+ should also differ, it is clear that the stoichiometric Cl^- concentration differs from the concentration of the free Cl^- which is the term to be used in eq 6 and 7. This and other limitations were discussed previously,[5b,c] and they emphasize the need for caution when comparing α' values which were obtained with different salts and concentrations.

activity is much higher for the formation of the ion **31** and is somewhat higher for the formation of ion **32**.

Ion pairs were not involved in the solvolysis of compounds **21** and **33**, but they were involved in the accompanying $E \rightleftharpoons Z$ isomerization.[5b,34] For example, 20.3% of the initially formed ion pairs in the acetolysis of **33**-*E*



33-*E*

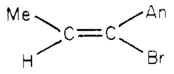
returned to **33**-*E*, 17.7% returned to **33**-*Z*, and 62% gave the product-forming free ion.[5b] Such an analysis became possible since the reactivities of **33**-*E* and **33**-*Z* were similar, and return gave an ~1:1 mixture of **33**-*E* to **33**-*Z*. Although similar information for our system is embodied in Figures 2–4, the analysis is more difficult since the k_{ion} values and the rate constants for return from the two sides of the vacant orbital are different. Comparison of Figures 3 and 4 show that addition of Cl^- increases the extent of isomerization at the expense of the solvolysis, and Table V shows that for **4**-*E* the sum of k_{isom} and $k_t{}^0$ remains constant, as expected for competing isomerization and product formation from **23**. However, the relatively sharp increase in the concentration of **4**-*E* at early reaction times in the solvolysis of **4**-*Z* (Figure 3) indicates the intermediacy of an ion pair which is involved only in the **4**-*E* $\rightleftharpoons$ **4**-*Z* isomerization. This is supported by the 2.6-fold higher $k_t{}^0$ in the presence of 0.01 M $LiClO_4$ than in its absence, and although this is only a single kinetic result, it is reminiscent of the "special salt effect".[33,53] Likewise, $k_t{}^0$ in the presence of strong nucleophiles is higher than in the presence of 2,6-lutidine (see below).

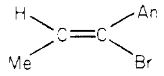
Solvolysis in TFE in the Presence of Strong Nucleophiles. The reaction in the presence of the strong nucleophiles p-$MeC_6H_4S^-$ and $CF_3CH_2O^-$ shows neither common-ion rate depression nor a **4**-*E* $\rightleftharpoons$ **4**-*Z* isomerization. This is consistent with a complete capture of **23** by these nucleophiles in preference to its reaction with the Cl^- ion. However, when a *b* value of 1.5 is used in the reaction with the $CF_3CH_2O^-$ ion (Table VII), the extrapolated k_t values are 3-fold (for **4**-*E*) and 3.5-fold (for **4**-*Z*) higher than those in the presence of 2,6-lutidine. Likewise, the rate constants for the vinyl thiolates formation are higher than those in the presence of 2,6-lutidine, but they are similar to those with $CF_3CH_2O^-$. We therefore ascribe the rate difference to capture of the intermediate ion pairs **24a** and **24b** which occurs at the expense of the ion-pair return. The effect of $LiClO_4$ and the product distributions[54] suggest that the ion pairs are solvent separated and that they intercovert rapidly before reaction with the nucleophile.

The difference between the reactions of p-$MeC_6H_4S^-$ in 80% EtOH and in TFE shows the role of the solvent in the delicate balance between the C–Nu bond formation and the C–Cl bond cleavage for a system such as **4** where both processes are feasible. In the more ionizing TFE the latter process precedes the former.

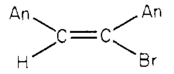
Relative Stabilities and Reactivities of 4-*E* and 4-*Z*. Compound **4**-*E* was found to be more stable by ca. 0.5 kcal mol^{-1} and 2.4–3.9 times more reactive than **4**-*Z* at 120 °C. The **4**-*E*/**4**-*Z* equilibrium ratio is very close to the average of the equilibrium ratios for α,α'-dimethylstilbene (45% of the cis isomer)[19] and α,α'-dichlorostilbene (75% of the cis isomer).[19] Combined steric and electronic interactions of the four substituents account for this behavior. The similar *E*/*Z* ratios for systems **9**, **11**, **12**, and **14** probably result from a similar combination of effects.

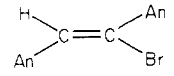
The higher reactivity of **4**-*E* reflects a higher heterolysis rate of the C–Cl bond since it was also observed in the absence of common-ion rate depression where k_t is presumably similar to k_{ion}. This is a transition-state effect since **4**-*E* is more stable than **4**-*Z*. To the extent that the rate difference has a steric origin, the $k(4\text{-}E)/k(4\text{-}Z)$ ratio can be estimated from the product of the reactivity ratios of compounds **8**-*E*, **8**-*Z*,[21] **34**-*E*, and **34**-*Z*.[7a] Indeed, the





	8-*E*	**8**-*Z*
rel k_t (80% EtOH)	6.90	0.83





	34-*E*	**34**-*Z*
rel k_t (80% EtOH)	5.45	0.12

$k(34\text{-}E)k(8\text{-}Z)/k(34\text{-}Z)k(8\text{-}E)$ product ratio is 5.45, approximating the $k(4\text{-}E)/k(4\text{-}Z)$ ratio. The ratio represents the higher reactivity of the systems with bulky substituents cis to the anisyl group, the low reactivity of the system with the *trans*-stilbene skeleton, and the inductive electron withdrawal by the β-aryl group which should be important for compounds **4**.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were determined with Cary 14 and Perkin-Elmer 402 instruments, infrared spectra with a Perkin-Elmer 377 instrument, and mass spectra with a Varian MAT 112 instrument. NMR spectra were recorded with a Varian XL-100 instrument, and the data are given in δ units downfield from internal tetramethylsilane. Dielectric constants were determined by using a DM 01 dipolmeter (Wiss-Techn. Werkstatten), and refractive indices were measured on a Zeiss refractometer. Potentiometric titrations were conducted with a Radiometer TTT-2b instrument.

Solvents and Materials. Ethanol and trifluoroethanol were dried according to the literature.[8b,55] Aqueous ROH solutions were prepared by mixing the appropriate volumes of the components. 2,6-Lutidine was dried over solid KOH and distilled before use. Sodium trifluoroethoxide was prepared by dissolving sodium in TFE. The RO^- concentration was determined by titration with HCl using bromophenol blue as an indicator. p-Toluenethiol (bp 195 °C, Aldrich) and p-*tert*-butylbenzenethiol [Aldrich, bp 92–94 °C (1 mm)] were distilled before use. The sodium thiolate solutions in aqueous EtOH were prepared by dissolving the thiol in $EtOH$–H_2O containing an equivalent amount of NaOH. Solutions of these salts in TFE were prepared by drying of the aqueous EtOH solution, crystallization of the formed salt from EtOH, and drying the salt in vacuo.

***p*-Methoxy-ω-(*p*-nitrophenyl)acetophenone (5).** p-Nitrophenylacetic acid (18.1 g, 0.1 mol) and anisole (11.9 g, 0.11 mol) were stirred with warming to 50–60 °C in polyphosphoric acid (85 mL) for 30 min. The black viscous oil was poured into water (300 mL), and the yellow solid was crystallized twice from EtOH, giving 19.7 g (75%) of yellow crystals of **5**: mp 117 °C; $\nu_{\max}$ (KBr)

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(53) (a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597–2598. (b) Fainberg, A. H.; Winstein, S. *Ibid.* **1956**, *78*, 2767–2770. (c) Fainberg, A. H.; Robinson, G. C.; Winstein, S. *Ibid.* **1956**, *78*, 2777–2779. (d) Winstein, S.; Clippinger, E. *Ibid.* **1956**, *78*, 2784–2788. (e) Winstein, S.; Robinson, G. C. *Ibid.* **1958**, *80*, 169–181. (f) Winstein, S.; Fainberg, A. H. *Ibid.* **1958**, *80*, 459–465. (g) Winstein, S.; Klinedinst, P. E., Jr.; Robinson, G. C. *Ibid.* **1961**, *83*, 885–895.

(54) The product distributions at early reaction times differ by several percent from that at infinity, but the distributions from both starting materials are similar. A nucleophilic **12**-*E* $\rightleftharpoons$ **12**-*Z* isomerization during the reaction is possible and small differences in the *E*/*Z* distribution may escape detection due to this reason.

(55) Lund, H.; Bjerrum, J. *Ber. Dtsch. Chem. Ges. B* **1931**, *64*, 210–213.

1665 (s, C=O), 1600 (s, C=C) $\mathrm{cm^{-1}}$; δ ($CDCl_3$) 3.85 (3 H, s, MeO), 4.30 (2 H, s, CH_2), 6.8–8.2 (8 H, 2 q, Ar); *m/e* (relative intensity) 271 (4, M), 135 (100, AnCO), 121 (4, *p*-$O_2NC_6H_4CH$), 106 (5, M − CO − NO − An), 92 (22, C_6H_4O), 77 (73, Ph). Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.50; H, 4.80; N, 5.16. Found: C, 66.30; H, 4.84; N, 4.86.

1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)-1-propanone (6). A solution of sodium (4 g, 170 mmol) in absolute ethanol (100 mL) was added to a solution of 4-methoxy-ω-(*p*-nitrophenyl)acetophenone (15 g, 55 mmol) in ethanol (200 mL). The solution turned violet. Methyl iodide (92 g, 0.65 mol) was added slowly, and the mixture was refluxed for 30 min. After the mixture was allowed to stand for several hours at 25 °C, a yellow precipitate (13.4 g, 86%; mp 143–144 °C) was obtained. Crystallization from 95% EtOH gave **6**: mp 149–151 °C; ν_{max} 1650 (s, C=O), 1600 (s, C=C) $\mathrm{cm^{-1}}$; δ ($CDCl_3$) 1.53 (3 H, d, *J* = 7 Hz, Me), 3.75 (3 H, s, MeO), 4.7 (1 H, q, CH), 6.65–8.10 (8 H, 2 AA′BB′ q, Ar); *m/e* (relative intensity) 285 (2, M), 255 (5, M − NO), 136 (45, *p*-$O_2NC_6H_4CH_2$), 135 (AnCO), 107 (41, An), 92 (44, C_6H_4O), 77 (53, Ph). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.40; H, 5.26; N, 4.91. Found: C, 67.12; H, 5.21; N, 5.05.

1-(*p*-Methoxyphenyl)-1,1,2-trichloro-2-(*p*-nitrophenyl)propane (7). A mixture of 1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl)-1-propanone (3.4 g, 11.9 mmol) and phosphorus pentachloride (10 g, 48 mmol) in CCl_4 (100 mL) was refluxed for 48 h. The mixture was then washed successively with water and a dilute $NaHCO_3$ solution until the acids were completely neutralized and the organic layer was separated and dried ($MgSO_4$). The solvent was evaporated and crystallization from acetonitrile gave the trichloride: mp 138 °C; 3.3 g (74%); δ ($CDCl_3$) 2.34 (3 H, s, Me), 3.76 (3 H, s, MeO), 6.58–7.95 (8 H, m, Ar). Anal. Calcd for $C_{16}H_{14}Cl_3NO_3$: C, 51.20; H, 3.74; N, 3.74; Cl, 28.40. Found: C, 50.85; H, 3.68; N, 3.62; Cl, 28.03. A minor side product which sometimes accompanied the main product was eliminated during the crystallization.

(*E*)- and (*Z*)-1-Anisyl-2-(*p*-nitrophenyl)propen-1-yl Chlorides (4-*E* and 4-*Z*). A mixture of the trichloride **7** (20 g, 53 mmol) and sodium iodide (100 g, 0.66 mol) in acetone (500 mL) was refluxed for 90 h in the dark. If the reaction was not complete, the reflux was continued for an additional 30–60 h. The mixture was poured into water, extracted with CH_2Cl_2 (200 mL), washed with water (200 mL) and with dilute sodium thiosulfate solution (200 mL), and dried ($MgSO_4$), and the solvent was evaporated. A 70:30 mixture of **4**-*E* and **4**-*Z* (40% yield) was obtained. The isomers were separated by fractional crystallization from EtOH which gave varying yields of the nearly pure **4**-*E*: mp 101 °C; λ_{max} (EtOH) 260 nm (ϵ 16 800), 336 (6600); ν_{max} (Nujol) 2860 (s, MeO), 1600, 1590 (s, C=C), 1348 (s, NO_2), 1120 (m), 1100 (m), 782 $\mathrm{cm^{-1}}$ (s); δ ($CDCl_3$) 2.32 (3 H, s, Me), 3.67 (3 H, s, MeO), 6.76 (4 H, center of AA′BB′ q, *J* = 8 Hz, OMe), 7.47 (4 H, center of AA′BB′ q, *J* = 9 Hz, *p*-$O_2NC_6H_4$); *m/e* (relative intensity) 305, 303 ($M^{37}Cl$ and $M^{35}Cl$, 32 and 100), 273 (M − 2 Me, 15), 268 (M − Cl, 89), 238 (M − 2 Me − Cl, 11), 222 (M − Cl − NO_2, 39), 207 (M − Cl − Me − NO_2, 23), 178 (M − HCl − Me − NO_2 − CO, 32); μ (cyclohexane) 3.17 ± 0.10 D. On sunlight irradiation of the remaining ethanolic solution or of a solution of pure **4**-*E*, the other isomer (**4**-*Z*, mp 137–138 °C) was obtained: λ_{max} (EtOH) 254 nm (ϵ 16 600), 308 (sh, 8900); ν_{max} (Nujol) 2860 (s, MeO), 1600, 1590 (m, C=C), 1348 (s, NO_2), 1100 (m), 1075 $\mathrm{cm^{-1}}$ (m); δ ($CDCl_3$) 2.03 (3 H, s, Me), 3.78 (3 H, s, MeO), 7.04 (4 H, center of AA′BB′ q, *J* = 8 Hz, An), 7.76 (4 H, center of AA′BB′ q, *J* = 9 Hz, *p*-$O_2NC_6H_4$); *m/e* (relative intensity) 305, 303 ($M^{37}Cl$ and $M^{35}Cl$, 30 and 79), 273 (M − 2 Me, 27), 268 (M − Cl, 100), 238 (M − 2 Me − Cl, 23), 222 (M − Cl − NO_2, 47); μ (cyclohexane) 5.70 ± 0.06 D. Anal. Calcd for $C_{16}H_{14}ClNO_3$: C, 63.26; H, 4.62; N, 4.61; Cl, 11.70. Found (for **4**-*Z*): C, 62.68; H, 4.66; N, 4.48; Cl, 11.61. Found (for **4**-*E*): C, 63.01; H, 4.61; N, 4.52; Cl, 11.93.

(*E*)- and (*Z*)-1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)propen-1-yl Ethyl Ethers (9-*E* and 9-*Z*). Compound **4**-*E* (70 mg, 0.2 mmol) and $AgNO_3$ (40 mg, 0.24 mmol) in absolute EtOH (7 mL) were kept at 120 °C for 7 days. The AgCl was filtered, and the solvent was evaporated. NMR showed the presence of **9**-*E*, **9**-*Z*, **10**, and other compound(s). The mixture of the two ethers was separated from the other compounds by several crystallizations from methanol: δ ($CDCl_3$) 1.05, 1.16 (6 H, 2 t, 2 Me, **9**-*E* and **9**-*Z*), 1.93 (3 H, s, Me, **9**-*Z*), 2.16 (3 H, s, Me, **9**-*E*), 3.3–3.8 (4 H, 2 q, CH_2, **9**-*E* and **9**-*Z*), 3.71 (3 H, s, MeO, **9**-*E*), 3.8 (3 H, s, MeO, **9**-*Z*), 6.58–8.24 (16 H, m, Ar, **9**-*E* and **9**-*Z*); *m/e* (relative intensity) 313 (66, M), 282 (15, M − MeO), 256 (100, *p*-$O_2NC_6H_4C(Me)An$), 238 (11, M − 2 Me − OEt). Anal. Calcd for $C_{18}H_{19}NO_4$: C, 69.01; H, 6.07; N, 4.47. Found: C, 69.52; H, 5.91; N, 4.03.

(*E*)- and (*Z*)-1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)propen-1-yl Trifluoroethyl Ethers (11-*E* and 11-*Z*). An ampule containing **4**-*E* (60 mg, 0.2 mmol) in a solution of 0.3 M of sodium trifluoroethoxide in TFE (15 mL) was kept at 120 °C for 48 h. The mixture was then poured into water, extracted with CH_2Cl_2, washed with dilute HCl and water, and dried ($MgSO_4$), and the solvent was evaporated. An oily mixture of 70% **11**-*E* and 30% **11**-*Z* (by NMR) was obtained but was not separated: δ ($CDCl_3$) 1.95 (3 H, s, Me, **11**-*Z*), 2.18 (3 H, s, Me, **11**-*E*), 3.71 (3 H, s, MeO, **11**-*E*), 3.81 (3 H, s, MeO, **11**-*Z*), 3.56–3.98 (4 H, 2 q, OCH_2CF_3, **11**-*E* and **11**-*Z*), 6.6–8.13 (16 H, 4 q, Ar, **11**-*E* and **11**-*Z*); *m/e* (relative intensity) 367 (72, M), 336 (16, M − MeO), 309 (16), 256 (100, *p*-$O_2NC_6H_4C(Me)An$), 238 (23, M − 2 Me − OCH_2CF_3), 234 (33, M − MeO − CF_3CH_2OH), 217 (27), 195 (27). Anal. Calcd for $C_{18}H_{16}F_3NO_4$: C, 58.85; H, 4.36; N, 3.81. Found: C, 57.13; H, 4.48; N, 3.76.

(*E*)- and (*Z*)-1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)propen-1-yl *p*-Toluenethiolates (12-*E* and 12-*Z*). Compound **4**-*Z* (137 mg, 0.45 mmol) was dissolved in an ampule containing dry dimethylformamide (10 mL). Nitrogen was bubbled through the solution for 15 min, dry sodium *p*-toluenethiolate (200 mg, 1.4 mmol) was added, and the ampule was kept for 4 h at 120 °C. The mixture was poured into water (50 mL), extracted with CH_2Cl_2 (2 × 50 mL), washed with water, and dried ($MgSO_4$), and the solvent was evaporated. The oil contained (by NMR) 35% of **12**-*E* and **12**-*Z*, 15% of **13**, and 50% of an unidentified compound. Separation of **12**-*E* and **13**-*E* from the other materials was performed on a preparative silica TLC plate by using 10% acetone–90% petroleum ether: δ ($CDCl_3$) 2.07 (3 H, s, Me, **12**-*Z*), 2.17 (6 H, 2 s, C_6H_4SMe, **12**-*E* and **12**-*Z*), 2.47 (3 H, s, Me, **12**-*E*), 3.58 (3 H, s, MeO, **12**-*E*), 3.70 (3 H, s, MeO, **12**-*Z*), 6.34–8.12 (24 H, m, 6 Ar, **12**-*E* and **12**-*Z*); *m/e* (relative intensity) 391 (33, M), 269 (44, M − *p*-$O_2NC_6H_4$), 191 (11), 184 (33), 178 (55), 136 (100, *p*-$O_2NC_6H_4CH_2$), 121 (77), 108 (89). Anal. Calcd for $C_{23}H_{21}NO_3S$: C, 70.59; H, 5.37; N, 3.58; S, 8.18. Found: C, 69.92; H, 5.19; N, 3.20; S, 7.50.

(*E*)- and (*Z*)-1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)propen-1-yl *p*-*tert*-Butylbenzenethiolates (14-*E* and 14-*Z*). Compound **4**-*Z* (50.8 mg, 0.17 mmol) was dissolved in a solution of 0.3 M sodium *p*-*tert*-butylbenzenethiolate in 80% EtOH (10 mL). The mixture was kept in a sealed ampule at 120 °C for 75 h and then poured into water containing 0.8 M $Cu(NO_3)_2 \cdot 2H_2O$ (40 mL) for precipitation of the cupric *p*-*tert*-butylbenzenethiolate. The remainder was extracted with CH_2Cl_2 (2 × 40 mL), dried ($MgSO_4$), and evaporated. NMR analysis showed the presence of a mixture of **14**-*E*, **14**-*Z*, and **15**: δ ($CDCl_3$, for the mixture) 1.2–1.3 (3 s, *t*-Bu of **14**-*E*, **14**-*Z*, **13**), 2.06 (s, Me, **14**-*Z*), 2.46 (s, Me, **14**-*E*), 3.58 (s, MeO, **14**-*E*), 3.70 (s, MeO, **14**-*Z*), 6.34–8.16 (m, Ar, **14**-*E*, **14**-*Z*, and **15**).

Isomerization Experiments. (a) A solution of either **4**-*E* or **4**-*Z* (40 mg, 0.13 mmol) in dry Me_2SO (20 mL) was refluxed for 1 h in the dark. After the mixture was washed with water and extracted with CH_2Cl_2, the extract dried, and the solvent evaporated, the NMR of the remainder showed no isomerization. (b) When a solution of either pure **4**-*E* or **4**-*Z* in nitrobenzene was kept at 120 °C for 13 h and worked up as above, isomerization was not observed. (c) A solution of **4**-*E* (40 mg, 0.13 mmol) in a 1:3 cyclohexane–chloroform mixture (8 mL) containing 2 mL of a 0.2 M HCl solution was kept at 120 °C for 18 h. Dichloromethane (5 mL) was then added, the solution was washed with water and dried ($MgSO_4$), and the solvent was evaporated. Analysis of the remainder by NMR showed the presence of 70% **4**-*E* and 30% **4**-*Z*. The same reaction of **4**-*Z* gave 20% **4**-*E* to 80% of **4**-*Z* after 2 or 22 h at 120 °C. (d) An ampule containing **4**-*E* or **4**-*Z* (30 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) and one drop of concentrated H_2SO_4 was kept at 120 °C for 12 h. NMR analysis after the workup showed that most of the substrate had been destroyed. (e) A mixture of **4**-*E*, **4**-*Z* (19 mg, 0.06 mmol), and iodine (6 mg, 0.02 mmol) in CCl_4 (3 mL) was irradiated for 20 h in a 1-cm quartz cell with a 400-W mercury lamp with a yellow filter which transmits wavelengths >490 nm. A 4:1 4-*Z*/4-*E* mixture was obtained from 4-*Z* and a 3:1 4-*E*/4-*Z* mixture was obtained from 4-*E*.

Determination of the Dipole Moments. The dipole moments were determined in cyclohexane by Smith's and Palit's modifications[14] of the Guggenheim method.[13] Six or seven solutions of each isomer with a weight fraction between 0.5×10^{-3} and 5×10^{-3} were studied, and the changes in the dielectric constant and the refraction index as compared with pure cyclohexane were determined at 33 °C.

Kinetic Procedure. Due to the low solubility, the substrate was weighed separately for each kinetic point into a pressure (Pyrex) ampule (Sovirel), and a 5-mL solution of the base or the nucleophile was added. The ampules were shaken after 1 min at the reaction temperature in order to facilitate dissolution and then kept in the dark in a thermostated bath with a temperature reading accurate to ±0.1–0.2 °C. The ampules were then cooled with ice–water, and their content was either titrated or analyzed spectrally.

The solvolysis was followed by potentiometric titration of the Cl^- with $AgNO_3$ using a calomel electrode immersed in a K_2SO_4/agar-agar solution. In the presence of 2,6-lutidine or NaOAc the kinetic samples were diluted with water (15 mL) before the titration. In the presence of CF_3CH_2ONa, water (15 mL) and AcOH (3–4 mL) were added before the titration, and for the product analysis studies the acid was neutralized with dilute aqueous NaOH after the titration.

In the experiments in the presence of thiolate ions the sample was diluted by water (20 mL) and a solution of 9.8 M of $Cu(NO_3)_2 \cdot 2H_2O$ (5 mL). The excess thiolate ions were precipitated as the cupric salts together with the starting material and the product. The solution was filtered, and the Cl^- ion was titrated. The precipitate was dissolved in CH_2Cl_2 and analyzed spectrally. Control experiments showed that the addition of the cupric salt had no effect on the relative proportions of the products.

Product Analysis. At the end of the reaction the mixture was poured into a mixture of CH_2Cl_2 (15 mL) and water (15 mL). The organic layer was separated and washed with dilute HCl in the reactions in the presence of 2,6-lutidine, NaOAc, or $NaOCH_2CF_3$. In the presence of thiolate ions the mixtures were first washed with NaOH and then with water. The organic solution was dried ($MgSO_4$), the solvent was evaporated, and the product distribution was analyzed by NMR and occasionally by IR.

4-*E* $\rightleftharpoons$ 4-*Z* Isomerization. The positions of the Me, MeO, and aromatic signals of 4-*E* and 4-*Z* are sufficiently separated for a convenient follow-up of the 4-*E* $\rightleftharpoons$ 4-*Z* isomerization. The methyl signals of the products are sufficiently away from those of 4-*E* and 4-*Z*, enabling a concurrent follow-up of the isomerizations and the solvolysis.

Registry No. (*E*)-**4**, 74684-45-0; (*Z*)-**4**, 74684-46-1; **5**, 20765-22-4; **6**, 74684-47-2; **7**, 74684-48-3; (*E*)-**9**, 74684-49-4; (*Z*)-**9**, 74684-50-7; **10**, 100-19-6; (*E*)-**11**, 74684-51-8; (*Z*)-**11**, 74684-52-9; (*E*)-**12**, 74684-53-0; (*Z*)-**12**, 74684-54-1; **13**, 103-19-5; (*E*)-**14**, 74684-55-2; (*Z*)-**14**, 74684-56-3; **15**, 7605-48-3; *p*-nitrophenylacetic acid, 104-03-0; anisole, 100-66-3; sodium *p*-toluenethiolate, 10486-08-5; sodium *p*-*tert*-butylbenzenethiolate, 54166-35-7.

Supplementary Material Available: Table I, 4-*E* $\rightleftharpoons$ 4-*Z* isomerization data; Table II, solvolysis products of **4** in EtOH; Table IV, solvolysis products of **4** in 60% TFE; Table VI, product and precursor distributions in the solvolysis of 4-*E* and 4-*Z*; Table IX, data for the reaction of 4-*E* with sodium *p*-toluenethiolate; Table X, 4-*E* $\rightleftharpoons$ 4-*Z* isomerization data during solvolysis in 80% EtOH/RS^- (6 pages). Ordering information is given on any current masthead page.

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. 9. Reaction of Phenol with 1-Propanol[1a]

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At 250–350 °C in the presence of alumina, phenol (1) reacts with excess 1-propanol to give mainly (>90%) C-alkylation to form mono- to penta-*n*-propylphenols plus some O-alkylation to form *n*-propyl aryl ethers. The principal component of the product mixture from 1 is 2,6-di-*n*-propylphenol (26–50 mol % yield). With 4-*n*-propylphenol as substrate (instead of 1), tri-, tetra-, and penta-*n*-propylphenols are formed in 48–79% combined yield. On the average, only 3% of the total C_3H_7 groups in the product mixture are isopropyl ones. Deoxygenation is not observed. It is proposed that the principal products result from an S_N2-type reaction mechanism which involves nucleophilic attack (variously by C-2, C-4, C-6, or O) of an adsorbed ambident phenoxide ion onto C-1 of an adsorbed *n*-propoxide group. *n*-Propylation at C-3 and C-5 of the phenol ring results from surface-catalyzed dienone–phenol rearrangement. Isopropylation may occur via a side reaction of S_N1 type.

Previous papers in this series[2-7] concerned alumina-catalyzed reactions of methanol with naphthols, indanol, hydroxybiphenyls, and hydroaromatic ketones of the benzene and naphthalene systems in a flow apparatus at 220–550 °C. In general terms, processes of (a) O-alkylation to give alkyl aryl ethers, (b) C-alkylation to give alkylarenols and alkylated hydroaromatic ketones, and (c) alkylation–deoxygenation to form alkylarenes variously occurred with the hydroxyarene substrates. Analogous interactions between phenol and methanol were reported by other investigators.[8] On the basis of mechanisms proposed in our studies,[2,3] one would expect that any primary or secondary alcohol should undergo processes b and c without skeletal rearrangement of the alkyl group. This paper and the following one[9] report the results of inter-

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