Bull. Chem. Soc. Jpn., 72, 163—170 (1999)

Headline Articles

Solvolysis of Styryliodonium Salt: Products, Rates, and Mechanisms

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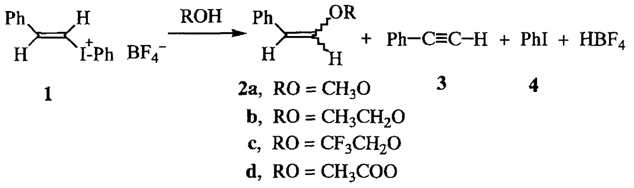
(Received September 10, 1998)

The solvolysis of phenyl[(*E*)-styryl]iodonium tetrafluoroborate in various solvents was examined at 50—70 °C by means of product and kinetic studies with the normal and labeled substrates. The reactions involved are α-elimination and substitutions with configurational retention and inversion. In methanol and ethanol, the main reaction is α-elimination, along with about 5% of substitution with the ratio of inversion/retention from 4/6 to 3/7. As the basicity of the solvent decreases, the reaction rate and the fraction of α-elimination decrease, and at the same time the ratio of inversion/retention of substitution also decreases. In 2,2,2-trifluoroethanol, only the substitution with retention was observed. Labeling experiments showed that complete isotope scrambling occurred between the olefinic hydrogens of the retained product while the deuterium remained at the original position of the inverted product. The substitution mechanism is concluded to involve parallel pathways: an $\mathrm{S_N1}$-type with a vinylenebenzenium ion intermediate leading to retention and a vinylic $\mathrm{S_N2}$-type with a direct attack by the nucleophilic solvent leading to inversion.

Vinyliodonium salts readily undergo nucleophilic substitution and elimination reactions due to a high nucleofugality of the iodonio group. A cyclohexenyliodonium salt was found to undergo solvolysis via cyclohexenyl cation as an intermediate,[1)] while 1-alkenyliodonium salts undergo one-step $\mathrm{S_N2}$ reaction without a cationic intermediate.[2—4)] Styryliodonium salt showed intermediate behavior that it undergoes solvolysis both via a vinylenebenzenium ion intermediate with retention and $\mathrm{S_N2}$ substitution with inversion of configuration depending on the reaction conditions.[5,6)] The present paper describes a full account of the solvolysis reaction of phenyl[(*E*)-styryl]iodonium tetrafluoroborate (**1**) that involves the $\mathrm{S_N1}$ and $\mathrm{S_N2}$-type substitutions as well as α-elimination.

Results

Product Analysis. Reactions of **1** in some alcohols, acetic acid, and mixed aqueous alcoholic solvents were carried out at 50—70 °C. Solvolysis products involve those of substitution, (*E*)- and (*Z*)-1-alkoxy (or acetoxy)-2-phenylethene (**2**), 1,1-dialkoxy-2-phenylethane (**5**), and phenylacetaldehyde (**6**), and the elimination product, phenylacetylene (**3**) as well as accompanying iodobenzene (**4**) (Eqs. 1, 2, and 3).



(1)

$$2 + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \underset{\mathbf{5}}{\mathrm{PhCH_2CH(OR)_2}} \qquad (2)$$

$$2 \text{ or } 5 + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \underset{\mathbf{6}}{\mathrm{PhCH_2CHO}} \qquad (3)$$

The secondary products, **5** and **6**, must be formed from **2** by the reaction catalyzed by the acid generated during the reaction (Eqs. 2 and 3), and their yields vary with reaction conditions.

Yields of these products were determined by gas chromatography; the results under typical conditions are summarized in Table 1. The main product is **3** formed from elimination in methanol and ethanol, but the substitution becomes a main reaction in less basic solvents like acetic acid and 2,2,2-trifluoroethanol (TFE). The ratios of substitution to elimination (S/E) are given in the last column of Table 1. The fraction of substitution changes from 4—7% in meth-

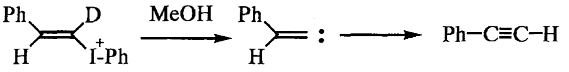
Table 1. Product Distribution in the Solvolysis of **1** in Various Solvents

Solvent	Additive	Temp	Time	Yield/%			S/E[a]
	(concn/mol dm^{-3})	°C	h	**2** (*Z*/*E*)	**3**	**4**	
MeOH	None	50	50	1.4 (43/57)	26	26	5/95
MeOH	TFA (0.001)	60	50	2.2 (34/66)[b]	75	75	6/94
MeOH	AcONa (0.05)	50	4	0	68	70	0/100
MeOH	CF_3CO_2Na (0.05)	50	20	0.5 (38/62)	65	59	0.8/99.2
EtOH	None	50	50	1.4 (39/61)	27	28	4/96
EtOH	TFA (0.001)	60	50	2.4 (30/70)[c]	70	69	7/93
20E[d]	TFA (0.001)	60	50	11[e]	23	27	32/68
TFE	None	50	240	78 (0/100)[f]	0	86	100/0
AcOH	None	50	76	2.2 (17/83)	0.2	4.2	90/10
AcOH	None	70	120	38 (14/86)	7	54	85/15

a) The ratio of substitution to elimination. b) Also obtained were 0.4% of **5** and 2.3% of **6**. c) Also obtained were 1.8% of **5** and 1.1% of **6**. d) 20% (v/v) aqueous ethanol. e) Aldehyde **6**. f) Also obtained was 22% of **5**.

anol and ethanol in the absence of base to 85% in acetic acid and to 100% in TFE. The results are in-between (about 30% of substitution) in aqueous ethanol. The increase in substitution relative to elimination seems to depend on the solvent basicity. Addition of a base (carboxylate) accelerates the reaction and completely results in elimination. It is also noticeable that the isomeric ratio of *Z*/*E* of **2** changes with the solvent employed, from roughly 4/6 in methanol and ethanol to 15/85 in acetic acid and to 0/1 in TFE. The fraction of the retained product, (*E*)-**2**, increases with acidity of the solvent, where the reaction is very slow and the elimination is largely inhibited.

Labeling Experiments. Reactions were also carried out with the α-deuterated substrate (**1-αD**),[7] and the deuterium distributions of the products were analyzed by means of mass or ^{1}H NMR spectroscopy. The deuterium content of the elimination product **3** obtained from the reactions of **1-αD** in methanol without any additive was evaluated from the GC MS spectrum of the product mixture. The relative heights of the molecular peaks $m/z = 102$ and 103 for **3** show that the label is essentially lost during the reaction. A comparison of the relative peak heights is rather a crude method for the determination of the deuterium content, but it shows that the excess deuterium content is less than 1% for the reaction in neutral methanol. A control experiment shows that the deuterated phenylacetylene **3-d** does undergo isotope exchange under the reaction conditions but only partially (7.5% in 50 h at 50 °C in neutral methanol). If **3-d** were formed during the reaction, it must have remained largely deuterated. That is, most of the deuterium of the substrate **1-αD** was lost during the elimination reaction. This is in marked contrast to the results found in the presence of bromide ion in acetonitrile, where the deuterium was completely retained in the product **3**.[6] The latter elimination is the β-elimination, while the elimination observed in methanol occurs via the α-elimination, that is, through an alkylidenecarbene as an intermediate. These results are along the same line as those observed for 1-alkenyliodonium salts which undergo α-elimination induced by the base, while β-elimination is induced by adding bromide and chloride ions.[2—4]

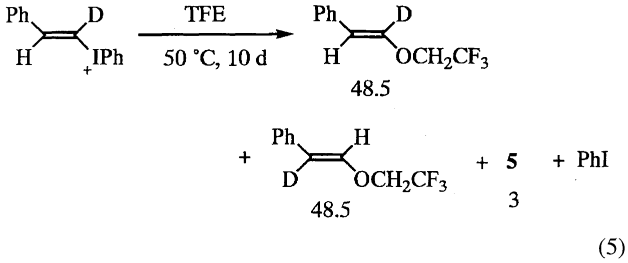


1-αD

(4)

The elimination product **3** obtained from **1-αD** in the presence of 0.05 mol dm^{-3} of tetrabutylammonium bromide in methanol was also examined. The reaction at 50 °C for 25 h resulted in 30% yield of **3** containing about 39% excess of deuterium in addition to the substitution products.[6] Since **3-d** was found to lose about 2% of the label under the same reaction conditions, both the β- and α-eliminations of **1** must take place in the presence of the bromide in methanol.

Deuterium contents in the substitution products were examined by ^{1}H NMR for the reactions of **1-αD** in TFE, acetic acid, and methanol. The results are illustrated in Eqs. 5, 6, and 7, showing molar ratios of the products deduced from GC and NMR analyses. The ^{1}H NMR spectra of product mixtures obtained from reactions in TFE and methanol are shown in Figs. 1 and 2, respectively.



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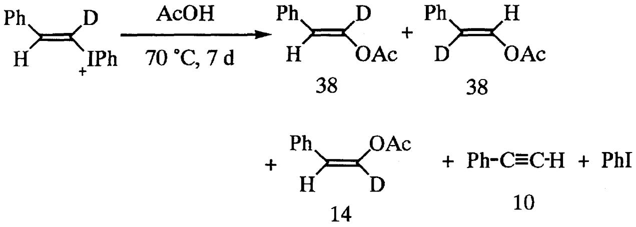

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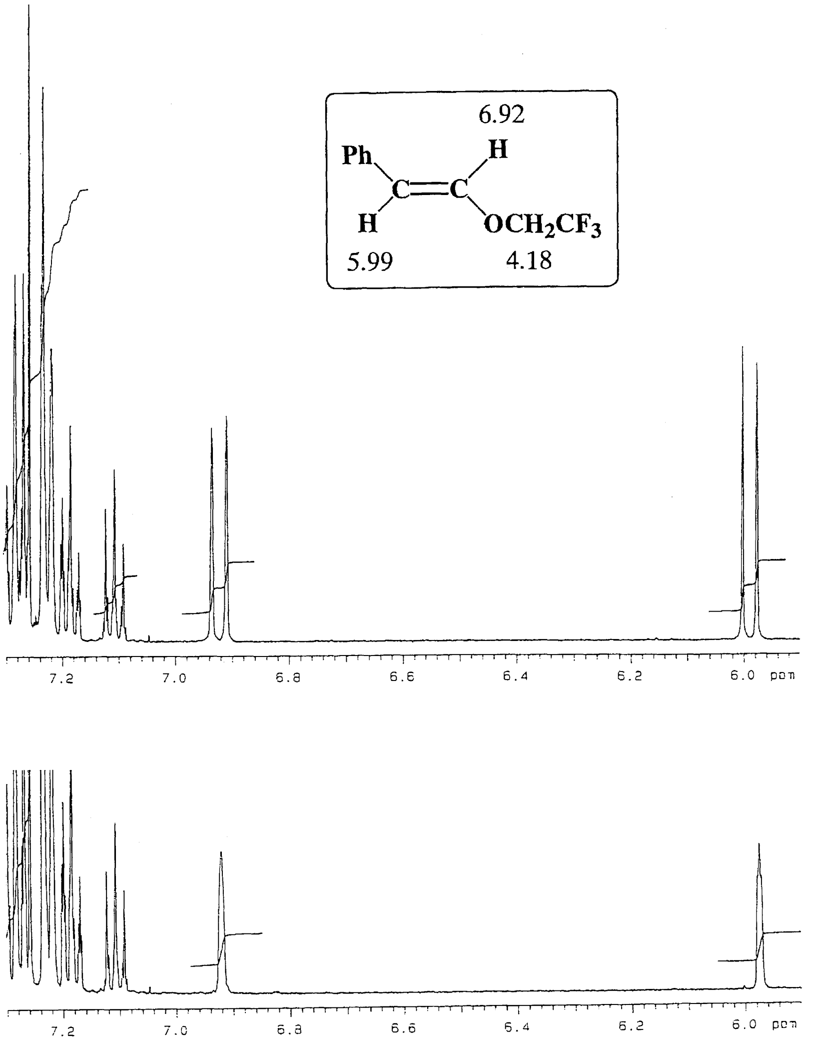
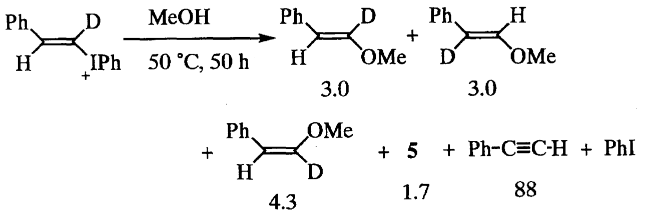


Fig. 1. ^{1}H NMR spectra of solvolysis products of **1** (upper) and **1-αD** (lower) in TFE.



(7)

In TFE, the only primary product formed is (*E*)-**2c**, a substitution product of retention, and the deuterium is completely scrambled between the α and β positions.[7] This crucial point is concluded from the NMR observations (Fig. 1): The geometry is assigned as *E* from the olefinic proton coupling of 13.0 Hz. Two olefinic proton signals at 5.99 and 6.92 ppm were found in the spectrum of the (*E*)-**2c** obtained from **1-αD**. However, both of them coalesce into broad singlets and their intensities are about a half of the amount expected, compared to the intensity of the methylene signal of the trifluoroethoxy group (the observed intensities of the 5.99 and 6.92 ppm signals are 0.59 and 0.51 relative to 2.00 for the CH_2). The coalescence of the doublet to singlet indicates that the counterpart hydron is replaced by a deuteron and the total intensity of about unity corresponds to the original β-proton of **1-αD**.

In acetic acid, (*E*)-**2d** and (*Z*)-**2d** were both obtained at a ratio of 85/15; the deuterium is scrambled in the *E* isomer while it is retained at the original position of the *Z* isomer as summarized in the Experimental Section and in a preliminary communication.[5]

The substitution products are minor in methanolysis and the ratio (*E*)-**2a**/(*Z*)-**2a** is about 6/4. Here again, the deuterium is scrambled in (*E*)-**2a** but it remains at the original position of (*Z*)-**2a**. This conclusion was reached from the following NMR observations (Fig. 2): Two olefinic signals for the (*E*)-**2a** obtained from **1-αD** were seen at 5.80 and 7.04 ppm as poorly separated triplets (due to coupling with the counterpart deuteron). Intensities of these peaks are nearly a half of that expected from the intensity of the methoxy signal at 3.68 ppm. On the other hand, the signal for the β-proton of (*Z*)-**2a** was observed at 5.22 ppm as a broad singlet while the α-proton signal was hardly seen at the expected position of 6.12 ppm. The intensity of the β-proton signal is about 1/3 of that of the methoxy signal at 3.77 ppm. Relative intensities of those signals at 5.22 and 5.80 ppm

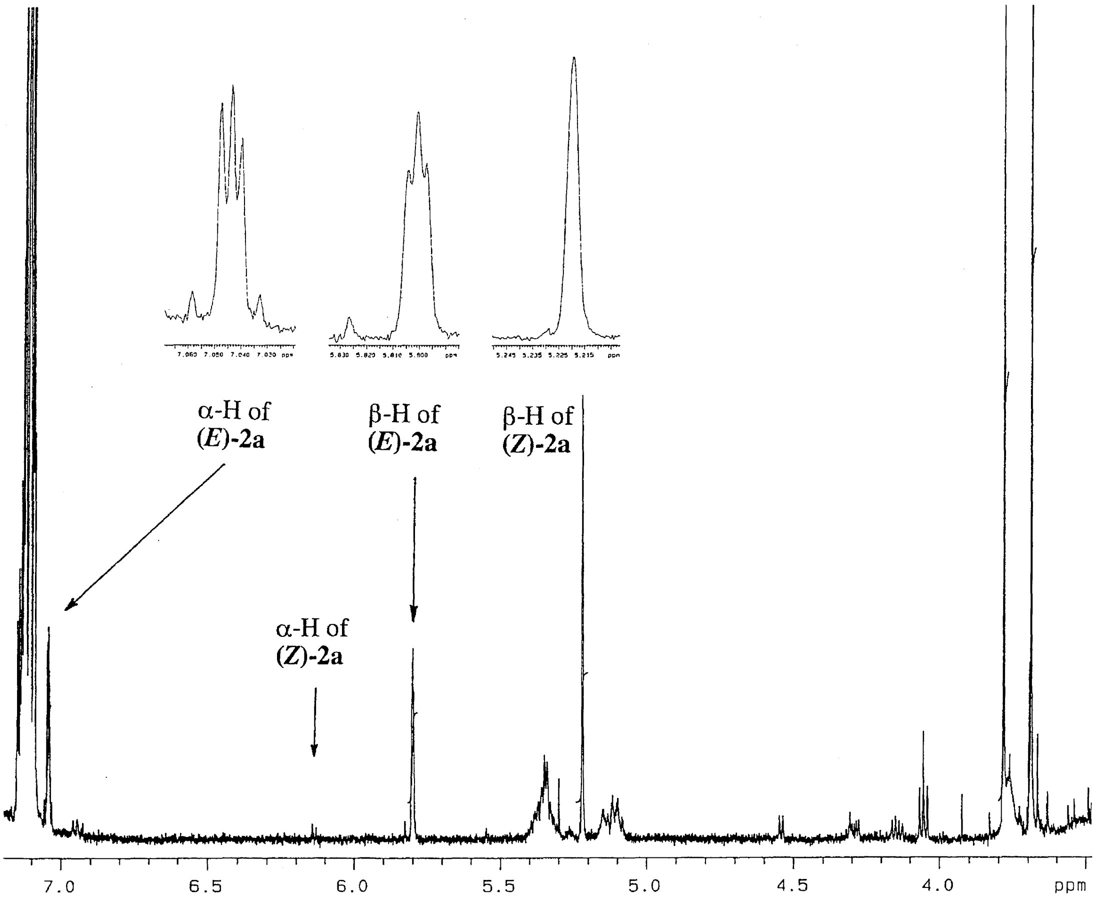


Fig. 2. ^{1}H NMR spectrum of the solvolysis products of **1-αD** in methanol.

are 1.00 : 0.71, in agreement with the GC peak ratios ((*Z*)-**2a**/[(*E*)-**2a**/2] = 4.3/3.0). (The proton signal at 7.04 ppm is on the tail of aromatic signals, so reliable intensity values could not be obtained.)

Reaction Rates. The UV spectrum of a solution of **1** shows an absorption maximum at 268 nm in an alcohol; the spectrum usually changes smoothly with time with isosbestic points at about 222 and 246 nm. However, the reproducibility of the time-dependent spectral change easily becomes poor unless the solvent is carefully prepared. Contamination with an undetectably small amount of base seems to accelerate the apparent reaction at the low concentration of the substrate employed for the spectrophotometric kinetic measurements (ca. 5×10^{-5} mol dm^{-3}), although product profiles (at higher concentrations) are not affected by the methods of solvent preparation. The methanol of a commercial "dry grade" induced an instantaneous reaction of **1** viewed from the UV spectral change, and the methanol prepared by a usual distillation from metal magnesium (magnesium methoxide) resulted in the same observation. We thought that a basic contamination induced a very facile α-elimination of **1** (see below). Since the solvolysis reaction of **1** was found not to be influenced by small amounts of added acid, we used for kinetic measurements freshly distilled solvents containing about 1 mmol dm^{-3} of trifluoroacetic acid. The reaction was monitored by a decrease in the absorbance at 268 nm at 60 °C. The pseudo-first-order rate constants k_{obsd} were calculated from the time-dependent absorbance change.

The results are summarized in Table 2; k_{obsd} are logarithmically plotted against the solvent ionizing power Y_{OTs}[8] and nucleophilicity N_{T}[9] parameters in Fig. 3. Scattering of the plots is large especially in that against Y_{OTs}, that shows a tendency

Table 2. Rate Constants for Solvolysis of **1** in Various Solvents at 60 °C

Solvent	Y_{OTs}[a]	N_{T}[b]	$10^5k_{\text{obsd}}/\text{s}^{-1}$
MeOH	−0.92	0.17	0.92
EtOH	−1.92	0.37	1.7
TFE	1.77	−3.93	0.25
H_2O	4.0	−1.38	0.70
80E[c]	0	0	1.12
60E[c]	0.95	−0.39	0.98
40E[c]	1.92	−0.74	0.64
20E[c]	3.32	−1.26	0.33
80ET[d]	−1.18	0.08	1.3
60ET[d]	−0.44	−0.34	0.64
40ET[d]	0.21	−0.94	0.44
20ET[d]	0.98	−1.76	0.23
90Tw[e]	1.88	−2.55	0.18
70Tw[e]	2.0	−1.98	0.22
50Tw[e]	2.14	−1.73	0.32

a) Ref. 8. b) Ref. 9. c) Volume % ethanol of aqueous ethanol. d) Volume % ethanol of mixed ethanol–TFE. e) Weight % TFE of aqueous TFE.

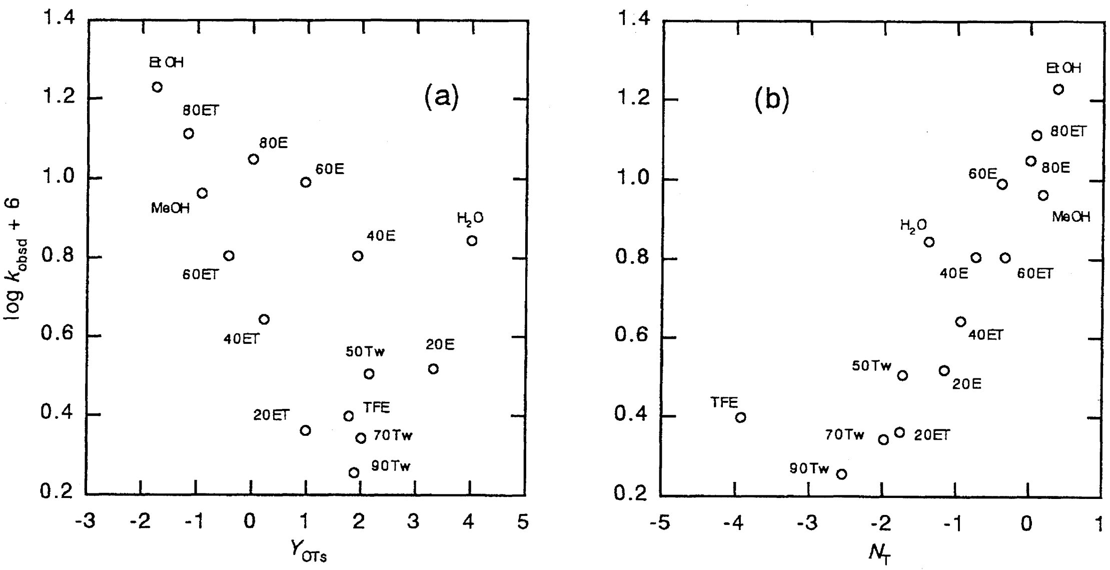


Fig. 3. Logarithmic plots of solvolysis rate constants k_{obsd} for **1** obtained at 60 °C against solvent parameters Y_{OTs} (a) and N_T (b). For abbreviations of solvents, see Table 2.

of decreasing rates with solvent ionizing power. The plot against N_T shows a trend that the rate increases with solvent nucleophilicity. A two-parameter fitting of the data resulted in the relationship: $\log k_{obsd} = -0.022\ (\pm 0.035) Y_{OTs} + 0.21\ (\pm 0.05) N_T - 5.13\ (\pm 0.06)$; Dependence on Y_{OTs} is very small and its inclusion does not significantly improve the correlation with the single parameter N_T.

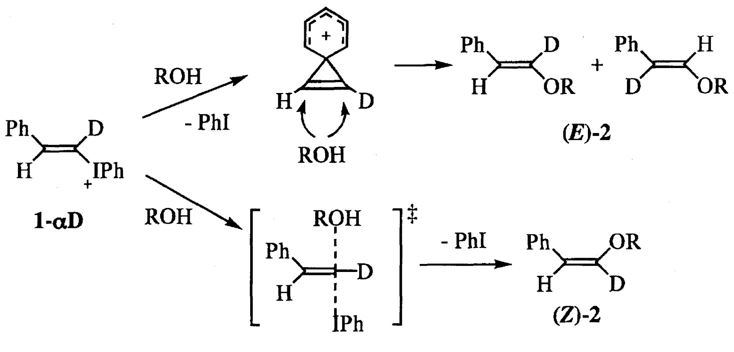
Discussion

Let us summarize the experimental observations on the solvolysis reactions of the styryliodonium salt **1**: (1) In methanol and ethanol, the main reaction is α-elimination; (2) In more acidic solvents, the reaction becomes slower and the fraction of substitution increases; (3) In these acidic solvents, the fraction of retention of configuration increases at the cost of inversion of substitution. In TFE, the observed reaction is exclusively the substitution with retention. (4) The deuterium of the labeled substrate **1-αD** is completely scrambled between the α and β positions of the retained product of substitution (*E*)-**2**, while it remains at the original position of the inverted product (*Z*)-**2**.

These results show that the solvent basicity most greatly affects the α-elimination. The substitution processes are best accounted for by a mechanism (Scheme 1) involving a vinylenebenzenium ion intermediate to lead to the substitution with retention and a parallel direct reaction of the nucleophilic solvent from the back side of the leaving iodonio group to give an inverted product. The latter process corresponds to a unique in-plane vinylic S_N2 reaction observed for the reaction of this and other vinylic iodonium salts with halide ions.[2—4,6]

The participation of the β-phenyl group in the leaving of the iodonio group of **1** to lead to 1,1-vinylenebenzenium ion occurs in competition with the attack by an external nucleophile (solvent). The poorest of the solvents as a nucleophile, TFE ($N_T = -3.93$), cannot compete with the phenyl participation, but can only trap the intermediate benzenium ion to give solely the retained product, (*E*)-**2c**. Acetic acid is more nucleophilic ($N_T = -1.78$) than TFE, and about 15% of the inverted product, (*Z*)-**2d**, was observed. A still higher proportion of inversion was found for the reaction in methanol. The extreme case of such a process would be the reaction with bromide ion in an aprotic solvent (acetonitrile), which resulted in more than 99% of the substitution with inversion.[6)]

A similar benzenium intermediate was previously suggested for the solvolysis of 1-methyl-2-phenyl-1-propenyl



Scheme 1.

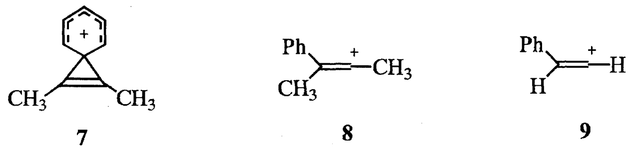


Chart 1.

triflate.[10] The results of kinetic, stereochemical, and labeling experiments were explained by a mechanism involving both a dimethyl-substituted vinylenebenzenium ion **7** and a linear secondary vinyl cation **8** (Chart 1). However, formation of a primary vinyl cation like **9** is unlikely in the present reaction because the primary cation is expected to be much less stable than the secondary cation; furthermore, the β-phenyl substitution is considered to destabilize vinyl cation while the β-methyl substitution stabilizes it.[11,12] Thus, the possibility that the inverted product (*Z*)-**2** is formed from a paired vinyl cation intermediate is excluded and the inversion must occur during the direct S_N2 substitution. This is compatible with the observation that no isotopic scrambling occurred during the formation of (*Z*)-**2** in contrast to the complete deuterium scrambling in (*E*)-**2**. It was recently reported that thermal decomposition of phenyl[(*E*)-2-phenyl-1-butenyl]iodonium trifluoromethanesulfonate (triflate) occurred with rearrangement of the phenyl group probably via a benzenium intermediate.[13]

A more nucleophilic alcohol is also a more basic solvent, which induces α-elimination; nearly 95% of the entire reaction is α-elimination in methanol and ethanol but this fraction decreases to 68% in 20% aqueous ethanol (20E in Table 1). Water is a less basic solvent (Taft's β[14] = 0.18 and $N_T = -1.38$) compared with methanol ($\beta = 0.62$ and $N_T = 0.17$) and ethanol ($\beta = 0.77$ and $N_T = 0.37$). The α-elimination was not observed in TFE, which has no basic property in terms of Taft's β value ($\beta = 0$).[14] By addition of sodium acetate as a base, the reaction of **1** becomes very rapid and gives exclusively the elimination product **3**.

The elimination via the α route is confirmed by the labeling experiments that show the label at the α-position of **1-αD** is lost in the product **3**. A comparison of the product ratios S/E in the reactions of **1** and **1-αD** in methanol allows us to evaluate the kinetic isotope effects. If we assume that the secondary kinetic isotope effects on the substitution can be neglected, the kinetic isotope effect on the elimination is calculated to be about 2.6 from the S/E values 5/95 and 12/88 for **1** and **1-αD**. This evaluation implies that the effect is primary and that the α-hydrogen is eliminated in the rate-determining step.

The observed rate constants seem to depend on the solvent nucleophilicity N_T, but much less on the solvent polarity (ionizing power Y_{OTs}). This observation can be explained by the fact that the α-elimination is more easily occurring in methanol, ethanol, and aqueous ethanol. The solvent basicity facilitates this reaction and N_T stands for the solvent basicity. The heterolysis of the ionic substrate **1** is expected not to be dependent very much on the solvent polarity, as observed previously.[1,15] The present heterolysis involving phenyl participation would be still less dependent on the solvent polarity. In fact such dependence is small and seems to be rather negative [Fig. 3(a)].

In summary, the three competing reactions in solvolysis of the styryliodonium salt **1** are largely dependent on the solvent basicity/nucleophilicity: The basic character of the solvent is responsible for the α-elimination, while the nucleophilicity controls the S_N2 substitution. The substitution with retention involving the phenyl-participation leading to heterolysis to form a vinylenebenzenium intermediate is largely independent of solvent polarity or nucleophilicity, and it shows up when both basic/nucleophilic processes become sluggish in a more acidic solvent, but the solvent is nucleophilic enough to trap the benzenium intermediate.

Experimental

^{1}H NMR spectra were recorded on a Varian INOVA 500 spectrometer and chemical shifts are given in ppm downfield from internal TMS. UV spectra were obtained on a Shimadzu UV-2200 spectrophotometer. Mass spectra (EI MS) were recorded at 70 eV on a mass spectrometer JEOL JMS-DX303HF. Analytical gas chromatography was conducted on a Shimadzu GC-14B gas chromatograph with a DB-1 capillary column (0.25 mm×30 m) and an integrator C-R6A.

Materials. Alcohols for kinetic runs are freshly distilled and kept in a quartz flask. Phenyl[(*E*)-styryl]iodonium tetrafluoroborate (**1**) and the α-deuterated substrate **1-αD** (the isotopic purity = 98.8%) were obtained as described previously.[6] Authentic samples of phenylacetylene (**3**, Wako Chemicals, Osaka), iodobenzene (**4**, Wako), and 1,1-dimethoxy-2-phenylethane (**5a**, TCI, Tokyo) were purchased. (*E*)- and (*Z*)-1-ethoxy-2-phenylethene (**2b**) are the samples prepared previously.[16]

1-Methoxy-2-phenylethene (**2a**) was prepared as an isomeric mixture of $E/Z = 6/4$ from **5a**.[17] ^{1}H NMR (CDCl$_3$), (*E*)-**2a**: δ = 3.68 (s, CH$_3$), 5.80 (d, J = 12.7 Hz, β-H), 7.04 (d, J = 12.7 Hz, α-H). (*Z*)-**2a**: δ = 3.77 (s, CH$_3$), 5.22 (d, J = 7.2 Hz, β-H), 6.12 (d, J = 7.2 Hz, α-H). MS *m/z* (%) **2a**: 134 (M$^+$; 100), 119 (15), 105 (3), 103 (3), 91 (68), 77 (5), 65 (10). **5a**: ^{1}H NMR (CDCl$_3$) δ = 2.91 (d, J = 5.5 Hz, CH$_2$), 3.34 (s, CH$_3$), 4.54 (t, J = 5.5 Hz, CH), 7.22 (m), 7.29 (m). MS *m/z* (%) 166 (M$^+$; 0.4), 135 (M−OCH$_3$; 17), 103 (9), 91 (14), 75 (M−PhCH$_2$; 100), 65 (5).

Product Analysis. A typical reaction was carried out with about 5 mg of **1**. A weighed sample of **1** was dissolved in 3 mL of the reaction solution and kept in a stoppered test tube at 50—70 °C. After the reaction time, water (usually 15 mL) and 1 mL of the pentane solution containing tetradecane (the internal standard for GC) were added to the cooled mixture, and the products were immediately extracted with pentane (3 mL) 3 times. The combined pentane layer was washed with water and dried over magnesium sulfate. The extract was analyzed by GC and by GC MS or ^{1}H NMR when required. The relative molar intensities of the GC peaks were determined with the authentic samples in comparison with the internal tetradecane or evaluated by comparing the relevant NMR peak areas with the GC peak areas. The relative intensities for the isomers were assumed to be the same.

Methanolysis. A sample of **1** (6.9 mg) was dissolved in 3 mL of methanol and kept at 50 °C for 50 h. Products were extracted with pentane after addition of a pentane solution of tetradecane and water as described above. GC determination showed that yields of **3**, **4**, and (*Z*)- and (*E*)-**2a** were 26, 26, 0.60, and 0.79%, respectively.

A trace amount of the acetal peak (**5a**) was also detected.

A sample of **1-αD** (41 mg) was dissolved in methanol (8 mL) and kept at 50 °C for 50 h. Products were extracted with pentane (5 mL×3) after addition of water (30 mL). The separated pentane layer was washed with water and dried over magnesium sulfate. GC shows formation of **4**, **3**, (*Z*)- and (*E*)-**2a**, and **5a** in a molar ratio of 98 : 88 : 4.3 : 6 : 1.7. Lower boiling **3** and a part of **4** were evaporated under vacuum before dissolving in $CDCl_3$ for the NMR measurement. The ^1H NMR spectrum (Fig. 2) shows a clear singlet peak at 5.22 ppm (β-H of (*Z*)-**2a**) and two slightly separated triplets at 5.80 and 7.04 ppm (olefinic protons of (*E*)-**2a**), but no peak around 6.1 ppm (α-H of (*Z*)-**2a**). The intensity ratio of the signals at 5.22/5.80 ppm is 1.00/0.71.

Trifluoroethanolysis. A sample of **1** or **1-αD** (8 mg) was dissolved in 5 mL of 2,2,2-trifluoroethanol (TFE) and kept at 50 °C for 10 d. Products were extracted with pentane (3 mL×3) after addition of water (20 mL). The products were collected in the same way as above and analyzed by GC, GC MS, and ^1H NMR (Fig. 1). GC peaks at retention times 7.5, 10.5, and 11.0 min are assigned to iodobenzene (**4**), (*E*)-1-phenyl-2-(2,2,2-trifluoroethoxy)ethene (**2c**), and 2-phenyl-1,1-bis(2,2,2-trifluoroethoxy)ethane (**5c**). Relative intensities of the peaks were 71 : 75 : 25 for **1** and 73 : 97 : 3 for **1-αD**, molar ratios evaluated being 86 : 78 : 22 and 86 : 97 : 3. The products from **1** showed: (*E*)-**2c**: ^1H NMR ($CDCl_3$) $\delta = 4.18$ (q, $J = 8.2$ Hz, CH_2), 5.99 (d, β-H, $J = 13.0$ Hz), 6.92 (d, α-H, $J = 13.0$ Hz), 7.2—7.3 (Ph). MS *m/z* (%) 202 (M^+; 100), 119 (29), 103 (3.6), 91 (81), 77 (5), 65 (11). **5c**: ^1H NMR ($CDCl_3$) $\delta = 2.99$ (d, $J = 5.7$ Hz, CH_2), 3.92 (m, CH_2), 4.94 (t, $J = 5.7$ Hz, CH). MS *m/z* (%) 211 ($M-PhCH_2$; 100), 203 ($M-OCH_2CF_3$; 22), 129 (2.7), 109 (4.3), 103 (9), 91 (12), 83 (11), 65 (2.4). The ^1H NMR spectrum of the product mixture from **1-αD** showed broad singlets at 5.99 and 6.92 ppm and a quartet at 4.18 ppm with relative intensities of 0.59 : 0.51 : 2.00, in addition to other signals in the 7—8 ppm region.

Acetolysis. A sample of **1** or **1-αD** (about 20 mg) was dissolved in 10 mL of acetic acid and kept at 70 °C for 7 d. Products were extracted with pentane (5 mL×3) after addition of 30 mL of water. The combined pentane layer was washed with water and dried over magnesium sulfate. The solvent was removed by vacuum evaporation. The remaining products were analyzed by GC, GC MS, and ^1H NMR. GC peaks at retention times 12.8 and 13.3 min are assigned to (*Z*)- and (*E*)-**2d**, respectively, relative intensities being about 15/85 both for the products from **1** and **1-αD**. These peaks of isomeric **2d** from **1** showed the same MS pattern consistent with the assigned structure. The products from **1** showed ^1H NMR ($CDCl_3$) δ (splitting, coupling constant, relative intensity, assignment) 2.19 (s, 3.00, CH_3CO of (*E*)-**2d**), 6.39 (d, $J = 12.7$ Hz, 0.99, β-H of (*E*)-**2d**), 7.84 (d, $J = 12.7$ Hz, 1.01, α-H of (*E*)-**2d**), 2.27 (s, 0.50, CH_3CO of (*Z*)-**2d**), 5.70 (d, $J = 7.1$ Hz, 0.16, β-H of (*Z*)-**2d**), 7.29 (d, $J = 7.1$ Hz, —, α-H of (*Z*)-**2d**). MS *m/z* (%) **2d**: 162 (M^+; 17), 120 (100), 91 (43), 65 (5.3). The products from **1-αD** showed ^1H NMR ($CDCl_3$) δ (splitting, relative intensity), 2.19 (s, 3.00), 6.39 (slightly separated t, 0.51), 7.84 (slightly separated t, 0.53), 2.27 (s, 0.53), 5.70 (broad s, 0.17).

Deuterium Content of 3. The deuterium content of **3** formed from the reaction of **1-αD** was evaluated by MS from the relative heights of the parent peaks at *m/z* 102 and 103, as before.[6] The relative peak height 102/103 was 100 : 9.33 (calcd for the natural isotopic abundances: 9.053) for the authentic protium sample of **3**. The product **3** obtained in the reaction of **1-αD** in methanol at 50 °C without any additive showed the peak ratio 102/103 of 100/10.13. This value corresponds to the excess deuterium content (after correction for the natural abundances) of 0.80%. The isolated deuterated phenylacetylene **3-d** (92% excess D, peak ratio 102/103 = 8.62/100) was treated at 50 °C for 50 h in methanol, and the recovered **3** was subjected to MS analysis; the peak ratio 102/103 was 17.24/100, corresponding to 7.5% isotope exchange.

The reaction of **1-αD** was carried out at 50 °C for 25 h in methanol containing 0.05 mol dm^{-3} of Bu_4NBr. The product **3** showed the peak ratio 102/103 of 100/63.0, corresponding to 38.6% excess in deuterium. The treatments of **3-d** under the same conditions resulted in 2% isotope exchange; the peak ratio 102/103 became 10.98/100 from 8.62/100.

Kinetic Measurements. Reaction rates were determined by monitoring the decrease in UV absorbance at 268 nm at 60 (±0.1) °C as described previously.[1] Freshly distilled solvents containing 10^{-3} mol dm^{-3} CF_3CO_2H were used for all the kinetic determinations, and pseudo-first-order rate constants k_{obsd} were usually obtained as averages of three determinations.

We thank Hiroshi Okuda and Kazuo Fukuda for measurements of NMR and MS spectra. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture.

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