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Reactions of Phenyl(styryl)iodonium Tetrafluoroborate with Halide Ions

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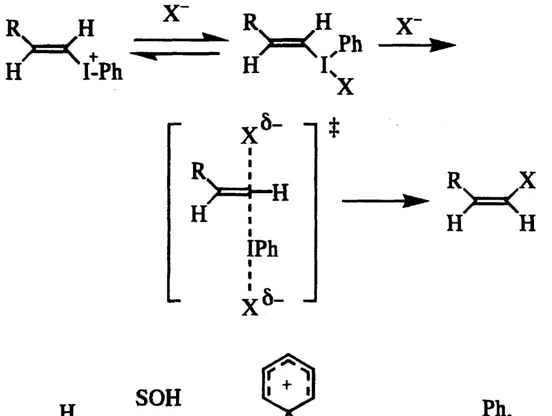
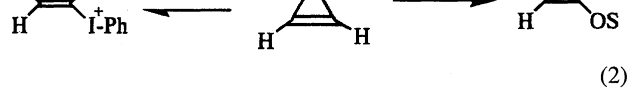
Reactions of (*E*)-phenyl(styryl)iodonium tetrafluoroborate with chloride, bromide, and iodide ions are examined under various conditions. The products are those of substitution and elimination, involving (*Z*)-1-halo-2-phenylethene (**2**), phenylacetylene (**3**), and iodobenzene as main products as well as minor products of (*E*)-**2** and 1-halo-1-phenylethene. Results of product analysis, UV absorption spectroscopy, and kinetic measurements are consistent with major pathways involving pre-equilibrium formation of halo-λ^3-iodane and iodate intermediates, leading to the in-plane vinylic S_N2 substitution to (*Z*)-**2** and the intramolecular β-elimination to **3**. The minor retained product (*E*)-**2** is concluded to be formed through the vinylenebenzenium ion intermediate in 2,2,2-trifluoroethanol through the ligand coupling within the λ^3-iodane intermediate in acetonitrile. 1-Bromo-1-phenylethene is considered to be derived from **3** by reaction with HBr formed during the reaction.

We have recently shown that β-alkyl-substituted vinyliodonium salts undergo a bimolecular in-plane vinylic (S_N2) substitution with halide nucleophiles to give the inverted product (Eq. 1).[1—3] This is recognized as the first and definitive example of this type of reaction, vinylic S_N2 reaction.[4,5] On the other hand, the β-phenyl-substituted derivative, styryliodonium salt, was found to form vinylenebenzenium ion as an intermediate in protic solvents (SOH) to lead to a solvolysis product with retention of stereochemistry (Eq. 2).[6] The reactions of phenyl(styryl)iodonium salt with halide ions were found to show interesting mixed behavior of these contrasting observations. The results will be given in the present paper.



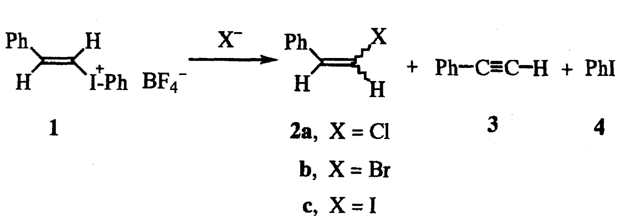
(1)



(2)

Results

Product Analysis. Reactions of (*E*)-phenyl(styryl)iodonium tetrafluoroborate (**1**) with tetrabutylammonium chloride, bromide, and iodide were carried out in various solvents, usually at 50 °C. Products involve 1-halo-2-phenylethene (**2**) and phenylacetylene (**3**) as well as accompanying iodobenzene (**4**), as shown by Eq. 3 and summarized in Table 1. A large part of the reaction is elimination, unlike that of 1-alkenylidonium salts where it is usually S_N2 substitution. The relative ratio of **2**/**3**, i.e., substitution/elimination (*s*/*e*), depends very much on the identity of halides, the halide concentration, and the solvent employed. The fraction of substitution increases in the order: $Cl^- < Br^- < I^-$, and with increasing concentration of halide [X^-]. The fraction of substitution tends to increase at lower temperature (Nos. 3 and 10).



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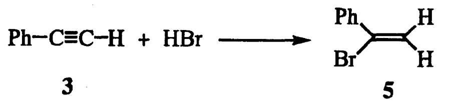
It is noticeable that the fraction of substitution is smaller in chloroform than in other aprotic polar solvents. In protic solvents, the reactions are much slower than in aprotic solvents. A considerable amount of 1-bromo-1-phenylethene (**5**) is formed during the reaction with bromide in acetic acid and 2,2,2-trifluoroethanol (TFE) (Nos. 20 and 21). This is considered to result from addition of HBr to **3** produced in the primary reaction, and **5** is included in the elimination products for the calculation of the *s*/*e* ratios. Formation of a trace amount of **5** was also noticed generally in other aprotic solvents by examination of the GC and of the GC-MS for selected runs.

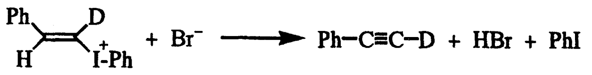
Table 1. Product Yields (%) in the Reaction of **1** with Halide Ions[a)]

No.	Solvent	Halide, X[b)] (concn/mol dm^{-3})	Time / h	**2** (Z/E)[d)]	**3** (s/e)[d)]	**4**
1	MeCN	Cl (0.01)	4	4.7 (96/4)	74 (6/94)	83
2	MeCN	Cl (0.1)	8	14 (99.8/0.2)	71 (16/84)	78
3	MeCN	Cl (0.1)	50[e)]	17 (99.7/0.3)	69 (20/80)	79
4	$CHCl_3$	Cl (0.001)	2.5	Trace (1/0)	91 (0/1)	82
5	$CHCl_3$	Cl (0.1)	5	6.7 (98.5/1.5)	73 (8.4/91.6)	77
6	MeCN	Br (0.002)	4	3.0 (79/21)	84 (3.4/96.6)	82
7	MeCN	Br (0.01)[f)]	3	11 (95.4/4.6)	76 (13/87)	86
8	MeCN	Br (0.05)[f)]	3	38 (98.7/1.3)	52 (42/58)	93
9	MeCN	Br (0.1)	3	48 (99.4/0.6)	43 (53/47)	87
10	MeCN	Br (0.1)	50[e)]	54 (99.6/0.4)	42 (56/44)	88
11	MeCN	Br (0.2)	3	50 (99.7/0.3)	39 (56/44)	86
12	$CHCl_3$	Br (0.001)	3	Trace (1/0)	85 (0/1)	78
13	$CHCl_3$	Br (0.05)	3	17 (96.8/3.2)	76 (18/82)	85
14	$CHCl_3$	Br (0.1)	3	26 (98.3/1.7)	72 (27/73)	91
15	Dioxane	Br (0.1)	1.5	45 (99.6/0.4)	40 (53/47)	82
16	THF	Br (0.1)	0.25	57 (99.8/0.2)	39 (59/41)	90
17	DMSO	Br (0.1)	5	19 (98.6/1.4)	17 (53/47)	29
18	MeOH	Br (0.05)	15	2.3 (91.8/8.2)	27 (8/92)	34
19	MeOH	Br (0.2)	20	6.5 (95.8/4.2)	56 (10/90)	63
20	TFE	Br (0.1)	120	17 (70/30)	12 (50/50)[g)]	41
21	AcOH	Br (0.1)	48[h)]	8 (89/11)	55 (9/91)[f)]	88
22	MeCN	I (0.01)[f)]	3	41 (91.7/8.3)	41 (50/50)	78
23	MeCN	I (0.1)	2	77 (98.8/1.2)	10 (89/11)	81

a) Reactions were carried out at 50 °C without adjusting the ionic strength unless noted otherwise. b) Tetrabutylammonium halide (Bu_4NX). c) The nucleophilic fragment X is the corresponding halogen. Isomeric ratios are given in parentheses. d) A trace amount of **5** was generally detected. The ratio *s*/*e* is that of substitution/elimination. e) At 25 °C. f) The ionic strength was adjusted at 0.10 with Bu_4NClO_4. g) 1-Bromo-1-phenylethene (**5**, 5%) and 1-phenyl-2-(2,2,2-trifluoroethoxy)ethene (3%) were also formed. h) At 70 °C. i) The product **5** (30%) was found.



3 **5** (4)

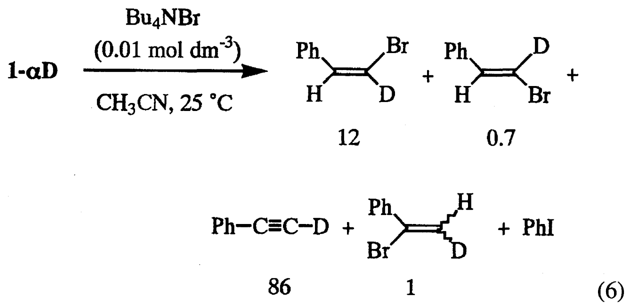


1-αD (5)

The substitution product **2** is predominantly in a *Z* configuration, but a considerable amount of the *E* isomer is formed, especially at low concentrations of halide and in protic solvents.

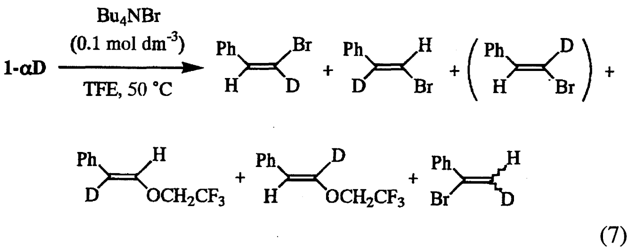
The deuterium content of the elimination product **3** from the reaction of the deuterated iodonium salt, (*E*)-phenyl(2-phenyl[1-^{2}H]vinyl)iodonium tetrafluoroborate (**1-αD**), with bromide ion in acetonitrile was evaluated by mass spectral analyses. The relative heights of the parent peaks $m/z = 102$ and 103 were 100 : 9.33 (calcd for natural isotopic abundances, 9.053) for the authentic protium sample of **3**. The products **3** obtained from **1-αD** at $[Br^-] = 0.10$ and 0.01 mol dm^{-3} showed the peak ratios 102/103 of 2.66/100 and 3.19/100, respectively. These values correspond to the deuterium contents of 97.4 and 96.9%, respectively. That is, more than 98% of the deuterium of the substrate **1-αD** (98.8% D purity) was retained in the elimination product **3**. This implies that the elimination occurs via a *syn* β-elimination, as was observed for the reaction of 1-alkenyliodonium salts with bromide ion.[1—3)] The NMR spectrum of the product mixture obtained from the reaction of **1-αD** in acetonitrile and TFE also suggests β-elimination, as discussed below.

Distribution of the deuterium in other (substitution) products obtained from **1-αD** was examined by the ^{1}H NMR spectrum of the product mixture. The reaction of **1-αD** with bromide in acetonitrile was carried out at $[Bu_4NBr] = 0.01$ mol dm^{-3} and at a lower temperature of 25 °C for 60 h to obtain more substitution products. The GC showed formation of **(*Z*)-2b**, **(*E*)-2b**, **3**, and **5** in an approximate ratio of 12 : 0.7 : 86 : 1. The ^{1}H NMR spectrum of the product mixture showed no peaks at the positions expected for the protons (β-H) on the carbon bearing the bromine of **(*Z*)-2b** and **(*E*)-2b** (6.43 and 6.77 ppm), although the geminal β protons of **5** were detected as singlets at 5.77 and 6.10 ppm in the intensity ratio of about 1 : 0.22. The singlet signals (the lack of coupling) of the **5** obtained indicate that the counterpart geminal hydrogen is deuterium, since the protium authetic sample of **5** shows a small but distinct geminal coupling of 2 Hz. That is, the primary product **3** has retained the deuterium of **1-αD**. In conclusion, the original deuterium of **1-αD** is not scrambled and is retained at the original position in all the products mentioned, as shown in Eq. 6.



(6)

The NMR spectrum of the product mixture obtained from the reaction of **1**-*α***D** with bromide in TFE showed a signal for the *β*-H (to the phenyl group, 6.77 ppm) of (*E*)-**2b** as a slightly separated triplet (coupling with D at the *trans* position). However, the corresponding signal (6.43 ppm) for (**Z**)-**2b**, which should be present in more than a two-fold amount of (*E*)-**2b** from GC, could not be seen. That is, the deuterium of **1**-*α***D** is retained at the original position of (**Z**)-**2b**, while it must be largely distributed at the carbon carrying the phenyl group of (*E*)-**2b** (isotopic scrambling). Unfortunately, the proton signals at this carbon (*α*-H) of **2b** at about 7.1 ppm cannot clearly be seen because of the overlap with aromatic proton signals of the accompanying product **4**. A solvolysis product, (*E*)-1-phenyl-2-(2,2,2-trifluoroethoxy)ethene, is also formed, and the broad signals observed at 5.97 and 6.92 ppm suggest coupling with the counterpart deuterium and complete scrambling of the deuterium between the two olefinic positions. This agrees with the previous observations in solvolysis in the absence of halide.[6,7] The olefinic proton signals at 5.77 and 6.10 ppm for the **5** in the product mixture are both singlets and the intensity ratio is about 1 : 0.3. The deuterium of **5** and so that of **3** formed in this reaction must be retained at the original position.



(7)

Kinetic Measurements. The tetrafluoroborate **1** has an absorption maximum at 267 nm. Stronger absorption develops immediately when it is dissolved in a halide solution as shown in Fig. 1, but it disappears slowly with time. Such an absorbance increase was not seen in a solution containing tetrabutylammonium perchlorate. The initial absorbances were determined by extrapolating the observed absorbances to the time of mixing for chloride and bromide solutions in acetonitrile (Fig. 2). The absorbance increases with increasing halide concentrations [X$^-$] but seems to saturate at the higher [X$^-$].

The disappearance of absorption follows nicely the pseudo-first-order rate law for at least 4 half-lives. The observed pseudo-first-order rate constants k_{obsd} are plotted against [X$^-$] in Figs. 3 and 4 for the reactions with chloride and bromide ions, respectively. The results are contrasting: The rate for the chloride reaction tends to decrease, while that for the bromide reaction increases with increasing concentration of the halide, but both with strong curvature. The rate for the reaction of **1** with iodide seems to show a similar tendency to that for the bromide reaction, as indicated in the data given in Table 2.

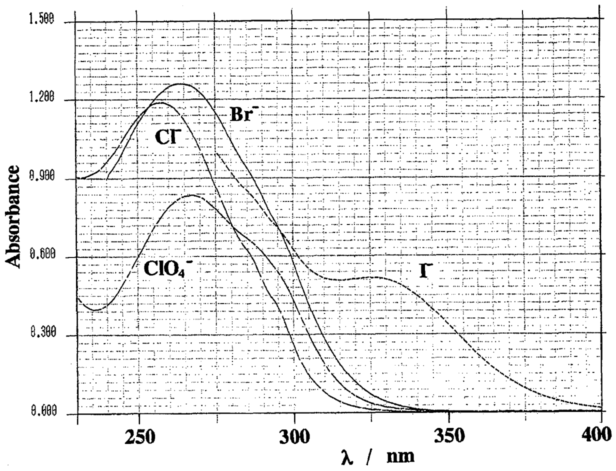


Fig. 1. The initial absorption spectra of **1** in acetonitrile in the absence (–·–) and in the presence of 0.01 mol dm^{-3} of Bu_4NCl (–––), Bu_4NBr (——), and Bu_4NI (····) at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4 and 25 °C. [**1**]=4.4×10^{-5} mol dm^{-3}.

The rate constants k_{obsd} for the deuterated substrate **1**-*α***D** are compared with the corresponding values for the protium **1** in Table 2. The deuterium compound **1**-*α***D** is slightly less reactive by about 20% than **1**.

Effects of pressure were examined on the rate for reaction of **1** with Bu_4NBr in chloroform at [Br$^-$] = 0.05 mol dm^{-3} and 45 °C for the sake of convenience of measurements. The rate decreases with pressure (Fig. 5) and affords the activation volume $\Delta V^{\ddagger}$=7.0 cm^3 mol^{-1}.[8]

Discussion

The reactions of **1** with halide ions to give the inverted substitution product (**Z**)-**2** and the elimination product **3** can be explained by a reaction mechanism similar to that proposed for 1-alkenyliodonium salts (Scheme 1).[2,3] That is, the substrate **1** and halide ions rapidly attain to equilibrium of formation of the 1 : 1 and 1 : 2 complexes $\mathbf{I_1}$ and $\mathbf{I_2}$. Then the substitution occurs via an in-plane vinylic S_N2 reaction of vinyliodonium ion **1** and the intermediate halo-λ^3-iodane $\mathbf{I_1}$, while the elimination takes place intramolecularly within the intermediate $\mathbf{I_1}'$ as a *syn β*-elimination. The problem remain, however, of how the minor retained substitution product (*E*)-**2** is formed. This point will be discussed below, and we will explain first the major kinetic and other observations in terms of Scheme 1.

The UV absorption behavior of **1** in halide solutions is consistent with rapid equilibrium formation of the halo-λ^3-iodane $\mathbf{I_1}$ (10-I-3 hypervalent species) and the iodate (12-I-4) $\mathbf{I_2}$.[2,3] The observed initial absorbance increase ΔA due

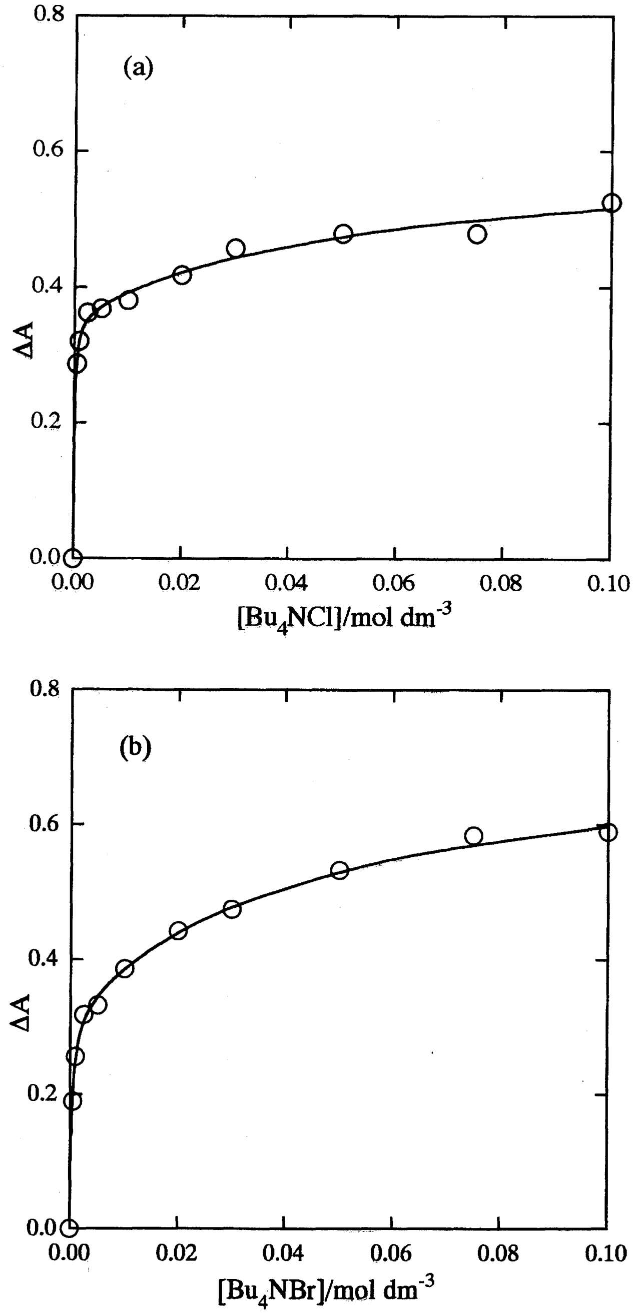


Fig. 2. Initial absorbance of **1** in acetonitrile solutions containing (a) Bu_4NCl at 260 nm and (b) Bu_4NBr at 270 nm measured at 50 °C, the ionic strength of 0.10 (Bu_4NClO_4), and $[\mathbf{1}] = 4.4\times10^{-5}$ mol dm^{-3}. Solid curves are calculated with the parameters given in Table 3.

to halide ions can be described by Eq. 8 for the equilibrium $\mathbf{1}\rightleftharpoons\mathbf{I}_1$ ($\mathbf{I}_1'$)$\rightleftharpoons\mathbf{I}_2$, where the two possible structural isomers, $\mathbf{I}_1$ and $\mathbf{I}_1'$, are not differentiated, since the interconversion between the two via pseudorotation must be rapid.[2,3]

$$\Delta A=(\Delta A_1K_1[X^-]+\Delta A_2K_1K_2[X^-]^2)/(1+K_1[X^-]+K_1K_2[X^-]^2),\quad(8)$$

where K_1 and K_2 are the equilibrium constants for the formation of the hypervalent intermediates, $\mathbf{I}_1$ ($\mathbf{I}_1'$) and $\mathbf{I}_2$, and ΔA_1 and ΔA_2 are the maximum absorbance increases due to the formation of $\mathbf{I}_1$ ($\mathbf{I}_1'$) and $\mathbf{I}_2$, respectively. The parameters were obtained by curve fittings with the nonlinear least-squares treatments of the data and are given in Table 3. The solid curves in Fig. 2 are calculated according to Eq. 8 with these parameters.

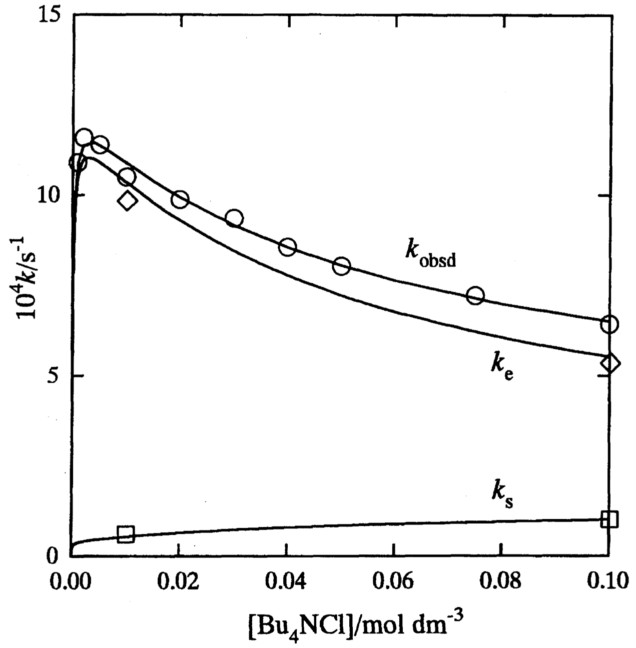


Fig. 3. The rate constants, k_{obsd} (○), k_s (□), and k_e (◇) for the reaction of **1** with chloride in acetonitrile at 50 °C and the ionic strength of 0.10 (Bu_4NClO_4). Solid curves are calculated with the parameters given in Table 3.

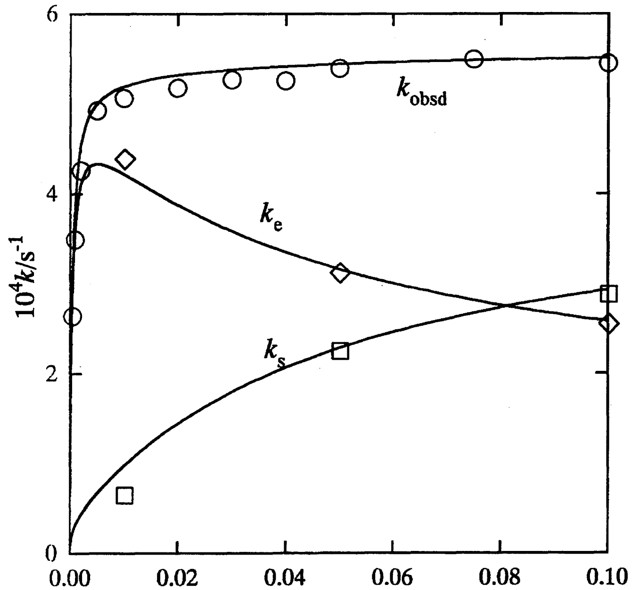


Fig. 4. The rate constants, k_{obsd} (○), k_s (□), and k_e (◇) for the reaction of **1** with bromide in acetonitrile at 50 °C and the ionic strength of 0.10 (Bu_4NClO_4). Solid curves are calculated with the parameters given in Table 3.

The observed rate constants are also expressed by Eq. 9 according to Scheme 1 with the rate constants defined.[2,3]

Table 2. Observed Rate Constants for the Reaction of **1** and **1-αD** under Some Selected Conditions[a)]

Halide, X	$[X^-]$ mol dm^{-3}	$10^4\ k_{obsd}/s^{-1}$ **1**	**1-αD**	k_H/k_D
Cl	0.01	10.5	8.56	1.23
Cl	0.10	6.42	5.12	1.25
Br	0.01	5.06	4.24	1.19
Br	0.10	5.45	4.53	1.20
I	0.01	7.52		
I	0.10	12.2		

a) Measured at 50 °C and the ionic strength of 0.10.

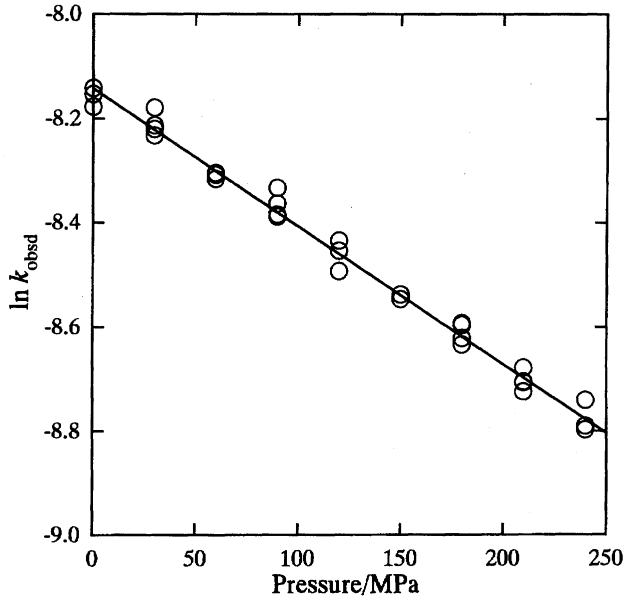


Fig. 5. Effects of pressure on the rate of reaction of **1** with Bu_4NBr (0.05 mol dm^{-3}) in chloroform at 45 °C.

$$k_{obsd} = \{(k_1 + k_2'K_1)[X^-] + (k_2K_1 + k_3'K_1K_2)[X^-]^2\} /(1 + K_1[X^-] + K_1K_2[X^-]^2). \qquad (9)$$

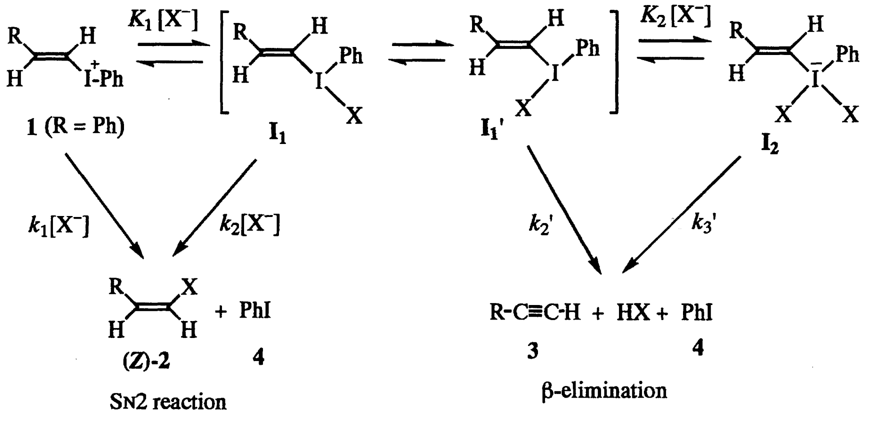
The solid curves in Figs. 3 and 4 are calculated with the parameters summarized in Table 3 according to Eq. 9 by using the equilibrium constants obtained from the initial absorbances (Fig. 2). The k_{obsd} are separated into the rate constants for the substitution (k_s) and the elimination (k_e) by the product ratios *s*/*e* (Table 1), and the values are shown in Figs. 3 and 4. The calculated curves for these separated rate constants are obtained from the corresponding terms of Eq. 9 by using the approximate parameters given in Table 3. Although the minor products are not considered here, the overall reactions are satisfactorily accounted for by Scheme 1. The decreasing tendency of apparent constant k_e is characteristic of an intramolecular reaction of the intermediate $\mathbf{I_1}$ ($\mathbf{I_1}'$). The concentration of $\mathbf{I_1}$ ($\mathbf{I_1}'$) decreases at higher $[X^-]$ due to the formation of $\mathbf{I_2}$. The apparent difference in the k_{obsd} curves between the chloride and bromide reactions is ascribed to different contributions from the two reaction pathways (k_s and k_e).

Table 3. Parameters Used for Simulation of the Absorbance and Kinetic Curves[a)]

Halide	Cl	Br
λ/nm	260	270
$10^{-3}K_1$/mol^{-1} dm^3	7.7 (2.5)	2.84 (0.50)
A_1	1.142 (0.016)	1.193 (0.016)
K_2/mol^{-1} dm^3	18 (10)	20 (6)
A_2	1.387 (0.052)	1.597 (0.038)
$k_1+k_2'K_1$/mol^{-1} dm^3 s^{-1}	9.6	1.5
$k_2K_1+k_3'K_1K_2$/mol^{-2} dm^6 s^{-1}	45	32
k_1/mol^{-1} dm^3 s^{-1}	0.3	0.1
10^3k_2/mol^{-1} dm^3 s^{-1}	2.4	8.5
$10^3k_2'$/s^{-1}	1.2	4.9
$10^4k_3'$/s^{-1}	2.0	1.4

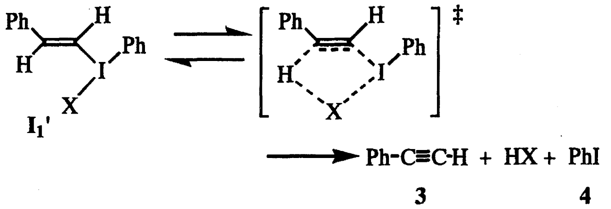
a) The initial concentration of **1** was 4.4×10^{-5} mol dm^{-3}. Values in parentheses are standard deviations for the fittings of the absorbance curves.

The elimination product **3** obtained from **1-αD** retains most of the original deuterium and is consistent with the intramolecular β-elimination within the λ^3-iodane $\mathbf{I_1}'$ (Eq. 10).[1—3)] The kinetic deuterium isotope effects, $k_H/k_D \approx 1.2$ (Table 2), observed for the reaction with halides where more than 80% of the reaction is elimination are compatible with the β-elimination mechanism. If it occurred via the alternative α-elimination and rearrangement, the primary isotope effects of $k_H/k_D \approx 3$ would have been observed.[1,2)] The observed activation volume of a small positive value



Scheme 1.

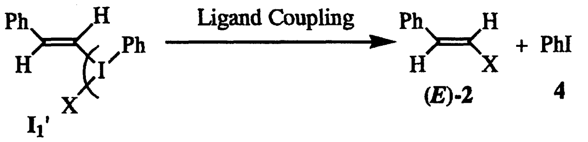
($\Delta V^{\ddagger} = 7.0\,\mathrm{cm^3\,mol^{-1}}$) is also consistent with the intramolecular elimination mechanism involving a conversion from the initial λ^3-iodane $\mathbf{I_1}'$ to a slightly expanded transition state without much solvent reorganization.



(10)

1-Bromo-1-phenylethene (**5**) must be formed from the elimination products, **3** and HBr. The relative intensities of the NMR signals for the geminal protons **5** obtained from **1-αD** suggest that the electrophilic addition of HBr to **3** occurred via 70—80% stereoselective *syn* addition, in agreement with the earlier observations.[9,10]

There are two possible pathways for the formation of the minor stereochemically retained substitution product (***E***)**-2**. One is a reaction through intermediate formation of vinylenebenzenium ion (Eq. 2), and the other is a ligand coupling mechanism within the intermediate $\mathbf{I_1}'$ or $\mathbf{I_2}$ (Eq. 11). The former mechanism was observed for the solvolysis of **1** in acetic acid and TFE.[6] If the vinylenebenzenium ion is captured by a halide ion, the resulting product will be (*E*)-2. In this case, the deuterium of the substrate **1-αD** should be completely scrambled in the product (*E*)-2, as was the case for the solvolysis products.[6] This is exactly the case found by the NMR analysis of the product mixture from the reaction of **1-αD** with bromide *in TFE*, but *this is not found in acetonitrile*.



(11)

If the vinylenebenzenium ion were also formed in acetonitrile and trapped by the halide, the scrambling of the deuterium should have been observed in the (*E*)-2 obtained under these reaction conditions. However, the ^{1}H NMR of the product mixture from the reaction of **1-αD** with bromide in acetonitrile did not show any sign of the scrambling. This contrasting result cannot be explained by the formation of vinylenebenzenium ion. Since the ionization to a primary vinyl cation is unlikely,[11] the alternative ligand coupling mechanism leading to the retained product is the most probable pathway in the aprotic solvent. The ligand coupling mechanism for the substitution with retention of configuration within halo-λ^3-iodane like $\mathbf{I_1}'$ has been observed with 2-halo-1-decenyliodonium salt[12] and with 1-decenyliodonium salt in TFE[2] when the other reaction pathways are retarded. The ligand coupling pathway may have shown up in the present reactions because the $\mathrm{S_N}2$ reaction of **1** is quite slow, **1** being about 10^2 times less reactive than 1-decenyl(phenyl)iodonium salt.[12b]

In conclusion, the reactions of the styryliodonium salt with halide ions occur mainly as the in-plane $\mathrm{S_N}2$ substitution and the intramolecular β-elimination of halo-λ^3-iodane intermediate by the mechanism shown in Scheme 1. The minor pathway leading to substitution with retention takes place through the vinylenebenzenium ion intermediate in polar solvents like TFE or alternatively through the ligand coupling within the halo-λ^3-iodane intermediate in aprotic solvents like acetonitrile.

Experimental

^{1}H NMR spectra were recorded on a Varian INOVA 500 spectrometer and chemical shifts are given in ppm downfield from internal TMS. IR and UV spectra were obtained by JASCO IRA-1 and Shimadzu UV-2200 spectrophotometers, respectively. 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. Melting points were measured on a Yanaco micro-melting-point apparatus and are not corrected.

Acetonitrile was distilled from calcium hydride. Chloroform of analytical grade stabilized with 2-methyl-2-butene was obtained from Tokyo Chemical Industry (TCI, Tokyo) and used without further purification. Tetrabutylammonium chloride (TCI), bromide (Wako, Osaka), iodide (Wako), and perchlorate (Fluka) were used as received. Iodobenzene (**4**), phenylacetylene (**3**), and 1-bromo-2-phenylethene (**2b**) and 1-bromo-1-phenylethene (**5**) for the authetic samples were purchased from Wako or TCI.

Curve fittings were carried out by a nonlinear least squares method (Marquardt–Levenberg Algorithm) using SigmaPlot (Jandel Scientific, San Rafael, CA) on a personal computer Macintosh 7600/200.

(*E*)-Phenyl(styryl)iodonium Tetrafluoroborate (1). The $\mathrm{BF_3}$-catalyzed silicon-iodonium exchange reaction between (*E*)-trimethylsilyl(styryl)silane and iodosylbenzene was carried out in the same way as described previously.[13]

(*E*)-Phenyl(2-phenyl[1-^{2}H]vinyl)iodonium Tetrafluoroborate (1-αD). The α-deuterated substrate **1-αD** (the isotopic purity = 98.8%) was prepared by Lewis acid-catalyzed boron-iodine(III) exchange reaction of dihydroxy[(*E*)-2-phenyl[1-^{2}H]vinyl]borane with (diacetoxyiodo)benzene.[14]

Product Analysis. A typical reaction was carried out with about 5 mg of **1**. A weighed sample of **1** was dissolved in 3 mL (or more to contain excess halide at low halide concentrations) of the reaction solution at 50 °C. After the reaction time, water (usually 15 mL) and 1 mL of the pentane solution containing 2.5×10^{-6} mol of 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 when required. The relative molar intensities of the GC peaks were determined with the authentic samples in comparison with the internal standard and were assumed to be the same for the isomers and halostyrenes. The deuterium content of **3** formed from **1-αD** was evaluated from the relative heights of parent peaks at *m*/*z* 102 and 103.

Reaction of 1-αD with Bromide Ion in Acetonitrile. A sample of **1-αD** (8 mg) was added to 3 mL of acetonitrile containing 0.01 $\mathrm{mol\,dm^{-3}}$ of $\mathrm{Bu_4NBr}$ and kept at 25 °C for 60 h. Products were extracted with pentane, and the GC of the extract showed formation of (**Z**)-**2b**, (**E**)-**2b**, **3**, **4**, and **5** in an approximate ratio of 12 : 0.7 : 86 : 100 :1. After evaporation of the volatile fraction, the nonvolatile residues were dissolved in $CDCl_3$ for NMR analysis. The GC of the NMR sample indicated that the mixture consisted of (**Z**)-**2b**, (**E**)-**2b**, **4**, and **5** in a molar ratio of about 50 : 3 : 4 : 100. The most of the **3** formed was lost during evaporation. The NMR spectrum showed two small singlets at 5.77 and 6.10 ppm in an intensity ratio of 1 : 0.22, in addition to strong signals in the 7—8 ppm region.

Reaction of 1-αD with Bromide Ion in TFE. A sample of **1-αD** (6 mg) was dissolved in 3 mL of TFE containing 0.1 mol dm^{-3} of Bu_4NBr and kept at 50 °C for 5d. Products were extracted with pentane and nonvolatile residues were dissolved in $CDCl_3$. The GC showed formation of (**Z**)-**2b**, (**E**)-**2b**, **4**, **5**, and (*E*)-1-phenyl-2-(2,2,2-trifluoroethoxy)ethene in an integral peak ratio of about 3.5 : 1.5 : 5 : 1 : 1. The NMR spectrum showed five olefinic proton signals, in addition to aliphatic (1—2 ppm) and aromatic signals (7—8 ppm), at 5.77 (s), 5.97 (bs), 6.10 (s), 6.77 (t), and 6.92 (bs) ppm in relative integral intensities of 3 : 4 : 1 : 6 : 4.

Initial Absorbance. Initial absorbances of the reaction mixture were determined at 50 °C, as described previously for 1-alkenyliodonium salts.[2,3]

Kinetic Measurements. Reaction rates were determined by monitoring the decrease in UV absorbance at 50 °C, as described previously.[2,3] High-pressure measurements were carried out in the same way as before.[2]

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References

1) M. Ochiai, K. Oshima, and Y. Masaki, *J. Am. Chem. Soc.*, **113**, 7059 (1991).

2) T. Okuyama, T. Takino, K. Sato, K. Oshima, S. Imamura, H. Yamataka, T. Asano, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **71**, 243 (1998).

3) T. Okuyama, T. Takino, K. Sato, and M. Ochiai, *J. Am. Chem. Soc.*, **120**, 2275 (1998).

4) Z. Rappoport, *Adv. Phys. Org. Chem.*, **7**, 1 (1969); *Recl. Trav. Chim. Pays-Bas*, **104**, 309 (1985); *Acc. Chem. Res.*, **25**, 474 (1992).

5) B. A. Shainyan and Z. Rappoport, *J. Org. Chem.*, **58**, 3421 (1993); M. Beit-Yannai, Z. Rappoport, B. A. Shainyan, and Y. S. Danilevich, *J. Org. Chem.*, **62**, 8049 (1997).

6) T. Okuyama and M. Ochiai, *J. Am. Chem. Soc.*, **119**, 4785 (1997).

7) T. Okuyama et al., to be published.

8) a) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967); b) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978); c) R. van Eldik, T. Asano, and W. J. le Noble, *Chem. Rev.*, **89**, 549 (1989).

9) a) No sign of formation of primary 1-alkenyl or 2-phenylvinyl cation was detected in TFE or acetic acid.[2,6] The β-phenyl substitution is demonstrated theoretically to destabilize vinyl cation.[9b] b) S. Kobayashi, T. Hori, T. Hasako, K. Koga, and H. Yamataka, *J. Org. Chem.*, **61**, 5274 (1996).

10) R. C. Fahey and D.-J. Lee, *J. Am. Chem. Soc.*, **88**, 5555 (1966); F. Marcuzzi and G. Melloni, *J. Am. Chem. Soc.*, **98**, 3295 (1976).

11) a) Chemical shifts of the geminal protons are assigned accordings to Ref. 11b. b) J. R. Blackborow, *J. Chem. Soc. Perkin Trans. 2*, **1973**, 1989; Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **96**, 6428 (1974).

12) a) M. Ochiai, K. Oshima, and Y. Masaki, *Chem. Lett.*, **1994**, 871; b) T. Okuyama, T. Takino, K. Sato, and M. Ochiai, *Chem. Lett.*, **1997**, 955.

13) M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, and E. Fujita, *Tetrahedron*, **44**, 4095 (1988).

14) M. Ochiai, M. Toyonari, T. Nagaoka, D.-W. Chen, and M. Kida, *Tetrahedron Lett.*, **38**, 6709 (1997).