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Vinylic S_N2 Reaction of 1-Decenyliodonium Salt with Halide Ions

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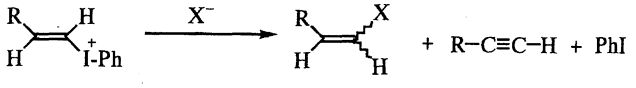
Reactions of (*E*)-1-decenyl(phenyl)iodonium salt with halide ions are examined under various conditions. The products are those of substitution and elimination, usually (*Z*)-1-halo-1-decene and 1-decyne, as well as iodobenzene, except for the reaction with fluoride which leads exclusively to elimination. The labeling experiments show that the elimination induced by fluoride occurs via an α mode, while that caused by the other halides is a *syn* β elimination. Kinetic results show that the substitution and β elimination occur mainly from the halo-λ^3-iodane intermediate; the substitution occurs as a bimolecular reaction with the external halide ion while the elimination is a unimolecular (intramolecular) reaction. The intermediacy of the hypervalent λ^3-iodane as well as of the iodate are also confirmed by UV spectroscopy. The secondary kinetic isotope effects, leaving group substituent effects, and pressure effects on the rate are compatible with the in-plane vinylic S_N2 mechanism for the substitution with inversion. Some retained substitution product, (*E*)-1-halo-1-decene, is formed in polar protic solvents like trifluoroacetic acid, formic acid, and 1,1,1,3,3,3-hexafluoro-2-propanol. The reaction is very slow in these solvents and no sign of formation of ionic intermediates is found. This slow substitution with retention is considered to occur via ligand coupling within the halo-λ^3-iodane intermediate.

Nucleophilic substitution at vinylic carbon may proceed via one of several possible mechanistic pathways, depending on the structure of the substrate.[1] The in-plane S_N2 reaction with inversion of configuration has been considered very unlikely to occur at the vinylic carbon,[2] and this pathway is generally rejected as a possible mechanism of vinylic substitution.[2b] The inversion has in fact rarely been observed for the nucleophilic vinylic substitution. Predominant, but not exclusive, inversion found in the solvolysis of some alkenyl triflates is accommodated with an ion-pair mechanism, where the initially formed ion pair is attacked by the nucleophile on the opposite side of the leaving group before dissociation.[3]

It has recently been found that 1-alkenyliodonium salts undergo nucleophilic substitution by halide ions with exclusive inversion of configuration.[4] This reaction was concluded to be the first example of vinylic S_N2 reaction by excluding a possibility of formation of ionic intermediates.[5] It was also reported that the reaction of 1,2-dibromo-1,2-difluoroethene with thiolate ion resulted in substitution with inversion,[6] while an intramolecular methide transfer within di-*t*-butylthiirenium ion was classified as an in-plane nucleophilic substitution at the vinylic carbon.[7] The theoretical calculations subsequently showed the feasibility of the in-plane S_N2 pathway.[8]

We have now examined in detail the mechanistic aspects of the reaction of (*E*)-1-decenyl(phenyl)iodonium (**1**) salt with halide ions to confirm the conclusion that this reaction occurs through the S_N2 pathway. Complete inversion of configuration has been observed for this reaction in a wide range of solvents, though limited amounts of the retained products were detected in some polar protic solvents. Kinetic analysis of this reaction showed the bimolecular nature of the rate-determining step. This paper summarizes results of comprehensive investigations on this characteristic reaction.



1 (R = *n*-C_8H_{17}) **2 a**, X = Cl; **b**, X = Br; **c**, X = I; **3**; **4** (1)

Results

Reaction Products. Reactions of **1** with halide ions were carried out in various solvents at room temperature to 50 °C and the products were determined by gas chromatography. The reactions of **1** with chloride, bromide, and iodide ions

resulted in formation of the substitution products, 1-halo-1-decene (**2**) and iodobenzene (**4**), as well as an accompanying elimination product, 1-decyne (**3**) (Eq. 1). Some representative results are summarized in Tables 1 and 2. In most of the reactions, the tetrafluoroborate salt of **1** (**1**·BF_4) was used as the substrate. The halide salts of **1** (**1**·**X**) can also be isolated as crystals, and they give the substitution and elimination products on standing in solution in a similar manner to the

Table 1. Selected Data of Product Distributions in the Reaction of **1** with Halides in Aprotic Solvents[a)]

Run	Halide (concn/mol dm^{-3})	Solvent	Ionic strength[b)]	Time h	Product yield/% (*Z*)-**2**[c)]	**3**	**4**	r[d)]
1	Bu_4NCl (0.001)	$CHCl_3$		8	25	68	86	27/73
2	Bu_4NCl (0.001)	$CHCl_3$	0.1	8	27	67	87	29/71
3	Bu_4NCl (0.1)	$CHCl_3$		10	85	15	85	85/15
4	Bu_4NCl (0.1)[e)]	$CHCl_3$	0.6	10	69	18	73	79/21
5	Bu_4NCl (0.08)[e)]	CH_2Cl_2		10	75	25	97	75/25
6	Bu_4NCl (0.002)	CH_3CN		5.5	18	45	51	29/71
7	Bu_4NCl (0.002)	CH_3CN	0.1	6	23	47	55	33/67
8	Bu_4NCl (0.1)	CH_3CN		1.5	54	6.2	59	90/10
9	Bu_4NCl (0.1)	THF		0.5	95	4.9	79	95/5
10	Bu_4NCl (0.15)[e)]	DMF		10	84	16	Nd[f)]	84/16
11	Bu_4NCl (0.14)[e)]	Hexane		10	91	3	80	97/3
12	Bu_4NBr (0.001)	$CHCl_3$		5	43	50	92	46/54
13	Bu_4NBr (0.001)	$CHCl_3$	0.1	6	46	42	88	52/48
14	Bu_4NBr (0.1)	$CHCl_3$		1.5	74	6.7	85	92/8
15	Bu_4NBr (0.1)	CH_3CN		1	55	2.4	65	96/4
16	Bu_4NI (0.1)	$CHCl_3$		1	91	9	Nd[f)]	91/9
17	Bu_4NI (0.1)	CH_3CN		0.5	79	0.3	70	99.6/0.4
18	Bu_4NF (0.026)[e)]	CH_2Cl_2		10	0	94	100	0/100
19	Bu_4NF (0.14)[e)]	CH_3CN		10	0	47	100	0/100

a) The substrate concentration [**1**] was lower than one fifth of the halide concentration. Reactions were carried out at 25 °C unless noted otherwise. b) The ionic strength was adjusted with added Bu_4NClO_4 if specified. c) Haloalkene **2a**, **2b**, or **2c** depending on the halide used. d) Product ratio r=[**2**]/[**3**]. e) At room temperature. f) Not determined.

Table 2. Product Distributions in the Reaction of **1** with Halides in Various Solvents[a)]

Run	Solvent (Y_{OTs}[b)])	Halide	Time h	Product yield/% **2** (*Z*/*E*)[c)]	**3**	**4**	r[d)]
21	$CHCl_3$	Bu_4NCl	0.2	43 (100/0)	27	70	61/39
22	CH_3CN	Bu_4NCl	0.2	54 (100/0)	17	67	76/24
23	CH_3OH (−0.92)	Bu_4NCl	1	60 (100/0)	15	52	80/20[e)]
24	CH_3OH (−0.92)	Bu_4NCl	20[f)]	27 (100/0)	5.6	24	83/17[g)]
25	TFE (1.80)	Bu_4NCl	25	80 (100/0)	4.7	89	94/6[h)]
26	97HFIP[i)] (3.61)	Bu_4NCl	50	48 (98.4/1.6)	4.0	61	92/8
27	AcOH (−0.61)	Bu_4NCl	6	66 (100/0)	9.8	86	87/13
28	HCO_2H[j)] (3.04)	Bu_4NCl	50	28 (96.9/3.1)[j)]	1.0	65	98/2[j)]
29	TFA[k)] (4.57)	Bu_4NCl	50	51 (85/15)[k)]	0	62	1/0
30	TFA[l)] (4.57)	Bu_4NCl[l)]	50	57 (15/85)[l)]	0	61	1/0
31	CH_3OH (−0.92)	Bu_4NBr	1	51 (100/0)	10	70	84/16
32	TFE (1.80)	Bu_4NBr	20	81 (100/0)	2.7	62	97/3
33	AcOH (−0.61)	Bu_4NBr	3	50 (100/0)	8	55	86/14
34	HCO_2H (3.04)	NaBr	24	81 (98.4/1.6)	1.3	53	98/2
35	TFA (4.57)	Bu_4NBr	24	87 (98.6/1.4)	0	78	1/0
36	TFA[m)] (4.57)	Bu_4NBr[m)]	25	100 (85/15)	0	96	1/0

a) Reactions were carried out at the halide concentration of 0.05 mol dm^{-3} and 50 °C unless noted otherwise. b) Taken from Ref. 22. c) **2a** or **2b**. d) Product ratio r=[**2**]/[**3**]. e) Substitution products, (*Z*)-**2d** (0.3%) and **5** (1.6%), were also detected. f) At 25 °C. g) Aldehyde **6** was also obtained in 2.8% yield. h) Aldehyde **6** (0.7%) was also detected. i) 97% (w/w) Aqueous 1,1,1,3,3,3-hexafluoro-2-propanol. j) Reproducibility was poor, and the fraction of the *E* isomer of **2** ranged from 2.0—4.8%. Aldehyde **6** (19%) was also obtained. k) Reproducibility was poor, and the fraction of the *E* isomer of **2** ranged from 12—23%. Aldehyde **6** (ca. 1%) and (*E*)-**2c** (0.7%) were also detected. l) [Bu_4NCl]=0.01 mol dm^{-3}. The fraction of the *E* isomer of **2a** ranged 80—95% and (*E*)-**2c** (3.5%) was also detected. m) [Bu_4NBr]=0.01 mol dm^{-3}. (*E*)-**2c** (0.6%) was also detected.

reaction systems of **1**·BF_4 plus Bu_4NX in the same solvent. Some reactions were carried out using the halide salts of **1**.

The substitution product, haloalkene **2**, obtained in aprotic solvents including chloroform, dichloromethane, acetonitrile, tetrahydrofuran (THF), dioxane, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexane is always exclusively the *Z* isomer, the product of inversion of configuration (Table 1). The ratio of substitution to elimination (r) varies with solvents without any clear tendency but largely depends on the concentration of halide. The fraction of substitution increases with increasing concentrations of the halide, as shown in Fig. 1, for the reactions in acetonitrile and chloroform at 25 °C. Chloride tends to lead to more elimination than bromide or iodide (Table 1) in accord with the higher basicity and lower nucleophilicity of chloride ion.

Reactions of **1** with chloride and bromide ions were also examined in protic solvents. The reactions are quite slow, and were carried out at 50 °C, maintaining the halide concentration mostly at 0.05 mol dm^{-3}. Products are mainly the haloalkene **2** as summarized in Table 2. Results in aprotic solvents at 50 °C are included for the sake of comparison (runs 21 and 22). The fraction of elimination is higher at a higher temperature (compare with values at $[Bu_4NX]$=0.05 mol dm^{-3} in Fig. 1). This tendency is also the case in methanol solution (runs 23 and 24). The fraction of elimination seems to decrease in polar protic solvents.

The stereochemistry of the haloalkene **2** is noteworthy: The haloalkene **2** obtained is exclusively in a *Z* configuration in most of the solvents employed, but in some polar acidic solvents a small amount of the *E* isomer was involved. In the chloride reaction, (*E*)-**2a** could not be detected in methanol or acetic acid, but a detectable amount of (*E*)-**2a** was

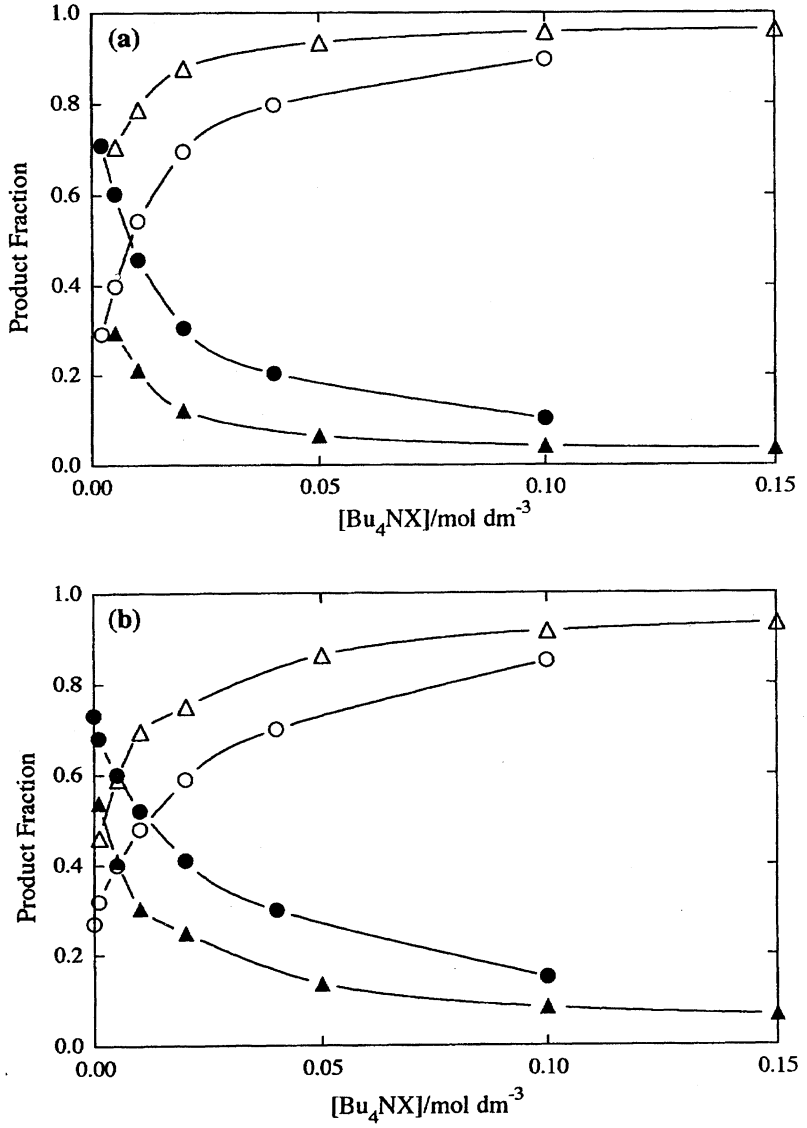
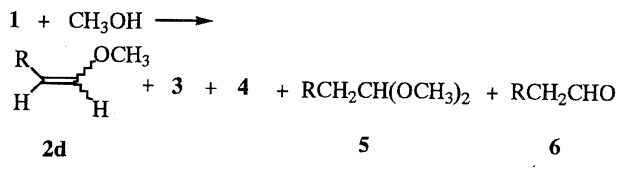


Fig. 1. Product distribution in the reaction of **1** with halide ions (a) in acetonitrile and (b) in chloroform solution at 25 °C. Fractions of (*Z*)-**2a** (○) and **3** (●) in the reaction with chloride and those of (*Z*)-**2b** (△) and **3** (▲) in the reaction with bromide ion are shown. The chloride salt of **1** was used for the reaction with Bu_4NCl in chloroform but the tetrafluoroborate salt was used under other conditions.

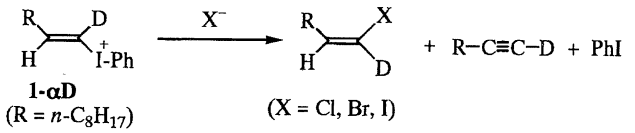
obtained in 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) containing 3 wt% of water. More *E* isomer was formed in formic and trifluoroacetic acids (TFA), although the results are not very reproducible for unknown reasons. At $[Bu_4NCl]=0.05$ mol dm^{-3} in TFA, 12—23% of **2a** was in an *E* configuration, i.e., the product of retention of configuration. Furthermore, up to 90% of the retained product, (*E*)-**2a**, was obtained at a low concentration of chloride, $[Bu_4NCl]=0.01$ mol dm^{-3} in TFA (run 30). It should also be pointed out that a small amount of the by-product, (*E*)-1-iodo-1-decene ((*E*)-**2c**), was obtained only under these conditions. The reaction with bromide ion was reproducible and a smaller but detectable amount of (*E*)-**2b** was formed in these acids at $[Bu_4NBr]=0.05$ mol dm^{-3}. At the low concentration of bromide (0.01 mol dm^{-3}) in TFA, the fraction of the retained product (*E*)-**2b** increased to 15% and (*E*)-**2c** was also detected (run 36).

Some solvolysis products were also found during the reaction in methanol (Eq. 2). The details of the solvolysis reactions of **1** will be presented elsewhere.



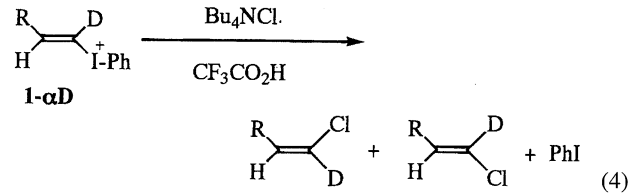
(2)

Labeling Experiments. Reactions were carried out with the labeled substrates, α- and β-deuterated **1** (**1-αD** and **1-βD**). The ratios of substitution/elimination (*r*) in the reactions with halides are summarized in Table 3. The fraction of elimination product is largely decreased by the β deuteration, while the results with **1-αD** are essentially the same as those with the protium substrate **1**. The results are consistent with the implication that the elimination occurs via a *syn* β mode. This was confirmed by the deuterium distribution in the products from the labeled substrates (Eq. 3). The 1-decyne product from **1-αD** was completely deuterated, while that from **1-βD** was the protium one. The deuterium in the haloalkene products remained at the original position.



(3)

The isotopic distributions in substitution products were also examined for the reaction of **1-αD** with chloride in TFA at $[Cl^-]=0.05$ and 0.01 mol dm^{-3} where the *E* isomer is formed. The deuterium was retained at the original position both in (*Z*)-**2a** and (*E*)-**2a** (Eq. 4). This was confirmed by examination of ^{1}H NMR spectra of the products. The olefinic proton signals of the protium products appear at $\delta=6.01$ (dt, $J=7.0$, 1.8 Hz, 1-H of (*Z*)-**2a**) 5.75 (q, $J=7.0$ Hz, 2-H of (*Z*)-**2a**), 5.93 (d, $J=13.0$ Hz, 1-H of (*E*)-**2a**), and 5.89 (dt, $J=13.0$, 6.5 Hz, 2-H of (*E*)-**2a**). However, the products from **1-αD** (97 atom %D purity) show the essential disappearance of the signals for protons at the 1 positions (1-H) both of (*Z*)- and (*E*)-**2a** as well as a change in coupling patterns of 2-H. The 2-H of (*Z*)-**2a** becomes a triplet of broad peaks while that of (*E*)-**2a** becomes a triplet of triplet ($J=7$ and 2 Hz) as shown in Fig. 2. This is due to the very weak coupling with deuterium at the 1 position. Small signals of the remaining 1-H maintain the original coupling pattern, indicating that the 2 position is not deuterated. The intensities of these signals are 3.0 and 3.5% of those of 2-H for (*Z*)-**2a** obtained at $[Bu_4NCl]=0.05$ mol dm^{-3} and (*E*)-**2a** obtained at $[Bu_4NCl]=0.01$ mol dm^{-3}, respectively.



(4)

Table 3. Product Ratios *r* in the Reactions of Deuterated **1** with Halide Ions[a)]

Halide (concn/mol dm^{-3})	Solvent	**1**	**1-βD**	**1-αD**
Cl^- (0)[b)]	$CHCl_3$	27/73	50/50	
Cl^- (0.02)[b)]	$CHCl_3$	59/41		59.2/40.8
Cl^- (0.04)[b)]	$CHCl_3$	70/30	87/13	69.2/30.8
Cl^- (0.05)[c)]	TFE	88.1/11.9	96.7/3.3	
Cl^- (0.05)[c)]	97HFIP	92.3/7.7	96.5/3.5	
Br^- (0.05)	$CHCl_3$	86.4/13.6	93.2/6.8	
Br^- (0.01)	CH_3CN	78.7/21.3	89.0/11.0	
Br^- (0.05)	CH_3CN	93.4/6.6	97.4/2.6	
I^- (0.02)	$CHCl_3$	78.0/22.0	90.3/9.7	
I^- (0.04)	$CHCl_3$	85.5/14.5	93.6/6.4	

a) Reactions were carried out in the presence of added tetrabutylammonium halide at 25 °C unless noted otherwise. $r=[\mathbf{2}]/[\mathbf{3}]$. b) The chloride salt of **1** was used as a substrate. c) At 50 °C.

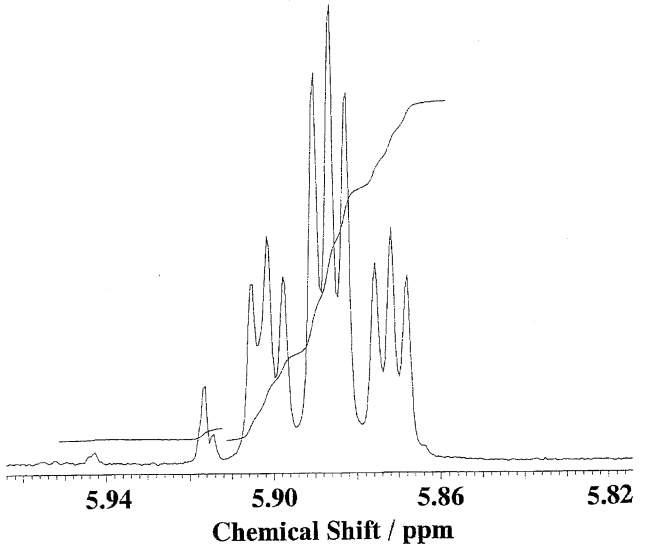
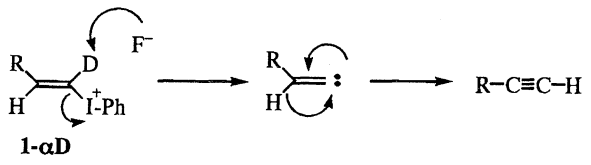


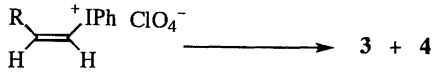
Fig. 2. ^{1}H NMR signals of olefinic protons of (*E*)-**2a** obtained from the reaction of **1-αD** with Bu_4NCl at 0.01 mol dm^{-3} in TFA.

Reaction with Fluoride. Reaction of **1** with tetrabutylammonium fluoride gives exclusively the elimination product **3** (runs 18 and 19) and no substitution products were detected. This reaction was found to be very rapid and to occur instantaneously. Examination of this reaction with the labeled substrates, **1-αD** and **1-βD**, shows that the α hydron (deuteron or proton) is lost and that the β hydron migrates to the terminal position of 1-decyne. That is, in contrast to the β elimination occurring during the reaction with the other halides, the reaction of **1** with tetrabutylammonium fluoride occurs through the α elimination, as illustrated by Eq. 5.[4] The carbene intermediate 1-alkenylidene undergoes exclusively migration of the β-hydron, but not of the alkyl group.[9]



(5)

The *Z* Isomer. Salts of the *Z* isomer of **1** ((*Z*-**1**) can be prepared, but they are quite unstable to give elimination products. This occurs because they undergo very facile *anti* β elimination.[10] Even in a nonbasic solvent like acetic acid the perchlorate salt of (*Z*)-**1** decomposed to give **3** and **4** at 17 °C. Furthermore, exposure of this perchlorate to tetrabutylammonium chloride in dichloromethane at 0 °C exclusively afforded the elimination products but no substitution product was obtained.



(*Z*)-**1** (R = *n*-C_8H_{17}) (6)

Reaction Rates. The tetrafluoroborate salt of **1** shows a strong UV absorption only below 240 nm. However, a longer wavelength absorption develops immediately on dissolution in a halide solution as shown in Fig. 3. This absorption disappears slowly following pseudo-first-order kinetics. In a solution of tetrabutylammonium fluoride, an instantaneous reaction seems to occur, the absorption in the 240—260 nm region being lower than that of **1·BF4** in a pure solvent.

The observed pseudo-first-order rate constants k_{obsd} were obtained at 25 °C from the time-dependent absorbance change. They can be separated into those for the substitution and elimination reactions, k_s and k_e, using the product ratio $r=[\mathbf{2}]/[\mathbf{3}]=k_s/k_e$, when available. The rate constants thus obtained in acetonitrile and chloroform solutions are plotted against the halide concentrations in Figs. 4, 5, and 6. The curves are not straightforward. The rate for substitution increases with increasing halide concentrations but the plots curve concave downward. By contrast, the rate for elimination tends to decrease with halide concentration probably following a steep increase in a very low concentration range of the halide. A similar curvature was observed for the reaction of [(*E*)-3,3-dimethyl-1-butenyl](phenyl)iodonium tetrafluoroborate with chloride ion, which only gives elimination products.[11] This unusual curve may result from a preequilibrium formation of a complex between **1** and the halide ion, as the UV absorption suggests.

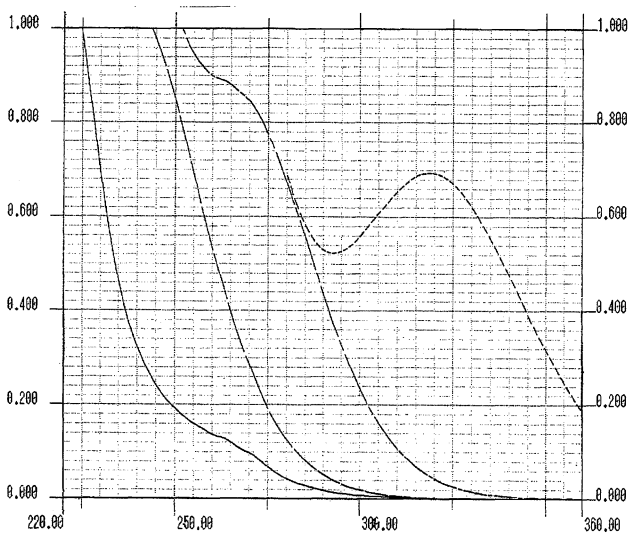


Fig. 3. UV Absorption spectra of **1·BF4** in acetonitrile solutions containing no salt (solid line), and 0.01 mol dm^{-3} of Bu_4NCl (– – – –), Bu_4NBr (–•–), and Bu_4NI (- - - - - -), respectively. Measured at 25 °C and [**1**]=6.55×10^{-5} mol dm^{-3}.

Effects of Ionic Strength. Effects of nonnucleophilic salts like tetrabutylammonium perchlorate on the reaction rates seemed to be rather small as observed for the reactions in acetonitrile. However, detailed examinations of the reaction in chloroform showed some complicated effects (Fig. 4b). The added salt enhances the observed rate at higher halide concentrations (>0.02 mol dm^{-3}) while it diminishes k_{obsd} at low concentrations of halide (<0.01 mol dm^{-3}). This may also be reflected to the product ratio *r* (Table 1); the fraction of substitution increases with ionic strength at the low [Cl^-] (run 2) while it decreases at the high [Cl^-] (run 4). The observed salt effects must arise largely from the preequilibrium formation of the association complex (see Discussion).

UV Absorption. The initial absorbances of **1** in acetonitrile solutions containing tetrabutylammonium halide were measured by extrapolating the decreasing absorbances at 250, 265, and 318 nm to the time of mixing for chloride, bromide, and iodide ions, respectively, at 25 °C. The absorbance increases with the concentration of halide, as shown for bromide in acetonitrile solution in Fig. 7. Other halides show similar saturation curves. At low halide concentrations, the absorbance is smaller when the ionic strength is increased to 0.10 with added tetrabutylammonium perchlorate. In chloroform solution the absorption increases in a similar manner by addition of halide ion, but the absorbance are already strong at 10^{-4} mol dm^{-3} of halide, decreasing slightly with halide concentration when the ionic strength is not adjusted (Fig. 8). However, added perchlorate salt causes some decrease in absorbance at low halide concentrations.

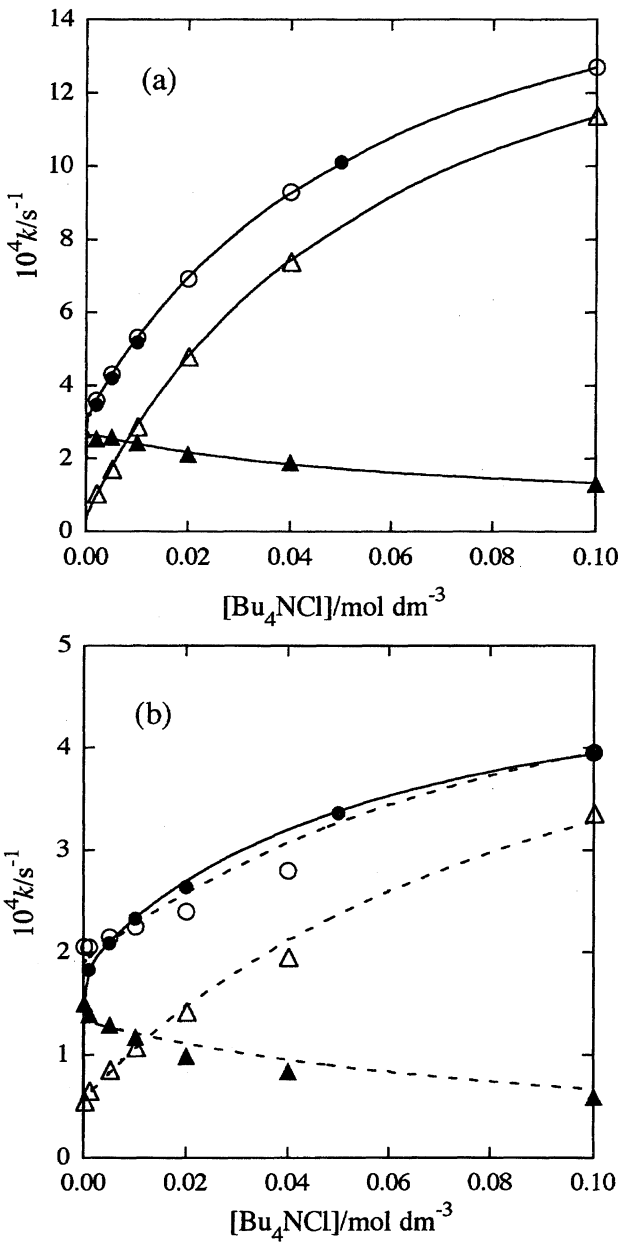


Fig. 4. The rate constants, k_{obsd} (○), k_s (△), and k_e (▲), for the reaction of **1** with Bu_4NCl (a) in acetonitrile and (b) in chloroform at 25 °C. Closed circles are k_{obsd} obtained at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4. Solid curves are calculated with the parameters given Table 5. Broken lines are obtained by trial calculations with $K_2=10$ according to Eq. 14. Other parameters (10^4 a/s^{-1}, 10^2 $b/mol^{-1}dm^3 s^{-1}$) employed are: k_{obsd} (1.9, 0.6), k_s (0.56, 0.6), and k_e (1.34, 0).

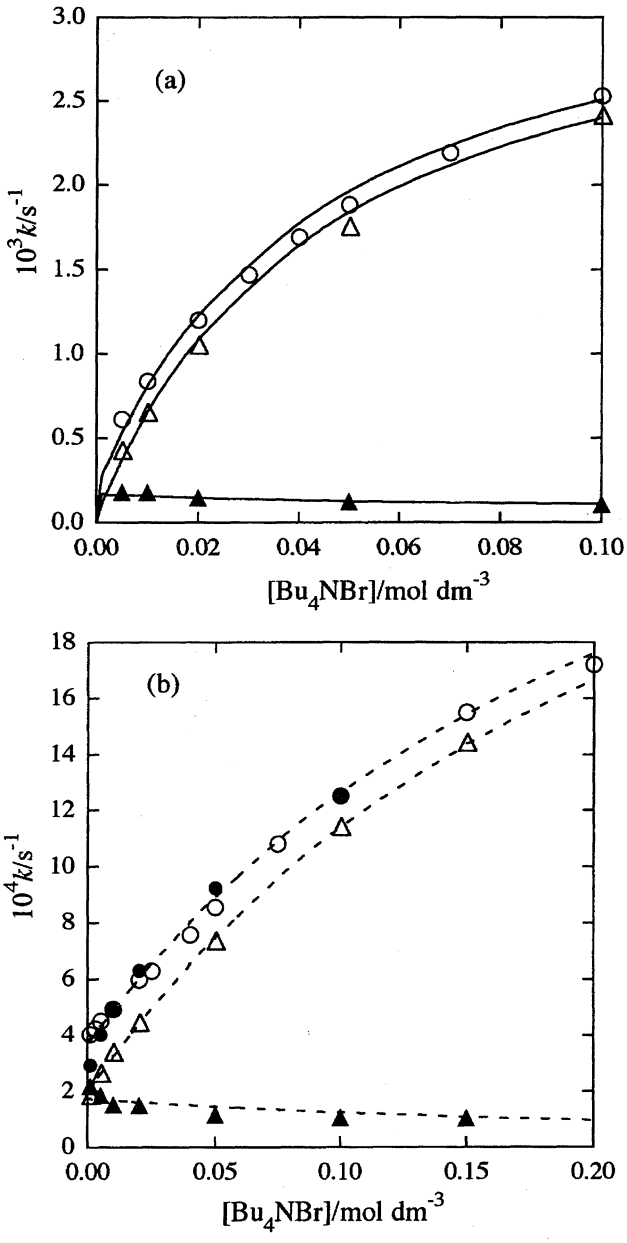


Fig. 5. The rate constants, k_{obsd} (○), k_s (△), and k_e (▲), for the reaction of **1** with Bu_4NBr (a) in acetonitrile and (b) in chloroform at 25 °C. Closed circles are k_{obsd} obtained at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4. Solid curves are calculated with the parameters given Table 5. Broken lines are obtained by trial calculations with $K_2=4$ according to Eq. 14. Other parameters (10^4 a/s^{-1}, 10^2 b/mol^{-1} $dm^3 s^{-1}$) employed are: k_{obsd} (3.7, 1.4), k_s (1.97, 1.4), and k_e (1.73, 0).

Solvent Effects. The kinetic results shown above are only those observed in chloroform and acetonitrile solutions, but the reactions in other solvents showed similar results. The overall rate constants for the reaction with bromide ion are compared in various solvents at [Bu_4NBr]=0.05 mol dm^{-3} (Fig. 9): k_{obsd} values are logarithmically plotted against the solvent polarity parameter $E_T(30)$.[12] Scattering of the data is large but k_{obsd} tends to decrease with increasing polarity of the solvent. Especially slow reactions in protic solvents are apparent.

Substituent Effects. Effects of the substituent in the leaving iodobenzene group of **1** were examined on the rate for the reaction with chloride ion in chloroform. The overall rate constants were measured at [Bu_4NCl]=0.05 mol dm^{-3} for the three substrates, *p*-methyl, *p*-chloro, and unsubstituted ones. The k_{obsd} increases with increasing electron-

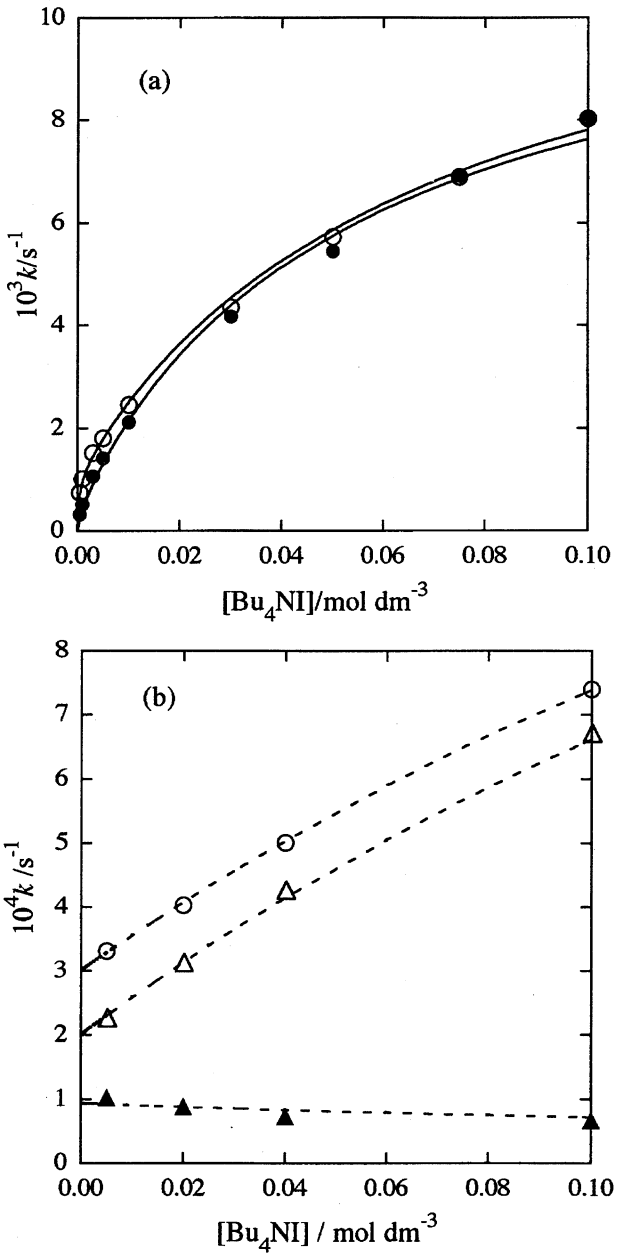


Fig. 6. The rate constants, k_{obsd} (○), k_2 (△), and k_e (▲), for the reaction of **1** with Bu_4NI (a) in acetonitrile and (b) in chloroform at 25 °C. Closed circles are k_{obsd} obtained at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4. Solid curves are calculated with the parameters given Table 5. Broken lines are obtained by trial calculations with K_2=3 according to Eq. 14. Other parameters (10^4 a/s^{-1}, 10^2 b/mol^{-1} dm^3 s^{-1}) employed are: k_{obsd} (3.0, 0.22), k_s (2.0, 0.22), and k_e (0.94, 0).

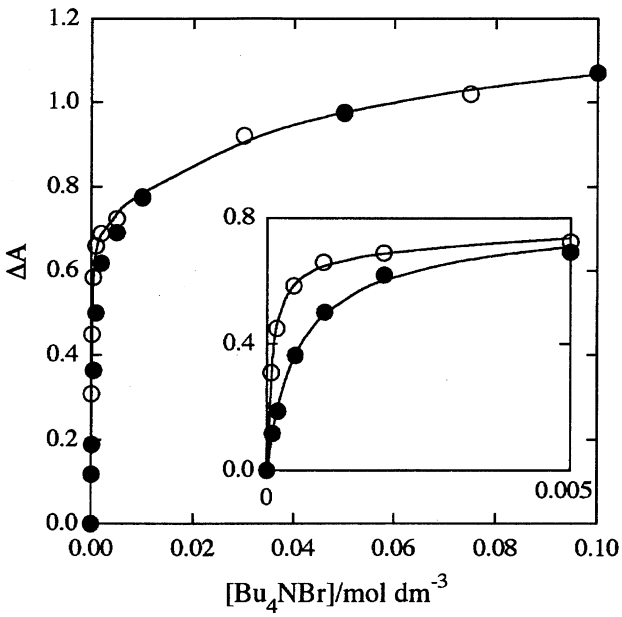


Fig. 7. Initial absorbance of **1** in acetonitrile solutions containing Bu_4NBr at 25 °C and [**1**]=6.79×10^{-5} mol dm^{-3}. Closed circles are values obtained at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4. Solid curves are calculated with the parameters given in Table 5. The inset shows details at low halide concentrations.

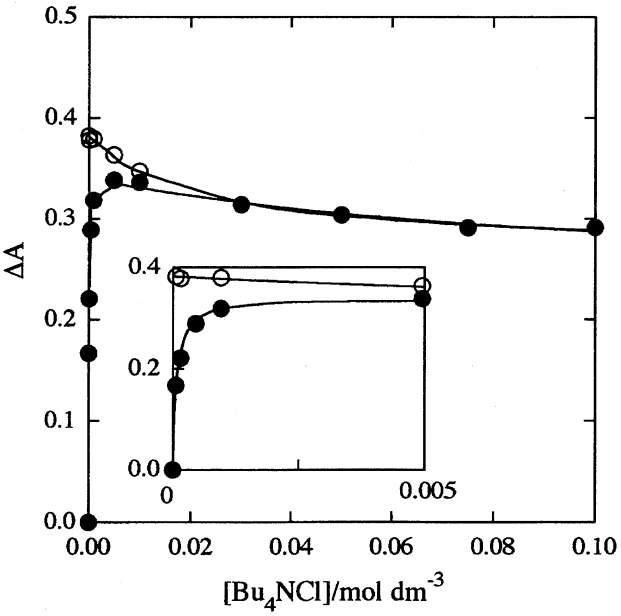


Fig. 8. Initial absorbance of **1** in chloroform solutions containing Bu_4NCl at 25 °C and [**1**]=5.20×10^{-5} mol dm^{-3}. Closed circles are values obtained at the constant ionic strength of 0.10 maintained with added Bu_4NClO_4. Solid curves are calculated with the parameters given in Table 5. The inset shows details at low halide concentrations.

withdrawing ability of the substituent as shown in Fig. 10 by a logarithmic plot against the Hammett σ values. The slopes ρ are roughly 0.83 and 0.75 at 25 and 35 °C, respectively.

Kinetic Isotope Effects. The reaction rates for the β and α deuterium substrates (**1-βD** and **1-αD**) are compared with those for the protium substrate (**1**) under various reaction conditions. Since the observed rate constants k_{obsd} are composites of the k_s and k_e values, the separation of the isotope effects on the two reactions is necessary. At selected concentrations of halide ions, product ratios r were also determined for the deuterium substrates (Table 3), and k_s^D and k_e^D values were obtained in the same way as for the protium substrate. The isotope effects k_H/k_D for substitution and elimination un-

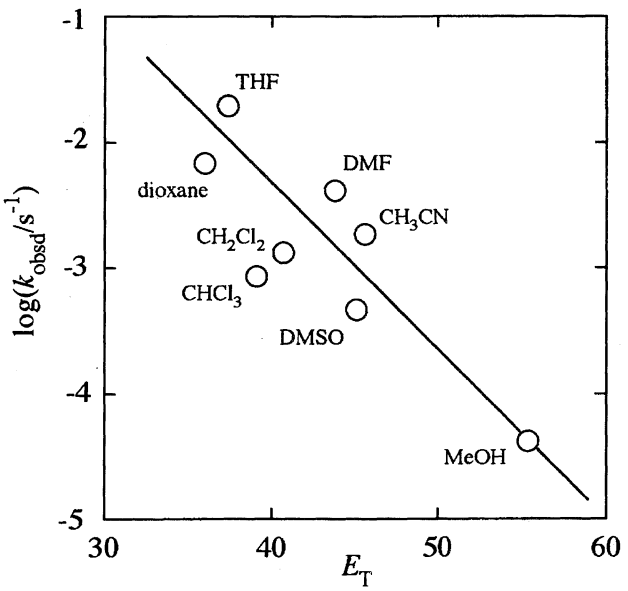


Fig. 9. Solvent effects of the observed rate constants for the reaction of **1** with Bu_4NBr (0.05 mol dm^{-3}) at 25 °C.

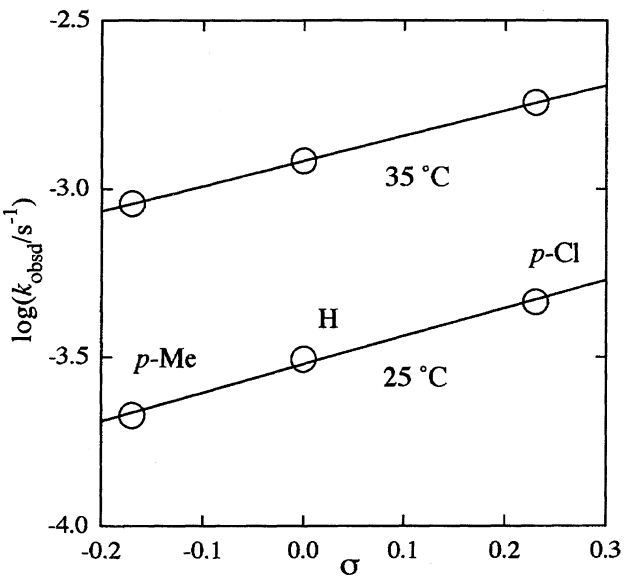


Fig. 10. Effects of the leaving group substituents on the rate of reaction of **1** with Bu_4NCl (0.05 mol dm^{-3}) in chloroform at 25 and 35 °C.

der the specified conditions were calculated from these data and are summarized in Table 4.

However, we could not determine the product ratios for the labeled substrates under all the reaction conditions where the rates were measured. When the product ratio was not available for the deuterium substrate, the separation of rate constants was performed as follows. With use of the product ratio, $r=k_s/k_e$, for the protium substrate and the reciprocal isotope effects for the substitution and the elimination, $s=k_s^D/k_s$ and $e=k_e^D/k_e$,[13] the observed overall reciprocal isotope effect k_D/k_H is presented by Eq. 7.

$$k_D/k_H = (sr+e)/(1+r). \quad (7)$$

This is rearranged to Eq. 8.

$$(k_D/k_H)(1+r) = sr+e. \quad (8)$$

From this relationship, the separate reciprocal isotope effects, s and e can be obtained by the least-squares calculations for the range of halide concentrations. The results obtained in this way are also given as the normal isotope effects in Table 4. Agreements of the values obtained from the two methods are satisfactory. The secondary kinetic isotope effect of the β deuterium on substitution is 1.1—1.2, while that of the α deuterium is about 1.13. The β deuterium shows primary isotope effect of about 3 on the elimination.

Effects of Pressure. The effects of high pressure on

Table 4. Kinetic Isotope Effects on the Substitution and Elimination in the Reactions of **1** with Halide Ions[a]

Position of deuterium	Halide (concn/mol dm^{-3})	Solvent	k_H/k_D Substitution	k_H/k_D Elimination
β	Cl^- (0—0.1)[b]	$CHCl_3$	1.18±0.02	2.72±0.07
β	Cl^- (0.04)	$CHCl_3$	1.13	3.25
β	Cl^- (0.05)[c]	TFE	1.09	(4.3)
β	Cl^- (0.05)[c]	97HFIP	1.08	(2.5)
α	Cl^- (0—0.1)[b]	$CHCl_3$	1.13±0.03	1.15±0.03
α	Cl^- (0.04)	$CHCl_3$	1.12	1.08
α	Cl^- (0.05)[c]	TFE	1.15[d]	
α	Cl^- (0.05)[c]	97HFIP	1.12[d]	
β	Br^- (0.05)	$CHCl_3$	1.24	2.7
β	Br^- (0.01)	CH_3CN	1.16	2.54
β	Br^- (0.05)	CH_3CN	1.23	3.3
β	I^- (0—0.1)[b]	$CHCl_3$	1.20±0.02	2.97±0.38
β	I^- (0.04)	$CHCl_3$	1.20	2.98

a) Reactions were carried out in the presence of tetrabutylammonium halide at 25 °C unless noted otherwise. b) The halide salt of **1** was used as the substrate. Calculated by the least squares method as described in text and given with the standard deviations. c) At 50 °C. d) The ratio of k_{obsd} for **1** and **1-αD**.

the reaction rates of **1** with bromide ion (0.05 mol dm^{-3}) were determined in chloroform at 20 °C for the convenience of rate measurements. The observed rate constants decrease with pressure as shown in Fig. 11 to give an apparent volume of activation $\Delta V^{\ddagger}$ of 4.6 cm^3 mol^{-1}.[14]

Discussion

Reaction Pathways. Reactions of the iodonium salt **1** with chloride, bromide, and iodide ions give both substitution and elimination products. Although our primary interest is in the mechanism of vinylic substitution, we first look into the elimination reactions. The rate constant k_e for elimination shows very characteristic dependence on the halide concentrations [X$^-$] when k_e is separated from the substitution rate k_s, as seen in Figs. 4, 5, and 6. The rate k_e decreases with increasing [X$^-$], following an initial sharp increase. The retardation observed at higher [X$^-$] may best be explained by formation of an unreactive complex. It should also be pointed out that fluoride induces exclusively α elimination, while other halides eliminate the β proton. This difference may arise from a high basicity of fluoride (pK_a of HF=3.17).

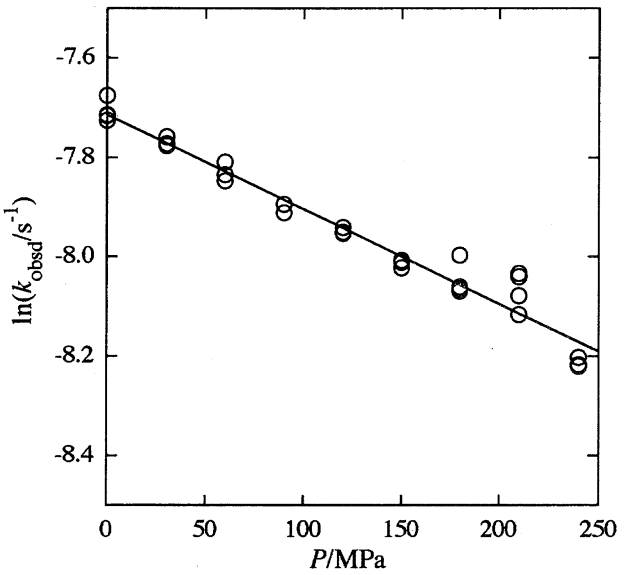


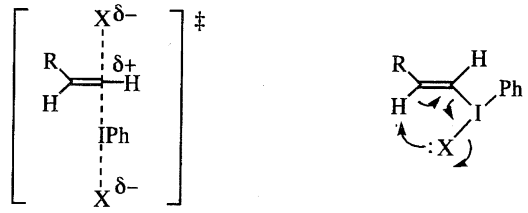
Fig. 11. Effects of pressure on the rate of reaction of **1** with Bu_4NBr (0.05 mol dm^{-3}) in chloroform at 20 °C.

Other poorly basic halides only lead to an intramolecular elimination within an intermediate complex (see below).

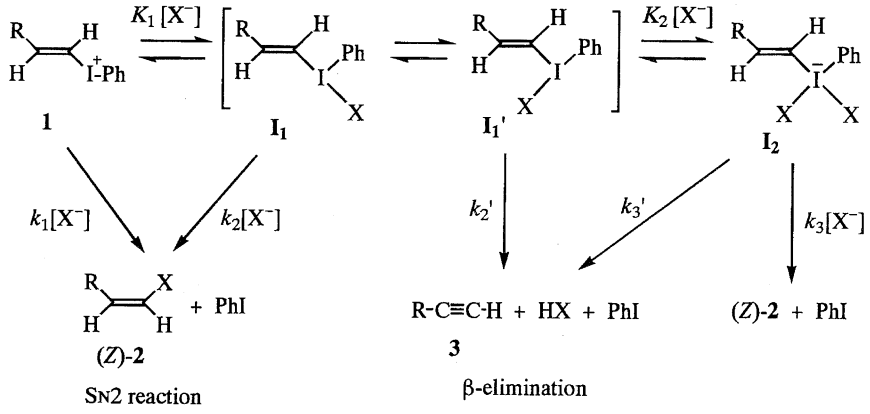
UV spectral observations are also compatible with a rapid equilibrium formation of complex(es) between **1** and halide ion. Although similar observations of red-shifted UV absorption of diphenyliodonium halide in aprotic solvents were ascribed to the charge-transfer band,[15] the strong absorbance observed for **1** (Fig. 3) may more reasonably be accommodated with a complex involving a hypervalent bonding. That is, the halide forms a 10-I-3 halo-λ^3-iodane[16] (**I$_1$**) by association with **1**. The characteristic curve for k_e forces us to assume further formation of a less reactive intermediate to retard the elimination at higher [X$^-$]. A second hypervalent species of 12-I-4 type, iodate (**I$_2$**) can be postulated as an additional intermediate of the molar ratio of 1 : 2 of **1** and X$^-$.[17] The overall reactions involved in the present reaction system are illustrated in Scheme 1.

The halo-λ^3-iodane will take one of the two probable structures, **I$_1$** and **I$_1$**′, where the more electronegative halogen X occupies one of the apical positions.[18] The interchanges among these conformers of the hypervalent intermediates must occur very rapidly via pseudorotation,[19] and may not be differentiated kinetically. The intermediate **I$_1$**′ will intramolecularly undergo β elimination, while **I$_1$** will lead to nucleophilic substitution by an external halide from the back side (S_N2). The anionic iodate intermediate **I$_2$** must be less reactive toward a nucleophile.

Both absorbance and kinetic curves can be reasonably explained according to Scheme 1. The saturation curves for the initial absorbance (Figs. 7 and 8) are accommodated with the rapid preequilibrium formation of the two complexes, **I$_1$** (**I$_1$**′) and **I$_2$** (Scheme 1), and can be simulated by a nonlinear least-squares method according to Eq. 9 and with the parameters



Scheme 2.



Scheme 1.

Table 5. Summary of the Parameters Used for Simulation of the Absorbance and Kinetic Curves[a)]

Halide (Solvent)	Cl^- (CH_3CN)	Br^- (CH_3CN)	I^- (CH_3N)	Cl^- ($CHCl_3$)
λ/nm	250	265	318	260
10^{-3} K_1/mol^{-1} dm^3	46.6±2.2 [7.16±0.31]	11.55±0.07 [2.13±0.16]	2.49±0.08 [0.439±0.022]	large [11.3±0.6]
K_2/mol^{-1} dm^3	16.8±2.9 [15.1±4.4]	21.7±3.7 [20.4±6.0]	14.6±2.2 [17.1±4.2]	45±6 [17.1±8.9]
$10^{-4}\epsilon_0$	0.288	0.199	0.003	0.315
$10^{-4}\epsilon_1$	1.20 [1.22]	1.22 [1.20]	1.09 [1.17]	0.735 [0.671]
$10^{-4}\epsilon_2$	1.67 [1.67]	2.02 [2.01]	1.85 [1.76]	0.515 [0.485]
$k_1+k_2'K_1$/mol^{-1} dm^3 s^{-1}	14.6	2.4	2.9 [0.45]	[2.1]
$k_2+K_1+k_3'K_1K_2$/mol^{-2} dm^6 s^{-1}	1440	900	450 [87]	[99]
k_1/mol^{-1} dm^{3}s^{-1}	1.9	0.4		
k_2K_1/mol^{-2} dm^{6}s^{-1}(k_2)	1400 (0.030)	800 (0.076)		
$k_2'K_1$/mol^{-1} dm^{3}s^{-1}(k_2')	12.6 (2.7×10^{-4})	20.0 (1.7×10^{-4})		
$k_3'K_1K_2$/mol^{-2} dm^{6}s^{-1}(k_3')	40 (5×10^{-5})	20 (8×10^{-5})		

a) Values in square brackets are those obtained at the ionic strength of 0.10 with added Bu_4NClO_4.

given in Table 5.

$$\Delta A = (\Delta A_1 K_1[X^-] + \Delta A_2 K_1 K_2 [X^-]^2)/(1 + K_1[X^-] + K_1K_2[X^-]^2). \quad (9)$$

Here ΔA is a difference between the initial absorbance (A_i) and that at $[X^-]=0$ (A_0), and K_1 and K_2 are the equilibrium constants for the formation of the hypervalent intermediates, $\mathbf{I_1}$ ($\mathbf{I_1}'$) and $\mathbf{I_2}$. The absorbances ΔA_1 and ΔA_2 correspond to the maximum absorbance increases due to the formation of $\mathbf{I_1}$ ($\mathbf{I_1}'$) and $\mathbf{I_2}$, respectively. The conformers of the λ^3-iodane, $\mathbf{I_1}$ and $\mathbf{I_1}'$, are not differentiated.

The association constant K_1 is very dependent on the ionic strength of the medium, but the magnitudes clearly decrease in the order: $Cl^- > Br^- > I^-$. That is, the stability of the halo-λ^3-iodanes decreases in this order. This order of the stability is reasonable since many difluoro- and dichloro-λ^3-iodanes are known, but dibromo-λ^3-iodanes are unstable.[20)] In chloroform, the association is essentially complete at very low concentration of halide ion if the ionic strength is not adjusted; i.e., K_1 is very large and the curve is fitted to an abbreviated Eq. 10.

$$\Delta A = (\Delta A_1 + \Delta A_2 K_2[X^-])/(1 + K_2[X^-]) \quad (10)$$

The curve fittings are satisfactorily performed even when the ionic strengths are not maintained constant, but the obtained parameters may not have much physical meaning since the equilibrium constants will change with the ionic strength.

Kinetic Eqs. 11 and 12 for substitution and elimination can be derived from Scheme 1 if one assumes that the formation of the hypervalent intermediates is a rapid preequilibrium. Kinetic curves obtained in acetonitrile solutions (Figs. 4, 5, and 6a) can be reasonably fitted to Eqs. 11, 12, and 13 using the equilibrium constants obtained from the absorbance curves (Table 5).

$$k_s = (k_1[X^-] + k_2K_1[X^-]^2 + k_3K_1K_2[X^-]^3) / (1 + K_1[X^-] + K_1K_2[X^-]^2), \quad (11)$$

$$k_e = (k_2'K_1[X^-] + k_3'K_1K_2[X^-]^2)/(1 + K_1[X^-] + K_1K_2[X^-]^2), \quad (12)$$

$$k_{obsd} = k_s + k_e. \quad (13)$$

The third-order term for k_s (k_3) in Eq. 11 is neglected in the concentration range studied. In spite of the unadjusted ionic strength employed for experimental data, all the kinetic curvatures are in conformity to the expected features of the proposed reaction scheme. It can also be pointed out that the first-order term order is $k_1 < k_2'K_1$ while the second-order term values $k_2K_1 > k_3'K_1K_2$ for both chloride and bromide reactions. That is, the main reactions occur from the halo-λ^3-iodane intermediate, though the reactivity of the iodonium ion is greater than the λ^3-iodane or iodate, i.e., $k_1 > k_2$ and $k_2' > k_3'$. Alternatively and more exactly by comparing the respective terms for substitution and elimination, $k_1/k_2K_1 = 1.4\times10^{-3}$ (Cl^-) or 0.5×10^{-3} (Br^-) mol dm^{-3} and $k_2'K_1/k_3'K_1K_2 = 0.3$ (Cl^-) or 0.1 (Br^-) mol dm^{-3}; that is, in the range of $[Cl^-]=0.0014$—0.3 and $[Br^-]=0.0005$—0.1 mol dm^{-3}, the main reactions occur from the halo-λ^3-iodane in acetonitrile.

The kinetic curves obtained in chloroform also have the same features, in accord with Scheme 1. The rate constant k_{obsd} obtained at the constant ionic strength of 0.10 for chloride (closed circles in Fig. 3b) can be reasonably reproduced by Eq. 13. The data obtained without adjusted ionic strength are fitted to Eq. 14, similar to Eq. 10 for the absorbance, assuming that K_1 is very large.

$$k = (a + b[X^-])/(1 + K_2[X^-]), \quad (14)$$

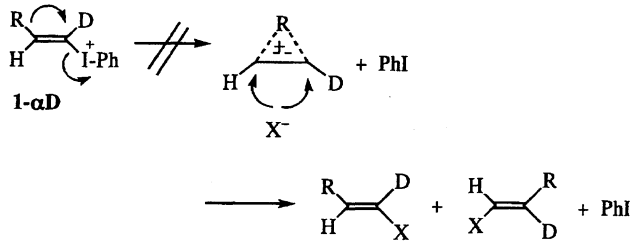
where a and b stand for the appropriate kinetic parameters. However, the fits are not satisfactory. Trial fittings are shown by broken lines in Figs. 4, 5, and 6b and the parameters used are given in the captions of the figures.

In conclusion, overall reactions of **1** with halide ions in solution are accommodated with Scheme 1 involving the hypervalent 10-I-3 and 12-I-4 intermediates. Main reactions occur in the usual concentration range of halide from the 10-I-3 haloiodane, $\mathbf{I_1}$ or $\mathbf{I_1}'$: The nucleophilic substitution occurs as a bimolecular reaction with $\mathbf{I_1}$ at a rate second order in $[X^-]$ (k_2 term) while the elimination takes place intramolecularly within $\mathbf{I_1}'$ at a rate first order in $[X^-]$ (k_2' term).

Vinylic S_N2 Mechanism. Nucleophilic substitution

is a bimolecular reaction occurring mainly with the λ^3-iodane intermediate $\mathbf{I_1}$ to lead to exclusive inversion, except for reactions in some polar protic solvents. The bimolecular reaction with inversion would occur through the concerted in-plane S_N2 mechanism, as suggested above. However, an alternative ion-pair mechanism should be excluded before reaching this conclusion. The ionization could occur in the presence of the nucleophile preassociated on the opposite side of the nucleofuge and the unstable vinyl cation generated could immediately be trapped by the nucleophile before dissociation of the ion pair.[3,21]

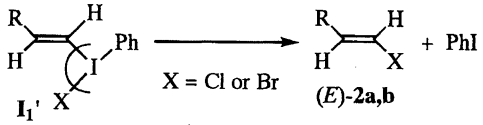
Solvent effects on the observed rate show that the reaction is slower in polar solvents (Fig. 9), in disagreement with an ionization mechanism. Some retention product (*E*)-**2** was observed in very ionizing solvents.[22] This was at first considered to be suggestive of an ion-pair mechanism. However, the reactions are extremely slow in these protic solvents. If ionization were occurring during the reaction, β-alkyl participation could have taken place and some rearranged product should have been involved in the retention product, as illustrated in Eq. 15 and as was observed with a β,β-dialkylvinyliodonium salt.[23,24]



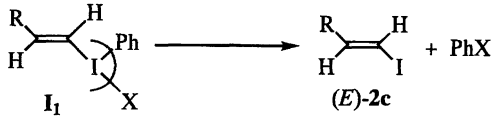
(15)

This was examined for the reaction of α-deuterated **1** with chloride in TFA, where the highest yield of (*E*)-**2a** was obtained. However, no sign of the rearrangement was detected by ^{1}H NMR spectra of the products. We conclude that ionization is impossible for the formation of primary β-monoalkylvinyl cation, although there is evidence for the formation of β,β-dialkylvinyl cation.[24] This conclusion is in accord with the observations[25] and theoretical calculations[25c,26] that the β-alkyl group stabilizes the vinyl cation. Although participation of β-phenyl group was observed during the acetolysis of (*E*)-styryliodonium salt, such participation was not found in the acetolysis of **1**.[5] Formation of primary vinyl cation was suggested during the decay of tritiated ethene[27] or in a superacid,[28] but such suggestions under normal solution conditions[29] do not seem conclusive. Possible 1,2-alkyl migrations were not observed in these instances.

Now, the problem remains of how the retention product was formed in the polar solvents. This would be a product of ligand coupling occurring within the halo-λ^3-iodane $\mathbf{I_1}'$ (Eq. 16). Because both S_N2 and β elimination routes are inhibited probably due to solvent hydrogen-bonding to the available lone-pair electrons on the halide ion and the coordinated halogen atom, a third slow route of ligand coupling can show up. This kind of ligand coupling leading to nucleophilic substitution was observed for the reaction of (*Z*)-β-halovinyliodonium salts with halide ions.[30] The accompanying formation of 1-iododecene ((*E*)-**2c**) was detected only when the formation of the retention product (*E*)-**2a** (or (*E*)-**2b** in the bromide reaction) was observed in TFA. This fact strongly supports the feasibility of the ligand coupling pathway. Ligand coupling within $\mathbf{I_1}$ should result in formation of (*E*)-**2c** and chlorobenzene (Eq. 17). Furthermore, the fraction of retention increase at low chloride concentration in TFA in consistent with the diminishing rate of the bimolecular reaction leading to inversion.



(16)



(17)

Effects of the leaving group are rather small: The approximate ρ value for the substituents of the phenyliodo group is 0.75 at 35 °C for the reaction with chloride (Fig. 10). Similar effects of the leaving iodonio group were previously examined for the solvolysis of (4-*t*-butyl-1-cyclohexenyl)-(phenyl)iodonium salt in 60% (v/v) aqueous ethanol at 35 °C and the ρ value of 1.8 was obtained.[31] The latter reaction occurs via rate-determining formation of the vinyl cation. The much smaller ρ value obtained for the present reaction is consistent with the concerted S_N2 mechanism, where much less charge development is expected at the transition state.

The α and β deuterium kinetic isotope effects have been used to differentiate the (concerted) S_N2 from S_N1 (ionization) mechanism of aliphatic nucleophilic substitution reactions.[32] A similar criterion can be employed to the present vinylic system. Small but significant secondary isotope effects of both α and β deuterium were observed on the rate of substitution (k_s) of **1** (Table 4). The effects of β deuterium isotope examined for the solvolysis of various alkenyl substrates to generate vinyl cations are summarized by Stang et al.[33] The k_H/k_D values range widely from 1.1 to 2.0. The vinyl cations concerned in the previous solvolysis are secondary cations stabilized by an α substituent and it was shown that the k_H/k_D value decreases with stability of the putative cation.[34] The primary vinyl cation should be very unstable, and if it were formed during the rate-determining step, the k_H/k_D value should have been larger. The observed isotope effects, $k_H/k_D < 1.2$, are at the lower limit of the values found for the formation of secondary vinyl cations and seem to be incompatible with formation of the unstable primary vinyl cation. The β deuterium isotope effects are generally about 10% ($k_H/k_D \approx 1.1$) per D for the formation of trivalent carbocation in aliphatic solvolysis,[32] but similar β effects on the formation of vinyl cation should be larger because of maximal overlapping between the β-hydron bond and the incipient p orbital, while the lower β effects are expected for the concerted S_N2 reaction. The present results

are compatible with the S_N2 mechanism.

The pressure effect measurements provide a small positive activation volume $\Delta V^{\ddagger}$=4.6 cm^3 mol^{-1}. Under the reaction conditions, the substrate is present completely in the form of the neutral associated form, bromo-λ^3-iodane **I$_1$** (**I$_1$'**). If it underwent ionization to give vinyl cation, the developing charge separation would have induced the solvent contraction and the negative $\Delta V^{\ddagger}$ would have resulted. The small positive value is not incompatible again with the concerted S_N2 mechanism, where partial desolvation of the anionic nucleophile and a new bond formation will occur at the transition state to result in a small volume change.

Conclusion. In the present reaction system no sign of formation of the primary vinyl cation was found even in very highly ionizing solvents. The reactions of **1** with halide ions occur mainly from the halo-λ^3-iodane: the nucleophilic substitution with exclusive inversion as a bimolecular reaction and the accompanying β elimination as an intramolecular reaction. The kinetic criteria are consistent with the in-plane vinylic S_N2 mechanism. In a highly polar protic solvent like TFA, the usual nucleophilic reactions become very slow and the intramolecular ligand coupling mechanism shows up to give a retained product of nucleophilic substitution.

Experimental

^{1}H NMR spectra were recorded on a JEOL JNM-FX200 or a Varian INOVA 500 spectrometer and chemical shifts are given in ppm downfield from internal TMS. IR and UV spectra were obtained by a JASCO IRA-1 and Shimadzu UV-2200 spectrophotometers, respectively. Mass spectrometers JEOL JMS-SX102A and JMS-DX303HF were used for MS. Analytical gas chromatography was conducted on a Shimadzu GC-14B or GC-15A gas chromatograph with a DB-1 capillary column (0.25 mm×30 m) or a packed column (20% silicone GE SF-96, 3m) and an integrator C-R6A, while preparative GC on a Shimadzu GC-14A with 20% silicone GE SF-96 (1 m). Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Melting points were measured on a Yanaco micromelting-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 TCI (Tokyo) and used without further purification. Tetrabutylammonium chloride (TCI), bromide (Wako, Osaka), iodide (Wako), fluoride (TCI), and perchlorate (Fluka) were used as received.

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 Centris 650.

(*E*)-1-Decenyl(phenyl)iodonium Tetrafluoroborate (1·BF$_4$). The BF_3-catalyzed silicon–iodonium exchange reaction between (*E*)-1-(trimethylsilyl)-1-decene and iodosylbenzene was carried out in the same way as described previously,[10] to give **1·BF$_4$** in 72% yield.

(*E*)-[1-^{2}H]-1-Decenyl(phenyl)iodonium Tetrafluoroborate (1-αD·BF$_4$). (*E*)-1-[Dimethyl(phenyl)silyl]-[1-^{2}H]-1-decene was prepared stereoselectively from [1-^{2}H]-1-decyne (96 atom %D) by the reaction with lithium bis[dimethyl(phenyl)silyl]cuprate in 65% yield according to the procedure developed by Fleming.[35] To a stirred suspension of iodosylbenzene (1.60 g, 7.26 mmol) and the vinylsilane (1.00 g, 3.63 mmol) in dichloromethane (30 mL) was added dropwise BF_3·Et_2O (1.03 g, 7.26 mmol) at 0 °C under nitrogen. The mixture was stirred for 2 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (8 g), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C to give 1.25 g (80%) of **1-αD·BF$_4$** (96 atom %D or 97 atom %D in another run) as a pale yellow oil: IR (Nujol) 2300, 1625, 1580, 1570, 1285, 1050, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.01 (d, *J*=7.8 Hz, 2H), 7.66 (t, *J*=7.3 Hz, 1H), 7.51 (dd, *J*=7.8, 7.3 Hz, 2H), 6.97 (t, *J*=7.5 Hz, 1H), 2.34 (q, *J*=7.5 Hz, 2H), 1.52—1.16 (m, 12H), 0.87 (t, *J*=7.0 Hz, 3H); FAB MS *m/z* 344 [(M−BF_4)$^+$].

(*E*)-[2-^{2}H]-1-Decenyl(phenyl)iodonium Tetrafluoroborate (1-βD·BF$_4$). (*E*)-1-[Dimethyl(phenyl)silyl]-[2-^{2}H]-1-decene was prepared stereoselectively from 1-decyne by the reaction with lithium bis[dimethyl(phenyl)silyl]cuprate and D_2O in 83% yield according to the procedure developed by Fleming.[35] In the same way as described for **1-αD·BF$_4$**, the vinylsilane (1.00 g, 3.63 mmol) was treated with iodosylbenzene (1.60 g, 7.26 mmol) and BF_3·Et_2O (1.03 g, 7.26 mmol) in dichloromethane (30 mL) at 0 °C for 2 h, to afford 1.31 g (84%) of **1-β·BF$_4$** (96 atom %D or 93 atom %D in another run) as a pale yellow oil: IR (Nujol) 2270, 1625, 1570, 1285, 1060, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.01 (d, *J*=7.8 Hz, 2H), 7.65 (t, *J*=7.3 Hz, 1H), 7.49 (dd, *J*=7.8, 7.3 Hz, 2H), 6.78 (br s, 1H), 2.33 (t, *J*=7.3 Hz, 2H), 1.52—1.16 (m, 12H), 0.87 (t, *J*=6.8 Hz, 3H); FAB MS *m/z* 344 [(M−BF_4)$^+$].

(*E*)-1-Decenyl(4-methylphenyl)iodonium Tetrafluoroborate. With use of a similar procedure for the preparation of **1-αD·BF$_4$**, (*E*)-1-(trimethylsilyl)-1-decene (100 mg, 0.471 mmol) was treated with 1-iodosyl-4-methylbenzene (176 mg, 0.752 mmol) and BF_3·Et_2O (107 mg, 0.752 mmol) in dichloromethane (7 mL) at 0 °C for 1 h, to afford 103 mg (49%) of the iodonium salt as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ=7.86 (d, *J*=8.5 Hz, 2H), 7.31 (d, *J*=8.5 Hz, 2H), 6.90 (dt, *J*=13.6, 7.0 Hz, 1H), 6.74 (d, *J*=13.6 Hz, 1H), 2.44 (s, 3H), 2.33 (q, *J*=7.0 Hz, 2H), 1.59—1.03 (m, 12H), 0.87 (t, *J*=6.4 Hz, 3H). HRFAB MS Calcd for $C_{17}H_{26}I$ [(M−BF_4)$^+$]: M, 357.1079. Found: *m/z* 357.1066.

(*E*)-1-Decenyl(4-chlorophenyl)iodonium Tetrafluoroborate. In the same way as above, (*E*)-1-(trimethylsilyl)-1-decene (100 mg, 0.471 mmol) was treated with 1-chloro-4-iodosylbenzene (192 mg, 0.753 mmol) and BF_3·Et_2O (120 mg, 0.848 mmol) in dichloromethane (3 mL) at 0 °C for 1.5 h, to give 141 mg (70%) of the iodonium salt as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ=7.96 (d, *J*=8.8 Hz, 2H), 7.42 (d, *J*=8.8 Hz, 2H), 7.02 (dt, *J*=13.7, 7.0 Hz, 1H), 6.77 (d, *J*=13.7 Hz, 1H), 2.31 (q, *J*=7.0 Hz, 2H), 1.56—1.06 (m, 12H), 0.87 (t, *J*=6.4 Hz, 3H). HRFAB MS Calcd for $C_{16}H_{23}ClI$ [(M−BF_4)$^+$]: M, 377.0533. Found: *m/z* 377.0544.

(*Z*)-1-Decenyl(phenyl)iodonium Perchlorate ((*Z*)-1·ClO$_4$). The BF_3-catalyzed silicon–iodonium exchange reaction between (*Z*)-1-(trimethylsilyl)-1-decene and (diacetoxyiodo)benzene was carried out in the same way as described previously,[36] to give **(*Z*)-1·ClO$_4$** in 42% yield.

A General Procedure for the Ligand Exchange of Vinyliodonium Tetrafluoroborate: Preparation of (*E*)-1-Decenyl(phenyl)iodonium Chloride (1·Cl). A solution of **1·BF$_4$** (226 mg, 0.525 mmol) in dichloromethane (5 mL) was shaken with a saturated aqueous NaCl solution (5 mL) at 0 °C three times using a separatory funnel. The organic layer was washed with water and concentrated under an aspirator vacuum to give an oil. The oil was washed several times with hexane by decantation at −78 °C to afford 155 mg (78%) of **1·Cl** as a white powder: Mp 61.3—62.0 °C; IR (Nujol) 990, 940, 735, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.94 (d, *J*=7.8 Hz,

2H), 7.59 (t, J=7.3 Hz, 1H), 7.45 (dd, J=7.8, 7.3 Hz, 2H), 6.77 (d, J=14.0 Hz, 1H), 6.58 (dt, J=14.0, 7.0 Hz, 1H), 2.23 (q, J=7.0 Hz, 2H), 1.49—1.14 (12H), 0.87 (t, J=7.3 Hz, 3H). Anal. Calcd for $C_{16}H_{24}ClI \cdot 1/3\ H_2O$: C, 49.95; H, 6.46%. Found: C, 50.14; H, 6.30%.

(*E*)-[1-^{2}H]-1-Decenyl(phenyl)iodonium Chloride (1-αD·Cl): White powder; IR (KBr) 2924, 2300, 1473, 1439, 991, 739, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.93 (d, J=7.8 Hz, 2H), 7.60 (t, J=7.3 Hz, 1H), 7.46 (dd, J=7.8, 7.4 Hz, 2H), 6.55 (t, J=7.5 Hz, 1H), 2.22 (q, J=7.5 Hz, 2H), 1.50—1.12 (m, 12H), 0.87 (t, J=6.3 Hz, 3H); FAB MS m/z 344 [(M−Cl)$^+$]. HRFAB MS Calcd for $C_{16}H_{23}DI$ [(M−Cl)$^+$]: M, 344.0986. Found: m/z 344.0991.

(*E*)-[2-^{2}H]-1-Decenyl(phenyl)iodonium Chloride (1-βD·Cl): White powder; IR (KBr) 2925, 2250, 1473, 1439, 1188, 991, 810, 739, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.94 (d, J=7.6 Hz, 2H), 7.58 (t, J=7.2 Hz, 1H), 7.44 (dd, J=7.6, 7.2 Hz, 2H), 6.75 (br s, 1H), 2.22 (t, J=7.1 Hz, 2H), 1.49—1.06 (m, 12H), 0.87 (t, J=6.5 Hz, 3H). HRFAB MS Calcd for $C_{16}H_{23}DI$ [(M−Cl)$^+$]: M, 344.0986. Found: m/z 344.0995.

(*E*)-1-Decenyl(phenyl)iodonium Bromide (1·Br): White powder; mp 62.5—63.2 °C; IR (Nujol) 1605, 1310, 1195, 1160, 1105, 990, 945, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.96 (d, J=7.8 Hz, 2H), 7.57 (t, J=7.3 Hz, 1H), 7.43 (dd, J=7.8, 7.3 Hz, 2H), 6.78 (d, J=14.2 Hz, 1H), 6.65 (dt, J=14.2, 7.0 Hz, 1H), 2.21 (q, J=7.0 Hz, 2H),1.50—1.10 (m, 12H), 0.87 (t, J=6.6 Hz, 3H). Anal. Calcd for $C_{16}H_{24}BrI$: C, 45.41; H, 5.72%. Found: C, 45.28; H, 5.67%.

(*E*)-1-Decenyl(phenyl)iodonium Iodide (1·I): Yellow powder; mp 51.5—52 °C; IR (Nujol) 1560, 1190, 1160, 985, 940, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.91 (d, J=7.8 Hz, 2H), 7.59 (t, J=7.3 Hz, 1H), 7.44 (dd, J=7.8, 7.3 Hz, 2H), 6.80 (d, J=13.7 Hz, 1H), 6.64 (dt, J=13.7, 6.8 Hz, 1H), 2.22 (q, J=6.8 Hz, 2H), 1.45—1.10 (m, 12H), 0.87 (t, J=6.6 Hz, 3H). Anal. Calcd for $C_{16}H_{24}I_2$: C, 40.87; H, 5.15%. Found: C, 40.37; H, 5.43%.

Product Determination for Reactions of 1. A sample of **1·BF$_4$** (2—5 mg) was dissolved in the reaction solution containing the specified concentrations of tetrabutylammonium halide, and kept standing for the reaction time. The amount of the halide solution was decided so that the halide would be at least 5 times in excess of the substrate. The reaction mixture was diluted with water and the products were extracted 3 times with pentane containing tetradecane (2.5×10^{-6} mol) for a GC internal standard. The combined pentane layer was washed with water, dried over $MgSO_4$, and analyzed by GC before and after concentration. GC MS was examined when necessary.

Pure samples of (*Z*)-**2** and **3** were isolated by preparative GC or TLC from a large scale reaction of **1** with ammonium halide, while the *E* isomers of **2** were obtained from the reaction of **1** with copper(I) halide-pottasium halide.[4)]

(*Z*)-2a:[37)] IR ($CHCl_3$) 2935, 2850, 1620, 1570, 1465, 1435, 1050, 1005, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.01 (dt, J=7.2, 1.5 Hz, 1H), 5.75 (q, J=7.2 Hz, 1H), 2.22 (dq, J=1.5, 7.2 Hz, 2H), 1.50—1.15 (12H), 0.89 (t, J=7.0 Hz, 3H).

(*E*)-2a:[37)] IR ($CHCl_3$) 2930, 2850, 1635, 1460, 930, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.93 (d, J=13.0 Hz, 1H), 5.89 (dt, J=13.0, 6.5 Hz, 1H), 2.04 (q, J=6.5 Hz, 2H), 1.50—1.15 (12H), 0.88 (t, J=6.8 Hz, 3H).

(*Z*)-2b:[39)] IR ($CHCl_3$) 2935, 2850, 1610, 1565, 1460, 1430, 1005, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.17—6.04 (m, 2H), 2.19 (q, J=6.8 Hz, 2H), 1.50—1.15 (12H), 0.88 (t, J=6.6 Hz, 3H).

(*E*)-2b:[38)] ^{1}H NMR ($CDCl_3$) δ=6.18 (dt, J=13.5, 6.8 Hz, 1H), 6.00 (dt, J=13.5, 1.3 Hz, 1H), 2.03 (dq, J=1.3, 6.8 Hz, 2H), 1.50—1.15 (12H), 0.88 (t, J=6.5 Hz, 3H).

(*Z*)-2c:[40)] IR ($CHCl_3$) 2930, 2860, 1610, 1465, 1375, 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.23—6.12 (m, 2H), 2.13 (q, J=7.3 Hz, 2H), 1.50—1.15 (12H), 0.89 (t, J=6.4 Hz, 3H).

(*E*)-2c:[40)] IR ($CHCl_3$) 2930, 2845, 1600, 1460, 1370, 1180, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.51 (dt, J=14.4, 7.1 Hz, 1H), 5.97 (dt, J=14.4, 1.0 Hz, 1H), 2.05 (dq, J=1.0, 7.1 Hz, 2H), 1.50—1.15 (12H), 0.88 (t, J=6.6 Hz, 3H).

3: ^{1}H NMR ($CDCl_3$) δ=2.18 (dt, J=2.6, 6.8 Hz, 2H), 1.93 (t, J=2.6 Hz, 1H), 1.60—1.20 (12H), 0.88 (t, J=6.6 Hz, 3H).

Reaction of 1-αD with Tetrabutylammonium Chloride. To a stirred solution of 11 mg (0.026 mmol) of **1-αD·BF$_4$** (97 atom %D purity) in dichloromethane (1.5 mL) was added tetrabutylammonium chloride (15 mg, 0.052 mmol) at room temperature. The mixture was stirred for 10 h. After addition of water, the mixture was extracted with pentane. Analytical GC with undecane as the internal standard showed the formation of **3** and (*Z*)-**2a** in 37 and 62% yields, respectively. Both **3** and (*Z*)-**2a** were found to be deuterated at the 1 position to the degree of 100 and 96 atom %, respectively, by ^{1}H NMR and GC-MS.

Reaction of 1-βD with Tetrabutylammonium Chloride. Reaction of 20 mg (0.046 mmol) of **1-βD·BF$_4$** (93 atom %D) with tetrabutylammonium chloride (26 mg, 0.092 mmol) was carried out in dichloromethane (3 mL) at room temperature for 5h. Analytical GC with undecane as the internal standard showed the formation of **3** and (*Z*)-**2a** in 18 and 80% yields, respectively. The ^{1}H NMR and GC-MS showed that the **3** obtained was deuterated at the 1 position by about 7 atom % and the (*Z*)-**2a** at the 2 position by 95 atom %.

Reaction of 1-αD with Tetrabutylammonium Fluoride. Reaction of 26 mg (0.060 mmol) of **1-αD·BF$_4$** (97 atom %D) with tetrabutylammonium fluoride trihydrate (19 mg, 0.060 mmol) was carried out in dichloromethane (3 mL) at room temperature for 10 h. Analytical GC with undecane as the internal standard showed the formation of **3** in 86% yield. No deuterium incorporation was detected in the **3** obtained either by GC-MS or ^{1}H NMR.

Reaction of 1-βD with Tetrabutylammonium Fluoride. Reaction of 11 mg (0.026 mmol) of **1-βD·BF$_4$** (93 atom %D) with tetrabutylammonium fluoride trihydrate (8 mg, 0.026 mmol) was carried out in dichloromethane (1.5 mL) at room temperature for 10 h. Analytical GC with undecane as the internal standard showed the formation of **3** in 93% yield. The ^{1}H NMR and GC-MS showed that the **3** obtained contained 95 atom % of deuterium at the 1 position.

Decomposition of (*Z*)-1 in Acetic Acid. A solution of (*Z*)-**1·ClO$_4$** (51 mg, 0.11 mmol) in acetic acid (23 mL) was stirred at 17 °C for 2 h under nitrogen. After addition of water, the mixture was extracted with hexane 3 times. The combined hexane layer was washed with water and dried over Na_2SO_4. Analytical GC showed the formation of **3** (76%) and **4** (76%).

Reaction of (*Z*)-1 in the Presence of Tetrabutylammonium Chloride. To a stirred solution of (*Z*)-**1·ClO$_4$** (9 mg, 0.02 mmol) in dichloromethane (1.5 mL) was added tetrabutylammonium chloride (58 mg, 0.21 mmol) at 0 °C. The mixture was stirred for 0.5 h at 0 °C. After addition of water, the mixture was extracted with pentane. Analytical GC showed the formation of **3** (98%) and **4** (100%).

Reaction of 1 with Tetrabutylammonium Chloride in TFA. About 10 mg, of **1** or **1-αD** (97 atom %D) was dissolved in 5 mL of TFA containing 0.05 mol dm^{-3} Bu_4NCl (or 10 mL of TFA at [Bu_4NCl]=0.01 mol dm^{-3}) and kept at 50 °C for 50 h. The products were extracted with pentane as described above. The residues after evaporation of the solvent under vacuum were dissolved in $CDCl_3$, and analytical GC and ^{1}H NMR (500 MHz) measurements were performed on this solution. The ratios of (*Z*)-**2a**/(*E*)-**2a** were

essentially the same for the products from **1** and **1-αD** and the agreements were satisfactory between the GC and NMR determinations: (*Z*)-**2a**/(*E*)-**2a**=85/15 and 10/90 at [Bu_4NCl]=0.05 and 0.01 mol dm^{-3}, respectively. In the NMR spectra of the products from **1-αD**, the ^1H signal for the 1 position (1-H) was hardly recognized for the minor isomer of **2a** but that for the major isomer was 3.0—3.5% of the intensity of 2-H (Fig. 2). ^1H NMR ($CDCl_3$): (*Z*)-**2a-αD** δ=5.75 (t, *J*=7.0 Hz), (*E*)-**2a-αD** δ=5.89 (tt, *J*=7.0, 2 Hz).

Initial Absorbance. To 3.0 mL of the reaction solution equilibrated at 25 °C in a quartz cuvette inserted in the cell compartment of the spectrophotometer, the stock solution of **1·BF_4** in acetonitrile or chloroform (30 μL) was added from a microsyringe. After rapid mixing, the absorbance at the specified wavelength was recorded for a few minutes and extrapolated to the time of addition on a chart of an analog recorder.

Kinetic Measurements. Reaction rates were measured by monitoring the decrease in absorbance usually at 25 °C as described previously.[31] A high-pressure optical vessel similar to the one described in the literature[41] was used in the pressure effect study.

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