Solvolysis of 1-Decenyl(phenyl)iodonium Tetrafluoroborate: Mechanisms of Nucleophilic Substitution and Elimination

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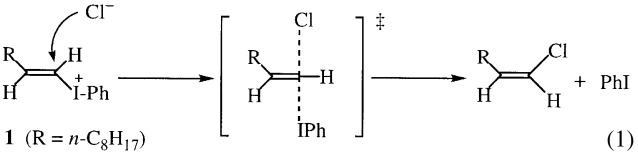
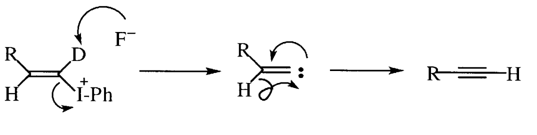
(Received September 25, 2000)

Solvolysis of (*E*)-1-decenyl(phenyl)iodonium tetrafluoroborate **1** was carried out in some alcohols, acetic acid, and mixed aqueous alcoholic solvents at 50–60 °C and the effects of added carboxylates and other salts were also examined in methanol. Reaction products include enol derivatives (substitution) and 1-decyne (elimination) as well as iodobenzene. Rates for the solvolysis increase with increasing nucleophilicity of the solvent but have no correlation with the solvent ionizing power. The substitution occurs mostly via inversion of configuration, and is concluded to follow the in-plane S_N2 mechanism with a minor concomitant out-of-plane S_N2 pathway. The reactions with the deuterated substrates show that stronger bases of pK_a of the conjugate acid > 3 induce exclusively α-elimination of **1** in methanol. However, both α- and β-elimination occur in neutral methanol in a ratio of about 3/1 besides the substitution. Mechanisms for these reactions are proposed.

Vinylic iodonium salts show a wide variety of reactivities toward nucleophiles/bases[1] due to the high nucleofugality[1,2] and strongly electron-withdrawing nature of the iodonio group. The reactions include formation of vinylic cation (S_N1 and E1), in-plane (σ^*) and out-of-plane (π^*) S_N2 reaction, and α-elimination (αE) and β-elimination (βE). (*E*)-1-Decenyl(phenyl)iodonium (**1**) tetrafluoroborate is a typical salt that undergoes the in-plane S_N2 reaction with chloride ion to give a completely inverted 1-chloro-1-alkene (Eq. 1), while the reaction with fluoride ion leads to αE (Eq. 2).[3] The αE of primary 1-alkenyliodonium salts occurs quite easily to afford a free alkylidenecarbene intermediate which provides an alkyne (by 1,2-shift) or insertion products.[4] This reaction was initially carried out with a strong base such as potassium *t*-butoxide and then with a milder one, triethylamine. Fluoride ion was also found to be basic enough (pK_a of the conjugate acid = 3.17) to effect exclusively the α-elimination.[3] We have recently found that even neutral methanol can induce partially the αE of 2-phenylvinyl-[5] or 2,2-dialkylvinyliodonium tetrafluoroborate[6] during the methanolysis reactions and that carboxylates are generally basic enough to effect exclusively the αE of 1-alkenyliodonium salts.



1 (R = n-C_8H_{17}) (1)

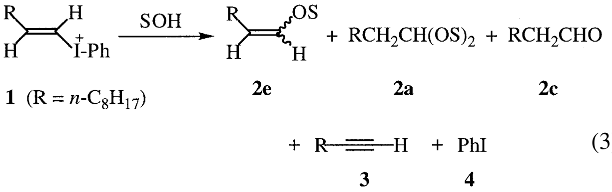


(2)

In the present paper are presented results of studies of reactions of 1-decenyliodonium salt **1** in various alcoholic and aqueous solutions in the absence or presence of a base/nucleophile of changing reactivity (pK_a). The reactions were found to take place through αE and βE as well as S_N2 pathways, and no sign of formation of the primary vinylic cation was detected.

Results

Products. Reactions of (*E*)-1-decenyl(phenyl)iodonium (**1**) tetrafluoroborate were carried out in some alcohols, acetic acid, and mixed aqueous alcoholic solvents at 50–60 °C. Reaction products include those of substitution **2** and elimination **3** as well as iodobenzene **4** (Eq. 3). The substitution products in SOH are enol ether (or acetate) **2e**(S), acetal **2a**(S), and aldehyde **2c**. The acetal **2a**(S) is formed by addition of the alcohol (SOH) to the initial product **2e**(S), catalyzed by the acid HBF_4 generated during the reaction, and **2c** is a product in aqueous solution or that of acid-catalyzed hydrolysis of **2e**(S) and **2a**(S). Yields of these products were determined by gas chromatography with tetradecane as an internal standard and are summarized in Table 1. The enol products **2e**(S) obtained in methanol and ethanol are mostly in a *Z* form but a small amount of the *E* isomer was also detected. The product of acetolysis is exclusively (*Z*)-1-acetoxy-1-decene (**2e**(Ac)). 1-Decyne (**3**) may be produced either by αE or βE.



1 (R = n-C_8H_{17}) **2e** **2a** **2c** **3** **4** (3)

Table 1. Reaction Products of Solvolysis of **1** in Various Solvents at 50 °C

		Product yield/%					
Solvent	Time/h	**2e** (Z/E)$^{a)}$	**2a**	**2c**	**3**	**4**	$s/e^{b)}$
MeOH	5	24 (97.7/2.3)	9.0	2.0	12.6	48	74/26
50% MeOH–H_2O	20	0	0	79	6.3	81	92.6/7.4
EtOH	6	23 (99.4/0.6)	14	4.0	12	55	77/23
60% EtOH–H_2O	15	0	0	67	7.7	93	90/10
AcOH	28	51 (100/0)	0	0	0	43	100/0
HCO_2H	52	0	0	33	0	24	100/0

a) Isomeric ratio. b) Ratio of substitution and elimination products.

Effects of Additives. Effects of some additives including bases/nucleophiles were examined in methanol solution, and product yields obtained at 50 °C are summarized in Table 2. A small amount of acid or a neutral salt, tetrabutylammonium perchlorate, diminishes the formation of the elimination product (from ca. 25% of elimination to 10%) as is the case for the reaction in aqueous alcoholic solution compared with that in wholly alcoholic solutions. These results must be due to the decrease in medium basicity. Addition of a base greatly accelerates the reaction; the products are mostly those of elimination, **3** and **4**. Added bases of pK_a (of the conjugate acid) greater than 3 induce exclusively elimination. Those bases include pyridines, carboxylates, and typical nucleophiles like cyanide, azide, and nitrite. In these cases, the basic character overwhelms the nucleophilic reactivity to lead to α-elimination (see below). Bases of pK_a lower than 3 afford some product of substitution by methanol. Even trifluoroacetate (pK_a = 0.23) increases considerably the fraction of elimination. Effects of the base become sluggish only when the pK_a is less than –1.

Labeling Experiments. In order to examine the mode of elimination, αE or βE, the deuterium content of product **3** obtained from α- and β-deuterated substrates, **1-αD** and **1-βD**, were evaluated from the ^{1}H NMR spectra of the product mixture as summarized in Table 3. The amount of remaining 1-H (1.93 ppm) of **3** was compared with the integrated area for the 3-methylene signal (2.18 ppm). Enol ether product **2e** was converted to acetal **2a** prior to this determination, because the 3-methlene signal of **2e** overlaps with that of 1-H of **3** in ^{1}H NMR spectra. The deuterated product RC≡C–D may undergo isotope exchange with the solvent proton under the reaction conditions. This possibility was examined with the authentic sample of [1-^{2}H]-1-decyne, and it was found that no appreciable D/H exchange occurred in the reaction time under any of the reaction conditions employed. Correction for the D/H exchange of the product is not necessary. Thus, the ^{1}H NMR spectra of the product mixtures obtained in the presence of sodium acetate (0.05 mol dm^{-3}) show that **3** was formed with complete removal of the α deuterium from **1-αD** but with the total retention of the D of **1-βD**. That is, the reaction involved is essentially αE

Table 3. Remaining Deuterium Atom% in 1-Decyne **3** Formed from the Deuterated Substrates **1-αD** and **1-βD** and the Ratio of α- and β-Elimination$^{a)}$

Additive	Reaction	Atom% D in **3** from		
(conc/mol dm^{-3})	Time/h	**1-αD** (% αE)$^{b)}$	**1-βD** (% αE)$^{b)}$	αE/βE$^{c)}$
None	8	~35 (64)	~80 (86)	3/1
CH_3CO_2Na (0.05)	0.1	0 (100)	97 (100)	1/0
CF_3CO_2Na (0.05)	5	29 (70)	84 (90)	4.5/1

a) Reaction in methanol at 50 °C. b) The percentage fraction of α-elimination corrected for the deuterium purity of the substrate. c) The ratio of α- to β-eliminarion corrected for the primary isotope effects assuming k_H/k_D = 2.

Table 2. Product Distribution in the Reaction of **1** in Methanol in the Presence of Various Additive$^{a)}$

Additive			Product yield/%					
(Concn/mol dm^{-3})	p$K_a$$^{b)}$	Time/h	**2e** (Z/E)$^{c)}$	**2a**	**2c**	**3**	**4**	$s/e^{d)}$
CF_3CO_2H (0.001)		4	9.4 (94.6/5.4)	27	1.0	3.7	43	90/10
Bu_4NClO_4 (0.1)	−10.00	4	25 (97.8/2.2)	3.0	0	3.4	34	89/11
Na_2CO_3 (0.04)	10.33	4	0	0	0	72	69	0/100
KCN (0.05)	9.40	4	0	0	0	74	79	0/100
2,6-Lutidine (0.03)	6.77	4	0	0	0	96	87	0/100
Pyridine (0.1)	5.17	1	0	0	0	87	84	0/100
CH_3CO_2Na (0.05)$^{e)}$	4.76	0.1	0	0	0	71	64	0/100
Bu_4NN_3 (0.01)	4.72	4	0	0	0	88	81	0/100
HCO_2Na (0.05)	3.77	4	0	0	0	80	74	0/100
$NaNO_2$ (0.1)	3.29	6	0	0	0	81	77	0/100
Bu_4NF (0.05)	3.17	5	0	0	0	90	86	0/100
$ClCH_2CO_2Na$ (0.05)$^{e)}$	2.86	3	2.1 (33/67)	0.1	0	69	63	3/97
NaH_2PO_4 (satd)	2.12	6	1.5 (72/28)	0	0.13	82	62	2/98
Cl_2CHCO_2Na (0.05)	1.35	4	4.5 (98.9/1.1)	0.2	3.0	68	58	10/90
F_3CCO_2Na (0.05)	0.23	6	23 (97/3)	12	12	33	76	58/42
$NaClO_3$ (0.1)	−1.0	6	10 (95.4/4.6)	18	1.7	7.6	58	80/20
$NaNO_3$ (0.1)	−1.3	6	15 (89/11)	14	3.7	9.5	72	78/22
Bu_4NCl (0.05)$^{f)}$	−7	1	60$^{g)}$ (100/0)	1.6	0	15	52	80/20

a) Reaction at 50 °C unless noted otherwise. b) pK_a of the conjugate acid of the added base. c) Isomeric ratio. d) Ratio of substitution and elimination products. e) Reaction at 25 °C. f) Data taken from ref. 3b. g) 1-Chloro-1-decene. 0.3% of (Z)-**2e**(Me) was also detected.

in the presence of acetate. In contrast, the acetylene **3** obtained in neutral methanol or in the presence of sodium trifluoroacetate (0.05 mol dm^{-3}) contains a considerable amount of D both from **1-αD** and **1-βD**, suggesting that both αE and βE occur under these conditions. In these determinations, the precision of values was poor for the reaction in neutral methanol due to the low yield of **3**, but the isotope distribution pattern is undoubtedly similar to that observed in the presence of trifluoroacetate but not to that with acetate. These results are compatible with the mass spectral data of the same products. Since the MS of **3** does not show a clear molecular peak, evaluation of the deuterium contents from the MS is not accurate. Nonetheless, the relative intensities of the fragment peaks at *m*/*z* 109 and 110 (M – C_2H_5) are consistent with the results obtained from ^{1}H NMR spectra.

Kinetics. Rates of solvolysis were measured spectrophotometrically in various solvents at 60 °C. The reaction follows the pseudo-first-order kinetics and the observed rate constants k_{obsd} are summarized in Table 4. Reaction rates for elimination were also determined as a function of concentration of added base. The elimination reaction is very rapid, and kinetics were carried out at 25 °C to follow at a reasonable rate. The rate constants are very much dependent on the solutions prepared, and we suspected effects of a trace amount of contaminating heavy metals.[7] We obtained reasonably good reproducible data when the solutions were treated with the Chelex 100 resin supplied from Bio-Rad. The rate constant obtained after this treatment was usually several times smaller than those obtained without treatments. However, product distributions were not affected by this treatment. The observed pseudo-first-order rate constants are plotted against concentrations of carboxylate in Fig. 1 for some typical carboxylates. Concentration dependences are obviously not simple and suggest some complexity of the mechanism. Kinetic isotope effects were determined, though not precisely, with **1-αD** and **1-βD** for the reactions in methanol in the presence of acetate, formate, and chloroacetate at 0.05 mol dm^{-3} to give k_H/k_D = 1.6–2.1 for **1-αD** and k_H/k_D = 1.0–1.2 for **1-βD**.

Table 4. Observed Rate Constants for the Solvolysis of **1** in Various Solvents at 60 °C

Solvent	$10^5k_{obsd}/s^{-1}$
EtOH	23.4
MeOH	15.0
H_2O	4.65
TFE	0.38
80E[a)]	15.7
60E[a)]	11.5
40E[a)]	8.26
20E[a)]	5.92
80ET[b)]	18.0
60ET[b)]	10.5
40ET[b)]	4.23
20ET[b)]	1.59
90Tw[c)]	1.32
70Tw[c)]	2.67
50Tw[c)]	3.60

a) Aqueous ethanol giving vol % ethanol in number. b) Ethanol-TFE mixture giving vol % ethanol in number. c) Aqueous TFE giving weight % of TFE in number.

Discussion

Substitution. Nucleophilic substitution is the main reaction of solvolysis of **1** in neutral media, as values *s*/*e* in the last column of Table 1 show, and the primary products **2e** are composed exclusively or mostly of the *Z* isomer, the inverted product. We showed previously that a substitution reaction of **1** with halide ions, Cl^-, Br^-, and I^-, occurs completely by inversion of configuration[3] and we concluded that the reaction proceeds through nucleophilic attack toward the σ^* orbital of the substrate,[8] i. e., the in-plane S_N2 mechanism (Eq. 1).[9] What does it mean that a small portion of the retained product (*E*)-**2e** is formed in methanol or ethanol? Three possibilities are conceivable: (1) An ion-pair mechanism involving formation of a primary vinylic cation-molecule pair followed by nucleophilic trapping largely from the opposite side of the paired leaving group, iodobenzene, to give the inverted product but also leading to the retained product as a minor one. (2) Concurrent bimolecular nucleophilic substitutions (S_N2) via in-plane (inversion) and out-of-plane (retention) routes. (3) Largely in-plane S_N2 pathway but concomitant formation of the retained product via solvent insertion to the alkylidenecarbene generated by α-elimination.

The third α-elimination-insertion route was observed for the formation of the stereo-divergent product in substitution of a 2,2-dialkylvinyliodonium sustrate,[6] but the 2-monoalkyl derivative **1** gives exclusively the acetylenic product **3** when the carbene is generated in the presence of a base (see below). The 1,2-hydride shift of the alkylidenecarbene to give alkyne is much faster than the alcoholic insertion, and the third possibility is ruled out.

There is little definitive evidence to exclude the first possibility, which suggests formation of the primary vinylic cation. However, if this cation were formed, 1,2-hydride shift to afford a more stable secondary vinylic cation (Eq. 4) should have occurred without barrier as theoretical calculations suggest.[6] Thus, the vinylic cation route (S_N1) is unlikely.

(4)

The second possibility that the S_N2 pathways occur mainly by the in-plane attack toward the σ^* orbital with a concomitant out-of-plane attack toward the π^* orbital is most probable. These two S_N2 pathways are both demonstrated theoretically to be feasible.[8,10–12] A similar concurrent S_N2 mechanism has recently been proposed for the reaction of 2,2-dialkylvinyliodonium salt with halide nucleophiles.[13,14]

Kinetic results are also compatible with a rate-determining nucleophilic reaction. The observed rate constants k_{obsd} for the solvolysis are logarithmically plotted against the solvent ionizing power Y_{OTs}[15] and the solvent nucleophilicity N_T[16] in Fig. 2. The former plot is largely scattered without showing any tendency but the latter plot against nucleophilicity shows a reasonable linear dependence; such a result implies a nucleophilic

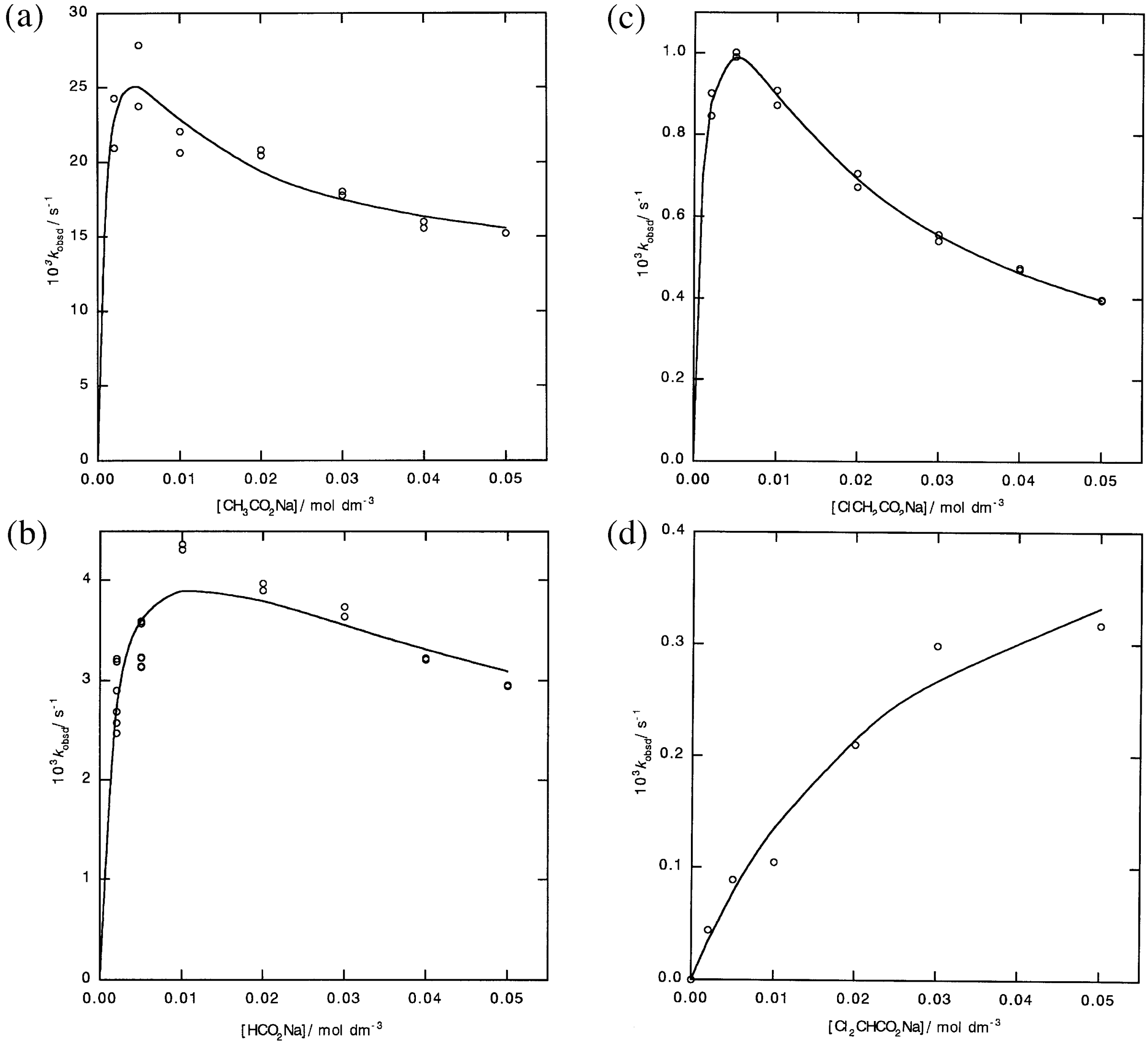


Fig. 1. Observed rate constants for the reaction of **1** in methanol in the presence of varying concentrations of sodium carboxylates measured at 25 °C and the ionic strength of 0.5 maintained with Bu_4NClO_4. (a) Acetate, (b) formate, (c) chloroacetate, and (d) dichloroacetate.

process in the rate-determining step. These kinetic observations are in conformity to the S_N2 mechanism but not to the S_N1-type ion-pair mechanism. Rate constants for the S_N1-type solvolysis of a vinylic iodonium salt were found to depend on Y_{OTs}[2] if the slope is very small.

Elimination. The elimination product **3** can be derived either via αE or βE. It was previously found that fluoride and strong bases induce αE of 1-alkenyliodonium salts[3,4] while other halide ions (very weak bases) effect βE in addition to S_N2 reaction.[3,9] 2,2-Dialkylvinyl- and 2-phenylvinyliodonium salts were found to undergo partially αE even in neutral methanol solution.[5,6] We now examined a mode of elimination of **1** under the present conditions using the deuterated substrates **1-αD** and **1-βD**. The results summarized in Table 3 clearly show that acetate exclusively induces αE of **1-αD** and **1-βD**, while both αE and βE occur under the other two conditions. To evaluate the ratio of αE/βE for normal substrate **1**, it is necessary to correct for primary kinetic isotope effects. We observed the isotope effects of $k_H/k_D \approx 2$ for the reaction of **1-αD** in the presence of acetate, formate and chloroacetate in methanol but almost no effects for the reaction of **1-βD**. The isotope effects of $k_H/k_D = 2$ is assumed both for **1-αD** on αE and for **1-βD** on βE.[17] These corrections give a ratio αE/αE of about 3/1 in neutral methanol and about 4.5/1 in the presence of trifluoroacetate (Table 3).

The αE no doubt occurs readily due to the relatively high acidity of the α hydrogen of **1**. The βE can compete with the αE only when the base is very weak, which can coordinate to the iodine of **1** and can participate in the intramolecular elimination of the less acidic β hydrogen as suggested for the chloride-induced βE.[3,9] Thus, carboxylate-induced elimination may be illustrated as in Scheme 1. Here, the coordination of the carboxylate to the iodine reversibly forms λ^3-iodane (**I$_1$**). The direct reaction of carboxylate at the α hydrogen leads to αE, while the intramolecular reaction of the coordinated carboxylate with the β hydrogen within **I$_1$** results in βE. This can occur

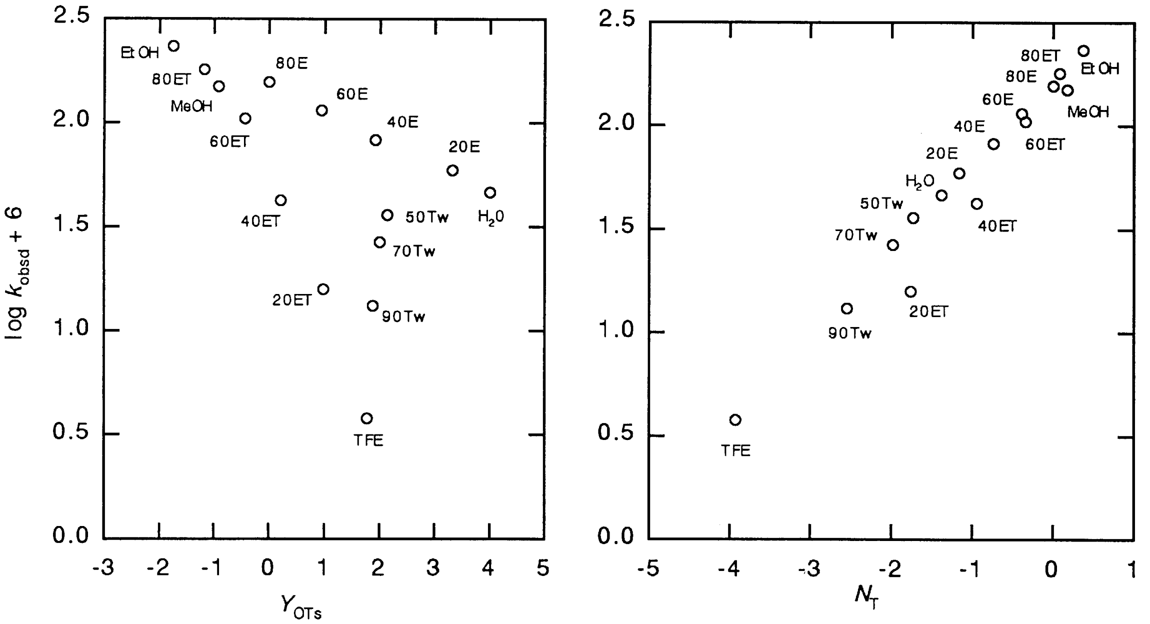
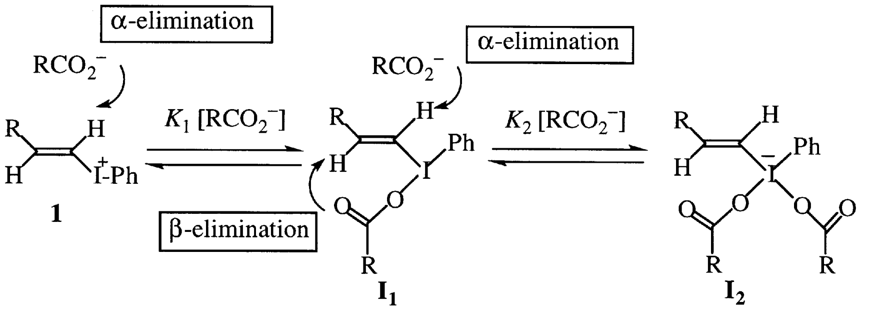


Fig. 2. Observed rate constants for solvolysis of **1** in various solvents logarithmically plotted against the ionizing power Y_{OTs} and the nucleophilicity N_T of the solvents.



Scheme 1.

with a very weak carboxylate like trifluoroacetate that cannot effectively react with the acidic α hydrogen. These considerations suggest that the βE induced in neutral methanol occurs from coordination of methanol on the iodine of **1**.

Rate constants for elimination reaction of **1** in methanol show unexpected concentration dependence on the base (Figs. 1a–1d). The curvatures for acetate, formate, and chloroacetate (Figs. 1a–1c) are similar to those observed for β-elimination of (*E*)-3,3-dimethyl-1-butenyl(phenyl)iodonium salts by chloride[9] or for ligand-coupling substitution reaction of (*Z*)-2-bromo-1-decenyl(phenyl)iodonium salt with bromide ion,[18] where the addition intermediates, λ^3-iodane ($\mathbf{I_1}$) and iodate ($\mathbf{I_2}$), play an important role. The reaction scheme compatible with the kinetic results is shown in Scheme 1. Coordination of the base on the iodine of the substrate reduces the acidity of α hydrogen to retard the αE, while it makes an intramolecular β-elimination feasible. The decrease in rate at higher concentration of carboxylate implies that a dicoodinated intermediate $\mathbf{I_2}$ is unreactive. Although reliable kinetic simulations of the curves according to the reaction scheme were difficult because of experimental uncertainties of the kinetic measurements, treatments similar to those for the halide reactions[3b,9,13,18] give solid curves in Fig. 1 with unreliable kinetic parameters which are not recorded here. The apparent curvature for dichloroacetate (Fig. 1d) is different from those for more basic carboxylates. However, the saturation tendency of the plot suggests formation of an intermediate complex in equilibrium, and the reaction may be explained by the same reaction scheme as that for other carboxylates. This weak base has low reactivity and low coodination ability to the iodine, and no contribution from the dicoordinated intermediate $\mathbf{I_2}$ that reduces the apparent rate has been observed yet.

In conclusion, substitution in solvolysis of **1** in methanol and ethanol occurs mostly via the in-plane S$_N$2 mechanism with a minor concomitant out-of-plane route. Elimination in neutral methanol was found to take place both via α- and β-elimination routes. Bases with pK_a > 3 induce exclusively α-elimination, while very weak bases like trifluoroacetate and chloride promote the β-elimination of **1**.

Experimental

Experimental procedures are the same as described previously for treatments of materials[3b] and for solvolysis.[2]

Materials. The samples of iodonium salt **1** and deuterated ones, **1-αD** (97 atom% D) and **1-βD** (93 atom% D) prepared previously[3b] and stored at –20 °C were used. Iodobenzene (**4**), 1-decyne (**3**), and decanal (**2c**) were obtained commercially. Methanol was distilled before use. Salts and other organic additives were used as received.

E/*Z* mixtures of 1-methoxy- and 1-ethoxy-1-decene (**2e**(Me) and **2e**(Et)) were prepared by phosphoric acid-catalyzed dealkoxylation of the corresponding 1,1-dialkoxydecane (**2a**)[19] which were obtained from **2c** by a standard method.[20]

(*Z*)-1-Acetoxy-1-decene (**2e**(Ac)) was isolated from the acetolysis products of **1** by preparative gas chromatography. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.3 (m, 12H), 1.5 (m, 2H), 2.14 (s, 3H), 4.86 (dt, $J = 6.4$, 8.5 Hz, 1H), 6.98 (dt, $J = 6.4$, 1.6 Hz, 1H). From the coupling constant of 6.4 Hz for olefinic protons, the geometry is assigned as *Z* compared with $J_{\text{cis}} = 6.3$ and $J_{\text{trans}} = 12.4$ Hz for 1-methoxy-1-decene. MS *m*/*z* (relative intensity) 198 (M^+; 10.5), 156 (9.5), 138 (25), 110 (17), 96 (41), 82 (49), 68 (20), 57 (38), 43 (100). HRMS Found: *m*/*z* 198.1615. Calcd for $C_{12}H_{22}O_2$ M, 198.1620.

[1-^{2}H]-1-Decyne (97 atom% D) was obtained by quenching the lithium acetylide of **3** with D_2O.

Product Determination. Reaction products were extracted with pentane and determined by gas chromatography, as described previously.[2,3b]

The products from the deuterated substrates were obtained in a larger scale and analyzed by ^{1}H NMR spectroscopy at 400 MHz (JEOL EXcalibur 400) and GC MS (JEOL JMS-DX303HF). A sample of **1-αD** or **1-βD** (ca. 10 mg) was dissolved in a methanol solution (5 mL) in a Pyrex tube, and the tube was immediately immersed in a water bath controlled at 50 °C. After the specified reaction time, the products were extracted with pentane and washed with water. The product mixture obtained in the acetate solution was directly subjected to analysis. Those obtained in neutral methanol and the trifluoroacetate solution were treated with methanol containing 0.05 mol dm^{-3} trifluoroacetic acid for 5 h at room temperature to convert **2e** to **2a**. The products were extracted again with pentane, washed with water, and analyzed.

Kinetic Measurements. Reaction rates were determined by monitoring the decrease in UV absorbance (240 nm) as described previously[2,6] at 60 (± 0.1) °C for solvolysis (without added base) and at 25 (± 0.1) °C in the presence of carboxylates. In the absence of added salts, freshly distilled solvents containing 10^{-3} mol dm^{-3} of trifluoroacetic acid were used for kinetic runs. Various solutions of carboxylates were prepared at 0.05 mol dm^{-3} by weighing and were diluted to the required concentrations with a 0.05 mol dm^{-3} solution of Bu_4NClO_4. These solutions were treated with the Chelex 100 resin (Bio-Rad) before use to remove heavy metal ions.

We thank Professor Masahito Ochiai of the University of Tokushima for the gift of the iodonium samples and for helpful discussions. We are also grateful to Dr. Morifumi Fujita (Himeji Institute of Technology) for the measurements of NMR spectra and to Kazuo Fukuda (Osaka University) for MS measurements.

References

1 a) M. Ochiai, in "Chemistry of Hypervalent Compounds," ed by K.-y. Akiba, Wiley-VCH, New York (1999), Chap. 12. b) T. Okuyama, *Rev. Heteroatom Chem.*, **21**, 257 (1999).

2 T. Okuyama, T. Takino, T. Sueda, and M. Ochiai, *J. Am. Chem. Soc.*, **117**, 3360 (1995).

3 a) M. Ochiai, K. Oshima, and Y. Masaki, *J. Am. Chem. Soc.*, **113**, 7059 (1991). b) T. Okuyama, T. Takino, K. Sato, K. Oshima, S. Imamura, H. Yamataka, T. Asano, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **71**, 243 (1998).

4 a) M. Ochiai, Y. Takaoka, and Y. Nagao, *J. Am. Chem. Soc.*, **110**, 6565 (1988). b) M. Ochiai, M. Kunishima, S. Tani, and Y. Nagao, *J. Am. Chem. Soc.*, **113**, 3135 (1991). c) M. Ochiai, K. Uemura, and Y. Masaki, *J. Am. Chem. Soc.*, **115**, 2528 (1993). d) M. Ochiai, T. Sueda, K. Uemura, and Y. Masaki, *J. Org. Chem.*, **60**, 2624 (1995).

5 T. Okuyama, Y. Ishida, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **72**, 163 (1999).

6 T. Okuyama, H. Yamataka, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **72**, 2761 (1999).

7 M. C. Caserio, D. L. Glusker, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 336 (1959); F. M. Beringer, E. M. Gindler, M. Rapoport, and R. J. Taylor, *J. Am. Chem. Soc.*, **81**, 351 (1959).

8 T. Okuyama and H. Yamataka, *Can. J. Chem.*, **77**, 577 (1999).

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

10 M. N. Glukhovtsev, A. Pross, and L. Radom, *J. Am. Chem. Soc.*, **116**, 5961 (1994).

11 V. Lucchini, G. Modena, and L. Pasquato, *J. Am. Chem. Soc.*, **117**, 2297 (1995).

12 C. K. Kim, K. H. Hyun, C. K. Kim, and I. Lee, *J. Am. Chem. Soc.*, **122**, 2294 (2000).

13 T. Okuyama, K. Sato, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **73**, 2341 (2000).

14 The transition state for the out-of-plane S_N2 pathway is the same as that for the ligand-coupling mechanism occurring within an adduct of the substrate with the nucleophile (λ^3-iodane).[8] The former is bimolecular while the latter is unimolecular. When there is no evidence for formation of the adduct, the term "out-of-plane S_N2" is more general, since the overall reaction is kinetically of the second order.

15 F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976); T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.*, **17**, 121 (1990).

16 D. N. Kevill and S. W. Anderson, *J. Org. Chem.*, **56**, 1845 (1991); D. N. Kevill, in "Advances in Quantitative Structure-Property Relationships," ed by M. Charton, JAI Press, Greenwich, Connecticut (1996), Vol. 1, pp. 81–115.

17 The β deuterium isotope effects on βE induced by halide ions were evaluated to be $k_H/k_D \approx 3$,[3b] but this value gives inconsistent results from the data obtained with **1-αD** and **1-βD**.

18 T. Okuyama, T. Takino, K. Sato, and M. Ochiai, *Chem. Lett.*, **1997**, 955.

19 (a) T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Am. Chem. Soc.*, **89**, 5826 (1967). (b) E. Taskinen and P. Liukas, *Acta Chem. Scand.*, **B28**, 114 (1974).

20 R. N. Icke, C. E. Redemann, B. B. Wisegarver, and G. A. Alles, *Org. Syn.* Coll. Vol. 3, 644 (1955).