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In-Plane Vinylic S_N2 Substitution and Intramolecular β Elimination of β-Alkylvinyl(chloro)-λ^3-iodanes

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Abstract: The reactions of four (*E*)-β-alkylvinyl(phenyl)iodonium salts with chloride ion were examined in acetonitrile and in several other solvents at 25 °C. The β-methyl-, β-octyl-, and β-isopropyl-substituted iodonium salts undergo competitive bimolecular nucleophilic substitution to form the corresponding (*Z*)-1-chloro-1-alkene with inversion of configuration at the vinylic carbon and elimination to form the 1-alkyne. The β-*tert*-butyl-substituted iodonium salt affords only the products of the elimination reaction. The UV absorption spectra of the reactants show the rapid coversion of chloride and iodonium ions to an equilibrium mixture of the corresponding chloro-λ^3-iodane, with an association constant of 5600−7600 mol^{-1} dm^3. A kinetic analysis shows that most of the substitution and elimination products form from reaction of the λ^3-iodane. Evidence is presented that the substitution reaction proceeds by a concerted bimolecular S_N2 mechanism and that the elimination reaction proceeds by a unimolecular reaction mechanism with intramolecular transfer of the β-proton to the leaving group.

Nucleophilic substitution reactions at vinylic carbon have been shown to proceed by several different reaction pathways, depending upon the substrate,[1] but substitution by an in-plane S_N2 reaction mechanism is considered to be highly improbable.[2] In fact, the possibility of concerted bimolecular nucleophilic displacement at vinylic carbon has been excluded by at least one elementary textbook in organic chemistry.[2b] Nucleophilic vinylic substitution with complete inversion of configuration has rarely been observed, in contrast to this well-established stereochemistry for S_N2 displacement reactions at saturated carbon. The predominant, but not exclusive, inversion of configuration observed for the products of solvolysis of some alkenyl triflates is consistent with an ion-pair reaction mechanism, where the dissociation of the initially formed ion pair is slow compared with the trapping of the vinylic carbocation by backside addition of solvent.[3]

We recently observed that 1-decenyliodonium salts undergo nucleophilic substitution by halide ions with exclusive inversion of configuration.[4] To the best of our knowledge, the only other reported example of bimolecular vinylic substitution occurring with complete inversion of configuration is nucleophilic reaction of thiolate ions with 1,2-dibromo-1,2-difluoroethene.[5] An intramolecular methanide transfer at di-*tert*-butylthiirenium ion was classified as an in-plane nucleophilic substitution at the vinylic carbon.[6] These results prompted theoretical calculations which were consistent with the proposal that in-plane concerted bimolecular substitution is a viable mechanism for nucleophilic subsitution at vinylic carbon.[7] Despite this experimental and theoretical evidence for in-plane concerted S_N2 reactions at vinylic carbon, there is still considerable skepticism in the organic community about the viability of this reaction mechanism.

Nucleophilic substitution with inversion of the configuration of a vinyliodonium salt has been concluded to occur by a concerted S_N2 reaction mechanism,[4] because the experimental results exclude the possibility of formation of an ionic reaction intermediate.[8] To strengthen and extend this conclusion, we have examined the kinetics of the reactions of some β-alkyl-substituted vinyliodonium salts (**1**) with chloride ion. When the β substituent is a primary or secondary alkyl group, both substitution and elimination reactions are observed to give the corresponding (*Z*)-1-chloro-1-alkene (**3**) or 1-alkyne (**4**) and iodobenzene (**5**). By contrast, the β-*tert*-butyl group completely inhibits the reaction by the substitution pathway so that the reaction of **1d** affords only the elimination product (**4d**). Kinetic analyses of the reactions of **1** show that the major reaction pathway is through a chloro-λ^3-iodane reaction intermediate (**2**) and that the direct reaction of the iodonium ion **1** is a minor pathway. Both **1** and **2** undergo concerted bimolecular nucleophilic substitution by chloride ion while **2** also undergoes a unimolecular (intramolecular) β-elimination of iodobenzene and

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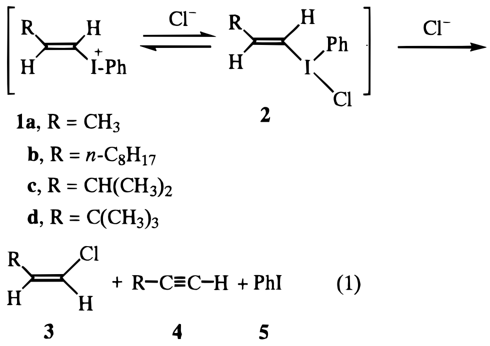
Table 1. Product Ratios and Observed Rate Constants Obtained at $[Cl^-] = 0.01$ mol dm^{-3} [a]

substrate β-R	**1a** CH_3	**1b** n-C_8H_{17}	**1c** i-Pr	**1d** t-Bu
3/**4**	72/28	54/46	41/59	0/100
$10^4\ k_{obsd}/s^{-1}$	2.61	5.32	5.51	7.21
$10^4\ k_s/s^{-1}$	1.88	2.87	2.26	0
$10^4\ k_e/s^{-1}$	0.73	2.45	3.25	7.21

[a] At 25 °C in acetonitrile or acetonitrile-d_3 without adjusting the ionic strength.

HCl. The results of this work provide strong support for a concerted in-plane S_N2 pathway for vinylic nucleophilic substitution reactions.



1a, R = CH_3
b, R = n-C_8H_{17}
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$

2

3 **4** **5**

(1)

Results

Reaction Products. The reactions of (E)-1-decenyl(phenyl)iodonium salt **1b** with halide ions were previously examined under various conditions and the product yields were determined by gas chromatographic analyses.[4] (Z)-1-Halo-1-decene (**3b**) and 1-decyne (**4b**) are the major products of the reaction of all halide ions except fluoride ion. The ratio of the yields of the products of nucleophilic substitution and elimination, [**3b**]/[**4b**], increases with increasing concentrations of halide ion. Similar results were obtained in studies of the reactions of the β-methyl (**1a**) and the β-isopropyl derivatives (**1c**). Because of the low boiling points of the products of these substitution and elimination reactions, they were examined in sealed NMR tubes in a solution of acetonitrile-d_3 which contained 0.01 mol dm^{-3} tetramethylammonium chloride at 25 °C. The ^{1}H NMR spectra of the reaction mixtures were recorded directly. The ratios of the yields of **3** and **4** were determined from the integral intensities of these compounds and are summarized in Table 1. Essentially all of the nucleophilic substitution reaction is with inversion of configuration at carbon to give **3** with the (Z) configuration and there is no detectable formation of the (E) isomer of **3**. These reactions were usually carried out with the tetrabutylammonium salt of chloride ion. However, since the butyl groups of this salt interfered with our in-situ NMR analysis of the reaction products, tetramethylammonium chloride was used for all of these experiments. The concentration of chloride ion used in these NMR experiments was limited by the low solubility of tetramethylammonium choride in organic solvents.

The products of the reactions of the β-*tert*-butyl derivative **1d** with chloride ion were determined by both GC and in-situ NMR analyses. The only products detected were 3,3-dimethyl-1-butyne (**4d**) and iodobenzene (**5**) from the elimination reaction. No substitution product was detected by either GC or in-situ NMR analyses. Similar results were obtained in a study of the reaction of **1d** with bromide ion and in some other solvents.

Reaction Rates. The UV absorption of the tetrafluoroborate salts of **1** only becomes strong at wavelengths below 240 nm, while the chloride salts show significant UV absorption at longer wavelengths. This absorption develops immediately when the fluoroborate salts are dissolved in a solution which contains chloride ion (Figure 1), and the UV absorption decays slowly in accord with a pseudo-first-order rate law. First-order rate constants k_{obsd} were obtained from an analysis of the disappearance of the absorbing species. The initial absorbances A_i at 250 nm was obtained by extrapolation of the absorbance readings to the time of initial mixing of reactants. Figure 2 shows a plot of ΔA against the concentration of chloride ion for the reaction of **1a**, where ΔA is the difference between the values of A_i and A_0 measured when $[Cl^-] = 0$. Downward curvature at high concentrations of chloride ion is observed in Figure 2. A UV spectral analysis of the reactions of other salts of **1** shows a similar chloride ion dependent accumulation and decay of a reaction intermediate.

The values for the observed first-order rate constants k_{obsd} determined for reactions in acetonitrile which contains 0.01 mol dm^{-3} Bu_4NCl are reported in Table 1. Figures 3 and 4 show plots of values of k_{obsd} obtained at 25 °C and constant ionic strength ($\mu = 0.10$, Bu_4NClO_4) against the concentration of Bu$_4$-

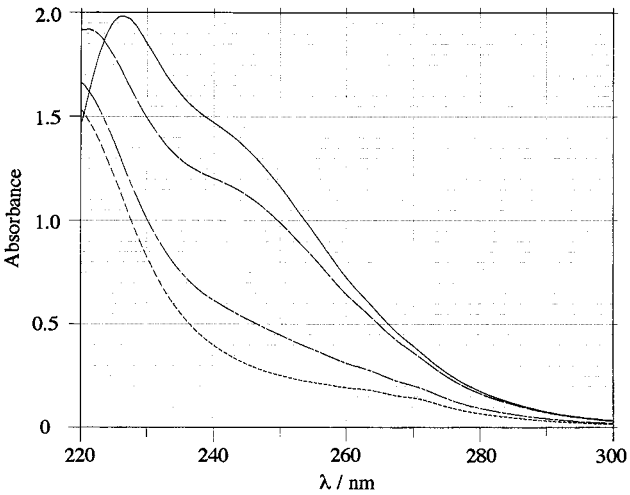


Figure 1. UV absorption spectra of **1a** (BF_4^-) recorded immediately after dissolving in acetonitrile in the absence and presence of Bu_4NCl at $\mu = 0.10$ (Bu_4NClO_4), [**1a**] $= 7.16 \times 10^{-5}$ mol dm^{-3}, and 25 °C. $[Bu_4NCl] = 0$ (---), 10^{-4} (-‑—), 0.01, (— —), and 0.10 mol dm^{-3} (—).

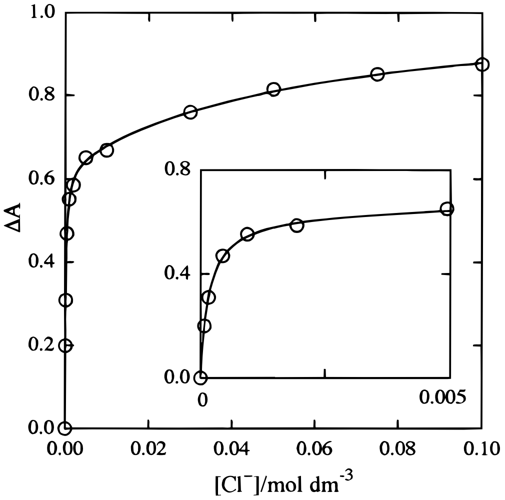


Figure 2. The initial absorbance of **1a** at 250 nm in Bu_4NCl solution in acetonitrile measured at $\mu = 0.10$ (Bu_4NClO_4), [**1a**] $= 7.16 \times 10^{-5}$ mol dm^{-3}, and 25 °C. The solid curves are the theoretical ones calculated as described in the text. The inset shows data at low $[Cl^-]$.

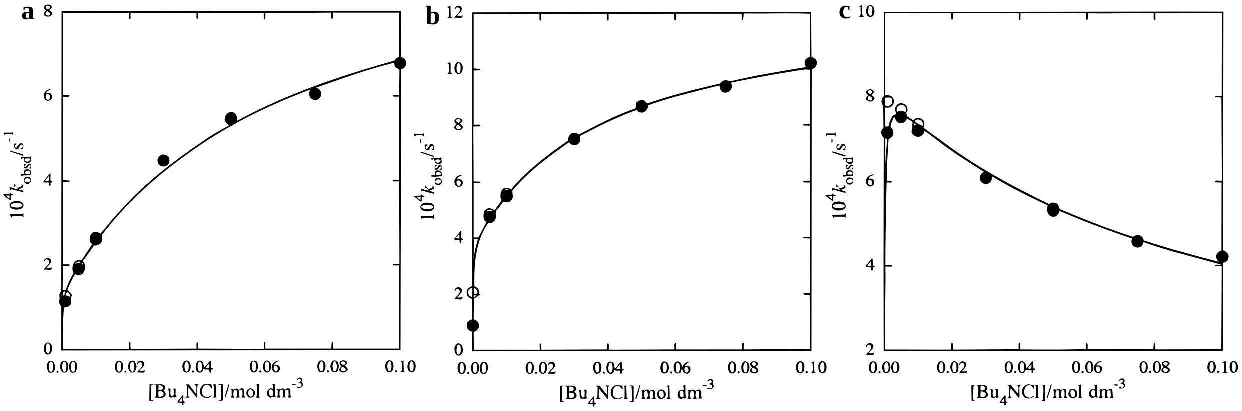


Figure 3. Observed rate constants for the reactions of **1a** (a), **1c** (b), and **1d** (c) with chloride ion in acetonitrile at 25 °C. The closed circles indicate values at $\mu = 0.10$ and the open circles indicate those obtained without adjusting the ionic strength. The solid curves are calculated as described in the text.

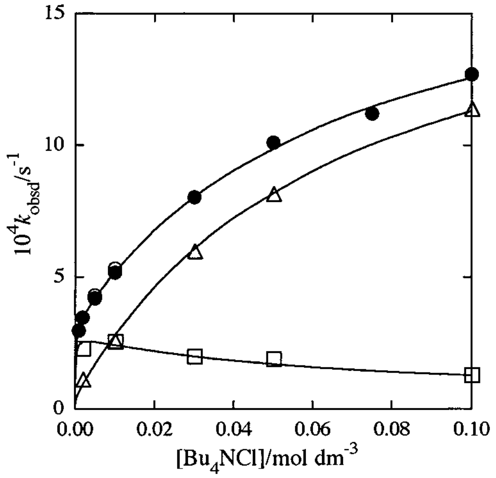


Figure 4. Rate constants for the reactions of **1b** with chloride ion in acetonitrile at $\mu = 0.10$ and 25 °C: (●) k_{obsd}; (△) k_s; (□) k_e; and (○) k_{obsd} obtained without adjusting the ionic strength. The solid curves are calculated as described in the text.

NCl. Downward curvature is observed in the plot of rate constants k_{obsd} for the reactions of **1a**, **1b**, and **1c** against [Cl⁻]. By contrast a much more complicated chloride ion concentration dependence is observed for the reaction of **1d** (Figure 3c). Here the values of k_{obsd} are observed to first increase to a maximum and then decrease at higher concentrations of chloride ion. This unusual concentration dependence may be related to the observation that only elimination products are observed for the reaction of **1d**, while the other substrates react by both substitution and elimination pathways. This behavior was also observed for the reaction of **1d** in chloroform (Figure 5). The rate retardation caused by chloride ion was stronger and more clearly observed when constant ionic strength was not maintained. The effect of changing ionic strength on a reaction in acetonitrile is smaller than that observed in chloroform, but the values of k_{obsd} are slightly larger for reactions at low ionic strength (open circles in Figures 3 and 4).

The value of k_{obsd} for the reactions of **1** is equal to the sum of the rate constants for the nucleophilic substitution and elimination reactions ($k_s + k_e$). The individual rate constants k_s and k_e were calculated from the values for k_{obsd} and the product ratio [**3**]/[**4**] = k_s/k_e determined by ¹H NMR analyses. The results for reactions in the presence of 0.01 mol dm⁻³ chloride ion are given in Table 1. The rate constants for the substitution reactions of **1a**, **1b**, and **1c** are similar, but this reaction is dramatically inhibited by the *tert*-butyl group at **1d**.

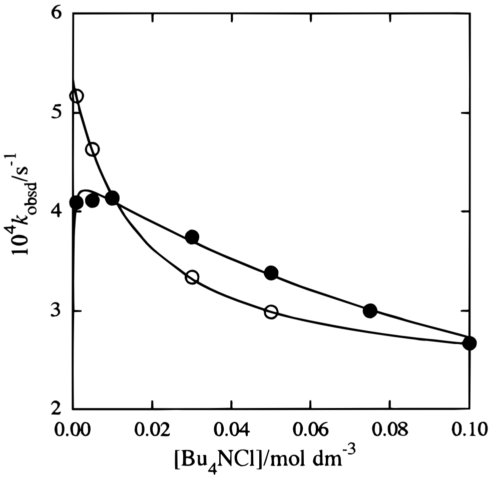


Figure 5. Observed rate constants for the reaction of **1d** with chloride ion at 25 °C in chloroform at $\mu = 0.10$ (●) and unadjusted ionic strength (○). The solid curves are calculated as described in the text.

Table 2. Observed Rate Constants for the Reaction of **1b** with Chloride Ion in Various Solvents at 25 °C[a]

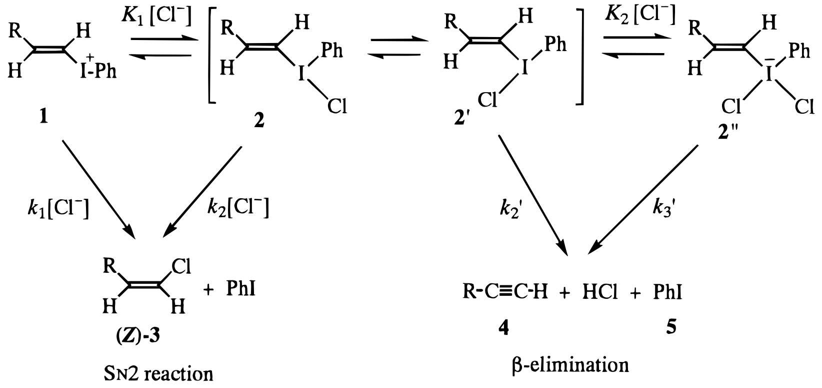
solvent	$10^4\ k_{obsd}/s^{-1}$	ϵ^b	$E_T^{N\ c}$
THF	52.0	7.47	0.207
DMF	37.7	37.07	0.404
propylene carbonate	14.4	62.93	0.472
acetonitrile	12.7	36.0	0.460
dichloromethane	6.45	9.02	0.309
DMSO	5.11	46.71	0.444
chloroform	3.95	4.89	0.259
ethanol	0.441	25.0	0.654
methanol	0.122	32.35	0.762

[a] The initital concentrations of **1b** and added Bu₄NCl were 7 × 10⁻⁵ and 0.1 mol dm⁻³, respectively. [b] Dielectric constant at 20 °C. [c] Normalized $E_T(30)$.[15]

The rate constants for the elimination reaction increase in the following order, **1a** < **1b** < **1c** < **1d**.

Product ratios [**3**]/[**4**] = k_s/k_e were determined for the reaction of **1b** in the presence of several different concentrations of chloride ion by gas chomatographic analyses. These product ratios were combined with the corresponding values of k_{obsd} for reactions of **1b** to give values of k_s and k_e for nucleophilic substitution and elimination. Figure 4 shows the dependence of k_{obsd}, k_s, and k_e for the reaction of **1b** on the concentration of added chloride ion. Simple downward curvature is observed in the plot of the values of k_s. By contrast, the rate constant k_e first increases and then decreases with increasing concentrations

Scheme 1



of chloride ion. The shape of this curve is similar to that observed for the elimination reaction of **1d** (Figure 3c), and is apparently a characteristic feature of this reaction pathway.

The effects of changing solvent on the values of k_{obsd} were determined for the reaction of **1b** under typical reaction conditions (0.1 mol dm^{-3} of chloride ion at 25 °C). The results of these experiments are summarized in Table 2. The variation in the rate constants determined for reactions in aprotic solvents is only 13-fold, but the reactions in protic alcohol solvents are typically 100−500-fold slower than in aprotic solvents.

Discussion

Stereochemistry of the Substitution Reaction. The products **3** of nucleophilic substitution of chloride ion at the (*E*) isomer of **1** form exclusively with the inverted (*Z*) configuration. The products of the reaction of the (*Z*) isomers of **1** were examined in this work in an attempt to definitively establish the stereochemical course for this vinylic nucleophilic substitution reaction. The (*Z*) isomer of **1b** was prepared as the perchlorate salt and the products of its reaction in a variety of solvents were examined.[4b] The (*Z*) isomer of **1b** is unstable and within 30 min at room temperature undergoes reaction in chloroform, acetonitrile, acetic acid, and 2,2,2-trifluoroethanol, in either the presence or the absence of chloride ion, to form predominantly the elimination products **4** and **5**.[4b] We were not able to isolate any substitution products from the reaction of the (*Z*) isomer of **1b**. The instability of the (*Z*) isomer must be due to the facile β-elimination of proton and iodobenzene located at the antiperiplanar positions.

However, the substitution product **(*Z*)-3** is not usually the more stable isomer and cannot be a thermodynamic product; 1-chloropropene (**3a**) is slightly more stable in the (*Z*) configuration than in the (*E*) form, and the (*E*) isomer becomes progressively more stable as the β-alkyl group of 1-chloro-1-alkene **3** becomes bulkier.[9] Furthermore, other nucleophiles such as bromide, iodide, thiol, and dialkyl sulfide (to form the vinylsulfonium salt) give the inverted (*Z*) substitution products on reaction with (*E*)-**1b**.[4,10a] Therefore, our failure to observe the products of a nucleophilic substitution reaction of chloride ion with the (*Z*) isomer of **1** does not affect our earlier conclusion that nucleophilic substitution reactions at the vinylic carbon of **1** occur with inversion of configuration.

It will also be worth mentioning here that β,β-dialkylvinyl iodonium salts undergo less stereoselective nucleophilic substitutions with extensive rearrangement due to the involvement of vinylic cation intermediates.[10]

Reaction Pathways. The reactions of the iodonium salts **1a**, **1b**, and **1c** with chloride ion give both substitution and elimination products while the β-*tert*-butyl derivative **1d** reacts to form only the products of elimination. The values of k_{obsd} for the reactions of these two classes of substrates also show sharply different changes with changing concentrations of chloride ion. This difference is simply accounted for by the following: (1) the difference in the products of reactions of **1a**−**c** (both substitution and elimination) and for reaction of **1d** (elimination only), and (2) the different effects of chloride ion on the rate constants k_s and k_e for the substitution and elimination reactions. Figure 3c shows that k_{obsd} for the reaction of **1d** increases sharply to a maximum value and then decreases. This corresponds to the chloride ion dependence of k_e for the reaction of **1d** since $k_e = k_{obsd}$ for the reaction of this substrate. By contrast, simple downward curvature is observed in plots of k_{obsd} against [Cl$^-$] for the reactions of **1a** and **1c** (Figure 3, parts a and b, respectively). Separation of the contribution of the rate constants k_e and k_s to k_{obsd} for the reaction of **1b** shows that the dependence of k_e on chloride ion concentration is the same as that for the reaction of **1d** and very different from the chloride ion dependence of k_s (Figure 4). The downward curvature observed for a plot of k_s against [Cl$^-$] is consistent with a fast second-order reaction of chloride ion with **1b** at low concentrations of chloride ion, and conversion of **1b** at higher chloride ion concentrations to a complex which is less reactive toward addition of chloride ion than the free substrate. The sharp decrease in k_e observed for the reactions of **1b** and **1d** at higher concentrations of chloride ion is consistent with the unimolecular nature of the reaction and the formation of a complex that is less reactive toward elimination.

The overall reactions which we propose to occur in this system are illustrated in Scheme 1. The UV spectral data show the accumulation of an intermediate species, which reaches a maximum level at high concentrations of chloride ion (Figure 2). This is consistent with the rapid establishment of a chemical equilibrium for complex(es) between **1** and chloride ion. Although similar observations of red-shifted UV absorption of diphenyliodonium halide in aprotic solvents were ascribed to a charge-transfer band,[11] the strong absorbance observed for **1** at >240 nm in the presence of chloride ion (Figure 1) may more reasonably be accommodated with formation of a complex involving hypervalent bonding to iodine. That is, we propose that chloride ion reacts with **1** to form a chloro-λ^3-iodane (10-I-3) **2**. The sharp decrease in k_e observed at higher concentrations of chloride ion is consistent with the formation of a second, less reactive complex at high [Cl$^-$]. We postulate that a second

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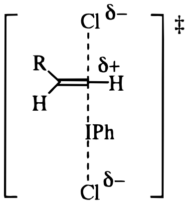
Table 3. Equilibrium and Kinetic Parameters Used for the Curve Fittings[a]

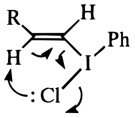
substrate	**1a**	**1b**	**1c**	**1d**	**1d**[b]
β-R	CH_3	*n*-C_8H_{17}	*i*-Pr	*t*-Bu	*t*-Bu
10^{-3} K_1/mol^{-1} dm^3	5.90 (0.26)	7.16 (0.31)	7.60 (1.19)	5.64 (0.35)	17 (8)
$10^{-4}\epsilon_1$	1.237 (0.011)	1.189 (0.010)	1.110 (0.039)	1.204 (0.015)	
K_2/mol^{-1} dm^3	15.7 (3.6)	15.1 (4.4)	25.1 (10.4)	10.8 (4.6)	6 (4)
$10^{-4}\epsilon_2$	1.796 (0.056)	1.679 (0.061)	1.502 (0.062)	1.809 (0.134)	
$k_1 + k_2'K_1$/mol^{-1} dm^3 s^{-1}	0.819	2.30[c]	2.91	4.65	7.5 (0.2)
$k_2K_1 + k_3'K_1K_2$/mol^{-2} dm^6 s^{-1}	95.7	203[d]	239	0.93	0

[a] Values in parentheses are standard deviations obtained by the nonlinear least-squares treatments of the absorbance curves. [b] In chloroform at $\mu = 0.10$. K_1 and K_2 are obtained from the kinetic curve. [c] $k_1 = 0.3$ and $k_2'K_1$ 2.0 mol^{-1} dm^3 s^{-1} ($k_2' = 2.8 \times 10^{-4}$ s^{-1}) from the separated k_s and k_e. [d] $k_2K_1 = 200$ mol^{-2} dm^6 s^{-1} ($k_2 = 0.28$ mol^{-1} dm^3 s^{-1}) and $k_3'K_1K_2 = 3$ mol^{-2} dm^6 s^{-1} ($k_3' = 2.8 \times 10^{-5}$ s^{-1}) from the separated k_s and k_e.

hypervalent species of 12-I-4 type, iodate (**2″**), is a less reactive intermediate of these reactions.[12]

There are two probable structures, **2** and **2′**, of the chloro-λ^3-iodane. The most electronegative chlorine ligand is expected to prefer the apical positions. The interchanges among the conformers of the hypervalent intermediates must occur very rapidly via pseudorotation,[13] so that these isomers cannot be simply distinguished by our kinetic experiments. The chloroiodane **2′** is expected to undergo an intramolecular β-elimination reaction, while **2** should undergo backside (S_N2) nucleophilic addition of an external chloride ion as illustrated below. The electron-rich anionic 1:2 complex of **1** and chloride ion (**2″**) is expected to be essentially unreactive toward further nucleophilic addition of chloride ion.





It has been confirmed by the labeling experiments that the reaction of fluoride ion with **1b** gives only the products of an α-elimination reaction, while the reaction of other halides occurs at the β-proton of **1b**.[4] This difference may arise because of the high basicity of fluoride ion (pK_a of HF = 3.17), since other simple moderately strong bases such as carboxylate ions or amines also undergo exclusive α-elimination reactions with **1b**. Weakly basic halide ions such as chloride and bromide ions react by the β-elimination pathway, and this behavior is best accounted for by an intramolecular reaction in which the β-proton is abstracted by the leaving group at the halo-λ^3-iodane complex. The elimination reactions of other iodonium salts **1** induced by chloride are also expected to occur by the same intramolecular reaction mechanism.

The UV spectral and kinetic data can both be explained by the reaction mechanism shown in Scheme 1. The initial absorbance observed for the reaction of **1** first increases sharply with increasing concentrations of choride ion due to formation of a chloride ion adduct to **1** and appears to approach a limiting absorbance at high [Cl$^-$] (Figure 2, inset). However, a further increase in the initial absorbance is observed at larger [Cl$^-$]. This is consistent with formation of a second adduct (**2″**), which contains two chloride ions. These data are consistent with Scheme 1, where the absorbance change observed at low concentrations of chloride ion is attributed to rapid formation of the complexes **2** (**2′**), and the further increase in the initial absorbance observed at the highest concentrations of chloride ion is attributed to the rapid formation of **2″** (Scheme 1). The absorbance data can be simulated by a nonlinear least-squares method according to eq 2[14] by using the parameters given in Table 3. The concentrations of free chloride ion at low [Cl$^-$] are adjusted by the iterative calculations by using the K_1 value determined, because [Cl$^-$] is affected by the magnitude of K_1.

$$\Delta A = (\Delta A_1 K_1[\mathrm{Cl}^-] + \Delta A_2 K_1 K_2[\mathrm{Cl}^-]^2)/(1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2) \quad (2)$$

Here, K_1 and K_2 are the equilibrium constants for the formation of λ^3-iodane **2** (**2′**) and iodate **2″**, respectively. The value of ΔA_1 corresponds to the theoretical absorbance increase for a reaction in which **1** is converted quantitatively to **2** (**2′**) and the value of ΔA_2 is that for a reaction in which there is quantitative formation of **2″**. The isomeric λ^3-iodanes, **2** and **2′**, cannot be differentiated by our experimental results.

The expression in eq 3 shows the relationship between $k_{obsd} = k_s + k_e$ and the rate and equilibrium constants in Scheme 1. This equation was derived with the assumption that the hypervalent reaction intermediates form in rapid equilibrium addition of chloride ion to **1**.[14] It is assumed that the nucleophilic substitution reaction of the anionic intermediate **2″** can be neglected over the concentration range studied. The solid lines in Figures 3 and 4 show the fits of the kinetic data to eq 3 obtained by using the equilibrium constants determined by our analysis of the initial aborbance for **1** in the presence of increasing concentration of chloride ion (Table 3).

$$k_{obsd} = \{(k_1 + k_2'K_1)[\mathrm{Cl}^-] + (k_2K_1 + k_3'K_1K_2)[\mathrm{Cl}^-]^2\}/(1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2) \quad (3)$$

The kinetic data can also be fit to expressions which relate the individual rate constants k_s and k_e for the nucleophilic substitution and elimination reactions to k_1, k_2 and k_2', k_3', respectively. Such analyses were carried out for **1b** as shown in Figure 4. The values determined for the rate constants for the reaction of **1b** are given as footnotes *c* and *d* for Table 3. The term in the rate law that is first order in [Cl$^-$] is mainly due to the pathway leading to formation of elimination products ($k_2'K_1$) while the term which is second order in chloride ion arises mainly from the pathway leading to the products of nucleophilic substitution (k_2K_1). That is, in the normal range of choride ion concentrations used in these experiments (10^{-4}–

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(14) Equations 2 and 3 can be derived by using the equilibrium fractions of **1**, **2** (**2′**), and **2″** at a given [Cl$^-$] which are expressed as $1/(1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2)$, $K_1[\mathrm{Cl}^-]/(1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2)$, and $K_1K_2[\mathrm{Cl}^-]^2/(1 + K_1[\mathrm{Cl}^-] + K_1K_2[\mathrm{Cl}^-]^2)$, respectively. A detailed derivation of the equations is presented in Supporting Information.

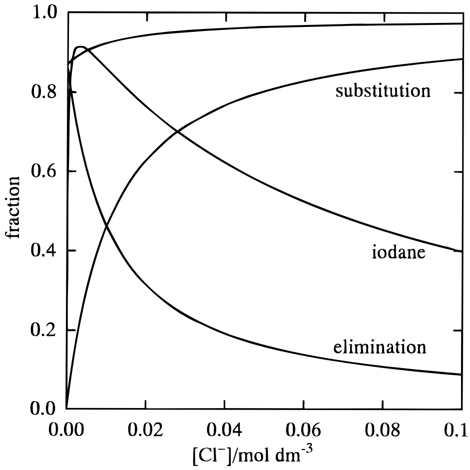


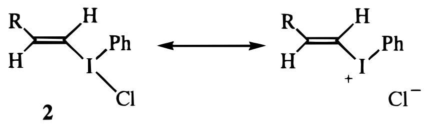
Figure 6. Calculated curves of the contribution of chloro-λ^3-iodane (**2**) to the reaction of **1b** with chloride in acetonitrile. The curves are calculated by equations similar to eq 3 with the parameters given in Table 3. The top thick curve indicates a fraction of the reactions (substitution plus elimination) occurring with **2**, while the line identified by "iodane" shows a fraction of **2** in the equilibrium of **1**, **2**, and **2″**.

0.1 mol dm^{-3}), both the nucleophilic substitution and elimination reactions of **1b** occur mainly through the chloroiodane **2** reaction intermediate, rather than by the direct reaction of the iodonium ion **1** (Figure 6).

The curves in Figure 6 were calculated by using the kinetic and equilibrium constants for the reaction of **1b** listed in Table 3. These data define (1) the fraction of these reactions (substitution and elimination) which occur from the iodane intermediate and (2) the fraction of the substrate that exists in the iodane form. The results provide evidence that as much as 87−97% of the products of the reaction of **1b** form from the iodane reaction intermediate and that the fraction of the **1b** which has been coverted to the iodane varies from 42% (when $[\mathrm{Cl}^-] = 10^{-4}$ mol dm^{-3}) to 40% (at 0.1 mol dm^{-3}) and this fraction passes through a maximum of 91% when $[\mathrm{Cl}^-] = 0.004$ mol dm^{-3}.

The effects of changing solvents on the observed rate constant for the reaction of **1b** in the presence of 0.1 mol dm^{-3} chloride ion are relatively small (Table 2) and they show no clear dependence on polarity of the solvent as measured by the dielectric constants or the polarity parameter $E_T{}^N$.[15] These results are consistent with the conclusion that the major pathway for this reaction involves nucleophilic addition of chloride ion to the neutral λ^3-iodane, because there is no disappearance or creation of the charge occurring during the reaction but only the dispersion of the negative charge on proceeding from the initial state to the transition state. The rate constants for these reactions are depressed in the protic solvents, methanol and ethanol. This result is consistent with a reduction in the nucleophilic reactivity of chloride ion due to hydrogen bonding to these solvents.

The relative reactivity of iodonium ion (**1**) and chloroiodane (**2**) toward nucleophlic substitution by chloride ion is about 10 ($k_1/k_2 = 0.3$ mol^{-1} dm^3 s^{-1}/0.028 mol^{-1} dm^3 s^{-1} ≈ 10) for the reaction of **1b**, while the relative reactivity of chloroiodane (**2**) and iodate (**2″**) toward elimination is between 10 and 60 ($k_2' = 2.8 \times 10^{-4}$ and $k_3' = 2.8 \times 10^{-5}$ s^{-1} for the reaction of **1b** and $k_2' = 8.2 \times 10^{-4}$ and $k_3' = 1.5 \times 10^{-5}$ s^{-1} for the reaction of **1d**). In general, similar chemical and physical properties of iodonium ions and λ^3-iodanes make it difficult to distinguish these compounds from one another in solution.[16] This is because the hypervalent bonding of chloride ion at the polyvalent iodo group is weak,[16] which can be represented by assignment of a large contribution of a no-bond resonance form to the structure of the λ^3-iodane.



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The present work provides an interesting example of a distinction between these compounds that is based upon the small, but experimentally significant, difference in the nucleofugality of the positive iodonio and the neutral polyvalent iodo groups.

The kinetic data for the reaction of **1d** in chloroform were analyzed by the same procedure described above. The value of the association constant K_1 at $\mu = 0.10$ is considerably larger than that in acetonitrile (Table 3). The value of K_1 determined for reaction in the absence of added salt ($\mu = [\mathrm{Bu_4NCl}]$) is extremely large, so that there is essentially no dissociation of the chloroiodane to form **1d** under these reaction conditions. Now, the only detectable effect of added chloride ion is an inhibition of the elimination reaction of **1d** (Figure 5). The theoretical curve in Figure 5 was determined by fitting the experimental data to an equation for k_{obsd}: $k_{\mathrm{obsd}} = (k_2' + k_3'K_2[\mathrm{Cl}^-])/(1 + K_2[\mathrm{Cl}^-])$ with $k_2' = 5.3 \times 10^{-4}$ s^{-1}, $k_3' = 2.2 \times 10^{-4}$ s^{-1}, and $K_2 = 61$ mol^{-1} dm^3. However, the physical meanings of these derived parameters are unclear because it is not possible to evaluate whether they are constant or change with changing ionic strength. These experimental results are consistent with the conclusion that elimination involves the intramolecular reaction of the chloroiodane reaction intermediate.

In conclusion, the reactions of **1** with chloride ion in solution are consistent with the mechanism written in Scheme 1 which includes the hypervalent 10-I-3 and 12-I-4 reaction intermediates. The main reactions which occur in the range of chloride ion concentrations examined in this work involve the 10-I-3 chloro-λ^3-iodanes, **2** or **2′**. We propose that the intermediate **2** undergoes concerted bimolecular nucleophilic substitution by chloride ion (k_2, Scheme 1), while the intermediate **2′** undergoes intramolecular elimination to form the corresponding alkyne (k_2', Scheme 1).

Vinylic S_N2 Mechanism. Nucleophilic vinylic substitution reactions of chloride ion occur both at the iodonium ion (**1**) and λ^3-iodane (**2**), which is in equilibrium with **1**. Although **1** is about 10 times more reactive than **2** toward addition of chloride ion, **2** is the major species at chemical equilibrium under our reaction conditions and the reaction of this species with exclusive inversion of configuration is the major reaction pathway leading to formation of substitution products (Figure 6). This bimolecular substitution reaction with inversion occurs through the concerted in-plane S_N2 pathway suggested above. An alternative ion-pair mechanism has been excluded by the observations, indicating that a simple primary vinyl cation cannot be formed even in polar protic solvents.[8,10a] The bulky *β-tert*-butyl group at **1d** creates a large steric barrier to backside nucleophilic attack of chloride ion but has relatively little effect on the rate of elimination, which is the only reaction pathway observed for this compound. Other changes in the secondary and primary alkyl substituents at **1** do not have a large effect

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on the rate constant k_s for the substitution reaction of chloride ion (Table 1). Free carbon−carbon bond rotation allows these smaller alkyl substituents to adopt a conformation that can avoid interfering with the incoming nucleophile. The nucleophile is assumed to approach the vinylic carbon from the direction of the α-hydrogen atom and may in fact form a stabilizing hydrogen bond to this α-hydrogen. This hydrogen bond has been detected in theoretical calculations of the reaction coordinate for S_N2 nucleophilic substitution reactions at vinylic carbon.[7a,17]

In conclusion, it is now established that the in-plane S_N2 substitution occurs at the vinylic carbon of primary vinyl-λ^3-iodane/iodonium substrates.

Experimental Section

^{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 JASCO IRA-1 and Shimadzu UV-2200 spectrophotometers, respectively. Mass spectrometers JEOL JMS-SX102A and JMS-DX303HF were used for MS. Gas chromatography was conducted on a Shimadzu GC-14B with a DB-1 capillary column (0.25 mm × 30 m). 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 obtained from TCI (Tokyo) was used without purification. Other solvents are of the best grade commercially available. Acetonitrile-d_3 containing 99.6 atom % of D and 0.03% of TMS and $CDCl_3$ (99.9 atom % D) were obtained from Aldrich. Tetrabutylammonium chloride (TCI) and perchlorate (Fluka) and tetrmethylammonium chloride (Wako, Osaka) were used without further purification. 1-Decyne (**4b**, TCI), 3,3-dimethyl-1-butyne (**4d**, TCI), and iodobenzene (**5**, Wako) were purchased for authentic samples.

(*E*)-1-Propenyl(phenyl)iodonium Tetrafluoroborate (1a). (*E*)-1-(Trimethylsilyl)-1-propene was prepared stereoselectively from 3-(trimethylsilyl)-1-propene by $Fe(CO)_3$-catalyzed photoisomerization in 27% yield according to a literature procedure.[18] To a stirred suspension of iodosylbenzene (4.70 g, 21.4 mmol) and (*E*)-1-(trimethylsilyl)-1-propene (1.22 g, 10.7 mmol) in dichloromethane (67 mL) was added dropwise BF_3-Et_2O (3.98 g, 28.1 mmol) at 0 °C under nitrogen, and the mixture was stirred for 50 h at 0 °C and then for 1 h at room temperature. The mixture was stirred with a saturated aqueous solution of sodium tetrafluoroborate (15 g) for 30 min and then extracted with dichloromethane. The organic layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane by decantation at −78 °C. Recrystallization from hexane−dichloromethane gave the vinyliodonium salt **1a** (1.11 g, 31%) as colorless crystals: mp 67.5−68 °C. IR (KBr) 3030, 1472, 1441, 1063, 992, 735, 680, 522 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.51 (dd, J = 8.0, 7.3 Hz, 2H), 7.03 (dq, J = 13.7, 6.8 Hz, 1H), 6.80 (dq, J = 13.7, 1.4 Hz, 1H), 2.05 (dd, J = 6.8, 1.4 Hz, 3H). HRFAB MS calcd for $C_9H_{10}I$ [(M − BF_4)$^+$] 244.9827. Found 244.9817. Anal. Calcd for $C_9H_{10}BF_4I$: C, 32.57; H, 3.04. Found: C, 32.51; H, 2.98.

(*E*)-1-Decenyl(phenyl)iodonium Tetrafluoroborate (1b). 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.[19] The yield of **1b** was 72%.

(*E*)-3-Methyl-1-butenyl(phenyl)iodonium Tetrafluoroborate (1c). (*E*)-3-Methyl-1-(trimethylsilyl)-1-butene was prepared in 69% yield by the benzenesulfinic acid catalyzed isomerization[20] of the (*Z*) isomer, which was obtained by hydroalumination-protonolysis[21] of 3-methyl-1-(trimethylsilyl)-1-butyne. By a similar procedure used for **1a**, (*E*)-3-methyl-1-(trimethylsilyl)-1-butene (220 mg, 1.55 mmol) was treated with iodosylbenzene (614 mg, 2.79 mmol) and BF_3-Et_2O (396 mg, 2.79 mmol) in dichloromethane (8 mL) for 5 h at room temperature under nitrogen. Recrystallization from hexane−dichloromethane gave the vinyliodonium salt **1c** (94 mg, 17%) as colorless crystals: mp 91.5−92 °C. IR (KBr) 2964, 1563, 1471, 1306, 1095, 740, 681, 651, 522 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.52 (dd, J = 7.8, 7.4 Hz, 2H), 6.96 (dd, J = 14.3, 7.0 Hz, 1H), 6.78 (d, J = 14.3 Hz, 1H), 2.64 (octet, J = 7.0 Hz, 1H), 1.09 (d, J = 7.0 Hz, 6H). HRFAB MS calcd for $C_{11}H_{14}I$ [(M − BF_4)$^+$] 273.0140. Found 273.0150. Anal. Calcd for $C_{11}H_{14}BF_4I$: C, 36.71; H, 3.92. Found: C, 36.45; H, 3.90.

(*E*)-3,3-Dimethyl-1-butenyl(phenyl)iodonium Tetrafluoroborate (1d). (*E*)-3,3-Dimethyl-1-(trimethylsilyl)-1-butene was prepared in 68% yield by the hydroalumination-protonolysis[22] of 3,3-dimethyl-1-(trimethylsilyl)-1-butyne. By a similar procedure used for **1a**, the vinylsilane (2.07 g, 13.2 mmol) was treated with iodosylbenzene (4.37 g, 19.9 mmol) and BF_3-Et_2O (2.82 g, 19,9 mmol) in dichloromethane (66 mL) for 3 h at room temperature under nitrogen. Recrystallization from hexane−dichloromethane gave the vinyliodonium salt **1d** (2.37 g, 48%) as colorless needles: mp 147−147.5 °C. IR (KBr) 3092, 2964, 1470, 1446, 1263, 1080, 990, 742, 680, 523 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.00 (d, J = 8.0, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (dd, J = 8.0, 7.5 Hz, 2H), 6.99 (d, J = 14.4 Hz, 1H), 6.78 (d, J = 14.4 Hz, 1H), 1.11 (s, 9H). HRFAB MS calcd for $C_{12}H_{16}I$ [(M − BF_4)$^+$] 287.0297. Found 287.0312. Anal. Calcd for $C_{12}H_{16}BF_4I\cdot{}^1/_4H_2O$: C, 38.08; H, 4.26. Found: C, 38.07; H, 4.27.

Product Determination for Reaction of 1b. A sample of **1b** (2−5 mg) was dissolved in acetonitrile solution containing the specified concentrations of tetrabutylammonium chloride and perchlorate and kept at 25 °C for about 10 half-lives. The amount of the chloride solution was decided for the chloride to be at least 5 times 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 **3b**[23] and **4b** were isolated by preparative GC (20% silicone GE SF-96, 1 m) from a large-scale reaction of **1b**. **3b**: IR ($CHCl_3$) 2935, 2850, 1620, 1570, 1465, 1435, 1050, 1005, 990 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.01 (dt, J = 7.3, 1.5 Hz, 1H), 5.75 (q, J = 7.3 Hz, 1H), 2.22 (dq, J = 1.5, 7.3 Hz, 2H), 1.50−1.15 (12H), 0.89 (t, J = 6.5 Hz, 3H). **4b**: ^{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).

Products of Reaction of 1d. Reaction products of **1d** were determined by GC in the same way as those of **1b** by comparison with the authentic samples of **4d** and **5**. No sign of formation of **3d** was found.

NMR Determination of Product Ratio. Reaction was carried out at the substrate concentration of 2 mmol dm^{-3} in acetonitrile-d_3 containing 0.01 mol dm^{-3} tetramethylammonium chloride and 0.03% TMS in an NMR tube. For the reactions of **1a** and **1c**, the tube was sealed by fusion to avoid evaporation of the products, but it was only stoppered with a cap for **1d**. The required amount (0.2 mL) of the stock solution of **1** in chloroform (0.01 mol dm^{-3}) was placed in a flask, the solvent was completely removed under vacuum, and 1 mL of the ammonium chloride solution in acetonitrile-d_3 was added. The solution was transferred in an NMR tube and kept at 25 °C for 5 h and subjected to the NMR measurements. From the relative integral intensities of the olefinic and the acetylenic signals or those of the

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methyl groups, relative amounts of the products, chloroalkene **3** and acetylene **4**, were evaluated. ^{1}H NMR (CD_3CN): **3a**, δ 1.74 (dd, $J = 6.7, 1.7$ Hz), 5.90 (quintet, $J = 6.7$ Hz), 6.12 (dq, $J = 6.7, 1.7$ Hz); **4a**, δ 1.78 (d, $J = 2.9$ Hz), 2.00 (q, $J = 2.9$ Hz); **3c**, δ 1.00 (d, $J = 7$ Hz), 2.84 (m), 5.78 (dd, $J = 9, 7$ Hz), 6.02 (dd, $J = 7, 1.2$ Hz); **4c**, δ 1.15 (d, $J = 7$ Hz), 2.23 (d, $J = 2$ Hz), 2.56 (m); **4d**, δ 1.21 (s), 2.29 (s).

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 was added the stock solution of **1** in acetonitrile (30 μL) from a microsyringe. After rapid mixing, the absorbance at 250 nm was recorded for a few minutes and extrapolated to the time of addition on a chart of an analogue recorder.

Kinetic Measurements. Reaction rates were measured by monitoring the decrease in absorbance at 250 nm at 25 °C as described previously.[24]

Curve Fittings: The curve fittings were carried out by a nonlinear least-squares method (Marquardt−Levenberg Algorithm) with use of SigmaPlot (Jandel Scientific, San Rafael, CA) on a personal computer Macintosh Centris 650.

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Supporting Information Available: Derivation of eqs 2 and 3 (1 page, print/PDF). See any current masthead page for ordering and Web access instructions.

JA972267C

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