Reactions of Cyclohexenyl Iodonium Tetrafluoroborate with Bromide Ion: Retardation Due to the Formation of λ^3-Bromoiodane
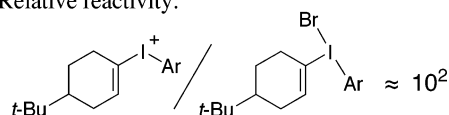
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Relative reactivity:

The reaction of 4-*tert*-butylcyclohex-1-enyl(phenyl)iodonium tetrafluoroborate (**1a**) and the 4-chlorophenyl derivative (**1b**) with bromide ion was examined in methanol, acetonitrile, and chloroform. Products include those derived from the intermediate cyclohexenyl cation as well as 1-bromocyclohexene. Kinetic measurements show that the reaction of **1** is strongly retarded by the added bromide. The curved dependence of the observed rate constant on the bromide concentration is typical of a pre-equilibrium formation of the intermediate adduct with a fast bromide-independent reaction (solvolysis of the iodonium ion). The formation of the adduct, λ^3-bromoiodane, was also confirmed by the UV spectral change. The relative reactivity of the iodonium ion and λ^3-bromoiodane is evaluated to be on the order of 10^2. The bromide substitution product forms both via the S_N1 reaction of the free iodonium ion and via the ligand coupling of the iodane.

Introduction

A secondary vinylic iodonium salt, cyclohex-1-enyl(aryl)-iodonium tetrafluoroborate, **1**, undergoes S_N1-type solvolysis in alcoholic solvents via a vinylic cation as an intermediate (eq 1).[1] Thermolysis of **1** in chloroform to give 1-fluorocyclohexene,
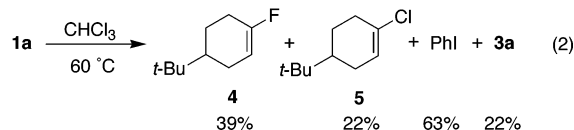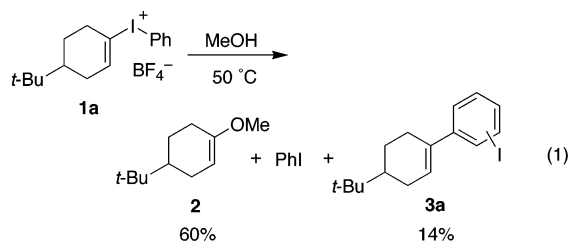
4, was also suggested to follow the S_N1-type mechanism (eq 2).[2] Weak bases such as acetate and amines induce β-elimination

of **1** to give cyclohexyne, and the reaction with an amine was concluded unexpectedly to occur via the E1 mechanism, in contrast to the reaction with acetate proceeding via the E2 mechanism.[3] That is, cyclohexenyl cation **6** is readily generated thermally even in aprotic solvents (Scheme 1).
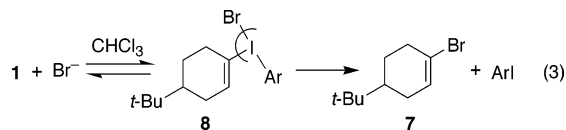
The reaction of **1** with bromide ion provides 1-bromocyclo-hexene **7** in a high yield in chloroform, and this product was suggested to form by ligand coupling within the hypervalent adduct, λ^3-bromoiodane **8** (eq 3), instead of a possible S_N1-type mechanism.[3] Reactions of simple alk-1-enyl iodonium salts with a halide ion other than fluoride give 1-haloalk-1-ene with
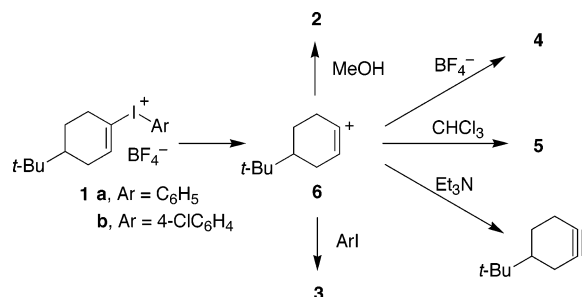
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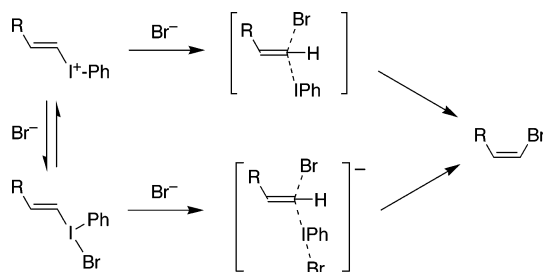(2) Okuyama, T.; Fujita, M.; Gronheid, R.; Lodder, G. *Tetrahedron Lett.* **2000**, *41*, 5125−5129.

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SCHEME 1

SCHEME 2

FIGURE 1. Observed rate constants for the reaction of **1b** in methanol in the presence of tetrabutylammonium perchlorate ($\square$), tetrabutylammonium tetrafluoroborate (Δ), and tetrabutylammonium bromide ($\bigcirc$) at 50 °C.

FIGURE 2. Initial absorbance ($\bullet$) at 255 nm and observed rate constants ($\bigcirc$) for the reaction of **1b** in methanol at 50 °C in the presence of tetrabutylammonium bromide and at the constant ionic strength of 0.20 mol dm^{-3}, maintained with tetrabutylammonium perchlorate. The solid curves are those calculated with the parameters given in Table 2.

complete inversion of configuration,[4] which are concluded to occur via the vinylic S_N2 ($S_NV\sigma$) mechanism.[5] In this and other reactions, a halide is known first to form a λ^3-haloiodane intermediate like **8**,[8-11] and this intermediate as well as the free iodonium ion undergoes ensuing reactions such as $S_NV\sigma$ in the case of alk-1-enyl iodonium salts (Scheme 2).[6,7] When the $S_NV\sigma$ and other reactions become sluggish, the ligand-coupling (or $S_NV\pi$)[7] reaction may show up, as in the case of 2-haloalk-1-enyliodonium salt.[8,9]

The nucleophilic substitution of **1** can occur via the S_N1 or the ligand-coupling mechanism, as mentioned above (the $S_NV\sigma$ mode of reaction is not possible with the cyclic substrate), and kinetic analysis allows the differentiation between the two mechanisms.[9] One purpose of this study is to address this point for the reaction of **1** with bromide ion. The reactivity of λ^3-iodane in comparison with that of the iodonium ion is also an interesting issue to identify the true reactive species to afford the products. The effects of an added bromide salt on the reaction rates for **1** in different solvents are examined in this study, showing that the λ^3-bromoiodane is much less reactive than the free iodonium ion in polar solvents.

Results

The reactions of 4-*tert*-butylcyclohex-1-enyl(phenyl)iodonium tetrafluoroborate (**1a**) and the 4-chlorophenyl derivative (**1b**) were carried out in methanol, acetonitrile, and chloroform at
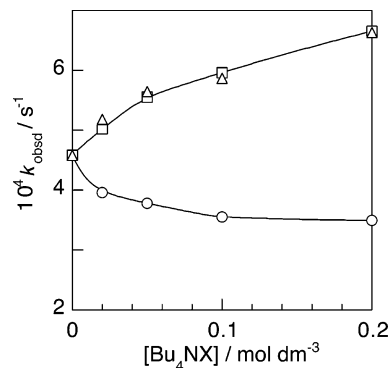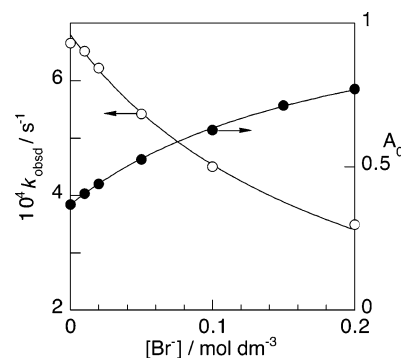
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50−60 °C in the presence of tetrabutylammonium bromide and other salts. The yields of the enol ether derivatives were determined as their hydrolysis product, 4-*tert*-butylcyclohexanone (**2′**). The product distributions for the reactions of **1a** under varied conditions are summarized in Table 1.

Kinetic measurements were performed with **1a** and **1b** by monitoring the decrease in UV absorption. When the tetrafluoroborate salt of **1** is dissolved in a solution containing bromide (or chloride ion), a new absorption band immediately develops at a longer wavelength, as observed for other vinyl iodonium salts.[5,6,9-11] This absorbance decays following the pseudo-first-order kinetic law to provide the observed rate constants k_{obsd}. The extrapolated initial absorbance A_0 can also be measured in the same way as described previously.[5,6] The results obtained in methanol, acetonitrile, and chloroform are presented in Figures 1−4.

Discussion

Solvolysis in Methanol. The solvolysis of **1** in various alcoholic solvents affords the recombination products **3** in addition to the expected enol derivative **2** (or cyclohexanone **2′**), and the rate is only slightly dependent on solvent polarity, which is consistent with the reaction of an ionic substrate giving an ionic product (intermediate).[1] The recombination products **3** are of the Friedel−Crafts type and are always abundant in the ortho (about 80%) of the three isomers, to imply recombina-

TABLE 1.   Product Yields of the Reactions of 1a under Varied Conditions

					product yield (%)				
						3a			
no.	solv.	temp (°C)	time (h)	[Bu$_4$NBr] (mol dm^{-3})	other salt (concn; mol dm^{-3})	2′	(o/m/p)	5	7	PhI
1	CHCl$_3$	60	1.0	0	Bu$_4$NClO$_4$ (0.10)		28 (n.d.)	42		nd
2	CHCl$_3$	60	25	0.10	none		1.5 (86:6:8)		98	90
3	CHCl$_3$	60	25	0	Bu$_4$NCl (0.10)		1.8 (86:6:8)	98		80
4	MeCN	50	1.0	0	Bu$_4$NClO$_4$ (0.20)	39	7.9 (81:6:13)			72
5	MeCN	50	1.5	0.01	Bu$_4$NClO$_4$ (0.19)	31	8.7 (79:9:12)		21	75
6	MeCN	50	2.5	0.02	Bu$_4$NClO$_4$ (0.18)	30	6.8 (86:7:7)		40	78
7	MeCN	50	4.0	0.05	Bu$_4$NClO$_4$ (0.15)	23	4.5 (86:7:7)		62	83
8	MeCN	50	4.0	0.10	Bu$_4$NClO$_4$ (0.10)	18	5.1 (84:7:9)		76	88
9	MeCN	50	6.0	0.20	none	17	2.5 (87:8:5)		80	84
10	MeCN	50	11.5	0	Bu$_4$NCl (0.20)	18	3.8 (79:9:12)	70		75
11	MeOH	60	1.5	0	Bu$_4$NClO$_4$ (0.20)	36	6.7 (81:6:13)			57
12	MeOH	60	2.0	0.10	Bu$_4$NClO$_4$ (0.10)	42	9.7 (81:9:10)		7.8	75
13	MeOH	60	3.0	0.20	none	47	5.8 (79:12:9)		13	73
14	MeOH	60	3.0	0	Bu$_4$NCl (0.20)	49	9.0 (81:7:12)	7.4		62

SCHEME 3
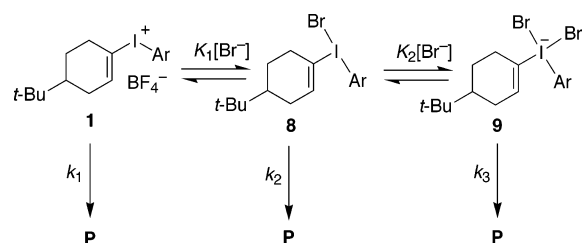
TABLE 2.   Kinetic Parameters Used for the Simulation of the Kinetic Curves of Figures 2−4 for the Reaction of 1b with Bromide Ion[a]

	MeOH	MeCN[b]	CHCl$_3$	MeCN[c]
K_1 (mol^{-1} dm^3)	5.0	690 (370)	1600	7160
K_2 (mol^{-1} dm^3)	∼0	∼0 (0.7)	3.3	15.1
$10^4 k_1$ (s^{-1})	6.8	30 (40)	8.1	(0.30)[d]
$10^4 k_2$ (s^{-1})	∼0	0.6 (2)	1.5	(0.028)[d]
k_1/k_2	large	50 (20)	5.4	(11)[d]

[a] Reactions were carried out at 50 °C and with an ionic strength of 0.20 mol dm^{-3} in methanol and acetonitrile or 0.10 mol dm^{-3} in chloroform, maintained with Bu$_4$NClO$_4$. [b] Values in parentheses are those obtained for the reaction of **1a** at 60 °C. [c] Data taken from ref 6 for the reaction of dec-1-enyl(phenyl)iodonium tetrafluoroborate with chloride at 25 °C and with an ionic strength of 0.10 mol dm^{-3}. [d] Second-order rate constant in mol dm^{-3} s^{-1} for the S$_N$2 (S$_N$Vσ) reaction.

tion occurring within the tight ion−molecule pair.[1] This product, **3**, was always observed in the thermal reactions of **1** in the range of the solvents given in Table 1, suggesting intermediary formation of the cyclohexenyl cation **6** at least partially under any conditions employed.

The effects of added salts on the reaction rate for the 4-chloro substrate **1b** were examined in methanol at 50 °C, and the results are shown in Figure 1. The addition of tetrabutylammonium bromide and chloride (not shown) decelerates the reaction, while neutral salts, perchlorate and tetrafluoroborate, accelerate it. The effects of perchlorate and fluoroborate are much the same. The increased ionic strength must enhance the polarity of the medium and accelerate heterolytic reactions. Halides provide some substitution products, **7** (or **5**), but the neutral salts do not much affect the products, just a small decrease in the fractions of the recombination products **3**, which may be ascribed to the dissociation of the ion−molecule pair. Because the ionic strength increases significantly the reaction rate of the iodonium salts **1**, all the measurements hereafter were undertaken at the constant ionic strength of 0.1 or 0.2 mol dm^{-3}.

More significant deceleration by added bromide is apparent when the ionic strength is kept constant at 0.2 mol dm^{-3} with Bu$_4$NClO$_4$ in methanol (Figure 2). The initial absorbance A_0 at 255 nm increases with increasing bromide concentration [Bu$_4$NBr], as shown in Figure 2. Both the rate and the absorbance curves show saturation with [Bu$_4$NBr]. These curves may be Scheme 3 and Table 2 explained by a reaction scheme with a pre-equilibrium formation of the adduct (iodane **8** as well as iodate **9**, if applicable), as shown in Scheme 3.[5,6,10,11] The absorbance increase, $\Delta A_0 = A_0 - A_0$ at [Br$^-$] = 0, and the rate constant k_{obsd} can be represented by eqs 4 and 5, respectively, if all three species contribute to the reaction.[5,6,10,11]

$$\Delta A_0 = (\Delta A_1 K_1[Br^-] + \Delta A_2 K_1 K_2[Br^-]^2)/$$
$$(1 + K_1[Br^-] + K_1 K_2[Br^-]^2) \quad (4)$$

$$k_{obsd} = (k_1 + k_2 K_1[Br^-] + k_3 K_1 K_2[Br^-]^2)/$$
$$(1 + K_1[Br^-] + K_1 K_2[Br^-]^2) \quad (5)$$

The absorbance and rate curves are simulated by a nonlinear least-squares method to give solid curves shown in Figure 2 with the parameters $K_1 = 5.0$ mol^{-1} dm^3 and $k_1 = 6.8 \times 10^{-4}$ s^{-1}; contributions from **9** (K_2) and the reaction of **8** (k_2) can be neglected here. Reasonable curve fittings with these kinetic parameters show that the reaction of the free iodonium ion **1** is retarded by the formation of iodane **8** and that the reactivity of **8** is negligibly small (probably more than two orders of magnitude smaller than **1**) in methanol. The formation of the bromide-substitution product **7** (up to 13% at [Br$^-$] = 0.2 mol dm^{-3}) must occur via the S$_N$1 mechanism from the iodonium ion **1** (the rate-determining step does not involve the bromide ion). Intermediate cation **6** is trapped by bromide as well as by the methanol solvent.

Reaction in Acetonitrile. The reaction products of **1a** in acetonitrile are those of the solvolysis type, **2′** and **3a** after workup, in the absence of an added nucleophile (no. 4 in Table 1). The primary product must be enamide, a product of the Ritter reaction, which is readily hydrolyzed to cyclohexanone **2′**. When bromide is added to the reaction mixture, bromocyclohexene **7** is formed up to nearly 80% at [Br$^-$] = 0.2 mol dm^{-3} (nos. 5−9, Table 1). Similar results were obtained with chloride (no. 10, Table 1).

The remarkable change in the rate was observed with added bromide (Figures 3 and 4). Figure 3 shows the results for the
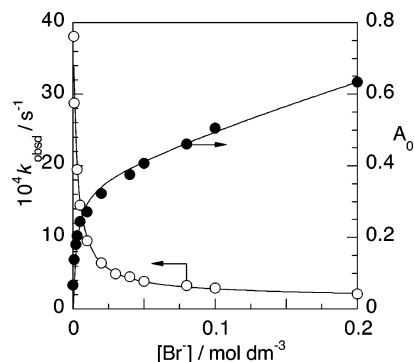
FIGURE 3. Initial absorbance (●) at 270 nm and observed rate constants (○) for the reaction of **1a** in acetonitrile at 60 °C in the presence of tetrabutylammonium bromide and at the constant ionic strength of 0.20 mol dm^{-3}, maintained with tetrabutylammonium perchlorate. The solid curves are those calculated with the parameters given in Table 2.
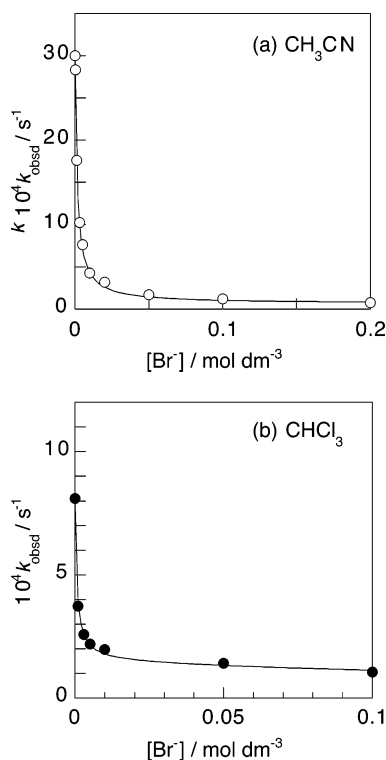

FIGURE 4. Observed rate constants for the reaction of **1b** in the presence of tetrabutylammonium bromide at 50 °C in acetonitrile (a) at the ionic strength of 0.20 mol dm^{-3} and in chloroform (b) at the ionic strength of 0.10 mol dm^{-3}, adjusted with tetrabutylammonium perchlorate. The solid curves are those calculated with the parameters given in Table 2.

reaction of **1a** in acetonitrile at the ionic strength of 0.2 mol dm^{-3}, maintained with Bu$_4$NClO$_4$ at 60 °C. The absorbance at 270 nm increases with [Br$^-$], while k_{obsd} sharply decreases at very low concentrations of Br$^-$. These curves are simulated according to eqs 4 and 5, respectively. The solid curves in Figure 3 are calculated with $K_1 = 370$ mol^{-1} dm^3, $K_2 = 0.7$ mol^{-1} dm^3, $k_1 = 4.0 \times 10^{-3}$ s^{-1}, and $k_2 = 2 \times 10^{-4}$ s^{-1} (Table 2). The relative rate for the reaction of free **1a** and λ^3-bromoiodane **8a** is evaluated to be about 20 (k_1/k_2) under these conditions. The absorbance change observed seems to show the formation of iodate **9a** at a higher concentration of bromide, as found

previously with other iodonium salts,[5,6,10,11] but the contribution from **9a** to the reaction (k_3) may be negligible in the concentration range studied. The reactivity of the iodate should be still lower than that of the iodane.

The reaction rates for **1b** in acetonitrile at 50 °C, shown in Figure 4a, are also simulated by eq 5, with parameters given in Table 2. The formation of iodate **9b** (K_2) cannot be evaluated only from the rate measurements as a result of it being too small of a contribution. A satisfactory fitting of the curve was obtained with $K_2 = 0$ (Figure 4a) to give the apparent iodonium/iodane reactivity (k_1/k_2) of about 50.

These kinetic analyses show that both λ^3-bromoiodane **8** and free iodonium ion **1** are reactive species of the reaction in the presence of bromide ion. The contribution from each species can be calculated from eq 5, with the parameters given in Table 2, and trial calculations show that the fraction of the bromide product **7** formed is always greater than the calculated contribution from **8**. This indicates that **7** forms not only from **8** but also from free **1**. Although the formation of **7** from **8** should occur via ligand coupling, the formation of **7** from **1** must proceed through the S$_N$1 mechanism. The latter mechanism accompanies the formation of **2′** and **3**.

Reaction in Chloroform. The thermolysis of **1a** in chloroform affords fluoride- and chloride-substitution products, **4** and **5**, as well as the recombination product **3a** (eq 2).[2] When 0.1 mol dm^{-3} of perchlorate, Bu$_4$NClO$_4$, was added, the formation of fluoride **4** was essentially inhibited and chloride **5** (42%) and **3a** (28%) were obtained as the main products (no. 1, Table 1). The addition of excess perchlorate leads to the dissociation of the tetrafluoroborate of **1a**, which prohibits the intermediate cation **6** from picking up fluoride. The reaction of **1a** with bromide in chloroform was found to proceed efficiently to give a high yield of the substitution product **7**.[3] However, a careful reexamination of this reaction showed the formation of a small amount (1.5% at [Bu$_4$NBr] = 0.1 mol dm^{-3}) of **3a** in addition to **7** (no. 2, Table 1). Similar results are also seen with chloride (no. 3, Table 1). These observations suggest the formation of **7** via the S$_N$1 mechanism, if only in a small fraction. This is compatible with the results of the kinetic analysis.

Although the bromide (and the chloride) ion induces an effective substitution reaction of **1** in chloroform, the reaction rate sharply decreases with the addition of a bromide salt (Figure 4b). The rate curve can be reproduced satisfactorily by eq 5, with the parameters of Table 2. In this case, a rough value of K_2 could be evaluated, but the contribution from **9** to the reaction seems to be too small in the range of the [Br$^-$] studied. The k_3 is neglected in the simulation of the kinetic curve. The relative rate constant, k_1/k_2, is rather small (5.4) in this reaction.

Iodonium and Iodane Reactivity. The relative reactivity of the free iodonium ion **1** and iodane **8** evaluated from the k_1/k_2 values is very dependent on the solvent employed, as seen in the last line of Table 2. Both of the processes responsible for k_1 and k_2 are unimolecular, but the reactions involved are not the same: the former involving only spontaneous heterolysis of **1**, while the latter involves ligand coupling as well as spontaneous heterolysis. The ease of unimolecular heterolysis should be dependent on the polarity of the solvent, but an intramolecular ligand-coupling reaction would not depend much on the solvent. The relatively larger contribution of the latter reaction in a less polar solvent must give rise to the apparently smaller relative reactivities of **1** and **8**. So, the intrinsic relative reactivities of **1** and **8** compared for the same reaction, for

example, spontaneous heterolysis, should be large, as observed in methanol and could be evaluated at least to the order of 10^2. The value obtained in chloroform may be the result of competition of different reactions, spontaneous heterolysis and ligand coupling. From the previous kinetic analysis of the $S_NV\sigma$ reaction of dec-1-enyliodonium salt[6] (the last column of Table 2), the relative reactivities of iodonium and iodane are evaluated to be 11. This rather small value may be a result of the nature of the transition state of the bimolecular substitution.

Iodonium salts are often called iodane[12,13] because species represented by R$_2$IX can exist either in an ionic or in a covalent form; an electronegative ligand X may be anionic or may form a hypervalent (covalent) bond to the iodine. There is a strong argument in favor of the iodane nomenclature[13] on the basis of the structure of the iodonium salts in a crystalline form, where the iodine moiety is T-shaped and the counteranion locates on the apical direction of the polyvalent iodine.[13-15] There is hypervalent interaction, but the separation between the iodine and the stable anion, like tetrafluoroborate or triflate, is quite large, suggesting the ionic character of this bonding.[14,15] The triflate in iodonium crystals has a weak interaction with the iodine through one of the three oxygen atoms of the sulfonate group, but these oxygen atoms are apparently equivalent,[16] characteristic of the triflate anion. Furthermore, the iodane obviously dissociates in solution, as the UV spectrum suggests. Molecular weight[17] and conductivity measurements[18] show that the dissociation in solution results in the formation of the iodonium ion. That is, both iodonium and iodane forms do exist in solution in a proportion that is dependent on the concentration and the dissociation constant, which is very dependent on the counteranion and solvent.

The other problem is the relative reactivities of the two species. In the beginning of this study, we assumed that the iodanyl group (PhIX−) could be a better leaving group than the iodonio group (PhI$^+$−) because the hypervalent C−I bond of iodane is longer than the C−I bond involved in the iodonium ion,[19,20] and, thus, the former may be weaker than the latter. However, this hypothesis is clearly disproved by the present kinetic results. The leaving ability of the iodanyl group is about 10^2 times smaller than that of the iodonio group. Our previous conclusion that the leaving ability of the phenyliodonio group (PhI$^+$−) is about 10^6 times greater than that of triflate was obtained from the solvolysis in aqueous ethanol,[1] and this refers to the iodonio group. The iodanyl group (PhIBr−) is only 10^4-fold better than triflate as a leaving group.

Experimental Section

Substrates **1a** and **1b**, solvents, and tetrabutylammonium salts were obtained as described previously.[1,5,6] All the products were characterized by NMR and MS spectra and compared with reported data.[1,3]

Reactions were carried out on a scale of a 1−5 mL solution containing 1−10 mg of the substrate **1**, and products were determined by vapor-phase chromatography in the same way as before.[1,5,6] The UV absorbance changes were recorded on a spectrophotometer Shimadzu UV-2200. The measurements of the initial absorbance and the reaction rates were also done in the same way as described for similar iodonium salts.[1,5,6]

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