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Effects of stereochemistry and β-substituents on the rates of vinylic S_N2 reaction of hypervalent vinyl(phenyl)-λ^3-iodanes with tetrabutylammonium halides

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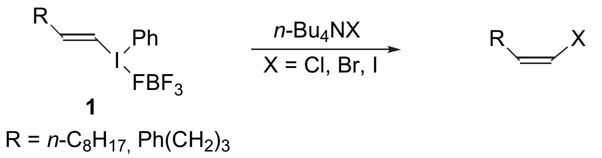
ABSTRACT

Both stereoisomers of β-(2-phenylethoxy)vinyl-λ^3-iodane and (*Z*)-β-aroyloxyvinyl-λ^3-iodane were prepared stereoselectively. These substituted vinyl-λ^3-iodanes undergo nucleophilic vinylic substitutions with *n*-Bu_4NX (X=Cl, Br, I) under mild conditions, yielding vinyl halides. The observed inversion of configuration at the *ipso* vinylic carbon atom is compatible with a concerted vinylic S_N2 mechanism. Kinetic measurements indicated that the rates for vinylic S_N2 reaction of (*Z*)-vinyl-λ^3-iodane are greater than those of the *E*-isomer, probably because of the higher ground state energy of the *Z*-isomer. Electronic effects of β-substituents of vinyl-λ^3-iodanes in the vinylic S_N2 reaction are also discussed.

1. Introduction

Bimolecular nucleophilic substitution (S_N2 reaction) at a vinylic sp^2 carbon atom involves the attack of a nucleophile to the $\sigma*$ orbital of a vinylic C–L bond (L=a leaving group) from the side opposite the leaving group and proceeds with exclusive inversion of configuration in a concerted manner without forming an intermediate. This process has been considered to be a high-energy pathway on the basis of steric factors and of early calculations,[1] and in fact was rarely observed.[2] In 1991, we reported that a nucleophilic vinylic substitution of (*E*)-β-alkylvinyl(phenyl)(tetrafluoroborato)-λ^3-iodanes **1** with tetrabutylammonium halides (Cl, Br, and I) proceeds with complete inversion of configuration on the vinylic *ipso* carbon atom even at room temperature (Scheme 1).[3] This is the unambiguous example of a vinylic S_N2 reaction.[4–6]



Scheme 1. Vinylic S_N2 reaction of vinyl-λ^3-iodanes **1** with halides.

All of the kinetic data, the secondary isotope effects, substituent effects of the leaving groups, the solvent effects, the pressure effects as well as stereochemistry of the substitutions firmly establish the in-plane vinylic S_N2 mechanism.[3,4] Hypernucleofugality of the phenyl(tetrafluoroborato)-λ^3-iodanyl group,[7] being a much better nucleofuge than superleaving triflate,[8] is responsible for the unique vinylic S_N2 reaction. Dialkyl sulfides and selenides,[5b] phosphoroselenoates,[9a] dithiocarbamates,[9b] carboxylic acids,[10] amides,[11] and thioamides[12] serves as efficient nucleophiles in the vinylic S_N2 reactions of vinyl-λ^3-iodanes **1**.

To understand in depth the mechanism of bimolecular nucleophilic substitution at a vinylic carbon atom, it is highly desirable to compare the differences in reactivity between both (*E*)- and (*Z*)-stereoisomers of vinyl-λ^3-iodanes **1**. The attempted substitution of (*Z*)-derivatives of β-alkylvinyl-λ^3-iodanes **1** with halides, however, resulted in an exclusive formation of terminal alkynes, probably via facile *anti* β-elimination and/or α-elimination-1,2-rearrangement sequence.[13] No evidence for the vinylic S_N2 displacement of the (*Z*)-isomers of **1** with halides was observed in these reactions. The only example of vinylic S_N2 reaction of (*Z*)-vinyl-λ^3-iodanes was reported recently:[13] thus, reaction of (*Z*)-(β-aroyloxyvinyl)phenyl-λ^3-iodanes **2** with *n*-Bu_4NX undergoes a bimolecular nucleophilic substitution selectively to give inverted (*E*)-vinyl halides. Unfortunately, however, no methods for the synthesis of (*E*)-isomers of **2** are available in the literature (Scheme 2).

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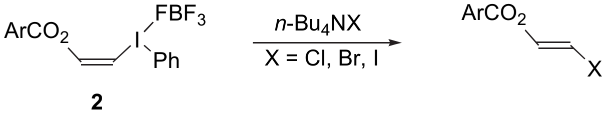


Scheme 2. Vinylic S_N2 reaction of (*Z*)-vinyl-λ^3-iodanes **2**.

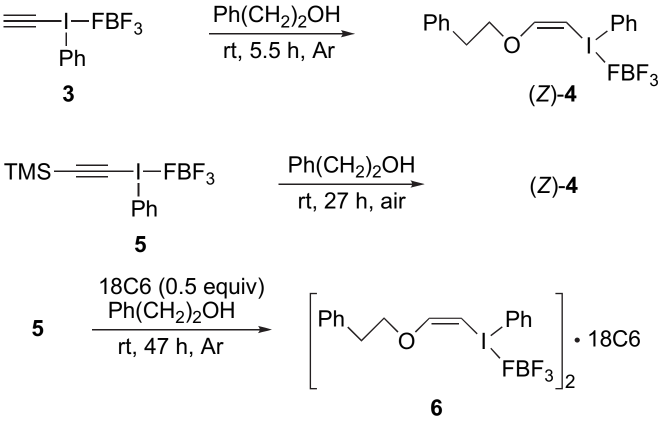
Intramolecular nucleophilic substitution of 2-bromobut-2-enylamines afforded 2-ethyleneaziridines by way of stereochemical inversion at the vinylic carbon atom.[14] Intramolecular vinylic S_N2-type reaction of vinyl halides was also reported by Narasaka and co-workers:[15] thus, vinyl halides with hydroxy, sulfonamide, and active methine groups afforded the corresponding hetero- and carbocycles by the exposure to a base with inversion of configuration. Recently, formation of a transition state model compound for vinylic S_N2 reaction with a very short lifetime was detected by Yamamoto and co-workers in the laser flash photolysis of vinyl bromide derived from 1,8-dimethoxythioxanthen-9-one.[16]

We report herein the stereoselective synthesis of both stereoisomers of β-alkoxyvinyl-λ^3-iodanes **4**. These vinyliodanes **4** undergo vinylic S_N2 displacement by the reaction with *n*-Bu_4NX stereospecifically under mild conditions and the rates for these nucleophilic substitutions are compared each other, indicating higher reactivity of (*Z*)-isomer (*Z*)-**4** than that of (*E*)-**4** toward halide nucleophiles. Effects of the β-substituents (alkyl, alkoxy, and aroyloxy groups) of vinyl-λ^3-iodanes are also evaluated.

2. Results and discussion

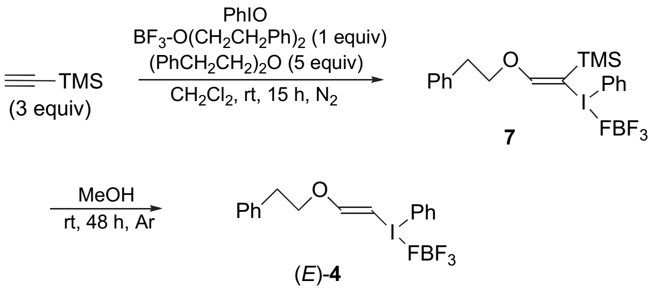
2.1. Synthesis of β-alkoxyvinyl-λ^3-iodanes

Synthetic method of (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane (*Z*)-**4** is straightforward: it was directly prepared from the commercially available ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**3**) through *anti* Michael-type addition of phenethyl alcohol (Scheme 3).[17] Thus, exposure of ethynyl-λ^3-iodane **3** to a large excess of phenethyl alcohol at room temperature afforded a 73% yield of (*Z*)-β-alkoxyvinyl(phenyl)(tetrafluoroborato)-λ^3-iodane (*Z*)-**4** stereoselectively as colorless crystals. Michael addition of the alcohol toward trimethylsilylethynyl-λ^3-iodane **5**,[18] accompanied by protodetrimethylsilylation, also afforded (*Z*)-vinyl-λ^3-iodane (*Z*)-**4** (72%) under ambient conditions. Stereochemistry of (*Z*)-**4** was determined by the small vicinal coupling constant of 3.3 Hz between the vinylic protons. Alkoxyvinyl-λ^3-iodane (*Z*)-**4** is rather thermally labile but complexation with 18-crown-6 (18C6) increases its stability in the solid state.[17,19] Thus, no decomposition was observed when the colorless prisms of 2:1 (*Z*)-β-alkoxyvinyl-λ^3-iodane·18C6 complex **6**, prepared from silylethynyl-λ^3-iodane **5** in the presence of 18C6 (0.5 equiv) in a 69% yield, were left standing under ambient conditions for several days.



Scheme 3. Stereoselective synthesis of (*Z*)-β-alkoxyvinyl-λ^3-iodanes.

In 1988, we reported a unique method for the synthesis of (*E*)-β-ethoxyvinyl(phenyl)(tetrafluoroborato)-λ^3-iodane: the method involves an initial Lewis acid (BF_3–Et_2O)-catalyzed *anti* ethoxy-λ^3-iodanation of trimethylsilylacetylene with iodosylbenzene, followed by the protodesilylation of the resulting (*E*)-α-trimethylsilyl-β-ethoxyvinyl-λ^3-iodane with water in the presence of triethylamine.[20] The alkoxy group of (*E*)-β-ethoxyvinyl-λ^3-iodane originates from the ligand Et_2O of Lewis acid BF_3. The method was slightly modified for the stereoselective synthesis of (*E*)-**4** (Scheme 4).[21]



Scheme 4. Stereoselective synthesis of (*E*)-β-alkoxyvinyl-λ^3-iodane (*E*)-**4**.

Treatment of iodosylbenzene with 3 equiv of trimethylsilylacetylene in the presence of BF_3–$O(CH_2CH_2Ph)_2$ (1 equiv)[22] and bis(phenethyl) ether (5 equiv) in dichloromethane at room temperature resulted in an *anti*-selective alkoxy-λ^3-iodanation of a carbon–carbon triple bond, yielding pure (*E*)-α-trimethylsilyl-β-(2-phenylethoxy)vinyl-λ^3-iodane **7** in a 26% yield as a pale yellow oil. Low yield of (*E*)-**7** is partly due to the formation of trimethylsilylethynyl-λ^3-iodane **5** as a by-product: the alkynyliodane **5** was selectively removed from a crude reaction mixture by the exposure to an aqueous NaBr solution (see Experimental), which probably produces bromo(trimethylsilyl)acetylene through tandem Michael addition–alkylidene carbene rearrangement of **5**.[23] Under the conditions, vinyl-λ^3-iodane (*E*)-**7** remains intact: neither Michael-type addition nor bimolecular nucleophilic substitution of (*E*)-**7** with bromide anion takes place. Subsequent protodesilylation of vinyl-λ^3-iodane (*E*)-**7** with methanol, developed by Kunishima,[21] proceeded in an exclusively stereoselective manner with retention of configuration and gave (*E*)-β-(2-phenylethoxy)vinyl-λ^3-iodane (*E*)-**4** at room temperature in an 85% yield. A large vicinal coupling constant (J=12.9 Hz) of the vinylic protons in (*E*)-**4** is in a good agreement with the reported value (12.5 Hz) for (*E*)-β-ethoxyvinyl-λ^3-iodane.[20]

To investigate the electronic effects of β-aroyloxy substituents of vinyl-λ^3-iodanes in vinylic S_N2 reaction, (*Z*)-β-aroyloxyvinyl-λ^3-iodanes **2a**–**d** were prepared in good yields according to the reported method (Scheme 5).[13,24]

$$\mathbf{3}\ \xrightarrow[\text{MeOH, rt, Ar}\\ \text{then aq NaBF}_4]{\text{ArCO}_2\text{H (9 equiv)}\\ \text{ArCO}_2\text{Na (0.2 equiv)}}\ \mathbf{2}$$

2a: Ar = Ph, **2b:** Ar = *p*-MeC_6H_4, **2c:** Ar = *p*-ClC_6H_4, **2d:** Ar = *p*-$CF_3C_6H_4$

Scheme 5. Stereoselective synthesis of (*Z*)-**2**.

2.2. Structure of vinyl-λ^3-iodanes

X-ray crystallographic analysis of vinyl-λ^3-iodane (*Z*)-**4** (Fig. 1) illustrates an asymmetric dimer structure with two independent but closely related molecules. Each λ^3-iodane molecule in the dimer unit shows a T-shaped structure, ligated with one fluorine

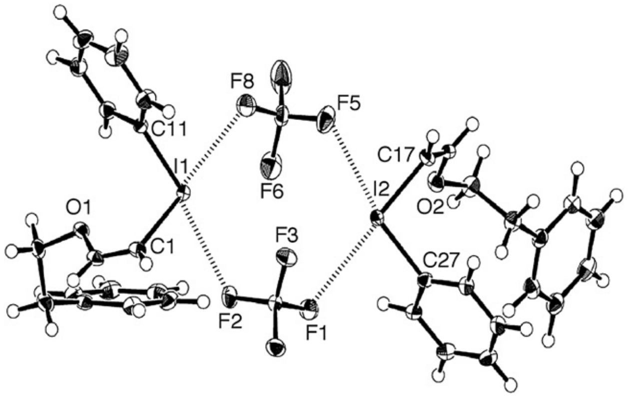


Figure 1. ORTEP drawing of vinyl-λ^3-iodane (*Z*)-**4**. Selected bond lengths (Å) and angles (deg): C1–I1 2.076(2), C11–I1 2.109(2), I1···F8 2.8969(15), I1···F2 3.0748(15), I1···F3 3.3161(17), I1···F6 3.3798(19), I1···O1 3.1317(16), C17–I2 2.079(2), C27–I2 2.119(2), I2···F5 2.9076(16), I2···F1 2.9893(13), I2···F6 3.298(2), I2···F3 3.3098(14), I2···O2 3.0826(18), C1–I1–C11 97.27(9), C17–I2–C27 94.80(9).

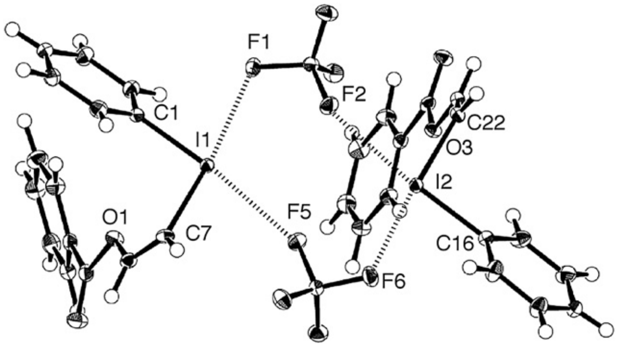


Figure 2. ORTEP drawing of vinyl-λ^3-iodane (*Z*)-**2a**. Selected bond lengths (Å) and angles (deg): I1–C1 2.1084(13), I1–C7 2.0850(14), I1···F5 2.8530(8), I1···F1 2.9424(8), I2–C16 2.1160(14), I2–C22 2.0780(14), I2···F2 2.8572(8), I2···F6 3.0691(8), C1–I1–C7 97.43(5), C16–I2–C22 96.51(5).

atom (F8 or F5) of tetrafluoroborate at an apical site of the iodine center with a distance of I1···F8 2.8969(15) Å or I2···F5 2.9076(16) Å and with a near linear triad, C1–I1···F8 (171.10°) or C27–I2···F5 (169.27°).[25] Including an another close contact between I1···F2 3.0748(15) Å or I2···F1 2.9893(13) Å, each iodane molecule adopts a distorted square-planar arrangement around the iodine atom with rms deviation (0.177(1) Å for I1, C1, C11, F2, and F8, or 0.041(1) Å for I2, C17, C27, F1, and F5) from the least squares plane. Other I···F and I···O interactions (I1···F3, I1···F6, I2···F3, I2···F6, I1···O1, and I2···O2) are very weak and considerably deviate from the linearity of hypervalent 3c–4e bonding.[26]

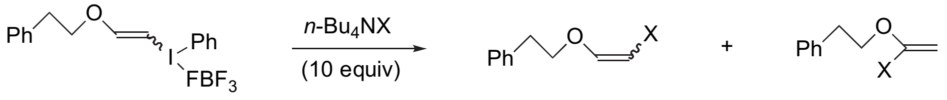
Figure 2 shows a similar dimeric structure of (*Z*)-β-benzoyloxy-vinyl-λ^3-iodane **2a**. Two closely related molecules in the dimer unit adopt a distorted square-planar arrangement around the iodine atoms.

2.3. Product analysis

The results for vinylic substitution of (*E*)- and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodanes **4** with *n*-Bu$_4$NX (X=Cl, Br, and I) are shown in Table 1. Reactions were carried out by using an excess of *n*-Bu$_4$NX (10 equiv) under heating. All of the reactions afforded good yields of vinyl halides **8** via nucleophilic displacement at the *ipso* vinylic position with halides, except for the reaction of (*Z*)-vinyl-λ^3-iodane (*Z*)-**4** with *n*-Bu$_4$NCl in THF (Table 1, entry 2). It is noted that these substitutions predominantly proceed with inversion of configuration at the α-vinylic carbon atom of **4**, which is compatible with the in-plane vinylic S$_N$2 mechanism. In THF and 1,4-dioxane as solvents, both (*E*)- and (*Z*)-**4** by the reaction with chloride and bromide anions afforded the inverted β-(2-phenylethoxy)vinyl chloride **8a** and bromide **8b** with more than 97% stereoselectivity (entries 1–6). Slightly decreased inversion of configuration was observed in the reactions in acetonitrile (entries 7–10). Therefore, the reaction is highly stereoselective and the overall substitutions are stereospecific. In addition, the vinylic substitutions of (*Z*)-**4** seem to be more rapid than those of the *E*-isomer (*E*)-**4**.

In contrast to the reaction of (*E*)-**4** with chloride in THF at 65 °C (entry 1), which produced (*Z*)-vinyl chloride **8a** selectively through vinylic S$_N$2 reaction, *Z*-isomer (*Z*)-**4** gave regioisomeric vinyl chloride **9a** as a major product (58%, entry 2), in which a chlorine atom is introduced at the β-vinylic carbon atom of **4**. Vinyl bromide **9b** was also produced in the reaction of (*Z*)-**4** with bromide anion, albeit in a low yield (5%). Scheme 6 depicts a possible reaction pathway, leading to the formation of vinyl halides **9a** and **9b**: the

Table 1
Nucleophilic substitutions of (*E*)- and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodanes **4** with *n*-Bu$_4$NX[a]



4

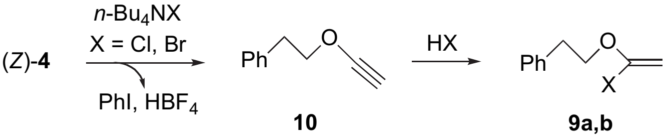
8a: X = Cl
8b: X = Br
8c: X = I

9a: X = Cl
9b: X = Br

Entry	λ^3-Iodane **4**	X	Solvent	Temp. (°C)	Time (h)	Product, Yield[b] (%)				
						8a (*E*/*Z*)	**8b** (*E*/*Z*)	**8c** (*E*/*Z*)	**9a**	**9b**
1	(*E*)-**4**	Cl	THF	65	72	74 (3:97)	—	5 (100:0)	—	—
2	(*Z*)-**4**	Cl	THF	65	4	13 (100:0)[c]	—	—	58	—
3[d]	(*E*)-**4**	Br	THF	65	24	—	61 (3:97)	5 (100:0)[c]	—	—
4	(*Z*)-**4**	Br	THF	65	2	—	67 (97:3)	—		5[c]
5	(*E*)-**4**	Br	1,4-Dioxane	65	67	—	80 (<1:>99)	1 (100:0)	—	—
6	(*Z*)-**4**	Br	1,4-Dioxane	65	4	—	77 (98:2)	—	—	1[c]
7	(*E*)-**4**	Br	CH$_3$CN	81	36	—	75 (15:85)	—	—	—
8	(*Z*)-**4**	Br	CH$_3$CN	81	5	—	66 (95:5)	—	—	—
9	(*E*)-**4**	I	CH$_3$CN	81	18	—	—	88 (11:89)	—	—
10	(*Z*)-**4**	I	CH$_3$CN	81	1.5	—	—	87 (96:4)	—	—

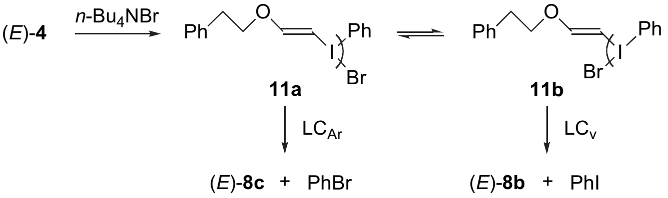
[a] Initial concentration: vinyl-λ^3-iodane **4**, 0.01 M; *n*-Bu$_4$NX, 0.1 M.
[b] Isolated yields.
[c] NMR yields.
[d] PhI (56%) and PhBr (2%) were obtained.

reaction probably involves a stereoelectronically preferred *anti* β-elimination of phenyl-λ^3-iodanyl group[27] and/or an α-elimination-1,2-rearrangement sequence,[13,28] yielding ynol ether **10**. Subsequent addition reaction of hydrogen chloride and bromide, generated in situ, toward ynol ether **10** will occur in a Markovnikov fashion to give vinyl halides **9**.[29] A higher yield of vinyl chloride **9a**, compared to that of vinyl bromide **9b**, probably reflects the differences in basicity between chloride and bromide anions.[30,31]



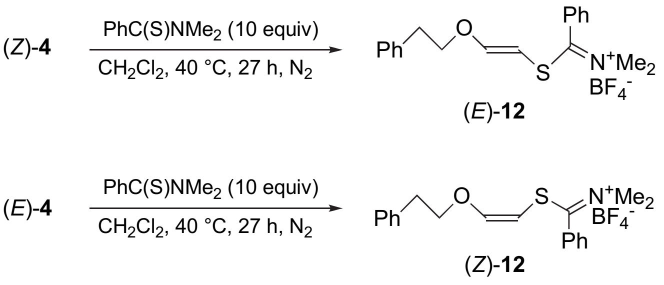
Scheme 6. A possible reaction pathway for formation of **9**.

Reaction of (*E*)-**4** with *n*-Bu$_4$NBr in THF produced (*Z*)-vinyl bromide (*Z*)-**8b** (59%) and PhI (56%) as major products (entry 3). Detailed product analysis further indicated the formation of a small amount of (*E*)-**8b** (2%), (*E*)-vinyl iodide (*E*)-**8c** (5%), and PhBr (2%). As discussed in our previous report,[13] these results clearly indicate that the vinylic S$_N$2 reaction of (*E*)-**4** with bromide, yielding (*Z*)-**8b** and PhI, competes with a ligand coupling reaction on iodine(III) of bromo-λ^3-iodane intermediates **11** to a discernible extent (Scheme 7).[32] Thus, the ligand coupling on aromatic *ipso* carbon atom (LC$_{Ar}$) of **11a** produces (*E*)-vinyl iodide (*E*)-**8c** and bromobenzene, while that on vinylic *ipso* carbon atom (LC$_V$) of **11b** affords (*E*)-vinyl bromide (*E*)-**8b** with retention of configuration and iodobenzene.



Scheme 7. A competing ligand coupling reaction.

Thioamides have been shown to be good nucleophiles in the vinylic S$_N$2 reaction of (*E*)-β-alkylvinyl-λ^3-iodanes **1**.[12] In fact, reaction of (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane (*Z*)-**4** with *N*,*N*-dimethylthiobenzamide in dichloromethane (40 °C/27 h) proceeded in an exclusive inversion of configuration via S$_N$2 displacement and afforded (*E*)-*S*-vinylthioimidonium tetrafluoroborate (*E*)-**12** quantitatively (Scheme 8). Under the conditions, (*E*)-**4** similarly produced inverted (*Z*)-imidonium salt (*Z*)-**12** selectively, but in contrast the yield was found to be very low (14%) and a large amount (79%) of (*E*)-**4** was recovered unchanged. These results again indicate lower reactivity of (*E*)-**4** toward vinylic S$_N$2 reaction than that of the *Z*-isomer. Highly basic methoxide ion (NaOMe/MeOH/rt/1 h) resulted in an exclusive elimination reaction of (*Z*)-**4** and produced ynol ether **10** in a high yield (87%), while interestingly (*E*)-**4** was recovered unchanged under the conditions.



Scheme 8. Vinylic S$_N$2 reaction with a thioamide.

2.4. Kinetic measurements

Rates for nucleophilic substitutions of various kinds of β-substituted vinyl-λ^3-iodanes **1**, **2**, and **4** with tetrabutylammonium halides were measured spectrophotometrically by monitoring the decrease in an absorbance in the range of 250–330 nm. Pseudo-first-order rate constants k_{obsd} were obtained throughout each runs and the values for 2–5 runs were averaged. Table 2 shows the values for the observed first-order rate constants k_{obsd} determined for the reactions of vinyl-λ^3-iodanes (6×10^{-5} M) in acetonitrile, THF, and 1,4-dioxane, which contain an excess *n*-Bu$_4$NX (0.02 M). It is noted that the observed value of 7.9×10^{-4} s^{-1} for the reaction of (*Z*)-**4** with *n*-Bu$_4$NCl in THF at 50 °C (Table 2, entry 13) probably reflects the rate of the *anti* β- and/or α-elimination, as shown in Table 1 (entry 2).

Table 2
Observed rate constants for the reaction of vinyl-λ^3-iodanes with tetrabutylammonium halides[a]

Entry	λ^3-Iodane	X	Temp. (°C)	Solvent	10^5k_{obsd}/s^{-1}
1	(*E*)-**1**[b]	Br	25	CH$_3$CN	120
2	(*E*)-**1**[b]	Br	22	THF	1040
3	(*E*)-**1**[b]	I	25	CH$_3$CN	339
4	(*Z*)-**2a**	Br	60	CH$_3$CN	13.2
5	(*Z*)-**2a**	Br	50	THF	79.0
6	(*Z*)-**2b**	Br	60	CH$_3$CN	13.4
7	(*Z*)-**2c**	Br	60	CH$_3$CN	12.4
8	(*Z*)-**2d**	Br	60	CH$_3$CN	10.5
9	(*Z*)-**4**	Br	60	CH$_3$CN	42.8
10	(*Z*)-**4**	Br	50	THF	227
11	(*Z*)-**4**	Br	50	1,4-Dioxane	47.0
12	(*Z*)-**4**	I	60	CH$_3$CN	130
13	(*Z*)-**4**	Cl	50	THF	79.0
14	((*Z*)-**4**)$_2$·18C6	Br	60	CH$_3$CN	43.0
15	(*E*)-**4**	Br	60	CH$_3$CN	0.794
16	(*E*)-**4**	Br	50	THF	50.3
17	(*E*)-**4**	Br	50	1,4-Dioxane	33.9
18	(*E*)-**4**	I	60	CH$_3$CN	4.68

[a] Initial concentration: vinyl-λ^3-iodane, 6×10^{-5} M; *n*-Bu$_4$NX, 0.02 M.
[b] R=*n*-C$_8$H$_{17}$.

As shown by the previous report of Okuyama, Ochiai, and coworkers,[4a] nucleophilic substitutions of the β-substituted vinyl-λ^3-iodanes with bromide anion in THF are always faster than those in acetonitrile. A more effective hydrogen bonding between the latter solvent and the halide anion, leading to the reduced nucleophilicity of the anion, will be responsible at least in part for the decreased rates of substitutions in acetonitrile.[33]

2.5. Discussion

The observed rate constants, shown in Table 2, indicate that the vinylic S$_N$2 reactions of (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane (*Z*)-**4** with halides (Br, I) proceed more rapidly than those of the *E*-isomer, especially for the reactions in acetonitrile solution. For instance, reactions of (*Z*)-**4** with bromide and iodide in acetonitrile are 54 and 28 times faster than those of (*E*)-**4**, respectively (compare entries 9 and 15; 12 and 18). A similar tendency for the reactivity difference between (*Z*)- and (*E*)-**4** but to a lesser extent ($k_{Z\text{-}4}/k_{E\text{-}4}$=4.5 and 1.4) was observed for the vinylic substitutions with bromide in THF and 1,4-dioxane (compare entries 10 and 16; 11 and 17).

The greater reactivity of the *Z*-isomer (*Z*)-**4** toward the vinylic S$_N$2 reactions is probably ascribed to its higher ground state energy due to a vicinal steric interaction between sterically demanding Ph(CH$_2$)$_2$O and I(Ph)BF$_4$ groups.[34,35] In other words, steric assistance[36] would efficiently increase the reaction rates of (*Z*)-**4** compared to that of (*E*)-**4**, because the vicinal steric interaction of the *Z*-isomer will be attenuated to some extent in the concerted vinylic S_N2 transition state. The β-(2-phenylethoxy) group of (*E*)-**4** could cause steric and electrostatic repulsions toward the incoming halide ion in the in-plane S_N2 transition state.[4a] The rate of nucleophilic substitutions depends on halide anions and decreases in the order *n*-Bu_4NI>*n*-Bu_4NBr (entries 1, 3, 9, 12, 15, and 18).

Table 2 shows that, in both acetonitrile and THF solutions, magnitude of the observed rate constants for the reactions of vinyl-λ^3-iodanes with *n*-Bu_4NBr decreases in the order (*E*)-**1**>(*Z*)-**4**>(*Z*)-**2a**>(*E*)-**4** (entries 1, 9, 4, and 15 in acetonitrile; entries 2, 10, 5, and 16 in THF). These reactivity orders seem to suggest that the presence of an inductively electron-withdrawing group at the β-position of vinyl-λ^3-iodanes decreases the rate of nucleophilic vinylic substitutions.[37] In fact, introduction of an electron-withdrawing *p*-Cl or *p*-CF_3 group at the β-benzoyloxy substituent of (*Z*)-vinyl-λ^3-iodane (*Z*)-**2a** tends to slightly decrease the rates of nucleophilic vinylic substitutions in acetonitrile. A linear free energy relationship ($\rho=-0.15$) for the substituent effects in the reaction of (*Z*)-**2** with bromide anion with a correlation coefficient *r* of 0.97 was found between log k_{Ar}/k_{Ph} and Hammett σ_p constants (Fig. 3).

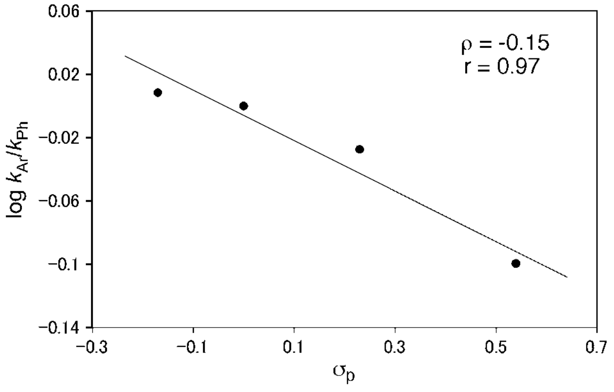
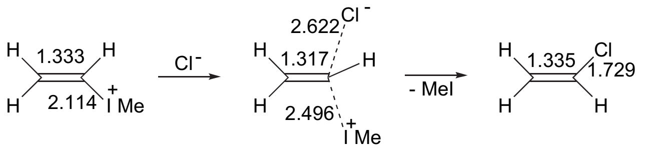


Figure 3. Hammett plot of log k_{Ar}/k_{Ph} vs σ_p constants for the reaction of (*Z*)-**2**.

Okuyama and Yamataka reported an ab initio MO (MP2/DZ+d) calculation for the vinylic S_N2 reaction of vinyl(methyl)iodonium ion with chloride anion (Scheme 9), which indicates that the transition state geometry of the concerted vinylic S_N2 displacement is quite loose with a small degree of C–Cl bond formation (2.622 Å) and with a large extent of C–I(III) bond cleavage (2.496 Å).[6b] Therefore, a considerable positive charge will be developed at the vinylic *ipso* carbon atom in the transition state. Double bond distance (1.317 Å) becomes significantly shorter than that of the vinyl(methyl)iodonium ion, probably reflecting the substantial hyperconjugative stabilization between σ(Cβ–H) and σ*(Cα–I) orbitals, evoked by the buildup of partial positive charge at the vinylic α-carbon atom. Similar MO calculations have been reported for the gas-phase vinylic S_N2 reaction of vinyl chloride with nucleophiles.[6d,e]



Scheme 9. Calculated vinylic S_N2 reaction of vinyl(methyl)iodonium ion with chloride.

Ab initio MO calculations indicate that, for the β-substituted vinyl cations $XCH{=}CH^+$, both the hyperconjugative effect between σ(C–X) and empty 2p(C^+) orbitals and the X inductive effect control the stability of the vinyl cations, and the vinyl stabilization energies estimated from isodesmic reactions decrease in the order of β-Me>H>β-OH>β-F.[38] A similar order of substituent effects on the gas-phase S_N2 reaction of imidoyl chlorides XN=CHCl (X=Me, H, F) with chloride anion has been calculated at the G2(+)//MP2/6-311+G** level.[6e] Thus, it seems reasonable to assume that the ability of a β-substituent to stabilize the vinylic S_N2 transition state of vinyl-λ^3-iodanes by hyperconjugative and inductive effects will increase in the order β-$PhCO_2$<β-$Ph(CH_2)_2O$<β-*n*-C_8H_{17}, which is in good agreement with our experimental results shown in Table 2.

3. Conclusion

Both isomers of (*E*)- and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodanes **4** and (*Z*)-β-aroyloxyvinyl-λ^3-iodanes (*Z*)-**2** were prepared stereoselectively. These β-substituted vinyl-λ^3-iodanes undergo nucleophilic vinylic substitution reactions with tetrabutylammonium halides (Cl, Br, and I). The observed inversion of configuration at the *ipso* vinylic carbon atom in the reactions is compatible with a concerted vinylic S_N2 mechanism. Kinetic measurements indicated that the rates for vinylic S_N2 reaction of vinyl-λ^3-iodane (*Z*)-**4** with halides are larger than those of the *E*-isomer, probably because of the higher ground state energy of (*Z*)-**4** caused by a vicinal steric interaction between sterically demanding $Ph(CH_2)_2O$ and $I(Ph)BF_4$ groups. The observed rate constants for the reactions of vinyl-λ^3-iodanes with *n*-Bu_4NBr decreased in the order (*E*)-**1**>(*Z*)-**4**>(*Z*)-**2a**>(*E*)-**4**. Since buildup of partial positive charge at the vinylic *ipso* carbon atom in the transition state of the concerted vinylic S_N2 reaction is expected, vinyl-λ^3-iodanes with a β-substituent, showing the more efficient hyperconjugative and inductive effects, react faster.

4. Experimental

4.1. General information

IR spectra were recorded on Perkin–Elmer 1720 FT-IR spectrometer. ^1H and ^{13}C NMR were recorded on a JEOL JNM-AL300 or AL400 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on either JEOL JMS-DX 300, JEOL-SX 102A, Waters LCT Premier, or SHIMADZU Model GCMS-QP505 spectrometer. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected.

Substrates. (*E*)-1-Decenyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**1**)[27] was prepared by boron–iodine(III) exchange reaction. Ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**3**)[18] and trimethylsilylethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**5**)[18] were purchased from Tokyo Kasei Kogyo Co. Ltd.

4.2. Synthesis of β-(2-phenylethoxy)vinyl-λ^3-iodanes (*Z*)- and (*E*)-4, and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane·18C6 2:1 complex 6

*4.2.1. Reaction of ethynyl(phenyl)-λ^3-iodane **3** with phenethyl alcohol: preparation of (Z)-[β-(2-phenylethoxy)vinyl](phenyl)(tetrafluoroborato)-λ^3-iodane (Z)-(**4**).* Ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**3**) (14 mg, 0.044 mmol) was dissolved in phenethyl alcohol (1.3 mL) under argon and the solution was stirred for 5.5 h at room temperature. Evaporation of the solvent under reduced pressure, followed by repeated decantation at room temperature with hexane and then with diethyl ether, gave (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane **4** (15 mg, 73%): colorless prisms (recrystallized from dichloromethane/hexane at −20 °C); mp 61–61.5 °C; IR (KBr) 3120, 1614, 1285, 1150–900, 744, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J*=8.2 Hz, 2H), 7.55 (t, *J*=7.7 Hz, 1H), 7.37 (dd, *J*=8.2, 7.7 Hz, 2H), 7.33–7.19 (m, 3H), 7.15 (d, *J*=7.0 Hz, 2H), 6.97 (d, *J*=3.3 Hz, 1H), 5.97 (d, J=3.3 Hz, 1H), 4.38 (d, J=6.6 Hz, 2H), 2.95 (d, J=6.6 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 160.1, 136.7, 134.6, 132.3, 132.2, 129.1, 128.9, 127.6, 110.9, 76.1, 70.6, 36.0. Anal. Calcd for $C_{16}H_{16}BF_4IO$: C, 43.87; H, 3.68. Found: C, 43.70; H, 3.66.

4.2.2. Reaction of trimethylsilylethynyl-λ^3-iodane ***5*** *with phenethyl alcohol: preparation of (Z)-vinyl-λ^3-iodane (Z)-**4**.* Trimethylsilylethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**5**) (60 mg, 0.16 mmol) was dissolved in phenethyl alcohol (1.2 mL) and the solution was stirred for 27 h at room temperature. After addition of dichloromethane (1 mL), diethyl ether (1 mL), and hexane (10 mL), the mixture was allowed to stand at room temperature for 1 h. The supernatant was removed and the residue was washed several times with hexane and diethyl ether by decantation at room temperature to give λ^3-iodane (Z)-**4** (49 mg, 72%) as a pale yellow oil. Recrystallization from dichloromethane/hexane at −20 °C gave colorless prisms.

4.2.3. Reaction of trimethylsilylethynyl-λ^3-iodane ***5*** *with phenethyl alcohol in the presence of 18C6: preparation of (Z)-vinyl-λ^3-iodane·18C6 2:1 complex* ***6***. To a mixture of trimethylsilylethynyl-λ^3-iodane **5** (300 mg, 0.77 mmol) and 18-crown-6 (102 mg, 0.39 mmol) was added phenethyl alcohol (22 mL) at room temperature and the solution was stirred for 47 h. After addition of ethyl acetate (20 mL) and hexane, the reaction mixture was allowed to stand at −20 °C for 30 min to give the complex **6** (310 mg, 69%): colorless prisms (recrystallized from dichloromethane/hexane at −20 °C); mp 90–91 °C; IR (Nujol) 3130, 1610, 1232, 1150–900, 833, 736, 704 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J=8.0 Hz, 4H), 7.62 (d, J=7.0 Hz, 2H), 7.41 (dd, J=8.0, 7.0 Hz, 4H), 7.36–7.21 (m, 6H), 7.17 (d, J=7.3 Hz, 4H), 6.89 (d, J=3.5 Hz, 2H), 5.93 (d, J=3.5 Hz, 2H), 4.43 (t, J=5.9 Hz, 4H), 3.67 (s, 24H), 3.02 (t, J=5.9 Hz, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 159.6, 136.7, 134.8, 132.0, 131.8, 128.9, 128.7, 126.9, 111.4, 75.7, 71.0, 69.8, 35.9. Anal. Calcd for $C_{44}H_{56}B_2F_8I_2O_8$: C, 46.34; H, 4.94. Found: C, 46.04; H, 4.87.

*4.2.4. Preparation of (E)-[α-trimethylsilyl-β-(2-phenylethoxy)vinyl](phenyl)(tetrafluoroborato)-λ^3-iodane (**7**).* To a stirred solution of iodosylbenzene (0.18 g, 0.80 mmol), bis(phenethyl) ether (0.90 g, 4.0 mmol), and ethynyl(trimethyl)silane (0.24 g, 2.4 mmol) in dichloromethane (6.0 mL) was added 1.0 M dichloromethane solution of BF_3–bis(phenethyl) ether complex (0.8 mL, 0.80 mmol) at 0 °C under nitrogen and the mixture was stirred at room temperature for 15 h. After addition of a cold water, the mixture was extracted with dichloromethane four times. The combined organic phase was washed with a cold saturated aqueous solution of NaBr (2 mL) two times, and then with saturated aqueous solution of NaBF$_4$ (2 mL) four times. After filtration of the organic phase, dichloromethane was evaporated under aspirator vacuum to give an oil, which was washed several times with hexane by decantation at room temperature to give (E)-α-trimethylsilyl-β-(2-phenylethoxy)vinyl-λ^3-iodane **7** (120 mg, 26%) as a pale yellow oil: IR (neat) 3060, 1574, 1266, 1167, 1150–950, 847, 738 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (s, 1H), 7.83 (d, J=8.5 Hz, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.46 (dd, J=8.5, 7.4 Hz, 2H), 7.35–7.18 (m, 5H), 4.52 (t, J=7.0 Hz, 2H), 3.05 (t, J=7.0 Hz, 2H), 0.11 (s, 9H); HRMS (ESI, positive) calcd for $C_{19}H_{24}IOSi$ [(M−BF$_4$)$^+$] 423.0641, found 423.0653.

*4.2.5. Synthesis of (E)-[β-(2-phenylethoxy)vinyl](phenyl)(tetrafluoroborato)-λ^3-iodane (E)-(**4**).* Vinyl-λ^3-iodane **7** (120 mg, 0.21 mmol) was dissolved in methanol (4.0 mL, 99 mmol) under argon and the solution was stirred for 48 h at room temperature. Evaporation of the solvent under reduced pressure, followed by repeated decantation with hexane at 0 °C gave (E)-β-(2-phenylethoxy)vinyl-λ^3-iodane (E)-**4** (78 mg, 85%) as a pale yellow oil; IR (neat) 3092, 1586, 1160, 1130–1000, 990, 739 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, J=8.2 Hz, 2H), 7.65 (d, J=12.9 Hz, 1H), 7.63 (t, J=7.4 Hz, 1H), 7.48 (dd, J=8.2, 7.4 Hz, 2H), 7.35–7.17 (m, 5H), 6.11 (d, J=12.9 Hz, 1H), 4.29 (d, J=6.9 Hz, 2H), 3.04 (d, J=6.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.0, 136.9, 134.0, 132.3, 132.1, 129.0, 128.6, 126.8, 112.2, 72.8, 70.7, 35.2; HRMS (FAB, positive) calcd for $C_{16}H_{16}IO$ [(M−BF$_4$)$^+$] 351.0246, found 351.0241.

4.3. General procedure for preparation of (*Z*)-β-aroyloxyvinyl(phenyl)(tetrafluoroborato)-λ^3-iodanes 2a–d. A typical example: (*Z*)-(β-benzoyloxyvinyl)(phenyl)(tetrafluoroborato)-λ^3-iodane (2a)

To a mixture of ethynyl(phenyl)(tetrafluoroborato)-λ^3-iodane (**3**) (650 mg, 2.1 mmol), benzoic acid (2.3 g, 19 mmol), and sodium benzoate (59 mg, 0.41 mmol) was added methanol (50 mL) at room temperature under argon and the solution was stirred for 2 h. The solvent was evaporated under reduced pressure. To remove excess benzoic acid, the residue was washed several times with diethyl ether by decantation. The crude product was dissolved in methanol and the solution was vigorously shaken with a saturated aqueous NaBF$_4$ solution two times. The organic layer was filtered and concentrated under aspirator vacuum to give (Z)-(β-benzoyloxyvinyl)phenyl-λ^3-iodane **2a** (690 mg, 76%). Recrystallization from dichloromethane/hexane gave colorless needles.[13]

*4.3.1. (Z)-[β-(4-Methylbenzoyloxy)vinyl](phenyl)(tetrafluoroborato)-λ^3-iodane (**2b**).* Colorless needles (recrystallized from dichloromethane/ether at −20 °C): mp 129–130 °C; IR (KBr) 1749, 1607, 1150–900, 742 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, J=3.9 Hz, 1H), 8.01 (d, J=8.4 Hz, 2H), 7.98 (d, J=8.4 Hz, 2H), 7.61 (t, J=7.2 Hz, 1H), 7.45 (t, J=8.4 Hz, 2H), 7.35 (t, J=8.4 Hz, 2H), 6.60 (d, J=3.9 Hz, 1H), 2.45 (s, 3H); HRMS (FAB, positive) calcd for $C_{16}H_{14}IO_2$ [(M−BF$_4$)$^+$] 365.0039, found 365.0088. Anal. Calcd for $C_{16}H_{14}BF_4IO_2$: C, 42.52; H, 3.12. Found: C, 42.29; H, 3.41.

*4.3.2. (Z)-[β-(4-Chlorobenzoyloxy)vinyl](phenyl)(tetrafluoroborato)-λ^3-iodane (**2c**).* Colorless prisms (recrystallized from dichloromethane/hexane at −20 °C); mp 138–139 °C; IR (KBr) 1752, 1591, 1150–900, 742 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, J=4.1 Hz, 1H), 8.06 (d, J=8.4 Hz, 2H), 8.00 (d, J=8.4 Hz, 2H), 7.63 (t, J=7.7 Hz, 1H), 7.53 (d, J=8.4 Hz, 2H), 7.47 (dd, J=8.4, 7.7 Hz, 2H), 6.61 (d, J=4.1 Hz, 1H); HRMS (FAB, positive) calcd for $C_{15}H_{11}ClIO_2$ [(M−BF$_4$)$^+$] 384.9492, found 384.9492. Anal. Calcd for $C_{15}H_{11}BF_4ClIO_2\cdot 2/5H_2O$: C, 37.56; H, 2.48. Found: C, 37.85; H, 2.88.

*4.3.3. (Z)-{β-[4-(Trifluoromethyl)benzoyloxy]vinyl}(phenyl)(tetrafluoroborato)-λ^3-iodane (**2d**).* Colorless needles (recrystallized from dichloromethane/ether/hexane at −20 °C); mp 106–107 °C; IR (KBr) 1749, 1626, 1200–950, 735 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, J=7.9 Hz, 2H), 8.22 (d, J=3.8 Hz, 1H), 8.01 (d, J=8.2 Hz, 2H), 7.81 (d, J=7.9 Hz, 2H), 7.63 (t, J=7.3 Hz, 1H), 7.47 (dd, J=8.2, 7.3 Hz, 2H), 6.67 (d, J=3.8 Hz, 1H); HRMS (ESI, positive) calcd for $C_{16}H_{11}F_3IO_2$ [(M−BF$_4$)$^+$] 418.9756, found 418.9731.

4.4. General procedure for the reaction of (*E*)- and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodanes 4 with tetrabutylammonium halides. A typical example (Table 1, entry 3)

To a stirred solution of (E)-vinyl-λ^3-iodane (E)-**4** (4.3 mg, 0.0097 mmol) in THF (1 mL) was added tetrabutylammonium bromide (31 mg, 0.096 mmol) at room temperature under nitrogen and the mixture was heated at 65 °C for 24 h. After cooling, the mixture was poured into water and extracted with pentane (5 mL). The combined organic phase was washed with water four times, filtered, and analyzed by GC using a capillary column of FFS ULBON HR-1 (0.25 mm×50 m, 100 °C, undecane as an internal standard): iodobenzene (56%) and bromobenzene (2%). The mixture was dried over anhydrous Na_2SO_4 and concentrated at 0 °C under an aspirator vacuum to give an oil. The yields of (*E*)-β-(2-phenylethoxy)vinyl bromide (*E*)-(**8b**) (2%) and (*E*)-β-(2-phenylethoxy)vinyl iodide (*E*)-(**8c**) (5%) were determined by integration of the ^1H NMR spectrum of the crude reaction mixture. Preparative TLC (hexane/diethyl ether, 9:1) gave (*Z*)-β-(2-phenylethoxy)vinyl bromide (*Z*)-(**8b**) (1.3 mg, 59%) as a colorless oil: IR (neat) 3107, 2935, 1643, 1496, 1454, 1317, 1238, 1105, 750, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16 (m, 5H), 6.57 (d, *J*=4.0 Hz, 1H), 5.10 (d, *J*=4.0 Hz, 1H), 4.10 (t, *J*=7.3 Hz, 1H), 3.00 (t, *J*=7.3 Hz, 1H); MS *m*/*z* (relative intensity) 228 [7%, M^+ (^{81}Br)], 226 [7, M^+ (^{79}Br)], 105 (100), 91 (12), 79 (20), 77 (21); HRMS *m*/*z* calcd for $C_{10}H_{11}BrO$ (M^+) 225.9993, found 226.0001.

*4.4.1. (E)-β-(2-Phenylethoxy)vinyl chloride (E)-(**8a**).* A colorless oil; IR (neat) 3101, 2925, 1620, 1496, 1454, 1387, 1317, 1176, 748, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.16 (m, 5H), 6.67 (d, *J*=11.3 Hz, 1H), 5.49 (d, *J*=11.3 Hz, 1H), 3.90 (t, *J*=6.9 Hz, 2H), 2.97 (t, *J*=6.9 Hz, 2H); MS *m*/*z* (relative intensity) 182 (2%, M^+), 105 (100), 91 (8), 79 (14), 77 (15); HRMS (ESI, positive) calcd for $C_{10}H_{11}ClNaO$ $[(M+Na)^+]$ 205.0396, found 205.0401.

*4.4.2. (Z)-β-(2-Phenylethoxy)vinyl chloride (Z)-(**8a**).* A colorless oil; IR (neat) 3103, 2931, 1651, 1496, 1454, 1329, 1246, 1113, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.16 (m, 5H), 6.31 (d, *J*=4.0 Hz, 1H), 5.12 (d, *J*=4.0 Hz, 1H), 4.09 (t, *J*=7.5 Hz, 2H), 3.00 (t, *J*=7.5 Hz, 2H); MS *m*/*z* (relative intensity) 182 (2%, M^+), 105 (100), 91 (7), 79 (2), 77 (3); HRMS (ESI, positive) calcd for $C_{10}H_{11}ClNaO$ $[(M+Na)^+]$ 205.0396, found 205.0402.

*4.4.3. (E)-β-(2-Phenylethoxy)vinyl bromide (E)-(**8b**).* A colorless oil; IR (neat) 3101, 2924, 1632, 1601, 1496, 1454, 1321, 1163, 749, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.18 (m, 5H), 6.76 (d, *J*=11.8 Hz, 1H), 5.37 (d, *J*=11.8 Hz, 1H), 3.92 (t, *J*=7.0 Hz, 2H), 2.97 (t, *J*=7.0 Hz, 2H); MS *m*/*z* (relative intensity) 228 [10%, M^+ (^{81}Br)], 226 [10, M^+ (^{79}Br)], 105 (100), 79 (42), 77 (36); HRMS *m*/*z* calcd for $C_{10}H_{11}BrO$ (M^+) 225.9993, found 226.0005.

*4.4.4. (E)-β-(2-Phenylethoxy)vinyl iodide (E)-(**8c**).* A colorless oil; IR (neat) 3084, 2924, 1626, 1597, 1456, 1219, 1146, 1097, 750, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.16 (m, 5H), 6.81 (d, *J*=12.5 Hz, 1H), 5.06 (d, *J*=12.5 Hz, 1H), 3.96 (t, *J*=7.3 Hz, 2H), 2.98 (t, *J*=7.3 Hz, 2H); MS *m*/*z* (relative intensity) 274 (10%, M^+), 105 (100), 91 (12), 79 (30), 77 (24); HRMS *m*/*z* calcd for $C_{10}H_{11}IO$ (M^+) 273.9855, found 273.9856.

*4.4.5. (Z)-β-(2-Phenylethoxy)vinyl iodide (Z)-(**8c**).* A colorless oil; IR (neat) 3091, 2929, 1626, 496, 1454, 1309, 1221, 1097, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5H), 6.57 (d, *J*=3.8 Hz, 1H), 4.93 (d, *J*=3.8 Hz, 1H), 4.13 (t, *J*=7.3 Hz, 2H), 3.00 (t, *J*=7.3 Hz, 2H); MS *m*/*z* (relative intensity) 274 (44%, M^+), 105 (100), 91 (13), 79 (16), 77 (17); HRMS *m*/*z* calcd for $C_{10}H_{11}IO$ (M^+) 273.9855, found 273.9856.

*4.4.6. α-(2-Phenylethoxy)vinyl chloride (**9a**).* A colorless oil; IR (neat) 3030, 2925, 2854, 1637, 1454, 1192, 1173, 1022, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.17 (m, 5H), 4.35 (d, *J*=3.7 Hz, 1H), 4.31 (d, *J*=3.7 Hz, 1H), 4.05 (t, *J*=7.3 Hz, 2H), 3.02 (t, *J*=7.3 Hz, 2H); MS *m*/*z* (relative intensity) 182 (12%, M^+), 105 (100), 91 (12), 79 (28), 77 (29); HRMS (ESI, positive) calcd for $C_{10}H_{11}ClNaO$ $[(M+Na)^+]$ 205.0396, found 205.0393.

Formation of α-(2-phenylethoxy)vinyl bromide (**9b**) was detected by ^1H NMR and GC/MS, but it was too labile to be isolate.

*4.4.7. α-(2-Phenylethoxy)vinyl bromide (**9b**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.15 (m, 5H), 4.74 (d, *J*=3.7 Hz, 1H), 4.55 (d, *J*=3.7 Hz, 1H), 4.05 (t, *J*=7.3 Hz, 2H), 3.02 (t, *J*=7.3 Hz, 2H); MS *m*/*z* (relative intensity) 228 [<0.1%, M^+ (^{81}Br)], 226 [<0.1%, M^+ (^{79}Br)], 105 (100), 79 (19), 77 (15).

4.5. Nucleophilic substitutions of (*E*)- and (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane 4 with thioamide. A representative example: reaction of (*Z*)-4 with *N*,*N*-dimethylthiobenzamide

To a stirred solution of (*Z*)-vinyl-λ^3-iodane **4** (8.0 mg, 0.018 mmol) in dichloromethane (1.3 mL) was added *N*,*N*-dimethylthiobenzamide (30 mg, 0.18 mmol) at room temperature under argon and the mixture was heated at 40 °C for 27 h. After the solution was concentrated under an aspirator vacuum to one-half of its original volume, addition of hexane (5 mL) separated a pale yellow oil, which was washed several times with hexane/diethyl ether by decantation to give (*E*)-*S*-[β-(2-phenylethoxy)vinyl]-*N*,*N*-(dimethyl)thiobenzimidonium tetrafluoroborate (*E*)-(**12**) (7.4 mg, 100%) as a pale yellow oil; IR (neat) 2947, 1616, 1601, 1496, 1288, 1100–1000, 758, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56–7.46 (m, 3H), 7.42–7.33 (m, 2H), 7.33–7.18 (m, 3H), 7.05 (d, *J*=7.0 Hz, 2H), 6.84 (d, *J*=16.1 Hz, 1H), 4.65 (d, *J*=16.1 Hz, 1H), 3.80 (s, 3H), 3.72 (t, *J*=6.6 Hz, 2H), 3.47 (s, 3H), 2.76 (t, *J*=6.6 Hz, 2H); HRMS (FAB, positive) calcd for $C_{19}H_{22}NOS$ $[(M-BF_4)^+]$ 312.1422, found 312.1426.

*4.5.1. (Z)-S-[β-(2-Phenylethoxy)vinyl]-N,N-(dimethyl)thiobenzimidonium tetrafluoroborate (Z)-(**12**).* A pale yellow oil; IR (neat) 2925, 1620, 1446, 1286, 1200–950, 760, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.44 (m, 3H), 7.42–7.18 (m, 7H), 6.30 (d, *J*=4.8 Hz, 1H), 4.47 (d, *J*=4.8 Hz, 1H), 4.11 (t, *J*=6.8 Hz, 2H), 3.82 (s, 3H), 3.46 (s, 3H), 2.98 (t, *J*=6.8 Hz, 2H); HRMS (ESI, positive) calcd for $C_{19}H_{22}NOS$ $[(M-BF_4)^+]$ 312.1422, found 312.1407.

4.6. Reaction of (*Z*)-β-(2-phenylethoxy)vinyl-λ^3-iodane (*Z*)-4 with sodium methoxide

To a stirred solution of (*Z*)-vinyl-λ^3-iodane **4** (5.4 mg, 0.012 mmol) in methanol (1 mL) was added a 0.49 M methanol solution of sodium methoxide (25 μL, 0.012 mmol) at room temperature under argon and the mixture was stirred for 1 h. The mixture was poured into water and extracted with dichloromethane four times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated at 0 °C under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexane/ethyl acetate, 9:1) to give (2-phenylethoxy)acetylene (**10**) (1.6 mg, 87%) as a colorless oil; IR (neat) 3313, 2952, 2148, 1496, 1456, 1375, 1103, 748, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 2H), 7.29–7.18 (m, 3H), 4.26 (t, *J*=7.3 Hz, 2H), 3.08 (t, *J*=7.3 Hz, 2H), 1.59 (s, 1H); MS *m*/*z* (relative intensity) 146 (3%, M^+), 105 (100), 91 (66), 77 (47); HRMS (ESI, positive) calcd for $C_{10}H_9Na_2O$ $[(M-H+2Na)^+]$ 191.0449, found 191.0458.

4.7. Kinetic study (Table 2)

Rates for the reaction of vinyl-λ^3-iodanes with tetrabutylammonium halides were measured by monitoring the decrease in absorbance at 250–330 nm at different temperatures in the range of 22–60 °C on Shimadzu UV-160A spectrophotometer. The reaction temperature was controlled by CPS-240A controller and accurate to within ±0.1 °C. A stock solution of vinyl-λ^3-iodanes was prepared by weighting and dissolving in 1,4-dioxane (0.017 M) and stored in a refrigerator at −20 °C. The reaction solutions were prepared by weighting of *n*-Bu_4NX and dissolving in CH_3CN, THF, and 1,4-dioxane (0.02 M) at room temperature. To a solution (3.0 mL) of *n*-Bu_4NX in a quartz cuvette inserted in a cell compartment of the spectrophotometer and equilibrated at the reaction temperature was added 10 μL of stock solution vinyl-λ^3-iodane from a microsyringe. The absorbance change was fed to a computer

NEC PC-9821V13 through an interface and processed by a pseudo-first-order kinetics program. The reaction followed pseudo-first-order kinetics for at least four half-lives and pseudo-first-order rate constants k_{obsd} were calculated.

4.8. Crystallographic data

Crystallographic data were recorded on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo KR radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct methods[39] and expanded using Fourier techniques.[40] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[41] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[42] All calculations were performed using the teXsan[43] crystallographic software package of Molecular Structure Corp.

X-ray data for (*Z*)-**4**: $C_{16}H_{16}BF_4IO$, $M=438.01$, $T=93$ K, triclinic space group *P*-1 (No. 2), $a=10.596(3)$ Å, $b=12.079(3)$ Å, $c=14.684(3)$ Å, $\alpha=110.52(2)^\circ$, $\beta=99.34(2)^\circ$, $\gamma=99.06(2)^\circ$, $V=1689.5(7)$ Å^3, $Z=4$, $D_c=1.722$ g cm^{-3}, μ (Mo Kα)=19.347 cm^{-1}. A total of 16,263 reflections were collected; 7656 were unique. $R=0.024$, $R_w=0.083$. CCDC registration number 761728.

X-ray data for **2a**: $C_{15}H_{12}BF_4IO_2$, $M=437.97$, $T=153$ K, triclinic space group *P*-1 (No. 2), $a=10.085(5)$ Å, $b=11.354(6)$ Å, $c=14.386(7)$ Å, $\alpha=100.19(4)^\circ$, $\beta=101.84(5)^\circ$, $\gamma=97.10(5)^\circ$, $V=1564.8(13)$ Å^3, $Z=4$, $D_c=1.859$ g cm^{-3}, μ (Mo Kα)=20.936 cm^{-1}. A total of 15,352 reflections were collected; 7098 were unique. $R=0.026$, $R_w=0.045$. CCDC registration number 761727.

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.04.041. These data include MOL files and InChIKeys of the most important compounds described in this article.

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