Bull. Chem. Soc. Jpn., 73, 2341—2349 (2000)

Reactions of 2,2-Dialkylvinyl Iodonium Salt with Halide Ions

Tadashi Okuyama,* Koichi Sato,† and Masahito Ochiai†

Faculty of Science, Himeji Institute of Technology, Kamigori, Hyogo 678-1297

†Faculty of Pharmaceutical Sciences, University of Tokushima, Tokushima 770-8505

(Received April 27, 2000)

Reactions of (*E*)- and (*Z*)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium (**1**) salts with halide ions were examined in various solvents at 50 or 60 °C. The main products are those of substitution, 1-halo-2-methyl-5-phenyl-1-pentenes, mainly of inversion but involving some retained products. Varying amounts of rearranged products are also formed. Reaction follows pseudo-first-order kinetics at [**1**] ≪ [halide ion]. The observed rate constants show curved dependence on halide concentration typical of reactions involving a pre-equilibrium formation of the adduct, λ^3-haloiodane, and first-, second-, and third-order reaction pathways. The first-order rate constant for the *E* isomer, (*E*)-**1**, is greater than that for (*Z*)-**1**, while the opposite is the case for the second- and third-order terms. The main reaction is considered to proceed via a vinylic in-plane S_N2 mechanism to lead to inversion while some retention routes via out-of-plane S_N2 and/or ligand coupling mechanism are also possible. Competing rearrangement reactions occur by the β-alkyl participation and no evidence for formation of the primary vinylic cation was obtained.

We have found that 2-monoalkylvinyliodonium salts undergo substitution by halide ions via a vinylic in-plane S_N2 pathway with inversion of configuration.[1—3] The only accompanying reaction was β-elimination of intermediate λ^3-haloiodane adducts. Hinkle and co-workers[4] have recently found that 2,2-dialkylvinyliodonium triflates thermally decompose with rearrangement and suggested that a primary vinylic cation was involved in this reaction. We have found that a similar salt, 2-methyl-5-phenyl-1-pentenyl(phenyl)-iodonium tetrafluoroborate (**1·BF$_4$**), undergoes solvolysis with extensive rearrangement, but the 1,2-alkyl migration is concluded mainly to occur via β-alkyl participation to directly lead to the rearranged secondary vinylic cations.[5] However, the primary vinylic cation seemed to be partially involved in some poorly nucleophilic solvents. On the other hand, careful examinations of solvolysis of a chiral 4-methylcyclohexylidenemethyliodonium salt show that formation of the rearranged products does not involve an achiral primary vinylic cation as intermediate.[6]

We now examine reactions of both geometrical isomers of **1**, (*E*)-**1** and (*Z*)-**1**, with halide ions in various solvents. These reactions result in formation of the unrearranged substitution products mainly of inversion with accompanying products of retention as well as rearranged ones. The reaction seems to take place via an intermediary formation of vinylic cations. However, various lines of evidence are incompatible with formation of the primary vinylic cation as a possible intermediate under the reaction conditions. The reactions involved are concluded to be primarily the in-plane vinylic S_N2 reaction with inversion and a minor retention pathway of the out-of-plane vinylic substitution (of S_N2 and ligand-coupling types) as well as heterolysis with β-alkyl participation leading to the rearranged secondary vinylic cations which mainly result in elimination.

Results

Product Analysis. Reactions of the salts of (*E*)-**1** and (*Z*)-**1** with chloride, bromide, and iodide ions were carried out at 50 °C in the presence of tetrabutylammonium halide in acetonitrile (AN) and chloroform as well as in some other aprotic solvents. The tetrafluoroborate **1·BF$_4$** was usually used as the substrate but the chloride **1·Cl** was sometimes employed for the reaction with chloride ion. It was found that both of the salts behaved in the same way in solutions containing excess chloride ion (see below). The ionic strength of the reaction solution was adjusted with tetrabutylammonium perchlorate when required. The products were extracted with pentane containing tetradecane as an internal standard for gas-chromatographic determination. Some products were isolated and identified by their spectra, while others were compared with the authentic samples. Those include iodobenzene (**2**), haloalkenes **3X**, and rearranged elimination products **6—8** (Eq. 1). Their yields were determined by gas chromatography; results are summarized in Table 1. When the product mixtures were carefully examined, a very small amount of iodoalkene **3I** of retained structure was detected ($< 0.5\%$ yield). Although a careful search for **3I** was not always conducted, it was usually detected when the yield of the retained substitution product **3X** is higher than 10%. Some other small GC peaks ($< 1\%$) that seem to correspond to the halide-trapping products of the rearranged cations were occasionally seen but could not be identified.

The reactions of **1** with bromide and chloride ions were also examined in protic solvents at 60 °C. In addition to the substitution products **3X**, solvolysis products **3—5** as well as cyclopentene derivative **9** (Chart 1) were obtained in these

Table 1. Product Distribution in the Reactions of **1** with Halide Ions in Aprotic Solvents at 50 °C

No.	Structure of **1**	Solvent	X[a](concn) mol dm^{-3}	μ[b]	Reaction time h	Product yield/% **2**	**3X** (*Z*/*E*)	**6**	**7**	**8**	Rearrangement %
1	*E*	AN	Cl (0.2)	0.2	40	80	74 (81/19)	7.2	0.9	0	9.9
2	*E*	AN	Cl (0.04)	0.2	40	77	70 (75/25)[c]	11	0.5	0	14.1
3	*E*	AN	Cl (0.04)	0.04	40	86	80 (75/25)[c]	12	0.6	0.2	13.8
4	*E*	AN	Cl (0.01)	0.2	25	76	63 (73/27)[c]	12	0.3	0.2	16.6
5	*E*	AN	Cl (0.01)	0.01	25	79	73 (73/27)[c]	12	0.2	0.2	14.5
6	*E*	AN	Cl (0.001)	0.2	40	79	25 (75/25)	30	0.8	0	55
7	*E*	AN	Cl (0.001)	0.001	40	83	47 (72/28)	18	0.3	0	28
8	*Z*	AN	Cl (0.2)	0.2	40	87	87 (8/92)	1.6	0	0	1.8
9	*Z*	AN	Cl (0.04)	0.2	30	75	87 (9/91)[c]	2.9	0	trace	3.3
10	*Z*	AN	Cl (0.01)	0.2	22	100	82 (10/90)[c]	2.9	0	0	3.4
11	*Z*	AN	Cl (0.001)	0.2	45	83	65 (10/90)	11	0	0.7	15.3
12	*Z*	AN	Cl (0.001)	0.001	40	84	72 (13/87)	4.0	0	trace	5.3
13	*E*	$CHCl_3$	Cl (0.2)	0.2	22	82	89 (80/20)	5	2	0	7.3
14	*E*	$CHCl_3$	Cl (0.04)	0.2	20	78	72 (77/23)	5	trace	0	6.5
15	*E*	$CHCl_3$	Cl (0.01)	0.2	18	73	71 (78/22)	6	trace	0	7.8
16	*E*	$CHCl_3$	Cl (0.01)	0.01	22	95	94 (75/25)	2.0	0	0	2.1
17	*E*	$CHCl_3$	Cl (0.001)	0.2	65	80	42 (77/23)	21	2.1	0.6	36
18	*E*	$CHCl_3$	Cl (0.001)	0.001	65	93	96 (75/25)	1.4	trace	0	1.5
19	*Z*	$CHCl_3$	Cl (0.04)	0.04	24	43	61 (8/92)	0	0	0	0
20	*Z*	$CHCl_3$	Cl (0.01)	0.2	22	54	69 (5/95)	trace	0	0	small
21	*Z*	$CHCl_3$	Cl (0.01)	0.01	22	84	93 (9/91)	trace	0	0	small
22	*Z*	$CHCl_3$	Cl (0.001)	0.2	65	79	84 (7.5/92.5)	1.8	0	0	2.1
23	*Z*	$CHCl_3$	Cl (0.001)	0.001	65	91	98 (9/91)	0	0	0	0
24	*E*	THF	Cl (0.04)	0.2	38	72	90 (68/32)	2	3	0	5.3
25	*Z*	THF	Cl (0.04)	0.2	16	57	74 (15/85)	0	0	0	0
26	*E*	DMF	Cl (0.04)	0.2	28	64	69 (74/26)	7	1	0	10
27	*Z*	DMF	Cl (0.04)	0.2	35	68	83 (11/89)	2	0	trace	2.4
28	*E*	AN	Br (0.04)	0.1	20	85	84 (77/23)[c]	5.2	0.3	0.1	6.1
29	*Z*	AN	Br (0.04)	0.1	20	88	98 (8/92)[c]	0.9	0	trace	0.9
30	*E*	AN	I (0.04)	0.04	17	86	90 (71/29)	1.2	0	0	1.3
31	*Z*	AN	I (0.04)	0.04	16	94	96 (11/89)	0	0	0	0

a) Bu_4NX. b) Ionic strength adjusted with tetrabutylammonium perchlorate. c) Retained **3I** (< 0.5 %) was also detected.

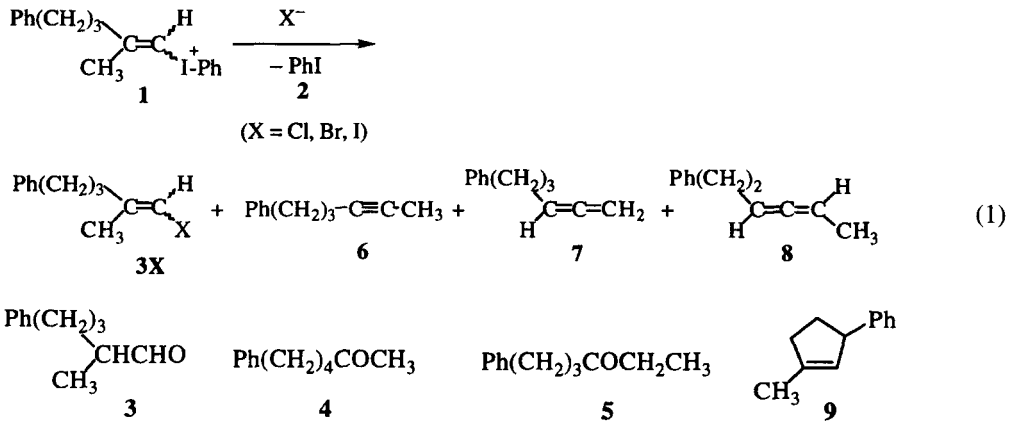


Chart 1.

solvolytic solvents as minor products (Table 2). Details of the solvolysis reactions were presented in a separate paper.[5b]

The product data given in Tables 1 and 2 can be summarized as follows: (1) Effects of the substrate geometry are clear. The stereoselectivity for inversion to give **3X** is greater with the *Z* isomer (*Z*)-**1** (90—97% inversion) than with (*E*)-**1** (70—86% inversion), except for the reactions in aqueous solution (Nos. 40—43). (2) The stereoselectivity is only slightly affected by concentration of chloride ion (Nos. 1—23). An increase in [Cl^-] tends to increase the fraction of inversion at the constant ionic strength (0.2) if the effects are small. (3) Effects of the reaction media are small but there is some clear tendency that the stereoselectivity for inversion is greater in more polar solvents. Although we do not

Table 2. Product Distribution in the Reactions of **1** with Halide Ions in Protic Solvents at 60 °C

No.	Structure of **1**	Solvent	X[a] (concn) mol dm^{-3}	Reaction time h	Product yield/% 2	3X (*Z*/*E*)	3	4	5	6	7	8	9	4+7 5+8	Rearrangement %
32	*E*	MeOH	Br (0.05)	25	57	18 (80/20)	12	11	0.5	17	4.2	0.2	0.6	95/5	52
33	*Z*	MeOH	Br (0.05)	25	68	45 (4.4/95.6)	7.5	0.6	4.6	8.5	0	2.1	trace	8/92	23
34	*E*	TFE	Br (0.05)	25	76	11 (86/14)	0.3	11	3.5	39	2.4	0.5	trace	77/23	83
35	*Z*	TFE	Br (0.05)	25	56	37 (2.6/97.4)	1.1	1.3	2.2	15	trace	0.6	1.0	32/68	34
36	*E*	TFE	Br (0.01)	30	75	5.6 (78/22)	0.5	12	4.0	34	1.4	trace	trace	71/29	90
37	*Z*	TFE	Br (0.01)	30	65	19 (6.0/94.0)	4.9	2.0	2.3	17	trace	trace	4.0	46/54	39
38	*E*	50M	Br (0.05)	25	45	1.2 (80/20)	1.9	7.6	0.5	20	4.5	0.2	0.3	94/6	92
39	*Z*	50M	Br (0.05)	25	54	9.0 (4.0/96.0)	7.3	0.9	6.1	17	0	4.0	1.0	8/92	63
40	*E*	H_2O	Br[b] (0.1)	50	58	0.7 (55/45)	2.0	19	1.3	27	4.6	0.3	0	94/6	95
41	*Z*	H_2O	Br[b] (0.1)	50	54	1.2 (13/87)	7.4	2.2	18	11	0	2.2	0.1	10/90	80
42	*E*	H_2O	Cl[c] (0.1)	30	57	0.2 (35/65)	2.9	16	1.0	16	2.1	0.1	0.2	94/6	92
43	*Z*	H_2O	Cl[c] (0.1)	30	55	1.0 (25/75)	6.1	1.6	13	22	0.2	5.5	0.1	9/91	86

a) Bu_4NX unless noted otherwise. b) NaBr. c) NaCl.

see any clear trend in chloride reactions in aprotic solvents (compare the data at [Cl$^-$] = 0.04 mol dm^{-3} and μ = 0.2 (or 0.04) given in Nos. 2/3, 9, 14, 19, and 24—27), the bromide reactions in a wider range of solvents including protic ones (Nos. 28, 29, and 32—35) show a clearer tendency of the increasing selectivity both for (*E*)-**1** and (*Z*)-**1** in the order AN (E_T^N = 0.460) < MeOH (0.762) < 2,2,2-trifluoroethanol (TFE) (0.898), solvent polarity shown by the E_T^N parameter[7] in parentheses. An increase in ionic strength of the solution in AN or $CHCl_3$ at a low chloride concentration ([Cl$^-$] = 0.001 mol dm^{-3}, Nos. 6 vs. 7, 11 vs. 12, 17 vs. 18, and 22 vs. 23) enhances the stereoselectivity for inversion in substitution, but it results in a larger fraction of the rearrangement. The salt effects to enhance rearrangement at low [Cl$^-$] are very large. (4) In aqueous solution, amounts of the halide substitution products are very small and the stereoselectivity is poor. (5) The *Z* isomer (*Z*)-**1** always gives fewer rearranged products than (*E*)-**1** under the same conditions as the values of % rearrangement (last column) show. The major rearrangement products are those of migration of the alkyl group *trans* to the leaving iodonio group as the values of (**4**+**7**)/(**5**+**8**) in Table 2 show. (6) Effects of different halide ions in AN on the stereoselectivity of substitution are small, but the fraction of substitution increases in the order Cl$^-$ < Br$^-$ < I$^-$.

Kinetic Measurements. The UV absorption spectrum of the substrate **1** is similar to other 1-alkenyliodonium salts:[2,3] the tetrafluoroborate **1**·BF_4 has strong absorption only below 240 nm, but the chloride salt **1**·**Cl** shows some absorbance at longer wavelengths. The strength of this absorption of **1**·**Cl** depends on the solvent and increases with concentration of added chloride ion (tetrabutylammonium chloride). Furthermore, in the presence of excess chloride ion, absorption spectra of **1**·BF_4 and **1**·**Cl** are essentially the same. The absorption of the solution containing chloride ion decreases with time following the pseudo-first-order kinetic law, but the initial absorbances A_i at 250 nm were determined by extrapolation of the decreasing absorbance to the time of mixing. The absorbances A_i obtained for (*E*)-**1** and (*Z*)-**1** in AN at 50 °C are plotted against [Cl$^-$] in Fig. 1 to give saturation

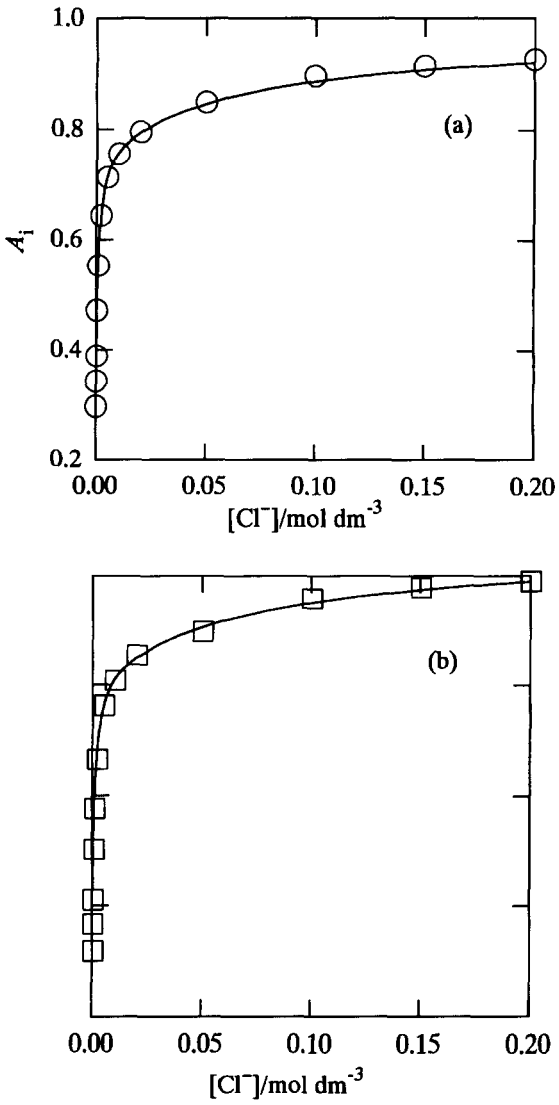
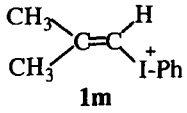


Fig. 1. Initial absorbances of (*E*)-**1** (a) and (*Z*)-**1** (b) in acetonitrile solution containing chloride ion at 250 nm and 50 °C. The ionic strength was maintained at 0.20 with tetrabutylammonium perchlorate.

curves as observed for similar salts.[2,3]

Pseudo-first-order rate constants k_{obsd} were determined for the reactions of both **(*E*)-1** and **(*Z*)-1** with chloride ion in AN and $CHCl_3$ at the constant ionic strength of 0.20 and at 50 °C. The k_{obsd} obtained are plotted against $[Cl^-]$ in Figs. 2 and 3. Rates for the reaction of 2-methyl-1-propenyliodonium tetrafluoroborate (**1m·BF$_4$**) were also determined in $CHCl_3$ for comparison (Chart 2, Fig. 3). Similar results were also obtained for the reactions with bromide ion (not shown). The *E* isomer **(*E*)-1** is more reactive at low $[Cl^-]$ than **(*Z*)-1**, but the relative reactivity is reversed at higher $[Cl^-]$. The k_{obsd} decreases gradually with $[Cl^-]$ after a sharp increase below $[Cl^-] = 0.001$ mol dm^{-3}. The simpler iodonium salt **1m** was found to be less reactive.



1m

Chart 2.

Discussion

Reaction Products. As is expected from the high nucleofugality of iodobenzene **(2)**[8] and nucleophilicity of the halide ions X^- involved, the main product is that of substitution, **3X** (Tables 1 and 2). The substitution is however not stereospecific in contrast to those observed with 2-monoalkylvinyliodonium salts, where the products are exclusively inverted ones in aprotic solvents and are concluded to be formed through the in-plane vinylic S_N2 mechanism.[1—3] Considerable amounts of elimination products of rearranged structure, **6—8**, are also formed, and this strongly suggests

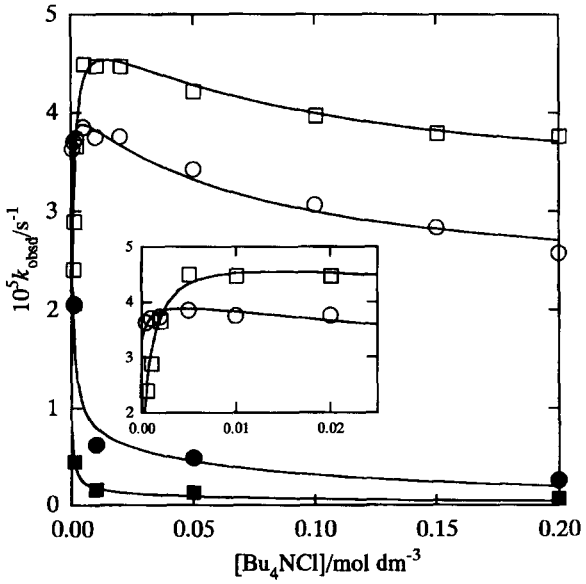


Fig. 2. Observed rate constants for the reaction of **(*E*)-1** (○) and **(*Z*)-1** (□) with chloride ion in acetonitrile at 50 °C and the ionic strength of 0.20. Closed symbols show partial rate constants evaluated for the rearrangement. The solid lines are calculated as described in text. The inset shows details at low chloride concentrations.

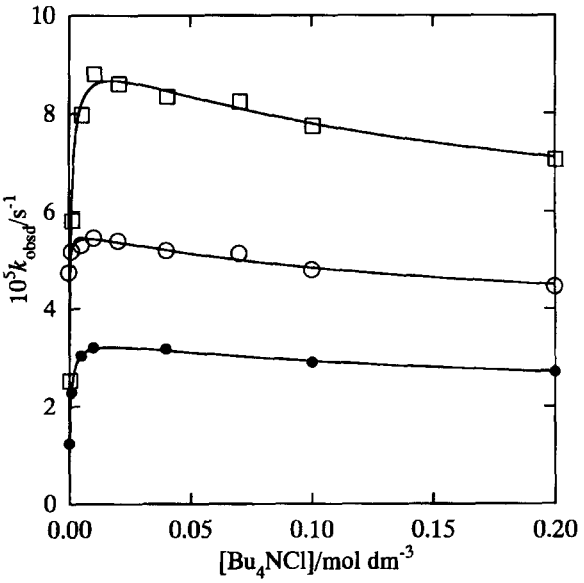
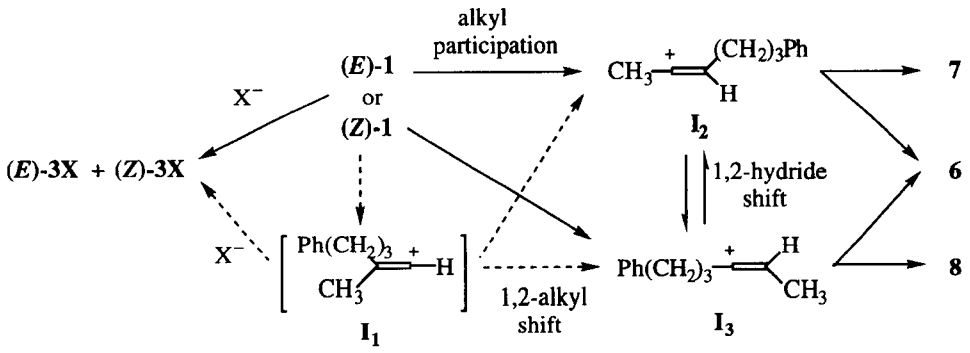


Fig. 3. Observed rate constants for the reaction of **(*E*)-1** (○), **(*Z*)-1** (□), and **1m** (●) with chloride ion in chloroform at 50 °C and the ionic strength of 0.20. The solid lines are calculated as described in text.

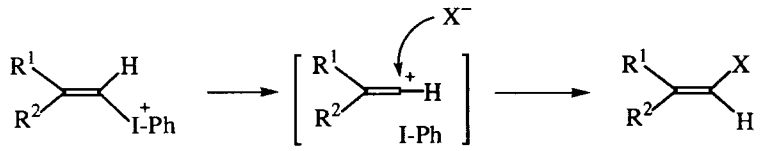
formation of vinylic cation intermediates as was found in the solvolysis reactions.[5] Overall reactions can be summarized in Scheme 1.

Disproof of Intermediacy of Primary Vinylic Cation. It is a controversial issue whether or not the primary vinylic cation like $\mathbf{I_1}$ is formed as a discrete intermediate under normal reaction conditions, even as a short-lived ion pair.[4,5,9—11] Our results can be analyzed by focusing on this question. The observed non-stereospecificity of the substitution with accompanying rearrangement appears to imply that the product **3X** has resulted from a nucleophilic capture by halide ion of the ion pair involving the primary vinylic cation $\mathbf{I_1}$ (ion-pair mechanism, Scheme 2) as some authors simply suggest.[4,10,11] The rearranged products arise from 1,2-migration of the β-alkyl groups; i.e., they must be derived from the secondary vinylic cations, $\mathbf{I_2}$ and $\mathbf{I_3}$, that could be generated by 1,2-alkyl shift of the putative primary cation $\mathbf{I_1}$. However, they can also be formed directly from **1** by the β-alkyl participation, as discussed in the previous papers.[5] Although the participation should occur stereospecifically only from the β-alkyl group *trans* to the leaving group, interconversion of the two secondary cations, $\mathbf{I_2}$ and $\mathbf{I_3}$, by 1,2-hydride shift can be quite rapid[5b] (Scheme 1). Observed rearrangements, even if they are not stereospecific, do not necessarily mean that the primary cation $\mathbf{I_1}$ is involved.

The medium effects observed may be argued against an ion-pair mechanism involving the primary vinylic cation $\mathbf{I_1}$. The ion-pair mechanism implies that the incipient cation paired with the leaving nucleofuge is mainly captured by the halide ion from the opposite side of the nucleofuge, resulting mainly but not exclusively in inversion of stereochemistry (Scheme 2). In more polar solvents or at higher salt concentrations, the ion pair should tend to dissociate or become looser, and so the nucleophilic trapping of the paired cation



Scheme 1.



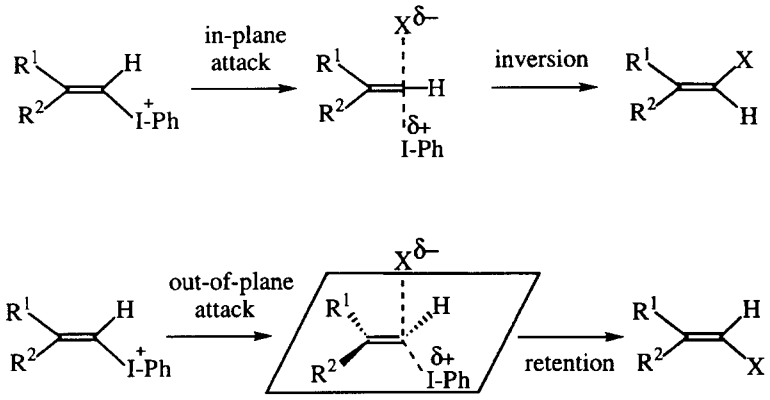
Scheme 2. Ion-pair mechanism.

would become less stereoselective, contrary to the observations. Furthermore, the nucleofuge is neutral in the present case and the counter anion is mainly halide ion under the reaction conditions (see below). So, the ion pair is actually a cation-molecule pair or a neutral molecule-shared cation-anion pair. Under these circumstances, the stereoselectivity cannot be so good. The observed medium effects are incompatible with the ion-pair picture.

Vinylic S_N2 Mechanisms and Rearrangement. Results with the geometrically isomeric substrates show that the substitution is mainly inversion, and both the stereoselectivity for inversion and the chemoselectivity for substitution (compared with rearrangement) are better with **(*Z*)-1** than with **(*E*)-1**. These results seem to be compatible with the view that the substitution is mainly the vinylic S_N2 reaction and the rearrangement occurs through the β-alkyl participation. The participation occurs in an anti-periplanar mode and the migratory aptitude of 3-phenylpropyl group is greater than that of methyl group.[5] So, **(*E*)-1** undergoes rearrangement more readily than **(*Z*)-1**, and the fraction of the competing reaction of the nucleophile X^- becomes smaller. Nucleophilicity of halide affects the fraction of substitution ($Cl^- < Br^- < I^-$) in accord with the bimolecular nucleophilic substitution mechanism. In a wholly aqueous solution, effective hydration of halide ions largely reduces their nucleophilicity and the reaction in this medium would well result in a small fraction of substitution.

Bimolecular nucleophilic substitution with inversion by halide ion was concluded to occur through the in-plane vinylic S_N2 (nucleophilic attack to the σ^* orbital) pathway[1–3] and the main reaction of **1** must also follow this pathway (Scheme 3). In contrast, the retained substitution products may be formed via the out-of-plane or perpendicular attack (to the π^* orbital) of the nucleophile at the vinylic carbon (Scheme 3). This pathway is theoretically possible[12–16] and was called as "a concerted addition-elimination route".[12] Some possible examples are suggested[12b] but no definitive examples seem to be reported.

A closely related out-of-plane pathway of the reaction of some vinyliodonium salts with halide ions was previously regarded as the ligand-coupling (LC) mechanism, since the nucleophilic halide ion has interaction with the iodine atom at the transition state[16] and the halide can come from the intermediate λ^3-haloiodane **1X**; i.e., the reaction is intramolecular

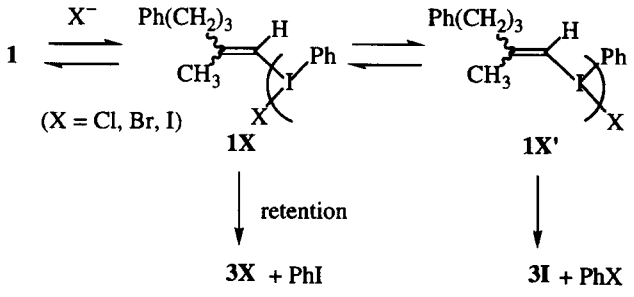


Scheme 3. Vinylic S_N2 mechanisms.

in nature (Scheme 4).[2,17] Furthermore, noticeable formation of iodoalkene **3I** of retained structure accompanies the retained product **3X** in this case. The former is a product of the cleavage of the iodine-phenyl bond of the iodane and is a characteristic by-product of LC.[2,17] The ligand coupling within **1X** gives stereospecifically the retained substitution product **3X**. Formation of **1X** is also inferred from the UV spectrum as discussed below. The by-product **3I** must be derived from a conformational isomer (**1X′**) of **1X** (Scheme 4). In the previous examples of LC substitution of 2-halo-1-decenyliodonium salt, the ratio of retained haloalkene/iodoalkene (the value corresponding to retained **3X/3I**) was about 10/1,[17] but the value of **3X/3I** in the present system ranges from 30 to 60 or greater. This makes detection of **3I** hard and the detection was possible only when the yield of the retained **3X** is > 10%. These results could be explained from the relative instability of the conformational isomer **1X′** due to the poor apicophilicity of the 2,2-dialkylvinyl group compared with the 2-halovinyl group that is more electronegative.[18]

However, the retained **3X** may be formed also by the bimolecular substitution pathway, i.e., the out-of-plane S_N2 mechanism. The stereoselectivity of substitution is not much dependent on [Cl^-], as is seen from the data in Table 1, which implies that the molecularity of the reactions to lead to inversion and retention is similar. Both reactions should be bimolecular. We propose that much of the retained **3X** obtained in the present reaction is formed through the out-of-plane S_N2 mechanism. A slight increase in inversion with increasing [Cl^-] suggests that a minor portion of the retained product is derived from the unimolecular LC mechanism which contributes more at lower [Cl^-].

In the previous results, the bimolecular reactions of 2-monoalkylvinyliodonium salts with halide ions gave exclusively the inverted product via the in-plane S_N2 mechanism in aprotic solvents,[1–3] while 2-halovinyliodonium salts gave exclusively the retained product via the LC mechanism.[17] Why could the out-of-plane S_N2 pathway be observed for the present system of 2,2-dialkylvinyliodonium salt **1**? Reactivity of **1** toward halide ion is in-between those of 2-monoalkylvinyl- and 2-halovinyliodonium salts. These results can be reasonably explained as follows: The in-plane S_N2 reaction is the most facile for 2-monoalkylvinyliodonium salts, but it is retarded by 2,2-dialkyl substitution; as a result, the out-of-plane S_N2 reaction shows up in the reactions of 2,2-dialkylvinyl substrates. 2-Alkyl-2-halovinyliodonium salts are much less reactive toward the nucleophile and the intramolecular LC becomes the sole reaction of the λ^3-haloiodane intermediate.[17] Higher stereoselectivity for inversion of the reaction of **(Z)-1** may be attributed to the steric effects of the β-alkyl group. The steric effects against in-plane nucleophilic attack at the vinylic carbon must be greater in the *E* geometry, where the bulkier group is located on the same side as the attack, than in the *Z* form, while the out-of-plane attack feels less steric effects. This is in accord with the kinetic results discussed below.

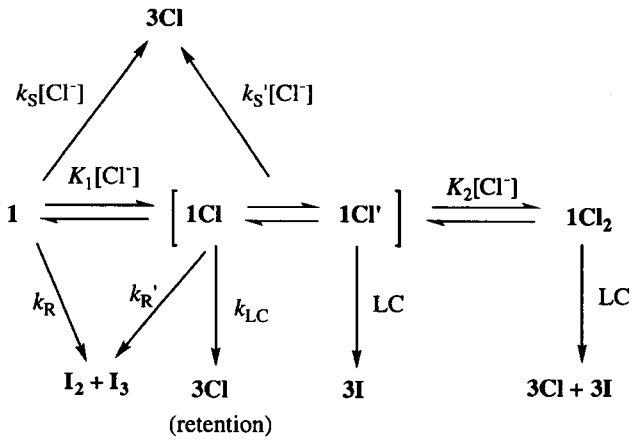


Scheme 4. Ligand coupling mechanism.

Kinetic Analysis. The UV absorption spectra of the iodonium ion **1** in solutions containing chloride ion, including a solution of the salt **1·Cl**, strongly suggest formation of adducts between **1** and Cl^-, as discussed previously for similar salts.[2,3] The saturation curves of the initial absorbances A_i shown in Fig. 1 are best accounted for by the rapid equilibrium formation of λ^3-chloroiodane **1Cl** and iodate **1Cl$_2$** (Scheme 5). Conformational isomers, **1Cl** and **1Cl′**, are assumed not to be differentiated spectroscopically or kinetically. Distinction between the salt **1·Cl** and the iodane **1Cl** is subtle in the solid state,[19] but both forms are present in solution depending on the concentrations and the medium employed. The observed initial absorbance is represented by Eq. 2, according to the equilibria shown in Scheme 5.[2,3]

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

Here, the absorbance increase ΔA is the difference between the initial absorbance A_i and that at [Cl^-] = 0, and K_1 and K_2 are the equilibrium constants for the formation of **1Cl** (**1Cl′**) and **1Cl$_2$**, respectively. The value of ΔA_1 corresponds to the theoretical absorbance increase attained when **1** is converted quantitatively to **1Cl** (**1Cl′**) and the value of ΔA_2 is that attained by quantitative formation of **1Cl$_2$**. The absorbance data can be simulated by a nonlinear least-squares method according to Eq. 2 and the curves in Fig. 1 are drawn with the equilibrium constants given in Table 3. Since we used the chloride salt **1·Cl** as the substrate in these experiments, the absorbance at [Cl^-] = 0 was not directly determined but was calculated during the simulation. The concentrations of free



Scheme 5. Kinetic scheme.

Table 3. Kinetic Parameters for the Reactions of the Iodonium Salts with Chloride Ion[a)]

	Acetonitrile		Chloroform		
Parameter	(*E*)-**1**	(*Z*)-**1**	(*E*)-**1**	(*Z*)-**1**	**1m**
$10^{-3}K_1$/mol^{-1} dm^3	1.26 (0.07)[b)]	1.12 (0.08)[b)]	1.0[c)]	1.0[c)]	1.0[c)]
K_2/mol^{-1} dm^3	14 (3)[b)]	12 (4)[b)]	6[c)]	6[c)]	6[c)]
10^5k_0/s^{-1}	3.27 (0.14)	0.88 (0.15)	4.74 (0.08)	2.50 (0.15)	1.23 (0.03)
10^2k_1/mol^{-1} dm^3 s^{-1}	5.16 (0.10)	5.60 (0.09)	5.62 (0.06)	9.38 (0.11)	3.45 (0.03)
$10k_2$/mol^{-2} dm^6 s^{-1}	3.88 (0.16)	4.27 (0.15)	2.14 (0.09)	3.16 (0.17)	1.27 (0.04)
10^5k_R/s^{-1}	3.27	0.88			
$10^6k'_R$/s^{-1}	7.1	1.25			
$10^4k'_S$/mol^{-1} dm^3 s^{-1}	3.1	3.8			

a) Measured in acetonitrile or chloroform at the ionic strength of 0.20 and at 50 °C. Values in parentheses are standard deviations. b) Obtained from the initial absorbances at 250 nm. c) Approximate values evaluated from the values calculated from the kinetic data for the three substrates.

chloride ion at low [Cl^-] are approximated by the iterative calculations using the value of K_1 obtained, because [Cl^-] is affected by the magnitude of K_1.

The curved dependence of k_{obsd} on [Cl^-] can be simulated by Eq. 3 involving pre-equilibrium formation of the adducts and reactions of zero-th, first, and second orders of [Cl^-] in a similar way to that described before.[2,3] The solid lines in Figs. 2 and 3 show the fits of the kinetic data to Eq. 3 calculated with the equilibrium and rate constants summarized in Table 3. Here, the equilibrium constants, K_1 and K_2, spectrophotometrically determined were used for simulations of the data in AN, while the equilibrium constants in $CHCl_3$ were chosen as average values of those kinetically obtained for the three substrates, since the convergency of simulations was poor due to too many parameters for the limited number of data. That is, the kinetic curves were simulated using predetermined equilibrium constants.

$$k_{obsd} = (k_0 + k_1[Cl^-] + k_2[Cl^-]^2)/(1 + K_1[Cl^-] + K_1K_2[Cl^-]^2) \quad (3)$$

Possible reaction pathways are shown in Scheme 5, where rearrangement and LC occur unimolecularly with **1** and/or **1Cl** (**1Cl'**) while the S_N2 reactions (in-plane and out-of-plane) take place as bimolecular reactions of **1** and **1Cl**. Thus, the kinetic parameters in Eq. 3 can be expressed by

$$k_0 = k_R,$$
$$k_1 = k_S + k'_RK_1 + k_{LC}K_1, \text{ and}$$
$$k_2 = k'_SK_1$$

according to the rate constants given in Scheme 5. (The reactions with no rate constant in Scheme 5 are neglected in the kinetic treatments for simplicity.)

In order to evaluate the magnitudes of individual rate constants in AN solution, the rate constants for rearrangement (k_{rearr}) was calculated from k_{obsd} and the % rearrangement. These values for (*E*)-**1** and (*Z*)-**1** are plotted with closed symbols in Fig. 2 and are simulated according to Eq. 4. The results are given in Table 3.

$$k_{rearr} = (k_R + k'_RK_1[Cl^-])/(1 + K_1[Cl^-] + K_1K_2[Cl^-]^2) \quad (4)$$

The term k'_RK_1 (0.9×10^{-2} and 0.1×10^{-2} mol^{-1} dm^{-3}s^{-1} for ***E*-1** and ***Z*-1**, respectively) makes a very small contribution to the k_1 value. The first-order terms of k_S and $k_{LC}K_1$ cannot be evaluated separately. Since the product ratio of inversion/retention is independent of chloride concentration, the fractions of the two processes must be nearly the same in the k_S and k'_S reactions and the contribution from the k_{LC} retention process must also be very small. That is, the k_1 value is largely composed of the k_S term.

The kinetic results are compatible with the product distributions and exhibit some interesting features. The values of k_R and k'_R show that rearrangement occurs more easily in the *E* form ((*E*)-**1**) than in the *Z* form ((*Z*)-**1**), in agreement with a better migratory aptitude of 3-phenylpropyl than methyl group. In contrast, magnitudes of k_S (k_1) and k'_S show the opposite trend, (*Z*)-**1** > (*E*)-**1**; i.e., the relative reactivity is reversed between the unimolecular rearrangement and bimolecular substitution reaction. This result may be rationalized by adverse steric effects on the major bimolecular reaction, in-plane attack of the nucleophile in the S_N2 mechanism.

The lower reactivity of the 2,2-dimethylvinyl derivative **1m** than (*Z*)-**1** or (*E*)-**1** is rather unexpected. However, it is compatible with the previous observation of the reactivities of 2-monoalkylvinyliodonium salts that decrease in the order: 2-alkyl = *t*-Bu > *i*-Pr > *n*-Bu > Me.[3]

Conclusions.

The reaction of **1** with halide ions involves pre-equilibrium formation of λ^3-haloiodane intermediate **1X** and proceeds mainly through the in-plane S_N2 leading to inversion with accompanying out-of-plane S_N2 pathway as well as ligand-coupling substitution with retention. Unimolecular heterolysis with β-alkyl participation can also compete with the substitution depending on the reaction conditions and results in rearrangement. No evidence for formation of the primary vinylic cation $\mathbf{I_1}$ was found.

Experimental

Most of the experimental procedures are essentially the same as described in a previous paper.[2] ^{1}H NMR spectra were recorded on a JEOL JNM-FX200 or a Varian INOVA 500 spectrometer. An IR

spectrometer JASCO IRA-1, a UV spectrophotometer Shimadzu UV-2200, and mass spectrometers JEOL JMS-SX102A and JMS-DX303HF were used for recording respective spectra. Analytical gas chromatography was carried out on a Shimadzu GC-14B with a DB-1 capillary column, while preparative GC was done on a Shimadzu GC-14A with a packed column of 20% silicone GE SF-96.

Materials. Solvents and salts used were obtained as before[2] or were of the best analytical grade available.

(*E*)- and (*Z*)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (**1·BF$_4$**) were samples used previously.[6] Chloride salts of **1** (**1·Cl**) were prepared by the ligand exchange[2] of **1·BF$_4$**. **(*E*)-1·Cl**: Colorless needles, mp 146.5—147.5 °C (CH_2Cl_2–Et_2O). IR (KBr): 3023, 2927, 1603, 1568, 1496, 1474, 1440, 1274, 1256, 1141, 994, 774, 729, 701, 682 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 7.95 (d, J = 8.3 Hz, 2H), 7.51—7.03 (m, 8H), 6.69 (br s, 1H), 2.59 (t, J = 7.6 Hz, 2H), 2.41 (br t, J = 7.3 Hz, 2H), 2.15 (br s, 3H), 1.91—1.71 (m, 2H). HRFAB MS Calcd for $C_{18}H_{20}I$ [$(M-Cl)^+$]; M, 363.0610. Found: *m/z* 363.0594. Anal. Calcd for $C_{18}H_{20}ClI$: C, 54.22; H, 5.06%. Found: C, 54.00; H, 5.01%. **(*Z*)-1·Cl**: Colorless needles, mp 156.0—157.0 °C (CH_2Cl_2–Et_2O). IR (KBr): 3023, 2927, 1600, 1567, 1440, 1256, 743, 701, 683 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 7.91 (br d, J = 7.8 Hz, 2H), 7.53—7.06 (m, 8H), 6.68 (br s, 1H), 2.60 (t, J = 7.8 Hz, 2H), 2.55—2.44: (m, 2H), 2.09 (br s, 3H), 1.83—1.64 (m, 2H). HRFAB MS Calcd for $C_{18}H_{20}I$ [$(M-Cl)^+$]: M, 363.0610. Found: *m/z* 363.0605. Anal. Calcd for $C_{18}H_{20}ClI·1/2H_2O$: C, 53.03; H, 4.94%. Found: C, 53.06; H, 4.93.

2-Methyl-1-propenyl(phenyl)iodonium tetrafluoroborate (**1m·BF$_4$**) was obtained as described previously.[20]

Product Analysis. A sample of **1·BF$_4$** or **1·Cl** was reacted in a solution containing halide salt. Products were extracted with pentane and analyzed by gas chromatography or isolated as described previously.[2]

Identifications of elimination products, **2** and **6—9**, and carbonyl compounds, **3—5**, were described in the previous paper.[6] Substitution products, **3Cl** and **3Br**, were isolated by preparative GC from reaction mixtures. The iodoalkene **3I** was assigned from GCMS: two GC peaks showed the same MS and that of shorter retention time was assumed to correspond to the *Z* isomer, since the retention time of the *Z* isomer of other haloalkenes is always shorter than that of the *E* isomer.

(*E*)-1-Chloro-2-methyl-5-phenyl-1-pentene ((*E*)-3Cl): Pale yellow oil. IR (film) 2920, 1495, 1450 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 7.36—7.10 (m, 5H), 5.08 (br s, 1H), 2.57 (t, J = 7.5 Hz, 2H), 2.10 (br t, J = 7.5 Hz, 2H), 1.85—1.66 (5H). MS *m/z* (rel. intensity) 194 (6), 117 (8), 104 (100), 91 (40), 77 (10), 65 (12), 53 (9). HRMS Calcd for $C_{12}H_{15}^{37}Cl$, M 196.0833, $C_{12}H_{15}^{35}Cl$, M, 194.0862. Found: *m/z* 196.0861 (M^+, ^{37}Cl), 194.0864 (M^+, ^{35}Cl).

(*Z*)-1-Chloro-2-methyl-5-phenyl-1-pentene ((*Z*)-3Cl): Pale yellow oil. IR (film) 2937, 1604, 1497, 1454, 747, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ = 7.37—7.13 (m, 5H), 5.79 (br s, 1H), 2.63 (t, J = 7.6 Hz, 2H), 2.27 (t, J = 7.6 Hz, 2H), 1.86—1.66 (5H). MS m/z (rel intensity) 194 (9), 117 (15), 104 (100), 91 (57), 77 (14), 65 (16), 53 (12). HRMS Calcd for $C_{12}H_{15}^{37}Cl$: M, 196.0833, $C_{12}H_{15}^{35}Cl$; M, 194.0862. Found: *m/z* 196.0828 (M^+, ^{37}Cl), 194.0858 (M^+, ^{35}Cl).

(*E*)-1-Bromo-2-methyl-5-phenyl-1-pentene ((*E*)-3Br): Pale yellow oil. IR (film) 2916, 2851, 1708 (br), 1470, 1216, 761 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ = 7.32—7.15 (m, 5H), 5.90 (br s, 1H), 2.59 (t, J = 7.6 Hz, 2H), 2.15 (t, J = 7.6 Hz, 2H), 1.82—1.72 (5H). MS m/z (rel intensity) 240 (2), 238 (3), 159 (8), 149 (12), 117 (10), 104 (100), 91 (52), 73 (23). HRMS Calcd for $C_{12}H_{15}^{81}Br$: M, 240.0337; $C_{12}H_{15}^{79}Br$: M, 238.0357. Found: *m/z* 240.0315 (M^+, ^{81}Br), 238.0336 (M^+, ^{79}Br).

(*Z*)-1-Bromo-2-methyl-5-phenyl-1-pentene ((*Z*)-3Br): Pale yellow oil. ^{1}H NMR ($CDCl_3$); δ = 7.32—7.15 (m, 5H), 5.89 (br s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.27 (br t, J = 7.6 Hz, 2H), 1.81—1.71 (5H). MS *m/z* (rel intensity) 240 (8), 238 (8), 159 (42), 117 (35), 104 (100), 91 (93), 77 (15). HRMS Calcd for $C_{12}H_{15}^{81}Br$: M, 240.0337; $C_{12}H_{15}^{79}Br$, M, 238.0357, Found: *m/z* 240.0333 (M^+, ^{81}Br), 238.0349 (M^+, ^{79}Br).

Stereochemistry of the haloalkenes **3Cl** and **3Br** was determined by measurements of an NOE enhancement between the vinylic and allylic protons.

1-Iodo-2-methyl-5-phenyl-1-pentene (3I): MS *m/z* (rel intensity) 286 (20), 159 (84), 117 (27), 104 (77), 91 (100), 81 (24), 65 (15), 55 (18).

Initial Absorbance. To 3.0 mL of the solution containing tetrabutylammonium chloride (and perchlorate) equilibrated at 50 (±0.1) °C in a quartz cuvette was added the freshly prepared stock solution of **1·Cl** in AN (0.6×10^{-2} mol dm^{-3}, 30 μL). After rapid mixing, the absorbance at 250 nm was recorded on an analogue recorder and extrapolated to the time of addition.

Kinetic Measurements. Reaction rates were measured by monitoring the decrease in absorbance at 250 nm at 50 (± 0.1) °C as before.[2]

Curve fittings were carried out by a nonlinear least squares method (Marquardt-Levenberg Algorism) using SigmaPlot (Jandel Scientific, San Rafael, CA) on a personal computer Macintosh 7600/200.[2,3]

References

1 M. Ochiai, K. Oshima, and Y. Masaki, *J. Am. Chem. Soc.*, **113**, 7059 (1991).

2 T. Okuyama, T. Takino, K. Sato, K. Oshima, S. Imamura, H. Yamataka, T. Asano, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **71**, 243 (1998).

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

4 a) R. J. Hinkle and D. B. Thomas, *J. Org. Chem.*, **62**, 7534 (1997). b) R. J. Hinkle, A. J. McNeil, Q. A. Thomas, and M. N. Andrews, *J. Am. Chem. Soc.*, **121**, 7437 (1999).

5 a) T. Okuyama, K. Sato, and M. Ochiai, *Chem. Lett.*, **1998**, 1177. b) T. Okuyama, H. Yamataka, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, **72**, 2761 (1999).

6 M. Fujita, Y. Sakanishi, and T. Okuyama, *J. Am. Chem. Soc.*, in press.

7 C. Reichardt, *Chem. Rev.*, **94**, 2319 (1994).

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

9 M. Hanack, R. Markl, and A. G. Martinez, *Chem. Ber.*, **115**, 772 (1982).

10 M. G. Moloney, J. T. Pinhey, and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2645.

11 R. Pellicciari, B. Natalini, R. M. Sadeghpour, M. Marinozzi, J. P. Snyder, B. L. Williamson, J. T. Kuethe, and A. Padwa, *J. Am. Chem. Soc.*, **118**, 1 (1996).

12 a) Z. Rappoport, *Acc. Chem. Res.*, **14**, 7 (1981). b) Z. Rappoport, *Recl. Trav. Chim. Pays-Bas*, **104**, 309 (1985). c) Z. Rappoport, *Acc. Chem. Res.*, **25**, 474 (1992).

13 R. D. Bach and G. J. Wolber, *J. Am. Chem. Soc.*, **106**, 1410 (1984).

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

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

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

17 a) M. Ochiai, K. Oshima, and Y. Masaki, *Chem. Lett.*, **1994**, 871. b) T. Okuyama, T. Takino, K. Sato, and M. Ochiai, *Chem. Lett.*, **1997**, 955.

18 For apicophilicity, see: a) S. Tippett, *Pure Appl. Chem.*, **40**, 595 (1974). b) R. R. Holms, *J. Am. Chem. Soc.*, **100**, 433 (1978). c) R. S. McDowell and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **107**, 5849 (1985). d) P. Wang, Y. Zhang, R. Glaser, A. E. Reed, P. v. R. Schleyer, and A. Streitwieser, *J. Am. Chem. Soc.*, **113**, 55 (1991).

19 T. Okuyama, *Rev. Heteroatom Chem.*, **21**, 257 (1999).

20 M. Ochiai, T. Sueda, and K. Uemura, *J. Org. Chem.*, **60**, 2624 (1995).