ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 611 (2000) 494–508

Journal of Organometallic Chemistry

Review

Nucleophilic vinylic substitutions of λ^3-vinyliodanes

Masahito Ochiai *

Faculty of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan

Received 9 March 2000; accepted 26 March 2000

Abstract

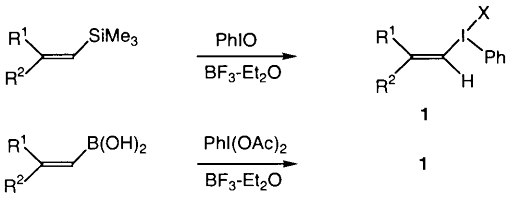
Because of the excellent nucleofugality of the λ^3-phenyliodanyl group, which shows a leaving group ability about 10^6 times greater than triflate, λ^3-vinyl(phenyl)iodanes serve as highly reactive species in nucleophilic substitutions. This review summarizes the nucleophilic vinylic substitutions of λ^3-vinyl(phenyl)iodanes. The reaction rates and mechanism of the nucleophilic vinylic substitutions change depending on the structure of λ^3-vinyliodanes; the nature of the substituents at the β-vinylic carbons is especially important. β-Monoalkyl-λ^3-vinyliodanes undergo bimolecular nucleophilic vinylic substitutions (S_N2) with exclusive inversion of configuration under mild conditions, which, hitherto, has been considered to be impossible on the bases of experimental results and theoretical calculations. Vinylic S_N1 reactions generating vinyl cations, ligand coupling reactions on hypervalent iodine(III), and addition–elimination and elimination–addition reactions, are also discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Substitution; Vinyliodane; Hypervalent element; S_N2 reaction; Ligand coupling; Vinyl cation; Inter-element linkage

---

1. Introduction

In spite of numerous studies on the chemistry of λ^3-diaryliodanes (ArAr′IX), the synthetic methods and utility of λ^3-vinyl(phenyl)iodanes (**1**) with an alkenyl group as a ligand on the hypervalent iodine(III) atom were limited and often inefficient [1]. In 1985, a general and practical method was reported for the synthesis of λ^3-vinyliodanes (**1**) ($X = BF_4$). It involves a silicon- or tin-λ^3-iodane exchange of vinylsilanes or vinylstannanes with hypervalent λ^3-phenyliodanes in the presence of a Lewis acid, $BF_3{-}Et_2O$ (Scheme 1) [2a–c]. These reactions are exclusively stereospecific to the limits of ^1H-NMR (400 MHz) detection with retention of the olefin geometry. Upon exposure to hypervalent phenyliodanes in the presence of $BF_3{-}Et_2O$ in dichloromethane, vinylboronic acids and esters also undergo boron-λ^3-iodane exchange, yielding λ^3-vinyliodanes (**1**) stereoselectively with retention of configuration [2d]. Development of these synthetic reactions makes it possible to investigate the nucleophilic vinylic substitutions of λ^3-vinyl(phenyl)iodanes (**1**).



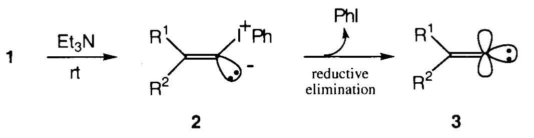
Scheme 1.

Let us discuss two important features of λ^3-aryliodanyl groups, associated with the high reactivity of λ^3-vinyl(aryl)iodanes in nucleophilic vinylic substitutions. Hammett substituent constants of aryliodanyl groups have been estimated by ^{19}F-NMR spectroscopy of *m*- and *p*-substituted fluorobenzenes [3]. As expected, the λ^3-phenyliodanyl group, $Ph(BF_4)I-$, is an inductively strong electron-withdrawing group ($\sigma_p = 1.37$) with large σ_I (1.34) and small σ_R (0.03) values. The electron-withdrawing nature of the phenyliodanyl group makes the α-C–H bonds of λ^3-vinyliodanes **1** quite acidic. Thus, a weak base such as triethylamine

---

* Tel.: +81-88-633-5187; fax: +81-88-633-9504.
E-mail address: mochiai@ph2.tokushima-u.ac.jp (M. Ochiai).

PII: S0022-328X(00)00487-3



Scheme 2.

could abstract the acidic α-vinylic hydrogen of **1** even at room temperature, generating the vinyliodonium ylide (**2**) (Scheme 2).

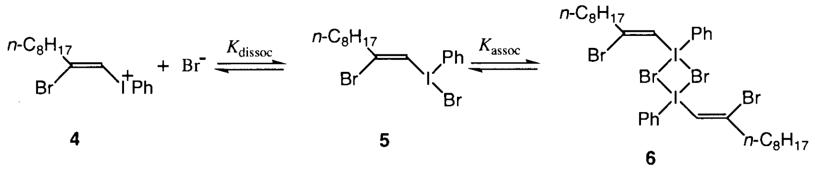
It is difficult, however, to use the resulting vinyliodonium ylide (**2**) as a reactive intermediate in organic synthesis, probably because of the very high nucleofugality of the λ^3-phenyliodanyl group, which shows a leaving group ability about 10^6 times greater than the superleaving group, triflate, described in detail in a later section [4]. Thus, the ylide **2** generated immediately decomposes to the alkylidene carbene (**3**) with reductive elimination of iodobenzene. In fact, repeated attempts to trap the ylide **2** with an aldehyde were fruitless.

This review attempts to summarize the nucleophilic vinylic substitutions of λ^3-vinyl(phenyl)iodanes, in which these natures of λ^3-aryliodanyl groups play an essential role in determining the product profiles and stereochemistry, the reaction rates, and the mechanism.

2. Structure of λ^3-vinyl(phenyl)iodanes in solution

Cryoscopic and conductance measurements have shown extensive dissociation of λ^3-diaryliodanes (Ar_2IX: $X = BF_4$, Cl, Br, OAc) into iodonium ions in polar solvents such as H_2O, MeOH, and DMSO [5]. Vapor pressure osmometric and spectroscopic studies on the molecular association and dissociation of (*Z*)-(2-bromo-1-decenyl)(phenyl)iodane (**5**) in chloroform solution indicate the equilibrium formation of the dimer **6** as well as the iodonium ion **4** (Scheme 3) [6].

The molecular weight of the λ^3-vinylbromoiodane (**5**) in chloroform solution was measured by vapor pressure osmometry. The average molecular weights (M_{obsd}) were concentration dependent: i.e. increasing the concentration of **5** tended to gradually increase the average molecular weight, approaching twice the molecular weight of the monomer, which suggests formation of the dimer **6** at higher concentrations. A plot of M_{obsd} against the concentration of **5** shows a downward curvature as depicted in Fig. 1. The data obtained nicely fit the dissociation–association equilibrium model shown in Scheme 3, and dissociation and association constants of **5** were calculated by least squares estimation to yield $K_{dissoc} = 2.66 \times 10^{-5}$ M and $K_{assoc} = 2.6 \times 10^2$ M^{-1}, respectively.



Scheme 3.

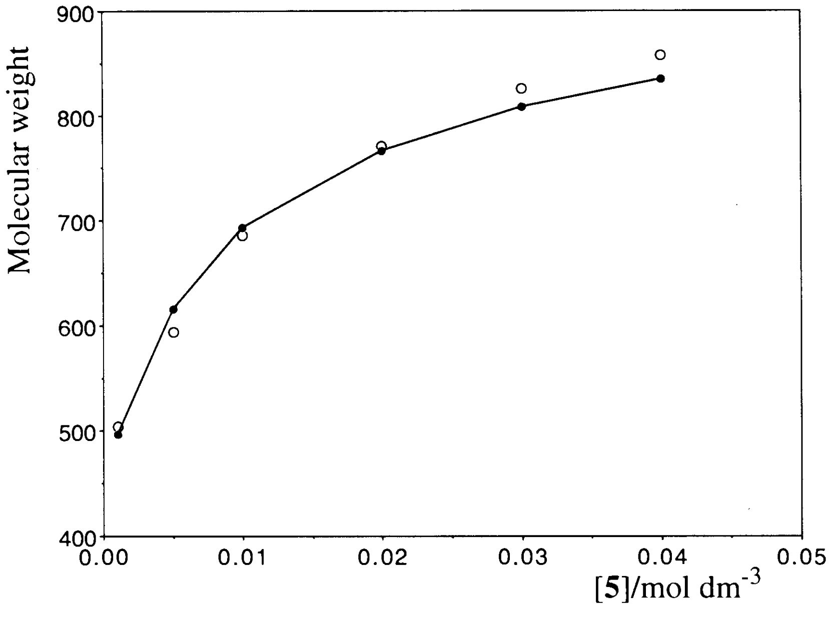
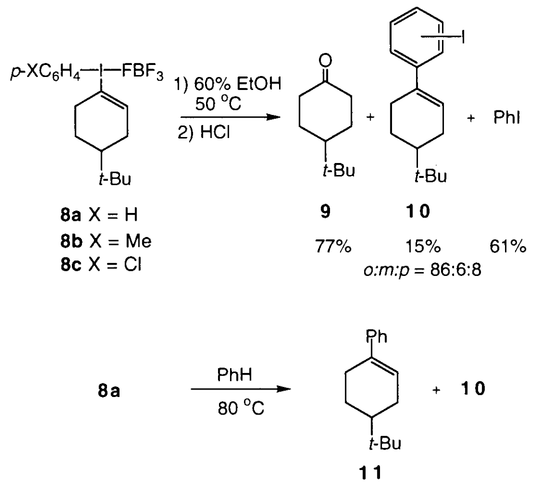
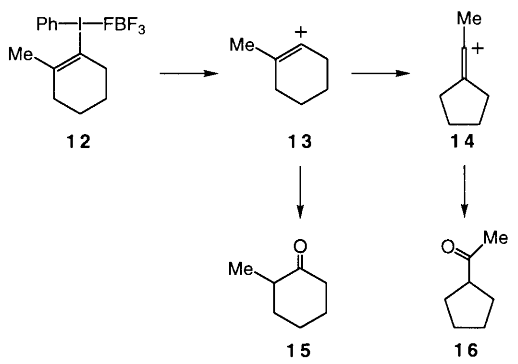


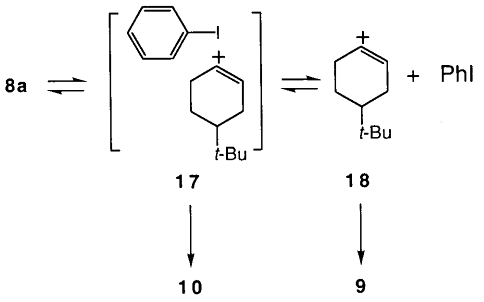
Fig. 1. Molecular weights of λ^3-iodane (**5**) in chloroform solution measured by VPO at 25°C (○). Calculated molecular weights (●).



Scheme 4.



Scheme 5.



Scheme 6.

Further evidence for the dissociation and association equilibria of λ^3-iodane (**5**) in chloroform solution comes from ^{1}H-NMR measurements. Chemical shifts of the vinylic and aromatic protons of λ^3-iodane **5** in $CDCl_3$ are concentration dependent. The resonances of the vinylic proton move increasingly downfield with increasing concentration of **5**, whereas the signals of the *meta* and *para* protons shift upfield.

Evidence for the aggregation of the λ^3-vinylbromoiodane (**5**) to the dimeric form **6** was also obtained from FAB mass spectrometry. When a solution of a 1:1 mixture of (*Z*)-(2-bromo-1-decenyl)iodane (**5**) and (*Z*)-(2-bromo-1-nonenyl)iodane (**7**) was analyzed by FAB-MS, formation of a heterodimer (**5** + **7**) was clearly observed in addition to homodimers (**5** + **5**) and (**7** + **7**). These results are indicative of a dimeric structure **6** even in the gas phase, in which the strength of the coordination bonds in **6** is close to the scope of mass spectroscopy.

3. Vinylic $\mathrm{S_N}1$ reaction: hyperleaving ability of λ^3-aryliodanyl groups

Solvolysis of (1-cyclohexenyl)phenyliodane (**8a**), prepared by BF_3-catalyzed silicon- or tin-λ^3-iodane exchange of vinylsilanes or stannanes with iodosylarenes [2], proceeds at a reasonable rate in aqueous alcohol solutions, even at room temperature, and generates cyclohexenyl cation with reductive elimination of iodobenzene [4]. The reaction in 60% aqueous ethanol at 50°C affords 4-*tert*-butylcyclohexanone (**9**) (77%) as a major product after acid workup, along with a mixture of rearranged products **10**, the *ortho* isomer being a major one (Scheme 4). Heating of **8a** in benzene at 80°C results in a Friedel–Crafts vinylation of benzene and affords a mixture of 1-phenylcyclohexene (**11**) (44%) and rearranged products **10** (53%) [7].

Intermediacy of the cyclohexenyl cation was firmly established by the observation of carbocation rearrangement during the solvolysis of **12**, in which an initially generated bent vinyl cation **13** with sp^2 hybridization rearranges to a more stable linear vinyl cation **14** with sp hybridization. The ratio of the rearranged **16** to the unrearranged ketone **15** depends on the nature of solvents used and changed from 14:86 in 60% aqueous ethanol to 46:54 in the less nucleophilic 2,2,2-trifluoroethanol (TFE) (Scheme 5).

The reaction mechanism for solvolysis of cyclohexenyliodane (**8a**) is shown in Scheme 6, which involves generation of the intimate cyclohexenyl cation-iodobenzene pair **17**. Friedel–Crafts vinylation of iodobenzene within the intimate ion-molecular pair **17** will produce a mixture of rearranged products **10** with selective formation of the *ortho* regioisomer. The fact that solvolysis of **8a** in methanol in the presence of an excess amount (50 equivalents) of *p*-methyliodobenzene at 35°C affords the exchanged vinyliodane **8b** (4%) in addition to the formation of **10** (*o*:*m*:*p* = 86:5:9) and the recovered vinyliodane **8a** (49%) suggests the reversible generation of the cyclohexenyl cation **18** during solvolysis, as shown in Scheme 6.

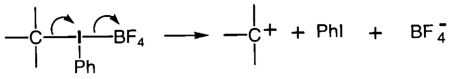
Pseudo-first-order rate constants for the solvolysis of **8** at 35–69°C are shown in Table 1. The leaving group ability of the λ^3-aryliodanyl groups increases with an increase in the electron-withdrawing nature of the ring substituents. Comparison of the solvolysis rate for **8a**

Table 1
Rate constants ($10^4 k_{obsd}$ (s^{-1})) for solvolysis of **8** in 60:40 ethanol–water

Iodane **8**	Temperature (°C)			$\Delta H\ddagger$ (kcal mol^{-1})	$\Delta S\ddagger$ (cal mol^{-1} K^{-1})
	35	50	69		
8a	0.229	2.32	26.9	28.7	13.3
8b	0.114	1.23	14.0	28.5	11.8
8c	0.594	5.74	60.3	27.9	12.8

with that of 1-cyclohexenyl triflate indicates that the λ^3-phenyliodanyl group $Ph(BF_4)I-$ is a remarkably good nucleofuge with a leaving group ability about 10^6 times greater than triflate, a so-called ‘superleaving’ group. The aryliodanyl groups are the most efficient leaving groups that have been evaluated quantitatively.

A nucleofuge such as the aryliodanyl group is termed a hyperleaving group [1m]. The hyperleaving group must not only show a leaving group ability higher than that of a superleaving group such as TfO but also must be a hypervalent leaving group. As shown in the following equation, the leaving process of a hyperleaving group must involve an energetically preferable reduction of the hypervalent atom to the normal valency of octet structure, which is the origin of the high leaving group ability. The positively charged dimethylsulfonio group with tetrahedral geometry, and hence with no hypervalency, shows poor leaving group ability. Furthermore, the leaving process of a hyperleaving group is associated with an increase in entropy, since the hypervalent molecule decomposes into three components, as shown in the equation.



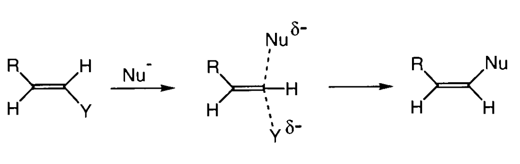
$$-\overset{|}{\underset{|}{C}}-\underset{\underset{Ph}{|}}{I}-BF_4 \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + PhI + BF_4^-$$

4. Vinylic S_N2 reaction

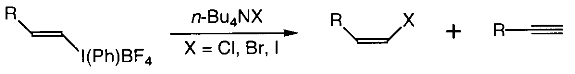
The S_N2 reaction involves the attack of a nucleophile from the side opposite the leaving group and proceeds with exclusive inversion of configuration in a concerted manner without forming an intermediate. The bimolecular nucleophilic substitution at the aliphatic carbon atom is one of the most popular organic reactions. On the other hand, the S_N2 reaction at the vinylic carbon atom, which involves the attack of a nucleophile to a σ^*_{C-Y} orbital (Y = leaving group) through a planar transition state, has been considered to be a high-energy pathway (Scheme 7). Textbooks of organic chemistry traditionally reject this mechanism on steric grounds [8]. Early theoretical calculations support this view and predict preferential attack of a nucleophile to the π-system [9].

The inversion of configuration has rarely been observed for nucleophilic vinylic substitutions. Predominant, but not exclusive, inversion was reported in the solvolysis of vinyl triflates, in which an ion-pair mechanism was proposed [10]. In 1991, we reported that a nucleophilic vinylic substitution of (*E*)-β-alkylvinyl-λ^3-iodanes (**19**) with halides proceeds with exclusive inversion of configuration (Scheme 8) [11]. This is the first clear example of a vinylic S_N2 reaction.

Nucleophilic substitution of (*E*)-β-alkylvinyl-λ^3-iodanes (**19b**, **19c**) with n-Bu_4NCl in dichloromethane takes place at room temperature and affords alkenyl halides (**20b**, **20c**) with (*Z*)-stereochemistry in a completely stereoselective manner [11a]. This reaction competes with an alkyne-forming elimination with the concomitant formation of iodobenzene. Complete inversion of configuration was observed in a variety of solvents including hexane, acetonitrile, and methanol, as shown in Table 2. Substitutions with n-Bu_4NBr and n-Bu_4NI similarly gave the corresponding (*Z*)-alkenyl halides (**20**) with complete inversion. On the other hand, n-Bu_4NF afforded only 1-alkyne (**21**). Note that the selectivity for substitution over elimination decreases in the order of n-$Bu_4NI > n$-$Bu_4NBr > n$-$Bu_4NCl \gg n$-Bu_4NF, reflecting the decreasing softness and the increasing basicity of halide ions. Most importantly, the ratios of substitution to elimination depend on the concentration of halide ions, and the fraction of substitution increases with increasing concentration of halides.



Scheme 7.



19a-e **20a-e** **21a-e**

a: R = Me, **b**: R = n-C_8H_{17}, **c**: R = $Ph(CH_2)_3$, **d**: R = i-Pr, **e**: R = t-Bu

Scheme 8.

Table 2
Nucleophilic vinylic substitutions of (*E*)-alkenyl(phenyl)-λ^3-iodanes (**19**) with n-Bu_4NX [a]

Run	λ^3-Iodane **19**	Reagent	Solvent	Reaction time (h)	Product, yield (%)			Ratio **20:21**
					20		**21**	
1	**19b**	n-Bu_4NF	CH_3CN	10	**20b** (X = F)	0	47	0:100
2	**19b**	n-Bu_4NCl	CH_2Cl_2	10	**20b** (X = Cl)	83	14	85:12
3	**19b**	n-Bu_4NCl	hexane	10	**20b** (X = Cl)	91	3	97:3
4	**19b**	n-Bu_4NCl	THF	10	**20b** (X = Cl)	92	8	92:8
5	**19b**	n-Bu_4NCl	MeOH	10	**20b** (X = Cl)	76	14	84:16
6	**19b**	n-Bu_4NCl	DMF	10	**20b** (X = Cl)	84	16	84:16
7	**19b**	n-Bu_4NCl	CH_3CN	10	**20b** (X = Cl)	91	9	91:9
8	**19b**	n-Bu_4NBr	CH_3CN	10	**20b** (X = Br)	95	5	95:5
9	**19b**	n-Bu_4NI	CH_3CN	10	**20b** (X = I)	88	2	98:2
10	**19c**	n-Bu_4NCl	CH_3CN	1	**20c** (X = Cl)	86	14	86:14
11	**19c**	n-Bu_4NBr	CH_3CN	10	**20c** (X = Br)	96	3	97:3
12	**19c**	n-Bu_4NI	CH_3CN	24	**20c** (X = I)	99	1	99:1

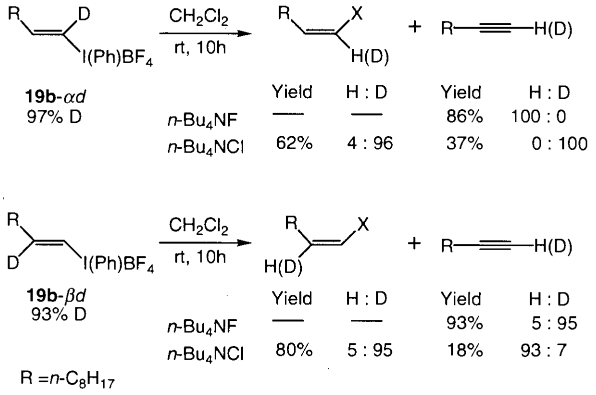
[a] Reactions were carried out using 10 equivalents of reagents at room temperature.

Primary kinetic deuterium isotope effects and the observed deuterium content of the product 1-decyne (**21b**) in the reaction of α- and β-deuterated alkenyl-λ^3-iodane **19b**-*αd* and **19b**-*βd* with n-Bu_4NCl in CH_2Cl_2 clearly indicate that 1-decyne (**21b**) was produced predominantly as the result of *syn* β-elimination; however, α-elimination generating the alkylidene carbene, followed by the 1,2-shift of hydrogen, was found to occur in the reaction with n-Bu_4NF yielding 1-decyne (**21b**) (Scheme 9) [11a,12].

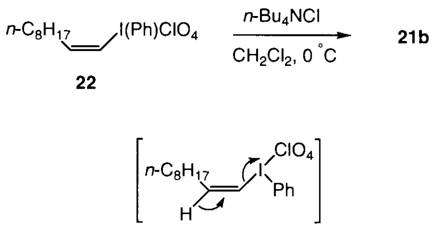
The (*Z*)-β-alkylvinyl-λ^3-iodane (**22**) does not undergo nucleophilic substitution in the reaction with halides, but, instead, affords 1-decyne (**21b**) quantitatively (Scheme 10). The (*Z*)-iodane **22** is very labile and decomposes with a half-life of 20 min to **21b** in chloroform solution at room temperature without using halides [13]. Stereoelectronically preferable *anti* β-elimination as shown in Scheme 10 accounts for this facile decomposition.

These results, combined with those from the kinetic analysis, suggest the reaction mechanism shown in Scheme 11 . Fluoride ion selectively attacks an α-hydrogen of alkenyliodane **19b**, which is most acidic because of a large inductive effect of the electron-withdrawing phenyliodanyl group [3,11], and induces a reductive α-elimination of iodobenzene to generate the alkylidene carbene (**23**). 1,2-Shift of α-hydrogen of **23** to the terminal position is more facile than the 1,5-carbon–hydrogen insertion that yields the corresponding cyclopentenes [12a], and affords 1-decyne (**21b**) (reaction mechanism A in Scheme 11). In marked contrast to the fluoride ion with high basicity, other less basic halide ions (Cl^-, Br^-, I^-) undergo a rapid ligand exchange on iodine(III) and produce halo-λ^3-iodanes such as **25** and **26**. This ligand exchange was firmly established by ^{1}H-NMR tube experiments.

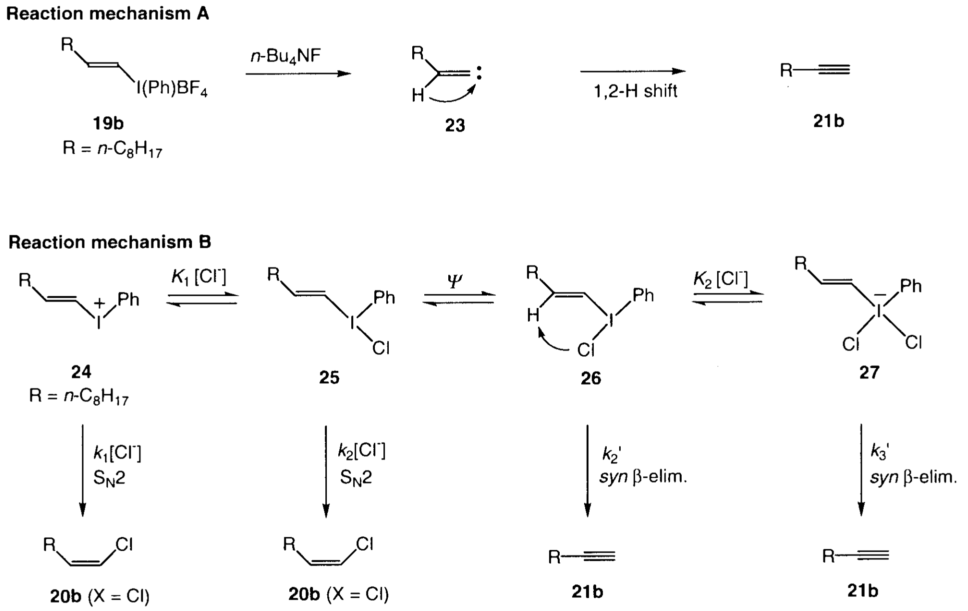
The initial UV absorbances of an acetonitrile solution of **19b** in the presence of n-Bu_4NX (X = Cl, Br, I) depend on the concentration of halide ions and indicate a rapid preequilibrium formation of the iodonium ion **24**, the halo-λ^3-iodanes **25** and **26**, and the dihaloiodate **27**. Intervention of dimers of the halo-λ^3-iodanes **25** and **26** is not important because of the low concentration of these iodanes. Stereoisomerization between the iodanes **25** and **26** via pseudorotation on iodine(III) will be very fast [14] and, therefore, these isomers cannot be differentiated kinetically. The isomer **26** with an equatorial alkenyl group undergoes intramolecular reductive



Scheme 9.

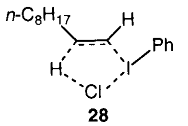


Scheme 10.

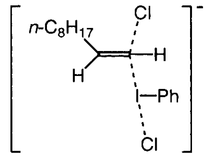


Scheme 11.

syn β-elimination via a five-membered cyclic transition state **28** yielding 1-decyne (**21b**), whereas **25** with an apical alkenyl group undergoes vinylic S_N2 reaction by the rear side attack of external halides via the transition state **29** yielding (*Z*)-alkenyl halides (**20b**) with inversion of configuration. The hyperleaving group ability of the phenyliodanyl group would be the origin of this unusual inversion of configuration in the nucleophilic vinylic substitutions.



28



29

Kinetic parameters for the reaction of **19b** with *n*-Bu_4NX in acetonitrile solution at 25°C are shown in Table 3. The magnitude of the association constant K_1 of the iodonium ion **24** with halides decreases in the order $Cl^- > Br^- > I^-$, which is in good agreement with the decreasing apicophilicity of halide ions. Both the iodonium ion **24** and the iodane **25** undergo vinylic S_N2 reaction. Comparison of the kinetic parameters $k_1/k_2K_1 = 1.4 \times 10^{-3}$ M for Cl^- and 0.5×10^{-3} M for Br^- clearly indicates that the hypervalent iodane **25**, but not the iodonium ion **24**, is the major species responsible for the vinylic S_N2 reaction in the normal range of halide ion concentrations. These kinetic analyses establish that the nucleophilic substitution occurs mainly as a bimolecular reaction of the iodane **25** at a rate that is second order in $[X^-]$, whereas the major part of the elimination takes place intramolecularly within the iodane **26** at a rate that is first order in $[X^-]$. Therefore, the relative ratios of the substitution to the alkyne-forming elimination depend on the concentration of halide ions, which is compatible with the results.

Substituent effects of the leaving aryliodanyl groups are rather small, but the rate of nucleophilic substitution increases with an increase in the leaving ability of the aryliodanyl groups; the Hammett ρ value for the reaction of substituted **30** with *n*-Bu_4NCl in chloroform at 35°C is 0.75, which is in contrast to that ($\rho = 1.8$) for the S_N1 solvolysis of cyclohexenyliodanes (**8**) in 60% aqueous ethanol at 35°C. This smaller ρ value for the reaction of **30** is consistent with the concerted S_N2 mechanism. Deuterium isotope effects also support the vinylic S_N2 mechanism; a secondary kinetic isotope effect of the β deuterium of 1.1–1.25 is observed for the nucleophilic substitution of β-deuterated alkenyliodane

Table 3
Kinetic parameters for the reaction of (*E*)-alkenyl-λ^3-iodane (**19b**) with *n*-Bu_4NX in acetonitrile at 25°C

	n-Bu_4NCl	*n*-Bu_4NBr	*n*-Bu_4NI
K_1 (M^{-1})	4.66×10^4	1.16×10^4	2.49×10^3
K_2 (M^{-1})	16.8	21.7	14.6
k_1 (M^{-1} s^{-1})	1.9	0.4	
k_2 (M^{-1} s^{-1})	0.03	0.076	
k'_2 (s^{-1})	2.7×10^{-4}	1.7×10^{-4}	
k'_3 (s^{-1})	5×10^{-5}	8×10^{-5}	

Table 4
Rate constants and product ratios for the reaction of (*E*)-alkenyliodanes (**19**) with Cl^- [a]

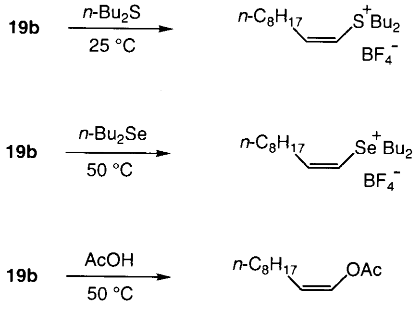
Iodane	Ratio [b]	$10^4\ k_{obsd}$ (s^{-1})	$10^4\ k_s$ (s^{-1}) [c]	$10^4\ k_e$ (s^{-1}) [d]
19a	72:28	2.61	1.88	0.73
19b	54:46	5.32	2.87	2.45
19d	41:59	5.51	2.26	3.25
19e	0:100	7.21	0	7.21

[a] In acetonitrile at 25°C.

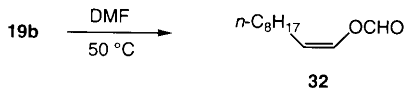
[b] Ratios of **20**:**21** (substitution:elimination).

[c] k_s rate constants for nucleophilic substitution.

[d] k_e rate constants for elimination.

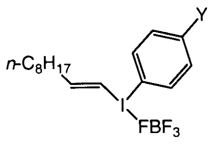


Scheme 12.



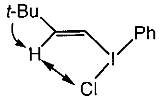
Scheme 13.

19b-*βd* with *n*-Bu_4NX (X = Cl, Br, I) in chloroform or acetonitrile at 25°C, whereas the β deuterium primary kinetic isotope effect for the *syn* β-elimination is 2.5–3.3. Effects of solvents on the rate of the reaction of alkenyliodane **19b** are small, probably because there is no charge disappearance and creation in the S_N2 transition state **29**. The rate of reaction is slow in protic solvents, methanol and ethanol, which provide extensive solvation toward halide ions and therefore decrease the nucleophilicity of these ions.



30

Effects of β-alkyl groups of vinyliodanes **19** on the rates and the ratios of substitution to elimination in the reaction with chloride ion are summarized in Table 4. The β-methyl- **19a**, β-*n*-octyl- **19b**, and β-isopropylvinyliodane **19d** undergo both vinylic S_N2 and elimination reactions, while β-*tert*-butylvinyliodane (**19e**) affords only the products of elimination. The sterically demanding β-*tert*-butyl group of **19e** will cause a severe steric repulsion toward the incoming chloride ion in the S_N2 transition state and inhibits the nucleophilic vinylic substitution, but rather, the β-*tert*-butyl group accelerates the *syn* β-elimination yielding the alkyne **21e**, probably because of a large buttressing effect [15]. The β-*tert*-butyl group buttresses the β-hydrogen geminal with it and thus prevents the β-hydrogen from bending outward, which would cause decrease in the distance between the β-hydrogen and the chlorine ligand of the intermediate vinylchloro-λ^3-iodane (**31**). This effect on *syn* β-elimination would cause the steric acceleration and would account for the observed increase in elimination rate constants k_e in the order **19a** < **19b** < **19d** < **19e**.



31

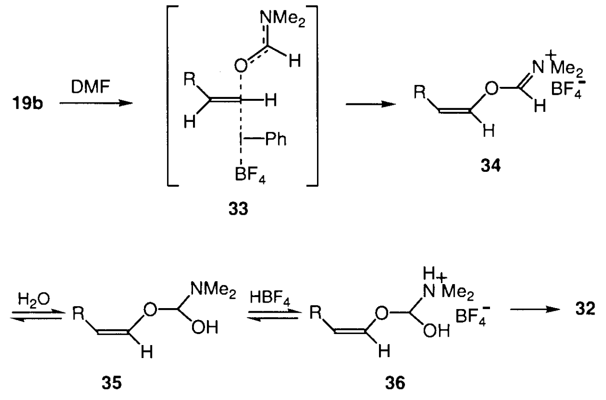
Nucleophiles that undergo vinylic S_N2 reaction involve sulfides [16], selenides [16], carboxylic acids [17], and phosphoroselenoates [18]. All of these reactions proceed with exclusive inversion of configuration (Scheme 12). These nucleophiles are only weakly basic or non-basic. More basic nucleophiles would result in a facile α-elimination of vinyliodanes generating alkylidene carbenes instead of the vinylic S_N2 reaction.

Although nucleophilicity of amides is rather low, amides serve as good nucleophiles in the vinylic substitutions of λ^3-vinyliodanes. Thus, *N*,*N*-dimethylformamide (DMF) by its reaction with (*E*)-β-alkylvinyl-λ^3-iodane (**19b**) at 50°C undergoes bimolecular nucleophilic vinylic substitution and affords the (*Z*)-vinyl formate **32** stereoselectively with inversion of configuration (Scheme 13) [19]. *N*,*N*-Diethylformamide and *N*-formyl cyclic amines, i.e. *N*-formyl-pyrrolidine, piperidine, and morpholine, similarly gave the (*Z*)-vinyl formate **32**. In contrast, the reaction course was dramatically changed when the sterically demanding *N*,*N*-diisopropylformamide was used as the nucleophile: a large amount of 1-decyne (**21b**) was produced as a byproduct via α-elimination, followed by 1,2-shift of the α-hydrogen of the resulting alkylidene carbenes. With *N*,*N*-dicyclohexylformamide, this elimination is the sole detectable pathway.

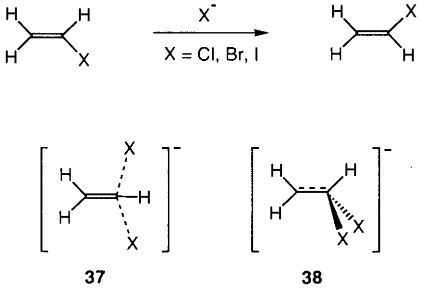
The oxygen atom of DMF selectively attacks the (*E*)-vinyliodane **19b** to produce the inverted (*Z*)-*O*-vinylimidonium salt **34** (Vilsmeier–Haack salt) via the vinylic S_N2 transition state **33**, which is stabilized by delocalization of the nitrogen lone-pair electrons. Subsequent attack of water produces *N*-protonated tetrahedral species **36**, which collapses to the (*Z*)-vinyl formate **32** with ammonio group being released (Scheme 14).

Methods for synthesis of vinyl formates are limited and thus this reaction provides an efficient route for stereoselective synthesis of (*Z*)-vinyl formates.

Early theoretical calculations suggest that the in-plane S_N2 process at the vinylic carbon atom is a high-energy pathway, compared with the alternative attack of a nucleophile on the π-system: extended Huckel calculations for hydride ion attack on ethylene indicated that the barrier for the S_N2 pathway to be 78 kcal mol^{-1}, whereas the barrier for attack on the π-system was found to be 18 kcal mol^{-1} [9]. However, a recent theoretical paper employing sophisticated computational techniques reports that an in-plane S_N2 approach of a halide ion to the α-carbon of vinyl halides in the gas phase is feasible with a transition state **37** that is lower in energy than the carbanionic intermediate **38** derived from the attack on the π-system (Scheme 15) [20].



Scheme 14.



Scheme 15.

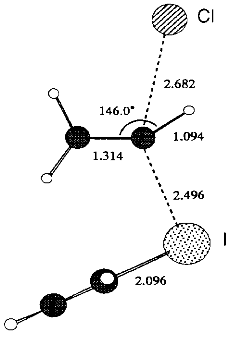
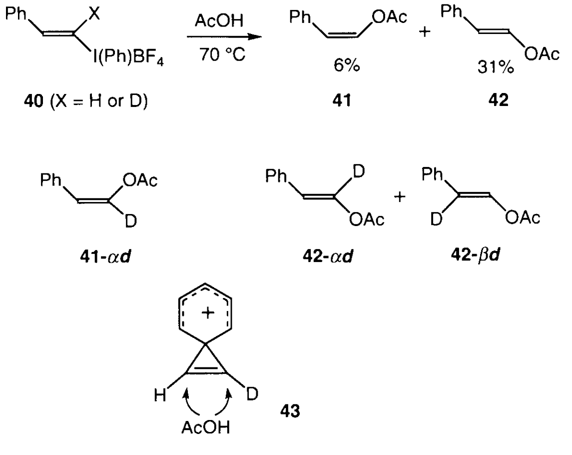
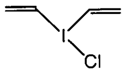


Fig. 2. Transition state geometry for the S_N2 reaction of divinyliodonium ion with chloride ion.



Scheme 16.

The ab initio MO (MP2) calculations of vinyl-λ^3-iodane at the double-zeta (DZ) + d level indicate that the σ* orbital for the C_{vinyl}–I bond is lower in energy than the π* orbital: for divinyl-λ^3-iodane (**39**), the σ* orbital (1.81 eV) for the C_{vinyl}–I apical bond is the LUMO, and the π* orbital (3.34 eV) of the apical vinyl group is the third lowest vacant orbital (LUMO + 2) [21]. The low-lying σ* orbital is an important feature of the vinyl-λ^3-iodanes and makes possible the in-plane bimolecular nucleophilic substitution (S_N2) at the vinylic carbon. Optimized geometry of the transition state for the vinylic S_N2 reaction of divinyliodonium ion with chloride anion is illustrated in Fig. 2.



39

5. Generation of vinylenebenzenium ion

Solvolysis of (*E*)-β-(phenylvinyl)iodane (**40**) (X = H) in acetic acid at 70°C gives a stereoisomeric mixture of vinyl acetates **41** and **42**, in which the retention product, (*E*)-vinyl acetate (**42**), was found to be a major stereoisomer (Scheme 16) [17,22]. Use of a more polar but less nucleophilic solvent TFE results in the exclusive formation of the retained (*E*)-vinyl 2,2,2-trifluoroethyl ether and formation of the (*Z*)-isomer was not detected in the reaction mixture. Deuterium distribution in the products was analyzed by ^{1}H-NMR spectroscopy for the solvolysis of α-deuterated (*E*)-β-(phenylvinyl)iodane (**40**) (X = D) in acetic acid:

the deuterium was found to be extensively scrambled in the (*E*)-vinyl acetate, i.e. a 1:1 mixture of **42**-*αd* and **42**-*βd* was observed, while deuterium was retained at the original position in the (*Z*)-isomer **41**-*αd*.

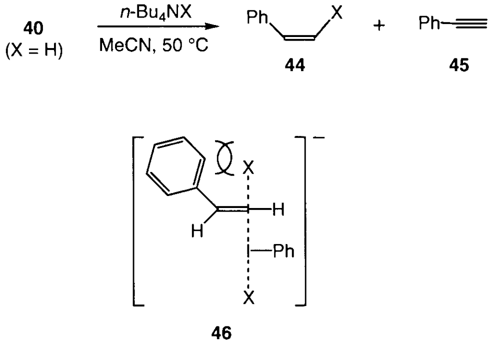
The deuterium scrambling in (*E*)-**42** suggests the involvement of a vinylenebenzenium ion intermediate **43** that would lead to the formation of the retained product. In contrast, retention of deuterium at the original position in (*Z*)-**41** indicates an attack of the nucleophilic solvent from the back side of the leaving λ^3-iodanyl group. The latter process corresponds to a vinylic S_N2 reaction. The less nucleophilic TFE ($N_T = -3.93$) cannot compete with the β-phenyl participation, but traps the intermediate benzenium ion **43** to give the retained product exclusively.

When the reaction of (*E*)-β-phenylvinyliodane (**40**) (X = H) was carried out in the presence of halide nucleophiles, the stereochemical outcome of the reaction was dramatically changed to produce inversion products selectively [23]. The rate of the nucleophilic substitutions of **40** with *n*-Bu_4NX decreased to about one tenth of that seen with (*E*)-β-alkylvinyliodane (**19b**). The results of substitutions of **40** with *n*-Bu_4NX in MeCN at 50°C, yielding halostyrene **44** and phenylacetylene (**45**), are summarized in Table 5 (Scheme 17). The fraction of nucleophilic substitutions tends to increase in the order of $Cl^- < Br^- < I^-$ and with increasing concentration of halides. The substitution product **44** is predominantly in a *Z* configuration but a small amount of the (*E*)-isomer is formed, especially at low concentrations of halide ions. Reaction of α-deuterated **40** (X = D) reveals that the elimination yielding phenylacetylene (**45**) occurs via a *syn* β-elimination. A severe steric repulsion between the β-phenyl group and the incoming halide ion in the vinylic S_N2 transition state **46**, producing (*Z*)-**44**, accounts for both the decreasing rate of the reaction and the increasing ratios of β-elimination to nucleophilic substitutions, compared to the reaction of (*E*)-β-alkylvinyliodane (**19b**).

Table 5
Nucleophilic substitutions of (*E*)-β-phenylvinyliodane (**40**) (X = H) with *n*-Bu_4NX [a]

Reagent (mol dm^{-3})	Reaction time (h)	Product, yield (%)	
		44 (*Z*:*E*)	**45**
n-Bu_4NCl (0.1)	8	14 (99.8/0.2)	71
n-Bu_4NBr (0.01)	3	11 (95.4/4.6)	76
n-Bu_4NBr (0.05)	3	38 (98.7/1.3)	52
n-Bu_4NBr (0.1)	3	48 (99.4/0.6)	43
n-Bu_4NI (0.01)	3	41 (91.7/8.3)	41
n-Bu_4NI (0.1)	2	77 (98.8/1.2)	1

[a] In acetonitrile at 50°C.

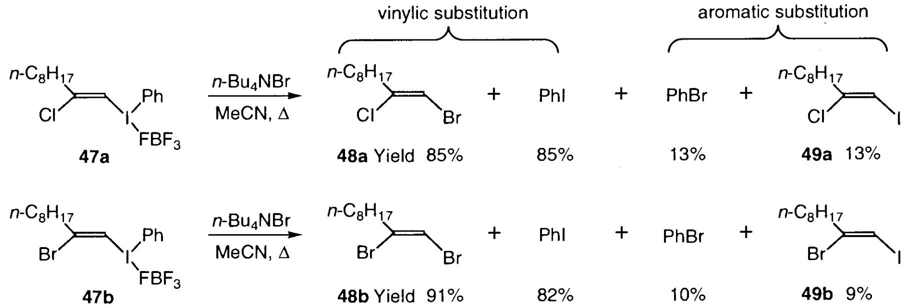


Scheme 17.

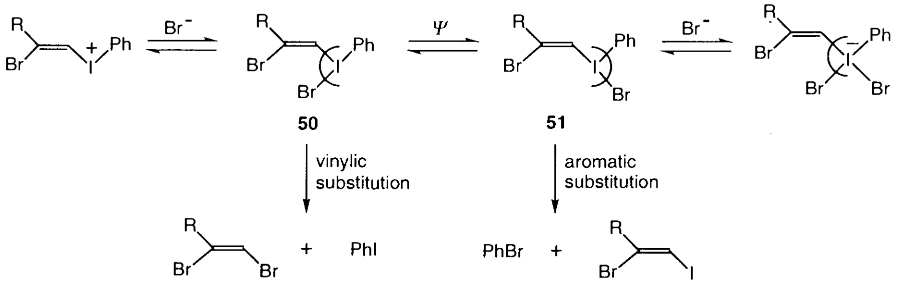
6. Ligand coupling reaction

Compared to the reaction of (*E*)-(β-alkylvinyl)-phenyliodanes (**19**) with *n*-Bu_4NX which proceed smoothly at room temperature, nucleophilic substitutions of (*Z*)-(β-halovinyl)phenyliodanes, prepared by conjugate addition of halide ions to alkynyl-(phenyl)iodanes using LiX (X = F, Cl, Br) in acetic acid at room temperature, become sluggish and generally require heating [24]. Interestingly, nucleophilic vinylic substitutions of (*Z*)-(β-halovinyl)phenyliodanes with *n*-Bu_4NX yielding vicinal (*Z*)-vinyl dihalides compete with nucleophilic aromatic substitutions affording halobenzenes; thus, treatment of (*Z*)-(β-chlorovinyl)iodane (**47a**) with *n*-Bu_4NBr in refluxing CH_3CN under nitrogen gave a mixture of the vinylic substitution products, the vicinal (*Z*)-β-chlorovinyl bromide (**48a**) (85%) and iodobenzene (85%), and the aromatic substitution products, the (*Z*)-β-chlorovinyl iodide (**49a**) (13%) and bromobenzene (13%) (Scheme 18). The nucleophilic vinylic substitution was completely stereoselective to the limits of NMR detection with retention of configuration. The rate of nucleophilic substitutions depends on the halide ions, and decreases in the order *n*-Bu_4NI > *n*-Bu_4NBr > *n*-Bu_4NCl. On the other hand, *n*-Bu_4NF does not undergo nucleophilic substitution but acts as a base for α-proton abstraction from **47**. For instance, the reaction of **47a** with *n*-Bu_4NF generates an α-chloroalkylidene carbene via α- and/or β-elimination, which undergoes intramolecular 1,5-carbon–hydrogen insertions as well as 1,2-migration of an α-chlorine atom [12c].

The product profiles, the stereochemical outcome, as well as the detailed kinetic analyses suggest a ligand coupling mechanism [25] on the iodine(III) of the intermediate halo-λ^3-iodanes **50** and **51** (Scheme 19) [26]. The major reaction pathways involve the ligand coupling of bromoiodane **50**, yielding products of the nucleophilic vinylic substitution, the vicinal (*Z*)-dibromide and iodobenzene, with retention of configuration. An alternative ligand coupling of bromoiodane **51** generated by pseudorotation [14] on iodine(III) will lead to



Scheme 18.



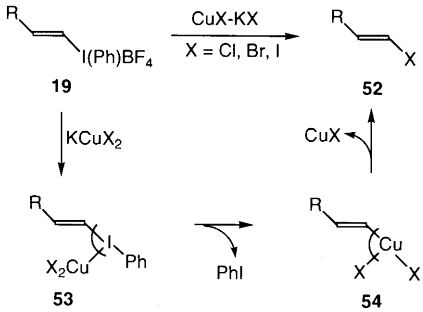
Scheme 19.

the formation of the nucleophilic aromatic substitution products, the (*Z*)-vinyl iodide and bromobenzene.

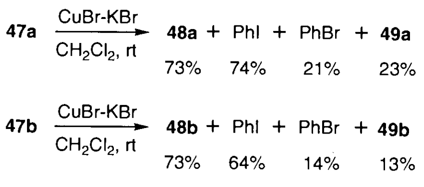
Nucleophilic substitutions of (*E*)-(β-alkylvinyl)-phenyliodanes (**19**) with halide anions, which proceed with inversion of configuration via S_N2 process, alter the reaction course, when the reaction is carried out in the presence of cuprous halides. The reaction in the presence of cuprous halides affords (*E*)-vinyl halides (**52**) with exclusive retention of configuration: thus, treatment of (*E*)-(β-alkylvinyl)phenyliodanes (**19**) with a combination of potassium halides (10 equivalents) and cuprous halides (10 equivalents) in dichloromethane at room temperature in the dark gives (*E*)-vinyl halides (**52**) in good yields (Scheme 20) [11a]. This reaction probably involves oxidative addition or ligand exchange of cuprates ($KCuX_2$) with formation of λ^3-iodane **53**, in which the copper ligand occupies an equatorial position because of its low electronegativity. Ligand coupling at the iodine(III) of **53** will produce the vinyl copper(III) species **54** with retention of stereochemistry of the double bond, followed by the reductive elimination at the copper(III) yielding the (*E*)-vinyl halides **52**.

Cuprous halide-catalyzed nucleophilic substitutions of (*Z*)-(β-halovinyl)phenyliodanes (**47**) with potassium halides compete with the nucleophilic aromatic substitutions, as was observed in the reaction with $n\text{-Bu}_4NX$. The reaction proceeds at room temperature in dichloromethane. For instance, reaction of (*Z*)-(β-chlorovinyl)iodane (**47a**) with CuBr–KBr gave the vinylic substitution products **48a** (73%) and iodobenzene (74%), and the aromatic substitution products **49a** (23%) and bromobenzene (21%) (Scheme 21) [24]. These results provide some evidence for the ligand coupling mechanism.

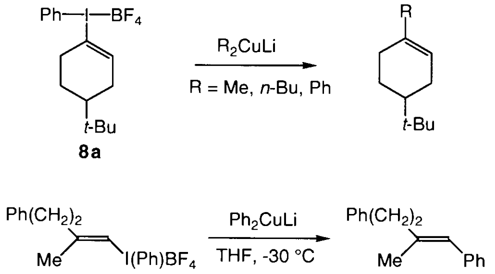
Reaction of λ^3-alkenyliodanes with alkyllithiums gave a complex mixture of products; however, dialkyl- and diarylcuprates undergo vinylic substitutions at the ipso position. Examples are shown in Scheme 22 [27]. The reaction is stereospecific and gives products of exclusive retention of configuration.



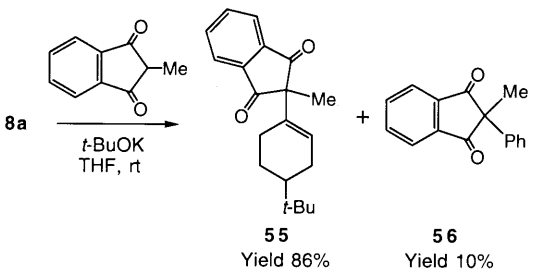
Scheme 20.



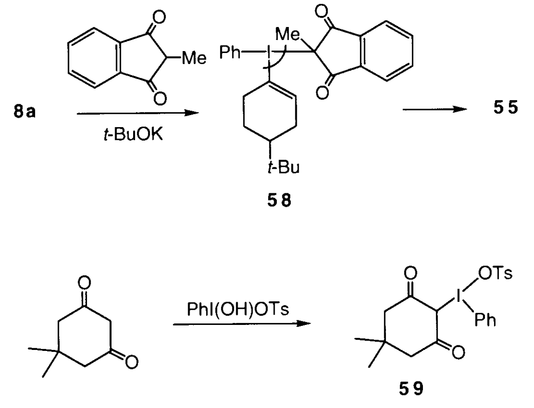
Scheme 21.



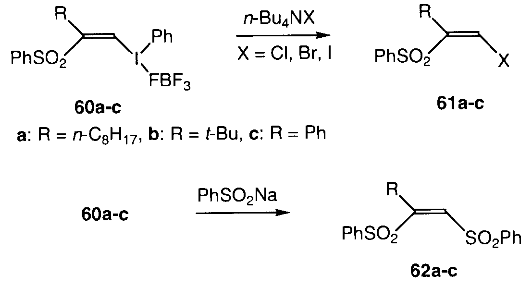
Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

Treatment of enolate anions derived from 1,3-dicarbonyl compounds with cyclohexenyl- and cyclopentenyl(aryl)iodanes at room temperature results in direct α-vinylations of carbonyl compounds (Scheme 23) [28]. In these reactions, the desired α-vinylations were generally accompanied by α-arylations as a competing side reaction; thus, exposure of the potassium enolate of 2-methyl-1,3-indandione to cyclohexenyl(phenyl)iodane (**8a**) in THF at room temperature afforded 2-cyclohexenyl-1,3-indandione (**55**) in 86% yield and 2-phenyl-1,3-indandione (**56**) in 10% yield. The electronic effects of substituents on the aromatic rings of alkenyl(aryl)iodanes play an essential role in determining the selectivity for vinylation and arylation; thus, use of alkenyl(*p*-methoxyphenyl)iodane (**57**) results in selective α-vinylation at the expense of the competing arylation of 1,3-dicarbonyl compounds. Use of an efficient aryl radical trap, 1,1-diphenylethylene, inhibits radical-induced decomposition of the alkenyl(aryl)iodanes, thereby improving the yields of α-vinylations of enolate anions derived from 1,3-dicarbonyl compounds.

This reaction probably involves the intermediate formation of the hypervalent organoiodane **58** by ligand exchange on the iodine(III). Subsequent ligand coupling on the iodine(III) of **58** would give rise to the vinylation product **55** (Scheme 24). A similar type of ligand exchange has been reported in which the reaction of dimedone with (hydroxy(tosyloxy)iodo)benzene in acetonitrile at room temperature gives 2-dimedonyl(phenyl)iodane **59** [29].

7. Addition–elimination reaction

7.1. *α-Addition–elimination reaction*

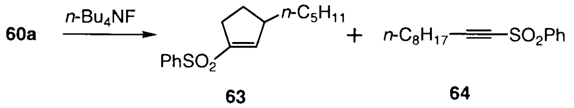
Nucleophilic vinylic substitution of (*Z*)-(β-(phenylsulfonyl)alkenyl)iodanes (**60**), prepared by stereoselective Michael addition of benzenesulfinic acid to alkynyl(phenyl)iodanes in methanol [12b], with n-Bu_4NCl (X = Cl, Br, I) in dichloromethane proceeds with exclusive retention of configuration at room temperature and affords (*Z*)-β-(phenylsulfonyl)vinyl halides (**61**) in high yields (Scheme 25) [30]. Reaction of **60** with sodium benzenesulfinate in THF at 0°C gives the retained (*Z*)-1,2-bis(phenylsulfonyl)alkenes (**62**) stereoselectively in good yields. Polymer supported benzenesulfinate anion also allows nucleophilic vinylic substitutions of **60** with retention of configuration [31]. The *Z* stereochemistry of **61** and **62** was established by the observation of a large nuclear Overhauser effect (NOE) enhancement (from 5% to 12%) between the vinylic and allylic protons.

As shown in Table 6, nucleophilic substitutions of **60b** and **60c** with the sterically demanding *tert*-butyl and phenyl groups at the β-position also give the corresponding (*Z*)-vinyl halides **61b** and **61c**. Note that, in general, the rate of substitutions with *n*-Bu_4NX decreases in the order *n*-Bu_4NI > *n*-Bu_4NBr > *n*-Bu_4NCl, reflecting the decreasing softness of halide ions. On the other hand, no substitution product was obtained in the reaction with *n*-Bu_4NF. For instance, the reaction of **60a** with *n*-Bu_4NF in dichloromethane at room temperature gave an 86:14 mixture of the alkylidene carbene-derived 1-(phenylsulfonyl)cyclopentene (**63**) and 1-(phenylsulfonyl)decyne (**64**) (Scheme 26).

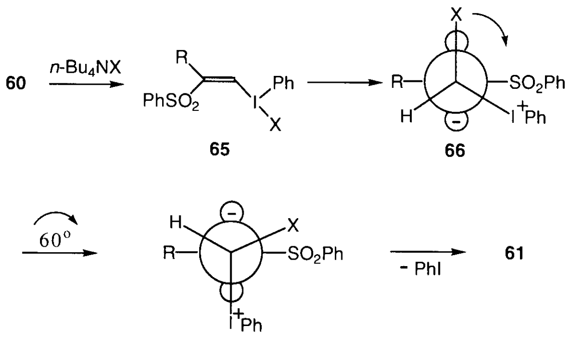
Table 6
Nucleophilic substitutions of (*Z*)-(β-(phenylsulfonyl)alkenyl)iodane (**60**) with *n*-Bu_4NX

60	*n*-Bu_4NX [a]	Time (h)	61	Yield (%)
60a	*n*-Bu_4NCl	4.5	**61a** (X = Cl)	95
60a	*n*-Bu_4NBr	3	**61a** (X = Br)	85
60a	*n*-Bu_4NI	1	**61a** (X = I)	79
60b	*n*-Bu_4NCl	11	**61b** (X = Cl)	100
60b	*n*-Bu_4NBr	9	**61b** (X = Br)	97
60b	*n*-Bu_4NI	1	**61b** (X = I)	83
60c	*n*-Bu_4NCl	1	**61c** (X = Cl)	100
60c	*n*-Bu_4NBr	0.5	**61c** (X = Br)	96
60c	*n*-Bu_4NI	5 min	**61c** (X = I)	93

[a] Reactions were carried out using 1.2 equivalents of *n*-Bu_4NX at room temperature.



Scheme 26.



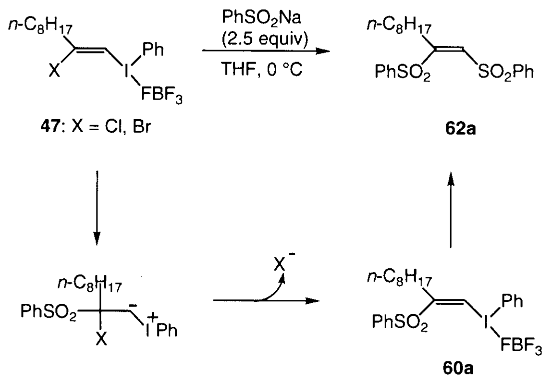
Scheme 27.

Scheme 27 shows a mechanism involving a ligand exchange of (*Z*)-(β-(phenylsulfonyl)alkenyl)iodanes (**60**) with halides and thereby formation of the (*Z*)-vinylhaloiodanes (**65**) as intermediates. It was established by ^1H-NMR that **65** is produced immediately after the addition of **60** to a solution of *n*-Bu_4NX in $CDCl_3$ at room temperature. The β-phenylsulfonyl group of **65** makes possible the perpendicular attack of halide ions to the π* orbital, which produces an α-sulfonyl-stabilized carbanion **66**. The internal 60° rotation of **66**, followed by reductive elimination of the hypernucleofuge, λ^3-phenyliodanyl group, would give (*Z*)-β-(phenylsulfonyl)vinyl halides (**61**) stereoselectively. Negative hyperconjugation between the hypernucleofuge and the carbanionic electron pair in **66** accounts for the preference of the 60° rotation over the 120° rotation of **66**.

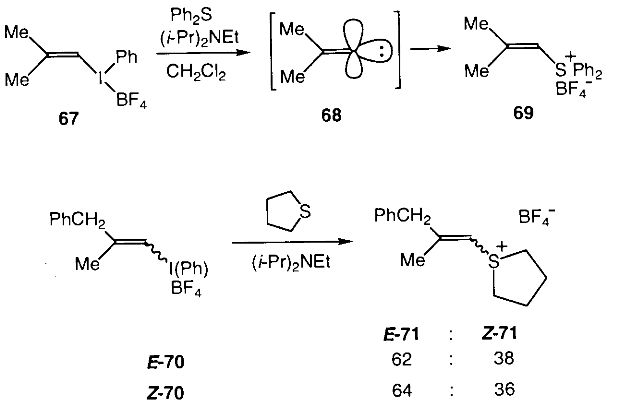
7.2. *β-Addition–elimination reaction*

Alkynyl(phenyl)iodanes are highly electron deficient species and act as good Michael acceptors for a variety of soft nucleophiles, including stable enolates of 1,3-dicarbonyl compounds, oxygen (carboxylates and phenoxides), nitrogen (azide and amide), and sulfur nucleophiles (sulfinates and thiocyanates) [11]. Michael addition of nucleophiles to the β-carbon of alkynyliodanes constitutes a key step for efficient cyclopentene annulation of alkynyliodanes via the tandem Michael-carbene insertion (MCI) reaction. In contrast, Michael addition to alkenyl(phenyl)iodanes at the β-carbon atom has rarely been observed [32].

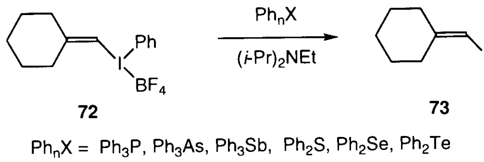
Nucleophilic vinylic substitutions of (*Z*)-(β-chloroalkenyl)- and (*Z*)-(β-bromoalkenyl)iodanes (**47**) with sodium benzenesulfinate in THF affords stereoselectively (*Z*)-1,2-bis(benzenesulfonyl)alkene (**62a**) with retention of configuration (Scheme 28) [33]. Intermediate formation of (*Z*)-(β-(benzenesulfonyl)alkenyl)-iodane (**60a**) was detected by ^1H-NMR experiments of the time courses of the reactions, especially at the early stages of the reactions. The formation of (*Z*)-**60a** involves a Michael addition of benzenesulfinate anion to the alkenyliodane **47** at the C_β atom, followed by halogen extrusion. Subsequent Michael addition of benzenesulfinate anion to (*Z*)-**60a** at the C_α atom, followed by reductive elimination of the λ^3-phenyliodanyl group yields (*Z*)-**62a**. This is the first firm evidence for a Michael addition of nucleophiles to alkenyl(phenyl)iodanes at the β-carbon atom.



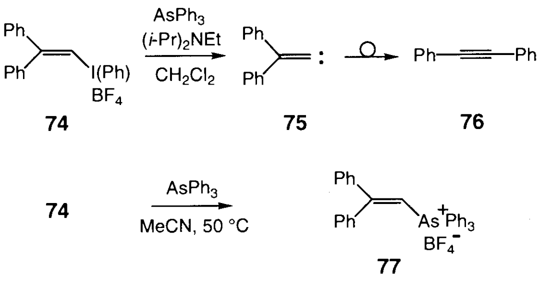
Scheme 28.



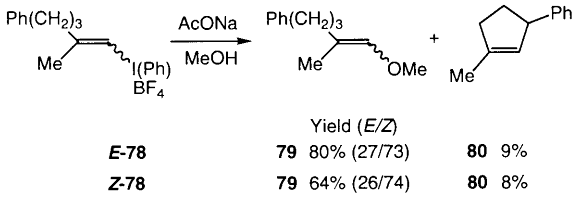
Scheme 29.



Scheme 30.



Scheme 31.



Scheme 32.

8. Elimination–addition reaction

As described above, base treatment of alkenyl(phenyl)iodanes under mild conditions results in reductive α-elimination of iodobenzene to generate alkylidene carbenes, because of the very high leaving group ability of the λ^3-phenyliodanyl group [4]. Subsequent nucleophilic trapping of the alkylidene carbenes constitutes formal nucleophilic vinylic substitution. Exposure of 2-methyl-1-propenyl-λ^3-iodane **67** to diphenyl sulfide in the presence of diisopropylethylamine in dichloromethane at room temperature allows the onium transfer reaction to proceed, yielding the alkenylsulfonium salt **69** in good yield (Scheme 29) [34]. This reaction involves intermediacy of the alkylidene carbene **68**, generation of which was firmly established by the observation that the reactive species derived from **67** via base-induced α-elimination readily undergoes cycloaddition to styrenes to give dimethylmethylenecyclopropanes [12d]. Furthermore, some alkylidene carbenes generated from alkenyl-λ^3-iodanes undergo 1,5-carbon–hydrogen insertions, providing a useful route for the construction of substituted cyclopentenes because of the high regio- and chemoselectivity [12].

The alkenyl group of (*E*)- and (*Z*)-1-alkenyl-λ^3-iodane (**70**) was selectively transferred to tetrahydrothiophene by the reaction with diisopropylethylamine to give a mixture of stereoisomers of the alkenylsulfonium salt **71**. The high degree of stereoconvergence of the olefin geometry in this onium transfer reaction yielding (*E*)- and (*Z*)-**71** provides evidence for the involvement of free alkylidene carbenes via base-induced reductive α-elimination. Both the complete stereoconvergence for intramolecular 1,5-carbon–hydrogen insertions of alkenyl-λ^3-iodanes yielding cyclopentenes [12a] and a small Hammett ρ value (-0.56) for the cycloaddition reaction of the vinyliodane **67** to ring-substituted styrenes [34] suggest the intermediacy of a free alkylidene carbene rather than a carbenoid.

Group 15 1-alkenyl(triphenyl)onium tetrafluoroborates (**73**) (X = P, As, Sb; n = 3) can be prepared by this onium transfer reaction of alkenyl-λ^3-iodane (**72**) under mild conditions in dichloromethane [35]. The reaction involves base-induced reductive α-elimination, followed by nucleophilic trapping of the resulting free alkylidene carbene with Group 15 element-centered nucleophiles. This onium transfer reaction also produced Group 16 1-alkenyl(diphenyl)onium tetrafluoroborates (**73**) (X = S, Se, Te; $n = 2$) in good yields (Scheme 30). 1,2-Migration of α-aryl groups of alkylidene carbenes is a low-energy process and proceeds rapidly [12c]. The attempted nucleophilic trapping of the alkylidene carbene **75** with triphenylarsine in dichloromethane to lead to the onium transfer cannot compete with the facile 1,2-phenyl migration yielding diphenylacetylene (**76**) (Scheme 31). Interestingly, however, 2,2-diphenylvinylarsonium tetrafluoroborate (**77**) was produced in a good yield when the reaction was carried out in acetonitrile at 50°C without using a base.

Competition between the nucleophilic vinylic substitution yielding the vinyl ether **79** and the intramolecular 1,5-carbon–hydrogen insertions of the intermediate alkylidene carbene to give the cyclopentene **80** was observed in the reaction of alkenyl-λ^3-iodane (**78**) with alcohols in the presence of a base (Scheme 32) [36]. Both geometrical isomers of **78** showed again the same product distributions at nearly the same rate. Decreasing the solvent nucleophilicity from MeOH to EtOH to

TFE tends to increase the fraction of the 1,5-carbon–hydrogen insertion product **80**.

9. Conclusions

Vinylic substitutions of λ^3-vinyl(phenyl)iodanes with nucleophiles are summarized. Halide anions act as good nucleophiles toward λ^3-vinyl(phenyl)iodanes, probably because of their low basicity and high nucleophilicity. Other nucleophiles involve sulfinate and enolate anions, alcohols, acids, amides, and Group 15 (phosphines, arsines, and stibines) and Group 16 (sulfides, selenides, and tellurides) compounds.

The nucleophilic vinylic substitutions of λ^3-vinyl(phenyl)iodanes occur under a variety of reaction mechanisms. Especially noteworthy is the bimolecular nucleophilic vinylic substitution of vinyliodanes affording products of exclusive inversion of configuration, which is the first clear example of the vinylic S_N2 reaction. The hyperleaving group ability of the λ^3-phenyliodanyl group would be the origin of this unusual inversion of configuration in the nucleophilic vinylic substitutions.

A veritable rainbow of reaction mechanisms is observable depending on the nature of the substituents at the β-vinylic carbons of λ^3-vinyl(phenyl)iodanes and on the reaction conditions, which include (1) vinylic S_N1 reactions generating vinyl cations, (2) in-plane vinylic S_N2 reactions, (3) nucleophilic substitutions with generation of vinylenebenzenium ion, (4) ligand coupling reactions, (5) addition–elimination reactions, and (6) elimination–addition reactions. Most importantly, in the nucleophilic vinylic substitutions of λ^3-vinyl(phenyl)iodanes with halides, the vinylic S_N2 reaction is more facile than the other vinylic S_N1 reaction, ligand coupling reaction, and addition–elimination reaction.

Acknowledgements

We wish to acknowledge our collaborations with Professor T. Okuyama, Himeji Institute of Technology, and financial support by a Grant-in-Aid for Scientific Research on Priority Areas (A) The Chemistry of Inter-Element Linkage (No. 09239102) from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] For reviews, see: (a) G.F. Koser, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Functional Groups, Supplement D, Wiley, New York, 1983, Chapter 25. (b) M. Ochiai, Y. Nagao, J. Synth. Org. Chem. Jpn. 44 (1986) 660. (c) M. Ochiai, Rev. Heteroatom. Chem. 2 (1989) 92. (d) R.M. Moriarty, R.K. Vaid, Synthesis (1990) 431. (e) R.M. Moriarty, R.K. Vaid, G.F. Koser, Synlett. (1990) 365. (f) A. Varvoglis, The Chemistry of Polycoordinated Iodine, VHC, New York, 1992. (g) Y. Kita, H. Tohma, T. Yakura, Trends Org. Chem. 3 (1992) 113. (h) P.J. Stang, Angew. Chem. Int. Ed. Engl. 31 (1992) 274. (i) G.F. Koser, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Functional Groups, Supplement D2, Wiley, New York, 1995, Chapter 21. (j) T. Kitamura, J. Synth. Org. Chem. Jpn. 53 (1995) 893. (k) P.J. Stang, V.V. Zhdankin, Chem. Rev. 96 (1996) 1123. (l) T. Muraki, H. Togo, M. Yokoyama, Rev. Heteroatom. Chem. 17 (1997) 213. (m) M. Ochiai, in: K. Akiba (Ed.), Chemistry in Hypervalent Compounds, Wiley-VCH, New York, 1999, Chapter 12.

[2] (a) M. Ochiai, K. Sumi, Y. Nagao, E. Fujita, Tetrahedron Lett. 26 (1985) 2351. (b) M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, Tetrahedron 44 (1988) 4095. (c) M. Ochiai, K. Oshima, Y. Masaki, J. Chem. Soc. Chem. Commun. (1991) 869. (d) M. Ochiai, M. Toyonari, T. Nagaoka, D.-W. Chen, M. Kida, Tetrahedron Lett. 38 (1997) 6709.

[3] A.A. Mironova, I.I. Maletina, S.V. Iksanova, V.V. Orda, L.M. Yagupolskii, Zh. Org. Chem. 25 (1989) 306.

[4] T. Okuyama, T. Takino, T. Sueda, M. Ochiai, J. Am. Chem. Soc. 117 (1995) 3360.

[5] (a) E.R. Kline, C.A. Kraus, J. Am. Chem. Soc. 69 (1947) 814. (b) O.A. Ptitsyna, G.G. Lyatiev, V.N. Krischchenko, O.A. Reutov, Izv. Akad. Nauk SSSR Ser. Khim. (1967) 955. (c) Y. Yamada, K. Kashima, M. Okawara, J. Polym. Sci. Polym. Lett. Ed. 14 (1976) 65. (d) F.M. Beringer, E.J. Geering, I. Kuntz, M. Mausner, J. Phys. Chem. 60 (1956) 141.

[6] M. Ochiai, M. Kida, K. Sato, T. Takino, S. Goto, N. Donkai, T. Okuyama, Tetrahedron Lett. 40 (1999) 1559.

[7] M. Ochiai, Y. Takaoka, K. Sumi, Y. Nagao, J. Chem. Soc. Chem. Commun. (1986) 1382.

[8] J. McMurry, Organic Chemistry, Brooks/Cole, Pacific Grove, 3rd ed., 1992, p. 369.

[9] D.R. Kelsey, R.G. Bergman, J. Am. Chem. Soc. 93 (1971) 1953.

[10] (a) T.C. Clarke, D.R. Kelsey, R.G. Bergman, J. Am. Chem. Soc. 94 (1972) 3626. (b) T.C. Clarke, R.G. Bergman, J. Am. Chem. Soc. 96 (1974) 7934. (c) R.H. Summerville, P.v.R. Schleyer, J. Am. Chem. Soc. 96 (1974) 1110.

[11] (a) M. Ochiai, K. Oshima, Y. Masaki, J. Am. Chem. Soc. 113 (1991) 7059. (b) T. Okuyama, T. Takino, K. Sato, M. Ochiai, J. Am. Chem. Soc. 120 (1998) 2275. (c) T. Okuyama, T. Takino, K. Sato, K. Oshima, S. Imamura, H. Yamataka, T. Asano, M. Ochiai, Bull. Chem. Soc. Jpn. 71 (1998) 243.

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

[13] M. Ochiai, K. Oshima, Y. Masaki, J. Chem. Soc. Chem. Commun. (1991) 869.

[14] M. Ochiai, Y. Takaoka, Y. Masaki, Y. Nagao, M. Shiro, J. Am. Chem. Soc. 112 (1990) 5677.

[15] (a) N.L. Allinger, M.A. Miller, F.A. VanCatledge, J.A. Hirsch, J. Am. Chem. Soc. 89 (1967) 4345. (b) M. Rieger, F.H. Westheimer, J. Am. Chem. Soc. 72 (1950) 19. (c) E.L. Eliel, S.H. Schroeter, T.J. Brett, F.J. Biros, J.-C. Richer, J. Am. Chem. Soc. 88 (1966) 3327.

[16] T. Sueda, M. Ochiai, unpublished results.

[17] T. Okuyama, M. Ochiai, J. Am. Chem. Soc. 119 (1997) 4785.

[18] J. Yan, Z.-C. Chen, Tetrahedron Lett. 40 (1999) 5757.

[19] M. Ochiai, S. Yamamoto, K. Sato, J. Chem. Soc. Chem. Commun. (1999) 1363.

[20] M.N. Glukhovtsev, A. Pross, L. Radom, J. Am. Chem. Soc. 116 (1994) 5961.

[21] (a) T. Okuyama, H. Yamataka, Can. J. Chem. 77 (1999) 577. (b) V. Lucchini, G. Modena, L. Pasquato, J. Am. Chem. Soc. 117 (1995) 2297.

[22] T. Okuyama, Y. Ishida, M. Ochiai, Bull. Chem. Soc. Jpn. 72 (1999) 163.

[23] T. Okuyama, H. Oka, M. Ochiai, Bull. Chem. Soc. Jpn. 71 (1998) 1915.

[24] M. Ochiai, K. Oshima, Y. Masaki, Chem. Lett. (1994) 871.

[25] (a) S. Oae, Y. Uchida, Acc. Chem. Res. 24 (1991) 202. (b) N. Furukawa, S. Ogawa, K. Matsumura, H. Fujihara, J. Org. Chem. 56 (1991) 6341. (c) J. Moc, A.E. Dorigo, K. Morokuma, Chem. Phys. Lett. 204 (1993) 65.

[26] T. Okuyama, T. Takino, K. Sato, M. Ochiai, Chem. Lett. (1997) 955.

[27] (a) M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, Tetrahedron 44 (1988) 4095. (b) M. Ochiai, K. Sumi, Y. Nagao, E. Fujita, Tetrahedron Lett. 26 (1985) 2351.

[28] M. Ochiai, T. Shu, T. Nagaoka, Y. Kitagawa, J. Org. Chem. 62 (1997) 2130.

[29] G.F. Koser, A.G. Relenyi, A.N. Kalos, L. Rebrovic, R.H. Wettach, J. Org. Chem. 47 (1982) 2487.

[30] M. Ochiai, K. Oshima, Y. Masaki, Tetrahedron Lett. 32 (1991) 7711.

[31] M. Ochiai, K. Oshima, Y. Masaki, M. Kunishima, S. Tani, Tetrahedron Lett. 34 (1993) 4829.

[32] T. Umemoto, Y. Gotoh, Bull. Chem. Soc. Jpn. 60 (1987) 3307.

[33] (a) M. Ochiai, Y. Kitagawa, M. Toyonari, K. Uemura, Tetrahedron Lett. 35 (1994) 9407. (b) M. Ochiai, Y. Kitagawa, M. Toyonari, K. Uemura, K. Oshima, M. Shiro, J. Org. Chem. 62 (1997) 8001.

[34] T. Sueda, T. Nagaoka, S. Goto, M. Ochiai, J. Am. Chem. Soc. 118 (1996) 10141.

[35] M. Ochiai, T. Sueda, R. Noda, M. Shiro, J. Org. Chem. 64 (1999) 8563.

[36] T. Okuyama, H. Yamataka, M. Ochiai, Bull. Chem. Soc. Jpn. 72 (1999) 2761.