REACTIONS OF VINYLSILANES WITH LEWIS ACID-ACTIVATED IODOSYLBENZENE:
STEREOSPECIFIC SYNTHESES OF VINYLIODONIUM TETRAFLUOROBORATES
AND THEIR REACTIONS AS HIGHLY ACTIVATED VINYL HALIDES

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Abstract: Alkenyl(phenyl)iodonium tetrafluoroborates 3 were
synthesized from alkenylsilanes 1 by the reaction with
iodosylbenzene and boron trifluoride-diethyl ether or
triethyloxonium tetrafluoroborate. The reaction proceeds
stereospecifically with retention of configuration of 1. X-ray
diffraction analysis of (4-*tert*-butylcyclohexenyl)phenyl-
iodonium tetrafluoroborate (3b) revealed the highly ionic
structure with the distorted T-shape arrangement. Iodonium
salts 3 behave like the highly activated species of vinyl
iodides due to the high leaving ability of the iodine(III)
substituents. Thus, a variety of substituted olefins including
a-cyano and a-nitro olefins, vinyl sulfides, vinyl halides, and
a,β-unsaturated esters, were synthesized from 3 under mild
conditions. A ligand coupling mechanism *via* the formation of
10-I-3 intermediate 27 containing a copper(III) ligand is
proposed for the substitutions of 3 with nucleophiles.

The versatility of alkenylsilanes in organic synthesis has been well
recognized.[1] They serve as vinyl anion equivalent species and react readily with
a wide range of electrophiles in a regio- and stereoselective manner to give
substitution products. In order to increase the synthetic utility of this
important class of compounds furthermore, we are interested in devising a new
method for achieving the reactivity umpolung of vinylsilanes. Our approach to
this problem involves the conversion of alkenylsilanes to vinylic compounds 2,
which should have a good leaving group X and therefore may act as vinyl cation
equivalent species. The choice of a hypervalent iodine(III) substituent as a
leaving group X seems to be highly desirable, because iodine(III) at the
hypervalent state is known to be an excellent leaving group.[2]
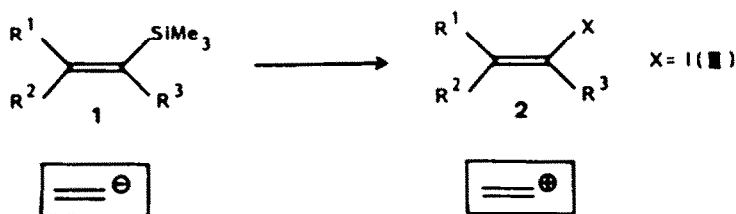
Scheme 1.

In spite of numerous studies on the chemistry of diaryliodonium salts, the
synthetic method and utility of the vinyl(aryl)iodonium salts are limited and
often inefficient.[2h] A few β-chlorovinyliodonium salts have been prepared and
they are mostly utilized as the source of acetylene itself.[3] Vinyl(aryl)iodonium

salts having no chlorine substituents in the vinyl moieties have been obtained by the reaction of vinylmercuric halides or vinyl(trichloro)stannane with (dichloroiodo)arenes.[4]   [Hydroxy(tosyloxy)iodo]benzene is   an   active   phenyl-iodinating species and condenses with alkynes in dichloromethane to give moderate yields of β-tosyloxyvinyl(phenyl)iodonium tosylates.[5]

We now wish to report a new, general, and stereoselective method for the synthesis of vinyl(phenyl)iodonium salts 3 from alkenylsilanes utilizing a hypervalent organoiodine compound, iodosylbenzene (ISB), and the utility of 3 in organic synthesis, especially in a sense of the activated, reactive species of vinyl iodides.[6]
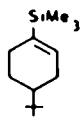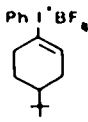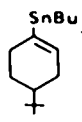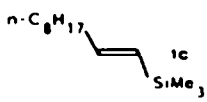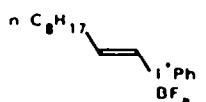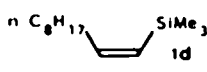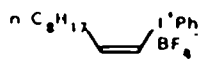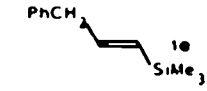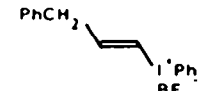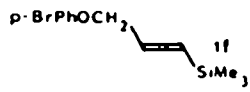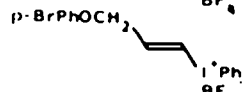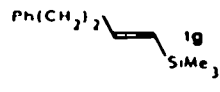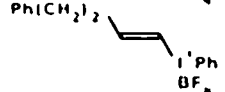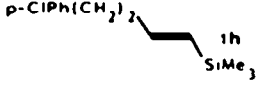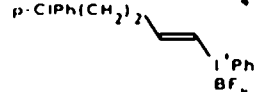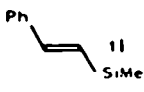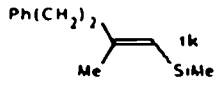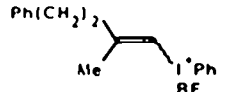
Synthesis of Vinyl(phenyl)iodonium Tetrafluoroborates 3

Reactivity of ISB toward weak nucleophiles such as organosilicon and organotin compounds is very low. For instance, allylsilanes do not react with ISB in dichloromethane at room temperature and are recovered unchanged.   The low reactivity of ISB may be attributable in part to the proposed polymeric nature and the very low solubility   toward common organic solvents (dichloromethane, tetrahydrofuran, dimethylsulfoxide, etc.).[7] However, we have reported that ISB is highly activated by the coordination of Lewis acids like boron trifluoride-diethyl ether to the oxygen atom, presumably *via* the formation of the electrophilic species $C_6H_5I^{\delta+}$-$OM^{\delta-}$ (M = Lewis acids). Thus, the boron trifluoride-activated ISB $C_6H_5I^{\delta+}$-$OBF_3^{\delta-}$ is now reactive enough   towards the nucleophilic attack of allylsilanes to afford the allyliodine(III) intermediate, which is an allyl cationic species and yields the allylation products by substitution reaction with a variety of nucleophiles including aromatic compounds, alcohols, carboxylic acids, and azides.[8,9] Recently, the oxidation of silyl enol ethers[10] and olefins[11] utilizing the boron trifluoride-activated ISB has been reported.

Reaction of alkenyl(trimethyl)silanes 1 with ISB (2.5 equiv.) in the presence of boron trifluoride-diethyl ether (2.5 equiv.) in dichloromethane followed by the treatment with excess amounts of aqueous sodium tetrafluoroborate (Method A) gave the corresponding alkenyl(phenyl)iodonium tetrafluoroborates 3 in good yields.[12] As an alternative to boron trifluoride, Meerwein's reagent triethyloxonium tetrafluoroborate, which may produce an active species of $C_6H_5I^+$-OEt BF_4^- by the reaction with ISB, was also found to be very useful for the synthesis of vinyliodonium salts 3.   Thus, 1 on   treatment with ISB (2.5 equiv.) and triethyloxonium tetrafluoroborate (2.5 equiv.) in dichloromethane (Method B) afforded 3.   The results are summarized in Table 1. Purification of 3 was carried out by recrystallization or by decantation. Some of the vinyliodonium salts 3 are labile at room temperature and should be kept in refrigerator.

Table 1 indicates that the reaction proceeds in a highly stereospecific manner with retention of configuration. *E*-1-(Trimethylsilyl)dec-1-ene (1c) gave the crystalline *E*-1-decenyliodonium tetrafluoroborate 3c in 72 % yield (Entry 5).   Its *E*-stereochemistry was determined by the large vicinal coupling constant (13.7 Hz) between two vinylic protons. On the other hand, the *Z*-vinylsilane 1d did not produce the corresponding *Z*-iodonium salt 3d and afforded the dehydrosilylation product dec-1-yne in good yield (Entry 6). Careful NMR tube experiment in CD_2Cl_2, however, showed the transient formation of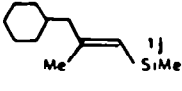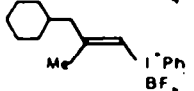 the labile salt 3d with a small coupling constant 6.0 Hz between vinylic protons in 21 % yield, after standing the reaction mixture for 4 h at room temperature with occasional shaking.   The presence of dec-1-yne (36 %) and 1d (43 %) was also detected. The ratio of 1d to 3d to dec-1-yne changed to 24:18:58 after standing for 6 h. Therefore, the rate of formation of 3d from 1d turned out to be comparable to that of the *anti*-β-

Table 1. Synthesis of alkenyl(phenyl)iodonium tetrafluoroborates 3

Entry	Vinylsilane 1	Method[a]	Reaction conditions	Vinyliodonium salts 3		Yield[b] %
1	1a	A	0 °C, 0.3 h	3a		94
	1b			3b		
2		A	0 °C, 0.25 h			80
3		B	0 °C, 1 h then RT,[c] 2.5 h			74
4	4	A	0 °C, 1.5 h	3b		67
5	1c	B	RT, 4 h	3c		72
6	1d	B[d]	RT, 5 h	3d		0[e]
7	1e	B	RT, 20 h	3e		69
8	1f	A	0 °C, 4.5 h	3f		72
9	1g	A	0 °C, 7.5 h	3g		77
10	1h	A	0 °C, 1.5 h	3h		75
11	1i	B	RT, 18 h	3i[f]		61
12	1j	A	0 °C, 0.2 h	3j		85
	1k			3k		
13	E/Z 98 2	A	0 °C, 0.1 h	E/Z 97 3		92
14	98 2	B	RT, 3 h	97 3		71
15	10 90	B	RT, 3.5 h	10 90		89

a) See the experimental section. b) Isolated yields. c) RT : room temperature. d) The reaction was carried out using 1.2 equiv. of ISB and 1 equiv. of triethyloxonium tetrafluoroborate. e) Dec-1-yne was obtained in 90% yield (GLC yield). f) Reference 4a.

elimination of a β-hydrogen and an organoiodine(III) substituent of 3d.[14] The
syn-β-elimination of E-3c, however, does not proceed under reaction conditions,
because of its unfavourable steric arrangement.[15] It has been well documented
that *anti*-dehydrohalogenation of vinyl halides by using bases is much faster than
syn-β-elimination.[16]

β,β-Disubstituted vinylsilanes 1j and 1k yielded the vinyliodonium salts 3j and
3k, respectively, with retention of stereochemistry (Entry 12 - 15). The
stereochemistry of these salts was determined by comparison of the nuclear
Overhauser effect (NOE): for instance, a 13 % NOE of the vinylic proton of Z-3k
was observed on irradiation of the protons of methyl group, while no such NOE was
observed in E-3k. (4-*tert*-Butyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate
3b was prepared from both vinylsilane 1b and vinylstannane 4 in a comparable yield
(Entry 2 - 4).

Aryl-silicon bonds can also be cleaved by the activated ISB to give
diaryliodonium salts. For instance, the reaction of phenyl(trimethyl)silane with
ISB and boron trifluoride resulted in the formation of diphenyliodonium
tetrafluoroborate (5)[17] in 75 % yield. Synthesis of diaryliodonium tosylate
utilizing arylsilanes and [hydroxy(tosyloxy)iodo]arenes has been reported by Koser
and his co-workers.[18] When the molecules containing both vinyl and aryl groups
attached to silicon atoms were allowed to react with the activated ISB,
competition between the formation of alkenyl(phenyl)iodonium salts and that of
diaryliodonium salts took place. In the reaction of alkenyl(phenyl)silane 6, the
high selectivity for the cleavage of vinyl-silicon over phenyl-silicon bonds was
observed and 3c and 5 were obtained in a ratio 93:7. Deactivation of the double
bond of 6 by the introduction of electron-withdrawing substituents such as
alkoxycarbonyl groups, however, reverses the chemoselectivity of the reaction.
Thus, vinylsilane 7 produced 5 exclusively in 68 % yield. In the reaction of
compound 8, the electron rich aromatic ring bearing three alkoxy groups but no
trimethylsilyl group was found to be a much better nucleophile toward the
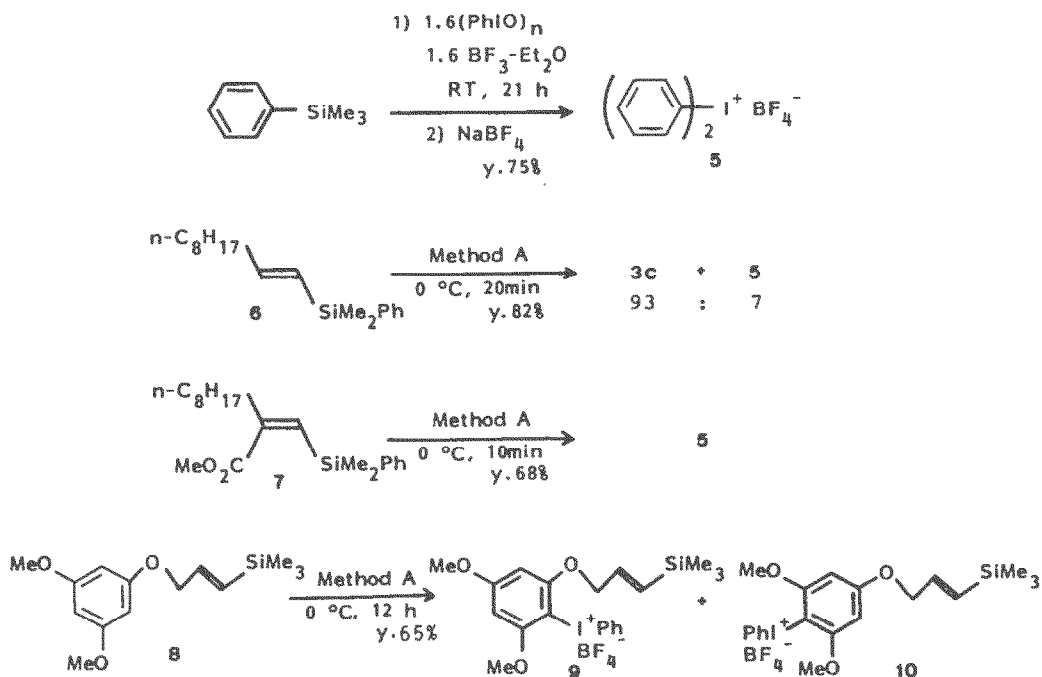
Scheme 2.

Table 2. ^{1}H and ^{13}C Chemical shifts of alkenyliodonium salts **3** and alkenyl iodides[a]

Compd.	^{1}H , δ (ppm)		^{13}C , δ (ppm)	
	Hα	Hβ	Cα	Cβ
3b	—	7.04	118.5	147.9
3c	6.78	6.98	96.5	155.9
3d	6.90	6.70	—[b]	—[b]
3e	6.81	7.11	98.0	153.4
3i	7.48	7.79	96.0	151.6
3k (Z)	6.58	—	95.3	159.1
11	5.95	6.50	74.4	146.6

a) The numbering system is as follows: $R-C_\beta H_\beta = C_\alpha H_\alpha - X$.
b) Not determined.

activated ISB than a vinylsilyl group and a regioisomeric mixture of diaryl-iodonium salts $\underline{9}$ and $\underline{10}$ in a ratio 64:36 was obtained.

Fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS) are used extensively for the analysis of organic onium salts such as ammonium, phosphonium, and sulfonium salts.[19] The positive ion FAB mass spectra of vinyliodonium tetrafluoroborates $\underline{3}$ showed relatively abundant fragments corresponding to the intact cations: for example, iodonium salts $\underline{3a}$ and $\underline{3b}$ produce abundant ions assigned to $(M-BF_4)^+$ at m/e 285 and 341, respectively (See experimental section). Busch has reported that the positive ion secondary ion mass spectra of $\underline{3b}$, 3c, and $\underline{3i}$ also contain the intact cations as the base peak.[19e] IR spectra of 3 showed very large broad bands at 1100-1000 cm^{-1} characteristic of the BF_4^- anion.

^{1}H and ^{13}C NMR chemical shifts of vinylic protons and carbons of $\underline{3}$ are shown in Table 2. Comparing the ^{1}H and ^{13}C NMR chemical shifts in E-1-decenyliodonium salt $\underline{3c}$ and E-1-iodo-1-octene $\underline{11}$, it is observed that in the iodonium salt 3c the α-hydrogen and α-carbon are much more deshielded (0.83 ppm for Hα and 22.1 ppm for Cα) than the β-hydrogen and β-carbon (0.48 ppm for Hβ and 9.3 ppm for Cβ), respectively. The observation may be partly interpreted in terms of the higher electronegativity of the phenyliodonium group compared to that of iodine.[20] In contrast to the above results, it has been shown that the β-carbons in methyl(vinyl)-bromonium and -chloronium salts are much more deshielded than the α-carbons.[24]

Crystal Structure of Phenyl(4-*tert*-butylcyclohexenyl)iodonium Tetrafluoroborate (3b)

Single-crystal X-ray diffraction analysis of alkenyl(phenyl)iodonium tetrafluoroborate $\underline{3b}$ was carried out to determine the stereo-structure. The structure of the bimolecular unit formed in the crystal of $\underline{3b}$ (Figure 1) reveals the distorted T-shape arrangement with the three bonds to iodine (I-C$_1$, I-C$_{.1}$, and I-F$_1$). The configuration is similar to other trivalent organoiodine compounds.[25] The selected bond lengths and bond angles are summarized in Table 3.

The I-F$_1$ bond distance (3.037 Å) is much longer than the computed covalent single bond length of 1.97 Å.[26] This fact clearly indicates that the iodonium salts $\underline{3b}$ is considerably ionic in character. Similar ionic structure for diphenyliodonium tetrafluoroborate ($\underline{5}$) with I-F bond distance of 2.96 Å has been reported by Struchkov and Khotsyanova.[27] The crystal structure contains three secondary bonds[28] between the electropositive trivalent iodine and the three
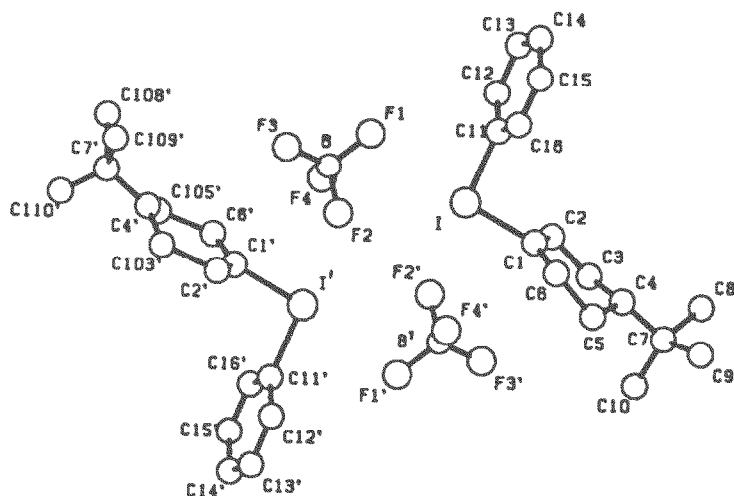
Figure 1. Molecular arrangement around an inversion center showing a bimolecular unit formed in the crystal of **3b**
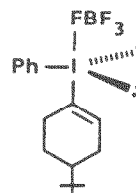
Figure 2. Trigonal bipyramidal structure of **3b**

Table 3. A) Selected interatomic distances (Å) and B) bond angles (degrees) of **3b**[a,b]

A)

I-F1	3.037(7)	I-F2	3.311(9)	I-F2'	3.189(9)
I-F4'	3.311(14)	I-C1	2.114(8)	I-C11	2.099(9)
C1-C2	1.41(1)	C1-C6	1.36(1)		

B)

F1-I-C1	161.6(3)	F1-I-C11	79.8(3)	C1-I-C11	98.5(3)

a) See experimental section. b) Numbers in parentheses are e.s.d. values.

fluorine atoms (F_2, $F_{2'}$, and $F_{4'}$). The intermolecular I-$F_{2'}$ secondary bond is stronger than the others. The deviation of F_1-I-C_1 bond angle of 161.6° from the ideal value of 180° for the hypervalent 3-center-4-electron bond may be interpreted in terms of the presence of these secondary bonds.

These results are compatible with the distorted trigonal bipyramidal configuration of 3b possessing the phenyl group and two lone pairs in equatorial positions as indicated in Figure 2. The more bulky cyclohexenyl group having an equatorial 4-*tert*-butyl group than the phenyl group as well as the highly electronegative fluorine of BF_4 occupy apical positions.

Reaction of Vinyliodonium Salts 3 with Nucleophiles

It seems reasonable to assume that in substitution reaction with nucleophiles vinyliodonium salts 3 exhibit high reactivity as the activated species of vinyl halides, especially vinyl iodides, because of the excellent leaving ability of the organoiodine(III) substituents. In this sense, 3 seems to be a very versatile intermediate in organic synthesis. In fact, *E*-β-phenylethenyliodonium salt on treatment with sodium p-toluenesulfinate in water has been shown to give a 65 %

yield of E-β-(p-tolyl)styrene.[4c]   Beringer   has   reported   the   synthesis   of
2-phenyl-2-(o-chlorostyryl)-1,3-indandione   by the reaction of β-chloro-β-phenyl-
ethenyliodonium salt with sodium 2-phenyl-1,3-indanedionate.[3d]

In   order   to   clarify the reactivity of vinyliodonium salts 3 as   well   as   to
establish their versatility in organic synthesis, we   have   investigated   the
substitution   reactions   with   a variety of nucleophiles in detail.   The   trans-
formations   shown   for   cyclic   vinyliodonium tetrafluoroborate 3b   in   Scheme   3
illustrate   the   broad range of utility of the salts 3.   It is   essential   to   the
success   of   these   reactions   that   the counter   ion BF_4^- associated   with   the
alkenyl(phenyl)iodonium cation   is   nonnucleophilic   in   character   to   avoid
competition with nucleophiles.

The attempted substitution of 3b with butyllithium in tetrahydrofuran at   -78°C
resulted   in formation of a complex mixture of 12 (R = Bu, 0.2 %), 17 (X = I,   25
%),   4-tert-butylcyclohexanone (17 %), and iodobenzene (40 %).   The use of   copper
salts   is   vital to the success of the substitution reactions.   With Bu_2CuLi in
diethyl ether at -78°C, the desired olefin 12 (R = Bu) was obtained in 84 % yield

12: R= Me, Bu, Ph
y.73% 84% 90%

CO₂Me → 18

CN → 13

PhI^+ BF_4^-

3b

14

17: X= Cl, Br, I
y.93% 69% 100%

G y.84%   A   B y.92%

F   C y.64%

E y.81%   D y.55%

SPh → 16

NO₂ → 15
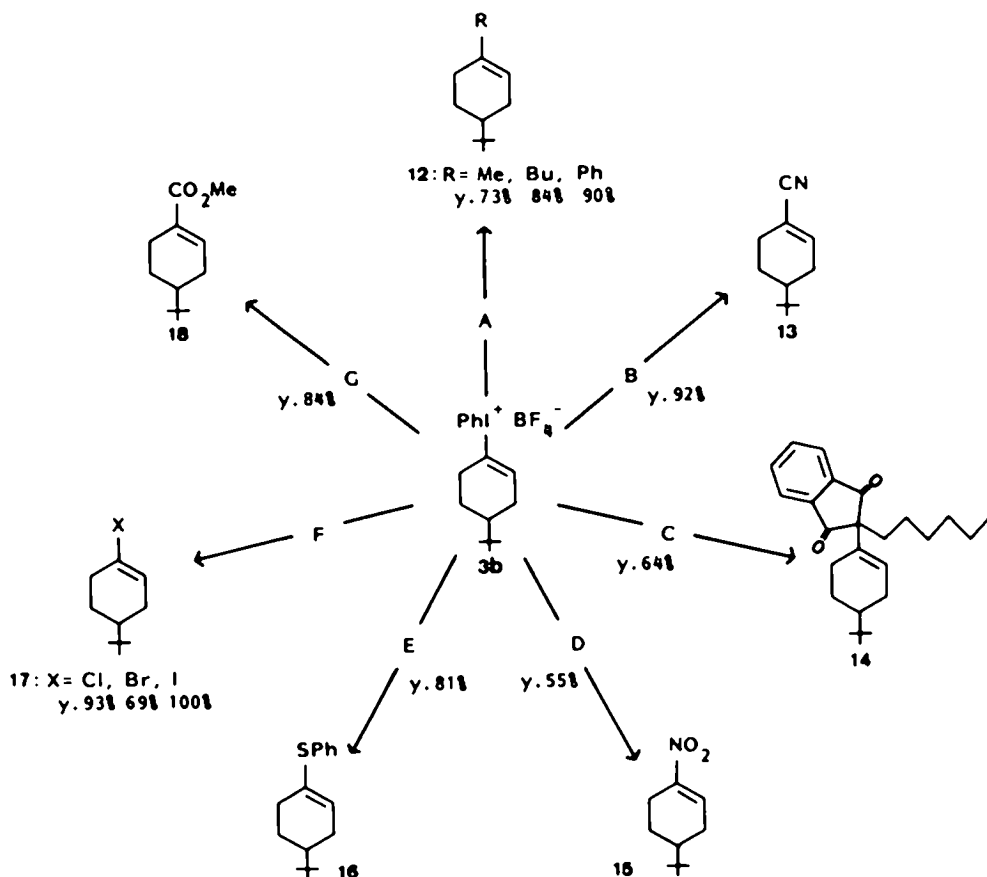
Scheme 3. Substitution reaction of 3b. The specific reagents and
reaction conditions are as follows: (A) Me_2CuLi, THF, -78 °C, 4 h;
Bu_2CuLi, Et_2O, -78 °C, 3 h; Ph_2CuLi, THF, -30 °C, 5 h; (B) $KCu(CN)_2$,
DMF, 25 °C, 12 h; (C) potassium 2-hexyl-1,3-indanedionate, THF,
25 °C, 0.5 h; (D) $NaNO_2$, $CuSO_4$, DMF-H_2O, 25 °C, 28 h; (E) PhSNa,
dioxane, 25 °C, 0.5 h; (F) CuCl, KCl, DMF, 25 °C, 12 h; CuBr, KBr,
DMF, 25 °C, 12 h; CuI, KI, DMF, 25 °C, 1 h; (G) cat.$Pd(OAc)_2$, CO,
n-Bu_3N, MeOH, 25 °C, 2 h.

with the reductive elimination of iodobenzene (62 %). Cuprous potassium cyanide in dimethylformamide at room temperature gave the unsaturated nitrile 13 in high yield. The enolate anion generated from 2-hexyl-1,3-indanedione undergoes substitution with production of 1,3-diketone 14. Conjugated nitro olefin 15[29] and vinyl sulfide 16 were readily prepared under mild conditions. The tetra-fluoroborate 3b reacts with a mixture of a cuprous halide and a potassium halide in dimethylformamide, yielding a variety of vinyl halides 17 (X = Cl, 93 %; X = Br, 69 %; X = I, 100 %) other than the corresponding fluoride 17 (X = F). The vinyl iodide 17 (X = I) was also obtained by the lithium aluminum hydride reduction or photochemical reaction in about 30 % yield. Palladium-catalyzed alkoxycarbonylation of 3b in the presence of a tertiary amine proceeds at room temperature to give the α,β-unsaturated ester 18 in good yield.[30]

Michael-type addition of a various nucleophiles toward vinylphosphonium salts[31] and vinylsulfonium salts[32] has been well documented. In addition, we have found the efficient cyclopentene annulations involving the conjugate addition of stable carbanions generated from 1,3-dicarbonyl compounds to the carbon-carbon triple bond of alkynyliodonium tetrafluoroborates as the key step.[33] In the case of vinyliodonium salts 3, however, the product derived from the Michael-type addition of nucleophiles to the double bonds was not observed. Especially noteworthy are the much milder conditions required for the substitutions of 3b, as compared with that of vinyl iodides. Elevated reaction temperature (110 – 150°C in *N*-methyl-pyrrolidinone) was required for the substitution reaction of vinyl iodides using copper(I) cyanide, phenylthiolate, and halides.[34] Palladium-catalyzed alkoxy-carbonylation of vinyl halides was usually carried out at 80 – 110°C.[35] On the other hand, the reactions B – G shown in Scheme 3 proceed readily at room temperature.

To determine the stereochemical course of the reaction of alkenyliodonium salts, both stereoisomers of 3k were treated with $(C_6H_5)_2$CuLi in tetrahydrofuran at -30°C (Scheme 4). The substitution reaction yielding the olefin 19 was found to be stereospecific and proceeded with essentially complete retention of configuration in good yield. *E*-Iodonium salt 3c produced selectively *E*-1-phenyl-decene 20 in 72 % yield. In this case, however, elimination reaction affording an alkyne becomes competitive and 1-decyne was obtained in 7 % yield.[4c,36] Similarly, palladium-catalyzed methoxycarbonylation of 3k (*E:Z* = 9:91) afforded
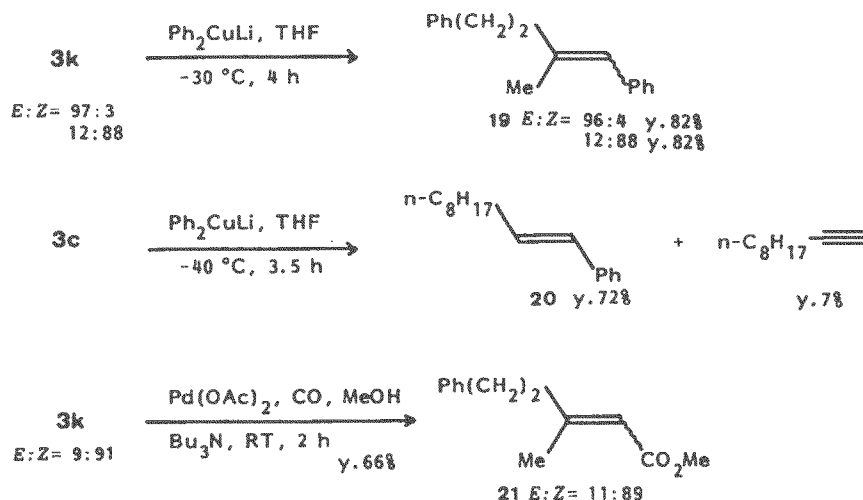
Scheme 4.

the unsaturated ester 21 (E:Z = 11:89) stereospecifically in 66 % yield. The stereochemistry of 19 and 21 was determined by NOE experiments.

The mechanism for substitutions of alkenyliodonium salts 3 with nucleophiles containing copper(I) is not yet clear. As one of the possible reaction pathway, the single electron transfer mechanism (Scheme 5) involving the formation of 9-I-2 intermediate 22 followed by its decomposition to yield radicals should be considered. Such a pathway has been proposed in the cuprous chloride-catalyzed thermal decomposition of diphenyliodonium chloride to chlorobenzene and iodobenzene.[37] In the cleavage of 22, path a is favored over path b because of the higher stability of a combination of vinyl radical 23 and iodobenzene than that of phenyl radical and vinyl iodide 24.[38] This explains the exclusive formation of vinylic compounds 25 instead of the phenylation of nucleophiles producing 26. However, the electron transfer mechanism seems unlikely since the complete retention of stereochemistry in the phenylation of 3k is not compatible with the formation of vinyl radical intermediate 23 which rapidly loses the stereochemistry.[40] We propose a reaction pathway involving the following three steps (Scheme 6): 1) Oxidative addition of cuprates with formation of 10-I-3 species 27, in which the copper(III) ligand probably occupies an equatorial position because of its low electronegativity. 2) Ligand coupling on the iodine atom producing the vinyl copper(III) species 28 with retention of the stereochemistry of the double bond.[41] 3) Ligand coupling on the copper atom between the alkenyl group and X to give the substitution product. Similar mechanism involving the ligand coupling of tricoordinate iodine(III) species has been suggested.[42]
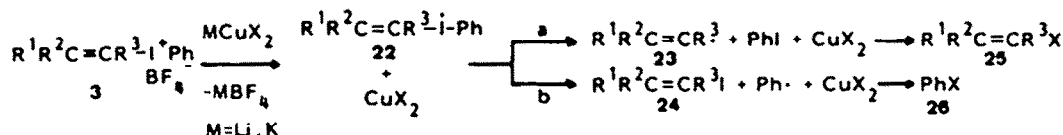
Scheme 5.
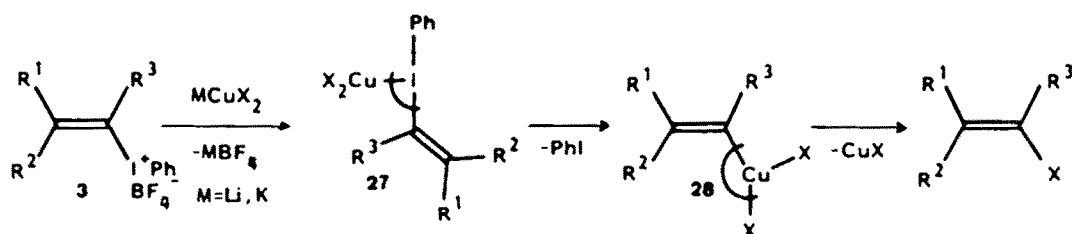
Scheme 6.

Conclusions

We have developed a general method for the synthesis of alkenyl(phenyl)iodonium tetrafluoroborates 3 from vinylsilanes 1 utilizing the Lewis acid-activated iodosylbenzene. X-ray data show that the iodonium salt 3b adopts a distorted trigonal bipyramidal configuration. Vinyliodonium salts 3 are highly effective as the activated species of vinyl iodides and a variety of nucleophiles can be introduced to the double bond of 3, accompanied by the reductive elimination of iodobenzene. Vinylsilanes 1 usually act as vinyl anion equivalent species. Therefore, the reaction described above offers a new methodology for the umpolung of reactivity of vinylsilanes.

EXPERIMENTAL

IR spectra were recorded with JASCO A-202 and JASCO IR-810 spectrophotometers. ^{1}H and ^{13}C NMR spectra were obtained with JEOL JNM-FX 100 and JEOL JNM-GX 400 spectrometers. Chemical shifts are reported relative to internal tetramethyl-silane. MS spectra were determined on a JEOL JMS-DX300 spectrometer. Analytical gas chromatography (GC) was carried out on a Shimazu GC-4CM gas chromatograph with 20% Silicon GE SF-96 on Chromosorb W. Preparative GC was performed on a Varian Aerograph model 920 gas chromatograph with a column of 20% Silicon GE SF-96 on Chromosorb W. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (Merk, Silica gel F-254). Kieselgel 60 (Merk) was used for column chromatography.

General procedure for synthesis of alkenyl(phenyl)iodonium tetrafluoroborates 3.

Method A: Boron trifluoride-diethyl ether (2.5 equiv. with respect to an alkenylsilane 1) was added dropwise to a stirred suspension of 1 and ISB (2.5 equiv. with respect to 1) in dichloromethane under nitrogen. A yellow color was developed. The mixture was stirred under the conditions described in Table 1. A saturated aqueous sodium tetrafluoroborate solution was added and the mixture was stirred vigorously for 0.5 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under aspirator vacuum to give an oil, which was washed several times with hexane and/or diethyl ehter by decantation. Purification of 3 was accomplished by repeated solution of the salt in dichloromethane or ethyl acetate followed by slow precipitation with hexane or diethyl ether.

Method B: A solution of triethyloxonium tetrafluoroborate (2.5 equiv. with respect to 1) in dichloromethane was added dropwise to a suspension of 1 and ISB (2.5 equiv. with respect to 1) in dichloromethane under nitrogen. A pale yellow color of the suspension turned gradually to a bright yellow color. After being stirred under the conditions described in Table 1, the reaction mixture was quenched by the addition of water, and extracted with dichloromethane. Purification was carried out according to the procedure described in Method A.

Phenyl(1-cyclohexenyl)iodonium tetrafluoroborate (3a). Colorless prisms (recrystallized from dichloromethane-hexane); mp 53 - 54 °C; IR (KBr) 3060, 1635, 1565, 1445, 1070, 745 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 1.50 - 2.00 (4H, m), 2.30 - 2.78 (4H, m), 7.05 (1H, m), 7.40 - 7.80 (3H, m), 7.90 - 8.12 (2H, m); MS (FAB) m/e 285 [(M-BF$_4$)$^+$].

Phenyl(4-*tert*-butyl-1-cyclohexenyl)iodonium tetrafluoroborate (3b). Colorless prisms (recrystallized from dichloromethane-hexane); mp 82 °C; IR (CHCl$_3$) 3030, 1560, 1465, 1050 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.85 (9H, s), 1.37 - 1.55 (2H, m), 1.88 - 1.96 (1H, m), 2.23 - 2.35 (1H, m), 2.43 - 2.54 (1H, m), 2.57 - 2.76 (2H, m), 7.02 - 7.07 (1H, m), 7.50 - 7.56 (2H, m), 7.60 - 7.73 (1H, m), 7.98 - 8.04 (2H, m); ^{13}C NMR (25 MHz, CDCl$_3$) δ 26.9 (q), 31.7 (t), 32.2 (s), 35.2 (t), 41.6 (d), 108.5 (s), 118.5 (s), 132.3 (d), 132.7 (d), 135.6 (d), 147.9 (d); MS (FAB) m/e 341 [(M-BF$_4$)$^+$]. Anal. Calcd for C$_{16}$H$_{22}$BF$_4$I: C, 44.89; H, 5.18; F, 17.75; I, 29.65. Found: C, 44.87; H, 5.22; F, 17.43; I, 29.59.

E-Phenyl(1-decenyl)iodonium tetrafluoroborate (3c). Colorless powder; mp 30 - 31 °C; IR (CHCl$_3$) 3075, 1560, 1465, 1440, 1050, 735 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.87 (3H, t, J=6.8 Hz), 1.17 - 1.33 (10H, m), 1.45 (2H, quint, J=7.3 Hz), 2.34 (2H, dq, J=1.3, 6.8 Hz), 6.78 (1H, dt, J=13.7, 1.2 Hz), 6.98 (1H, dt, J=13.7, 6.8 Hz), 7.46 - 7.55 (2H, m), 7.63 - 7.70 (1H, m), 7.98 - 8.03 (2H, m); ^{13}C NMR (25 MHz, CDCl$_3$) δ 14.1 (q), 22.6 (t), 27.7 (t), 29.0 (t), 29.1 (t), 31.8 (t), 35.3 (t), 96.5 (d), 110.1 (s), 132.4 (d), 132.7 (d), 135.6 (d), 155.9 (d); MS (FAB) m/e

343 [(M-BF$_4$)$^+$]. Anal. Calcd for C$_{16}$H$_{24}$BF$_4$I: C, 44.68; H, 5.62. Found: C, 44.43; H, 5.52.

<u>Z-Phenyl(1-decenyl)iodonium tetrafluoroborate (3d).</u> ^{1}H NMR (400 MHz, CD$_2$Cl$_2$)δ 2.43 (2H, m), 6.70 (1H, dt, J=6.0, 7.0 Hz), 6.90 (1H, d, J=6.0 Hz), 7.49 -7.59 (2H, m), 7.71 (1H, m), 7.92 - 7.98 (1H, m).

<u>E-Phenyl(3-phenyl-1-propenyl)iodonium tetrafluoroborate (3e).</u> Pale yellow oil; IR (film) 3080, 1600, 1560, 1440, 1050, 730 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.62 (2H, d, J=6.8 Hz), 6.81 (1H, dt, J=13.7, 1.5 Hz), 7.05 - 7.15 (3H, m), 7.15 -7.22 (1H, m), 7.22 - 7.29 (2H, m), 7.40 - 7.47 (2H, m), 7.55 - 7.62 (1H, m), 7.92 - 7.97 (2H, m); ^{13}C NMR (25 MHz, CDCl$_3$) δ 40.8 (t), 98.0 (d), 110.1 (s), 127.1 (d), 128.8 (d), 128.9 (d), 132.3 (d), 132.7 (d), 135.4 (d), 136.0 (s), 153.4 (d); MS (FAB) m/e 321 [(M-BF$_4$)$^+$].

<u>E-Phenyl(3-(p-bromophenoxy)-1-propenyl)iodonium tetrafluoroborate (3f).</u> Yellow oil; IR (CHCl$_3$) 3040, 1590, 1490, 1240, 1060, 820 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 4.72 (2H, m), 6.64 - 6.88 (2H, m), 7.04 - 7.72 (7H, m), 7.88 - 8.08 (2H,m); MS (FAB) m/e 415 [(M-BF$_4$)$^+$].

<u>E-Phenyl(4-phenyl-1-butenyl)iodonium tetrafluoroborate (3g).</u> Colorless oil; IR (film) 3070, 1605, 1445, 1070 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 2.44 - 3.0 (4H, m), 6.66 (1H, d, J=14.2 Hz), 6.80 - 7.90 (11H, m); MS (FAB) m/e 335 [(M-BF$_4$)$^+$].

<u>E-Phenyl(4-(p-chlorophenyl)-1-butenyl)iodonium tetrafluoroborate (3h).</u> Colorless needles (recrystallized from dichloromethane-diethyl ether); mp 45 - 46 °C; IR (CHCl$_3$) 3040, 1600, 1570, 1490, 1060 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.65 (2H, q, J= 7.3 Hz), 2.78 (2H, t, J=7.3 Hz), 6.71 (1H, dt, J=13.7, 1.2 Hz), 6.96 (1H, dt, J=13.7, 7.3 Hz), 7.02 - 7.05 (2H, m), 7.17 - 7.22 (2H, m), 7.44 - 7.50 (2H, m), 7.63 - 7.68 (1H, m), 7.83 - 7.88 (2H, m); MS (FAB) m/e 369 [(M-BF$_4$)$^+$].

<u>E-Phenyl(2-phenylvinyl)iodonium tetrafluoroborate (3i).</u> Colorless powder; mp 98 - 99 °C; IR (CHCl$_3$) 3050, 1560, 1465, 1440, 1050 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 - 7.39 (3H, m), 7.40 - 7.46 (4H, m), 7.48 (1H, d, J=14.2 Hz), 7.59 (1H, t, J=2.7 Hz), 7.79 (1H, d, J=14.2 Hz), 8.01 - 8.07 (2H, m); ^{13}C NMR (25 MHz, CDCl$_3$)δ 96.0 (d), 110.5 (s), 129.1 (d), 131.3 (d), 132.3 (d), 132.7 (d), 134.1 (s), 135.7 (d), 151.6 (d); MS (FAB) m/e 307 [(M-BF$_4$)$^+$]. Anal. Calcd for C$_{14}$H$_{12}$BF$_4$I: C, 42.68; H, 3.07; F, 19.29; I, 32.21. Found: C, 42.72; H, 3.15; F, 19.20; I, 31.93.

<u>E-Phenyl(3-cyclohexyl-2-methyl-1-propenyl)iodonium tetrafluoroborate (3j).</u> Colorless prisms (recrystallized from ethyl acetate-diethyl ether); mp 71 - 72 °C; IR (KBr) 3030, 1610, 1565, 1440, 1080, 735 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.8 - 2.0 (11H, m), 2.18 (3H, s), 2.38 (2H, d, J=6.8 Hz), 6.61 (1H, s), 7.30 - 8.04 (5H, m); MS (FAB) m/e 341 [(M-BF$_4$)$^+$].

<u>E-Phenyl(2-methyl-4-phenyl-1-butenyl)iodonium tetrafluoroborate (3k).</u> Pale orange plates (recrystallized from dichloromethane-hexane); mp 78 - 80 °C; IR (KBr) 3050, 1620, 1440, 1260, 1080, 740 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.20 (3H, d, J=1.0 Hz), 2.80 - 2.90 (4H, m), 6.58 (1H, q, J=1.0 Hz), 7.08 - 7.13 (2H, m), 7.16 - 7.27 (3H, m), 7.39 - 7.45 (2H, m), 7.56 - 7.62 (1H, m), 7.67 - 7.73 (2H, m); MS (FAB) m/e 349 [(M-BF$_4$)$^+$].

<u>Z- and E-Phenyl(2-methyl-4-phenyl-1-butenyl)iodonium tetrafluoroborate (3K).</u> A mixture of Z- and E-3k in a ratio 90:10; Pale reddish oil; IR (film) 3080, 1600, 1560, 1440, 1060, 735 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.17 (0.3H, d, J=1.0 Hz, E), 2.23 (2.7H, d, J=1.0 Hz, Z), 2.75 - 2.88 (4H), 6.60 (0.1H, q, J=1.0 Hz, E), 6.61 (0.9H, q, J=1.0 Hz, Z), 7.07 - 7.74 (10H); MS (FAB) m/e 349 [(M-BF$_4$)$^+$].

<u>Reaction of phenyl(trimethyl)silane with ISB.</u> Treatment of phenyl(trimethyl)-silane (2.0 g, 13.3 mmol) with ISB (4.68 g, 21.3 mmol) and BF$_3$-Et$_2$O (3.02 g, 21.3 mmol) in dichloromethane at room temperature for 21 h, followed by the quenching of the reaction mixture with a saturated aqueous sodium tetrafluoroborate

solution, gave diphenyliodonium tetrafluoroborate (5)[17] (3.65 g, 75%).

Reaction of the vinylsilane 6 with ISB. Reaction of 54.4 mg (0.198 mmol) of 6 (Method A, 0 °C, 20 min) gave a mixture of products (70.7 mg, 82%). Analysis by ^{1}H NMR spectroscopy indicated that this is a mixture of 3c and 5 in a ratio 93:7.

Reaction of the vinylsilane 7 with ISB. Reaction of 106 mg (0.318 mmol) of 7 (Method A, 0 °C, 10 min) gave 5 (79.2 mg, 68%).

Reaction of the vinylsilane 8 with ISB. Reaction of 42.5 mg (0.16 mmol) of 8 (Method A, 0 °C, 12 h) gave a mixture of 9 and 10 (57.9 mg, 65%) in a ratio 64:36. Colorless powder; IR (KBr) 3050, 1590, 1470, 1230, 1070, 870, 745 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.09 (s, 9), 0.10 (s, 10), 3.87, 3.91, 3.94 (each s), 4.63 (d, J=3.9 Hz, 10), 4.66 (d, J=4.4 Hz, 9), 5.98 (d, J=18.8 Hz, 9), 6.07 (dt, J=18.8, 4.4 Hz, 9), 6.09 (d, J=19.0 Hz, 10), 6.17 (dt, J=19.0, 4.0 Hz, 10), 6.18 (d, J=2.4 Hz, 9), 6.25 (s, 10), 6.26 (d, J=2.4 Hz, 9), 7.36 - 7.44 (m), 7.55 (t, J=7.6 Hz), 7.80 - 7.90 (m); MS (FAB) m/e 469 [(M-BF$_4$)$^+$].

Substitution reaction of 3b.

Reaction with butyllithium. To a solution of 3b (60 mg, 0.14 mmol) in tetrahydrofuran (2 ml) was added dropwise a hexane solution of butyllithium (1.6 M solution, 0.088 ml, 0.14 mmol) at -78 °C in nitrogen. After being stirred for 3 h at -78 °C, the mixture was quenched with water. Analytical GC showed the formation of 12 (R = Bu, 0.2%),[43] 17 (X = I, 25%), 4-*tert*-butylcyclohexanone (17%), and iodobenzene (40%).

Methylation with lithium dimethylcuprate. A solution of lithium dimethyl-cuprate was prepared by adding 0.94 ml (1.4 mmol) of 1.5 M methyllithium in diethyl ether to a stirred slurry of CuI (133 mg, 0.70 mmol) in 5 ml of tetrahydrofuran at -20 °C in nitrogen. The iodonium salt 3b (40 mg, 0.093 mmol) in 1 ml of tetrahydrofuran was added at -78 °C and the reaction mixture was stirred for 4 h at -78 °C. The mixture was quenched with water. Analysis by GC indicated a 73% yield of 12 (R = Me)[43] and a 79% yield of iodobenzene. A pure sample of 12 (R = Me) was obtained by preparative GC: IR (CHCl$_3$) 3025, 2930, 1460 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.84 (9H, s), 1.0 - 2.2 (7H), 1.62 (3H, s), 5.35 (1H, m); MS (electron impact) m/e 152 (M$^+$), 137, 95, 57. High resolution MS: Found 152.1586. Calcd for C$_{11}$H$_{20}$ (M$^+$) 152.1565.

Butylation with lithium dibutylcuprate. The iodonium salt 3b (40 mg, 0.093 mmol) was treated with lithium dibutylcuprate (0.7 mmol)[44] in diethyl ether at -78 °C for 3 h. Analytical GC showed the formation of 12 (R = Bu, 84%) and iodobenzene (62%). A pure sample of 12 (R = Bu) was obtained by preparative GC: IR (CHCl$_3$) 2950, 1465, 905 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.86 (9H, s), 0.89 (3H, t, J=7.3 Hz), 1.05 - 2.05 (13H), 5.38 (1H, m); MS (electron impact) m/e 194 (M$^+$), 179, 137, 81. High resolution MS: Found 194.2026. Calcd for C$_{14}$H$_{26}$ (M$^+$) 194.2033.

Phenylation with lithium diphenylcuprate. The iodonium salt 3b (40 mg, 0.093 mmol) was treated with lithium diphenylcuprate (0.7 mmol)[45] in tetrahydrofuran at -30 °C for 5 h. preparative TLC (pentane) afforded the olefin 12 (R = Ph, 18 mg, 90%).[43] IR (CHCl$_3$) 1645, 1600, 1500, 1365, 910, 695 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.89 (9H, s), 1.1 - 2.5 (7H), 5.98 - 6.14 (1H, m), 7.0 - 7.4 (5H, m); MS (electron impact) m/e 214 (M$^+$), 157, 143, 130. High resolution MS: Found 214.1721. Calcd for C$_{16}$H$_{22}$ (M$^+$) 214.1721.

Synthesis of the unsaturated nitrile 13. To a solution of 3b (30 mg, 0.07 mmol) in dimethylformamide (4ml) was added KCu(CN)$_2$ at room temperature in nitrogen. After being stirred for 12 h, the mixture was poured into water, and extracted with diethyl ether. After the usual work-up, preparative TLC [hexane-ethyl acetate (9:1)] gave the nitrile 13 (10.5 mg, 92%). The structure was confirmed by comparison of the product with an authentic sample prepared from

4-*tert*-butylcyclohexanone.[46]

Synthesis of the 1,3-diketone 14. A solution of 3b (218 mg, 0.51 mmol) in tetrahydrofuran (5 ml) was added to a suspension of potassium enolate of 2-hexyl-1,3-indanedione (0.42 mmol) in tetrahydrofuran (5 ml) at room temperature in nitrogen and the mixture was stirred for 30 min. The reaction mixture was poured into water and extracted with diethyl ether. A usual work-up gave an oil, which was chromatographed on a column of silica gel using hexane-ethyl acetate (9:1) to give 14 (100 mg, 64%). IR (CHCl$_3$) 1745, 1705, 1600, 1250 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.70 - 2.32 (29H), 5.52 - 5.68 (1H, m), 7.78 - 8.04 (4H, m); MS (electron impact) m/e 366 (M$^+$), 338, 295, 281, 231. High resolution MS: Found 366.2597. Calcd for C$_{25}$H$_{34}$O$_2$ (M$^+$) 366.2559.

Synthesis of the α-nitro olefin 15. A mixture of 3b (30 mg, 0.07 mmol), CuSO$_4$ (22 mg, 0.14 mmol), and NaNO$_2$ (48 mg, 0.7 mmol) in dimethylformamide (2 ml) and water (2 ml) was stirred at room temperature for 28 h in nitrogen. The α-nitro olefin 15 (7 mg, 55%) was isolated by preparative TLC [hexane-ethyl acetate (9:1)]. IR (CHCl$_3$) 1515, 1335 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.92 (9H, s), 1.10 - 2.95 (7H, m), 7.16 - 7.32 (1H, m); MS (electron impact) m/e 183 (M$^+$), 127, 57. High resolution MS: Found 183.1244. Calcd for C$_{10}$H$_{17}$NO$_2$ (M$^+$) 183.1259.

Synthesis of the vinyl sulfide 16. A solution of 3b (43 mg, 0.1 mmol) in dioxane (2 ml) was added to sodium thiophenoxide (0.2 mmol) at room temperature in nitrogen. After being stirred for 30 min, the mixture was poured into water, and extracted with diethyl ether. Preparative TLC [hexane-ethyl acetate (9:1)] afforded the sulfide 16 (20 mg, 81%). ^{1}H NMR (CDCl$_3$) δ 0.86 (9H, s), 1.0 - 2.3 (7H), 5.77 - 6.0 (1H, m), 6.90 - 7.23 (5H, m); MS (electron impact) m/e 246 (M$^+$), 189, 162. High resolution MS: Found 246.1433. Calcd for C$_{16}$H$_{22}$S (M$^+$) 246.1142.

Synthesis of the vinyl chloride 17 (X = Cl). A mixture of CuCl (50 mg, 0.5 mmol) and KCl (37 mg, 0.5 mmol) in dimethylformamide (1 ml) was stirred at room temperature for 1 h in the dark. The mixture was added to a solution of 3b (22 mg, 0.05 mmol) in dimethylformamide (1 ml). After being stirred at room temperature for 12 h, the reaction mixture was quenched with water and extracted with diethyl ether. A usual work-up gave an oil, which was purified by preparative TLC (hexane) to give the chloride 17 (X = Cl, 8 mg, 93%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.87 (9H, s), 1.23, - 1.40 (2H, m), 1.81 - 1.92 (2H, m), 2.07 - 2.15 (1H, m), 2.25 - 2.43 (2H, m), 5.76 - 5.81 (1H, m); MS (electron impact) m/e 172 (M$^+$), 116, 69, 57. High resolution MS: Found 172.0999. Calcd for C$_{10}$H$_{17}$Cl (M$^+$) 172.1018.

Synthesis of the vinyl bromide 17 (X = Br). The iodonium salt 3b (22 mg, 0.05 mmol) was converted to the bromide 17 (X = Br, 7.5 mg, 69%) using CuBr (72 mg, 0.5 mmol) and KBr (60 mg, 0.5 mmol) according to the procedure for the synthesis of 17 (X = Cl). ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.84 (9H, s), 1.10 - 2.53 (7H), 5.90 - 6.06 (1H, m); MS (electron impact) m/e 216 (M$^+$), 160, 137, 57. High resolution MS: Found 216.0485. Calcd for C$_{10}$H$_{17}$Br (M$^+$) 216.0514.

Synthesis of the vinyl iodide 17 (X = I). The iodonium salt 3b (30 mg, 0.07 mmol) was treated with a mixture of CuI (133 mg, 0.7 mmol) and KI (116 mg, 0.7 mmol) in dimethylformamide (4 ml) at room temperature for 1 h. Analytical GC showed the formation of 17 (X = I) in quantitative yield. A pure sample of 17 (X = I) was obtained by preparative GC. ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.85 (9H, s), 1.20 - 2.13 (5H, m), 2.42 - 2.68 (2H, m), 6.20 - 6.38 (1H, m); MS (electron impact) m/e 264 (M$^+$), 57. Reduction of 3b (58 mg, 0.14 mmol) with lithium aluminum hydride (5 mg, 0.14 mmol) in tetrahydrofuran (3 ml) at room temperature gave 17 (X = I, 11 mg, 31%). Irradiation of a solution of 3b in dichloromethane at room temperature for 2 h using a high-pressure mercury lamp also produced the iodide 17 (X = I, 32%).

Palladium-catalyzed methoxycarbonylation of 3b. A mixture of 3b (22 mg, 0.05 mmol), Pd(OAc)$_2$ (0.2 mg, 0.001 mmol), and tributylamine (28 mg, 0.15 mmol) in methanol (1 ml) was stirred at room temperature for 2 h under carbon monoxide (1 atm of pressure). After the evaporation of the solvent under reduced pressure, the reaction mixture was dissolved in ether and washed with 5% hydrochloric acid solution and brine. After the usual work-up, silica gel column chromatography using dichloromethane afforded the unsaturated ester 18 (8.2 mg, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.88 (9H, s), 1.13 (1H, dq, J=4.9, 12.7 Hz), 1.22 -1.32 (1H, m), 1.87 - 1.99 (2H,m), 2.06 - 2.29 (2H, m), 2.46 - 2.55 (1H, m), 3.73 (3H, s), 6.96 - 7.01 (1H, m); MS (electron impact) m/e 196 (M$^+$), 140, 57. High resolution MS: Found 196.1456. Calcd for C$_{12}$H$_{20}$O$_2$ (M$^+$) 196.1463.

Phenylation of the iodonium salt 3k. A stereoisomeric mixture of 3k (E:Z = 97:3, 43 mg, 0.1 mmol) was treated with lithium diphenylcuprate (0.75 mmol) in tetrahydrofuran at -30 °C for 4 h. Preparative TLC (hexane) gave a mixture of E- and Z-19 (18.1 mg, 82%) in a ratio 96:4. On the other hand, a mixture of 3k (E:Z = 12:88) afforded an 82% yield of 19 (E:Z = 12:88). E-19: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.90 (3H, d, J=1.0 Hz), 2.46 (2H, m), 2.83 (2H, m), 6.26 (1H, br s), 7.10 - 7.33 (10H, m); MS (electron impact) m/e 222 (M$^+$), 204, 131, 91. High resolution MS: Found 222.1384. Calcd for C$_{17}$H$_{18}$ (M$^+$) 222.1408. Z-19: IR (CHCl$_3$) 3050, 1645, 1600, 1500, 905, 690 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.94 (3H, d, J=1.5 Hz), 2.53 (2H, m), 2.79 (2H, m), 6.32 (1H, br s), 7.10 - 7.32 (10H, m); MS (electron impact) m/e 222 (M$^+$), 131, 91. High resolution MS: Found 222.1415. Calcd for C$_{17}$H$_{18}$ (M$^+$) 222.1408. A 15% NOE of the vinylic proton of Z- 19 was observed on irradiation of the protons of methyl group.

Phenylation of the iodonium salt 3c. The iodonium salt 3c (57 mg, 0.13 mmol) was treated with lithium diphenylcuprate (0.99 mmol) in tetrahydrofuran at -40 °C for 3.5 h. Analytical GC indicated a 7% yield of 1-decyne. Preparative TLC (hexane) afforded the olefin 20 (21 mg, 72%). 20: IR (CHCl$_3$) 3050, 1640, 1595, 1455, 960, 685 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.88 (3H, t, J=6.8 Hz), 1.20 - 1.53 (12H, m), 2.16 - 2.24 (2H, m), 6.22 (1H, dt, J=16.1, 6.8 Hz), 6.37 (1H, d, J=16.1 Hz), 7.15 - 7.37 (5H, m); MS (electron impact) m/e 216 (M$^+$), 131, 105, 77. High resolution MS: 216.1888. Calcd for C$_{16}$H$_{24}$ (M$^+$) 216.1878. A 10% NOE of the α-vinylic proton of 20 was observed on irradiation of the allylic protons.

Palladium-catalyzed methoxycarbonylation of 3k. A solution of 3k (E:Z = 9:91, 103 mg, 0.24 mmol) in methanol (4 ml) was added to a mixture of Pd(OAc)$_2$ (5.3 mg, 0.024 mmol) and tributylamine (131 mg, 0.71 mmol) in methanol (3 ml) under carbon monoxide (1 atm of pressure). The reaction mixture was stirred at room temperature for 2 h. After the removal of the solvent under reduced pressure, the reaction mixture was dissolved in diethyl ether and washed with 5% hydrochloric acid solution and brine. The usual work-up gave an oil, which was purified by preparative TLC [hexane-ethyl acetate (95:5)] to give the esters E-21 (3.4 mg, 7%) and Z-21 (28.3 mg, 59%). E-21: IR (CHCl$_3$) 3020, 1705, 1640, 1145 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.21 (3H, d, J=1.0 Hz), 2.45 (2H, m), 2.79 (2H, m), 3.68 (3H, s), 5.69 (1H, m), 7.13 - 7.32 (5H, m); MS (electron impact) m/e 204 (M$^+$), 172, 144, 91. High resolution MS: Found 204.1190. Calcd for C$_{13}$H$_{16}$O$_2$ (M$^+$) 204.1151. An 11% NOE of the vinylic proton of E-21 was observed on irradiation of the allylic methylene protons. Z-21: IR (CHCl$_3$) 3020, 1705, 1645, 1160 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.89 (3H, d, J=1.5 Hz), 2.78 (2H, m), 2.91 (2H, m), 3.68 (3H, s), 5.70 (1H, m), 7.16 - 7.32 (5H, m); MS (electron impact) m/e 204 (M$^+$), 144, 91. High resolution MS: Found 204.1158. Calcd for C$_{13}$H$_{16}$O$_2$ (M$^+$) 204.1151. A 12% NOE of the vinylic proton of Z-21 was observed on irradiation of the protons of β-methyl group.

<u>X-ray diffraction analysis of 3b.</u> Crystal data: $C_{16}H_{22}BF_4I$, $\underline{m}.\underline{w}.$ = 428.1, triclinic, space group $\overline{P1}$, crystal size 0.2x0.2x0.2 mm, μ(Mo) = 1.8 mm^{-1}, $\underline{a}$ = 11.348(5), $\underline{b}$ = 12.919(6), $\underline{c}$ = 6.587(2) Å, α = 100.29(3), β = 98.02(3), γ = 101.65(4)°, $\underline{Z}$ = 2, $\underline{V}$ = 915.1(7) Å^3, $\underline{D}_c$ = 1.554 g/cm^3. Intensity data of 3185 unique reflections with $2\theta \leq 50°$ were collected on a Rigaku diffractometer using graphite monochromated Mo $\underline{K\alpha}$ radiation.

The structure was solved by a conventional heavy-atom method. A difference electron density map suggested that the 4-<i>tert</i>-butylcyclohexene ring was disordered at the two locations [(I) and (II)] related, approximately, by a two-fold axis imagined to lie along the Cl-C4 direction: the ring of (I) consists of Cl~C10 and that of (II) consists of Cl, C2, C103, C4, C105, C6, C7, and C108~C110 (the atom-numbering system shown in Figure 1). No hydrogen atoms were located. The positional parameters of the non-hydrogen atoms and the anisotropic thermal parameters of the atoms excluding those of (I) and (II) for which individual isotropic temperature factors were used were refined by a block-diagonal least-squares method. The degree of occupancy of (I) was estimated to be about 60%. Final values of $\underline{R}$, $\underline{R}_w$, and $\underline{S}$ were respectively 0.065, 0.092, and 1.069 for 2540 observed reflections with $|F_o|>2\sigma(F_o)$.

In Figure 1, a bimolecular unit consisting of two molecules related by an inversion center in the crystal is shown. Symmetry related atoms in one of the pair are primed in the other. Although the structure of 4-<i>tert</i>-butylcyclohexene should be shown as a superposition of (I) and (II), (I) and (II) are separately drawn for clarity. The cyclohexene rings adopt a distorted half-chair form, in which the double bond is assumed to locate between Cl and C2 for (I) and between Cl and C6 for (II) based on consideration of the ring conformation. Bond lengths and bond angles are not resonable due to the disordered structure of the ring.

<u>Supplementary material available:</u> Atomic coordinates for <u>3b</u> has been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

REFERENCES AND NOTES

(1) For reviews, see: (a) Chan, T. H.; Fleming, I. Synthesis <u>1979</u>, 761. (b) Ager, D. J. Chem. Soc. Rev. <u>1982</u>, 11, 493. (c) Colvin, E. W. Chem. Soc. Rev. <u>1978</u>, 7, 15. (d) Fleming, I. Chem. Soc. Rev. <u>1981</u>, 10, 83. (e) Paquette, L. A. Science, <u>1982</u>, 217, 793. (f) Fleming, I. Comprehensive Organic Chemistry; Pergamon Press: Oxford, 1979, Vol. 3, Chapter 18. (g) Colvin, E. W. Silicon in Organic Synthesis; Butterworths: London, 1981. (h) Weber, W. P. Silicon Reagents for Organic Synthesis; Springer-Verlag: Berlin, 1983.

(2) For reviews of hypervalent organoiodine(III) compounds, see: (a) Sandin, R. B. Chem. Rev. <u>1943</u>, 32, 249. (b) Banks, D. F. Chem. Rev. <u>1966</u>, 66, 243. (c) Varvoglis, A. Chem. Soc. Rev. <u>1981</u>, 10, 377. (d) Umemoto, T. J. Synth. Org. Chem., Jpn. <u>1983</u>, 41, 251. (e) Varvoglis, A. Synthesis <u>1984</u>, 709. (f) Ochiai, M.; Nagao, Y. J. Synth. Org. Chem., Jpn. <u>1986</u>, 44, 660. (g) Moriarty, R. M.; Prakash, O. Acc. Chem. Res. <u>1986</u>, 19, 244. (h) Koser, G. F. The Chemistry of Functional Groups, Supplement D; Wiley: New York, 1983; Chapter 18, 25.

(3) Freidlina, R. Kh.; Brainina, E. M.; Nesmeyanov, A. N. Bull. Acad. Sci. USSR, Div. Chem. Sci. <u>1945</u>, 647. (b) Brainina, E. M.; Freidlina, R. Bull. Acad. Sci. USSR, Div. Chem. Sci. <u>1947</u>, 623. (c) Colichman, E. L.; Matschiner, J.

T. J. Org. Chem. <u>1953</u>, 18, 1124. (d) Beringer, F. M.; Galton, S. A. J. Org. Chem. <u>1965</u>, 30, 1930. (e) Beringer, F. M.; Mathan, R. A. J. Org. Chem. <u>1969</u>, 34, 685. (f) Beringer, F. M.; Nathan, R. A. J. Org. Chem. <u>1970</u>, 35, 2095.

(4)   (a) Nesmeyanov, A. N.; Tolstaya, T. P.; Sokalova, N. F.; Varfolomeeva, V. N.; Petrakov, A. V. Dokl. Akad. Nauk SSSR <u>1971</u>, 198, 115. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V. Dokl. Akad. Nauk SSSR <u>1971</u>, 197, 1337. (c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. Dokl. Akad. Nauk SSSR <u>1977</u>, 235, 591. (d) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. Dokl. Akad. Nauk SSSR <u>1978</u>, 238, 1109.

(5)   (a) Koser, G. F.; Rebrovic, L. J. Org. Chem. <u>1981</u>, 46, 4324. (b) Rebrovic, L.; Koser, G. F. J. Org. Chem. <u>1984</u>, 49, 4700.

(6)   A part of this work has been reported in a preliminary form: Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. Tetrahedron Lett. <u>1985</u>, 26, 2351.

(7)   (a) Schardt, B. C.; Hill, C. L. Inorg. Chem. <u>1983</u>, 22, 1563. (b) Bell, R.; Morgan, K. J. J. Chem. Soc. <u>1960</u>, 1209. (c) Siebert, H.; Handrich, M. Z. Anorg. Allg. Chem. <u>1976</u>, 426, 173.

(8)   (a) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. J. Chem. Soc., Chem. Commun. <u>1982</u>, 1108. (b) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. Tetrahedron Lett. <u>1983</u>, 24, 777. (c) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. Chem. Pharm. Bull. <u>1985</u>, 33, 41. (d) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. Chem. Pharm. Bull. <u>1985</u>, 33, 989.

(9)   The formation of boron trifluoride-activated ISB $C_6H_5I^{\delta+}-OBF_3^{\delta-}$ has not yet been firmly established. The posibility that the reaction proceeds on the ISB polymer surface activated by coordination of boron trifluoride to the oxygen atom can not be ruled out.

(10) (a) Moriarty, R. M.; Prakash, O.; Duncan, M. P. J. Chem. Soc., Chem. Commun. <u>1985</u>, 420. (b) Moriarty, R. M.; Prakash, O.; Duncan, M. P. Synthesis, <u>1985</u>, 943.   (c) Moriarty, R. M.; Prakash, O.; Duncan, M. P, Vaid, R. K. J. Org. Chem. <u>1987</u>, 52, 150. (d) Moriarty, R. M.; Prakash, O.; Duncan, M. P. J. Chem. Soc. Perkin Trans. I <u>1987</u>, 559.

(11) Zefirov, N. S.; Zhadankin, V. V.; Dankov, Y. V.; Sorokin, V. D.; Semerikov, V. N.; Kozmin, A. S.; Caple, R.; Berglund, B. A. Tetrahedron Lett. <u>1986</u>, 27, 3971.

(12) For the synthesis of vinyliodonium tetrafluoroborates <u>3</u>, the use of sodium tetrafluoroborate is not necessarily required. Thus, the reaction of <u>1b</u> with ISB (2.5 equiv.) and BF_3-Et_2O (2.5 equiv.) afforded directly the iodonium tetrafluoroborate <u>3b</u> in 79 % yield, without treatment of the reaction mixture with sodium tetrafluoroborate. The BF_4^- anion of <u>3b</u> may be produced during the reaction from BF_3. The similar finding has been reported in the synthesis of α-methoxyalkylphosphonium tetrafluoroborates by Oshima and Utimoto.[13]

(13) Tuckmantel, W.; Oshıma, K.; Utimoto, K. Tetrahedron Lett. <u>1986</u>, 27, 5617.

(14) β-Elimination of vinyliodonium salts with bases yielding alkynes has been reported.[4c,d]

(15) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. J. Chem. Soc., Chem. Commun. <u>1985</u>, 697.

(16) (a) Cristol, S. J.; Begoon, A.; Norris, W. P.; Ramey, P. S. J. Am. Chem. Soc. <u>1954</u>, 76, 4558. (b) Staley, S. W.; Doherty, R. F. J. Chem. Soc., Chem. Commun. <u>1969</u>, 288. (c) Cristol, S. J.; Whittemore, C. A. J. Org. Chem. <u>1969</u>, 34, 705.

(17) Ptitsyna, O. A.; Gurskii, M. E.; Reutov, O. A. J. Org. Chem. USSR 1974, 10, 2262.

(18) Koser, G. F.; Wettach, R. H.; Smith, C. S. J. Org. Chem. 1980, 45, 1544.

(19) (a) Unger, S. E.; Ryan, T. M.; Dooks, R. G. Anal. Chim. Acta 1980, 118, 169. (b) Ryan, T. M.; Day, R. J.; Cooks, R. G. Anal. Chem. 1980, 52, 2054. (c) Unger, S. E.; Vincze, A.; Cooks, R. G.; Chrisman, R.; Rothman, L. D. Anal. Chem. 1981, 53, 976. (d) McCreary, D. A.; Peake, D. A.; Gross, M. L. Anal. Chem. 1985, 57, 1181. (e) Duffin, K. L.; Busch, K. L. Int. J. Mass Spectrom. Ion Processes 1986, 74, 141.

(20) A good linear correlation between the coupling constant of olefinic protons of vinyl halides E-MeCH $=$ CHX (X = F, Cl, Br, and I) in the ^{1}H NMR spectra[21] and the electronegativity of halogens X[22] was obtained with a correlation coefficient $\gamma = -0.997$.[23] The equation is given by

$$Jtrans = -2.03\ Ex + 19.2$$

where Ex is the electronegativity of halogens. On this basis, the electronegativity of the phenyliodonium group is estimated to be about 2.7.

(21) Brugel, W. Handbook of NMR Spectral Parameters; Heyden: London, 1979; Vol. 2, Chapter 66.

(22) Pauling, L. The Nature of the Chemical Bonding; Cornell University Press: Ithaca, 1960; Chapter 3.

(23) (a) Laszlo, P.; Schleyer, P. R. Bull. Soc. Chim. France 1964, 87. (b) Schaefer, T. Can. J. Chem. 1962, 40, 1.

(24) Prakash, G. K. S.; Bruce, M. R.; Olah, G. A. J. Org. Chem. 1985, 50, 2405.

(25) (a) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. J. Am. Chem. Soc. 1987, 109, 228. (b) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Frenz, B. A. J. Org. Chem., 1976, 41, 3609. (c) Naae, D. G.; Gougoutas, J. Z. J. Org. Chem. 1975, 40, 2129. (d) Archer, E. M.; Schalkwyk, T. G. D. Acta Crysta. 1953, 6, 88. (e) Khotsyanova, T. L. Kristallografiya 1957, 2, 51.

(26) Reference 22, Chapter 7.

(27) Struchkov, Y. T.; Khotsyanova, T. L. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1960, 821.

(28) (a) Alcock, N. W.; Countryman, R. M. J. Chem. Soc. Dalton 1977, 217. (b) Alcock, N. W.; Countryman, R. M. J. Chem. Soc, Dalton 1979, 851. (c) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. J. Chem. Soc. Dalton 1979, 854.

(29) The formation of β-nitrostyrene by the reaction of 31 with aqueous sodium nitrite has been reported.[4a]

(30) For the methoxycarbonylation of diaryliodonium salts catalyzed by palladium species, see: Uchiyama, M.; Suzuki, T.; Yamazaki, Y. Nippon Kagaku Kaishi 1982, 236.

(31) (a) Posner, G. H.; Lu, S.-B. J. Am. Chem. Soc. 1985, 107, 1424. (b) Marino, J. P.; Laborde, E. J. Am. Chem. Soc. 1985, 107, 734. (c) Just, G.; O'Connor, B. Tetrahedron Lett. 1985, 26, 1799. (d) Kawamoto, I.; Muramatsu, S.; Yura, Y. Tetrahedron Lett. 1974, 4223.

(32) (a) Doering, W. E.; Schreiber, K. C. J. Am. Chem. Soc. 1955, 77, 514. (b) Garst, M. E.; Arrhenius, P. J. Org. Chem. 1983, 48, 16.

(33) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.; Fujita, E. J. Am. Chem. Soc. 1986, 108, 8281.

(34) Commercon, A.; Normant, J.; Villieras, J. J. Organometal. Chem. 1975, 93,

415.

(35)   Schoenberg, A.; Bartoletti, I.; Heck, R. F. J. Org. Chem. <u>1974</u>, 39, 3318.

(36)   Treatment of 3c with sodium methoxide in methanol at 0 °C afforded 1-decyne
        in quantitative yield.

(37)   Bachofner, H. E.; Beringer, F. M.; Meites, L. J. Am. Chem. Soc. <u>1958</u>, 80,
        4269.

(38)   The value of ΔH° in the following reaction has been calculated to be 2.4
        kcal/mol.[39]

$$C_6H_5I + H_2C = CH\cdot \longrightarrow C_6H_5\cdot + H_2C = CHI$$

(39)   Golden, D. M.; Benson, S. W. Chem. Rev. <u>1969</u>, 69, 125.

(40)   Stork, G.; Baine, N. H. J. Am. Chem. Soc. <u>1982</u>, 104, 2321.

(41)   (a) Oae, S. Croatica Chem. Acta <u>1986</u>, 59, 129. (b) Oae, S. Phosphorus and
        Sulfur <u>1986</u>, 27, 13.

(42)   (a) Lancer, K. M.; Wiegand, G. H. J. Org. Chem. <u>1976</u>, 41, 3360.   (b)
        Moriarty, R. M.; Ku, Y. Y.; Sultana, M. Tetrahedron Lett. <u>1987</u>, 28, 3071.
        (c) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A.
        G. J. Am. Chem. Soc. <u>1987</u>, 109, 228.

(43)   McMurry, J. E.; Scott, W. J. Tetrahedron Lett. <u>1980</u>, 21, 4313.

(44)   Whitesides, G. M.; Fischer, W. F.; Filippo, J. S.; Bashe, R. W.; House, H.
        O. J. Am. Chem. Soc. <u>1969</u>, 91, 4871.

(45)   Johnson, C. R.; Dutra, G. A. J. Am. Chem. Soc. <u>1973</u>, 95, 7777.

(46)   Oda, M.; Yamamuro, A.; Watabe, T. Chem. Lett. <u>1979</u>, 1427.