52-2; Bz-Phg-Val-OMe, 117370-53-3; PABz-Phg-Val-OMe, 117370-54-4; Z-Gly-Phe-Ala-OMe, 33062-38-3; Z-Gly-D-Phe-Ala-OMe, 117370-55-5; BOC-Gly-Phe-Ala-OMe, 59095-78-2; BOC-Gly-D-Phe-Ala-OMe, 117370-56-6; Fmoc-Gly-Phe-Ala-OMe, 117370-57-7; Fmoc-Gly-D-Phe-Ala-OMe, 117370-58-8; PAZ-Gly-Phe-Ala-OMe, 117370-59-9; PAZ-Gly-D-Phe-Ala-OMe, 117370-60-2; PABz-D-Ala-Ala-OMe, 117370-61-3; Bz-D-Phg-Val-OMe, 117370-62-4; PABz-D-Phg-Val-OMe, 117370-63-5; PABz-D-Val-Phe-OMe, 117370-64-6; PAZ-Gly-Phe-OBu-*t*, 117370-65-7; BOC-Gly-D-Phe-OH, 117370-66-8; Z-Cl, 501-53-1; Fmoc-Cl, 28920-43-6; PAZ-Cl, 55592-99-9; BOC-Gly-D-Phe-OCH$_2$Ph, 104869-66-1; PABz-D-Val-OH, 117370-67-9; PABz-D-Phe-OH, 117370-68-0; PABz-D-Ala-OH, 117370-69-1; Bz-D-Phg-OH, 10419-67-7; Fmoc-Gly-Cl, 103321-49-9; PAZ-Gly-OH, 4596-55-8; H-Phe-OBu-*t*·HCl, 15100-75-1.

Alkynyliodonium Tetrafluoroborates as a Good Michael Acceptor for an Azido Group. A Stereoselective Synthesis of (*Z*)-(β-Azidovinyl)iodonium Salts

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Alkynylphenyliodonium salts **1** are highly reactive and formally tetraphilic (Cα, Cα′, Cβ, and I) toward the attack of nucleophiles.[1] We have reported an efficient cyclopentene annulation utilizing **1** via the tandem Michael–carbene insertion (MCI) reaction. It was suggested that the reaction involved the formation of unstable iodonium ylides **2** by the conjugate addition of soft nucleophiles such as carbanions generated from 1,3-dicarbonyl compounds. Elimination of iodobenzene from **2** is a rapid process under basic conditions and results in formation of alkylidenecarbenes **3**, which undergo intramolecular 1,5-carbon–hydrogen insertion to give cyclopentenes.[2] However, if the unstable ylides **2** react with electrophiles at the Cα atom much faster than the reductive elimination of iodobenzene, the reaction would offer a new route to the synthesis of functionalized vinyliodonium salts **4**. Recently Stang and Kitamura reported the Michael type reaction of (β-phenylethynyl)iodonium tosylate (**1**: R = C$_6$H$_5$, X = OTs) with sodium azide in the presence of triethylsilane as a proton source in dichloromethane, which produces the corresponding (β-azidovinyl)iodonium tosylate. The reaction, however, is strongly dependent upon the nature of R groups and in some cases formation of alkylidenecarbene-derived insertion products results in a major pathway.[3]

Vinyliodonium salts behave similarly to the highly activated species of vinyl iodides because of the high leaving ability of the iodine(III) substituents. They serve as a useful precursor for the synthesis of a variety of functionalized olefins including α-cyano and α-nitro olefins, vinyl sulfides, vinyl halides, and α,β-unsaturated esters and also undergo Friedel–Crafts vinylation of aromatic compounds under mild conditions.[4-6] However, the synthetic method of vinyliodonium salts is very limited.[4,7] We report herein a stereoselective synthesis of (*Z*)-(β-azidovinyl)iodonium salts **5** via the Michael-type addition of an azido group to readily available alkynyliodonium salts **1**.

Scheme I

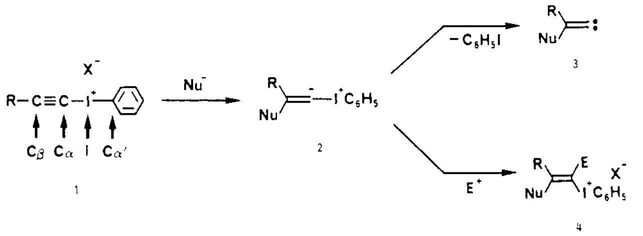
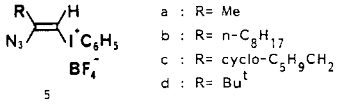


Table I. Synthesis of (*Z*)-(β-Azidovinyl)iodonium Tetrafluoroborates 5

1 (R)[a]	5	yield, %[b]	NOE, %[c]
1a (Me)	**5a**	79	10.3
1b (*n*-C$_8$H$_{17}$)	**5b**	91	7.5
1c (c-C$_5$H$_9$CH$_2$)	**5c**	87	8.9
1d (*t*-Bu)	**5d**	50	
1d[d]	**5d**	72	

[a] X = BF$_4$. [b] Isolated yield. [c] See text. [d] 3 molar equiv of trimethylsilyl azide and water were used.



5

When propynylphenyliodonium tetrafluoroborate (**1a**) was treated with trimethylsilyl azide (1.2 equiv) in dichloromethane in the presence of water (1.2 equiv) at −78 °C to room temperature under an atmosphere of nitrogen, Michael-type addition of an azido group to the electron-deficient β-carbon atom took place and (*Z*)-phenyl(2-azidopropenyl)iodonium tetrafluoroborate (**5a**) was obtained as a pale yellow oil in 79% yield. The results for the synthesis of (*Z*)-(β-azidovinyl)iodonium tetrafluoroborates **5** are shown in Table I. In the case of (β-*tert*-butylethynyl)iodonium tetrafluoroborate (**1d**),[1e] the yield of **5d** (50%) was somewhat lower than those of **5a–c**, most probably because of the large steric requirement of the bulky *tert*-butyl group for the conjugate addition of an azido group. Use of 3 equiv of trimethylsilyl azide and water increased the yield of **5d** up to 72%. Purification of **5** was carried out by decantation (with hexane) and/or recrystallization. Some of the vinyliodonium salts **5** are labile at room temperature and should be kept in a refrigerator.

The addition reactions were completely stereoselective to the limits of NMR detection at 100 MHz. The *Z* stereochemistry of **5a–c** was easily established by observation of a large nuclear Overhauser effect (NOE) enhancement between the vinylic and allylic protons: 7.5–10.3% NOE enhancement of vinylic protons of **5a–c**

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J. Org. Chem. **1988**, *53*, 6145–6147

was observed on irradiation of the allylic protons (Table I). The positive ion FAB mass spectra of **5** showed relatively abundant fragments corresponding to the intact cations. In this reaction the formation of substituted 1,2,3-triazoles was not observed. Thus the 1,3-dipolar cycloaddition of trimethylsilyl azide[8] to carbon–carbon triple bonds of **1** can not compete with the Michael-type additions yielding the (β-azidovinyl)iodonium salts **5**.

The use of water is essential to the success of this addition reaction. In the absence of water the reaction of decynyliodonium tetrafluoroborate (**1b**) with trimethylsilyl azide led to the considerable carbon–iodine bond cleavage, yielding a complex mixture of products: iodobenzene (48%), 1-iododecyne (12%), (β-azidovinyl)iodonium salt (**5b**, 17%), and **1b** (24%). It should be noted that trimethylsilyl azide is sensitive toward moisture.[9] On the basis of these results, the active species of this Michael-type reaction is most probably hydrazoic acid produced by the hydrolysis of trimethylsilyl azide in situ.

Thus, in contrast to vinyliodonium salts, alkynyliodonium salts serve as a useful Michael acceptor toward nitrogen nucleophiles as well as carbon nucleophiles and produce the (β-azidovinyl)iodonium salts in good yields.

Experimental Section

Physical Data. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-202 spectrophotometer. NMR spectra were recorded on either a JEOL JNM-FX 100, Varian VXR 200, or JEOL JNM-GX 400 spectrophotometer. Chemical shifts (^{1}H, ^{13}C) were reported in parts per million (ppm) downfield from internal tetramethylsilane. Mass spectra (MS) were taken on a JEOL JMS-DX 300 spectrometer.

Materials. Alkynyliodonium tetrafluoroborates **1a–c** were prepared from the corresponding alkynyltrimethylsilanes by the reaction with iodosylbenzene and boron trifluoride etherate in dichloromethane in 74–85% yields.[10] (β-*tert*-Butylethynyl)iodonium tetrafluoroborate (**1d**) was obtained by the reaction of (β-*tert*-butylethynyl)borate with iodosylbenzene and boron trifluoride etherate in dichloromethane in 85% yield.[1e] Trimethylsilyl azide was purchased from Tokyo Kasei Kogyo Co. and distilled from calcium hydride under nitrogen.

General Procedure for Synthesis of (β-Azidovinyl)iodonium Tetrafluoroborates 5. To a stirred suspension of alkynyliodonium tetrafluoroborate **1** (0.25 mmol) and water (0.30 mmol) in dichloromethane (5 mL) was added trimethylsilyl azide (0.30 mmol) dropwise at −78 °C under nitrogen. The mixture was stirred at −78 °C for 10 min and then allowed to warm to room temperature. Stirring was continued at room temperature until the reaction was complete to TLC (1.5–2.5 h). The mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under aspirator vacuum to give an oil. Purification of **5** was accomplished by repeated decantation using hexane and/or by recrystallization.

(*Z*)-Phenyl(2-azido-1-propenyl)iodonium tetrafluoroborate (5a): pale yellow oil; IR (film) 3100, 2150, 2125, 1595, 1310, 1070, 1025, 740, and 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2 H), 7.62 (t, $J = 7.3$ Hz, 1 H), 7.48 (m, 2 H), 6.18 (br s, 1 H), 2.42 (d, $J = 1.0$ Hz); ^{13}C NMR (25 MHz, CD_2Cl_2) δ 154.2, 135.2, 132.8, 132.6, 112.9, 77.9, 19.1; MS (FAB), m/z 286 [$(M - BF_4)^+$].

(*Z*)-Phenyl(2-azido-1-decenyl)iodonium tetrafluoroborate (5b): colorless needles (recrystallized from dichloromethane–diethyl ether), mp 60–60.5 °C; IR (KBr) 3050, 2930, 2110, 1595, 1310, 1070, and 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J = 7.4$ Hz, 2 H), 7.61 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.4$ Hz, 2 H), 6.18 (s, 1 H), 2.68 (t, $J = 7.5$ Hz, 2 H), 1.61 (quint, $J = 7.5$ Hz, 2 H), 1.4–1.2 (10 H), 0.87 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 157.4, 135.0, 132.5, 132.3, 111.7, 77.8, 33.4, 31.8, 29.1, 28.8, 27.1, 22.6, 14.0; MS (FAB), m/z 384 [$(M - BF_4)^+$]. Anal. Calcd for $C_{16}H_{23}BF_4IN_3$: C, 40.79; H, 4.92; I, 26.94; N, 8.92. Found: C, 40.60; H, 4.73; I, 26.82; N, 8.94.

(*Z*)-Phenyl(2-azido-3-cyclopentyl-1-propenyl)iodonium tetrafluoroborate (5c): pale yellow oil; IR (film) 3100, 2950, 2875, 2125, 1590, 1445, 1310, 1065, 1030, 740, and 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 2 H), 7.61 (t, $J = 7.5$ Hz, 1 H), 7.47 (t, $J = 7.5$ Hz, 2 H), 6.20 (s, 1 H), 2.69 (d, $J = 7.3$ Hz, 2 H), 2.08 (septet, $J = 7.3$ Hz, 1 H), 1.85–1.1 (8 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.8, 134.8, 132.4, 132.2, 111.7, 77.9, 39.2, 37.7, 32.2, 24.8; MS (FAB), m/z 354 [$(M - BF_4)^+$].

(*Z*)-Phenyl(2-azido-3,3-dimethyl-1-butenyl)iodonium tetrafluoroborate (5d): colorless needles (recrystallized from dichloromethane–hexane), mp 89–91 °C; IR (KBr) 3050, 2990, 2135, 1570, 1320, 1060, and 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2 H), 7.66 (t, $J = 7.5$ Hz, 1 H), 7.51 (t, $J = 7.5$ Hz, 2 H), 6.12 (s, 1 H), 1.38 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.6, 135.1, 132.5, 132.3, 111.0, 81.3, 40.5, 28.0; MS (FAB), m/z 328 [$(M - BF_4)^+$]. Anal. Calcd for $C_{12}H_{15}BF_4IN_3$: C, 34.73; H, 3.64; N, 10.13. Found: C, 34.46; H, 3.71; N, 9.98.

Registry No. **1a**, 105502-68-9; **1b**, 102987-32-6; **1c**, 105502-63-4; **1d**, 115505-36-7; **5a**, 117371-21-8; **5b**, 117371-23-0; **5c**, 117371-25-2; **5d**, 117371-27-4; $MeC{\equiv}CSiMe_3$, 6224-91-5; $C_8H_{17}C{\equiv}CSiMe_3$, 54559-17-0; c-$C_5H_9CH_2C{\equiv}CSiMe_3$, 72097-00-8; iodosylbenzene, 536-80-1; (β-*tert*-butylethynyl)borate, 117407-49-5; trimethylsilyl azide, 4648-54-8.

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Reaction of Pyridine with Phosgene: A Structural Reevaluation

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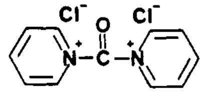
Several papers dealing with the reaction of tertiary amines with phosgene have appeared in the chemical literature.[1,2] Although both the 1:1 and the 1:2 adducts of phosgene with tertiary amines have been reported, no structural data indicative of the 1:2 configuration for the parent pyridine has been published; the originally proposed 1:2 structure (**1**) was deduced by analogy to the commonly observed 1:1 pyridinium salt.[1]



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Results and Discussion

The reaction of excess pyridine with phosgene in an aprotic medium is found to yield a canary-yellow flocculent material. Isolation of this precipitate, followed by drying under high vacuum, yielded a light yellow microcrystalline powder. This material is found to be sparingly soluble in most aprotic organic solvents other than methylene chloride and acetonitrile. The isolated salt is observed to be exceedingly hygroscopic and slightly photosensitive. On the basis of elemental analysis, the stoichiometric composition of this material corresponded to a 2:1 adduct of pyridine with phosgene.[3] Previously, Scholtissek[1] had

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[3] As noted in ref 1, the material occludes excess pyridine. Drying the material under vacuum (1–30 mmHg) for several hours removes the occluded material.

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