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Electrophilic Additions of Iodosylbenzene Activated by Trifluoromethanesulfonic Acid, [PhIO-TfOH], to Alkynes

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Abstract: A reagent [PhIO-TfOH] prepared by mixing iodosylbenzene and triflic acid undergoes electrophilic addition to various alkynes under mild conditions. The addition is a highly stereoselective anti-addition and provides (E)-[β-(trifluoromethanesulfonyloxy)vinyl]iodonium triflates in good to high yields.

Recently much attention has been paid to hypervalent iodine(III) compounds for organic synthesis. Many phenyliodine(III) reagents have been prepared so far and used as the phenyliodinating reagent for synthesis of novel organic iodine(III) compounds.[1] Reaction of the hypervalent iodine(III) reagents with alkynes is a general approach to prepare alkenyl or alkynyliodonium salts. Hydroxy(tosyloxy)iodobenzene [PhI(OH)OTs], Koser's salt, reacts with alkynes to yield a mixture of (E)- and (Z)-[β-(tosyloxy)vinyl](phenyl)iodonium tosylates and/or alkynyl(phenyl)iodonium tosylates.[2] The reactions with alkynylsilanes[3] and alkynylstannanes[4] are proven to be excellent ways to the preparation of alkynyl(phenyl)iodonium salts. On the other hand, triflate chemistry is also attractive and useful in organic synthesis.[5] The combination of a phenyliodine(III) reagent and trifluoromethanesulfonic acid (triflic acid) has been conducted by Zefirov et al.[6] When (diacetoxy)iodobenzene was treated with triflic acid in chloroform μ-oxo-iodine(III) reagent **3** was obtained.[6] This μ-oxo-iodine(III) reagent **3** was also prepared from iodosylbenzene and triflic anhydride.[7] A reagent prepared from iodosylbenzene and triflic acid has never before, to our knowledge, been reported. It is also expected that the reagent [PhIO-TfOH] shows a high electrophilicity similarly to the Zefirov's μ-oxo-iodine(III) reagent. In this paper we report our findings that the reagent [PhIO-TfOH] prepared from PhIO and TfOH adds to alkynes under mild conditions and the addition proceeds stereospecifically to yield only the (E) isomer of the expected adducts.[8]

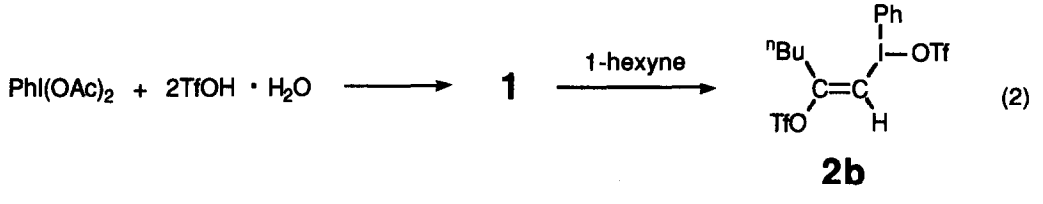
RESULTS AND DISCUSSION

Preparation of [PhIO-TfOH]

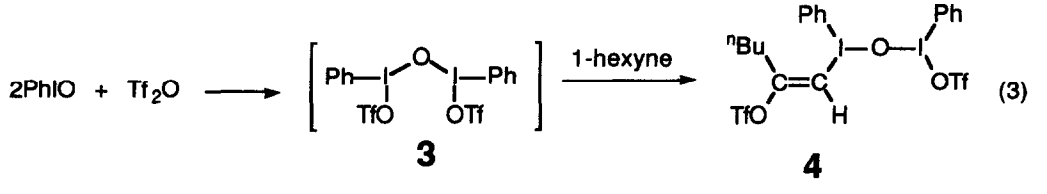
The reagent [PhIO-TfOH] was prepared by mixing iodosylbenzene and triflic acid in dichloromethane at 0 ^{o}C followed by warming up to a room temperature. The resulting, almost homogeneous pale yellow solution was used for the reaction with alkynes. When the solution was stood in a freezer (- 20 ^{o}C) for 24 h, pale yellow crystals were formed. The crystals were highly hygroscopic to melt when allowed to stand in the atmosphere. The ^{1}H and ^{13}C NMR spectra support the structure of PhI(OH)OTf (**1**) and the combustion analysis of the crystals prefers structure **1** to the Zefirov's reagent **3**. The products derived from the reaction with alkynes also support that structure as described later.

1 (1)

This structure is similar to Koser's reagent, hydroxy(tosyloxy)iodobenzene.[2] Accordingly, we conducted two experiments in order to get further the information about the structure. The same procedure as the preparation of Koser's reagent, PhI(OH)OTs,[2] was conducted to prepare the expected reagent [PhI(OH)OTf] and the reagent was allowed to react with 1-hexyne. The obtained crystalline product was the same as [2-(trifluoromethanesulfonyloxy)-1-hexenyl](phenyl)iodonium triflate (**2b**) which was prepared by the reaction of [PhIO-TfOH] with 1-hexyne. However, Zefirov's reagent **3**[7] prepared in situ from iodosylbenzene and triflic anhydride in a 2:1 molar ratio did not yield vinyliodonium triflate **2b** in the reaction with 1-hexyne but afforded the product **4** which still had a μ-oxo-bridged structure.



2b (2)



3 **4** (3)

Reaction with Alkynes

With Terminal Alkynes. A terminal alkyne was reacted with the reagent [PhIO-TfOH] prepared in situ from a 1:1 molar ratio of PhIO and TfOH in dichloromethane. The product was isolated by evaporation of the solvent followed by crystallization with ether-hexane. The isolated white crystalline products showed a single olefinic proton at δ 7.1-7.7 ppm in the ^{1}H NMR, two olefinic carbons at δ 93-97 and 159-163 ppm in the ^{13}C NMR, and an absorption of C=C stretching at 1625-1650 cm^{-1} in the IR spectrum. The combustion analyses (C, H) of the products were satisfied with the calculated values within ± 0.3%. Accordingly, the products were assigned to addition products, i.e., [β-(trifluoromethanesulfonyloxy)vinyl](phenyl)iodonium triflates (**2**). The geometry on the carbon-carbon double bond was determined by the NOE difference spectra of **2a** and **2b**. Although a large NOE enhancement (7-13%) was observed between the allylic and vinylic protons of vinyliodonium salts,[9] no meaning NOE enhancement (< 0.5%) was observed between those protons of **2a** and **2b**, while a small NOE enhancement (1%) was appeared between the allylic and aromatic *ortho* protons. From this experiment we determined the configuration of the vinyl moiety as the (E) isomer.

(4)

2

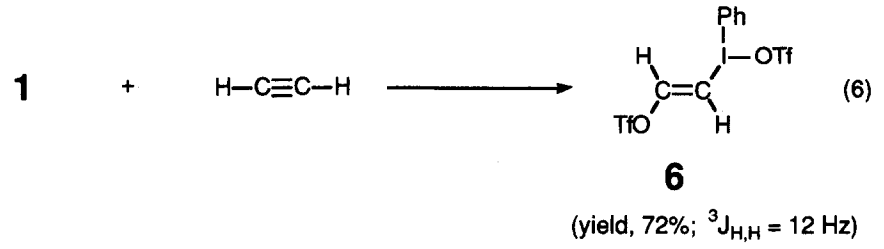
a: R^1 = ^{n}Pr (yield, 87%)
b: R^1 = ^{n}Bu (yield, 100%)
c: R^1 = ^{n}Hex (yield, 100%)
d: R^1 = Ph (62%)

Good to high yields of vinyliodonium triflates **2** were obtained as stable crystals. However, the reaction with *tert*-butylacetylene did not give the expected vinyliodonium triflate but provided *tert*-butylethynyl(phenyl)-iodonium triflate (**5**) in a 42% yield.

(5)

5 (yield, 42%)

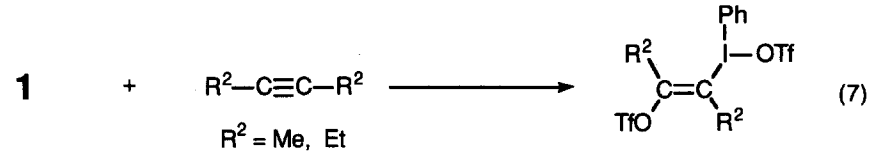
With Parent Acetylene, HC ≡CH. Acetylene gas was introduced into the solution of [PhIO-TfOH] in dichloromethane. An addition product, [β-(trifluoromethanesulfonyloxy)ethenyl](phenyl)iodonium triflate (**6**), was isolated in a 72% yield. The vinylic protons were appeared at δ 8.12 and 7.70 ppm as the AX quartet (J = 12 Hz). Since electronegative substituents diminish the magnitude of J_{trans} and J_{cis} in ethylenic compounds,[10] the value of J = 12 Hz is well in accord with *trans* geometry with respect to the carbon-carbon double bond.



6

(yield, 72%; $^3J_{H,H}$ = 12 Hz)

With Internal Alkynes. Symmetrical alkynes, 2-butyne and 3-hexyne were reacted with [PhIO-TfOH] to give the corresponding [β-(trifluoromethanesulfonyloxy)vinyl](phenyl)iodonium triflates (**7a** and **7b**), respectively, in 80 and 67% yields.



7

a: R^2 = Me (yield, 80%)
b: R^2 = Et (yield, 67%)

Reactivity of [PhIO-TfOH] toward Alkynes

The reagent [PhIO-TfOH] shows a high reactivity in the reaction with aromatic substrates.[11] Similarly, in the electrophilic addition to the carbon-carbon triple bond of alkynes, the reagent [PhIO-TfOH] was highly reactive. The addition reaction went to completion within a few hours at a room temperature and proceeds even at 0 °C. The addition of hypervalent iodine(III) reagents to alkynes has been studied by Koser et al. with hydroxy(tosyloxy)iodobenzene. Koser's reagent requires a refluxing temperature in chloroform for 3 h or 25 °C for 12-48 h to complete the addition reaction.[2] Therefore, this reagent [PhIO-TfOH] is considered to be more reactive than hydroxy(tosyloxy)iodobenzene. This high reactivity is attributed to the well-known nature of triflate ion.[5] Owing to the excellent leaving property of triflate group the iodine atom is considerably ionized and easily adds to the carbon-carbon triple bond of alkynes. However, alkynes with an electron-withdrawing group such as diethyl acetylenedicarboxylate and ethyl propiolate did not undergo the addition to lead vinyliodonium triflates **2**. The addition to the alkyne may produce an open vinyl cation or a bridged iodonium ion. Considering the (E) configuration of the products, the intermediate adduct should be a bridged iodonium structure rather than a open vinyl cation. Ring-opening by triflate ion leads to formation of [β-(trifluoromethanesulfonyloxy)vinyl]-(phenyl)iodonium ion with (E) geometry followed by ligand exchange of hydroxide to triflate ion.Therefore, the reaction of [PhIO-TfOH] with alkynes proceeds with highly stereospecific *anti* addition compared with Koser's reagent which provides a mixture of (E) and (Z) isomers.[2]

In coclusion, the reagent [PhIO-TfOH] prepared readily from iodosylbenzene and triflic acid is proven to be useful for preparation of β-[(trifluoromethanesulfonyl)oxy]vinyliodonium triflates. Due to the high stereoselectivity and polyfunctionality, the β-[(trifluoromethanesulfonyl)oxy]vinyliodonium triflates may be potent of a synthetic utility and be a precursor of alkynyliodonium triflates which are valuable in organic synthesis.[1]

EXPERIMENTAL

General. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained with a HITACHI R-600 (60 MHz), a BRUKER AC-250P (250 MHz), or a JEOL GSX-400 (400 MHz) spectrometer, and ^{13}C NMR spectra with a BRUKER AC-250P (62.9 MHz) or a JEOL GSX-400 (100.5 MHz) spectrometer. Chemical shifts are given in ppm units. IR spectra were recorded with a HITACHI 270-30 spectrometer. Microanalyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Iodosylbenzene was prepared from (diacetoxy)iodobenzene (Aldrich Chemical Co.) according to the reported procedure.[12]

Preparation of Reagent [PhIO-TfOH] (1)

The reagent [PhIO-TfOH] was prepared in situ by the procedure described below and used without the isolation for reaction with alkynes. To a suspension of iodosylbenzene (2.20 g, 10 mmol) in dichloromethane (20 mL) was added at 0 °C triflic acid (0.89 mL, 10 mmol), the mixture was warmed to room temperature and stirred for 2 h. For the reaction, an alkyne was added to the resulting pale yellow solution of [PhIO-TfOH].

In order to confirm the structure of the reagent [PhIO-TfOH], the isolation was attempted. Triflic acid (0.09 mL, 1 mmol) was added to a suspension of iodosylbenzene (229 mg, 1 mmol) in dichloromethane (3 mL) at 0 °C and the mixture was stirred for 1 h. The mixture was stood in a freezer (- 20 °C) for 24 h and the resulting pale yellow crystals were quickly filtered and dried in vacuo to yield 310 mg (84%). When the crystals were exposed to the atmosphere they melted gradually because of their high hygroscopic property. ^{1}H NMR (CD_3CN) δ 7.57-7.63 (m, 2H, ArH), 7.71-7.63 (m, 1H, ArH), 8.22-8.25 (m, 2H, ArH). ^{13}C NMR (CD_3CN) δ 123.21, 132.58, 134.70, 136.39. Anal. Calcd for $C_7H_6F_3IO_4S$: C, 22.72; H, 1.64. Found: C, 22.12; H, 1.65. Zefirov's reagent 3 ($C_{14}H_{10}F_6I_2O_7S_2$) requires C, 23.28; H, 1.40.

General Procedure for Reaction of [PhIO-TfOH] with Alkynes

An alkyne (12 mmol) was added dropwise at 0 °C to the dichloromethane solution of [PhIO-TfOH] prepared from iodosylbenzene (2.20 g, 10 mmol) and triflic acid (0.89 mL, 10 mmol) in dichloromethane (20 mL). The mixture was warmed to room temperature and stirred for 2 h. After filtration of the resulting insoluble materials, the solvent was evaporated to yield an oil or crystals. Ether and hexane were added to crystallize completely and the crystals were filtered, washed with hexane-ether, and dried in vacuo. Further purification for

microanalysis was carried out by recrystallization from dichloromethane and ether.

[2-[(Trifluoromethanesulfonyl)oxy]-1-pentenyl](phenyl)iodonium Trifluoromethanesulfonate (2a): 87% yield; mp 129-132 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7 Hz, 3H, Me), 1.28-1.90 (m, 2H, CH_2), 2.78 (t, J = 7 Hz, 2H, CH_2), 7.10 (s, 1H, =CH), 7.30-7.60 (m, 3H, ArH), 7.84-8.00 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.13, 19.50, 36.43, 93.08, 113.92, 132.24, 132.62, 134.87, 162.28; IR (Nujol) 1640 cm^{-1} (C=C). Anal. Calcd for $C_{13}H_{13}F_6IO_6S_2$: C, 27.38; H, 2.30. Found: C, 27.47; H, 2.29.

[2-[(Trifluoromethanesulfonyl)oxy]-1-hexenyl](phenyl)iodonium Trifluoromethanesulfonate (2b): 100% yield; mp 125-128 °C; ^{1}H NMR (CD_3CN) δ 0.90 (t, J = 6 Hz, 3H, Me), 1.33-1.41 (m, 2H, CH_2), 1.48-1.55 (m, 2H, CH_2), 2.88 (t, J = 6 Hz, 2H, CH_2), 7.35 (s, 1H, =CH), 7.56-7.60 (m, 2H, ArH), 7.73-7.77 (m, 1H, ArH), 8.05-8.07 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.52, 21.99, 27.98, 34.56, 93.05, 114.01, 132.21, 132.57, 134.87, 162.48; IR (Nujol) 1644 cm^{-1} (C=C). Anal. Calcd for $C_{14}H_{15}F_6IO_6S_2$: C, 28.78; H, 2.59. Found: C, 28.75; H, 2.57.

[2-[(Trifluoromethanesulfonyl)oxy]-1-octenyl](phenyl)iodonium Trifluoromethanesulfonate (2c): 100% yield; mp 120-123 °C; ^{1}H NMR ($CDCl_3$) δ 0.7-1.0 (m, 3H, Me), 1.1-1.8 (m, 8H, CH_2), 2.5-3.0 (m, 2H, CH_2), 7.10 (s, 1H, =CH), 7.3-7.7 (m, 3H, ArH), 7.8-8.0 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.90, 22.31, 25.94, 28.49, 31.27, 34.84, 92.83, 114.01, 132.23, 132.56, 134.80, 162.54; IR (Nujol) 1640 cm^{-1} (C=C). Anal. Calcd for $C_{16}H_{19}F_6IO_6S_2$: C, 31.38; H, 3.13. Found: C, 31.29; H, 3.14.

[2-[(Trifluoromethanesulfonyl)oxy]-2-phenylvinyl](phenyl)iodonium Trifluoromethanesulfonate (2d): 53% yield; mp 137-143 °C; ^{1}H NMR (CD_3CN) δ 7.44 (m, 2H, ArH), 7.55-7.61 (m, 4H, ArH), 7.66-7.70 (m, 4H, ArH), 7.69 (s, 1H, =CH); ^{13}C NMR (CD_3CN) δ 96.78, 114.48, 130.36, 130.62, 133.38, 134.23, 136.52, 158.78; IR (Nujol) 1626 cm^{-1} (C=C). Anal. Calcd for $C_{16}H_{11}F_6IO_6S_2$: C, 31.80; H, 1.84. Found: C, 31.73; H, 1.84.

[3-[(Trifluoromethanesulfonyl)oxy]-2-butenyl](phenyl)iodonium Trifluoromethanesulfonate (7a): 80% yield; mp 130-132 °C; ^{1}H NMR (CD_3OD) δ 2.61 (q, J = 1.5 Hz, Me), 2.72 (q, J = 1.5 Hz, Me), 7.60-7.67 (m, ArH), 7.76-7.83 (m, ArH), 8.17-8.23 (m, ArH); ^{13}C NMR (CD_3OD) δ 22.16, 22.81, 114.30, 115.09, 133.50, 134.32, 136.86, 154.14. IR (Nujol) 1674 cm^{-1} (C=C). Anal. Calcd for $C_{12}H_{11}F_6IO_6S_2$: C, 25.91; H, 1.99. Found: C, 25.86; H, 2.03.

[4-[(Trifluoromethanesulfonyl)oxy]-3-hexenyl](phenyl)iodonium Trifluoromethanesulfonate (7b): 67% yield; mp 80-90 °C; ^{1}H NMR ($CDCl_3$) δ 0.9-1.5 (m, 6H, Me), 2.5-3.3 (m, 4H, CH_2), 7.108.1 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 10.78, 13.28, 28.28, 30.22, 112.36, 123.27, 132.23, 132.56, 134.55, 156.77; IR (Nujol) 1652 cm^{-1} (C=C). Anal. Calcd for $C_{14}H_{15}F_6IO_6S_2$: C, 28.78; H, 2.59. Found: C, 28.88; H, 2.68.

[2-[(Trifluoromethanesulfonyl)oxy]vinyl](phenyl)iodonium Trifluoromethanesulfonate (6). A large excess of acetylene gas generated by addition of water to calcium carbide was introduced into the solution of [PhIO-TfOH]. After the workup described in general procedure the product was obtained as crystals in 72% yield: mp 110-112 °C; ^{1}H NMR (CD_3OD) δ 7.57-7.63 (m, 2H, ArH), 7.70 (d, J = 12 Hz, 1H, =CH), 7.74-7.78 (m, 1H, ArH), 8.12 (d, J = 12 Hz, 1H, =CH), 8.15-8.20 (m, 2H, ArH); ^{13}C NMR (CD_3OD) δ 94.75, 115.13, 133.33, 134.11, 136.61, 151.34; IR (Nujol) 1626 cm^{-1} (C=C). Anal. Calcd for $C_{10}H_7F_6IO_6S_2$: C, 22.74; H, 1.34. Found: C, 22.16; H, 1.28.

Reaction of [PhIO-TfOH] with 3,3-Dimethyl-1-butyn

The similar procedure described in general procedure was conducted in the case of 3,3-dimethylbutyne. Workup and crystallization gave white crystals of (3,3-dimethyl-1-butenyl)(phenyl)iodonium trifluoromethanesulfonate (**5**) in 42% yield: mp 140-144 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9H, Me), 7.31-7.61 (m, 3H, ArH), 7.85-8.10 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.13, 29.98, 116.54, 118.94, 132.35, 132.42, 133.67; IR (Nujol) 2148, 2184 cm^{-1} (C≡C). Anal. Cacld for $C_{13}H_{14}F_3IO_3S$: C, 35.96; H, 3.25. Found: C, 36.19; J, 3.33.

Reaction of 1-Hexyne with a Reagent Prepared from (Diacetoxy)iodobenzene and Triflic Acid Monohydrate

To a suspension of (diacetoxy)iodobenzene (0.644 g, 2 mmol) in dichloromethane (10 mL) was added at 0 °C trifluoromethanesulfonic acid (0.35 mL, 4 mmol) and water (0.07 mL, 4 mmol), and the mixture was warmed to room temperature and stirred for 2 h. 1-Hexyne (0.28 mL, 2.4 mmol) was added to the mixture at 0 °C and stirred at room temperature for 2 h. After removal of the insoluble materials, the solvent was evaporated to form crystals. Ether and hexane were added to complete the crystallization. The crystals were filtered, washed with ether-hexane, and dried in vacuo. From analyses by ^{1}H and ^{13}C NMR, the crystals were identified as [2-[(trifluoromethanesufonyl)oxy]-1-hexenyl](phenyl)iodonium trifluoromethanesulfonate (**2b**) (55% yield).

Reaction of Zefirov's Reagent with 1-Hexyne

To a suspension of iodosylbenzene(2,20 g, 10 mmol) in dichloromethane (20 mL) was added dropwise at 0 °C trifluoromethanesulfonic acid anhydride (0.84 mL, 5 mmol) and the mixture was stirred at room temperature for 2 h. 1-Hexyne (1.38 mL, 12 mmol) was added at 0 °C to the mixture and stirred at room temperature for 2 h. After filtration of the insoluble materials, crystals were obtained by evaporation of the solvent. The crystals were filtered, washed with ether-hexane, and dried in vacuo. The crystals were identified as a oxo-bridged iodine compound (**4**) (30% yield): mp 120-130 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6 Hz, 3 H, Me), 1.31-1.36 (m, 2 H, CH_2), 1.47-1.51 (m, 2 H, CH_2), 2.80 (t, J = 6 Hz, 2 H, CH_2), 7.16 (s, 1 H, =CH), 7.42-7.50 (m, 4 H, ArH), 7.58-7.64 (m, 2 H, ArH), 7.97-8.01 (m, 4 H, ArH). ^{13}C NMR (CDC_3) δ 13.52, 21.99, 27.96, 34.55, 92.97, 113.55, 114.03, 132.12, 132.19, 132.41, 132.53, 134.82, 135.28, 162.46; IR (Nujol) 1644 cm^{-1} (C=C). Anal. Calcd for $C_{20}H_{20}F_6I_2O_7S_2$: C, 29.85; H, 2.49. Found: C, 29.98; H, 2.53.

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