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Novel Alkynyl-substituted (*p*-Phenylene)bisiodonium Ditriflates. Preparation and Reaction with Thiocyanate Ion

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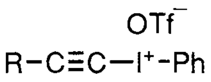
Novel alkynyl(*p*-phenylene)bisiodonium ditriflates were prepared in good to high yields by reaction of trimethylsilylalkynes with PhIO activated with 2 equivalents of triflic acid. Reaction of the alkynylbisiodonium salts with potassium thiocyanate gave alkynyl thiocyanates in high yields and suggested that the alkynylbisiodonium salts serve as an agent for alkynylation of a nucleophilic substrate.

Recently much attention has been paid to hypervalent iodine(III) compounds for organic synthesis.$^{1)}$ Among the synthetically useful organoiodine(III) compounds, alkynyl(phenyl)iodonium salts (**1**) are especially valuable in synthetic utility since they act as Michael acceptors, as synthons for "alkynyl cations", and as 1,3-dipolarophiles.$^{1f, h, k)}$



$$\overset{\mathrm{OTf}^-}{\mathrm{R{-}C{\equiv}C{-}I^+{-}Ph}}$$

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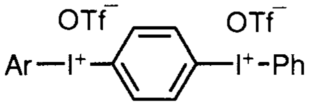

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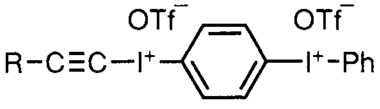

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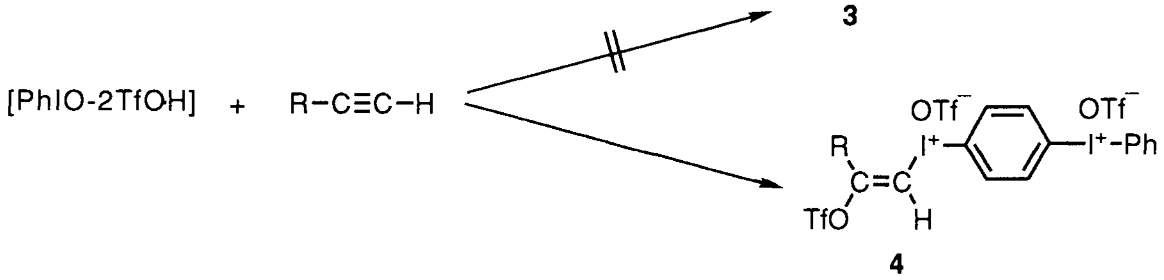
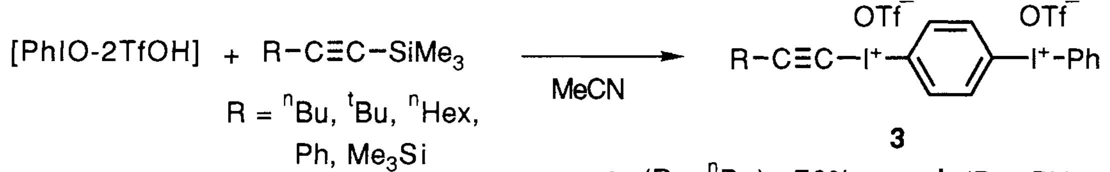
Very recently, we have found that diaryl(*p*-phenylene)bisiodonium ditriflates (**2**) can be prepared by reaction of iodosylbenzene (PhIO) with trifluoromethanesulfonic anhydride followed by treatment with aromatic substrates.$^{2)}$ However, alkynyl(*p*-phenylene)bisiodonium ditriflates (**3**) can not be obtained by this method using terminal alkynes, although alkynyl(phenyl)iodonium tosylates are prepared by using Koser's salt, PhI(OH)OTs.$^{3)}$ Thus, we conducted the preparation of novel alkynyl(*p*-phenylene)bisiodonium ditriflates **3** by reaction of trimethylsilylalkynes with PhIO activated by 2 equivalents of triflic acid and examined the substitution reaction by thiocyanate ion.

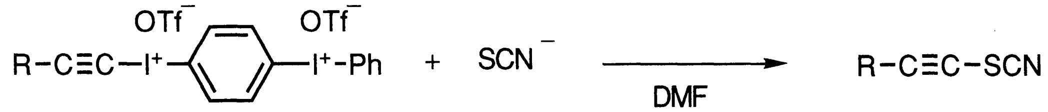


1-Trimethylsilylhexyne was treated with a reagent [PhIO-2TfOH] prepared *in situ* by addition of 2 equivalents of triflic acid to a stirred suspension of PhIO in dichloromethane. But this treatment was found to give a ca 1:1 mixture of desirable hexynyl-substituted bisiodonium ditriflate (**3a**) and addition product, 2-[(trifluoromethylsulfonyl)oxy]vinyl-substituted bisiodonium ditriflate (**4a**). The latter product **4a** has been prepared by reaction of [PhIO-Tf_2O] with 1-hexyne.[2)] Then, we conducted the alkynylation reaction after isolation of the reagent. The reagent [PhIO-2TfOH] was prepared as above and then concentrated in vacuo. Addition of dry diethyl ether to the crude reagent gave pale yellow crystals which were quickly filtered and dried in vacuo. Interaction of the crystalline reagent with 1-trimethylsilylalkynes in acetonitrile at room temperature yielded the desired alkynyl(*p*-phenylene)bisiodonium ditriflates (**3**)[4)] as crystals in good to high yields. The isolated alkynyl bisiodonium ditriflates **3** are stable crystals and have high melting points (decomposition). The ^{1}H NMR shows a characteristic *ortho* aromatic protons to the iodine(III) atom at 8.2-8.5 ppm. The ^{13}C NMR indicates the sp carbons of the triple bond around 25-30 and 110 ppm for alkyl-substituted ditriflates **3a-c**. Typical absorption of the stretching band due to the triple bond appears at 2190 cm^{-1} in the IR spectrum for **3a-c**. Introduction of alkynyl groups in the reagent can be applied successfully to several substituted silylated alkynes (R = *n*-butyl, *t*-butyl, *n*-hexyl, phenyl, and trimethylsilyl). The combustion analysis (C, H) is well in accord with the calculated values within ± 0.4%.



a (R = ^{n}Bu) 76%
b (R = ^{t}Bu) 83%
c (R = ^{n}Hex) 49%
d (R = Ph) 82%
e (R = Me_3Si) 76%

As a preliminary reaction of the alkynyl(*p*-phenylene)bisiodonium ditriflates **3**, the reaction with thiocyanate ion was adopted since good yields of the products were observed in the reactions of alkynyl(phenyl)iodonium tosylates5) and triflates.6) Treatment of alkynyl(*p*-phenylene)bisiodonium ditriflates with potassium thiocyanate (3 equivalents) in DMF gave the corresponding alkynyl thiocyanates **5** in high yields. The spectral data (^{1}H, ^{13}C NMR, and IR) of alkynyl thiocyanates **5** are consistent with the reported ones.6,7) Although there are several possible reaction sites in the alkynyl(*p*-phenylene)bisiodonium ditriflates **3**, the alkynyl group is apparently superior to the other aryl positions in the reaction with thiocyanate ion. The merit of the use of alkynyl(*p*-phenylene)bisiodonium ditriflates **3** is that the pure product (>95%) is obtained only by extraction with ether. In the cases of alkynyl(phenyl)iodonium salts **1** the product mixture usually contains iodobenzene which should be separated by a chromatography or distillation.



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a (R = ^{n}Bu): 94% **c** (R = ^{n}Hex): 97%
b (R = ^{t}Bu): 90% **d** (R = Ph): 87%

In summary, we have found a novel type of (*p*-phenylene)bisiodonium ditriflates **3** which bear a synthetically valuable carbon-carbon triple bond. This simple preparation involves alkynylation of the isolated reagent [PhIO-2TfOH] with silylated alkynes. As well as the known alkynyl(phenyl)iodonium salts **1**,1f,h,k) the alkynyl-substituted (*p*-phenylene)bisiodonium ditriflates **3** serve as the alkynylating agent in the reaction with thiocyanate ion and provide a potent utility for organic synthesis.

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4) **3a:** Mp 200-205 °C (dec); ^{1}H NMR (250 MHz, DMSO-d_6) δ 0.78 (t, J = 7, Me), 1.24-1.30 (m, CH_2), 1.38-1.44 (m, CH_2), 2.58 (t, J = 7, CH_2), 7.54-7.59 (m, ArH), 7.65-7.70 (m, ArH), 8.30-8.40 (m, ArH); ^{13}C NMR (62.9 MHz, MeOH-d_4) δ 13.64, 20.60, 22.72, 24.53, 30.70, 111.66, 116.32, 121.77, 124.26, 133.38, 134.07, 136.89, 138.51, 139.39; IR (Nujol) 2192 cm^{-1} ($C{\equiv}C$). **3b:** Mp 220-223 °C (dec); ^{1}H NMR (250 MHz, DMSO-d_6) δ 1.19 (s, Me), 7.53-7.59 (m, ArH), 7.67-7.73 (m, ArH), 8.28-8.44 (m, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 29.08, 29.28, 29.54, 114.30, 116.89, 120.42, 122.34, 131.84, 132.30, 135.28, 136.91, 137.73; IR (Nujol) 2199, 2164 cm^{-1} ($C{\equiv}C$). **3c:** Mp 198-201 °C (dec); ^{1}H NMR (250 MHz, DMSO-d_6) δ 0.81 (t, J = 7, Me), 1.19-1.25 (m, CH_2), 1.40-1.42 (m, CH_2), 2.58 (t, J = 7, CH_2), 7.51-7.59 (m, ArH), 7.65-7.74 (m, ArH), 8.29-8.43 (m, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 13.76, 19.43, 21.83, 27.08, 27.56, 29.23, 30.41, 107.73, 116.85, 120.42, 122.56, 131.88, 132.37, 135.42, 137.17, 137.81; IR (Nujol) 2192 cm^{-1} ($C{\equiv}C$). **3d:** Mp 188-192 °C (dec); ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.48-7.59 (m, ArH), 7.67-7.73 (m, ArH), 8.30-8.50 (m, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 41.53, 103.44, 116.95, 119.32, 120.63, 122.82, 129.17, 131.48, 132.01, 132.48, 132.73, 135.48, 137.33, 137.97; IR (Nujol) 2172 cm^{-1} ($C{\equiv}C$). **3e:** Mp 218-221 °C (dec); ^{1}H NMR (250 MHz, DMSO-d_6) δ 0.16 (s, Me), 7.52-7.58 (m, ArH), 7.67-7.73 (m, ArH), 8.28-8.31 (m, ArH), 8.37-8.45 (m, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ -1.05, 53.77, 113.99, 116.87, 120.57, 122.45, 131.85, 132.31, 135.30, 137.16, 137.84.

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7) *n*-Octynyl thiocyanate (**5c**): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.90 (t, J = 7, Me), 1.26-1.43 (m, CH_2), 1.49-1.61 (m, CH_2), 2.36 (t, J = 7, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.04, 20.11, 22.52, 27.76, 28.50, 31.23, 52.36, 102.52, 107.33; IR (neat) 2204 ($C{\equiv}C$), 2166 cm^{-1} (SCN).

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