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Alkenyl- and Alkynyl-Substituted (*p*-Phenylene)bisiodonium Ditriflates by Reactions of a (*p*-Phenylene)bisiodine(III) Reagent with Alkynes and 1-Trimethylsilyl-1-alkynes

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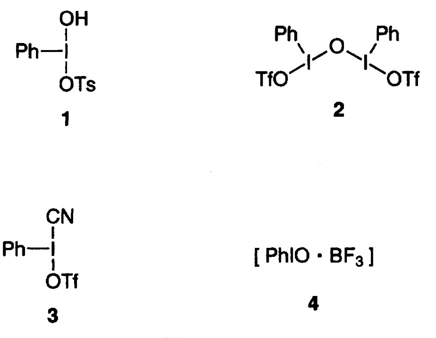
A (*p*-phenylene)bisiodine(III) reagent prepared from iodosylbenzene and trifluoromethanesulfonic acid or the anhydride showed a high reactivity to alkynes. The reaction of alkynes proceeded with stereoselective addition to the carbon–carbon triple bond to give *trans*-alkenyl(*p*-phenylene)bisiodonium ditriflates, whereas the reaction of 1-trimethylsilyl-1-alkynes afforded alkynyl(*p*-phenylene)bisiodonium ditriflates. These reactions indicate that the (*p*-phenylene)bisiodine(III) reagent is accessible for a (*p*-phenylene)bisiodine(III) transfer agent.

Hypervalent iodine(III) reagents are useful in organic synthesis.[1] Much attention has recently been paid to functionalized iodonium salts because of their unique properties and synthetic utility. Alkenyl- and alkynyl(phenyl)iodonium salts are especially valuable in organic synthesis.[2]

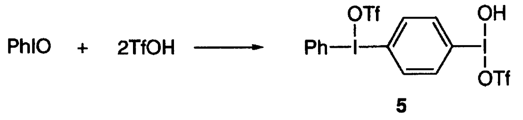
Recently several hypervalent iodine reagents have been developed in order to synthesize these functionalized iodonium salts. [Hydroxy(tosyloxy)iodo]benzene (**1**),[3] μ-oxybis[phenyl(trifluoromethylsulfonyloxy)iodine(III)] (**2**),[4] [cyano(trifluoromethylsulfonyloxy)iodo]benzene (**3**),[5] and iodosylbenzene activated with boron trifluoride (**4**)[6] are conveniently used as phenyliodine(III) transfer reagents (Chart 1).



1 **2** **3** **4**

Chart 1.

We have used trifluoromethanesulfonic acid (triflic acid) (TfOH) in order to increase the reactivity of hypervalent iodine reagents and we have prepared a reagent by reaction of iodosylbenzene (PhIO) or (diacetoxyiodo)benzene [$PhI(OAc)_2$] with TfOH.[7] The reagent [PhIO–TfOH] or [$PhI(OAc)_2$–2TfOH] reacts with aromatic substrates and can be applied for a convenient preparation of diaryliodonium triflates. In the course of the studies on the activation of PhIO by TfOH, we have noticed that PhIO dimerizes with an excess of TfOH to form 1-[hydroxy(trifluoromethylsulfonyloxy)iodo]-4-[phenyl(trifluoromethylsulfonyloxy)iodo]benzene (**5**) (Eq. 1).[8,9] This reagent has two iodine(III) atoms at the para position in the aromatic ring and is conveniently referred to as a (*p*-phenylene)bisiodine(III) reagent. The (*p*-phenylene)bisiodine(III) reagent **5** is readily prepared by reaction of PhIO with double the molar quantity of TfOH and indicates a high reactivity to aromatic substrates, even less reactive halogenated benzenes.[8,9] Reaction of aromatic substrates with (*p*-phenylene)bisiodine(III) reagent **5** provides 1,4-bis(aryliodonio)benzene ditriflates,[8] which show an interesting behavior that double substitution with some nucleophiles takes place, since two phenyliodonio groups are present at the para position of the aromatic ring. Accordingly, (*p*-phenylene)bisiodine(III) reagent **5** is useful as a transfer reagent of (*p*-phenylene)bisiodine(III) group and can be utilized in synthesis of (*p*-phenylene)bisiodonium salts. Thus, we examined reactions of (*p*-phenylene)bisiodine(III) reagent **5** with alkynes and silylalkynes in order to lean the utility of reagent **5** as the (*p*-phenylene)-bisiodine(III) transfer agent.



(1)

Results and Discussion

Reaction of (*p*-Phenylene)bisiodine(III) Reagent 5 with Alkynes. Electrophilic addition of hypervalent iodine reagents to alkynes is a general route to synthesis of alkenyl and alkynyliodonium salts. [Hydroxy(tosyloxy)iodo]benzene **1** adds to alkynes to give (*E*)- and (*Z*)-(phenyl)[β-(tosyloxy)vinyl]iodonium tosylates, while the reactions of **1** with terminal alkynes afford (alkynyl)(phenyl)iodonium tosylates and/or (*E*)- and (*Z*)-(phenyl)[β-(tosyloxy)vinyl]iodonium tosylates.[10] On the other hand, a more reactive reagent [PhIO–TfOH] prepared from PhIO and TfOH undergoes a stereoselective addition to alkynes, even terminal alkynes, to afford (*E*)-(phenyl)[β-(trifluoromethylsulfonyloxy)vinyl]iodonium triflates.[7] But, only in the case of a bulky *t*-butylacetylene, (*t*-butylethynyl)(phenyl)iodonium triflate is obtained. Furthermore, in the reaction with aromatic substrates, (*p*-phenylene)bisiodine(III) reagent **5** indicates a higher reactivity than [PhIO–TfOH] reagent.[8] We also expect that (*p*-phenylene)bisiodine(III) reagent **5** will show a high reactivity to alkynes.

A solution of (*p*-phenylene)bisiodine(III) reagent **5** was prepared by addition of TfOH (2 mol amt.) to a suspension of PhIO in CH_2Cl_2. The reagent solution could be used for the following reaction of alkynes without isolation (Method A in Scheme 1). The (*p*-phenylene)bisiodine(III) reagent **5** can also be prepared by reaction of PhIO with trifluoromethanesulfonic anhydride (Tf_2O).[8] In Method B, (*p*-phenylene)bisiodine(III) reagent **5** was prepared by addition of Tf_2O (1 mol amt.) to a suspension of PhIO in CH_2Cl_2 and then allowed to react with alkynes without isolation. (*p*-Phenylene)bisiodine(III) reagent **5** are stable crystals and can be stored for a long time in a refrigerator. Accordingly, the isolated (*p*-phenylene)bisiodine(III) reagent **5** can be conveniently used for the reaction of alkynes. (*p*-Phenylene)bisiodine(III) reagent **5** was dissolved in MeCN and reacted with alkynes (Method C). The results of the reaction are given in Table 1.

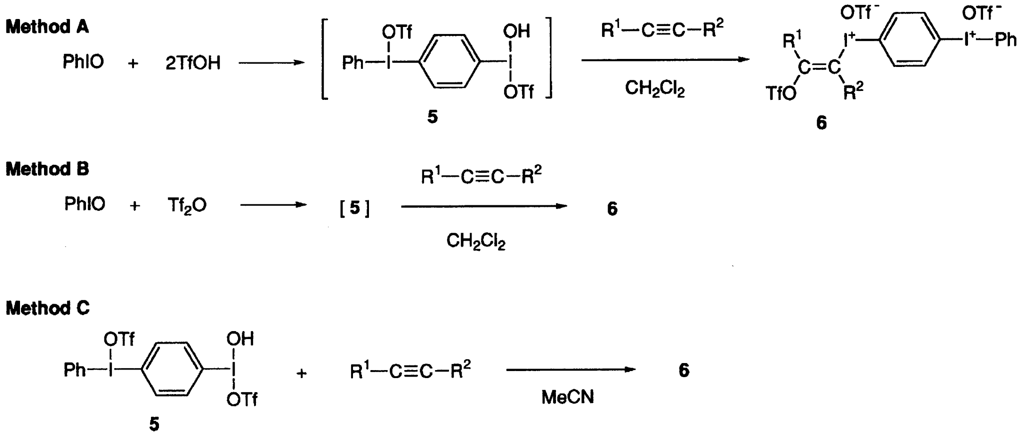
All methods operated successfully to give addition products, phenyl[(*E*)-2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflates (**6**) in good yields. All alkynes employed in the present study undergo addition reactions even in the cases of *t*-butylacetylene and phenylacetylene. In the case of *t*-butylacetylene, however, the addition reaction proceeded nonstereoselectively to yield a 1 : 1 mixture of (*E*)- and (*Z*)-[2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflates (**6d**).

The isolated [2-(trifluoromethylsulfonyloxy)vinyl]-(1,4-phenylene)bisiodonium ditriflates **6** are stable crystals and have relatively high melting points

Table 1. Addition of (*p*-Phenylene)bisiodine Reagent 5 to Alkynes

Alkyne	Method	Product	Yield/%[a]
n-PrC≡CH	A	**6a**: R^1=*n*-Pr, R^2=H	63
	B		70
	C		44
n-BuC≡CH	A	**6b**: R^1=*n*-Bu, R^2=H	65
	B		68
	C		53
n-HexC≡CH	A	**6c**: R^1=*n*-Hex, R^2=H	53
	B		61
	C		41
t-BuC≡CH	A	**6d**: R^1=*t*-Bu, R^2=H	58[b]
	B		43[b]
EtC≡CEt	A	**6e**: R^1=R^2=Et	54
	C		50
PhC≡CH	C	**6f**: R^1=Ph, R^2=H	53
HC≡CH	C	**6g**: R^1=R^2=H	53

a) Based on 2 equivalents of PhIO or **5**. b) A 1 : 1 mixture of (*E*) and (*Z*) isomers.



Scheme 1.

(decomposition). The ^{1}H NMR shows a characteristic *ortho* aromatic proton to the iodine(III) atoms at 8.2—8.5 ppm and a vinylic proton at 7—8 ppm. The ^{13}C NMR indicates the sp^2 carbons of the double bond at 99—110 and 158—160 ppm for aliphatic [2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflates **6a**—**c**. In the parent [2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflate **6g**, the sp^2 carbons of the double bond absorb at 98 and 150 ppm. A typical absorption of the stretching band due to the double bond appears at 1630—1650 cm^{-1} in the IR spectra. The configuration of [2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflates **6** was determined by the NOE experiment of **6b** and the proton coupling constant of the parent [2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflate **6g**. Although a large NOE enhancement was observed between the allylic and vinylic protons of vinyliodonium salts,[11] no NOE enhancement (<1%) was observed between those protons of [2-(trifluoromethylsulfonyloxy)-1-hexenyl](1,4-phenylene)bisiodonium ditriflate **6b**, as shown in Fig. 1. The vinylic protons of the parent [2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflate **6g** appeared at $\delta=8.26$ and 7.96 as the AX quartet ($J=12$ Hz), which value of the coupling constant is in good accord with a *trans* configuration with respect to the carbon–carbon double bond.[7]

Reaction of (*p*-Phenylene)bisiodine(III) Reagent 5 with 1-Trimethylsilyl-1-alkynes. Reaction of organoiodine(III) reagents with silylalkynes and stannylalkynes provides a good method for preparation of alkynyliodonium salts,[2] since facile desilylation or destannylation by electrophilic iodine(III) reagents takes place in such unsaturated silanes or stannanes.

We examined the reaction of the (*p*-phenylene)bisiodine(III) reagent **5** with alkynlsilanes. 1-Trimethylsilyl-1-hexyne was added to the reagent solution prepared in situ by mixing iodosylbenzene and double the molar quantity of triflic acid in CH_2Cl_2. However, this reaction using the in situ prepared reagent **5** gave a mixture of 1-hexynyl(1,4-phenylene)bisiodonium ditriflate **7a** and (*E*)-[2-(trifluoromethylsulfonyloxy)vinyl](1,4-phenylene)bisiodonium ditriflate **6b** in the ratio of 1 : 1 (Eq. 2). Vinyl derivative **6b** is formed from the addition reaction which should occur after protonation–desilylation giving 1-hexyne. Double the molar quantity of triflic acid is required to accomplish completely the self-condensation of iodosylbenzene by triflic acid, yielding the (*p*-phenylene)bisiodine(III) reagent **5**. Accordingly, the in situ prepared reagent solution contains extra amounts of triflic acid,[9] which cause the desilylation before the desired reaction.

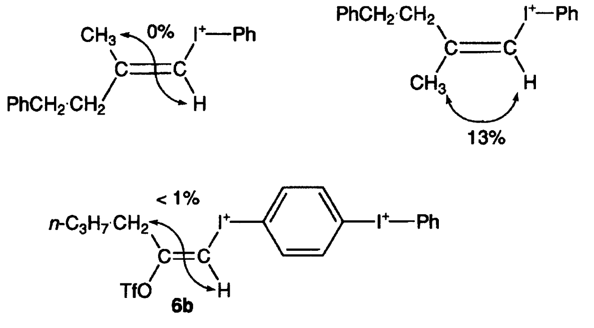
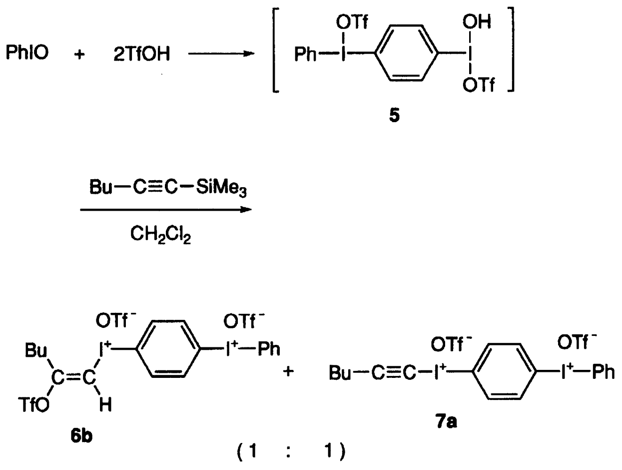
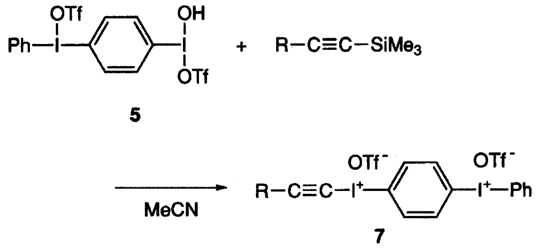


Fig. 1. NOE measurements for alkenyliodonium salts[11] and alkenyl(1,4-phenylene)bisiodonium triflate **6b**.



(2)

Then, we used the isolated crystalline bisiodine(III) reagent **5** similarly to method C. Interaction of the crystalline reagent **5** with 1-trimethylsilyl-1-alkynes in acetonitrile at room temperature gave alkynyl(*p*-phenylene)bisiodonium ditriflates **7** in good to high yields (Eq. 3). The results are given in Table 2.



(3)

The isolated alkynyl(*p*-phenylene)bisiodonium ditriflates **7** are fairly stable crystals and have relatively high melting points (decomposition). The ^{1}H NMR shows characteristic aromatic protons ortho to the iodine(III) atoms at 8.2—8.5 ppm. The ^{13}C NMR indicates

Table 2. Reaction of (*p*-Phenylene)bisiodine(III) Reagent **5** with 1-Trimethylsilyl-1-alkynes

Trimethylsilylalkyne	Yield/%
n-BuC≡CSiMe$_3$	76 (**7a**: R=n-Bu)
t-BuC≡CSiMe$_3$	83 (**7b**: R=t-Bu)
n-HexC≡CSiMe$_3$	68 (**7c**: R=n-Hex)
PhC≡CSiMe$_3$	82 (**7d**: R=Ph)
Me$_3$SiC≡CSiMe$_3$	76 (**7e**: R=Me$_3$Si)

the sp carbons of the triple bond around 25—30 and 110 ppm for aliphatic alkynyl(*p*-phenylene)bisiodonium ditriflates **7**. Typical absorption of the stretching band due to the triple bond appears at 2190 cm^{-1} in the IR spectra.

As the (*p*-Phenylene)bisiodine(III) Transfer Reagent. 1-[Hydroxy(trifluoromethylsulfonyloxy)iodo]-4-[phenyl(trifluoromethylsulfonyloxy)iodo]benzene (**5**) shows a high reactivity to alkynes and affords alkenyl- or alkynyl(*p*-phenylene)bisiodonium ditriflates. The products possess the (*p*-phenylene)bisiodonium moiety derived from reagent **5**. Accordingly, in addition to the reaction with aromatic substrates,[8] reagent **5** directly supplies the (*p*-phenylene)bisiodonium functionality to the products. Taking into account the high utility of hypervalent iodine compounds, a convenient preparation of functionalized (*p*-phenylene)bisiodonium salts is expected to provide a potential synthetic application.

Experimental

Melting points were measured with a Yanaco micromelting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained with Bruker AC-250P (250 MHz) and JEOL GSX400 (400 MHz) spectrometers, and ^{13}C NMR spectra with Bruker AC-250P (62.9 MHz) and JEOL GSX (100 MHz) spectrometers. Chemical shifts are given in ppm units. IR spectra were obtained with a Horiba FT-200 spectrometer. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Iodosylbenzene (PhIO) was prepared from (diacetoxyiodo)benzene (Aldrich Chemical Co.) according to the reported procedure.[12] 1-[Hydroxy(trifluoromethylsulfonyloxy)iodo]-4-[phenyl(trifluoromethylsulfonyloxy)iodo]benzene (**5**) was prepared by reaction of PhIO with trifluoromethanesulfonic acid (TfOH) according to our procedure.[8,9] TfOH was a gift from Central Glass Co.

Reaction of (*p*-Phenylene)bisiodine(III) Reagent 5 with Alkynes. Method A: To a stirred suspension of PhIO (0.44 g, 2.0 mmol) in CH_2Cl_2 (5 ml) was added TfOH (0.35 ml, 4.0 mmol) at 0 °C. The mixture was stirred for 3 h at room temperature. Then the reagent solution was used for reaction with alkynes without isolation. An alkyne (2.0 mmol) was added to the reagent solution, the mixture was stirred for 2 h and then concentrated under reduced pressure. Dry ether was added to the residue to crystallize it. The crystals were filtered, washed with ether, and dried in vacuo.

Method B: To a stirred suspension of PhIO (0.44 g, 2.0 mmol) in CH_2Cl_2 (5 ml) was added Tf_2O (0.34 ml, 2.0 mmol) at 0 °C. The mixture was stirred for 3—12 h at room temperature. An alkyne (2.0 mmol) was added to the reagent solution. The product was obtained by a procedure similar to Method A.

Method C: To a solution of crystalline (*p*-phenylene)bisiodine(III) reagent **5** (0.722 g, 1.0 mmol) in MeCN (4 ml) was added an alkyne (1.0 mmol). The mixture was stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and ether was added to crystallize it. The crystals were filtered, washed with ether, and dried in vacuo. The results are given in Table 1.

1-Phenyliodonio-4-[(*E*)-2-(trifluoromethylsulfonyloxy)-1-pentenyliodonio]benzene Ditriflate (6a): Mp 208—215 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) δ=0.79 (t, J=7 Hz, 3H), 1.36—1.45 (m, 2H), 2.83 (t, J=7 Hz, 2H), 7.51—7.57 (m, 2H), 7.65—7.71 (m, 1H), 7.84 (s, 1H), 8.23—8.32 (m, 4H), and 8.40—8.43 (m, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ=12.64, 18.95, 35.22, 99.23, 117.01, 120.03, 120.59, 131.81, 132.27, 135.24, 137.58, 137.73, and 160.37; IR (Nujol) 1632 cm^{-1}. Found: C, 26.20; H, 1.81%. Calcd for $C_{20}H_{17}F_9I_2O_9S_3$: C, 26.04; H, 1.86%.

1-Phenyliodonio-4-[(*E*)-2-(trifluoromethylsulfonyloxy)-1-hexenyliodonio]benzene Ditriflate (6b): Mp 182—188 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) δ=0.80 (t, J=7 Hz, 3H), 1.20—1.42 (m, 4H), 2.84 (t, J=7 Hz, 2H), 7.50—7.56 (m, 2H), 7.65—7.71 (m, 1H), 7.82 (s, 1H), 8.23—8.29 (m, 4H), and 8.38—8.42 (m, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ=13.58, 21.41, 27.71, 33.66, 99.06, 117.09, 120.08, 120.65, 131.97, 132.44, 135.47, 137.70, 137.88, and 160.72; IR (Nujol) 1634 cm^{-1}. Found: C, 26.99; H, 2.02%. Calcd for $C_{21}H_{19}F_9I_2O_9S_3$: C, 26.93; H, 2.05%.

1-Phenyliodonio-4-[(*E*)-2-(trifluoromethylsulfonyloxy)-1-octenyliodonio]benzene Ditriflate (6c): Mp 182—188 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) δ=0.80—0.83 (m, 3H), 1.19—1.41 (m, 8H), 2.85 (t, J=7 Hz, 2H), 7.51—7.57 (m, 2H), 7.66—7.72 (m, 1H), 7.84 (s, 1H), 8.24—8.32 (m, 4H), and 8.39—8.43 (m, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ=13.71, 21.70, 25.35, 27.52, 30.59, 33.64, 98.92, 116.92, 119.91, 120.50, 131.81, 132.29, 135.27, 137.52, 137.71, and 160.58; IR (Nujol) 1632 cm^{-1}. Found: C, 28.76; H, 2.33%. Calcd for $C_{23}H_{23}F_9I_2O_9S_3$: C, 28.64; H, 2.41%.

1-[3,3-Dimethyl-2-(trifluoromethylsulfonyloxy)-1-butenyliodonio]-4-phenyliodoniobenzene Ditriflate (6d): A 1:1 mixture of (*E*)- and (*Z*)-isomers. ^{1}H NMR (400 MHz, CD_3CN) δ=1.22 (s, Me), 1.38 (s, Me), 7.27 (s, =CH), 7.51—7.55 (m, ArH), 7.67—7.70 (m, ArH), 7.85 (s, =CH), 8.10—8.22 (m, 4H), and 8.38—8.42 (m, 2H). Found: C, 27.20; H, 1.96%. Calcd for $C_{21}H_{19}F_9I_2O_9S_3$: C, 26.93; H, 2.05%.

1-Phenyliodonio-4-[(*E*)-4-(trifluoromethylsulfonyloxy)-3-hexen-3-yliodonio]benzene Ditriflate (6e): Mp 154—164 °C (decomp); ^{1}H NMR (250 MHz, CD_3OD) δ=1.14—1.24 (m, 6H), 2.77 (q, J=7 Hz, 2H), 3.09 (q, J=7 Hz, 2H), 7.53—7.60 (m, 2H), 7.69—7.76 (m, 1H), 8.23—8.30 (m, 4H), and 8.35—8.40 (m, 2H); ^{13}C NMR (62.9 MHz, CD_3OD) δ=11.40, 13.65, 29.23, 31.13, 116.36, 120.68, 124.83, 133.46, 134.14, 136.91, 139.41, 139.55, and 158.70; IR (Nujol) 1654 cm^{-1}. Found: C, 26.96; H, 1.99%. Calcd for $C_{21}H_{19}F_9I_2O_9S_3$: C, 26.93; H, 2.05%.

1-Phenyliodonio-4-[(*E*)-2-phenyl-2-(trifluoromethylsulfonyloxy)ethenyliodonio]benzene Ditriflate (6f): Mp 135—137 °C (decomp); ^{1}H NMR (250 MHz, CD_3OD) δ=7.38—7.64 (m, ArH), 7.71—7.78 (m, ArH), 7.85—7.97 (m, ArH), 8.21—8.28 (m, ArH), and 8.35—8.42 (m, ArH); ^{13}C NMR (62.9 MHz, CD_3OD) δ=101.32, 116.34, 120.12, 124.29, 129.98, 133.44, 134.13, 134.18, 136.93, 138.18, 138.68, 139.19, 139.52, and 142.52.

1-Phenyliodonio-4-[(*E*)-2-(trifluoromethylsulfonyloxy)vinyliodonio]benzene Ditriflate (6g): Mp

256—257 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=$ 7.52—7.58 (m, 2H), 7.67—7.72 (m, 1H), 7.96 (d, $J=12$ Hz, 1H), 8.26 (d, $J=12$ Hz, 1H), 8.26—8.33 (m, 4H), and 8.42—8.45 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) $\delta=97.64$, 116.99, 119.55, 120.54, 131.88, 132.33, 135.37, 137.69 (2 signals overlapped), and 149.71. Found: C, 23.51; H, 1.30%. Calcd for $C_{17}H_{11}F_9I_2O_9S_3$: C, 23.20; H, 1.26%.

Reaction of (*p*-Phenylene)bisiodine(III) Reagent 5 with 1-(Trimethylsilyl)-1-alkynes. To a stirred solution of crystalline (*p*-phenylene)bisiodine(III) reagent **5** (0.722 g, 1.0 mmol) in MeCN (5 ml) was added an trimethylsilylalkyne (1.0 mmol). The mixture was stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and ether was added to crystallize it. The crystals were filtered, washed with ether, and dried in vacuo. The results are given in Table 2.

1-(1-Hexynyliodonio)-4-phenyliodoniobenzene Ditriflate (7a): Mp 203—207 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=0.78$ (t, $J=7$ Hz, 3H), 1.24—1.30 (m, 2H), 1.38—1.44 (m, 2H), 2.58 (t, $J=7$ Hz, 2H), 7.54—7.59 (m, 2H), 7.65—7.70 (m, 1H), and 8.30—8.40 (m, 6H); ^{13}C NMR (62.9 MHz, DMSO-d_6) $\delta=13.64$, 20.60, 22.74, 24.53, 30.70, 111.66, 116.32, 121.77, 124.26, 133.38, 134.07, 136.89, 138.51, and 139.39; IR (Nujol) 2192 cm^{-1}. Found: C, 30.31; H, 2.27%. Calcd for $C_{20}H_{18}F_6I_2O_6S_2$: C, 30.55; H, 2.31%.

1-(3,3-Dimethy-1-butynyliodonio)-4-phenyliodoniobenzene Ditriflate (7b): Mp 204—208 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=1.19$ (s, 9H), 7.53—7.59 (m, 2H), 7.67—7.73 (m, 1H), and 8.28—8.44 (m, 6H); ^{13}C NMR (62.9 MHz, DMSO-d_6) $\delta=29.08$, 29.28, 29.54, 114.30, 116.89, 120.42, 122.34, 131.84, 132.30, 135.28, 136.91, and 137.73; IR (Nujol) 2199 and 2164 cm^{-1}. Found: C, 30.47; H, 2.33%. Calcd for $C_{20}H_{18}F_6I_2O_6S_2$: C, 30.55; H, 2.31%.

1-(1-Octynyliodonio)-4-phenyliodoniobenzene Ditriflate (7c): Mp 198—201 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=0.81$ (t, $J=7$ Hz, 3H), 1.19—1.25 (m, 6H), 1.40—1.42 (m, 2H), 2.58 (t, $J=7$ Hz, 2H), 7.51—7.59 (m, 2H), 7.65—7.74 (m, 1H), and 8.29—8.43 (m, 6H); ^{13}C NMR (62.9 MHz, DMSO-d_6) $\delta=13.76$, 19.43, 21.83, 27.07, 27.56, 29.23, 30.41, 107.73, 116.85, 120.42, 122.56, 131.88, 132.37, 135.42, 137.17, and 137.81; IR (Nujol) 2192 cm^{-1}. Found: C, 31.77; H, 2.59%. Calcd for $C_{22}H_{22}F_6I_2O_6S_2$: C, 32.44; H, 2.73%.

1-(Phenylethynyliodonio)-4-phenyliodoniobenzene Ditriflate (7d): Mp 188—192 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=7.48$—7.59 (m, 7H), 7.67—7.73 (m, 4H), and 8.30—8.50 (m, 6H); ^{13}C NMR (62.9 MHz, DMSO-d_6) $\delta=41.53$, 103.44, 116.95, 119.32, 120.63, 122.82, 129.17, 131.48, 132.01, 132.48, 132.73, 135.48, 137.33, and 137.97; IR (Nujol) 2172 cm^{-1}. Found: C, 32.46; H, 1.72%. Calcd for $C_{22}H_{14}F_6I_2O_6S_2$: C, 32.75; H, 1.74%.

1-Phenyliodonio-4-(trimethylsilylethynyliodonio)benzene Ditriflate (7e): Mp 218—221 °C (decomp); ^{1}H NMR (250 MHz, DMSO-d_6) $\delta=0.16$ (s, 9H), 7.52—7.58 (m, 2H), 7.67—7.73 (m, 1H), 8.28—8.31 (m, 2H), and 8.37—8.45 (m, 4H); ^{13}C NMR (62.9 MHz, DMSO-d_6) $\delta=-1.05$, 53.77, 113.99, 116.87, 120.57, 122.45, 131.85, 132.31, 135.30, 137.16, and 137.84. Found: C, 28.51; H, 2.19%. Calcd for $C_{19}F_{18}F_6I_2O_6S_2Si$: C, 28.44; H, 2.27%.

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