

Self-condensation of Iodosylbenzene. Formation of a (*p*-Phenylene) Type of Bisiodine(III) Reagents

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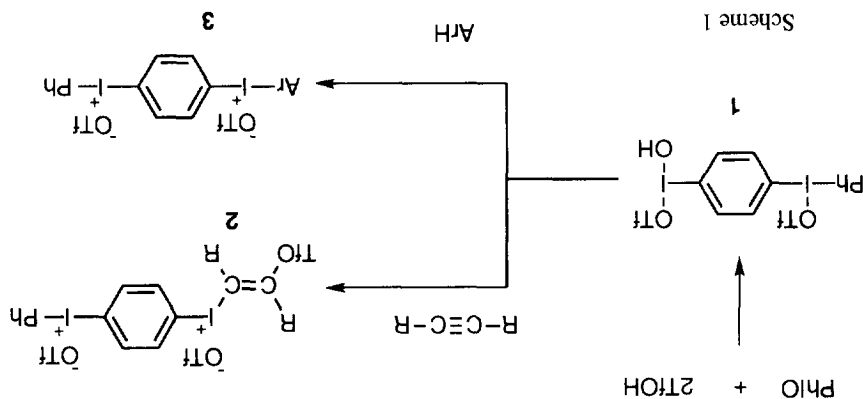
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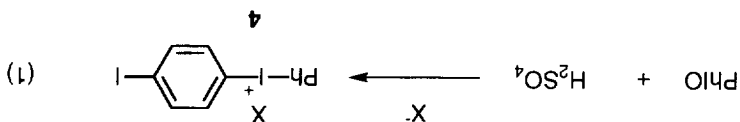
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Abstract: Reaction of iodosylbenzene (PhIO) with H_2SO_4 was reexamined. When PhIO was treated with excess H_2SO_4 , followed by reaction with aromatic substrates such as benzene, toluene, and bromobenzene, aryl(phenyl)*p*-phenylene(bisiodonium) salts were obtained in good to high yields. In stead of aromatic substrates, treatment of the reagent prepared from PhIO and H_2SO_4 with KI afforded *p*-iodophenyl(phenyl)iodonium iodide. Similarly, the *p*-phenylene type of bisiodonium salts were obtained with a fairly strong acid ($-H_0 > 8.0$) such as chlorosulfonic acid and trifluoromethanesulfonic acid. These results indicate that the reaction of PhIO with a strong acid gives rise to the formation of *p*-phenylene(bisiodine(III)) type of reagent, which leads to *p*-iodophenyl(phenyl)iodonium salt by the self-decomposition or to *p*-phenylene(bis(aryl)iodonium) salts by the reaction with aromatic substrates. The self-condensation of iodosylbenzene to *p*-phenylene(bisiodine(III)) type of reagents is discussed.

Recently it has been reviewed that hypervalent iodine(III) reagents are useful in organic synthesis.^{1,2} Previously we found that a reagent prepared from iodosylbenzene (PhIO) and trifluoromethanesulfonic acid (TfOH) shows a high reactivity toward unsaturated substrates such as alkynes and aromatics, and provides vinyl- and arylidonium triflates, respectively.³ Interestingly, when a reagent prepared by reaction of PhIO with double the molar quantity of TfOH was treated with alkynes and aromatics, vinyl- and aryl-substituted *p*-phenylene(bisiodonium) ditriflates (2 and 3) were obtained respectively,⁴ as shown in Scheme 1.



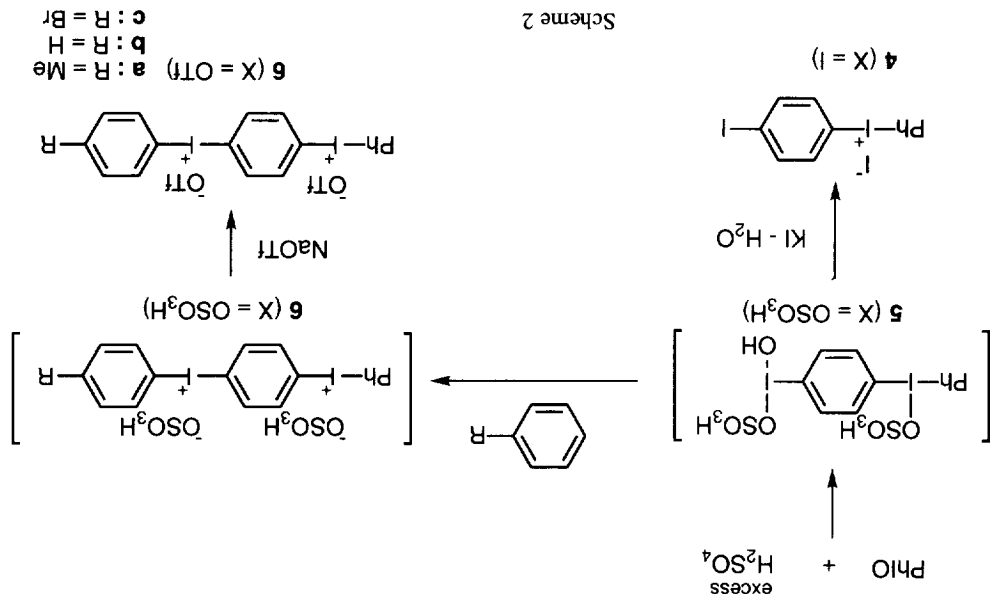


The formation of the (*p*-phenylene)bisiodonium salts **2** and **3** reminded us of the first example of diaryliodonium salts by Hartmann and Meyer⁴ that (*p*-iodophenyl)(phenyl)iodonium salt (**4**) is formed by treatment of PhIO with H₂SO₄ (eq. 1).⁵ We considered that formation of the (*p*-iodophenyl)(phenyl)iodonium salt is very close to our previous results⁴ on the formation of the (*p*-phenylene) type of bisiodine(III) compounds **2** and **3** because two iodine atoms incorporate with phenyl ring at the *para* position. Here we reexamine the reaction of PhIO with H₂SO₄ and propose a mechanism for the formation of (*p*-iodophenyl)(phenyl)iodonium salt via a (*p*-phenylene) type of bisiodine(III) reagent. Furthermore, we reveal the factors affecting the formation of (*p*-phenylene) type of bisiodine(III) compounds and discuss the mechanism of the self-condensation of iodobenzene with acids.

RESULTS AND DISCUSSION

Reaction of PhIO with H₂SO₄

In order to clarify the mechanism of the formation of *p*-iodophenyliodonium salt **4**, we reexamined the experiment conducted by Hartmann and Meyer,⁵ i.e., the self-condensation of PhIO by H₂SO₄. First, to examine that the reaction with H₂SO₄ proceeds in a similar manner to the previous reaction with TfOH,⁴ we checked the presence of the intermediate reagent related to the (*p*-phenylene) type of the bisiodine(III) reagent (**1**). If the intermediate (*p*-phenylene) type of bisiodine(III) reagent similar to **1** is generated by the reaction of PhIO with H₂SO₄, it can be trapped by aromatics such as toluene since the (*p*-phenylene) type of the bisiodine(III) reagent **1** is highly reactive toward aromatics.⁴



Iodosylbenzene was treated with an excess of concentrated H_2SO_4 and then reacted with toluene. Exchanging the ligand with NaOTf, (*p*-methylphenyl)(phenyl)(*p*-phenylene)bis(iodosonium) ditriflate (**6**) was obtained in 85% yield (Scheme 2). The same reactions with benzene and bromobenzene gave the corresponding (*p*-phenylene)bis(iodosonium) ditriflates (**6**, X = OTf) in 74 and 69% yields, respectively. These results indicate that the intermediate bis(iodosine(III)) species (**5**) is generated even in the reaction with H_2SO_4 and react with aromatic substrates to afford the (*p*-phenylene)bis(iodosonium) ditriflates **6** (X = OTf) after treatment of **6** (X = OSO_3H) with NaOTf.

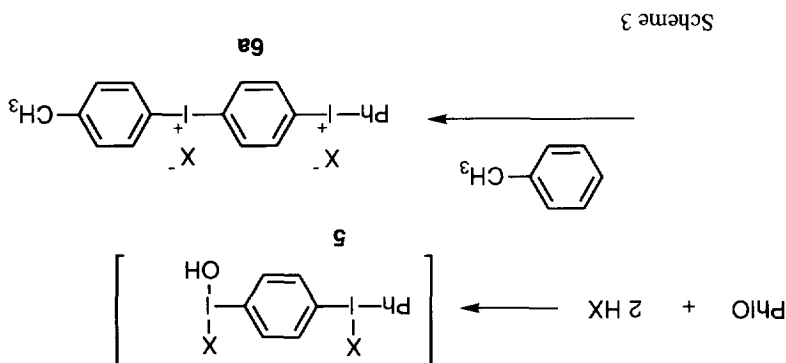
Next, we investigated whether the intermediate **5** prepared above gives (*p*-iodophenyl)(phenyl)iodonium salt **4**. When the reaction was worked up with H_2O and successively treated with KI, (*p*-iodophenyl)-(phenyl)iodonium iodide **4** (X = I) was obtained. This result is the same as that by Hartmann and Meyer.⁵ Accordingly, it is concluded that the formation of (*p*-iodophenyl)(phenyl)iodonium salts **4** is due to decomposition of the intermediate (*p*-phenylene) type of bis(iodosine(III)) reagent (**5**).

Reaction of PhIO with 2 Equivalents of TfOH

As reported preliminarily,^{4b} when PhIO was reacted with 2 equivalents of TfOH, (*p*-phenylene)bis(iodosine(III)) reagent (**1**) was obtained in 94% yield as stable crystals. This reagent reacts with aromatics and alkynes, and provides various substituted (*p*-phenylene)bis(iodosonium) salts **2** and **3**.^{4a}

Effect of Acids on Formation of a (*p*-Phenylene) Type of Bis(iodosine(III)) Reagents

It was found that a (*p*-phenylene) type of bis(iodosine(III)) reagents is generated in the reaction of PhIO with double the molar quantity of TfOH or with excess of H_2SO_4 . Then, we examined the effect of acid employed in the reaction of PhIO in order to clarify the property of the acid promoting the self-condensation of PhIO to the (*p*-phenylene) type of bis(iodosine(III)) reagents (**5**). The formation of the bis(iodosine(III)) reagent **5** was confirmed by obtaining (*p*-phenylene)bis(iodosonium) salts **6a** by reaction with toluene as a reactive aromatic substrate (Scheme 3).



To check the efficiency of the acid for the self-condensation of PhIO, double the molar quantity of the acid were treated with PhIO and followed by the reaction with toluene. (*p*-Phenylene)bis(iodosonium) salts **6a** were obtained only in the cases of H_2SO_4 (97%), TfOH, and chlorosulfonic acid, respectively, in 17, 82, and 43% yields. Other acids employed (H_3PO_4 (85%), HCl (37%), HNO_3 (60%), $\text{CF}_3\text{CO}_2\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$, HClO_4 (60%), and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ (60%)) did not afford (*p*-phenylene)bis(iodosonium) salts at all. Although diaryliodonium salts have been mainly prepared by acid-catalyzed arylation of PhIO or PhI(OAc)₂,⁶ the (*p*-phenylene) type of bis(iodosonium) salts have not been obtained. The present study indicates

that the formation of the (*p*-phenylene) type of bisdiodonium salts requires a fairly strong acid such as 97% H_2SO_4 , TfOH, and chlorosulfonic acid.

Factors Affecting Formation of the (*p*-Phenylene) Type of Bisdiodine(III) Reagents.

Correlation of the formation of the (*p*-phenylene) type of bisdiodine(III) reagents with the Hammett acidity function (H_0^7) as a measure of the acidity strength was examined by using a mixture of H_2SO_4 and H_2O . The formation of the bisdiodine(III) reagent (5) was confirmed by the formation of *p*-diodobenzene which was obtained by decomposition of the bisdiodine(III) reagent by KI. The result is shown in Figure 1. Figure 1 indicates that a high acidity of the acid ($-H_0 > 8.0$) is required to generate (*p*-phenylene) type of bisdiodine(III) reagents. Accordingly, H_2SO_4 (97%) ($-H_0 = ca 10.1$), $^{7,9}TfOH$ ($-H_0 = 14.1$), 8,10 and chlorosulfonic acid ($-H_0 = 13.8$), 8,11 are the reagents satisfying the above requirement.

Although the (*p*-phenylene) type of bisdiodine(III) reagents 1 was prepared by using 2 equivalents of TfOH to $PhIO_4$, the amount of TfOH should also affect the formation of bisdiodine reagent 1. Then, the formation of the bisdiodine(III) reagent 1 was checked by changing the amount of TfOH from 1 to 2 equivalents to $PhIO_4$. Similarly, the formation of the bisdiodine(III) reagent 1 is determined by the formation of *p*-diodobenzene after decomposition by KI. Figure 2 shows that the formation of the bisdiodine(III) reagent increased linearly from ca. 1.5 equivalents of TfOH.

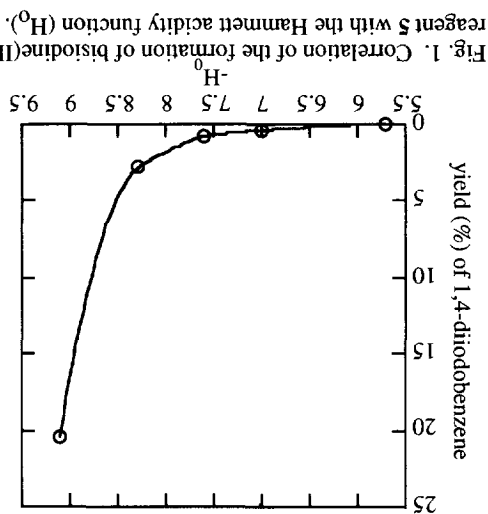


Fig. 1. Correlation of the formation of bisdiodine(III) reagent 5 with the Hammett acidity function (H_0).

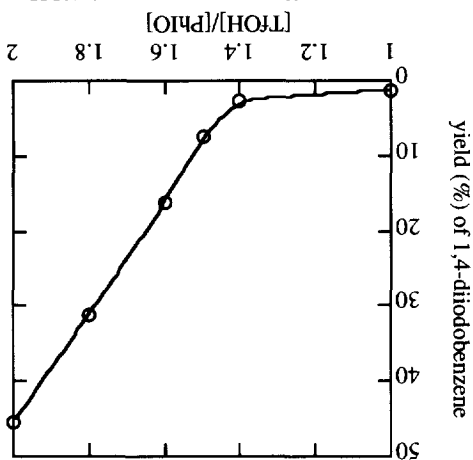


Fig. 2. Effect of the amount of TfOH.

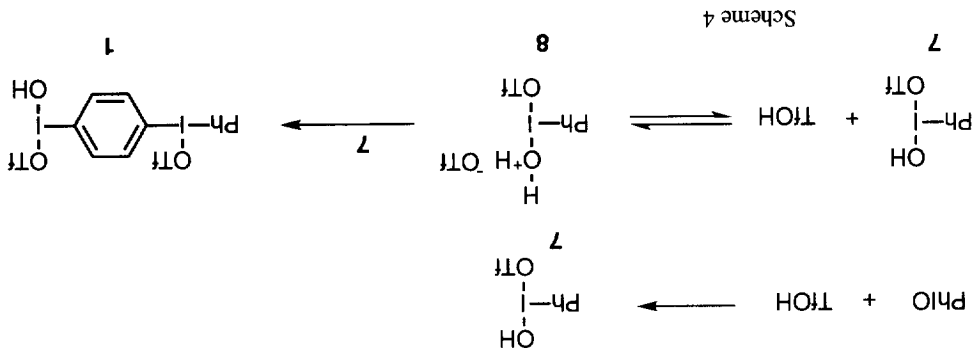
It was found that the formation of the (*p*-phenylene) type of bisdiodine(III) compounds is attributed to the

strength and the quantity of the employed acid.

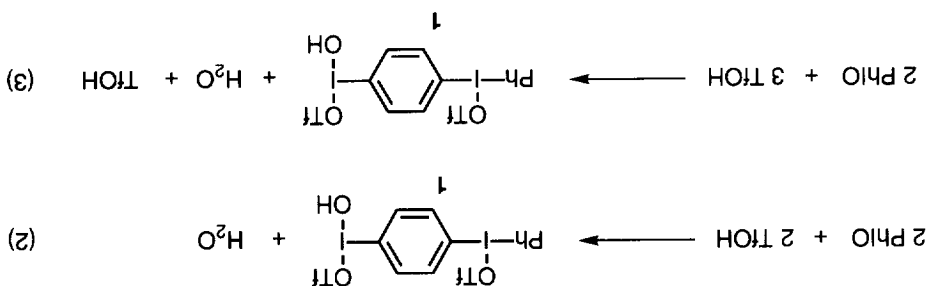
Generally, in acid-catalyzed arylation reactions of $PhIO_6$ reactive species [$PhIO_6H_2X^-$] are formed by protonation of $PhIO_4$ and react with aromatics to give diaryliodonium salts. The reaction of $PhIO_4$ in the cases of H_2SO_4 , chlorosulfonic acid, and TfOH also proceeds in the similar manner. In the present case with TfOH, as the example, the formation of [$PhIO_6H_2OTf$] (7) and the protonation of OH group of 7 are essential for the generation of the (*p*-phenylene) type of bisdiodine(III) reagents 1. [$PhIO_6H_2OTf$] 7 has an electrophilic nature but is inactive toward deactivated aromatics such as $PhIO_4$ or aromatics bearing electron-withdrawing I(III) group.

Self-condensation of $PhIO_4$ with Acids.

However, when a strong acid ($-\text{H}_0 > 8.0$) is present in excess, protonation of $[\text{PhI}(\text{OH})\text{OTf}]$ takes place to produce a highly reactive species **8**. The species **8** is the real intermediate leading to the self-condensation of PhIO .¹²



The protonated species **8** is expected to have a dicationic character such as " PhI^{2+} " because of the high nucleofugacity of OTf and H_2O^+ groups. The enhanced reactivity of **8** causes electrophilic attack to the phenyl group of $[\text{PhI}(\text{OH})\text{OTf}]$ which is inactive under usual conditions. The high *para* selectivity⁴ is due to the contribution by the lone pair on the iodine(III) atom and the steric hindrance of the *ortho* position by the iodine(III) group. Accordingly, both of a high acidity ($-\text{H}_0 > 8.0$) of acids and the excess quantity are required in order to generate a reactive dicationic species **8**.



Since 2 equivalents of PhIO and 2 equivalents of TfOH provide stoichiometrically the (*p*-phenylene)-bisdiodine(III) reagent **1** and H_2O , it may be expected that a 1:1 molar ratio of PhIO and TfOH is enough to cause the self-condensation of PhIO (eq. 2). However, the formation of the reagent $\text{PhI}(\text{OH})\text{OTf}$ **7** from a 1:1 molar ratio of PhIO and TfOH is very fast compared with the self-condensation of PhIO to the bisdiodine(III) reagent **1**, because the reaction of PhIO with TfOH (with the 1:1 molar ratio) gives rise to $\text{PhI}(\text{OH})\text{OTf}$ but the reaction does not cause the condensation to (*p*-phenylene)bisdiodine(III) compounds. Furthermore, as discussed above, it is necessary to generate the activated species **8** for the formation of the bisdiodine(III) reagent **1**. From Scheme 4, (*p*-phenylene)bisdiodine(III) reagent **1** is formed from two molecules of $\text{PhI}(\text{OH})\text{OTf}$ and one molecule of TfOH , that is, equation 3 is obtained. This means that 1.5 equivalents of TfOH is required toward PhIO for the self-condensation of PhIO . This is in accord with the above experimental results.

Therefore, it is concluded that the formation of the (*p*-phenylene) type of bisdiodine(III) reagents (**1** and **5**)

is due to the *in situ*-generation of a highly reactive species **8** which is expected to possess a dicationic property and undergo electrophilic substitution to yield **1** and **5**.

In summary, we have found that the (*p*-phenylene) type of bis(iodine(III)) reagents is formed by use of the acid possessing a high acidity ($-H^0 > 8.0$) and the excess amount of the acid. On the basis of the findings, various (*p*-phenylene) types of bis(iodine(III)) reagents can be synthesized and applied to organic synthesis.

EXPERIMENTAL

Melting points were measured with a Yanaco micromelting point apparatus and are uncorrected. 1H NMR spectra were obtained with Bruker AC-250P (250 MHz) and JEOL GSX400 (400 MHz) spectrometers, and ^{13}C NMR spectra were obtained 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 Horiba FT-200 spectrometer. Gas chromatographic analysis was conducted by Shimadzu GC-9A equipped with a glass column (2.0 m) packed with OV-17, programming from 100 to 150 °C at 10 °C/min. Elemental analyses 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.¹³

Reaction of PhIO with Concentrated H_2SO_4 .

To a stirred suspension of PhIO (0.66 g, 3.0 mmol) in CH_2Cl_2 (3.5 mL) was added dropwise concentrated H_2SO_4 (97%) (0.35 mL, 10 mmol) at 0 °C and the mixture was stirred at 0 °C for 3 h. Then, toluene (1.6 mL, 15 mmol) was added at 0 °C and the mixture was stirred for 2.5 h. After evaporation of the solvent, the residue was crystallized by adding aqueous NaOTf (NaOTf, 10 mmol). The crystals were filtered and dried in vacuo giving 1.013 g of (*p*-methoxyphenyl)(*p*-phenyl)(*p*-phenylene)bis(iododanium) diriflate (**6a**: X = OTf) (85%).

The same treatment of PhIO with concentrated H_2SO_4 (97%) was conducted and reacted with aromatic substrates (benzene and bromobenzene). After treatment with aqueous NaOTf, the corresponding (*p*-phenylene)bis(aryliodonium) diriflates were obtained as crystals: (*1*-(*p*-phenylene)bis(phenyliodonium) diriflate (**6b**: X = OTf) (74%) and (*p*-bromophenyl)(*p*-phenyl)(*p*-phenylene)bis(iododanium) diriflate (**6c**: X = OTf) (69%).

The same treatment of PhIO (0.66 g, 3.0 mmol) in CH_2Cl_2 (35 mL) with concentrated H_2SO_4 (97%) (0.55 mL) was conducted. Crushed ice (ca. 10 g) was added and then aqueous KI (KI, 1.66 g, 10 mmol) was added. The resulting crystals were filtered and washed with water. The yellow crystals were dried in vacuo to yield (*p*-iodophenyl)(*p*-phenyl)iododanium iodide **4** (X = I),⁵ quantitatively.

Reaction of PhIO with TfOH.

Trifluoromethanesulfonic acid (1.78 mL, 20 mmol) was slowly added dropwise at 0 °C to a stirred suspension of PhIO (2.20 g, 10 mmol) in dry CH_2Cl_2 (20 mL) and the mixture was further stirred at room temperature for 4 h. After evaporation of the solvent, dry ether was added to the residue to crystallize. The crystals were filtered, washed with dry ether, and dried in vacuo to give 3.40 g of (*p*-hydroxy)((trifluoromethylsulfonyloxy)iodo)-4-((phenyl)((trifluoromethylsulfonyloxy)iodo)benzene (**1**)^{4b} (94%), mp 125–132 °C (dec). 1H NMR (400 MHz, DMSO- d_6) δ 7.56 (t, J = 7.6 Hz, 2 H, ArH), 7.70 (t, J = 7.6 Hz, 1 H, ArH), 8.26 (d, J = 8.5 Hz, 2 H, ArH), 8.30 (d, J = 7.6 Hz, 2 H, ArH), 8.41 (d, J = 8.5 Hz, 2 H, ArH). ^{13}C NMR (100 MHz, DMSO- d_6) δ 116.79, 120.15, 126.43, 131.84, 132.30, 135.29, 136.41, 137.11, IR (Nujol) 1269, 1242, 1225, 1190 cm^{-1} . Anal. Calcd for $C_{14}H_{10}F_6I_2O_7S_2$: C, 23.28; H, 1.40%. Found: C, 23.35; H, 1.34%.

In order to confirm the *p*-phenylene structure of the reagent **1**, the reagent **1** was decomposed to diiodobenzene by the known reaction with iodide ion.^{6b} A solution of the reagent **1** (1.445 g, 2.0 mmol) in DMF (10 mL) was refluxed for 24 h in the presence of NaI (3.216 g, 21.5 mmol). The reaction mixture was poured into water, treated with aqueous Na₂S₂O₃, and extracted with ether. The etheral solution was washed with water and saturated brine, and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was evacuated to remove iodobenzene to give crystalline diiodobenzene (0.584 g, 89%), which was 1,4-diiodobenzene (99% in purity by GC).

Reaction of PhIO with Other Acids.

An acid (2.0 mmol) was added dropwise at 0 °C to a suspension of PhIO (220 mg, 1.0 mmol) in CH₂Cl₂ (4 mL) and the mixture was stirred for 2 h. Toluene (0.05 mL, 1.0 mmol) was introduced and the mixture was further stirred for 2 h. After evaporation of the solvent, ether was added to the residue to crystallize the (*p*-phenylene)bisiodonium salt. The resulting crystals were filtered and dried in vacuo. The formation of the (*p*-phenylene)bisiodonium salt was checked by ¹H NMR (250 MHz) showing the characteristic absorption at δ 8.0-8.4 which is not observed in diaryliodonium salts.

The employed acids were H₃PO₄ (85%), HCl (37%), HNO₃ (60%), CF₃CO₂H, CH₃SO₃H, HClO₄ (60%), *p*-CH₃C₆H₄SO₃H-H₂O, H₂SO₄ (97%), TfOH, and chlorosulfonic acid. The reactions with H₂SO₄ (97%), TfOH, and chlorosulfonic acid gave the corresponding (*p*-methylphenyl)(phenyl)(*p*-phenylene)bisiodonium salts **6a** in 17, 82, and 43% yields, respectively.

Effect of Concentration of H₂SO₄ in the Reaction of PhIO with H₂SO₄.

To a suspension of PhIO (0.22 g, 1.0 mmol) in CH₂Cl₂ (4 mL) were added dropwise 60%, 80%, 85%, 90%, and 97% H₂SO₄ (2.0 mmol), respectively, and the each mixture was stirred for 2 h. After evaporation of the solvent, KI (10 mmol) and DMF (4 mL) were added to the residue and the solution was then refluxed for 1 h. The mixture was poured into water and treated with aqueous Na₂S₂O₃. The products were extracted with ether, the extract was washed with water and saturated brine, and dried over anhydrous Na₂SO₄. After evaporation of the solvent, iodobenzene and 1,4-diiodobenzene, were analyzed by GC. The results are plotted in Figure 1.

Effect of Quantity of TfOH in the Reaction of PhIO with TfOH.

To a suspension of PhIO (0.44 g, 2.0 mmol) in CH₂Cl₂ (10 mL) were added dropwise at 0 °C 2.0 mmol (1.0 equiv), 2.8 mmol (1.4 equiv), 3.6 mmol (1.8 equiv), and 4.0 mmol (2.0 equiv) of TfOH, respectively, and the each mixture was stirred for 4 h. After evaporation of the solvent, KI (1.66 g, 10 mmol) and DMF (10 mL) were added to the residue and the mixture was refluxed for 1 h. The mixture was poured into water and treated with aqueous Na₂S₂O₃. The products were extracted with ether, the extract was washed and dried. 1,4-Diiodobenzene was analyzed by GC. The results are plotted in Figure 2.

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