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Oligomerization of (Diacetoxyiodo)benzene with Trifluoromethanesulfonic Acid. Preparation and Structure of Hypervalent Iodine Oligomers

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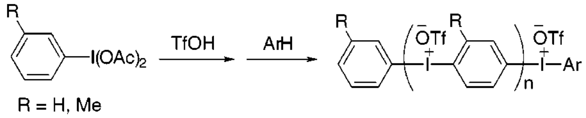
ABSTRACT



Treatment of (diacetoxyiodo)benzene with an excess amount of trifluoromethanesulfonic acid (TfOH) gives hypervalent iodine oligomers after quenching by aqueous NaBr. The thermolysis by KI yielding *p*-diiodobenzene and iodobenzene indicates that the structure for the oligomers consists of *p*-phenylene unit. The iodine oligomers in situ generated react with aromatic substrates such as benzene, toluene, and chlorobenzene to give the corresponding arylated iodine oligomers.

Applications of hypervalent iodine compounds to organic synthesis have recently attracted a great deal of attention.[1] Furthermore, hypervalent iodine compounds have been utilized as functional materials and applied to photopolymerization processes and chemical amplification in imaging systems.[2] Considering such developments, hypervalent iodine polymers are expected to create new functionality as a new type of polymers. However, electrophilic polymerization of hypervalent iodine compounds is quite difficult because hypervalent iodine groups such as diacetoxyiodo, iodosyl, dichloroiodo, and bis(trifluoroacetoxy)iodo have a high electron-withdrawing property. The extent of the inductive effect is similar to or stronger than those of nitro and cyano groups.[3]

In our study on highly reactive hypervalent iodine reagents, we have unexpectedly found that self-condensation of iodosylbenzene (PhIO) proceeds in the presence of trifluoromethanesulfonic acid (TfOH) to give a (*p*-phenylene)-

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(2) Fouassier, J. P.; Burr, D.; Crivello, J. V. J. M. S. *Pure Appl. Chem.* **1994**, *A31*, 677−701. Ito, H.; Ueda, M. *J. Photopolym. Sci. Technol.* **1989**, *2*, 1−10. Willson, C. G.; Bowden, M. J. *CHEMTECH* **1989**, *19*, 102−111. Yagci, Y.; Schnabel, W. *Makromol. Chem., Macromol. Symp.* **1988**, *13*−*14*, 161−174. Pappas, S. P. *Prog. Org. Coat.* **1985,** *13*, 35−64. Crivello, J. V. *Adv. Polym. Sci.* **1964**, *62*, 342−351.

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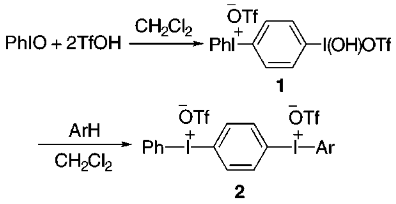
bisiodine(III) compound **1** (Scheme 1).[4] The bisiodine(III) compound **1** does not polymerize furthermore because of the low solubility. However, the bisiodine compound **1** reacts with aromatic substrates to give bisiodonium salts,[5] as shown in Scheme 1. This reaction suggests that the bisiodine(III) compound **1** still has a reactive site to enable the further reactions. Thus, we have examined the polymerization of (diacetoxyiodo)benzene [PhI(OAc)$_2$] under several conditions and obtained hypervalent iodine oligomers.

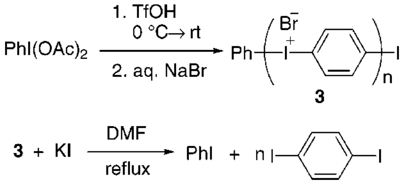
Scheme 1



During the course of our study, we found a paper describing the oligomerization of PhI(OAc)$_2$.[6] However, the structure proposed in that paper is different from the structure we have considered. In this paper we report our findings on the preparation and structure of novel hypervalent iodine oligomers derived from PhI(OAc)$_2$ and TfOH. Also, we describe the synthesis of the arylated hypervalent iodine oligomers.

The oligomerization reaction was conducted by adding PhI(OAc)$_2$ (2.5 mmol) to a solution of TfOH (4.5 mL) at 0 °C, followed by stirring the mixture at room temperature for 64 h. The reaction mixture was treated with aqueous NaBr. The resulting precipitates were filtered, washed with water and methanol, and dried in vacuo to give pale yellow solid **3** [0.73 g, mp 149−157 °C (dec)] (Scheme 2).

Scheme 2

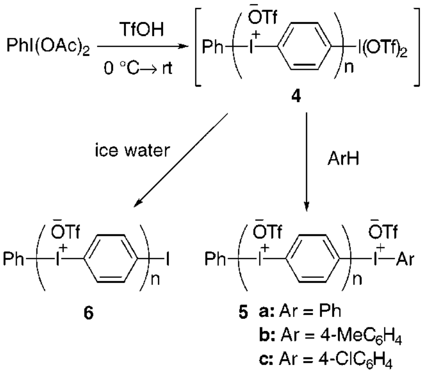


The product **3** was decomposed by thermolysis with KI since **3** was not dissolved in organic polar solvents such as CH$_2$Cl$_2$, DMF, and DMSO. The decomposition method using KI has been conventionally used to determine the structure of diaryliodonium slats.[7] The product **3** was decomposed by refluxing the mixture of **3** and KI in DMF. The decomposition products were analyzed by GC and NMR to verify that iodobenzene and 1,4-diiodobenzene were formed, as shown in Scheme 2. No other isomers of diiodobenzene were detected. This result means that the structure of the product **3** is composed of a *p*-phenylene unit. Quantitative analysis of iodobenzene and 1,4-diiodobenzene by GC indicated that the number average degree of polymerization was 3.0−3.9. Therefore, the product **3** was determined to have iodine(III) oligomers bearing *p*-phenylene structure.

It is presumed that the iodine oligomers **3** should have a reactive terminal site, bis(trifluoromethylsulfonyloxy)iodanyl group, similar to that of **4** before quenching with aqueous NaBr. It is, therefore, expected that this terminal iodine group can react with aromatic substrates. Then, we examined the arylation of the terminal group of the oligomers **4**. When the iodine oligomers **4** prepared from PhI(OAc)$_2$ as above were treated with benzene, toluene, and chlorobenzene, the corresponding arylated iodine oligomers **5** were obtained in good yields (0.64−0.85 g).[8]

The ^{1}H NMR of the oligomers **5a** showed the characteristic aromatic protons next to the iodine(III) group (8.2−8.3 ppm) together with other aromatic protons (7.5−7.7 ppm). However, it was found that the oligomers **5a** were contaminated with impurities (7.8−8.0 ppm) that were attributable to the unarylated iodine oligomers **6**. When the oligomers **5a** were decomposed by the thermolysis with KI, iodobenzene and 1,4-diiodobenzene were obtained. This result indicates that the iodine oligomer **5a** also has *p*-phenylene structure (Scheme 3).

Scheme 3



To examine the presence of the unarylated iodine oligomers **6**, the reactive iodine oligomers **4** were treated with ice water. After standing for 3 days, the resulting precipitates were collected (0.47 g) and analyzed by ^{1}H NMR. The NMR

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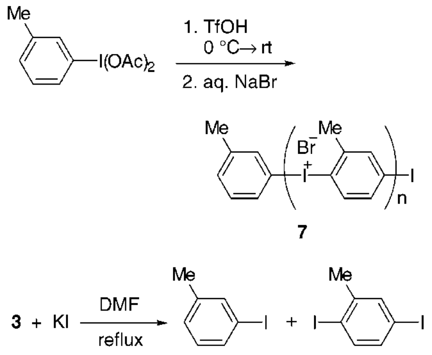
(8) **General Procedure for the Arylation of Iodine Oligomers 4.** (Diacetoxyiodo)benzene (0.8 g, 2.5 mmol) was added to TfOH (4.5 mL, 50 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. An aromatic substrate (10 mmol) was added, and the reaction mixture was stirred for 20 h and poured into ice water. The resulting precipitates were collected and dried in vacuo to afford white solids: **5a**, 0.81 g, ^{1}H NMR (CD$_3$OD) δ 7.52-7.57 (m), 7.69-7.73 (m), 8.20−8.30 (m); **5b**, 0.64 g, ^{1}H NMR (CD$_3$OD) δ 2.41 (bs), 7.36 (d, $J = 8$ Hz), 7.54 (t, $J = 7$ Hz), 7.68-7.77 (m), 8.05−8.10 (m), 8.20−8.30 (m); **5c**, 0.85 g, ^{1}H NMR (CD$_3$OD) δ 7.52-7.56 (m), 7.69−7.72 (m), 8.18−8.33 (m). The arylated iodine oligomers **5** were characterized by decomposition with KI, yielding 1,4-diiodobenzene, iodobenzene, and iodoarenes.

spectrum clearly showed the aromatic protons of the *p*-iodophenyl group at 7.90 (d, $J = 8.4$ Hz) and 8.00 (d, $J = 8.4$ Hz) ppm together with the *para* and *meta* protons of the phenyl group [7.54 (t, $J = 7.6$ Hz) and 7.68 (t, $J = 7.6$ Hz), respectively] and the other aromatic protons (8.2−8.3 ppm) of the *p*-phenylene and phenyl groups. The integration of these protons indicated that the number average degree of polymerization was 3.4. This value is also consistent with the value obtained by the decomposition of **3**.

To obtain further information on the orientation of the oligomerization process, we examined the reaction of *m*-(diacetoxyiodo)toluene with TfOH. A similar treatment of *m*-(diacetoxyiodo)toluene with an excess amount of TfOH followed by quenching with aqueous NaBr gave the corresponding iodine oligomers **7**. The thermolysis of **7** with KI in refluxing DMF yielded *m*-iodotoluene and 2,5-diiodotoluene. Again, this result suggests that the iodine oligomers **7** have a *p*-phenylene-type structure, as shown in Scheme 4. Therefore, it is concluded that the oligomerization of (diacetoxyiodo)benzene and -toluene proceeds in a *para*-directing manner to the hypervalent iodine group.

In summary, we have found that (diacetoxyiodo)arenes undergo oligomerization in the reaction with an excess amount of TfOH and provide a new *p*-phenylene type of hypervalent iodine oligomers. This oligomerization proceeds with a *para*-directing manner and is different from that proposed previously. The iodine oligomer has been found to be functionalized with aromatic substrates to give the arylated iodine oligomers.

Scheme 4



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