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Reaction of (diacetoxyiodo)benzene with excess of trifluoromethanesulfonic acid. A convenient route to *para*-phenylene type hypervalent iodine oligomers

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Abstract—Reaction of (diacetoxyiodo)benzene [PhI(OAc)₂] in trifluoromethanesulfonic acid (TfOH) resulted in oligomerization of PhI(OAc)₂. Quenching with NaBr gave the bromide salts of hypervalent iodine oligomers that were determined by thermolysis with KI to be a *para* phenylene type of oligomers. Neutralization of the reaction mixture of PhI(OAc)₂ and TfOH with aqueous NaHCO₃ yielded the triflate salts of iodine oligomers. Furthermore, quenching the reaction mixture with aromatic substrates afforded arylated iodine oligomers. These iodine oligomers were found to be 3–4 of the number average degree of polymerization (*P_n*) by GC analysis of the thermolysis products and ¹H NMR analysis. The major products, trimer and tetramer, were synthesized independently. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

Applications of hypervalent iodine compounds to organic chemistry have recently attracted a great deal of attention because they show high reactivity and have come into wide use in organic synthesis.¹ Since Hartmann and Meyer² reported the formation of (*p*-iodophenyl)(phenyl)iodonium salt (1) in Figure 1 as a stable hypervalent iodine compound. many diaryliodonium salts have been prepared. The preparation and chemistry of diaryliodonium salts have been summarized in early reviews.³ An extended type of the salts, *p*-phenylenebis(aryliodonium) salts (2), has been prepared recently by arylation of 1,4-bis(trifluoroacetoxyiodo)benzene.⁴ Okawara and his coworkers studied the synthesis of the tetramers of iodonium salts⁵ and suggested that the structure of the tetramers was composed of a metaphenylene skeleton. However, no further extended polymeric iodonium salts (3) have been prepared.

On the other hand, we found that the self-condensation of PhIO takes place in the presence of 2 equiv. of TfOH to give a bisiodine(III) reagent, 1-[(hydroxy)(trifluoromethyl-



Figure 1.

sulfonyloxy)iodo]-4-[(phenyl)(trifluoromethylsulfonyloxy)iodo]benzene (4),⁶ as shown in Scheme 1. This reagent 4 showed high reactivity to aromatic substrates and afforded



Scheme 1.

Keywords: Hypervalent iodine oligomer; (Diacetoxyiodo)benzene; Trifluoromethanesulfonic acid; *para*-Phenylene structure.

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(*p*-phenylene)bis(phenyliodonium) ditriflate (**5**) in the reaction with benzene. Furthermore, the reaction of **4** with diphenyl ether also gave oxygen-bridged tetraiodonium salt (**6**).^{6a} On the basis of the self-condensation of PhIO, the mechanism on the transformation of PhIO into **1** was elucidated.⁷

However, bisiodine(III) reagent 4 did not undergo polymerization to afford polymeric iodonium salts 3 although 4 had a reactive hypervalent iodonio group. The failure in polymerization was considered to be due to the reduced reactivity of the phenyl ring by the electronwithdrawing hypervalent iodine⁸ and to the insolubility of 4 in the organic solvent employed. Thus, we conducted the reaction of PhI(OAc)₂ using excess of TfOH and found that PhI(OAc)₂ underwent polymerization to give the oligomers.⁹ In this paper, we report in detail our findings on the formation and structure of the hypervalent iodine oligomers, and the independent synthesis of the hypervalent iodine trimer and tetramer to confirm the structure of the oligomers obtained by the reaction of PhI(OAc)₂.

2. Results and discussion

2.1. Oligomerization of PhI(OAc)₂ with TfOH. Isolation of hypervalent iodine oligomers as the bromide salts

PhI(OAc)₂ was treated with excess of TfOH and then the reaction was quenched with ice-water. However, no precipitates were formed on standing. When NaBr was added to the reaction mixture according to an early procedure¹⁰ to isolate diaryliodonium salts, pale yellow precipitates were formed. For example, the reaction of PhI(OAc)₂ (2.5 mmol) with TfOH (50 mmol) followed by treatment with aqueous NaBr gave 0.5–0.7 g of a pale yellow solid of the bromide (7), mp 149–157 °C (dec), as shown in Table 1 and Scheme 2. However, the solid

Table 1. Reaction of $\mbox{PhI}(\mbox{OAc})_2$ with TfOH followed by treatment with \mbox{NaBr}^a

Entry	Reaction time (h)	Yield of 7 (g)	$P_n^{\rm b}$
1	1	0.55	3.0
2	2	0.64	3.1
3	8	0.66	3.2
4	24	0.68	3.4
5	48	0.65	3.6
6	64	0.72	3.9
7	96	0.58	3.2
8	168	0.62	3.1

^a Reaction conditions: PhI(OAc)₂ (0.80 g, 2.5 mmol), TfOH (4.5 mL, 50 mmol) at room temperature.

^b Determined by GC after the decomposition with KI.



bromide 7 did not dissolve even in a polar organic solvent such as DMF, DMSO, or MeOH. To elucidate the structure of the solid, we conducted thermolysis with KI affording the corresponding organic iodides according to the conventional method¹¹ and analyzed the iodides with a capillary GC.

When the solid bromide 7 were reacted with KI in DMF under reflux conditions, iodobenzene and 1,4-diiodobenzene were formed. No isomers other than 1,4-diiodobenzene were detected. Therefore, the formation of 1,4diiodobenzene strongly indicates that the structure of bromide 7 is composed of a *para*-phenylene unit. On the basis of the quantitative GC analysis of iodobenzene and 1,4-diiodobenzene, the number average degree of polymerization (P_n) was calculated to be 3–4 as shown in Table 1. Therefore, the solid bromides were determined to be hypervalent iodine oligomers bearing a *p*-phenylene structure.

This result is different from Okawara's report⁵ that iodine oligomers (tetramers) have *meta*-phenylene units. However, our previous study⁶ on the dimerization of PhIO with TfOH supports this *para* orientation. It is, therefore, considered that the lone pairs on the iodine(III) atom govern the orientation of the oligomerization in the same way as the effect of halogen on electrophilic aromatic substitution of halobenzenes.

2.2. Isolation of hypervalent iodine oligomers as triflate salts

The bromide salt 7 of hypervalent iodine oligomers could not be analyzed by NMR since the solubility of 7 in organic solvents was extremely low. Then, we tried to isolate the hypervalent iodine oligomers as triflate salts and found that the neutralization of the reaction mixture with NaHCO₃ resulted in the formation of the precipitates of triflate (8), as shown in Scheme 3.

PhI(OAc)₂
$$\xrightarrow{0 \ ^{\circ}C \rightarrow r.t.}$$
 Ph $(OAc)_2$ $\xrightarrow{2. aq. NaHCO_3}$ Ph $(I \rightarrow R)$ Ph $(I \rightarrow R)$

Scheme 3.

For example, the reaction of PhI(OAc)₂ (2.5 mmol) with TfOH (50 mmol) for 8–48 h followed by neutralization with aqueous NaHCO₃ afforded white solids (0.5–0.6 g) of hypervalent iodine oligomers as shown in Table 2. The triffate salt **8** of oligomers dissolved in polar solvents such as DMSO and MeOH and this enabled the analysis by NMR. The ¹H NMR spectrum of **8** showed characteristic chemical shifts of hypervalent iodine compounds bearing a *p*-phenylene structure, indicating that the aromatic protons between the hypervalent iodines in the *p*-phenylene ring were observed around 8.32 ppm as a singlet. The terminal *p*-iodophenyl group showed a typical A₂B₂ pattern at 7.9–8.0 ppm and the *ortho* protons of the phenyl group appeared around 8.26 ppm as a doublet. The number average degree of polymerization *P_n* was determined to be 3.5–3.8 (entries

Table 2. Reaction of $PhI(OAc)_2$ with TfOH followed by treatment with $NaHCO_3^a$

Entry	TfOH (mmol)	Reaction time (h)	Yield of 8 (g)	P_n^{b}
1	12.5	24	0.26	2.3
2	25	24	0.48	3.3
3	50	24	0.64	3.7
4	75	24	0.55	3.7
5	50	8	0.53	3.5
6	50	48	0.62	3.8

^a Reaction conditions: PhI(OAc)₂ (0.80 g, 2.5 mmol) at room temperature.

^b Determined by ¹H NMR.



Scheme 4.

3–6 in Table 2) by the calculation of the integrals of these protons. This result is almost identical to that determined by the GC analysis of the thermolysis of 7 with KI. Therefore, the hypervalent iodine oligomers obtained in this study were found to be mostly composed of a trimer and a tetramer bearing a p-phenylene structure.

2.3. Arylation of hypervalent iodine oligomers

In the reaction mixture of PhI(OAc)₂ and TfOH, before quenching with NaBr or H₂O, it is presumed that there exists an intermediate hypervalent iodine species (**9**) having a reactive terminal site such as a bis(trifluoromethylsulfonyloxy)iodanyl group.¹² Since a PhI(OAc)₂/2TfOH reagent system shows high reactivity to aromatic substrates to give diaryliodonium salts,¹³ it is expected that this terminal iodine group can react with aromatic substrates to provide arylated hypervalent iodine oligomers. Thus, PhI(OAc)₂ was treated with excess of TfOH and then allowed to react with benzene, toluene, chlorobenzene, or bromobenzene, as shown in Scheme 4. The quenching and neutralization of the reaction mixture yielded the corresponding arylated hypervalent iodine oligomers (**10**) in good yields. The fact that the reaction with less reactive halobenzenes proceeds readily suggests that the terminal hypervalent iodine of **9** has a highly electrophilic character. The ¹H NMR spectra, however, showed that arylated iodine oligomers **10** were contaminated by small amounts of unarylated iodine oligomers **8**.

The thermolysis of phenylated iodine oligomers **10a** with KI similarly gave iodobenzene and 1,4-diiodobenzene. The quantitative GC analysis of iodobenzene and 1,4-diiodobenzene indicated that the number average degree of polymerization P_n was 3.5.

2.4. Independent synthesis of hypervalent iodine trimer and tetramer

From the above results, it is found that the reaction of $PhI(OAc)_2$ with excess of TfOH gives hypervalent iodine oligomers 7, 8, and 10 which are mostly composed of the trimer and the tetramer. Thus, we conducted an independent synthesis of the hypervalent iodine trimer, as illustrated in Scheme 5, to confirm its existence in the iodine oligomers 10a.

The self-condensation of PhIO with 2 equiv. of TfOH in CH₂Cl₂ gave bisiodine(III) reagent 4 in 84% yield. Arylation of 4 with 1,4-bis(tributylstannyl)benzene provided 4-(tributylstannyl)phenyl-substituted bisiodine(III) compound (11) in 61% yield. Reaction of 11 with a PhIO/ TfOH reagent followed by repeated recrystallization afforded hypervalent iodine trimer [10a (n=2)] in 26% yield. The ¹H NMR spectrum of **10a** (n=2) is almost identical with that of phenylated hypervalent iodine oligomers 10a. The triplet signals at 7.53 and 7.70 ppm are attributed to the *meta* and *para* protons of the terminal phenyl rings, respectively, and the doublet signal at 8.25 ppm to the *ortho* protons. Specially, the single peak observed at 8.34 ppm corresponds to all protons of the *p*-phenylene units. The ¹³C NMR spectrum showed characteristic high-field signals of ipso carbons bound to iodine(III) at 116.7, 120.3, and 120.5 ppm.

p-Phenylene-type hypervalent iodine tetramer [10a (n=3)]





Scheme 6.

was prepared by the reaction of 4 with excess of 1,4bis(tributylstannyl)benzene, as shown in Scheme 6. However, the procedure also provided mono-substituted compound 11. Accordingly, tetramer 10a (n=3) was isolated in 3% yield by repeated recrystallization. The ¹H NMR spectrum of tetramer 10a (n=3) was almost the same as that of trimer 10a (n=2), giving signals at 7.54 (triplet), 7.69 (triplet), and 8.26 (doublet) ppm corresponding to the meta, para, and ortho protons of the terminal phenyl rings, and the single peak at 8.34 ppm due to the protons of the para phenylene rings. The ¹³C NMR spectrum of 10a (n=3) indicated similarly high-field signals of the *ipso* carbon bound to iodine(III) at 116.7, 120.3, 120.5, and 120.6 ppm. The ¹H NMR spectra of trimer **10a** (n=2) and tetramer 10a (n=3) are very similar except for higher integration of the *p*-phenylene signal. Comparison of these spectra with phenylated oligomers 10a indicates that the ¹H NMR spectrum of **10a** is close to that of tetramer **10a** (n=3).

3. Conclusion

We have demonstrated that reaction of PhI(OAc)₂ in excess of TfOH gives hypervalent iodine oligomers comprising 3 or 4 units of $-C_6H_4I(X)$ -. The structure of the oligomers was characterized by GC analysis of the decomposition products with KI and by NMR. The oligomers obtained in this study have a *para* phenylene structure and 3–4 of P_n . Functionalization of the iodine oligomers 9 with aromatic substrates was readily performed to give aryl-substituted oligomers 10. As the practical applications, it has been reported that several types of diaryliodonium salts show strong biological activity.¹ Preliminarily, we examined the biological activity of the hypervalent iodine oligomers. Evaluation results of the biological activity indicate that these iodine oligomers show toxicity toward fungi and bacteria.¹⁴ Particularly, hypervalent iodine oligomers 10 exhibit in vitro toxicity against Aureobasidium pullulans and *Penicillium funiculosum* at the 50 ppm level and strong toxicity at the 25 ppm level against bacterial species such as Bacillus subtilis, Enterobacter aerogenes, Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Micrococcus luteus and Enterococcus faecalis. Independent syntheses of trimer 10a (n=2) and tetramer 10a (n=3)confirm the structure of the hypervalent iodine oligomers. As a future subject of study on hypervalent iodine oligomers, it will be very interesting to see the structure and property of these new types of hypervalent iodine oligomers because these oligomers contain many hypervalent iodines in the molecule.

4. Experimental

4.1. General

Melting points are uncorrected. Analytical GC evaluations of the product mixture were performed on a capillary gas chromatography using $30 \text{ m} \times 0.25 \text{ mm}$ capillary column (DB-5, J&J Scientific). Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

4.2. Oligomerization of PhI(OAc)₂ with TfOH. Isolation of hypervalent iodine oligomers 7 as bromide salts

(Diacetoxyiodo)benzene (0.80 g, 2.5 mmol) was added to TfOH (4.5 mL, 50 mmol) at 0 $^{\circ}$ C and the mixture was stirred at room temperature for the time given in Table 1. The reaction mixture was poured onto ice (45 g) and NaBr (7.72 g, 75 mmol) was added. The resulting precipitates were collected by suction, washed with water and methanol, and dried in vacuo. The oligomers 7 (0.55–0.72 g) were obtained as a pale yellow solid as shown in Table 1. The oligomers 7 decomposed in the range of 149–157 $^{\circ}$ C.

4.3. Decomposition of the oligomers 7 with KI

A mixture of oligomers 7 (50 mg) and KI (1.5 g, 9.0 mmol) in DMF (5 mL) was heated under reflux (163 °C) for 1 h. Water was added to the mixture and the products were extracted with ether. The organic layer was washed with water and aqueous sodium thiosulfate, and dried over anhydrous Na₂SO₄. The GC analysis of the products was performed on a Shimadzu gas chromatograph equipped with a capillary column (DB-5, J&W Scientific) using hexamethylbenzene as an internal standard. The products formed were iodobenzene and 1,4-diiodobenzene. The number average degree of polymerization (P_n) was calculated on the basis of the concentration of these products. Since the decomposition of 7 by KI affords a 1: n stoichiometric ratio of iodobenzene and 1,4-diiodobenzene, the P_n value is obtained by the following equation; $P_n = n - 1$, where n =[1,4-diiodobenzene]/[iodobenzene]. The results are given in Table 1. Because of the insolubility of 7 in organic solvents other methods for determination of P_n could not be applied.

4.3.1. Isolation of hypervalent iodine oligomers 8 as triflate salts. (Diacetoxyiodo)benzene (0.80 g, 2.5 mmol) was added to TfOH (the quantity described in Table 2) at 0 °C and the mixture was stirred at room temperature for the time given in Table 2. The reaction mixture was poured onto ice (50 g) and NaHCO₃ was carefully added until the solution was neutralized. The solution was kept standing for

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3 d. The resulting white precipitates were collected by suction, washed with water, and dried in vacuo to give oligomers **8** as a white solid as shown in Table 2. Mp 241–248 °C; ¹H NMR (300 MHz, DMSO- d_6) δ 7.54 (t, J= 7.8 Hz, ArH), 7.68 (t, J=7.5 Hz, ArH), 7.90 (d, J=8.4 Hz, ArH), 8.00 (d, J=8.4 Hz, ArH), 8.26 (d, J=7.8 Hz, ArH), 8.32 (s, ArH).

4.3.2. Arylation of hypervalent iodine oligomers. (Diacetoxyiodo)benzene (0.80 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 at room temperature. The reaction mixture was poured onto ice (50 g) and NaHCO₃ (4.41 g, 52.5 mmol) was added carefully. The solution was kept standing for 3 d. The resulting precipitates were collected by suction, washed with water, and dried in vacuo to give white solids of arylated oligomers 10. Phenylated oligomers 10a, 0.81 g, ¹H NMR (300 MHz, DMSO- d_6) δ 7.54 (t, J=8 Hz, ArH), 7.62–7.72 (m, ArH), 8.26 (d, J=8 Hz, ArH), 8.33 (s, ArH). 4-Methylphenylated oligomers **10b**, 0.64 g, ¹H NMR $(300 \text{ MHz}, \text{DMSO-}d_6) \delta 2.35 \text{ (s, Me)}, 7.35 \text{ (d, } J=8 \text{ Hz},$ ArH), 7.54 (t, J=8 Hz, ArH), 7.68 (t, J=8 Hz, ArH), 8.13 (d, J=8 Hz, ArH), 8.26 (d, J=8 Hz, ArH), 8.34 (s, ArH).4-Chlorophenylated oligomers **10c**, 0.85 g, ¹H NMR (300 MHz, DMSO-d₆) δ 7.51-7.56 (m, ArH), 7.62-7.72 (m, ArH), 8.26-8.29 (m, ArH), 8.33 (s, ArH). 4-Bromophenylated oligomers 10d, 0.81 g, ¹H NMR (300 MHz, DMSO-d₆) & 7.51–7.56 (m, ArH), 7.66–7.78 (m, ArH), 8.17-8.27 (m, ArH), 8.33 (s, ArH).

The phenylated iodine oligomers **10a** were also characterized by decomposition with KI. A mixture of oligomers **10a** (50 mg) and KI (1.5 g, 9.0 mmol) in DMF (5 mL) was refluxed for 1 h. After workup of the reaction mixture, the products were analyzed by GC using hexamethylbenzene as an internal standard. The products formed were iodobenzene and 1,4-diiodobenzene. The number average degree of polymerization (P_n) was calculated to be 3.5.

4.4. Preparation of hypervalent iodine trimer 10a (n=2) and tetramer 10a (n=3)

4.4.1. Preparation of 1-[(hydroxy)(trifluoromethylsulfonyloxy)iodo]-4-[(phenyl)(trifluoromethylsulfonyloxy)iodo]benzene (4). To a suspension of PhIO (1.1 g, 5.0 mmol) in CH₂Cl₂ (10 mL) was added TfOH (0.89 mL, 10 mmol) dropwise at 0 °C and the mixture was stirred for 4 h at room temperature. The solvent was removed by a rotary evaporator and ether was added to the residue. The resulting crystals were collected by suction, washed with ether, and dried in vacuo to afford 1.5 g (84%) of 4,⁶ mp 126–129 °C (dec).

4.4.2. Preparation of 1-[(phenyl)(trifluoromethylsulfonyloxy)iodo]-4-[(4-(tributylstannyl)phenyl)(trifluoromethylsulfonyloxy)]benzene (11). To a solution of 1,4bis(tributylstannyl)benzene¹⁵ (0.656 g, 1.0 mmol) in MeCN (10 mL) was added **4** (0.722 g, 1.0 mmol) at 0 °C and the mixture was stirred for 1 h at room temperature. The evaporation of the solvent gave crystals, which were collected by suction, washed with ether, and dried in vacuo to give 0.683 g (64%) of **11**: mp 238–242 °C (dec), ¹HMR (300 MHz, DMSO- d_6) δ 0.80 (t, J=7.2 Hz, 9H), 1.05 (t, J=7.5 Hz, 6H), 1.24 (m, 6H), 1.46 (m, 6H), 7.50– 7.69 (m, 5H), 8.17 (d, J=8.1 Hz, 2H), 8.26 (d, J=7.8 Hz, 2H), 8.33 (s, 4H); ¹³C NMR (75 MHz, DMSO- d_6) δ 9.31, 13.47, 26.57, 28.43, 116.77, 117.02, 119.99, 120.24, 131.91, 132.38, 134.18, 135.38, 137.63, 137.71, 139.24, 148.58.

4.4.3. Preparation of hypervalent iodine trimer, bis[4-[(phenyl)(trifluoromethylsulfonyloxy)iodo]phenyl](trifluoromethylsulfonyloxy)iodine [10a (n=2)]. To a suspension of PhIO (0.33 g, 1.5 mmol) in CH₂Cl₂ (5 mL) was added TfOH (0.13 mL, 1.5 mmol) dropwise at 0 °C and the mixture was stirred for 2 h at room temperature. A solution of 11 (0.536 g, 0.5 mmol) in MeCN (40 mL) was added to the resulting solution of PhIO/TfOH reagent at 0 °C and then the mixture was heated with stirring at 40 °C for 22 h. The solvent was evaporated by a rotary evaporator and ether was added to crystallize the residue. The crystals obtained from ether were recrystallized repeatedly from MeCN and ether to give 0.15 g (26%) of **10a** (n=2): mp 241–243 °C (dec); ¹H NMR (300 MHz, DMSO- d_6) δ 7.53 (t, J=7.8 Hz, 4H), 7.70 (t, J=7.2 Hz, 2H), 8.25 (d, J=7.8 Hz, 4H), 8.34 (s, 8H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 116.67, 120.34, 120.48, 131.84, 132.34, 135.27, 137.70, 137.77. Anal. Calcd for C₂₇H₁₈F₉I₃O₉S₃: C, 28.59; H, 1.60. Found: C, 28.59; H, 1.69.

4.4.4. Preparation of hypervalent iodine tetramer, 1,4bis[[4-[(phenyl)(trifluoromethylsulfonyloxy)iodo]phenyl](trifluoromethylsulfonyloxy)iodo]benzene [10a (n =3)]. To a solution of 1,4-bis(tributylstannyl)benzene (0.328 g, 0.5 mmol) in MeCN (100 mL) was added 4 (1.083 g, 1.5 mmol) at 0 °C and the mixture was stirred for 3 d at room temperature. At the end of the reaction, crystals were precipitated. The crystals were collected by suction, washed with ether, and finally recrystallized repeatedly from MeCN and ether to give 0.020 g (2.6%) of **10a** (n=3). Mp 235–238 °C (dec); ¹H NMR (300 MHz, DMSO- d_6) δ 7.54 (t, J=7.8 Hz, 4H), 7.69 (t, J=7.5 Hz, 2H), 8.26 (d, J=7.8 Hz, 4H), 8.34 (s, 12H); ¹³C NMR (75 MHz, DMSO-d₆) δ 116.69, 120.28, 120.48, 120.58, 131.87, 132.37, 135.30, 137.70, 137.80, 137.93. Anal. Calcd for C₃₄H₂₂F₁₂I₄O₁₂S₄: C, 27.47; H, 1.49. Found: C, 27.64; H, 1.65.

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