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# Safer Synthesis of (Diacetoxyiodo)arenes using Sodium Hypochlorite Pentahydrate ($NaClO•5H_2O$)

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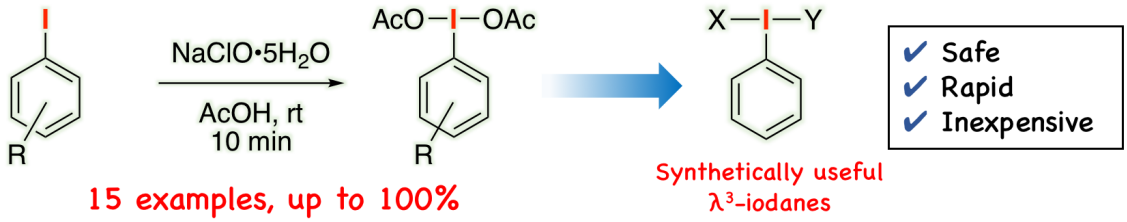
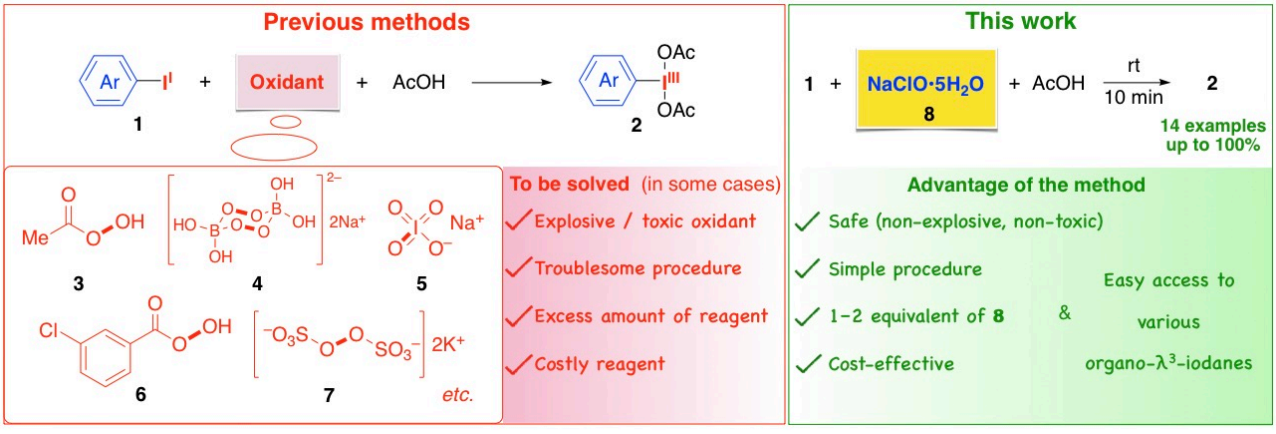
**ABSTRACT**: A practical method for the preparation of (diacetoxyiodo)arene $ArI(OAc)_2$ is described. The use of commercially available $NaClO•5H_2O$ enabled safe, rapid, and inexpensive oxidation of iodoarenes with electron-withdrawing and -donating substituents. The method allows tandem divergent access to synthetically useful organo $\lambda^3$-iodanes such as hydroxyl(tosyloxy)iodobenzene, iodosylbenzene, iodonium ylide, *etc*.




## Introduction

(Diacetoxyiodo)arene $ArI(OAc)_2$ **2** is one of the most synthetically useful oxidizing agents in the hypervalent organo-$\lambda^3$-iodane family.[1] The parent compound (diacetoxyiodo)benzene (**2a**) has enjoyed widespread application as a powerful and versatile oxidant and an excellent platform for construction of other di(hetero)iodoarenes, mainly because of its high thermal stability (storable indefinitely on the bench-top), non-explosive character and low toxicity. It can oxidize a wide range of functionalities, including alkenes, alkynes, alcohols, phenols, amines, sulfides, and carbonyl compounds under mild conditions.[1,2] However, despite its importance in synthetic organic chemistry, **2a** is still rather costly (available commercially at *ca.* 320 $/mol)[3a] compared to the precursor, iodobenzene (**1a**) (*ca.* 40 $/mol).[3a] This is partly because of the limitations of current synthetic methods (Scheme 1). For instance, a representative preparation method involves oxidation of iodoarenes **1** with excess amount of peracetic acid (**3**) in AcOH at 40 °C. This method requires strict temperature control: at lower temperature, the reaction rate slows down significantly, while at higher temperature over-oxidation to pentavalent iodine species occurs.[4a] More importantly, **3** is an *explosive* compound and has been the cause of serious accidents.[4b,c] In 1989, McKillop and Kemp reported a safer and more convenient method for the synthesis of **1** using sodium perborate tetrahydrate (**4**) in AcOH.[5a] Although this method is potentially applicable to variously functionalized iodoarenes, it generally requires the use of an excess amount of oxidant **4** (≥ 10 eq) and tedious work-up.[5b] Sodium periodate (**5**) oxidation in $Ac_2O$/AcOH is a promising method, but is

limited to electron-rich or weakly electron-deficient substrates **1**.[6] A combination of $CrO_3/H_2SO_4$ in $Ac_2O$-AcOH can oxidize highly electron-deficient iodoarenes such as *p*-nitroiodobenzene (**1b**),[7a] but this method requires special precautions to prevent explosions,[7b] and cannot be applied to electron-rich substrates.[7] In 2008, Togo and co-workers reported a simple and efficient method for the synthesis of **2** using *m*-chloroperbenzoic acid (**6**) in AcOH (Scheme 1).[8] This method shows wide applicability to both electron-rich and -deficient iodoarenes **1**, but the relatively high cost of **6** (*ca.* 244 $/mol)[3a] limits its applicability for large-scale synthesis. Although Kitamura's method using potassium peroxydisulfate (**7**) is economical ($K_2S_2O_8$ costs *ca.* 11$/mol),[3b] this method requires an excess of strong acid, such as $H_2SO_4$ or $CF_3SO_3H$, to activate **7**.[9] In this context, there is an urgent need for a safer, inexpensive, and operationally simple method for the preparation of **2** that is compatible with various iodoarenes (**1**). We report herein a new, practical preparation method for **2** using sodium hypochlorite pentahydrate ($NaClO{\bullet}5H_2O$) **8** as an oxidant, providing convenient access to various synthetically useful hypervalent iodine(III) reagents.




**Scheme 1.** Synthesis of (diacetoxyiodo)arene **2**: comparison between previous methods and the

present method.

## Results and Discussion

$NaClO•5H_2O$ (**8**) is a classical oxidant discovered about 100 years ago.[10] Little attention was paid to it as a reagent for organic synthesis until 2013,[11] but now **8** is widely available from various suppliers at low cost (*ca.* 15 $/mol).[3b] Considering its high purity and potent oxidation ability, we thought that the use of **8** for the preparation of **2** could overcome the above-mentioned difficulties in the oxidation of iodoarenes **1**. Indeed, **8** has already attracted attention as a clean and inexpensive oxidant for alcohols, 1,2-diols, thiols, sulfides, and phenols.[11]

We commenced this study by examining the direct oxidation of **1** with **8**. Exposure of **8** (2 mmol) to equimolar iodobenzene (**1a**) in the absence of solvent resulted in the recovery of **1a** after 1 hour at room temperature. This result indicates that the oxidation ability of **8** is insufficient under weakly basic conditions. However, when the reaction was carried out in AcOH, a pale yellow precipitate was formed within 10 min, and **2a** was obtained in 91% yield by means of a simple filtration-evaporation sequence (Table 1, entry 1). This reaction was not sensitive to the reagent concentration in the range of 0.3–2.6 M (entries 2–4). The optimized conditions could be easily scaled-up to 70 mmol (**1a**, 14 g) (entry 5). In a large-scale reaction, no significant evolution of heat was observed. Interestingly, when 4% aqueous NaClO solution was used instead of **8**, **2a** was not

obtained at all, but a large amount of iodylbenzene $PhIO_2$ (**9a**) was produced instead (entry 6), which is consistent with Zhdankin's report.[12] It is worth noting that the yield of **2a** was proportional to the concentration of aqueous NaClO solution (entries 1, 6–9; Figure 1), suggesting that $H_2O$ may promote the over-oxidation of **2a** to **9a** (see also Scheme 3). $Ca(ClO)_2•3H_2O$ also served as a good oxidant, but the reaction rate was slower, probably because of the lower solubility of this reagent in AcOH (entry 10). $NaClO•2.5H_2O$ also afforded **2a** in 91% yield under the same conditions. Use of a co-solvent was found to be effective to reduce the required amount of AcOH. Thus, in MeCN and $CH_2Cl_2$, the amount of AcOH could be reduced to 3.0 or 2.1 equivalents without any decrease in yield (entries 11–13), while the use of ethyl acetate, dimethyl carbonate, and acetone resulted in fair yields (entries 14–16). However, toluene was not effective for this reaction (entries 17 and 18). Propionic acid was also available for this transformation (entry 19).

Further studies on the scope and limitations indicated that this method is a powerful tool for rapid preparation of various (diacetoxyiodo)arenes. The optimized conditions are widely applicable not only to highly electron-deficient 4- and 3-nitroiodobenzenes (**1b** and **c**), 3,5-bis(trifluoromethyl)iodobenzene (**1d**), and pentafluoroiodobenzene (**1e**), but also to electron-rich 4-methoxyiodobenzene (**1j**), iodomesitylene (**1k**), and 1-iodonaphthalene (**1l**), affording the products in good to high yields (Table 2). It should be noted that the oxidation of **1b** with **6** was completed after only 10 min under our conditions, whereas when *m*-CPBA **6** was used,

the reaction required an elevated temperature (55 °C) and a prolonged reaction time (48 h).[8] Other recyclable iodoarenes **1m–o** were also good substrates.[13]

**Table 1.** Reaction of **1a** with NaClO•5$H_2O$ **8**.[a]

| entry | **1a** (mmol) | oxidant | solvent | (M) | time (min) | **2a** yield (%) |
|---|---|---|---|---|---|---|
| 1 | 2 | **8** | AcOH | 1.3 | 10 | 91 |
| 2 | 2 | **8** | AcOH | 0.3 | 5 | 70 |
| 3 | 2 | **8** | AcOH | 0.7 | 5 | 78 |
| 4 | 2 | **8** | AcOH | 2.6 | 10 | 69 |
| 5 | 70 | **8** | AcOH | 1.3 | 10 | 79 |
| 6 | 2 | 4% NaClO aq. | AcOH | 1.3 | 10 | 0[b] |
| 7 | 2 | 12% NaClO aq. | AcOH | 1.3 | 10 | 14 |
| 8 | 2 | 20% NaClO aq. | AcOH | 1.3 | 10 | 44 |
| 9 | 2 | 30% NaClO aq. | AcOH | 1.3 | 10 | 65 |
| 10 | 2 | $Ca(ClO)_2$•3$H_2O$[c] | AcOH | 1.3 | 30 | 73 |
| 11[d] | 2 | **8** | MeCN | 1.3 | 10 | 88 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 12[e] | 2 | **8** | MeCN | 1.3 | 20 | 92 |
| 13[d] | 2 | **8** | $CH_2Cl_2$ | 1.3 | 10 | 87 |
| 14[d] | 2 | **8** | AcOEt | 1.3 | 10 | 78 |
| 15[d] | 2 | **8** | $(MeO)_2CO$ | 1.3 | 10 | 78 |
| 16[d] | 2 | **8** | acetone | 1.3 | 10 | 66 |
| 17[d] | 2 | **8** | toluene | 1.3 | 10 | 28 |
| 18[d] | 2 | **8** | toluene | 1.3 | 120 | 36 |
| 19[f] | 2 | **8** | MeCN | 1.3 | 10 | 74[h] |

[a] Unless otherwise noted, reactions were carried out using exactly 1.0 eq of **8** in AcOH at room temperature under air. [b] $PhIO_2$ **9a** (90%) was obtained instead of **2a**. [c] 0.6 eq. [d] AcOH (3.0 eq). [e] AcOH (2.1 eq). [f] $EtCO_2H$ (3.0 eq). [g] $PhI(OCOEt)_2$ **10** was obtained.

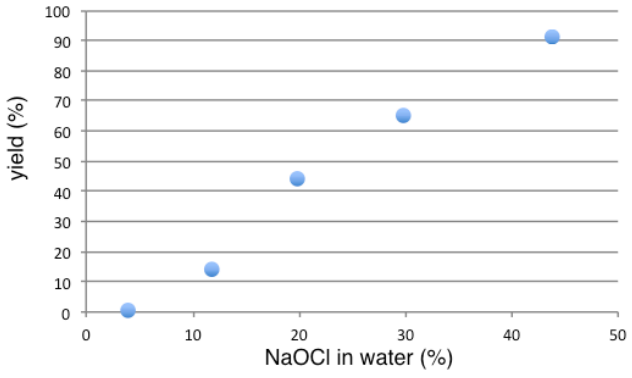
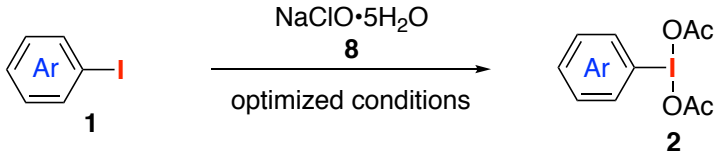



**Figure 1.** Relationship between concentration of NaClO and yield of **2a**.

**Table 2.** Synthesis of (diacetoxyiodo)arene **2**.[a]

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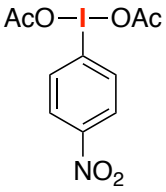
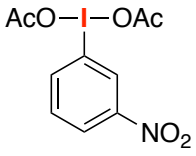
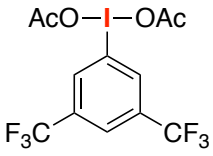
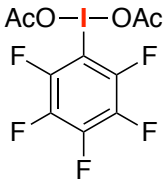
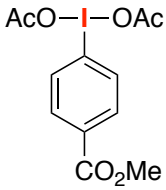
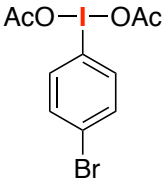
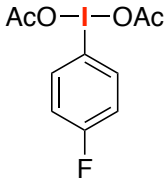
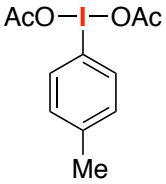
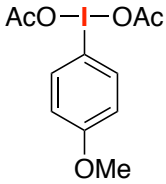
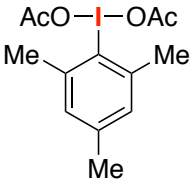
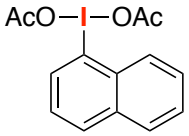
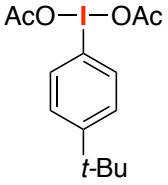
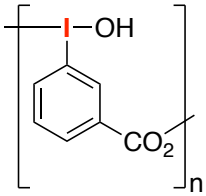
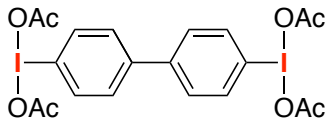
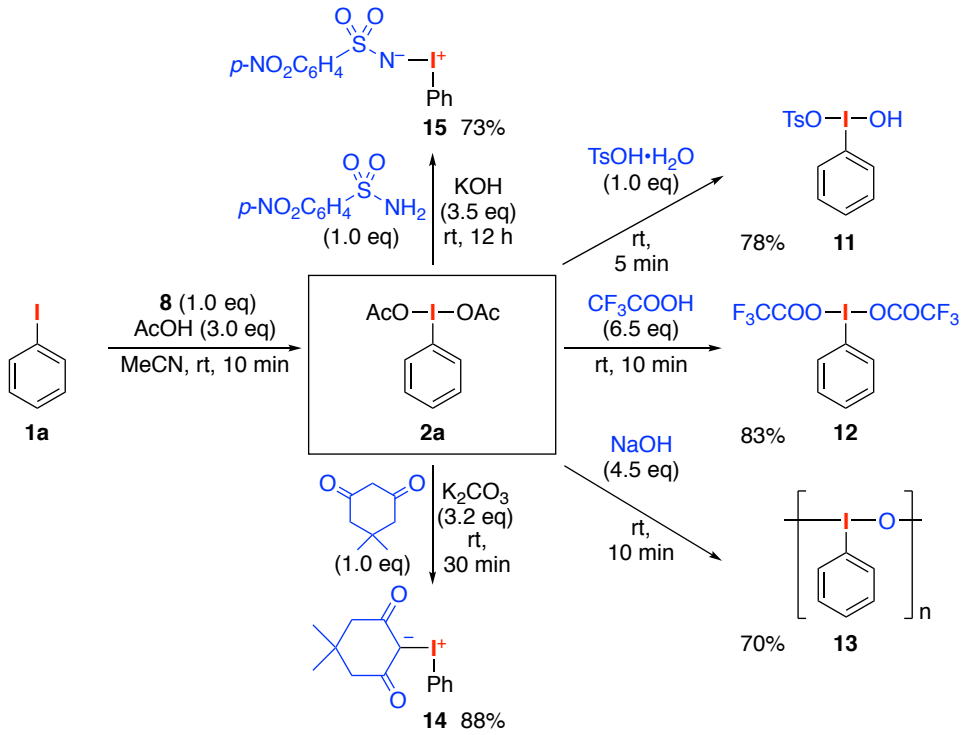
|  |  |  |  |  |
| **2b** | **2c** | **2d** | **2e** | **2f** |
| 76% | 91% | 63% | 87%[b] | 76%[c] |
|  |  |  |  |  |
| **2g** | **2h** | **2i** | **2j** | **2k** |
| 69% (74%)[d] | (78%)[d] | 78% (89%)[d] | 61%[c] (73%)[c,d] | 100% |
|  |  |  |  | |
| **2l** | **2m** | **2n** | **2o** | |
| 75% | 85%[c] | 81%[d,e] | 65%[c] | |

[a] Reaction conditions: **1** (2 mmol), **8** (1–1.4 eq), AcOH (1.5 mL), rt, air, 10 min. [b] **8** (2 eq). [c] *ca.* 5–10% of $\mu$-oxo dimers were contaminated. [d] AcOH (3 eq) in MeCN or $CH_2Cl_2$ (1.5 mL) was used. [e] Yield was determined by iodometry.

Our strategy can be extended to the divergent preparation of various hypervalent $\lambda^3$-iodanes (Scheme 2). Thus, after reaction of **1a** with **8** (1 eq) and AcOH (3 eq) in MeCN for 10 min (same as

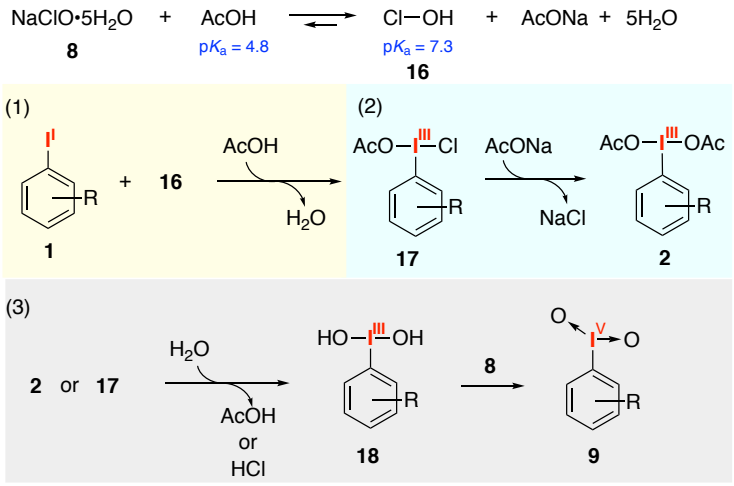
Table 1, entry 11), the **2a** obtained can be used directly for further transformations without purification. Thus, treatment of TsOH•$H_2O$, $CF_3CO_2H$, and NaOH resulted in the formation of hydroxy(tosyloxy)iodobenzene (**11**), bis(trifluoroacetoxy)iodobenzene (**12**), and iodosylbenzene (**13**) in fairly good yields; all of these compounds are important reagents in current synthetic organic chemistry.[14] Furthermore, reaction with dimedone and *p*-nitrobenzenesulfonamide under basic conditions afforded iodonium ylide **14** and imino-$\lambda^3$-iodane **15** in good to high yields.[15]




Scheme 2. Divergent synthesis of various hypervalent iodine(III) reagents.

A plausible reaction mechanism is illustrated in Scheme 3. (1) Nucleophilic attack of iodoarene **1** to hypochloric acid (HOCl) **16** generated by the reaction between **8** and acetic acid,[16] to form acetoxy(chloro)-$\lambda^3$-iodane intermediate **17**, followed by (2) ligand exchange with acetate ion results

in the formation of the more stable **2**. On the other hand, in the presence of a large amount of water, (3) a competitive ligand exchange yielding more electron-rich dihydroxy-$\lambda^3$-iodane **18** might occur. **18** thus generated would probably undergo further chlorination with **8** to afford pentavalent iodylarene **9**.




**Scheme 3.** Proposed reaction mechanism.

In conclusion, we have developed a very convenient method for the rapid, safe and efficient synthesis of (diacetoxyiodo)arenes **2** using sodium hypochlorite pentahydrate (**8**) and acetic acid. It is noteworthy that this method can be scaled up safely, since neither toxic molecular chlorine nor explosive peracetic acid was detected under the reaction conditions employed. This method provides a practical and rapid route to various synthetically useful organo $\lambda^3$-iodanes. Further studies on the preparation of tri/pentavalent organoiodine reagents with hypochlorite salt, as well as applications of this concept to iodoarene-catalyzed oxidation reactions are under investigation.

## EXPERIMENTAL SECTION

**General Information**

IR spectra were recorded on a FT-IR instrument. $^{1}H$ NMR, $^{13}C$ NMR, and $^{19}F$ NMR spectra were obtained on 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal $Me_4Si$. Low mass spectra (MS) were measured on TOF-MS with an ESI probe. Melting points were determined with melting points apparatus and are uncorrected.

**(Diacetoxyiodo)arenes 2 from Iodoarenes 1: General Procedure without Solvent**

To a vigorously stirred solid of $NaClO•5H_2O$ **8** (329 mg, 2.0 mmol) was added iodoarene **1** (2 mmol) and AcOH (1.5 mL) at room temperature under air and the mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (*ca.* 20 mL, it can be replaced by other solvent such as AcOEt or $CHCl_3$. If large amount of insoluble residue remained, addition of EtOH (*ca.* 5 mL) was very effective to re-dissolve it), the reaction mixture was filtered (removes NaCl and water) and solvents were removed under reduced pressure to give a pale yellow solid, which was washed several times with hexane or hexane-toluene by decantation to give (diacetoxyiodo)arene **2** in almost pure form. Further purification was achieved by 1) a short boiling of the crude **2** in AcOEt-$Ac_2O$ (>10:1) until it becomes clear solution and cooled to room temperature, 2) recrystallization by addition of excess hexane/$Et_2O$-hexane at 5 ºC or -20 ºC. Otherwise, the crude **2** was purified by following procedure. The crude residue (after evaporation) was added AcONa (4 mmol) and stirred in AcOEt (5 mL) at room temperature for 30 min, followed by the filtration and concentration under reduced pressure to

give pure **2** as a white solid. In several cases, small amount of corresponding μ-oxo dimer [ArI(OAc)⁻O⁻I(OAc)Ar] could not be separated.

**(Diacetoxyiodo)arenes 2 from Iodoarenes 1: General Procedure with Solvent**

To a vigorously stirred suspension of NaClO•5$H_2O$ **8** (329 mg, 2.0 mmol) in appropriate solvent (1.5 mL) was added iodoarene **1** (2 mmol) and AcOH (343 μL, 6.0 mmol) at room temperature under air and the mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (*ca.* 20 mL, it can be replaced by other solvent such as AcOEt or $CHCl_3$. If large amount of insoluble materials remained, addition of EtOH (*ca.* 5 mL) was very effective to re-dissolve it), the reaction mixture was filtered (removes NaCl and water) and solvents were removed under reduced pressure to give a pale yellow solid, which was washed several times with hexane or hexane-toluene by decantation to give (diacetoxyiodo)arene **2** in almost pure form. Analytically pure sample of **2** was obtained by following the above-mentioned procedures (general procedure without solvent).

**Large-scale synthesis of 2a**

In a well-ventilated food, to a vigorously stirred solid of NaClO•5$H_2O$ **8** (11 g, 70 mmol) in a 1 L beaker was added iodobenzene (7.5 mL, 67 mmol) in AcOH (100 mL) at room temperature under air. After 10 minutes, $CH_2Cl_2$ (200 mL) and toluene (200 mL) were added and separated aqueous

phase was removed and filtered. The filtrate was concentrated to a half of its original volume (*ca.* 50 mL) under reduced pressure to yield white suspension, which was then added excess hexane (~200 mL) and filtered to give **2a** (17 g, 79%) as a white solid. Analytically pure sample of **2a** was obtained by following the above-mentioned procedures (general procedure without solvent).

**(Diacetoxyiodo)benzene (2a)**:[5b] colorless prisms (586 mg, obtained from 2 mmol of starting material, purity 97% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.60 (dd, *J* = 8.4, 7.6 Hz, 2H), 2.01 (s, 6H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ = 176.3, 134.8, 131.6, 130.8, 121.5, 20.2.

**4-Nitro(diacetoxyiodo)benzene (2b)**:[8] colorless prisms (558 mg, obtained from 2 mmol of starting material, purity 97% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 9.1 Hz, 2H), 8.30 (d, *J* = 9.1 Hz, 2H), 2.04 (s, 6H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ = 176.7, 149.4, 136.0, 126.7, 125.6, 20.2.

**3-Nitro(diacetoxyiodo)benzene (2c)**:[5b] colorless prisms (668 mg, obtained from 2 mmol of starting material, purity 95% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.94 (m, 1H), 8.44 (m, 1H), 8.40 (m, 1H), 7.72 (t, *J* = 8.2 Hz, 1H), 2.04 (s, 6H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ = 176.8,

148.6, 140.4, 131.5, 130.1, 126.3, 120.6, 20.3.

**3,5-Bis(trifluoromethyl)(diacetoxyiodo)benzene (2d)**:[8] white microcrystalline solid (577 mg, obtained from 2 mmol of starting material, purity 100% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.50 (s, 2H), 8.07 (s, 1H), 2.05 (s, 6H); $^{19}$F NMR (470 MHz, $CDCl_3$): δ = -62.88 (s, 6F); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ = 177.0, 135.0, 133.8 (q, $^{2}J_{CF}$ = 34.7 Hz), 125.5 (br s), 122.2 (q, $^{1}J_{CF}$ = 273.0 Hz), 121.0, 20.3.

**2,3,4,5,6-Pentafluoro(diacetoxyiodo)benzene (2e)**: white microcrystalline solid (717 mg, obtained from 2 mmol of starting material, purity 97% by iodometry); mp 89–91 ºC; $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 6H); $^{19}$F NMR ($CDCl_3$, 470 Hz): δ = -120.90– -121.10 (m, 2F), -144.59 (tt, *J* = 20.7, 4.5 Hz, 1F), -156.42– -156.59 (m, 2F); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ = 178.2, 146.8–146.4 (m), 146.0–145.6 (m), 144.7–144.4 (m), 143.9–143.5 (m), 138.5–138.0 (m), 136.4–136.0 (m), 95.9 (t, $^{2}J_{CF}$ = 26.5 Hz), 20.0; HRMS (ESI, positive) *m/z* calcd for $C_{10}H_6F_5INaO_4$ [$(M + Na)^+$] 434.9129, found 434.9110.

**4-Methoxycarbonyl(diacetoxyiodo)benzene (2f)**:[8] white microcrystalline solid (638 mg, obtained from 2 mmol of starting material, purity 91% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.01

(d, $J$ = 9.1 Hz, 2H), 6.96 (d, $J$ = 9.1 Hz, 2H), 3.86 (s, 3H), 2.00 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 165.5, 134.9, 133.0, 131.8, 125.7, 52.7, 20.3.

**4-Bromo(diacetoxyiodo)benzene (2g)**:[17] colorless prisms (593 mg, obtained from 2 mmol of starting material, purity 96% by iodometry); $^{1}H$ NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, $J$ = 8.0 Hz, 2H), 7.62 (d, $J$ = 8.0 Hz, 2H), 2.01 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 136.5, 134.2, 126.8, 119.6, 20.3.

**4-Fluoro(diacetoxyiodo)benzene (2h)**:[5b] white microcrystalline solid (530 mg, obtained from 2 mmol of starting material, purity 99% by iodometry); $^{1}H$ NMR (500 MHz, $CDCl_3$): δ = 8.08 (dd, $J$ = 8.9 Hz, $^{4}J_{HF}$ = 5.2 Hz, 2H), 7.18 (dd, $J$ = 8.9 Hz, $^{3}J_{HF}$ = 8.2 Hz, 2H), 2.01 (s, 6H); $^{19}F$ NMR (470 MHz, $CDCl_3$): δ = -105.68 (s, 1F); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 164.3 (d, $^{1}J_{CF}$ = 254.3 Hz), 137.6 (d, $^{3}J_{CF}$ = 9.0 Hz), 118.6 (d, $^{2}J_{CF}$ = 22.4 Hz), 115.5 (d, $^{4}J_{CF}$ = 3.3 Hz), 20.3.

**4-Methyl(diacetoxyiodo)benzene (2i)**:[5b] white microcrystalline solid (598 mg, obtained from 2 mmol of starting material, purity 95% by iodometry); $^{1}H$ NMR (500 MHz, $CDCl_3$): δ =7.97 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 2.44 (s, 3H), 2.00 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.3, 142.5, 134.8, 131.6, 118.2, 21.3, 20.2.

**4-Methoxy(diacetoxyiodo)benzene (2j)**:[18] white microcrystalline solid (485 mg, obtained from 2 mmol of starting material, purity 88% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.00 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.4, 162.1, 137.1, 116.6, 111.6, 55.6, 20.3.

**2,4,6-Trimethyl(diacetoxyiodo)benzene (2k)**:[19] white microcrystalline solid (728 mg, obtained from 2 mmol of starting material, purity 99% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.10 (s, 2H), 2.71 (s, 6H), 2.36 (s, 3H), 1.97 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 143.2, 141.3, 129.5, 128.9, 26.7, 21.2, 20.3.

**1-(Diacetoxyiodo)naphthalene (2l)**:[20] white microcrystalline solid (558 mg, obtained from 2 mmol of starting material, purity 98% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.50 (dd, *J* = 7.5, 0.8 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.75–7.70 (m, 1H), 7.67–7.62 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 1.93 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.6, 137.1, 134.4, 133.5, 131.3, 129.6, 129.2, 129.1, 127.6, 126.6, 125.3, 20.2.

**4-*tert*-Butyl(diacetoxyiodo)benzene (2m)**:[21] white microcrystalline solid (718 mg, obtained from 2

mmol of starting material, purity 90% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 2.01 (s, 6H), 1.35 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.4, 155.5, 134.5, 128.2, 118.1, 31.1, 20.4.

**4,4'-Bis(diacetoxyiodo)biphenyl (2o)**:[22] white microcrystalline solid (874 mg, obtained from 2 mmol of starting material, purity 98% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.5 Hz, 4H), 7.67 (d, *J* = 8.5 Hz, 4H), 2.04 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.8, 142.7, 135.6, 129.7, 121.2, 20.2.

**(Dipropionyloxyiodo)benzene (10)**:[23] colorless prisms (518 mg, obtained from 2 mmol of starting material, purity 96% by iodometry); $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.59 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.49 (dd, *J* = 8.5, 7.5 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 4H), 1.07 (t, *J* = 7.6 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 179.5, 134.8, 131.6, 130.8, 121.7, 27.2, 9.8.

**Synthesis of 3-Iodosylbenzoic Acid (2n)**

To a vigorously stirred suspension of $NaClO{\bullet}5H_2O$ **8** (329 mg, 2.0 mmol) and 3-iodobenzoic acid (**1n**) (496 mg, 2 mmol) in MeCN (1.5 mL) was added AcOH (344 μL, 3.0 mmol) slowly at room temperature under air and the mixture was stirred for 10 minutes. After the reaction mixture was

added $H_2O$ (10 mL), the solid thus generated was filtered and washed twice with $H_2O$ (10 mL), followed by twice with acetone (10 mL) and $Et_2O$ (10 mL) (removes NaCl, starting materials, and water). The residue was dried at room temperature in the dark overnight to give 3-iodosylbenzoic acid (**2n**) (435 mg (98% purity), 81%) as a pale yellow solid. The purity of **2p** (98%) was determined by common iodometric titration using 10% KI aqueous solution, AcOH, and 0.1 M $Na_2S_2O_3$ aqueous solution.

**3-Iodosylbenzoic acid** (**2n**):[24] ATR-FTIR (neat) ν = 3082, 1650, 1622, 1265, 1171, 745, 707, 534 $cm^{-1}$; $^1H$ NMR ($CDCl_3$-TFA 20:1): δ = 8.95–8.93 (m, 1H), 8.51–8.45 (m, 2H), 7.83–7.79 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 169.9, 140.3, 136.9, 135.2, 132.4, 132.1, 127.3.

**Synthesis of Hydroxy(tosyloxy)iodobenzene 11**

To a vigorously stirred suspension of NaClO•$5H_2O$ **8** (329 mg, 2.0 mmol) and iodobenzene (**1a**) (224 μL, 2 mmol) in MeCN (1.5 mL) was added AcOH (343 μL, 6.0 mmol) slowly at room temperature under air and the mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (20 mL), the mixture was filtered and solvents were removed under reduced pressure to give a pale yellow solid, which was added *p*-toluenesulfonic acid monohydrate (380 mg, 2 mmol) in MeCN (1.5 mL) and stirred at room temperature for 10 minutes. After addition of $Et_2O$ (10 mL), the resulting white precipitate was collected by filtration. The residue was washed several times with acetone (5 mL)

and $Et_2O$ (5 mL) to give hydroxy(tosyloxy)iodobenzene **11** (612 mg, yield 78%) as a microcrystalline solid.

**Hydroxy(4-toluenesulfonyloxy)iodobenzene** (**11**):[25] $^1$H NMR (500 MHz, $CD_3CN$): δ = 8.10 (br d, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56–7.49 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): δ = 146.0, 138.2, 135.0, 132.9, 131.6, 128.6, 126.0, 124.0, 21.3.

**Synthesis of Bis(trifluoroacetoxy)iodobenzene (12)**

To a vigorously stirred suspension of NaClO•5$H_2O$ **8** (330 mg, 2.0 mmol) and iodobenzene (**1a**) (224 μL, 2 mmol) in MeCN (1.5 mL) was added AcOH (342 μL, 6.0 mmol) slowly at room temperature under air and the mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (20 mL), the reaction mixture was added trifluoroacetic acid (1.49 g, 13 mmol) and chlorobenzene (10 mL) and concentrated under reduced pressure. The residue was washed several times with hexane by decantation to give bis(trifluoroacetoxy)iodobenzene (**12**) (503 mg, 83%) as a microcrystalline solid.

**Bis(trifluoroacetoxy)iodobenzene** (**12**):[26] $^1$H NMR ($CDCl_3$, 500 MHz): δ = 8.22 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.75 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.62 (dd, *J* = 8.4, 7.5 Hz, 2H); $^{19}$F NMR ($CDCl_3$, 470 MHz): δ -73.45 (s, 6F); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): δ 161.1 (q, $^2J_{CF}$ = 40.8 Hz), 135.2, 133.7, 132.0,

122.8, 112.9 (q, $^1J_{CF}$ = 289 Hz).

**One-pot Synthesis of Iodosylbenzene (13)**

To a vigorously stirred suspension of NaClO•5$H_2O$ **8** (330 mg, 2.0 mmol) and iodobenzene (**1a**) (224 μL, 2 mmol) in MeCN (1.5 mL) was added AcOH (344 μL, 6.0 mmol) slowly at room temperature under air and the mixture was stirred for 10 minutes. After addition of 3 M NaOH aqueous solution (3 mL, 9 mmol), the mixture was stirred for 10 minutes. The yellow solid thus generated was filtered and washed three times with $H_2O$ (10 mL), followed by acetone (5 mL) and $Et_2O$ (5 mL). The residue was dried under reduced pressure overnight to give iodosylbenzene (**13**) (320 mg (97% purity), 70%) as light yellow powder. The purity of **13** was determined by common iodometric titration using 10% KI aqueous solution, AcOH, and 0.1 M $Na_2S_2O_3$ aqueous solution. **Iodosylbenzene** (**13**):[27] mp 208 ºC (dec); ATR-FTIR (neat) ν = 3048, 1672, 1567, 1470, 1439, 1172, 1047, 995, 800–650, 460 $cm^{-1}$; $^1$H NMR (MeOH-$d_4$, 500 MHz): δ = 8.01 (br d, $J$ = 7.3 Hz, 1.2H), 8.0 (br d, $J$ = 6.7 Hz, 0.8H), 7.7–7.5 (m, 3H). The splitted peaks in $^1$H NMR spectrum are probably responsible for the formation of (dimethoxyiodo)benzene-$d_6$ and its μ-oxo dimer [PhI($OCD_3$)OI(O$CD_3$)Ph].

**Synthesis of Iodonium Ylide 14**

To a vigorously stirred suspension of NaClO•5$H_2O$ **8** (467 mg, 2.8 mmol) and iodobenzene (**1a**) (318 μL, 2.8 mmol) in MeCN (1.5 mL) was added AcOH (480 μL, 8.4 mmol) slowly at room temperature under air and the mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (20 mL), the mixture was filtered and solvents were removed under reduced pressure to give a pale yellow solid, which was added dimedone (390 mg, 2.8 mmol), $K_2CO_3$ (1.26 g, 9.1 mmol), and EtOH (2.8 mL). After stirring the mixture at room temperature for 30 minute, the resulting orange suspension was added 5 mL of water and extracted with $CH_2Cl_2$ (5 mL X 4). The combined organic phase was dried over $Na_2SO_4$, filtered, and solvents were removed under reduced pressure to give iodonium ylide **14** (842 mg, 88%) as a white microcrystalline solid.

**5,5-Dimethyl-2-(phenyl-λ$^3$-iodanylidene)cyclohexane-1,3-dione** (**14**):[28] $^1$H NMR ($CDCl_3$, 500 MHz): δ = 7.83 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 8.0, 7.5 Hz, 2H), 2.51 (s, 4H), 1.07 (s, 6H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): δ = 188.4, 133.8, 131.5, 131.3, 112.0, 94.6, 50.6, 32.0, 28.1.

**Synthesis of Imino-λ$^3$-iodane 15**

To a vigorously stirred suspension of NaClO•5$H_2O$ **8** (328 mg, 2.0 mmol) and iodobenzene (**1a**) (224 μL, 2.0 mmol) in MeCN (1.5 mL) was added AcOH (340 μL, 6.0 mmol) slowly at room temperature under air and the mixture was stirred slowly at room temperature under air and the

mixture was stirred for 10 minutes. After addition of $CH_2Cl_2$ (20 mL), the mixture was filtered and solvents were removed under reduced pressure to give a pale yellow solid, which was added a mixture of *p*-nitrobenzenesulfonamide (404 mg, 2.0 mmol) and KOH (393 mg, 7.0 mmol) in MeOH (4.7 mL). After stirring the mixture overnight (12 h), the resulting suspension was filtered and washed with cold MeOH several times to give imino-$\lambda^3$-iodane **15** (594 mg, 73%) as pale yellow powder.

**[*N*-(4-Nitrophenylsulfonyl)imino](phenyl)-$\lambda^3$-iodane** (**15**):[29] ATR-FTIR (neat) ν = 3102, 3069, 1521, 1346, 1269, 1121, 1077, 851, 733, 616, 545, 463 $cm^{-1}$; $^1H$ NMR DMSO-$d_6$, 500 MHz): δ = 8.14–7.97 (m, 2H), 7.81–7.68 (m, 4H), 7.39 (t, *J* = 7.4 Hz 1H), 7.23 (t, *J* = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-$d_6$): δ = 151.5, 147.9, 133.4, 130.3, 130.0, 127.4, 123.6, 118.4.

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## ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx

Copies of $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra of all products.

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