Simple and Practical Method for Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and *m*-Chloroperoxybenzoic Acid

Masataka Iinuma, Katsuhiko Moriyama, Hideo Togo*

Graduate School of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan
Fax +81(43)2902792; E-mail: togo@faculty.chiba-u.jp

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Abstract: Various [(diacetoxy)iodo]arenes bearing 4-methylphenyl, phenyl, 4-nitrophenyl, 3-nitrophenyl, 4-cyanophenyl, 4-bromophenyl, 4-methoxycarbonyphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(*N*,*N*,*N*-trimethylammonium)methylphenyl groups were efficiently prepared by the treatment of iodoarenes with *m*-chloroperoxybenzoic acid in acetic acid. The great advantage of the present method is the easy preparation and isolation of [(diacetoxy)-iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 4-cyano, 4-methoxycarbonyl, and 3,5-bis(trifluoromethyl) groups, on the aromatic ring.

Key words: [(diacetoxy)iodo]arene, *m*-chloroperoxybenzoic acid, iodoarene, oxidation, acetic acid, electron-deficient aromatic ring

Hypervalent iodine reagents have received considerable attention for use in organic synthesis due to their nonmetallic and less toxic nature, making them environmentally benign as well as their excellent oxidation ability with high chemoselectivity.[1] Especially [(diacetoxy)iodo]-benzene (DIB) is one of the most typical and well-used hypervalent iodine reagents and can be used for various oxidative reactions.[2] As typical and practical methods for the preparation of [(diacetoxy)iodo]arenes, they are generally prepared by the reaction of iodoarenes with peracetic acid,[2a] which is generated from the reaction of acetic anhydride and hydrogen peroxide, and with sodium peroxoborate tetrahydrate ($NaBO_3 \cdot 4H_2O$),[3a] as less toxic and direct methods. Another method for the preparation of [(diacetoxy)iodo]arenes involves the two-step conversion of iodoarenes with CrO_3 in a mixture of sulfuric acid and acetic anhydride, followed by the treatment with ammonium acetate.[3b] This method has a strong oxidation ability furnishing [(diacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro and 4-cyano groups, in good yields. However, it requires two steps and CrO_3 is highly toxic. Recently, the preparation of [(diacetoxy)-iodo]arenes from the reaction of iodoarenes with potassium peroxodisulfate ($K_2S_2O_8$) in a mixture of sulfuric acid and acetic acid was reported as another less toxic method.[3c] However, the preparation of [(diacetoxy)iodo]arenes bearing electron-deficient aromatic groups, such as 4-nitro[(diacetoxy)iodo]benzene, 4-cyano[(diacetoxy)iodo]-benzene, 4-methoxycarbonyl[(diacetoxy)iodo]benzene, and 3,5-bis(trifluoromethyl)-1-[(diacetoxy)iodo]benzene, with peracetic acid,[2a] sodium peroxoborate in acetic acid,[3a] or potassium peroxodisulfate[3c] is very difficult and generally, the yields of [(diacetoxy)iodo]arenes bearing those electron-withdrawing groups are extremely low even if the reactions are carried out under heating conditions for a long reaction time. Recently, the preparation of [bis(trifluoroacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 3-nitro, and 4-trifluoromethyl groups on the aromatic ring, with iodoarenes and Oxone® in trifluoroacetic acid was reported.[4]

On the other hand, recently, in situ formation of hypervalent iodines from the reaction of iodobenzene and *m*-chloroperoxybenzoic acid (MCPBA) for use in organic synthesis has become very popular.[5] We previously reported the direct preparation of [(hydroxy)(tosyloxy)-iodo]arenes from the reaction of iodoarene and $PTSA \cdot H_2O$ with MCPBA,[6a] the α-tosyloxylation of ketones with iodobenzene, $PTSA \cdot H_2O$, and MCPBA,[6b–d] the preparation of oxazoles from ketones with nitriles, iodobenzene, MCPBA, and TfOH,[6e,f] and the formation of benzosultams from 2-arylethanesulfonamides, iodobenzene, and MCPBA.[6g,h] During this study, we found that [(diacetoxy)iodo]arenes can be isolated by the reaction of iodoarenes with MCPBA in acetic acid, and the products can be obtained by simple precipitation and subsequent filtration, after chloroform extraction of the reaction mixture. The great advantage of the present method is that [(diacetoxy)iodo]arenes bearing electron-withdrawing groups on the aromatic ring, such as 4-nitro, 3-nitro, 4-cyano, 4-methoxycarbonyl, 3,5-bis(trifluoromethyl), and 4-(*N*,*N*,*N*-trimethylammonium)methyl group, can be prepared in good yields by the simple experimental procedure. It is well known that MCPBA is a stronger oxidant than peracetic acid, because the 3-chlorophenyl group is an electron-withdrawing group connected to the peracid group in MCPBA.

Thus, to a solution of 4-iodonitrobenzene (**1c**) in acetic acid was added MCPBA, and the mixture was stirred at 55 °C for 48 hours. After the reaction, water was added to the mixture, and 4-nitro[(diacetoxy)iodo]benzene (**2c**) was extracted with chloroform. After being dried over Na_2SO_4, filtration, and removal of the solvent, diethyl ether and hexane were added to the residue to provide 4-nitro[(diacetoxy)iodo]benzene (**2c**) in 81% yield as a pure isolated product.[7] 4-Nitro[(diacetoxy)iodo]benzene could not be obtained by the peracetic acid method and the peroxoborate tetrahydrate method, respectively, in our study, due to the lower oxidation ability of those oxidants compared to MCPBA. The reaction progress was easily

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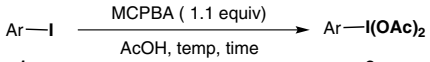
monitored by TLC. When 4-iodotoluene (**1a**) and iodobenzene (**1b**), which are much more reactive than 4-iodonitrobenzene (**1c**), were used, each mixture of 4-iodotoluene or iodobenzene with MCPBA in acetic acid was stirred at room temperature to provide 4-[(diacetoxy)iodo]toluene (**2a**) in 71% yield or [(diacetoxy)iodo]benzene (**2b**) in 83% yield, as a pure isolated product (Table 1, entries 1–3). Other [(diacetoxy)iodo]arenes could be obtained in good yields by the same procedure (Table 1, entries 4–9). Thus, using this method, both [(diacetoxy)iodo]arenes bearing an electron-deficient aromatic group, such as 4-nitrophenyl, 3-nitrophenyl, 4-cyanophenyl, 4-methoxycarbonylphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(*N*,*N*,*N*-trimethylammonium)-methylphenyl, and [(diacetoxy)iodo]benzene bearing an electron-rich aromatic group, such as 4-methylphenyl, could be obtained in good yields by the same procedure, although the reaction temperature and the reaction time would depend on the reactivity of the substrates.

Table 1 Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and MCPBA



1 **2**

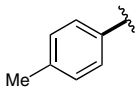
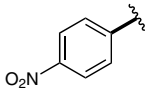
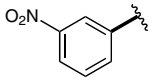
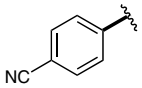
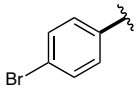
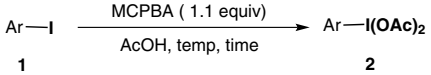
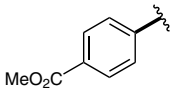
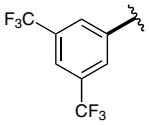
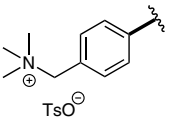
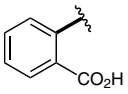
Entry	Ar	Temp (°C)	Time (h)	Product **2**	Yield (%)[a]
1	 **1a**	r.t.	24	**2a**	71
2	 **1b**	r.t.	15	**2b**	83
3	 **1c**	55	48	**2c**	81
4	 **1d**	55	24	**2d**	78
5	 **1e**	55	9	**2e**	80
6	 **1f**	r.t.	24	**2f**	76

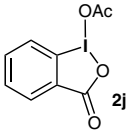
Table 1 Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and MCPBA (continued)



1 **2**

Entry	Ar	Temp (°C)	Time (h)	Product **2**	Yield (%)[a]
7	 **1g**	r.t.	24	**2g**	70
8	 **1h**	55	24	**2h**	66
9	 **1i**	55	24	**2i**	82
10	 **1j**	55	24	**2j**	80[b]

[a] Isolated yield.
[b] Product was compound **2j**.

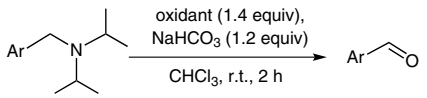


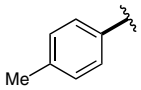
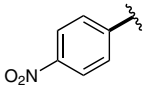
2j

1-Acetoxy-1,2-benziodoxole-3(1*H*)-one, a cyclic trivalent iodine, could also be obtained from 2-iodobenzoic acid with MCPBA in good yield (Table 1, entry 10). When the present reaction was carried out with 20 mmol of 4-iodonitrobenzene with MCPBA at 55 °C, 4-nitro[(diacetoxy)iodo]benzene was obtained in over 80% yield. Thus, the scale-up preparation of these [(diacetoxy)-iodo]arenes can be carried out easily.

The chemistry of 4-nitro[(diacetoxy)iodo]benzene (**2c**), which may has a stronger oxidation ability than DIB (**2b**), has not been studied well. Recently, the oxidative deamination of (*N*,*N*-diisopropylamino)methylarenes with DIB at 60 °C to produce aromatic aldehydes was reported.[8] Thus, we compared the reactivity of 4-nitro[(diacetoxy)iodo]benzene (**2c**) and DIB (**2b**) for the oxidative deamination of (*N*,*N*-diisopropylamino)methylarenes to produce aromatic aldehydes at room temperature, as shown in Table 2. The results indicate that 4-nitro[(diacetoxy)iodo]benzene (**2c**) is a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diiso-

Table 2 Oxidative Reaction of Tertiary Amines with **2b** and **2c**



Entry	Ar	Oxidant	Yield (%)[a]
1		**2b**	48
2		**2c**	95
3		**2b**	45
4		**2c**	91
5		**2b**	51
6		**2c**	92

[a] Isolated yield.

propylamino)methylarenes to give the corresponding aromatic aldehydes in good yields, while DIB (**2b**) is not effective at room temperature. Thus, 4-nitro[(diacetoxy)iodo]benzene (**2c**) has a stronger oxidation ability than DIB (**2b**). We believe the wide synthetic utility of 4-nitro[(diacetoxy)iodo]benzene (**2c**) compared to DIB (**2b**) will open doors to a new route in organic synthesis.

In conclusion, various [(diacetoxy)iodo]arenes bearing 4-methylphenyl, phenyl, 4-nitrophenyl, 3-nitrophenyl, 4-cyanophenyl, 4-bromophenyl, 4-methoxycarbonylphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(*N*,*N*,*N*-trimethylammonium)methylphenyl groups were efficiently prepared by the treatment of iodoarenes with MCPBA in acetic acid. The scale-up preparation of [(diacetoxy)-iodo]arenes is easily accomplished. The great advantage of the present method is the easy preparation and isolation of [(diacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 3-nitro, 4-cyano, 4-methoxycarbonyl, and 4-(*N*,*N*,*N*-trimethylammonium)methyl groups.

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(7) **Preparation of [(Diacetoxy)iodo]benzene (2b; Non-Electron-Deficient Iodoarene)**
To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H_2O (30 mL) was added to the reaction mixture and then it was extracted with $CHCl_3$ (3 × 20 mL). After being dried over Na_2SO_4, filteration, and removal of the solvent (residue ca. 3 mL), Et_2O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et_2O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield.
Preparation of 4-Nitro[(diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene)
To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred for 48 h at 55 °C. Then, H_2O (30 mL) was added to the reaction mixture and then it was extracted with $CHCl_3$ (3 × 20 mL). After being dried over Na_2SO_4, filteration, and removal of the solvent (residue ca. 3 mL), Et_2O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to –78 °C to induce precipitation (method B). After filtration, the solids were washed with a mixture of Et_2O and hexane to provide 4-nitro[(diacetoxy)iodo]benzene in 81% yield.

Conditions for the Precipitation of (Diacetoxyiodo)arenes

Method A

Et_2O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled at 0 °C for (diacetoxyiodo)benzene, 4-cyano(diacetoxyiodo)benzene, and 1-acetoxy-1,2-benziodoxole-3(1*H*)-one.

Method B

Et_2O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled at –78 °C for 4-nitro[(diacetoxy)iodo]benzene and 3-nitro[(diacetoxy)iodo]benzene.

Method C

Et_2O (20 mL) and hexane (40 mL) were added to the residue, and the mixture was cooled at –78 °C for 4-bromo[(diacetoxy)iodo]benzene, 4-methoxycarbonyl[(diacetoxy)iodo]benzene, (diacetoxy)iodotoluene, and 3,5-bis(trifluoromethyl)-1-[(diacetoxy)iodo]benzene.

Method D

Et_2O (30 mL) was added to the residue for 4-[(diacetoxy)iodo]benzyl-*N*,*N*,*N*-trimethylammonium tosylate.

(Diacetoxyiodo)toluene

Mp 102–103 °C (lit.[3c] mp 106–108 °C). IR (KBr): 663, 1267, 1410, 1567, 1649 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$ TMS): δ = 2.00 (s, 6 H), 2.45 (s, 3 H), 7.30 (d, 2 H, *J* = 8.3 Hz), 7.97 (d, 2 H, *J* = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.27, 21.43, 118.27, 131.65, 134.88, 142.57, 176.26.

(Diacetoxyiodo)benzene

Mp 156–158 °C (lit.[9] mp 161–162 °C). IR (KBr): 666, 743, 1271, 1644 cm^{-1}. ^1H NMR (500 MHz,$CDCl_3$, TMS): δ = 2.01 (s, 6 H), 7.49 (d, 2 H, *J* = 7.3 Hz), 7.60 (t, 1 H, *J* = 7.4 Hz), 8.10 (d, 2 H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.32, 121.57, 130.92, 131.69, 134.90, 176.37.

4-Nitro(diacetoxyiodo)benzene

Mp 103–104 °C (lit.[3c] mp 104–105 °C). IR (KBr): 673, 734, 849, 1274, 1348, 1414, 1515, 1570, 1644 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.03 (s, 6 H), 8.28 (d, 2 H, *J* = 9.1 Hz), 8.32 (d, 2 H, *J* = 9.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.27, 125.59, 126.72, 136.03, 149.40, 176.66.

3-Nitro(diacetoxyiodo)benzene

Mp 144–146 °C (lit.[3b] mp 148–150 °C). IR (KBr): 714, 815, 1346, 1569, 1647 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.04 (s, 6 H), 7.73 (t, 1 H, *J* = 8.2 Hz), 8.40 (d, 1 H, *J* = 9.7 Hz), 8.45 (d, 1 H, *J* = 9.3 Hz), 8.95 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.28, 120.60, 126.31, 130.07, 131.50, 140.37, 148.65, 176.78.

4-Cyano(diacetoxyiodo)benzene

Mp 168–170 °C (lit.[3b] mp 172–173 °C). IR (KBr): 673, 821, 1009, 1270, 1650, 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.03 (s, 6 H), 7.78 (d, 2 H, *J* = 8.9 Hz), 8.20 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.26, 115.65, 117.05, 125.20, 134.01, 135.54, 176.61.

4-Bromo(diacetoxyiodo)benzene

Mp 116–118 °C (lit.[3b] mp 120–122 °C). IR (KBr): 669, 746, 804, 1380, 1411, 1644 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.01 (s, 6 H), 7.62 (d, 2 H, *J* = 8.6 Hz), 7.95 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.31, 119.58, 126.80, 134.15, 136.41, 176.50.

4-Bromo(diacetoxyiodo)benzene

Mp 116–118 °C (lit.[3b] mp 120–122 °C). IR (KBr): 669, 746, 804, 1380, 1411, 1644 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.01 (s, 6 H), 7.62 (d, 2 H, *J* = 8.6 Hz), 7.95 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.31, 119.58, 126.80, 134.15, 136.41, 176.50.

4-Methoxycarbonyl(diacetoxyiodo)benzene

Mp 127–130 °C. IR (KBr): 670, 755, 826, 1284, 1410, 1566, 1642, 1716 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 2.02 (s, 6 H), 3.97 (s, 3 H), 8.13 (d, 2 H, *J* = 8.9 Hz), 8.17 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 20.25, 52.65, 125.67, 131.74, 133.00, 134.84, 165.45, 176.45. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{13}O_6INa$: 402.9649; found: 402.9639.

3,5-Bis(trifluoromethyl)-1-(diacetoxyiodo)benzene

Mp 102–104 °C (lit.[3c] mp 108–110 °C). IR (KBr): 670, 1131, 1185, 1278, 1349, 1369, 1649 cm^{-1}. ^1H NMR (125 MHz, $CDCl_3$, TMS): δ = 2.05 (s, 6 H), 8.09 (s, 1 H), 8.51(s, 2 H). ^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ = 20.24, 129.03, 123.21, 125.49, 133.73 (q, *J* = 34.4 Hz), 134.95, 176.97. ^{19}F NMR (500 MHz, $CDCl_3$, TMS): δ = –62.72 (CF_3).

4-[(Diacetoxy)iodo]benzyltrimethylammonium Tosylate

Oil. IR (neat): 566, 684, 1009, 1034, 1123, 1186, 1267, 1482, 1646 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 1.90 (s, 6 H), 2.28 (s, 3 H), 3.04 (s, 9 H), 4.60 (s, 2 H), 7.12 (d, 2 H, *J* = 7.8 Hz), 7.50 (d, 2 H, *J* = 7.7 Hz), 7.73 (d, 2 H *J* = 8.0 Hz), 8.07 (d, 2 H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.82, 21.11, 51.94, 67.05, 97.85, 125.52, 127.17, 128.16, 133.31, 134.86, 137.81, 145.59, 172.08. ESI-HRMS (+): *m/z* calcd for $C_{14}H_{21}O_4NI$: 394.0510; found: 394.0497. ESI-HRMS (anion): *m/z* calcd for $C_7H_7O_3S$: 171.0110; found: 171.0113.

1-Acetoxy-1,2-benziodoxole-3-(1*H*)-one

Mp 168–170 °C (lit.[10] mp 164–168 °C). IR (KBr): 743, 1563, 1613 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 1.90 (s, 3 H), 7.70 (t, 1 H, *J* = 7.2 Hz), 7.84 (d, 1 H, *J* = 8.0 Hz), 7.96 (t, 1 H, *J* = 7.6 Hz), 8.01 (d, 1 H, *J* = 7.5 Hz). ^{13}C NMR(500 MHz, DMSO-d_6): δ = 21.08, 120.45, 126.31, 130.40, 131.13, 131.52, 134.52, 167.77, 172.07.

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