Alternative, Easy Preparation of (Diacetoxyiodo)arenes from Iodoarenes Using Potassium Peroxodisulfate as the Oxidant

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Abstract: An easy, safe and effective method for preparing (diacetoxyiodo)arenes [ArI(OAc)$_2$], from iodoarenes is presented in this paper, using potassium peroxodisulfate as the oxidant. This procedure avoids the use of high temperature and severe reaction conditions. The reaction of the iodoarenes with potassium peroxodisulfate in acetic acid in the presence of concentrated sulfuric acid or trifluoromethane sulfonic acid at room temperature, efficiently generates the corresponding (diacetoxyiodo)arenes in high yield in a short reaction time.

Key words: (diacetoxyiodo)arenas, iodoarenes, potassium peroxodisulfate, hypervalent iodine, oxidation

(Diacetoxyiodo)arenes [ArI(OAc)$_2$], and particularly the parent compound, (diacetoxyiodo)benzene, [PhI(OAc)$_2$], have been known for a long time.[1–5] They are potent, often chemoselective oxidants, widely used in modern organic synthesis. They are also used for the facile synthesis of, for example, iodosylarenes, [bis(trifluoroacetoxy)iodo]arenes, [hydroxyl(tosyloxy)iodo]arenes (selective oxidants) and aromatic iodonium salts (arylating reagents), etc.[2–6] Several methods are available for the preparation of (diacetoxyiodo)arenes. Historically, the first member, (diacetoxyiodo)benzene was synthesized by Willgerodt in 1892, by dissolving iodosylbenzene in hot acetic acid.[7] The methods used so far are generally as follows:

i. Dissolution of iodosylarenes in glacial acetic acid;

ii. Oxidiation of iodoarenes in warm glacial acetic acid by either peracetic acid,[5] sodium perborate tetrahydrate,[8] chromium(VI)oxide,[9] or electrolytically;[3,4]

iii The exchange of chloride with acetoxy groups on (dichloroiodo)arenes using silver, lead(II) or sodium acetate, or by dissolving the substrate in acetic acid in the presence of mercury(II) oxide in chlorinated solvents;[10]

iv. The conversion of iodoarenes to (diacetoxyiodo)arenes by a two-step reaction – reaction with thionyl chloride to yield dichloroiodoarenes followed by treatment with aqueous acetic acid in pyridine;[11]

v. Refluxing iodoarenes for two hours in a solution of sodium periodate, acetic acid, acetic anhydride, and sodium acetate;[12]

vi. Oxidation of iodoarenes are using sodium percarbonate in an anhydrous ternary solvent system (Ac$_2$O–AcOH–CH$_2$Cl$_2$).[13]

The standard, and most general, method for the synthesis of (diacetoxyiodo)arenes (oxidative diacetoxylation of aryl iodide by warm peracetic acid solution) requires a very long reaction time (12–16 h), and the utmost care should be taken to maintain the temperature at exactly 40 °C. Two-step conversion of various aryl iodides to (diacetoxyiodo)arenes in the anhydrous chromium(III) oxide, acetic acid, acetic anhydride, concentrated sulfuric acid liquid system, followed by mixing with an excess of 20% aqueous ammonium acetate solution, gives (diacetoxyiodo)arenes in good yields. This procedure is 8–16 times faster and about five times less expensive than the method of McKillop and Kemp.[8] However, this method is not applicable to iodotoluenes [4-MeC$_6$H$_4$I(OAc)$_2$ was obtained from 4-MeC$_6$H$_4$I in only 20% yield]. For aryl iodides substituted with strong electron withdrawing groups, the sodium periodate system is not applicable.[12] In the sodium percarbonate method,[13] 4-iodotoluene and 4-chloroiodobenzene were unexpectedly oxidized to the corresponding iodylarenes. Here we wish to report an alternative, easy method for the preparation of (diacetoxyiodo)arenes from iodoarenes.

In our laboratory, we found a quick and efficient method for preparing (diacetoxyiodo)arenes in high yield in a short reaction time from the corresponding iodoarenes in acetic acid, using commercial potassium peroxodisulfate as the oxidant. The results are given in Table 1. Addition of concentrated sulfuric acid or trimethane sulfonic acid is essential to generate (diacetoxyiodo)arenes. Potassium peroxodisulfate is used as a strong oxidizing agent in many applications. It has the particular advantages of being almost non-hygroscopic, as well as being safe and easy to handle. The oxidation of iodoarenes to (diacetoxyiodo)arenes can be easily scaled up; given the advantages of potassium peroxodisulfate outlined above, together with the complete absence of effluent or by-product problems. The essence of our novel method is described in Scheme 1.

The oxidative reactions shown in Schemes 1 and 2 were carried out at room temperature (25 °C), in a mixture of acetic acid and concentrated sulfuric acid or trifluoromethane sulfonic acid. The presence of Potassium peroxodisulfate in the reaction mixture was indispensable

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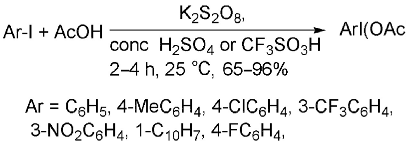
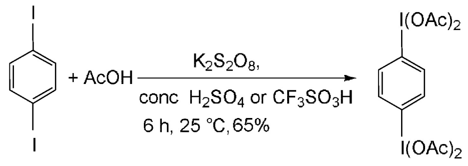


$$\text{Ar-I} + \text{AcOH} \xrightarrow[\text{2–4 h, 25 °C, 65–96\%}]{K_2S_2O_8,\ \text{conc } H_2SO_4 \text{ or } CF_3SO_3H} \text{ArI(OAc)}_2$$

Ar = C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 3-$CF_3C_6H_4$, 3-$NO_2C_6H_4$, 1-$C_{10}H_7$, 4-FC_6H_4,

Scheme 1



Scheme 2

Table 1 Preparation of (Diacetoxyiodo)arenes from Iodoarenes[a]

Entry	Iodoarenes	Additives (mmol)	Time (h)	Yield (%)
1	C_6H_5I	H_2SO_4 (4)	2	95.7
2	4-MeC_6H_4-I	H_2SO_4 (4)	2	75.2
3	4-ClC_6H_4-I	H_2SO_4 (4)	2	74.4
4	3-$CF_3C_6H_4$-I	CF_3SO_3H(6)	4	77.9
5	3-$NO_2C_6H_4$-I	CF_3SO_3H(6)	4	72.9
6	1-$IC_{10}H_7$	H_2SO_4 (4)	4	85.4
7	1,4-$I_2C_6H_4$	CF_3SO_3H(6)[b]	6	65.3
8	4-FC_6H_4-I	H_2SO_4 (4)	4	70.7

[a] The reaction of an iodoarene (1 mmol) was carried out in AcOH (5 mL) in the presence of $K_2S_2O_8$ (4 mmol) at 25 °C.

[b] CH_2Cl_2 (3 mL) was added.

because without its addition the oxidation reactions did not proceed. When potassium peroxodisulfate was replaced with sodium peroxodisulfate, the final yields of (diacetoxyiodo)arenes were lowered by about 11–16%. Iodoarenes bearing strong electron-withdrawing groups such as trifluoromethyl and nitro at the *meta* position also gave (diacetoxyiodo)arenes in good yields, but the reaction of 1-iodo-4-nitrobenzene and 1-iodo-3,5-bis(trifluoromethyl)benzene resulted in low yields (18–20%) of (diacetoxyiodo)arenes due to their decreased reactivity. This method was not applicable to iodoarenes with strong election-donating groups. For example, iodoanisoles were quickly oxidized in the reaction mixtures, but the reaction resulted in the decomposition and the formation of tarry products. This method was not applicable to trisubstituted iodoarenes due to the steric effect of the multiple substituents.

We have developed a novel preparative procedure, which is easy, quick, cheap, and possibly environmentally benign. The new method gives (diacetoxyiodo)arenes in high yields by the reaction of iodoarenes with potassium peroxodisulfate in acetic acid in the presence of concentrated sulfuric acid or trifluoromethane sulfonic acid at room temperature. We believe that the present method will be widely used because of its simplicity and convenience.

Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer and the chemical shifts are expressed in parts per million downfield from tetramethylsilane.

(Diacetoxyiodo)arenes from Iodoarenes; General Procedure
$K_2S_2O_8$ (4 mmol) was slowly added portionwise over 10 min to a stirred solution of an iodoarene (1 mmol) in AcOH (5 mL) with concd H_2SO_4 (4 mmol) or CF_3SO_3H (6 mmol) at r.t. (25 °C), and the mixture was stirred at r.t. until TLC analysis indicated completion of the reaction. In the case of 1,4-diiodobenzene, CH_2Cl_2 (3 mL) was added (this ensured the complete dissolution of 1,4-diiodobenzene). The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and H_2O (10 mL) was added. The resulting precipitate was collected by filtration, washed with H_2O (10 mL), and dried in air. A second crop of product was obtained by extraction of the filtrate with CH_2Cl_2 (3 × 10 mL) and the combined extracts were dried over anhyd Na_2SO_4; after filtration the solution was concentrated under reduced pressure. The combined crude products were purified by recrystallization from AcOH–hexane.

In the case of 1-iodo-4-nitrobenzene, CF_3SO_3H (12 mmol) was used as a promoter and 1,2-dichloroethane (5 mL) was added to dissolve the substrate.

(Diacetoxyiodo)benzene
Yield: 0.304 g (95.7%); mp 162–163 °C (lit.[14] 161.1–162.2 °C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.01$ (s, 6 H, $MeCO_2$), 7.47–7.53 (m, 2 H, ArH), 7.58–7.64 (m, 1 H, ArH), 8.07–8.12 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.19$, 134.77, 131.58, 130.79, 121.36, 20.18.

1-(Diacetoxyiodo)-4-methylbenzene
Yield: 0.250 g (75.2%); mp 106–108 °C (lit.[14] 106–110 °C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.00$ (s, 6 H, $MeCO_2$), 2.44 (s, 3 H, Me), 7.29 (d, $J = 8.6$ Hz, 2 H, ArH) 7.97 (d, $J = 8.6$ Hz, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.19$, 142.50, 134.82, 131.58, 118.14, 21.37, 20.21.

4-Chloro-1-(diacetoxyiodo)benzene
Yield: 0.265 g (74.4%); mp 110–112 °C (lit.[14] 109.8–113.2 °C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.01$ (s, 6 H, $MeCO_2$), 7.46 (d, $J = 8.6$ Hz, 2 H, ArH), 8.01 (d, $J = 8.6$ Hz, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.30$, 138.27, 136.22, 131.07, 118.68, 20.18.

1-(Diacetoxyiodo)-3-(trifluoromethyl)benzene[8]
Yield: 0.305 g (77.9%); mp 146–147 °C.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6 H, $MeCO_2$), 7.65 (t, $J = 7.9$ Hz, 1 H, ArH), 7.85 (d, $J = 7.9$ Hz, 1 H, ArH), 8.28 (d, $J = 7.9$ Hz, 1 H, ArH), 8.33 (s, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.54$, 138.10, 132.87 (q, $J_{CF} = 33.4$ Hz, CCF_3), 131.67 (q, $J_{CF} = 3.7$ Hz, $CCCF_3$), 131.21, 128.39 (q, $J_{CF} = 3.7$ Hz, $CCCF_3$), 122.72 (q, $J_{CF} = 272.8$ Hz, CF_3), 120.90, 20.18.

1-(Diacetoxyiodo)-3-nitrobenzene

Yield: 0.270 g (72.9%); mp 150–152 °C (lit.[14] 151–154.2 °C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.04$ (s, 6 H, $MeCO_2$), 7.72 (t, $J = 8.1$ Hz, 1 H, ArH), 8.39 (d, $J = 8.1$ Hz, 1 H, ArH), 8.44 (d, $J = 8.1$ Hz, 1 H, ArH), 8.94 (s, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.67$, 148.47, 140.35, 131.48, 129.94, 126.24, 120.46, 20.16.

1-(Diacetoxyiodo)naphthalene[8]

Yield: 0.309 g (85.4%); mp 174–175 °C.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.92$ (s, 6 H, $MeCO_2$), 7.51 (t, $J = 7.8$ Hz, 1 H, ArH), 7.62 (t, $J = 7.4$ Hz, 1 H, ArH), 7.71 (t, $J = 7.4$ Hz, 1 H, ArH), 7.89 (d, $J = 7.8$ Hz, 1 H, ArH), 8.09 (d, $J = 8.1$ Hz, 1 H, ArH), 8.10 (d, $J = 8.1$ Hz, 1 H, ArH), 8.49 (d, $J = 7.2$ Hz, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.49$, 137.01, 134.33, 133.46, 131.21, 129.54, 129.20, 129.07, 127.60, 126.54, 125.27, 20.16.

1,4-Bis(diacetoxyiodo)benzene

Yield: 0.290 g (65.3%); mp 226–228 °C (lit.[15] 220–223 °C).

^{1}H NMR ($CDCl_3$): $\delta = 1.96$ (s, 12 H, $MeCO_2$), 8.23 (s, 4 H, ArH).

1-(Diacetoxyiodo)-4-fluorobenzene

Yield: 0.240 g (70.7%); mp 176.5–177.5 °C (lit.[14] 177.0–179.8 °C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.01$ (s, 6 H, $MeCO_2$), 7.15–7.21 (m, 2 H, ArH), 8.07–8.13 (m, 2 H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.35$, 164.17 (d, $J_{CF} = 253.7$ Hz, CF), 137.45 (d, $J_{CF} = 8.7$ Hz, *C*CCF), 118.41 (d, $J_{CF} = 23.0$ Hz, *C*CF), 115.39 (d, $J_{CF} = 3.7$ Hz, *C*CCCF), 20.18.

1-(Diacetoxyiodo)-4-nitrobenzene[9]

Yield: 0.073 g (20.0%); mp 104–105 °C

^{1}H NMR (300 MHz, CD_3OD): $\delta = 1.96$ (s, 6 H, $MeCO_2$), 8.31 (d, $J = 8.8$ Hz, 2 H, ArH), 8.38 (d, $J = 8.8$ Hz, 2 H, ArH).

1-(Diacetoxyiodo)-3,5-bis(trifluoromethyl)benzene[16]

Yield: 0.083 g (18.0%); mp 108–110 °C.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.05$ (s, 6 H, $MeCO_2$), 8.07 (s, 1 H, ArH), 8.50 (s, 2 H, ArH).

(Diacetoxyiodo)benzene; Large-Scale

$K_2S_2O_8$ (100 mmol) was slowly added portion-wise over 20 min to a stirred solution of an iodobenzene (5.10 g, 25 mmol) in AcOH (125 mL) with concd H_2SO_4 (100 mmol) at r.t. (25 °C), and the mixture was stirred at r.t. for 4 h. The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and H_2O (100 mL) was added. The precipitate formed was collected by filtration, washed with H_2O (200 mL), and dried in air. A second crop of product was obtained by extraction of the filtrate with CH_2Cl_2 (3×25 mL); the combined extracts were dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The combined crude products were purified by recrystallization from AcOH–hexane; yield: 7.15 g (88.7%).

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