

Eco-friendly Oxidative Iodination of Various Arenes with Sodium Percarbonate as the Oxidant[†]

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Abstract: Six easy laboratory procedures are presented for the oxidative iodination of various aromatics, mostly arenes, with either molecular iodine or potassium iodide (used as the sources of iodinating species, I^+ or I^{3+}), in the presence of sodium percarbonate (SPC), a stable, cheap, easy to handle, and eco-friendly commercial oxidant.

Keywords: Iodoarenes, arenes, iodine, sodium iodide, sodium percarbonate as oxidant

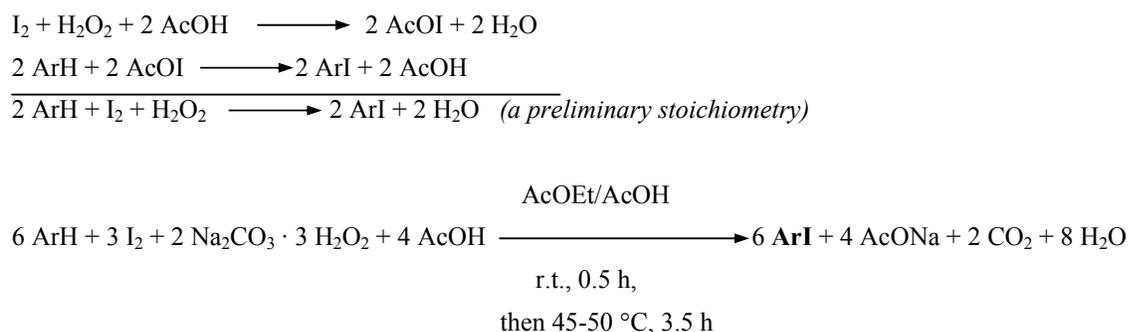
Introduction

Aromatic iodides are generally more reactive, albeit are more costly, than the respective bromides and chlorides. There are many different methods, direct and indirect, for their synthesis [1], and they are widely used in organic synthesis in chemical laboratories and, to a lesser extent, in industry. Moreover, they are able to form a variety of aromatic hypervalent iodine derivatives, which have found increasing applications in modern organic synthesis [2]. Our two latest reviews [3, 4] relate and explain a variety of direct oxidative iodination methods, suitable for both activated and deactivated aromatics, mostly arenes, devised in our laboratory since 1990, as well as our novel methods for preparing several classes of aromatic hypervalent iodine compounds, easily attainable from aromatic iodides. See also our former paper [5].

Three solid commercial products, viz. a urea–hydrogen peroxide adduct (UHP), $\text{H}_2\text{NCONH}_2 \cdot \text{H}_2\text{O}_2$, sodium perborate (SPB), $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ or $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, and sodium percarbonate (SPC), $2 \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, may be considered as ‘dry carriers’ of the hazardous and unstable hydrogen peroxide, are easy to handle, safe and stable at room temperature. Their ability to release oxidative species in water and organic media has made them useful oxidants in organic synthesis [6, 7]. The oxidative iodination reactions with using UHP [5] or SPB [7] were already reported. However, so far nobody has used SPC as a cheap [8] and eco-friendly oxidant in the oxidative iodination reactions of various aromatics, both activated and deactivated ones, which has been the aim of our present work (*vide infra*).

Results and discussion

First we have attempted to oxidatively monoiodinate four exemplary aromatic amines (Table 1) according to the stoichiometry shown in Scheme 1 (**Procedure 1**).



Scheme 1.

Supposedly, only some transient iodine(I) species, I^+ i.e. AcOI, are preponderantly acting here as weak electrophiles. Powdered diiodine was suspended in a mixture made up of ethyl acetate and glacial acetic acid (the latter was used in a large excess to decompose in full all Na_2CO_3 , releasing H_2O_2). SPC (in a 14% excess) was slowly added portionwise with stirring. Next, an aromatic amine was added, and the reaction mixture thus obtained was stirred first at room temperature for 30 min, and next at 45–50 °C for ca. 3.5 hours. The reactions were complete when the iodine coloration faded. After cooling, the reaction mixtures were quenched by pouring into excess aqueous Na_2SO_3 solutions (a reductant, used to destroy unreacted diiodine and any oxidized species). The oily or solid crude products were typically isolated and purified (see the Experimental section for details) to give the purified iodinated products in 67–86% yields (Table 1). When aniline was diiodinated in 85% yield, we added only half of the amount, i.e. 3 H-Ar-H equivalents (Scheme 1), to the starting iodinating mixture. However, *N,N*-dimethylaniline and 2-chloroaniline gave only some tarry products under the above reaction conditions. Such *easily oxidizable* aromatic amines were however readily monoiodinated according to the stoichiometry shown in Scheme 2 (**Procedure 2**).

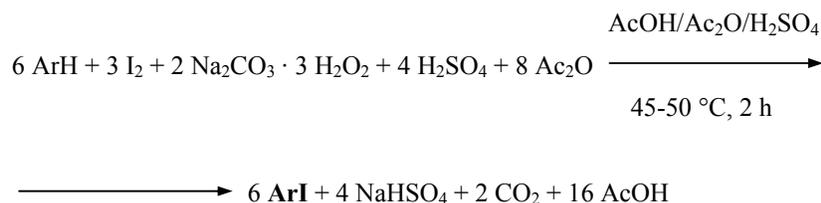


r.t., 0.5 h,
then 45–50 °C, 4 h

Scheme 2.

By comparing Schemes 1 and 2 one may deduce that the reaction media in Procedure 2 were notably *less acidic*, which was favorable for the successful oxidative iodination of the two aromatic amines. With the exception of this single important difference, the remaining reaction conditions and the reaction mechanism in Procedure 2 were nearly the same as those in Procedure 1, giving 4-iodo-*N,N*-dimethylaniline and 2-chloro-4-iodoaniline in 60 and 73% (purified) yields, respectively. However, the comparative monoiodinations of 2-bromoaniline and 2-toluidine were less effective than those in Procedure 1 (Table 1).

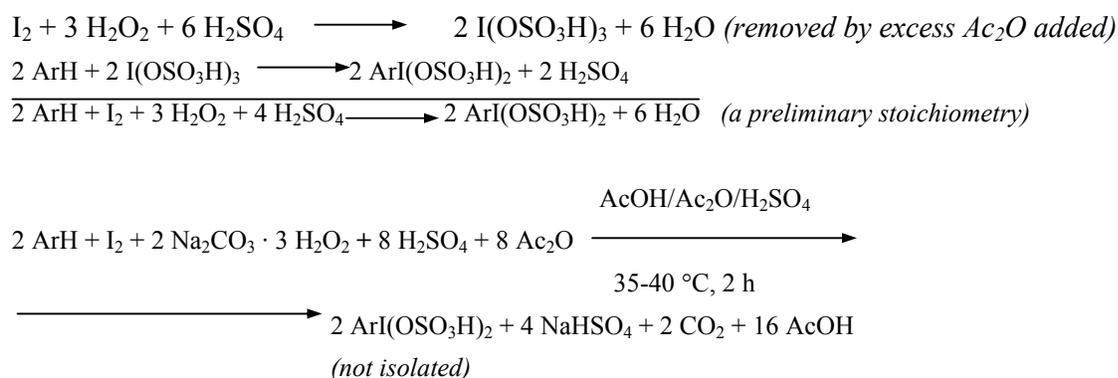
Uracil, benzene, two halobenzenes, and five weakly deactivated arenes (Table 1) were effectively oxidatively monoiodinated according to the stoichiometry shown in Scheme 3 (**Procedure 3**).



Scheme 3.

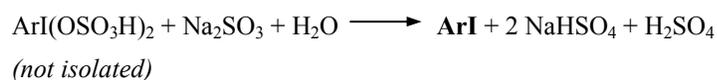
Supposedly, only some transient iodine(I) species, I^+ , i.e. IOSO_3H , are preponderantly acting there as moderate electrophiles. As above, powdered diiodine and SPC (in a 54% excess), and next a chosen arene were suspended in *anhydrous* AcOH/Ac₂O mixtures, then the mixtures were strongly acidified with *varied amounts* [9] of conc. (98%) H₂SO₄ slowly added dropwise with stirring and keeping the temperature below 10 °C. The reaction mixtures were next heated and stirred for 2 hours at 45–50 °C, where the following iodinating reactions underwent: $\text{ArH} + \text{IOSO}_3\text{H} \rightarrow \text{ArI} + \text{H}_2\text{SO}_4$. The reactions were quenched as above by pouring the final reaction mixtures into excess aqueous Na₂SO₃ solutions. The crude products were collected by filtration and worked up typically to give the purified iodinated products in 40–92% yields. When benzene was diiodinated in 83% yield, only half of the amount, i.e. 3 H-Ar-H equivalents (Scheme 3), was added to the starting iodinating mixture.

Five more strongly deactivated arenes were oxidatively monoiodinated according to the stoichiometry shown in Scheme 4 (**Procedure 4**).



Scheme 4.

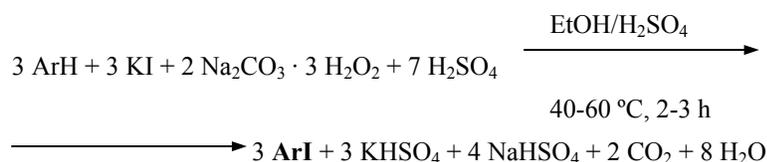
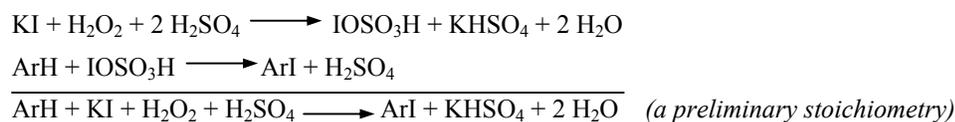
The oxidative iodination reactions were carried out in *anhydrous* AcOH/Ac₂O mixtures, containing diiodine, the said arenes and SPC, and next they were strongly acidified with *varied amounts* [9] of conc. (98%) H₂SO₄ (a catalyst and reactant, which also decomposed in full all Na₂CO₃, with releasing H₂O₂), while keeping the temperature below 10 °C. SPC was applied here in a 53% excess in respect to the amount demanded by the stoichiometry shown in Scheme 4. But in the said reaction mixtures some strongly electrophilic iodinating intermediates, I³⁺ i.e. I(OSO₃H)₃ [10], were generated, which readily reacted with the arenes to form the assumed, soluble organic iodine(III) intermediates, ArI(OSO₃H)₃ [10]. After completing the reactions carried out for 2 hours at 35–40 °C, the cooled final reaction mixtures were poured into excess aqueous Na₂SO₃ solutions to destroy any oxidizing and oxidized species and unreacted diiodine; see Scheme 5.



Scheme 5.

The crude monoiodinated products were isolated and purified similarly to those obtained in Procedures 1–3 (see the experimental section for details) to give pure monoiodinated arenes in 60–94% yields. When benzene and benzophenone were oxidatively diiodinated, we added only half of the amount, i.e. 1 H-Ar-H equivalent (Scheme 4), to the starting reaction mixtures; the purified 1,4-diiodobenzene was obtained in 83% yield, while pure 3,3'-diiodobenzophenone was afforded in 51% yield (Table 1). However, nitrobenzene was likewise monoiodinated in only ca. 5% yield; cf. Ref. 5.

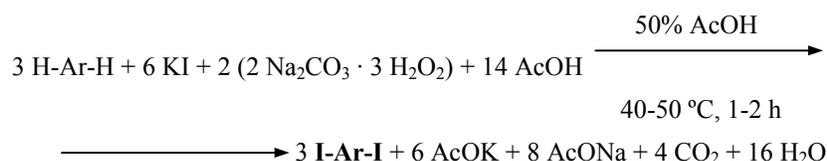
Anisole, two methoxynaphthalenes, and (for comparison) aniline were oxidatively monoiodinated using potassium iodide as the source of iodine(I) transient species, IOSO₃H. According to Merkushev [1c], a possibility of replacement of elemental iodine, usually requiring its careful grinding before use, by readily accessible and cheap alkali iodides, is often convenient – albeit larger quantities of the oxidants are spent in such oxidative iodination reactions. The said four monoiodination reactions obeyed the stoichiometry shown in Scheme 6 (**Procedure 5**).



Scheme 6.

Potassium iodide dissolved in a little water was added to stirred ethanol (which can be replaced by methanol). A chosen arene and next SPC (used in ca. 54% excess) were added portionwise with stirring. Next, a definite volume of conc. H_2SO_4 was slowly added dropwise with stirring, while keeping the temperature below 10°C . The reaction mixtures thus obtained were stirred and heated under a reflux condenser for 2–3 hours at $40\text{--}60^\circ\text{C}$; for more details see the experimental section. After cooling, the final reaction mixtures were poured into vigorously stirred $\text{CH}_2\text{Cl}_2/2\%$ aq. Na_2SO_3 biphasic mixtures. The separated organic layers dried over Na_2SO_4 were filtered, next the solvent was distilled off. The solid residues were recrystallized to give pure monoiodinated products in 53–68% yields. Recently, Iskra and co-workers [9] oxidatively iodinated several highly activated arenes with one equivalent of KI and two equivalents of 30% aqueous hydrogen peroxide solution, in methanol in the presence of conc. H_2SO_4 – it is close to our Procedure 5, however with avoiding the use of 30% aqueous H_2O_2 .

2- and 4-nitrophenol, 4-cresol, and 8-hydroxyquinoline were oxidatively diiodinated in 50% (v/v) aqueous acetic acid, using KI as the source of iodine(I) transient species, IOAc. The stoichiometry shown in Scheme 7 was obeyed (**Procedure 6**).



Scheme 7.

A definite amount of KI, a chosen phenol, and next SPC (used in ca. 84% excess) were subsequently slowly added to stirred 50% (v/v) aqueous acetic acid. The stirring was continued for 1–2 hours at $40\text{--}50^\circ\text{C}$. The cooled final reaction mixtures were poured into vigorously stirred $\text{CH}_2\text{Cl}_2/2\%$ aq. Na_2SO_3 biphasic mixtures. The separated organic layers dried over Na_2SO_4 were filtered, the solvent was distilled off, and the residues were recrystallized to give pure diiodinated products in 59–85% yields (Table 1). For comparison, we likewise monoiodinated aniline and 4-iodoaniline to obtain pure 4-iodo- and 2,4-diiidoaniline in 77 and 59% yields, respectively, with using the stoichiometry shown in Scheme 7, but corrected as follows: let one inserts there 6 ArH in place of 3 H-Ar-H to obtain the respective 6 ArI equivalents of the monoiodinated products.

Conclusions

Summing up, our easy and widely varied iodinating Procedures 1–6 reported in this paper gave mono- or diiodinated products from a large variety of different aromatics: highly activated arylamines and phenols, benzene, uracil, halobenzenes, and some activated or deactivated arenes in moderate to good yields (Table 1). The novel application of an eco-friendly, cheap [8], stable and easy to handle oxidant, viz. sodium percarbonate (SPC), makes our iodination methods to be attractive for organic chemists. In our opinion, the presented herein iodination reactions can be safely scaled up.

Experimental

General

The melting points of the freshly purified iodinated products are uncorrected and are compared with the literature data (Table 1). Their homogeneities were checked by TLC, next they were microanalyzed ($\% \text{I} \pm 0.4$), and finally their ^1H and ^{13}C NMR spectra (not shown here) were recorded at r.t. with a Bruker Avance DMX 400 MHz spectrometer in appropriate solvents, next compared with the same spectra of authentic samples and/or computed theoretical spectra. All the reagents and solvents were commercial (Aldrich, Lancaster) and were used without further purification. Elemental iodine (diiodine) should be finely powdered to facilitate its dissolution in the reaction mixtures. SPC (Aldrich) used in our iodinating experiments contained ca. 25% H_2O_2 [8] (theoretically, for $2 \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ calc. 32.5% H_2O_2).

Optimized iodinating procedures, with using sodium percarbonate (SPC) as the oxidant

Procedure 1, applicable for some arylamines

Powdered diiodine (0.51 g, 2.0 mmol; 0% excess) was suspended in a mixture made of AcOEt (8 mL) and glacial AcOH (10 mL), then SPC (0.31 g, 2.3 mmol H_2O_2 ; 14% excess) was slowly added portionwise, with stirring, within 20–30 min, next followed by an *aromatic amine* (4.2 mmol; 5% excess to prevent the possible diiodination) [when *aniline* was diiodinated, only 2.0 mmol (0% excess) of the aniline was added]. The stirring was continued for 30 min at r.t., next the temperature was raised to 45–50 °C, and the stirring was continued for a further 3.5 h under a reflux condenser. After cooling, the reaction mixtures were slowly added to stirred aq. Na_2SO_3 solutions (1 g Na_2SO_3 dissolved in 70 mL water). The precipitated crude products were collected by filtration, washed well with cold water until the filtrates were neutral, dried preliminarily by the suction, and next air-dried in the dark; they were recrystallized from appropriate organic solvents. If the semisolid crude products could not be efficiently isolated, they were extracted with CHCl_3 (3 x 10 mL), the combined extracts were washed with 2% aq. Na_2SO_3 and water, dried over anhydr. Na_2SO_4 , filtered, the solvent was distilled off, and the solidified residues were recrystallized from appropriate organic solvents to give the purified iodinated products in the yields shown in Table 1.

Procedure 2, applicable for easily oxidizable arylamines

Powdered diiodine (0.51 g, 2.0 mmol; 0% excess) was suspended in a mixture made of AcOEt (20 mL) and glacial AcOH (0.11 mL, 2.0 mmol), and SPC (0.31 g, 2.3 mmol H₂O₂; 14% excess) was slowly added portionwise, with stirring, within 20–30 min, next followed by an *aromatic amine* (4.2 mmol; 5% excess to prevent the possible diiodination). The reaction mixture was stirred at r.t. for 30 min and next at 45–50 °C for 4 h under a reflux condenser [only for the iodination of 2-toluidine: at 50–55 °C for 6 h]. After cooling, it was slowly poured, with stirring, into an aq. Na₂SO₃ solution (1 g Na₂SO₃ dissolved in 70 mL water) and the crude solid product was collected by filtration. The following workups were the same as those in Procedure 1 to give pure iodinated products in the yields shown in Table 1.

Procedure 3, applicable for benzene and some weakly deactivated arenes

Powdered diiodine (0.51 g, 2.0 mmol; 0% excess) was suspended in a mixture made of glacial AcOH (6 mL) and Ac₂O (3 mL), and next SPC (0.42 g, 3.1 mmol H₂O₂; 54% excess) was slowly added portionwise, with stirring, within 20–30 min. The stirred mixture was slowly warmed up to 30–35 °C, and a chosen *arene* (4.2 mmol; 5% excess to diminish the possible diiodination) or *benzene* (2.0 mmol; 0% excess – for its diiodination) were added. After cooling the reaction mixtures to 5–10 °C, the given below *varied amounts* [9] of conc. (98%) H₂SO₄ were slowly added dropwise with stirring and keeping the temperature below 10 °C:

- (a) 4.26 mL H₂SO₄ (7.84 g; 80 mmol) for the iodination of C₆H₅NHAc or uracil;
- (b) 4.80 mL H₂SO₄ (8.83 g; 90 mmol) for the iodination of C₆H₆, C₆H₅Br or C₆H₅Cl;
- (c) 5.33 mL H₂SO₄ (9.80 g; 100 mmol) for the iodination of 4-MeC₆H₄COOH, 4-MeC₆H₄COOMe, 4-O₂NC₆H₄Me or 4-O₂NC₆H₄OMe;
- (d) 7.50 mL H₂SO₄ (13.8 g; 140 mmol) for the diiodination of PhH.

The reaction mixtures were stirred at 45–50 °C for 2 h under a reflux condenser. After cooling, they were slowly poured, with stirring, into aq. Na₂SO₃ solutions (1 g Na₂SO₃ dissolved in 50 mL water). The precipitates were collected by filtration. The following workups were the same as those in Procedure 1 to give the purified iodinated products in the yields shown in Table 1.

Procedure 4, applicable for benzene and some more strongly deactivated arenes

Powdered diiodine (0.56 g, 2.2 mmol; 10% excess) was suspended in a mixture made of glacial AcOH (8 mL) and Ac₂O (5 mL), and next SPC (1.25 g, 9.2 mmol H₂O₂; 53% excess) was slowly added portionwise, with stirring, within 20–30 min. The reaction mixture was slowly warmed up to 30–35 °C, and a *deactivated arene* (4.0 mmol; 0% excess) or *benzene*, or *benzophenone* (2.0 mmol; 0% excess – for the diiodination reactions) were added. After cooling the reaction mixtures to 5–10 °C, the given below *varied amounts* [9] of conc. (98%) H₂SO₄ were slowly added dropwise with stirring and keeping the temperature below 10 °C:

- (a) 3.60 mL H₂SO₄ (6.60 g; 67.5 mmol) for the iodination of PhCOOH;

- (b) 4.80 mL H₂SO₄ (8.83 g; 90.0 mmol) for the iodination of PhI, PhCOOMe, 4-MeC₆H₄COOH, 4-O₂NC₆H₄Me, and for the diiodination of PhH;
(c) 6.80 mL H₂SO₄ (12.5 g; 127 mmol) for the diiodination of PhCOPh.

Next, the reaction mixtures were stirred at 35–40 °C for a further 2 h under a reflux condenser. After cooling, they were slowly added to stirred aq. Na₂SO₃ solutions (2 g Na₂SO₃ dissolved in 50 mL water). The precipitates were collected by filtration and further were worked up as those in Procedure 1 to give the purified iodinated products in the yields shown in Table 1.

Procedure 5, applicable for some aromatic ethers and aniline

KI (0.66 g, 4.0 mmol; 0% excess) prior dissolved in a little water (ca. 1 mL) was added with stirring to ethanol (20 mL). An *aromatic ether* or *aniline* (4.2 mmol; 5% excess to prevent the diiodination) and next SPC (0.84 g, 6.2 mmol H₂O₂; 54% excess) were slowly added portionwise with stirring, within 20–30 min. After cooling the mixtures to 5–10 °C, conc. (98%) H₂SO₄ (0.6 mL, 1.1 g; 11.2 mmol) was slowly added dropwise with stirring and keeping the temperature below 10 °C. Next, the reaction mixtures were stirred and heated under a reflux condenser as follows:

- (a) for 2 h at 40 °C for the iodination of PhOMe;
(b) for 2 h at 50–60 °C for the iodination of 1- or 2-MeOC₁₀H₇;
(c) for 3 h at 40 °C for the iodination of PhNH₂.

After cooling, the final reaction mixtures were slowly poured into vigorously stirred *biphasic* mixtures made of CH₂Cl₂ (50 mL) and 2% aq. Na₂SO₃ (40 mL). The organic phases were separated, washed with water, dried over anhydr. Na₂SO₄, filtered, and the solvent was distilled off. The crude solid products were recrystallized from appropriate organic solvents to give the purified iodinated products in the yields shown in Table 1.

Procedure 6, applicable for some phenols and aromatic amines

(a) For the *diiodination* of four phenols, KI (1.4 g, 8.5 mmol; 6.1% excess) prior dissolved in a little water (ca. 2 mL) was added with stirring to 50% (v/v) aq. AcOH (30 mL) containing a given *phenol* (4.0 mmol; 0% excess), next followed by slow addition of SPC (2.0 g, 14.7 mmol H₂O₂; 84% excess) within 20–30 min. The stirring was continued for 2 h at 40–50 °C under a reflux condenser. After cooling, the final reaction mixtures were slowly poured into vigorously stirred *biphasic* mixtures made of CH₂Cl₂ (50 mL) and 2% aq. Na₂SO₃ (40 mL). The following workups were the same as those in Procedure 5 to obtain pure diiodinated phenols in the yields given in Table 1.

(b) For the *monoiodination* of PhNH₂ or 4-IC₆H₄NH₂, KI (1.3 g, 8.0 mmol; 0% excess) prior dissolved in a little water (ca. 2 mL) was added with stirring to a solution of an *aromatic amine* (8.4 mmol; 5% excess to prevent the diiodination) in 50% (v/v) aq. AcOH (30 mL). SPC (2.0 g, 14.7 mmol H₂O₂; 84% excess) was slowly added portionwise with stirring within 20–30 min. The stirring was continued for 1 h at 40–50 °C under a reflux condenser. After cooling, the final reaction mixtures were slowly poured into vigorously stirred *biphasic* mixtures made of CH₂Cl₂ (50 mL) and 2% aq. Na₂SO₃ (40 mL). The following workups were the same as those in Procedure 5 to obtain pure monoiodinated arylamines in the yields given in Table 1.

Note. The final yields given in Table 1 for the purified iodinated products were calculated from the amounts of those reagents (arenes, diiodine or KI) which were used in the oxidative iodination reactions in strictly stoichiometric quantities (0% excess).

Table 1. Iodinated Pure Products Prepared.

Substrate	Procedure	Product	Yield (%) ^a	Mp (°C) (S), ^b or bp (°C/mmHg); Lit. [12] mp (°C), or bp (°C/mmHg)
PhNH ₂	1	4-IC ₆ H ₄ NH ₂	68	63–65 (H); 63–65
PhNH ₂	1	2,4-I ₂ C ₆ H ₃ NH ₂	85	93–94 (H); 95–96
4-IC ₆ H ₄ NH ₂	1	2,4-I ₂ C ₆ H ₃ NH ₂	78	96–97 (H); 95–96
2-BrC ₆ H ₄ NH ₂	1	2-Br-4-IC ₆ H ₃ NH ₂	67	71–74 (Hp); 71–72
2-MeC ₆ H ₄ NH ₂	1	4-I-2-MeC ₆ H ₃ NH ₂	86	86–87 (H); 88
PhNMe ₂	2	4-IC ₆ H ₄ NMe ₂	60	81–83 (E); 82
2-ClC ₆ H ₄ NH ₂	2	2-Cl-4-IC ₆ H ₃ NH ₂	73	60–61 (H); 62–63
2-BrC ₆ H ₄ NH ₂	2	2-Br-4-IC ₆ H ₃ NH ₂	62	70–73 (Hp); 71–72
2-MeC ₆ H ₄ NH ₂	2	4-I-2-MeC ₆ H ₃ NH ₂	48	87–88 (H); 86–88
PhH	3	PhI	40	bp 76–78/20; bp 78–80/25 [5]
PhH	3	1,4-I ₂ C ₆ H ₄	83	128–130 (L); 129
4-O ₂ NC ₆ H ₄ Me	3	2-I-4-O ₂ NC ₆ H ₃ Me	75	51–52 (N); 53–54
4-O ₂ NC ₆ H ₄ OMe	3	2-I-4-O ₂ NC ₆ H ₃ OMe	92	95–96 (L); 97
4-MeOC ₆ H ₄ CO ₂ Me	3	3-I-4-MeOC ₆ H ₃ CO ₂ Me	85	93–95 (N); 95–97
PhNHCOMe	3	4-IC ₆ H ₄ NHCOMe	62	183–185 (E); 184
PhCl	3	4-ClC ₆ H ₄ I	80	55–56 (E); 57
PhBr	3	4-BrC ₆ H ₄ I	68	91–92 (L); 91–92
uracil	3	5-iodouracil	84	276–276.5 (E); 276–278
4-RC ₆ H ₄ CO ₂ H ^c	3	3-I-4-RC ₆ H ₃ CO ₂ H ^c	92	238–239 (W); 230
PhH	4	1,4-I ₂ C ₆ H ₄	83	128–130 (L); 129
PhI	4	1,4-I ₂ C ₆ H ₄	94	128–129 (L); 129
PhCO ₂ H	4	3-IC ₆ H ₄ CO ₂ H	93	185–187 (C); 187–188
4-MeC ₆ H ₄ CO ₂ H	4	3-I-4-MeC ₆ H ₃ CO ₂ H	79	208–209 (C); 210–212
PhCO ₂ Me	4	3-IC ₆ H ₄ CO ₂ Me	60	52–53 (L); 54–55
4-O ₂ NC ₆ H ₄ Me	4	2-I-4-O ₂ NC ₆ H ₃ Me	87	51–53 (N); 53–54
PhCOPh	4	3-IC ₆ H ₄ COC ₆ H ₄ I-3'	51	140–142 (A); 141–143 [5]
C ₆ H ₅ OMe	5	4-IC ₆ H ₄ OMe	64	50–51 (H); 51–52
1-MeOC ₁₀ H ₇	5	4-I-1-MeOC ₁₀ H ₆	68	50–51 (E); 52–53 [11]
2-MeOC ₁₀ H ₇	5	1-I-2-MeOC ₁₀ H ₆	62	82–84 (E); 82–84 [11]
PhNH ₂	5	4-IC ₆ H ₄ NH ₂	53	60–62 (H); 63–65
2-O ₂ NC ₆ H ₄ OH	6	2,4-I ₂ -6-O ₂ NC ₆ H ₂ OH	80	93–94 (E); 94 [13]

Table 1. Cont.

4-O ₂ NC ₆ H ₄ OH	6	2,6-I ₂ -4-O ₂ NC ₆ H ₄ OH	72	149–150 (E); 150–151 [11]
4-CH ₃ C ₆ H ₄ OH	6	2,6-I ₂ -4-CH ₃ C ₆ H ₄ OH	83	58–59 (E); 55–58 [14]
8-hydroxyquinoline	6	5,7-diiodo-8-hydroxyquinoline	85	216–217 dec. (E); ca. 214 dec.
PhNH ₂	6	4-IC ₆ H ₄ NH ₂	77	60–62 (H); 63–65
4-IC ₆ H ₄ NH ₂	6	2,4-I ₂ C ₆ H ₃ NH ₂	59	95–96 (H); 95–96

^a Optimized yield of pure isolated product. Satisfactory microanalyses obtained for the purified products: 1% ± 0.4; their purities and homogeneities were checked by TLC and ¹H and ¹³C NMR solution spectra (not shown here).

^b S = Solvent used for recrystallization. A: acetone; C: CCl₄; E: EtOH; H: hexane; Hp: heptane; L: EtOH–H₂O (4:1); N: EtOH–H₂O (3:2); W: H₂O–EtOH (5:1).

^c R = 4-MeCONH.

References and Notes

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9. The varied amounts of conc. H₂SO₄ added to the reaction mixtures (established experimentally and given in the experimental section for each of the substrates iodinated) clearly depended on the relative reactivities of the arenes investigated. The more deactivated the arene, the more conc. H₂SO₄ had to be added to catalyze better the oxidative iodination reaction. For more details see Ref. 3, pp. 1334-1337.
10. Such strongly hygroscopic compounds as I₂(SO₄)₃, I(OSO₃H)₃, ArISO₄, ArI(OSO₃H)₂ are stable under strongly acidic and *anhydrous* conditions. For more details see the following review: Kasumov, T. M.; Koz'min, A. S.; Zefirov, N. S. The Chemistry of Inorganic Sulfates and Sulfonates of Polyvalent Iodine. *Usp. Khim.* **1997**, *66*, 936-952; *Russ. Chem. Rev.* **1997**, *66*, 843-857.
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Sample Availability: Contact the authors.