Ecofriendly Iodination of Activated Aromatics and Coumarins Using Potassium Iodide and Ammonium Peroxodisulfate

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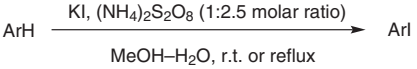
Abstract: An environmentally benign protocol for the iodination of activated aromatics, such as phenols, anilines, and hydroxycoumarins, using inexpensive commercially available potassium iodide and ammonium peroxodisulfate (1:2.5 molar equivalents per mole of substrate) in aqueous methanol (MeOH–H_2O, 6:1) at room temperature has been developed. The protocol provides for *ortho*-selective monoiodination as the predominant product without added acid and it is compatible with a number of common oxidizible functional groups, such as formyl, benzylic C–H, aromatic amines and hydroxymethyl. Good to acceptable yields of monoiodinated products in acceptable reaction times and exclusive *ortho*-iodination for 7-hydroxycoumarins, despite the presence of vinylogous electron-rich C3, are some of the key advantageous features of the method.

Key words: iodination, potassium iodide, ammonium peroxodisulfate, activated aromatics, coumarins

Iodinated aromatic and heteroaromatic compounds have attracted active contemporary interest because of their versatile synthetic utility ranging from precursors of organometallic compounds and benzynes to substrates for palladium-, nickel-, and copper-catalyzed cross-coupling reactions to form C–C, C–N, C–O, and C–S bonds.[1] Additionally, iodinated arenes possess a wide array of biological activity and find application in human and animal medicine.[2] Iodophenols, for example, are extensively used in non-evasive medical diagnostic techniques and radioiodinated photoprobes, hence they are of immense value as therapeutic and diagnostic aids. Iodocoumarins are utilized as fluorophores and intermediates for the synthesis of coumarin C-ribosides that are effective photophysical probes for the study of oligonucleotide dynamics.[3] Recently, iodinated umbelliferones have been elaborated into dihydrofuroangelicins and dihydrofuropsoralins with pronounced cytotoxicity against KB cells and they have properties that combat skin diseases such as psoriasis and vitiligo.[4] However, the iodofunctionalization of arenes and heteroarenes is frequently not facile due to the weak electrophilic nature of the iodonium ion coupled with the relatively weak bond strength of C–I compared to C–Br and C–Cl. The reversibility of the reaction with release of hydrogen iodide necessitates the use of oxidizers to make it practicable. Numerous oxidizing agents, including HgO,[5a] Oxone,[5b] Ag_2SO_4,[5c] $NaIO_4$,[5d] HIO_4,[5e] CrO_3,[5f] $Pb(OAc)_4$,[5g] I_2O_5,[5h] silica–$Bi(NO)_3$·5 H_2O,[5i] and TlOAc,[5j] have been used as a hydrogen iodide trap. However, these oxidizers are often harsh and involve toxic heavy metals, hence they are environmentally unacceptable. It was our aim to develop a mild, selective method for the iodofunctionalization of activated aromatics, particularly for phenols and hydroxycoumarins using commercially available inexpensive reagents under environmentally benign conditions. The oxyiodination strategy that utilizes an iodide salt in combination with a metal-free ecofriendly oxidizing agent appealed to us. In fact, halogenation in Nature occurs by way of oxidative halogenation involving haloperoxidase enzymes that oxidize halide salts into reactive hypohalous derivatives. To this end, potassium iodide in combination with ammonium peroxodisulfate was an attractive candidate. Potassium iodide is available in high purity and it is less expensive than sodium and ammonium iodide. It can be oxidized with ammonium peroxodisulfate, which is also an inexpensive, easily available reagent. It is a 'green' oxidizer that is widely used in industry for bleaching waste water treatment and it has been utilized to accomplish the oxidation of alkenes,[6] benzyl alcohols,[7] and substituted aromatics,[8] the cleavage of procarbonyl imine derivatives, such as oximes and phenylhydrazones,[9] the deprotection of allyl ethers,[10] and the solid-state microwave-assisted cleavage of 1,3-dithianes and dithiolanes on wet montmorillonite K-10 clay.[11] Herein, we describe the results of the iodination of a wide variety of aromatics and hydroxycoumarins with potassium iodide and ammonium peroxodisulfate in aqueous methanol (Scheme 1).



Scheme 1

We selected phenol as representative of activated aromatics and set out to optimize the iodination conditions. Selective monoiodination of phenol is elusive unless some directive influence of substituents is operative and, therefore, it was surmised that phenol represents a substrate that would give a good feel for the mildness as well as the selectivity of the iodinating reagent. Iodination of phenol with KI–$(NH)_4S_2O_8$ proved was unsuccessful in dry methanol and also in acetonitrile (Table 1, entries 1 and 2). On the other hand, iodination with the same reagent system in water, with and without anionic surfactant, sodium dodecyl sulfate (SDS) [H_2O (5 mL), SDS (0.4 mmol)] well

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above its critical miceller concentration (cmc), was also disappointingly sluggish even at elevated temperatures (50–60 °C) (entries 8–10). Attempted iodination in aqueous acetonitrile (MeCN–H_2O, 4:1) was also not encouraging either in terms of reaction time and yield of 2-iodophenol (**1a**) (entry 3). Aqueous methanol (6:1) was found to be the medium of choice furnishing **1a** and 2,6-diiodophenol (**1b**) in 65% and 10% yields, respectively in an acceptable reaction time (20 h) (entry 6). Observed regioselectively was in sharp contrast to exclusive *para*-iodination of phenol with iodine and tetrabutylammonium persulfate[12] in aprotic solvent, acetonitrile (20 °C, 30 h). Whereas iodine–thallium(I) acetate[5j] allowed *ortho*-selective iodination of phenols, the present method constitutes a metal-free *ortho*-selective iodinating system for phenols. For selective monoiodination, a stoichiometric ratio of substrate/iodide/oxidizer 1:1:2.5 was found to be rewarding from an iodine atom economy standpoint. Herein, we report the results of the iodination of a wide array of activated aromatics and coumarins using this reagent combination (Table 2). In view of the importance of polyiodinated phenols in medical diagnostics, we explored triiodination of phenol with 3.3 molar equivalents of potassium iodide along with 7 molar equivalents of ammonium peroxodisulfate at room temperature for ten hours and to our satisfaction, 2,4,6-triiodophenol (**1c**) was isolated as the exclusive product in 88% yield (entry 1). Notably, no mineral acid was added for the iodination of phenols. Previously, a combination of molecular iodine and potassium peroxodisulfate (0.5:2.2 molar ratio)[13] was utilized for the synthesis of iodoarenes, but this is effective only in the presence of concentrated sulfuric acid (3 mmol) or trifluoroacetic acid in dichloromethane as an activator; formation of resinous products and over-oxidation for electron-rich oxidation-prone aromatics are some of the serious limitations of this protocol. Successful iodination of anisole with potassium iodide and 30% hydrogen peroxide in methanol[14] also required one equivalent of concentrated sulfuric acid to arrest the decomposition of hydrogen peroxide to oxygen. We envisaged that the key to the efficacy of the present combination was the in situ generation of sulfuric acid upon hydrolysis of the acidic salt ammonium peroxodisulfate. Subsequent release of peroxomonosulfuric acid (Caro's acid) by way of hydrolysis of peroxodisulfuric acid and oxidation of iodide to iodine by either of the peracids under the acidic conditions follow. Oxidation of iodide to iodine with peroxodisulfuric acid and Caro's acid are not mutually exclusive and may compete with each other (Scheme 2). To support our contention, a solution of ammonium peroxodisulfate (2 mmol) in methanol–water (6:1, 4 mL) was found to exhibit a pH of 1.19 at 33 °C; addition of potassium iodide (1 mmol) to it sharply increased its pH to 6.43. These observations coupled with the fact that this combination proved ineffective in dry methanol strongly suggest the crucial role of water in the iodination process. The actual iodinating species involved is not clear to us. The facilitating role of methanol as solvent in iodination may be due to its solubilizing influence on iodine and the substrate as well. However, the possibility of liberated iodine being oxidized to a stronger iodonium ion equivalent in the form of methyl hypoiodite in the presence of an excess of a potent oxidizer such as peroxodisulfuric acid cannot be ruled out and there is literature precedent for an analogous reaction in the case of benzyltrimethylammonium dichloroperiodate based aromatic iodinations.[15]

Table 1 Optimization Experiments for the Oxyiodination of Phenol

Entry	Ratio[a] KI/$(NH_4)S_2O_8$	Solvent	Additive	Time (h)	Yield[b] (%)	
					1a	**1b**
1	1:2	MeOH	–	10	0	0
2	1:2	MeCN	–	10	8	0
3	1:2	MeOH–H_2O (4:1)	–	20	55	10
4	1:1.5	MeOH–H_2O (2:1)	–	30	45	6
5	1:2	MeOH–H_2O (6:1)	–	20	60	8
6	1:2.5	MeOH–H_2O (6:1)	–	20	65	10
7	1: 2	MeCN–H_2O (4:1)	–	20	35	8
8	1:2	H_2O	–	48	30	5
9	1:2	H_2O	–	40	20	8
10	1:2	H_2O	SDS (10 cmc)	40	30	10
11	1:2	*t*-BuOH–H_2O (6:1)	–	12	32	5
12	1:2	AcOH–H_2O (1:3)	–	10	40	15[c]

[a] Ratio = mol equiv ratio of KI/$(NH_4)S_2O_8$ per mmol of substrate; the iodination of phenol was carried on a 1-mmol scale.
[b] 2-Iodophenol (**1a**) and 2,6-diiodophenol (**1b**) were products of iodination of phenol.
[c] Several other products were formed in addition.

$$(NH_4)_2S_2O_8 + H_2O \longrightarrow (NH_4)_2SO_5 + H_2SO_4$$
$$(NH_4)_2S_2O_8 + H_2SO_4 \longrightarrow H_2S_2O_8 + (NH_4)_2SO_4$$
$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
$$2\,KI + H_2SO_5 + H_2SO_4 \longrightarrow I_2 + 2\,KHSO_4 + H_2O$$
$$2\,KI + H_2S_2O_8 \longrightarrow 2\,KHSO_4 + I_2$$

Scheme 2

ortho-Iodination of phenol is tentatively due to the hydrogen-bonding interaction of the phenolic OH with MeOI through a six-membered transition state thereby promoting delivery of iodine at C2 (Scheme 3). However, this is a purely hypothetical suggestion at this stage of the investigation. In case of 3-methylphenol the mono/diiodinated product ratio (**3a/3b**) was almost identical to that for **1a/1b**, *ortho*-monoiodinated product, 2-iodo-5-methylphenol, predominating in 60% yield (Table 2, entry 3).

Table 2 Oxidative Iodination of Activated Aromatics and Coumarins with Potassium Iodide and Ammonium Peroxodisulfate

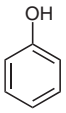
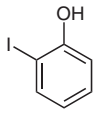
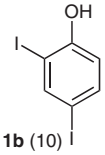
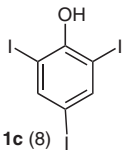
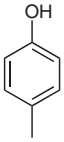
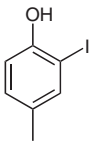
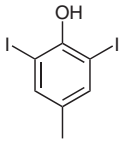
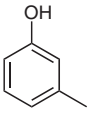
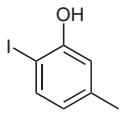
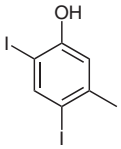
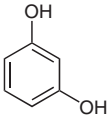
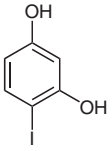
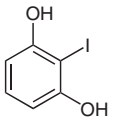
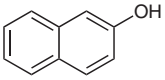
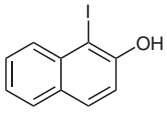
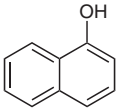
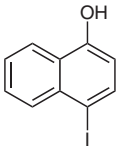
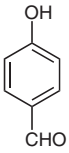
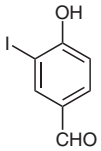
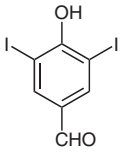
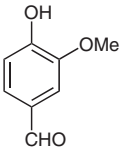
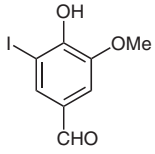
Entry	Substrate	Time[a] (h)	Product(s) [yield[b] (%)]
1		(i) 20	 **1a** (65)  **1b** (10)
		(ii) 10[c] (iii) 10[d]	**1b** (40)  **1c** (8) **1c** (88)
2		16	 **2a** (70)  **2b** (8)
3		12	 **3a** (60)  **3b** (10)
4		12	 **4a** (65)  **4b** (15)
5		12	 **5a** (95)
6		15	 **6a** (92)
7		20	 **7a** (80)  **7b** (5)
8		12	 **8a** (80)

Table 2 Oxidative Iodination of Activated Aromatics and Coumarins with Potassium Iodide and Ammonium Peroxodisulfate (continued)

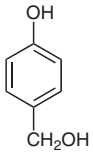
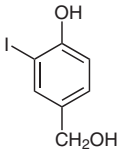
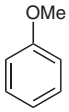
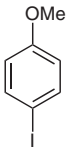
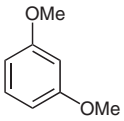
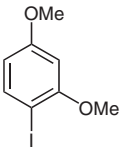
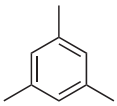
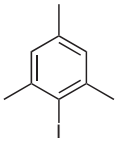
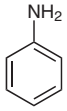
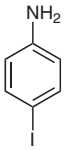
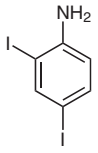
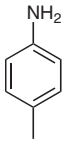
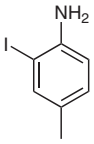
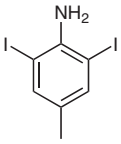
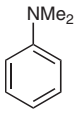
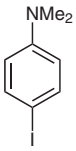
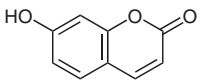
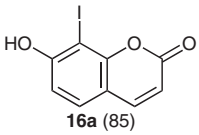
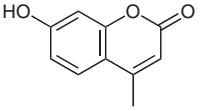
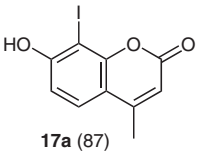
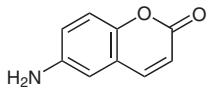
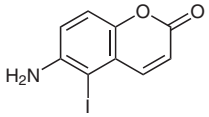
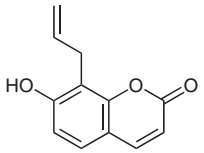
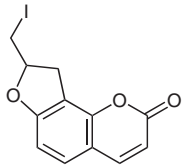
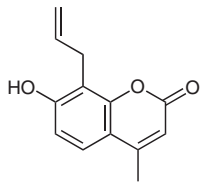
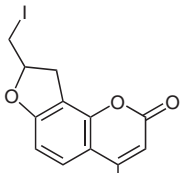
Entry	Substrate	Time[a] (h)	Product(s) [yield[b] (%)]
9		6	 **9a** (92)
10		16	 **10a** (92)
11		10	 **11a** (90)
12		12	 **12a** (94)
13		16[e]	 **13a** (55)  **13b** (8)
14		10	 **14a** (68)  **14b** (10)
15		10	 **15a** (58)
16		20	 **16a** (85)
17		24	 **17a** (87)

Table 2 Oxidative Iodination of Activated Aromatics and Coumarins with Potassium Iodide and Ammonium Peroxodisulfate (continued)

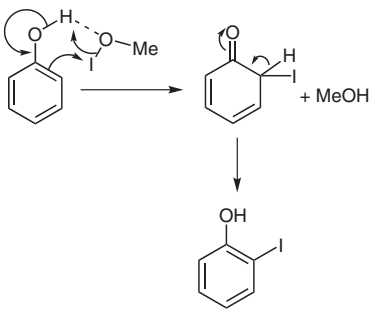
Entry	Substrate	Time[a] (h)	Product(s) [yield[b] (%)]
18		18[c]	 **18a** (75)
19		12[c]	 **19a** (66)
20		12[c]	 **20a** (68)

[a] Reaction conditions: substrate/KI/$(NH_4)_2S_2O_8$ 1:1:2.5, MeOH–H_2O (6:1), r.t.
[b] Yields refer to the chromatographically pure products characterized by spectral data (FT-IR, ^1H and ^{13}C NMR, and EIMS).
[c] Reaction conditions: substrate/KI/$(NH_4)_2S_2O_8$ 1:1:2:5, MeOH–H_2O (6:1), 50–60 °C.
[d] Reaction conditions: substrate/KI/$(NH_4)_2S_2O_8$ 1:3.3:7, MeOH–H_2O, r.t.
[e] Reaction conditions: substrate/KI/$(NH)_2S_2O_8$ 1:1:1.5, MeOH–H_2O, r.t.

ortho-Selectivity was further demonstrated in the iodination of benzene-1,3-diol which furnished 2-iodobenzene-1,3-diol (**4b**) in 15% yield despite unfavorable steric situation (entry 4). Oxidation-prone aromatic aldehydes and benzylic alcohol remained intact during the iodination (entries 7–9). However, in case of aniline, the use of 2.5 equivalents of oxidizer led to substantial formation of intractable colored oxidized products and successful *para* iodination was achieved only by its careful dropwise addition to a stoichiometric combination of potassium iodide and ammonium peroxodisulfate in 1:1.5 molar ratio (entry 13). Iodination of *N*,*N*-dimethylaniline led to 4-iodo-*N*,*N*-dimethylaniline (**15a**) as the only isolable product (entry 15). However, formation of the violet coloration characteristic of Methyl Violet dye was observed upon addition of *N*,*N*-dimethylaniline to the reagent system. Previous attempted of iodination of *N*,*N*-dimethylaniline with iodine–thallium(I) acetate[5j] resulted in the formation of **15a**, but the reaction was complicated due to the oxidation of *N*,*N*-dimethylaniline to 4,4′-methylenebis(*N*,*N*-dimethylaniline) and Methyl Violet. Analogous oxidation of *N*,*N*-dimethylaniline with iodine–silver(I) trifluoroacetate–dichloromethane[16] gave *N*,*N*,*N*′,*N*′-tetramethylbenzidine.

Iodination of 7-hydroxycoumarins (entries 16 and 17) was sluggish as expected due to the deactivating effect of the α-pyrone moiety, but it is remarkable that *ortho*-monoiodination occurred exclusively in the benzenoid ring despite substantial electron withdrawal to the vinylogous C3 position from the 7-OH group and this is so particularly for 7-hydroxy-4-methylcoumarin where C3 becomes further electron-rich due to the presence of electron-releasing 4-methyl group. Notably, exclusive bromination at C3 of 7-hydroxycourmarin was accomplished by us with *N*-bromosuccinimide in molten tetrabutylammonium bromide,[17] a hydrogen-bond base that discourages hydrogen bond formation of *N*-bromosuccinimide with the 7-OH group thereby preventing *ortho*-selective bromination. For substrates 8-allyl-7-hydroxycoumarin and 8-allyl-7-hydroxy-4-methylcoumarin bearing an allyl moiety *ortho* to the 7-OH group, iodolactonization took precedence over slower ring iodination process furnishing angular furanocoumarins (entries 19 and 20).

In conclusion, a mild ecofriendly protocol for the monoiodination of activated aromatics and coumarins using potassium iodide and ammonium peroxodisulfate has been developed. Use of commercially available, inexpensive reagents, simple procedure, good to acceptable yields and *ortho*-selective iodination for phenols and hydroxycoumarins without use of metal salts are key attractive features of the protocol.



Scheme 3

KI and $(NH_4)_2S_2O_8$ were procured from Merck, Germany and SRL, India respectively. IR spectra were recorded on a Perkin-Elmer FTIR L120-000A. NMR spectra were measured on Bruker AM-300L (300 MHz) and Bruker DPX-400 (400 MHz). Applied Biosystems MDS Sciex API 3200 were used for recording mass spectra of the compounds. Silica gel (60–120 mesh, Spectrochem, India) was used for column chromatographic separations and purification of regioisomeric and polyiodinated byproducts. PE = petroleum ether bp 60–80 °C. All products were known compounds unless otherwise given below, and their spectroscopic data were identical to those given in the literature.[18]

6-Amino-5-iodocoumarin (18a); Typical Procedure

To a stirred soln of $(NH_4)_2S_2O_8$ (570 mg, 2.5 mmol) in MeOH–H_2O (6:1, 7 mL) was added sequentially in small portions KOH (166 mg, 1 mmol) and 6-aminocoumarin (160 mg, 1 mmol). When the addition was complete the resulting mixture was heated at 50–60 °C for 18 h (TLC monitoring). MeOH was removed from the mixture under reduced pressure and the remaining material was extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed successively with 5% aq $Na_2S_2O_3$ soln (3 mL), H_2O (3 mL) and then dried (Na_2SO_4). Concentration of the dried extract followed by chromatography of the residue (silica gel, PE–EtOAc, 1:3) gave pure **18a** (215 mg, 75%); mp 138 °C.

IR (KBr): 3441, 3328, 2962, 2924, 1699, 1556, 1466, 1261, 1102, 1018, 802 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 9.6 Hz, 1 H), 7.18 (d, *J* = 9 Hz, 1 H), 6.96 (d, *J* = 9 Hz, 1 H), 6.45 (d, *J* = 9.6 Hz, 1 H).

LC-MS: *m*/*z* = 288 (M + 1).

8-(Iodomethyl)-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one (19a)

White solid; mp 164–166 °C.

IR (KBr): 3079, 3027, 1725, 1617, 1449, 1263, 1113, 1059, 836, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 9.6 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 6.23 (d, *J* = 9.6 Hz, 1 H), 5.07–5.03 (m, 1 H), 3.58–3.97 (m, 3 H), 3.22, 3.18 (2 d, *J* = 6.4, 6.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 160.9, 151.4, 143.9, 129.0, 113.3, 112.8, 112.5, 107.0, 83.4, 33.1, 8.2.

LC-MS: *m*/*z* = 329 (M + 1).

8-(Iodomethyl)-4-methyl-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one (20a)

White solid; mp 156–158 °C.

IR (KBr): 3031, 2968, 1735, 1615, 1456, 1382, 1365, 1249, 1068, 957, 840, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.4 Hz, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 6.11 (d, *J* = 0.8 Hz, 1 H), 5.07–5.02 (m, 1 H), 3.58–3.39 (m, 3 H), 3.22, 3.18 (2 d, *J* = 6.8, 6.4 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 160.9, 153.0, 150.8, 125.7, 114.4, 112.9, 111.5, 106.5, 83.5, 33.2, 19.0, 8.4.

LC-MS: *m*/*z* = 343 (M + 1).

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