

Direct halogenation of organic compounds with halides using oxone in water — A green protocol

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Abstract: Direct bromination and iodination of various aromatic compounds with NaBr and NaI using oxone (2KHSO₅·KHSO₄·K₂SO₄) in water was accomplished successfully in high-to-excellent yields. The main benefit of this protocol is the performance of the reactions in water in the presence of a harmless oxidant without the use of any organic solvents. Using NaBr and NaI as the safe sources of halogens is another advantage of the protocol. This method is easily applicable to the large-scale operations. We have also applied this method successfully for the iodocyclization of an unsaturated alcohol and an unsaturated carboxylic acid.

Key words: iodination, bromination, oxone, water.

Résumé : On a effectué avec succès la bromation et l'iodation directe de divers composés aromatiques avec du NaBr et du NaI à l'aide d'oxone (2KHSO₅·KHSO₄·K₂SO₄) dans l'eau; les rendements vont d'élevés à excellents. Le bénéfice principal de ce protocole réside dans le fait que les réactions sont effectuées dans l'eau, en présence d'un oxydant inoffensif, sans nécessité de solvant organique. L'utilisation de NaBr et de NaI comme source sécuritaire d'halogène est un autre avantage de cette méthode qui peut facilement être appliquée à des opérations d'envergure. On a aussi appliqué avec succès cette méthode à l'iodocyclisation d'un alcool et d'un acide carboxylique insaturés.

Mots-clés : iodation, bromation, oxone, eau.

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Introduction

Waste prevention rather than its treatment is of great concern for the industry and academia. For this aim, the use of less toxic materials as solvents and reagents is encouraged.¹ However, disposing organic solvents in pharmaceutical industries is their current major problem, as these solvents compose ~80% of their waste.^{2,3} Replacement of toxic, flammable, non-recyclable, expensive, and organic solvents with water in organic reactions is a great challenge for academia and chemical industries.^{4,5}

Using water is beneficial from different aspects. Water is a cheap, abundant, nontoxic, nonflammable, and green solvent. On the other hand, water with its chemical and physical properties imposes selectivity and reactivity in reactions, which cannot be achieved using organic solvents.⁶ In addition, organic compounds are insoluble in water; therefore, phase separation is easier and they can be easily isolated from aqueous media.

Recently, we have paid attention towards using water as a reaction medium. Along this line, Michael addition of amines and thiols to α,β -unsaturated ketones,⁷ regioselective iodination of aromatic compounds,^{7b} ring opening of epoxides with varieties of nucleophiles,^{7c} oxidation of sulfides to

their sulfoxides with H₂O₂,^{7d} Michael addition of indoles and pyrroles to α,β -unsaturated electron-deficient compounds,^{7e} conversion of epoxides to thiiranes and amino alcohols,^{7f} C–S bond formation via odorless thia-Michael addition,^{7g} C–C bond formation via Heck–Mizoroki reactions in water,^{7h} and highly efficient halogenation of organic compounds with halides catalyzed by CeCl₃·7H₂O using H₂O₂ as the terminal oxidant in H₂O⁷ⁱ are reported.

The aromatic halogenation reaction is an important electrophilic substitution reaction, and haloarenes are useful synthetic intermediates in the pharmaceuticals, pesticides, and agrochemical industries.⁸ In addition, haloarenes are useful and important substrates for the preparation of organometallic compounds. The other important uses of haloarenes are in Heck, Stille, Suzuki, and Sonogashira reactions.⁹ Halogenation of organic substrates requires using chlorine, bromine, or iodine. This reaction is associated with serious environmental hazards with respect to handling, transportation, and storage of chlorine, bromine, and iodine.¹⁰

Handling of halide salts is safer and easier than their molecular halogens. They are oxidized to the corresponding positive halogens or hypohalous acids by a variety of oxidants, including peroxy compounds.⁸ However, the articles describing the application of peroxy compounds for the oxidative halogenation of arenes include Ce(OH)₃/OH/SDS-H₂O,^{7b} KI/benzyltriphenylphosphoniumperoxy mono-sulfate/MeCN,¹¹ KI/H₂O₂(30%)/H₂SO₄/MeOH,¹² KI or I₂/PVP-supported H₂O₂/H₃PW₁₂O₄₀ in CH₂Cl₂,¹³ I₂ or KI/(Na₂CO₃·3H₂O),¹⁴ I₂/[(Bu₄N)₄(S₂O₈)]/MeCN or CH₂Cl₂,¹⁵ I₂/[(MePPh₃)₂(S₂O₈)]/MeCN,¹⁶ I₂/Na₂S₂O₈/MeCN,¹⁷ and NaI/H₂O₂/organotelluride cat. at pH-6 buffer in Et₂O/H₂O,¹⁸ KBr/benzyltriphenylphosphonium peroxydisulfate/ MeCN,¹⁹ Br₂ or LiBr/tetrabutylammonium peroxydisulfate/MeCN or CH₂Cl₂,²⁰ I₂/

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poly(4-vinylpyridine)-supported peroxydisulfate/MeCN,²¹ and NaI/Oxone/CH₃OH.²² The other methods using hydrogen peroxide include the use of NH₄I/H₂O₂/HOAc,²³ NH₄Br/H₂O₂/HOAc,²⁴ HX/H₂O₂/C₂H₄Cl₂/MW,²⁵ H₂O₂/I₂,²⁶ and NaBr/H₂O₂/H₂SO₄/CHCl₃.²⁷

Oxone is a ternary composite of 2KHSO₅, KHSO₄, and K₂SO₄ that is a stable peroxy inorganic compound. Oxone has a low order of toxicity when taken internally, based on animal studies. The approximate lethal dose (ALD) for rats is 2250 mg/kg.²⁸ Iodination of arenes with NH₄I in MeOH in the presence of oxone is recently reported.²⁹ This procedure encounters limitations such as the following: (i) it is applicable to electron-rich aryl compounds, (ii) usually long reaction times are required (8–48 h), and (iii) moderately deactivated aryl compounds such as bromobenzene remain intact even after 24 h.

In this article, we report a green method for the iodination and bromination of structurally different arenes by NaI and NaBr with oxone in H₂O in the absence of any organic co-solvents with high regioselectivity. In addition, halocyclization of unsaturated alcohols and a carboxylic acid with NaI/oxone system in water is also reported.

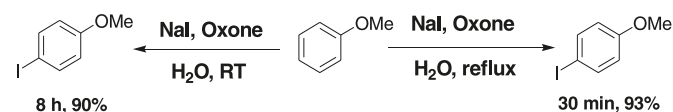
Results and discussion

In this study, we report a green procedure for the halogenation of structurally diverse arenes using NaBr and NaI salts as safe sources of halogens and oxone as a safe solid oxidant in water in the absence of any organic co-solvents. For optimization of the reaction conditions, we studied the reaction of anisole with NaI in the presence of oxone in water at room temperature. We found that the optimized molar ratio of anisole/NaI/Oxone was 1:1:0.5 mmol in 2 mL of water. The reaction proceeded well with excellent para selectivity, and after 8 h (GC or TLC), the *p*-iodoanisole was isolated in 90% yield. The structure of the isolated compound was confirmed by ¹H and ¹³C NMR and compared with an authentic sample. The reaction was also investigated under reflux conditions. The reaction proceeded to completion faster, and after 30 min (GC or TLC), the para isomer was isolated with excellent selectivity in 93% yield (Scheme 1).

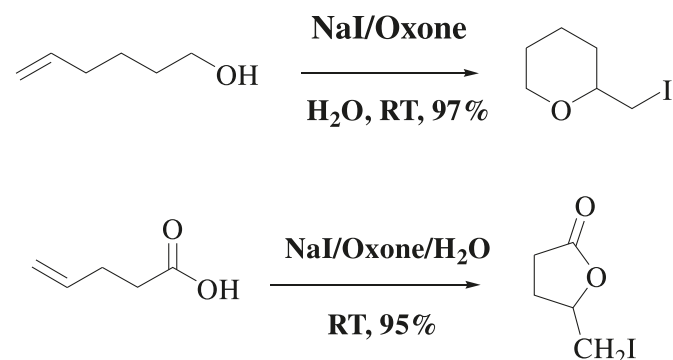
To show the general application of the method, the optimized conditions were applied to structurally different arenes. The results of this investigation are tabulated in Table 1. As it is evident from the results, this protocol is applicable to a broad spectrum of arenes, such as electron-rich aromatic compounds, toluene, benzene, bromo-, and chlorobenzenes. As shown in Table 1, electron-poor compounds like acetophenone and benzonitrile were also subjected to iodination reaction. The reaction of acetophenone proceeded very slowly, and after 48 h, the meta product was isolated in 40% yield. Benzonitrile was isolated intact from the reaction mixture after 48 h.

Bromination of arenes was also investigated by this protocol. For this purpose, we first optimized the reaction conditions for the bromination of anisole with NaBr in the presence of oxone in water as a model reaction. The optimized molar ratio of anisole/NaBr/oxone was 1:1:0.5 mmol in 2 mL of water at room temperature. In contrast to the iodination reaction, bromination proceeded well to completion after 10 min at room temperature, and the *para*-bromo com-

Scheme 1.



Scheme 2.



ound was isolated in 93% yield as the sole product. Then, we applied these conditions to electron-rich aromatic compounds, e.g., benzene, toluene, naphthalene, and chlorobenzene. The reactions proceeded well in high isolated yields. All the reactions were performed with high selectivity and only one product was isolated from the reaction mixtures. The structures of the products were also confirmed by ¹H and ¹³C NMR and were compared with authentic samples. The results are tabulated in Table 2.

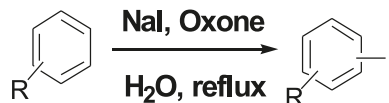
We also easily scaled up the bromination reaction of anisole, xylene, and naphthalene to 20 mmol. All the reactions proceeded well within the reaction times indicated in Table 2, and the mono-brominated compounds were isolated with the same yields as indicated in the table.

To show the advantage of using water as the reaction medium, we compared the results of the iodination of arenes with some of the reactions that proceeded in methanol,²⁹ as presented in Table 3.

Iodoetherification and iodolactonization are important and crucial reactions in organic synthesis and also for the structural elucidation of organic molecules.^{30,31} Examples include Corey's prostaglandin synthesis,³² total synthesis of tumor inhibitors, e.g., vernolepin and vernomenin,³³ and in vitamin D₂ and D₃ syntheses.³⁴

We were also interested in investigating halocyclization reactions, such as iodoetherification and iodolactonization, by this system. For this purpose, a similar molar ratio to the ratio used for the iodination of arenes was applied to the reaction of 5-hexene-1-ol and 4-pentene-1-oic acid as model compounds. Our preliminary studies show that iodination – ring-closure reaction proceeded immediately, and the corresponding iodocyclic ethers and the iodolactone were isolated in excellent yields as shown in Scheme 2.

Most of the products are known compounds, and their spectral data and physical constants along with their references are given in the Experimental section. The data of the known compounds have been found to be identical with those reported. For the unknown compounds, spectral data along with their elemental analyses are also given in the Experimental section.

Table 1. Mono-iodination of aromatic compounds using NaI/oxone/H₂O under reflux conditions.

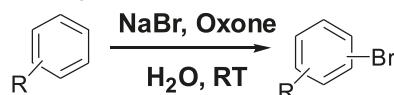
Entry	Substrate	product	Time	GC conversion (%)	Isolated yield (%)
1			15 min	100	98
2			30 min	100	93
3			10 min	100	85
4			15 min	100	89
5			15 min	100	90
6			3 h	100	90
7			3.5 h	100	87
8			6 h	100	88
9			12 h	100	85
10			12 h	100	83
11			48 h	45 ^a	40
12			48 h	–	–

^a *n*-Octane was used as an internal standard.

Conclusions

In conclusion, in this article, we have presented a green protocol for the halogenation of organic compounds using NaI or NaBr/oxone/H₂O system. We have modified the

previously reported protocol using NaI/oxone system in MeOH for the iodination of activated aromatic compounds with NaI/oxone system in H₂O as a green solvent. As we have shown, similar iodination reactions proceeded more efficiently in H₂O than in MeOH. NaI/oxone/H₂O system

Table 2. Bromination of aromatic compounds using NaBr/Oxone/H₂O at room temperature.

Entry	Substrate	product	Time (min)	GC conversion (%)	Isolated yield (%)
1			5	100	95
2			10	100	93
3			20	100	87
4			25	100	85
5			7	100	80
6			1.5 h	100	88
7			3 h	100	90
8			12 h	–	–

Table 3. A comparison between two procedures using NaI/oxone/MeOH²⁹ and NaI/oxone/H₂O for the iodination of different aromatic compounds.

Substrate	NaI/Oxone/MeOH		NaI/Oxone/H ₂ O	
	Time (h)	Conversion	Time (h)	Conversion
Bromobenzene	24	NR	12	85%
<i>m</i> -Xylene	24	99%	3	90%
Anisole	8	99%	0.5	93%

has been successfully applied to highly efficient and regioselective iodination and bromination of structurally different aromatic compounds. In addition, we have also successfully applied the protocol to highly efficient one-pot iodination/cyclization of unsaturated alcohols and iodination/lactonization of an unsaturated carboxylic acid. The method is also applicable to the large-scale reactions without any difficulties.

Experimental section

Typical procedure for the mono-iodination of 1,3-dimethoxybenzene with NaI/oxone system in H₂O

To a stirring mixture of 1,3-dimethoxybenzene (0.138 g,

1 mmol) and NaI (0.149 g, 1 mmol) in water (3 mL), oxone (0.307 g, 0.5 mmol) was added, and the mixture was refluxed for 15 min. The progress of the reaction was monitored by GC or TLC. The resulting reaction mixture was treated with Na₂S₂O₄ solution (10 mol%, 10 mL) and extracted with diethyl ether (2 × 10 mL). The ethereal solution was dried over anhydrous Na₂SO₄ and filtered. Evaporation of the solvent resulted in the desired crude product, which was further purified by plate chromatography technique to produce the pure compound in 98% (Table 1, entry 1).

Typical procedure for the mono-bromination of 1,3-dimethoxybenzene with NaBr/oxone system in H₂O

To a stirring mixture of 1,3-dimethoxybenzene (0.138 g,

1 mmol) and NaBr (0.102 g, 1 mmol) in water (3 mL), oxone (0.307 g, 0.5 mmol) was added. The reaction was completed within 5 min (GC or TLC). The resulting reaction mixture was treated with Na₂S₂O₄ solution (5 mol%, 30 mL) and extracted with diethyl ether. The organic layer was separated and dried over anhydrous Na₂SO₄, and after filtration and evaporation of the solvent, the desired mono-brominated crude product was obtained. Further purification was performed by plate chromatography technique to give the pure compound in 95% yield (Table 2, entry 1).

Typical procedure for the iodoetherification of 5-hexene-1-ol with NaI/oxone system in H₂O

To a stirring mixture of 5-hexene-1-ol (0.1 g, 1 mmol) and NaI (0.149 g, 1 mmol) in water (3 mL) was added oxone (0.307 g, 0.5 mmol). An immediate reaction occurred (GC or TLC). To the resulting reaction mixture, Na₂S₂O₄ solution (5 mol%, 30 mL) was added, and the mixture was extracted with diethyl ether. The organic layer was separated and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the resulting crude product was further purified by plate chromatography technique to give the desired iodocyclic ether in 97% yield (Scheme 2). The structure of the product was identified by ¹H and ¹³C NMR.

Typical procedure for the iodolactonization of 4-pentene-1-oic acid with NaI/oxone system in H₂O

To a stirring mixture of 4-pentene-1-oic acid (0.1 g, 1 mmol) and NaI (0.149 g, 1 mmol) in water (3 mL) was added oxone (0.307 g, 0.5 mmol). An immediate reaction occurred (GC or TLC). To the resulting reaction mixture, Na₂S₂O₄ solution (5 mol%, 30 mL) was added, and the mixture was extracted with diethyl ether. The organic layer was separated and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the resulting crude product was further purified by plate chromatography technique to give the desired iodolactone in 95% yield (Scheme 2). The structure of the product was identified by ¹H and ¹³C NMR.

Physical constants of known compounds

4-Iodo-1,3-dimethoxy benzene

Mp 39–41 °C (lit.⁴¹ mp 37–41 °C).

4-Iodoanisole

Mp 52–53 °C (lit.³⁵ mp 48–55 °C).

4-Iodo-N-methylaniline

Mp 30–32 °C (lit.³⁶ mp 31.5).

4-Iodo-N,N-dimethylaniline

Mp 75–76 °C (lit.³⁷ mp 77 °C).

4-Iodo-1,3-dimethylbenzene

Bp 229–230 °C (lit.³⁵ mp 229 °C).

4-Iodotoluene

Mp (petroleum ether) 33–35 °C (lit.³⁸ mp 34 °C).

Iodobenzene

Bbp 187–189 °C (lit.⁴¹ mp 188 °C).

4-Bromo-1-iodobenzene

Mp (petroleum ether) 91–93 °C (lit.³⁹ mp 95–97 °C).

4-Chloro-1-iodobenzene

Mp (diethyl ether) 55–57 °C (lit.³⁹ mp 54–56 °C).

4-Bromo-1,3-dimethoxy benzene

Mp (petroleum ether) 24–26 °C (lit.⁴¹ mp 25–26 °C).

4-Bromoanisole

Bp 222–224 °C (lit.⁴¹ mp 223 °C).

4-Bromo-1,3-dimethylbenzene

Bp 212–213 °C (lit.⁴¹ mp 214 °C).

4-Bromotoluene

Mp (petroleum ether) 24–26 °C (lit.⁴⁰ mp 25–26 °C).

1-Bromonaphthalene

Bp 280–282 °C (lit.⁴² mp 279–281 °C).

Bromobenzene

Bp 153–155 °C (lit.⁴¹ mp 156 °C).

4-Chloro-1-bromobenzene

Mp (diethyl ether) 66–68 °C (lit.⁴⁰ mp 65–66 °C).

Spectral data and elemental analysis for the unknown compounds

4-Iodo-N-ethylaniline

Mp(CHCl₃/diethyl ether) 79–81 °C. ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 1.11 (t, 3 H, *J* = 7.1 Hz), 2.97 (q, 2 H, *J* = 7.1 Hz), 3.37 (m, 1 H), 6.27 (d, 1 H, *J* = 4.9 Hz), 7.30 (d, 1 H, *J* = 4.8 Hz). ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 13.65, 37.26, 76.55, 113.89, 136.66, 146.84. Anal. calcd.: C, 38.88; H, 4.05; N, 5.67. Found: C, 38.69; H, 4.00; N, 5.38.

5-(Iodomethyl)dihydrofuran-2-one

Liquid. ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 7.39, 27.01, 27.89, 77.42, 175.38. Anal. calcd.: C, 31.85; H, 4.86. Found: C, 31.70; H, 4.07.

2-Iodomethyltetrahydropyran

Liquid. ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 1.18–1.80(m, 6 H), 3.10 (d, 2 H, *J* = 3.5), 3.21–3.40 (m, 1 H), 3.93–4.12 (m, 2 H). ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 9.10, 22.14, 24.56, 30.69, 67.77, 76.61. Anal. calcd.: C, 26.54; H, 3.09. Found: C, 26.22; H, 3.00.

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