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# Ionic Liquid/$H_2SO_4$ Catalyzed Aerobic Iodination of Alkoxyl-Substituted Benzenes and Naphthalines

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**Abstract**: The ionic liquid 1-butyl-3-methylimidazolium nitrate ([Bmim][$NO_3$]) was introduced as both the solvent and catalyst for the activation of the molecular oxygen related to the aerobic iodination of arenes, which provides an effective and practical strategy for the synthesis of aryl iodides. The presented procedure allows a series of alkoxyl-substituted benzenes and naphthalines to undergo the aerobic iodination in high yields and excellent selectivities at an ambient temperature of 40 ℃. Almost all the atoms in the iodine source can be transferred to the final products.

**Key words**: ionic liquid; catalysis; iodination; arenes
**CLC number**: O643.32　　**Document code**: A

Molecular oxygen, especially air, is an ideal oxidant for various organic reaction due to its inexpensive, readily available and environment-friendly character[1-3], thus many organic chemists have been fascinated to develop efficient methods for various aerobic reactions of organic compounds via the transition metal catalyzed-activation of the molecular oxygen[4-7]. However, the transition metals are a kind of nonrenewable resources and the utilization of them possibly results in the heavy metal waste, which is inconsistent with the criterion of the green and sustainable chemistry. Therefore the oxynitride species are very attractive as the non-transition metal catalyst for the activation of the molecular oxygen[8-10]. Considering that the ionic liquids have the potential ability relative to the green reaction media or catalysts for various organic reactions[11-12], our attention has been focused on developing a functional ionic liquid that can let out the oxynitride species to catalyze the activation of the molecular oxygen.

The aerobic iodination of arenes was selected to validate our idea. Iodination of arenes is a common and useful method for the preparation of aryl iodides that can serve as a kind of excellent electrophilic coupling partners for the cross-coupling reactions[13]. Compared with other synthesis methods including Sandmeyer reaction of aromatic amines[14] and ipso iodination of arylboron compounds[15], the iodination of arenes has several inherent advantages such as the use of readily available substrates and higher atom economy. Unfortunately, the inexpensive iodine sources including molecular iodine ($I_2$) and iodine salts ($I^-$) are less reactive towards most of aromatic compounds[16]. Thus much effort has been devoted to the development of

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many effective iodination reagents with a pronounced $I^+$ character, e. g. *N*-iodosuccinimide[17], *N*-iodosaccharin[18], iodine monochloride[19], IOAc[20] and polymer-supported dichloroiodate[21]. However, all the above-mentioned iodination reagents are not readily available, and the atom economy relative to the iodination reagent is poor, which is not only an economic problem but also an environmental one. In order to overcome these drawbacks, several methods for the aerobic iodination of arenes via the in-situ oxidation of readily available iodine sources by the molecular oxygen have been developed in the presence of various catalysts such as $Fe(NO_3)_3 \cdot 9H_2O$[22], $H_5PV_2Mo_{10}O_{40}$[23], $Bi(NO_3)_3$-$BiCl_3$[24], ceric ammonium nitrate[25], $NaNO_2$[26] and $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$[27]. In 2013, we have reported nitrogen dioxide catalyzed-aerobic iodination of arenes with acetonitrile as the solvent[28]. Unfortunately, this method suffers from the inherent disadvantages: both the toxic nitrogen dioxide catalyst and the evaporable acetonitrile solvent are not environment-friendly. The iodination of arenes rather than the aerobic iodination has also been effectively performed with the ionic liquids as the greener solvent[18, 29-30]. To our knowledge, there is no example for the aerobic iodination of arenes with the ionic liquids as both the solvent and the catalyst. Herein, we reported the aerobic iodination of arenes with the ionic liquid [Bmim][$NO_3$] as both the catalyst and the solvent.

## 1 Experimental

### 1.1 Materials and instruments

*n*-Butoxybenzene was synthesized from the reaction between the corresponding chloroalkane and substituted phenol (see Reference 28). Benzyl phenyl ethers were synthesized from the reactions between the corresponding substituted benzyl chloride and substituted phenols (see Reference 28). Other chemicals were commercially available and were used without further purification. For the quality and suppliers of the reagents, see Table S1.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker 400 MHz instrument with chemical shifts reported in ppm relative to the internal standard tetramethylsilane. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m × 0.32 mm). GC-MS spectra was recorded on an Agilent 6890/5973N gas chromatography-mass spectrometry instrument.

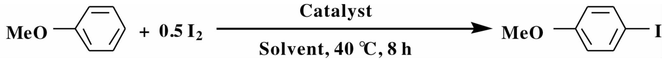
### 1.2 General experimental procedure for the aerobic iodination of arenes

To an about 40 mL tube equipped with a magnetic stirring, 1 mL [Bmim][$NO_3$], 0.5 mmol substrate, 0.25 mmol $I_2$ and 0.1 mL concentrated $H_2SO_4$(98%) were added (note: the air in the tube was not removed). Then the tube was sealed to perform the reaction for 8 h at 40 ℃. Once the reaction time was reached, the mixture was cooled to room temperature, 3 mL water and was added. Then the desired product was extracted with $CH_2Cl_2$(3 × 10 mL). GC analysis of the mixture provided the GC yield of the product. The product in another parallel experiment was purified by column chromatography, and identified by $^1$H-NMR and $^{13}$C-NMR.

## 2 Results and discussion

In the first set of experiments, we selected methoxybenzene as the model substrate to verify the catalytic efficiency of the ionic liquid [Bmim][$NO_3$]. The reaction was performed with 0.5 equiv. $I_2$ and 20% [Bmim][$NO_3$] in acetonitrile at 40 ℃. Under such a condition, the expected iodination product 4-methoxy-iodobenzene was obtained in 63% yield (Table 1, entry 4), while only small amount of iodination product was observed in the absence of [Bmim][$NO_3$] (Table 1, entry 1). These results revealed that the ionic liquid [Bmim][$NO_3$] served as the catalyst. According to the law of charge conservation, the presence of an oxidizing reagent was necessary for the iodination, which impelled us to ponder over who played the role of the oxidizing reagent in the presented reaction system. We guessed that the oxidizing reagent is the residual oxygen in the reaction tube, which was verified by the following experimental result: only small amount of 4-methoxy-iodobenzene product was obtained in the case of a removal of oxygen from the reaction system (Table 1, entry 5).

**Table 1 Aerobic iodination of methoxybenzene**[a]



| Entry | Catalyst | Solvent | Yield of /%[b] | Conversion /%[c] | Selectivity /%[c] |
|---|---|---|---|---|---|
| 1 | – | Acetonitrile | 7 | 20 | 36 |
| 2 | 5 mol% [Bmim][$NO_3$] | Acetonitrile | 15 | 51 | 29 |
| 3 | 10 mol% [Bmim][$NO_3$] | Acetonitrile | 22 | ~100 | 22 |
| 4 | 20 mol% [Bmim][$NO_3$] | Acetonitrile | 63 | ~100 | 63 |
| 5[c] | 20 mol% [Bmim][$NO_3$] | Acetonitrile | trace | 9 | – |
| 6 | – | [Bmim][$NO_3$] | 95 | ~100 | 95 |
| 7 | – | [Bmim]Cl | trace | 1 | – |
| 8 | – | [Bmim][$BF_4$] | trace | 10 | – |
| 9[d] | – | [Bmim][$NO_3$] | 94 | 98 | 96 |
| 10[d] | – | [Bmim][$NO_3$] | 96 | ~100 | 96 |
| 11[d] | – | [Bmim][$NO_3$] | 90 | ~100 | 90 |

a. Reaction conditions: 0.5 mmol methoxybenzene, 0.25 mmol $I_2$, 0.1 mL concentrated $H_2SO_4$(98%), 1 mL solvent, 40 ℃, 8 h, the air in the tube was not removed; b. Determined by GC with 1,2,4,5-tetramethylbenzene as an internal standard; c. The air inside the tube was replaced with $N_2$ gas by six vacuum/gas cycles; d. The reaction temperature is respectively 60 ℃ (entry 9), 80 ℃ (entry 10) and 100 ℃ (entry 11).

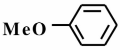
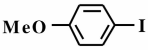
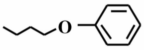
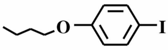
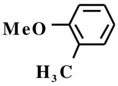
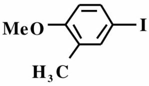
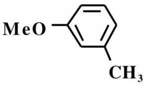
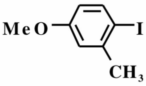
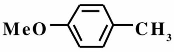
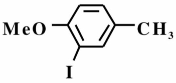
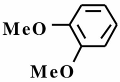
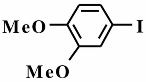
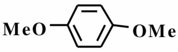
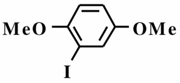
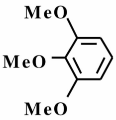
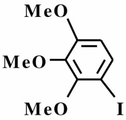
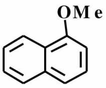
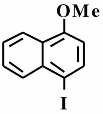
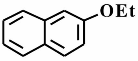
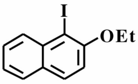
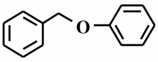
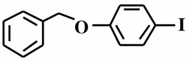
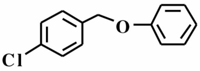
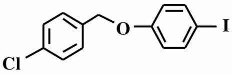
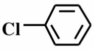
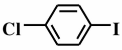
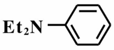
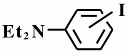
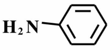
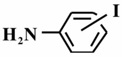
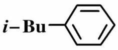
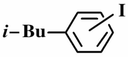
Whereafter, our attention was turned to the optimization of the reaction conditions. The yield of *para*-iodination product was not increased in the case of changing the acetonitrile to other solvents including dimethyl sulphoxide, *N*-methyl-2-pyrrolidone, *N*, *N*-dimethylformamide, tetrahydrofuran and toluene. When the ionic liquid [Bmim][$NO_3$] was employed as the solvent, the yield of the *para*-iodination product was increased to 95% (Table 1, entry 6). Moreover, the selectivity of the reaction was excellent, and hardly any other by-products apart from about 5% *ortho*-iodination was observed, while the reaction with acetonitrile as the solvent gave more by-products including 3% 4-nitro-methoxybenzene, 10% diiodination product and other unknown products (Table 1, entry 4). These results suggest that the ionic liquid [Bmim][$NO_3$] was not only an excellent catalyst but only the optimal solvent. The loading amount of the iodine source was also optimized, and the results showed that 0.5 equiv. $I_2$ was sufficient for the complete iodination of methoxybenzene. That is to say, basically all the atoms in the iodine source could be transferred to the final products, by contrast many previous methods have a very low atom economy relative to the iodine source[15-16, 27]. After the reaction temperatures ranged from 25 to 80 ℃ was tested, the reactions in the case of 60 and 80 ℃ gave similar results as that at 40 ℃, and the increase of the reaction temperature from 40 to 100 ℃ led to a decrease in the selectivity of the desired product (Table 1, entries 6, 9-11).

The present procedure for the aerobic iodination reaction with [Bmim][$NO_3$] as both the catalyst and the solvent was applicable to the iodination of various alkoxyl-substituted benzenes (Table 2). The mono-substituted benzenes containing alkoxy groups were a kind of excellent substrates (Table 2, entries 1 and 2),

**Table 2 Aerobic iodination of various substituted benzenes and naphthalines[a]**

$$\mathrm{ArH} + 0.5\ \mathrm{I_2} \xrightarrow[40\ ℃,\ 8\ \mathrm{h}]{[\mathrm{Bmim}]\mathrm{NO_3}} \mathrm{ArI}$$

Residual air in the reaction tube

| Entry | Substrate | Product[b] | GC yield /(%)[c] | Conversion /(%)[c] | Selectivity /(%)[c] |
|---|---|---|---|---|---|
| 1 |  |  | 95 | ~100 | 95 |
| 2 |  |  | 97 | ~100 | 97 |
| 3 |  |  | 90 | ~100 | 90 |
| 4 |  |  | 91 | ~100 | 91 |
| 5 |  |  | 96 | 97 | 99 |
| 6 |  |  | 89 | ~100 | 89 |
| 7 |  |  | 85 | ~100 | 85 |
| 8 |  |  | 95 | ~100 | 95 |
| 9 |  |  | 93 | ~100 | 93 |
| 10 |  |  | 89 | ~100 | 89 |
| 11 |  |  | ~100 | ~100 | 100 |
| 12 |  |  | 51 | 97 | 53 |
| 13 |  |  | 0 | 0 | 0 |
| 14 |  |  | 25 | ~100 | 25 |
| 15 |  |  | 11 | 18 | 62 |
| 16 |  |  | 0 | 0 | 0 |

a. Reaction conditions: 0.5 mmol substrate, 0.25 mmol $I_2$, 0.1 mL concentrated $H_2SO_4$(98%), 1 mL [Bmim]$NO_3$, 40 ℃, 8 h, the air in the tube was not removed; b. Determined by $^1$H-NMR, $^{13}$C-NMR and MS; c. Determined by GC with 1,2,4,5-tetramethylbenzene as an internal standard. Isolated yield is respectively 80% (entry 1), 84% (entry 2), 91% (entry 3), 86% (entry 4), 85% (entry 5), 75% (entry 6), 72% (entry 7), 81% (entry 8), 89% (entry 9), 86% (entry 10), 81% (entry 11), 49% (entry 12).

and the iodination occurred at the *para*-position with regard to alkoxy group in high yields and *para*-selectivity. The main by-product was from *ortho*-iodination of alkoxyl-substituted benzenes, while the nitration and diiodination of the benzene ring were not observed. Iodination of phenols also occurred, but the reaction selectivity was very poor, and the desired products were obtained in very low yields. Although amino groups are also strong activating group, the amino group-substituted benzenes gave the desired product in very low yields (Table 2, entries 14 and 15), which possibly resulted from the incompatibility between the alkaline character of amino groups and the acidic reaction condition.

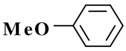
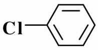
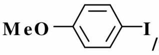
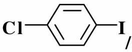
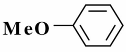
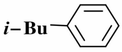
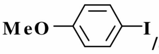
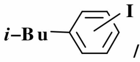
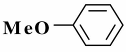
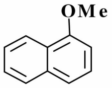
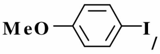
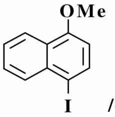
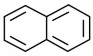
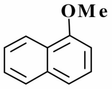
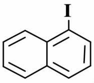
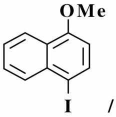
The disubstituted benzenes containing both an alkyl and an alkoxy group were also smoothly iodinated into the desired products under the present conditions (Table 2, entries 3-5). As expected, the iodination occurred at the *ortho-para* position of alkoxy group rather than alkyl group because the former was a stronger *ortho-para* directing group than the latter. For example, 2-methoxytoluene underwent the iodination to provide 90% 5-iodo-2-methoxytoluene product and a small amount of 3-iodo-2-methoxytoluene by-product. 2-Iodo-5-methoxytoluene product was obtained in 91% yield in the case of using 3-methoxytoluene as the substrate, but the *ortho*-iodination with regard to methoxy group was not observed. When 4-methoxytoluene was used as the substrate, only *ortho*-position of alkoxy group was selectively iodinated due to the absence of *para* C-H bond of alkoxy group, and the *ortho*-iodination product was obtained in as high as 96% GC yield, which was different from our previous report where 4-methoxytoluene was less reactive under the condition of nitrogen dioxide-catalyzed iodination[28]. Subsequently, iodination of dialkoxyl-substituted benzenes was tested (Table 2, entries 6 and 7). Iodination of *ortho* and *para*-dimethoxybenzene gave respectively 4-iodo-1,2-dimethoxybenzene and 2-iodo-1,4-dimethoxybenzene product in high yields. By comparison, *meta*-dimethoxybenzene was not a good substrate: although this substrate had a high reactivity, the reaction selectivity was poor and gave 23% diiodination by-product.

When 1,2,3-trimethoxybenzene was used as the substrate (Table 2, entry 8), 2,3,4-trimethoxy-1-iodobenzene product was obtained in 95% GC yield. Subsequently, the present protocol for the aerobic iodination reaction was applied into iodination of naphthalines (Table 2, entries 9 and 10). Iodination of 1-alkoxynaphthalene occurred at the 4-position of naphthalene ring, while 2-alkoxynaphthalene was selectively iodinated at its 1-position. The same site-selectivity was also observed in previous literatures with regard to the aerobic iodination of arenes[22-23, 28].

Next, the present method was applied to the iodination of benzene, alkylbenzenes and an electron withdrawing group-substituted benzene (Table 2, entries 13 and 16). Unluckily, these substrates were less reactive under the condition of 0.5 equiv. $I_2$ in [Bmim][$NO_3$] at 40 ℃. However, it is interesting that the alkoxybenzene rings could be selectively iodinated in the case of the substrates containing two arene rings. For example, only phenyl rings bonded to oxygen selectively underwent the iodination in high yield in the case of benzyl phenyl ethers (Table 2, entries 11 and 12). Such a selectivity was also verified by the following competition reactions between two substrates containing benzenes or naphthalene ring (Table 3). When both naphthalene and 1-methoxynaphthalene were added into the reaction system, only the latter underwent the iodination, while iodination of the former did not occur. In the coexistence of methoxybenzene and isobutylbenzene rings, only benzene ring of the former was selectively iodinated.

On the basis of the above results and discussion, the ionic liquid [Bmim][$NO_3$] is believed to play the roles of not only the solvent but also the catalyst precursor. Although we can not make certain who serves as the real catalytic species, it is reasonable to assume that the real catalytic species is formed from the $NO_3^-$ anion of [Bmim]$NO_3$ because it is known that the oxynitride species have the ability to catalyze the aerobic iodination of arenes[26, 28]. Indeed, only trace amount of iodination product was observed when [Bmim][$NO_3$] was replaced by the ionic liquids without $NO_3^-$ anion including [Bmim]Cl and [Bmim][$BF_4$]

**Table 3 Several competition reactions between different aromatic substrates**[a]

| Entry | Substrate 1 | Substrate 2 | GC yield of Product 1[b] | GC yield of Product 2 [b] |
|---|---|---|---|---|
| 1 |  |  |  /93% |  /0% |
| 2 |  |  |  /88% |  /0% |
| 3 |  |  |  /15% |  /68% |
| 4 |  |  |  /0% |  /85% |

a. Reaction conditions: 0.5 mmol Substrate 1, 0.5 mmol Substrate 2, 0.25 mmol $I_2$, 0.1 mL concentrated $H_2SO_4$(98%), 1 mL [Bmim]$NO_3$, 40 ℃, 8 h, the air in the tube was not removed; b. Determined by GC with 1,2,4,5-tetramethylbenzene as an internal standard.

(Table 1, entries 7 and 8). According to the previous literatures[31-32], $NO_3^-$ can be thermodynamically decomposed to give small amount of $NO_2$, $NO^+$ or $NO_2^+$ in the presence of Bronsted acid, thus one of these oxynitride species may be the real catalytic species[26, 28]. The molecular iodine is oxidized by oxygen via the catalytic cycle to give the highly reactive $I^+$ species[28, 33]. Then the resulting $I^+$ species may directly react with aromatic ring to afford the iodobenzene product[26, 33].

# 3 Conclusion

In summary, we have demonstrated an efficient method for the aerobic iodination of arenes via the oxidation of molecular iodine by 0.1 MPa air with the ionic liquid as both the catalyst and solvent. The reactions were performed at an ambient temperature of 40 ℃ and the used reaction reagents and additives are all simple and readily available, suggesting that this method is practical. Also, basically all the atoms in the iodine source can be transferred to the final products. Although the substrates were limited to alkoxyl-substituted benzenes and naphthalines, it offers an opportunity to the selective iodination of the alkoxyl-substituted aromatic rings in the case of the substrate containing two or more aromatic rings.

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# 离子液体/$H_2SO_4$ 催化烷氧基取代苯和萘的需氧碘化

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**摘要:** 使用离子液体[Bmim][$NO_3$]作为溶剂和催化剂, 进行分子氧的活化, 实现了芳烃的需氧碘化, 为碘代芳烃的合成提供了一种有应用潜力的方法. 在40 ℃的温和条件下, 一系列烷氧基取代苯和萘化合物能够顺利地进行需氧碘化, 得到的产率和选择性大部分高于85%. 由于碘源中的原子几乎都能够转移到最终产品中, 因此这个方法具有较高的原子经济性.

**关键词:** 碘化; 离子液体; 催化; 芳烃