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Nitrogen Dioxide-Catalyzed Electrophilic Iodination of Arenes

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Abstract: Nitrogen dioxide is demonstrated to be an effective catalyst precursor for the iodination of alkoxy-substituted benzenes and naphthalenes. Different from the transition metal catalysts, nitrogen dioxide can be easily separated from the final products, and is free of heavy metal waste. Although the present catalyst precursor is toxic, it does not stain the final products due to its low-boiling character. No other reagents apart from 0.5 equiv. of iodine (I_2), 6.5 mol% nitrogen dioxide and acetonitrile solvent were used in the iodination, and basically all the iodine atoms in the iodine source were transferred to the iodination products, showing that the presented protocol is highly atom-economic and practical.

Keywords: arenes; catalysis; iodination; nitrogen dioxide

Introduction

Aryl iodides have served as versatile intermediates for the synthesis of various organic products because they are excellent substrates for the formation of carbon-carbon and carbon-heteroatom bonds *via* transition metal-catalyzed cross-coupling reactions.[1] As a result, much effort has been devoted to the development of effective methods for the introduction of the iodo functional group onto aromatic rings.[2–5] Aryl iodides can be synthesized *via* iodo-deboronation of arylboron compounds,[2] halogen exchange of aryl halides[3] or the Sandmeyer reaction from aromatic amines.[4] In contrast, electrophilic iodination of aromatic compounds seems to be a more attractive alternative to the synthesis of aryl iodides due to the use of readily available substrates.[6] Different from chlorine and bromine, iodine is less reactive towards most aromatic compounds, thus electrophilic iodination requires the presence of the more reactive species with a pronounced I^+ character. One of the most effective solutions to this situation is the use of iodonium equivalents (I^+), for example, *N*-iodosuccinimide,[7] *N*-iodosaccharin,[8] iodine monochloride[9] and IOAc.[10] Another effective solution is the oxidative activation strategy where the electrophilic I^+-type species is generated through oxidation of iodine sources by oxidizing reagent systems, for example, CrO_3,[11] $Pb(OAc)_4$,[12] $Ce(OTf)_4$,[13] hydrogen peroxide,[14] H_5IO_6,[15] peroxodisulfate salts,[16] and ferrate salts.[17]

The use of molecular oxygen as the oxidant is a still desirable goal from environmental and economic perspectives.[18] Neumann and co-workers reported an effective method for the aerobic iodination of arenes *via* $H_5PV_2Mo_{10}O_{40}$-catalyzed oxidation of molecular iodine by oxygen gas.[19] Subsequently, the $Bi(NO_3)_3$-$BiCl_3$ system was found to be an effective catalyst for the aerobic iodination under an air atmosphere.[20] In 2007, Das and co-workers reported the ceric ammonium nitrate-catalyzed aerobic iodination of arenes,[21] but such a reaction required the use of 1 equivalent of I_2, thus a half of iodine source was wasted. Other examples relative to the aerobic iodination of arenes are the reactions using $I_2/NaNO_2$/air/silica-supported H_2SO_4[22] or KI/air/$NaNO_2/H_2SO_4$.[23] Considering the fact that NO_2 is free of heavy metal waste and easily separated from the final products, our attention was directed to developing a procedure with NO_2 as the catalyst precursor for the aerobic iodination, and the results are reported herein.

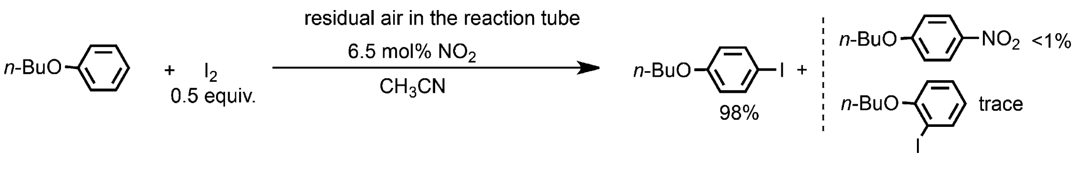
Results and Discussion

Our initial study aimed at the iodination of *n*-butoxybenzene as a model reaction to investigate the catalytic efficiency of NO_2. As shown in Scheme 1, the reaction proceeded efficiently using as low as 6.5 mol% NO_2 and gave the desired product in a high yield, along with a small amount of 4-nitro-4-*n*-butoxybenzene by-product resulting from the nitration of the benzene ring.[24] Although the *n*-butoxy group is an *ortho-para* directing group, only a small amount of *ortho*-iodination product was observed. Such an exclusive regioselectivity was also mentioned in several reports[25] where bromination of methoxybenzene and cyanation of multi-substituted benzenes were performed. As described in the literature,[25a] the exact reason for this excellent selectivity is not clear at the present stage. However, the steric effect seems to be one of the main reasons: the larger steric hindrance of the position *ortho* to the alkoxy group leads to less *ortho*-product,[26] and allows the reaction to give a high *para*-selectivity.

The reaction was highly dependent on the loading amount of NO_2: the aromatic substrate was less reactive in the absence of NO_2, and the optimal results were obtained in the case of 4.8–7.2 mol% NO_2 (see Table S2 in the Supporting Information). It is worth noting that an increase of the catalyst loading facilitates the nitration of the benzene ring, which leads to a decrease in the yield of the iodination product. For example, when the loading amount of NO_2 increased from 2.4 to 9.6 mol%, the yield of nitration product increased from 0 to 3.7% (Supporting Information, Table S2, entries 3–9). The type of solvent was found to have an important effect on the iodination. Of the screened solvents, acetonitrile was highly effective, while the iodinations using toluene, *N*,*N*-dimethylformamide, and *N*-methylpyrrolidone were very sluggish. Although dimethyl sulfoxide was also effective as the solvent (Supporting Information, Table S2, entry 18), we preferred the low-boiling acetonitrile because the use of high-boiling solvent was disadvantageous for the separation and purification of the products.

It was not necessary to use an excess of I_2. Hence, basically all the iodine atoms could be transferred to the iodination product. This highly atom-economic character contrasts sharply with that of the previous methods where only a low percentage of the iodine atom source ends up in the final products.[21,27] According to the law of charge conservation, the reaction requires the presence of an oxidizing reagent that plays a role of oxidizing the iodide molecule to the I^+ species. It was noted that there were about 43 mL of residual air (at atmospheric pressure) in the reaction tube before the reaction system was heated. Thus it is rational to assume that the residual oxygen in the reaction tube serves as the oxidizing reagent. Indeed, the removal of oxygen from the reaction system resulted in a remarkable decrease in the product yield (Supporting Information, Table S3, entry 7). The iodination reaction could proceed smoothly when the concentration of oxygen was decreased to 15 vol%, but a further decrease of the oxygen concentration to 10 vol% led to a lower yield (Supporting Information, Table S3, entries 4 and 5). Consistent with $H_5PV_2Mo_{10}O_{40}$-catalyzed iodination of arenes,[19] the use of I^- in place of I_2 did not result in significant iodination (Supporting Information, Table S2, entries 12–14), which suggested that no electrophilic I^+ species was formed from the formation and then oxidation of I^- under our experimental conditions using molecular iodine, thus it was possible that the molecular iodine was directly oxidized to two I^+-type species.[19]

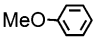
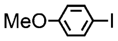
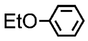
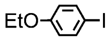
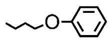
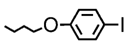
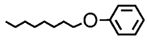
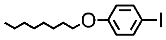
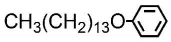
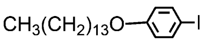
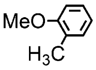
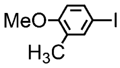
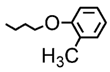
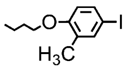
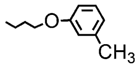
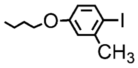
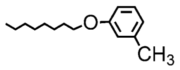
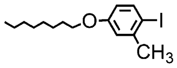
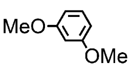
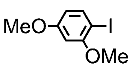
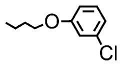
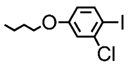
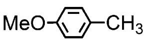
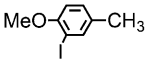
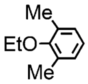
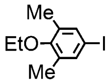
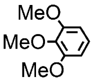
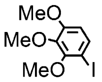
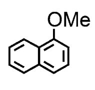
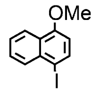
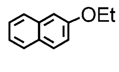
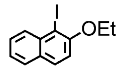
With the optimized conditions in hand, we set out to evaluate the scope of the present iodination protocol. When the mono-substituted benzenes containing alkoxy groups were employed as the substrates (Table 1, entries 1–8), all the iodination reactions proceeded efficiently with high yields and high *para*-selectivities. Surprisingly, the phenyl rings with other activated groups were converted into the desired products in poor yields (see Table S4 in the Supporting Information). One can argue that the alkoxy groups are stronger aromatic activating groups,[25b,28] and therefore this might be an explanation for the ease of iodination of alkoxybenzenes. However, it is difficult to understand why only alkoxyphenyl rings among so many types of electron-rich phenyl rings showed such high reactivities. Although the present method was limited to the iodinations of the benzenes with alkoxy groups, it was compatible with various groups including alkyl, acetamido, ester, carboxyl, nitro, chloro, bromo and iodo groups (Scheme 2), which seems to offer an opportunity for the selective functionalization of the alkoxybenzene rings in the case of the sub-



Scheme 1. NO_2-catalyzed iodination of *n*-butoxybenzene.

Table 1. NO_2-catalyzed iodination of various alkoxy-substituted benzenes and naphthalenes.[a]

$$\underset{}{ArH} + \underset{\text{0.5 equiv.}}{I_2} \xrightarrow[\substack{\text{1.5 mL } CH_3CN\text{, 40–120 °C, 10 h} \\ \text{residual air in the reaction tube}}]{\text{6.5 mol\% } NO_2} ArI$$

Entry	Substrate	Product[b]	Temperature [°C]	Isolated yield [%]
1			80	92
2			60	86
3			80	83
4			60	80
5			80	95
6			60	72
7			80	91
8			80	86
9			80	86
10			80	85
11			60	88
12			80	85
13			80	89
14			80	94
15			40	91
16			120	61
17			120	28
18			120	83
19			80	51
20			80	67
21			60	91
22			40	75
23			60	86
24			40	72

[a] *Reaction conditions:* 0.5 mmol substrate, 0.25 mmol I_2, 0.0325 mmol NO_2, 1.5 mL acetonitrile, 10 h, the air in the tube was not removed.

[b] The product was characterized by ^1H NMR and mass spectroscopy.

strates containing two or more activated benzene rings.

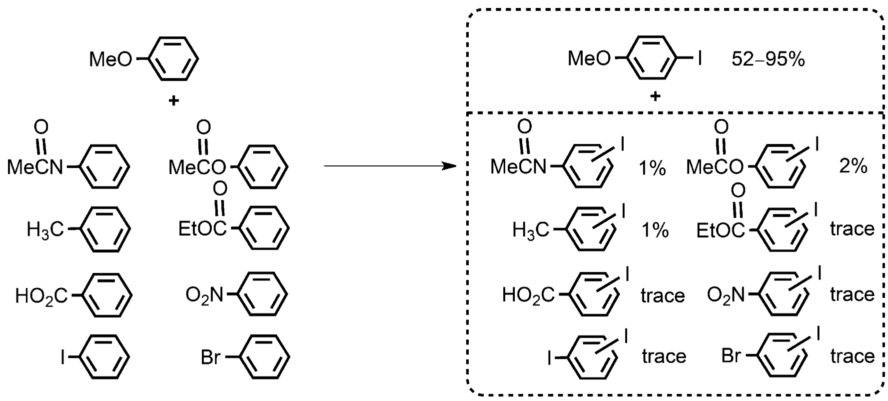
Among the tested disubstituted benzenes, *ortho*- and *meta*-substituted alkoxybenzenes were found to be good substrates for the iodinations (Table 1, entries 9–16), even the alkoxybenzene with a deactivating substituent was iodinated in moderate yield (Table 1, entry 16). In addition, the regioselectivity was excellent and the iodination of the tested disubstituted benzenes selectively occurred at the *para*-position with regard to alkoxy group. If the *para* C–H bonds of alkoxybenzenes were absent, it was difficult for the iodination to proceed efficiently. For example, 4-methoxytoluene underwent this transformation in poor yield (Table 1, entry 17), while the reaction selectivity was excellent and scarcely any other product was observed besides 3-iodo-4-methoxytoluene. Interestingly, 2,3,4-trimethoxy-1-iodobenzene, a key intermediate used in the manufacture of trimetazidines and some kinase inhibitor drugs,[29] was synthesized from 1,2,3-trimethoxybenzene by using the present procedure (Table 1, entry 20). Another kind of good substrate were the alkoxynaphthalenes (Table 21, entries 21–24), among which 1-alkoxynaphthalene was selectively iodinated at its 4-position, while 2-alkoxynaphthalene underwent this transformation at its 1-position. The same site-selectivity was also observed in the bismuth-catalytic iodination with molecular iodine.[20] We tried the iodination of several aromatic heterocycles including 1-methylimidazole, benzofuran, benzothiazole, indole and 2-phenylpyridine, but only a trace or small amount of iodination products was observed (Supporting Information, Table S4, entries 31–34).

At the end of reaction, only a small amount of NO_2 and other impurities were present in the solution of the resulting product, which offers an opportunity to further convert the iodine group to other functional groups in a one-pot process. As shown in Table 2, several benzonitrile products were effectively synthesized through the one-pot iodination and cyanation sequence.

Finally, our attention was drawn to the investigation of the catalytic species. NO_2 or its dimer can be diluted with many solvents to give small amounts of NO^+ and NO_3^- in some cases (Scheme 3).[30] The resulting NO^+ seems to be the real catalytic species because the oxidation of iodine to I^+ is possibly carried out by NO^+ in an inner-sphere electron transfer step,[31] which was also confirmed by our experimental result: the iodination with $NOBF_4$ instead of NO_2 proceeded efficiently with a high yield (Scheme 4).

It is known that NO^+ is effective in oxidizing a number of aromatics and heteroaromatics to the cation radicals,[32] hence the resulting aromatic radical cations should react with another aryl ring to generate the biaryl by-poducts.[33] However, no biaryl by-product was observed in all cases, which reveals that the mechanistic pathway *via* aryl radicals is ruled out under our experimental conditions (Scheme 5).

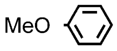
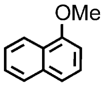
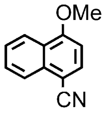
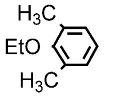
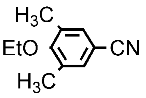
Considering that it is possible that the molecular iodine is oxidized by NO^+ to two I^+-type species,[31]



Scheme 2. Several competition reactions between methoxybenzene and some substituted benzenes (for the experimental procedure, see Scheme S1 in the Supporting Information).

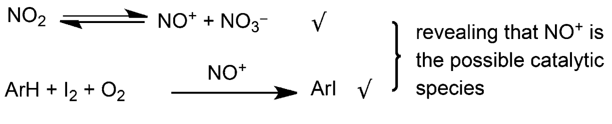
Table 2. Cyanation of several arenes through the one-pot iodination/cyanation.[a]

$$\text{Ar}-\text{H} \xrightarrow[\text{2) } K_3[Fe(CN)_6],\ Cu(NO_3)_2 \cdot 3\,H_2O]{\text{1) } I_2,\ NO_2,\ CH_3CN} \text{Ar}-\text{CN}$$

Entry	Substrate	Product	Isolated yield [%]
1			87
2			89
3			73

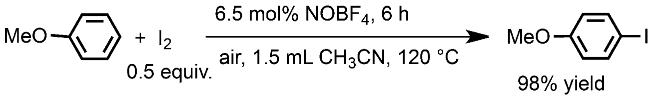
[a] For the experimental procedure, see Table S5 in the Supporting Information.

a tentatively proposed mechanism pathway is presented in Scheme 6. NO^+ plays the role of a mediator to bridge the gap between oxygen and I_2 to generate an electrophilic I^+ species.[31] Then the reaction between I^+ and phenyl ring gives the σ-complex intermediate, followed by an elimination of hydrogen to afford the iodobenzene product.[6a,34] It is worth noting that, although the elimination of hydrogen generates H^+ ions, the pH value of the reaction mixture is close to 7.0 after the completion of the reaction, which is possibly rationalized by assuming that the resulting H^+ ion is consumed in the oxidation of NO to NO^+.

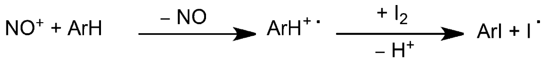


√ : confirmed by experiments or known in previous literature.

Scheme 3. Considerations on the catalytic species.



Scheme 4. Iodination of methoxybenzene catalyzed by $NOBF_4$.

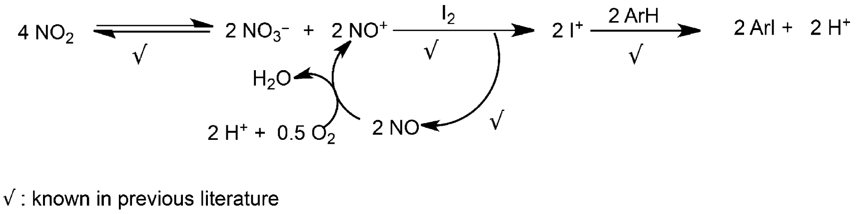


impossible pathway because no by-product from the coupling between two aromatic rings was observed

Scheme 5. Impossible mechanistic pathway.

Conclusions

In conclusion, an effective method was developed for the iodination of alkoxy-substituted benzenes and naphthalenes with nitrogen dioxide as the catalyst precursor. The used nitrogen dioxide can be easily separated from the final products, and is free of heavy metal waste. Although the present catalyst precursor is toxic, it does not stain the final products due to the low-boiling character. No other reagents apart from 0.5 equiv. I_2, 6.5 mol% nitrogen dioxide and acetonitrile solvent were used in the iodination, and basically all the iodine atoms could be transferred to the iodination products, indicating that the presented protocol is atom-economic and practical. Interestingly, among various phenyl hydrogens, those at the *para*-position with regard to alkoxy groups were selectively iodinated in excellent yields. In addition, several benzonitrile products were effectively synthesized through the one-pot iodination and cyanation sequence. Preliminary mechanistic investigations suggest that the reaction presumably involves NO^+ as



Scheme 6. Proposed mechanism for the iodination.

a mediator to bridge the gap between oxygen and I_2 to generate an electrophilic I^+ species.

Experimental Section

For the quality and suppliers of the reagents see Table S1 in the Supporting Information. *n*-Butoxybenzene, *n*-tetradecyloxybenzene, 2-*n*-butoxytoluene, 3-*n*-butoxytoluene, 1,3-dimethyl-2-ethoxylbenzene and 1-chloro-3-*n*-butoxybenzene were obtained from the reactions between the corresponding chloroalkanes and substituted phenols. Other chemicals were commercially available and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 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 an FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m × 0.32 mm). GC-MS were recorded on an Agilent 6890/5973N gas chromatography-mass spectrometry instrument.

General Procedure for the Iodinations

0.5 mmol substrate, 0.25 mmol I_2, 1.5 mL acetonitrile and 0.0325 mmol NO_2 were added to a dried 45-mL tube equipped with a magnetic stirring (note: NO_2 was withdrawn with a glass syringe from a flask filled with NO_2, and the air in the reaction tube was not removed). Then the reaction tube was sealed and placed in a constant-temperature oil bath to perform the reaction for 10 h. Once the reaction time was reached, the mixture was cooled to room temperature. The iodination product was purified by column chromatography, and identified by ^{1}H NMR and GC-MS.

Caution: Experiments using poisonous nitrogen dioxide gas are potentially hazardous and must only be carried out under rigorous safety precautions and using the appropriate equipment to avoid gas leakage.

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