


 Cite this: *RSC Adv.*, 2025, 15, 8523


Received 5th February 2025

Accepted 5th March 2025

DOI: 10.1039/d5ra00837a

rsc.li/rsc-advances

Halogenation of arenes using alkali metal halides/ Fe(NO₃)₃·9H₂O at room temperature†

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A simple, efficient and environmentally friendly methodology for the halodecarboxylation of anisole analogues using Fe(NO₃)₃·9H₂O/KBr or NaI at room temperature was developed. In this method, most substrates with an electron-donating group afforded corresponding products in good to excellent yields, whereas those with an electron-withdrawing group afforded low to moderate yields. More importantly, this protocol was also applicable for gram-scale synthesis. It is hoped that this methodology will be highly useful in organic synthesis.

Introduction

Aryl halides are very common structural units widely present in a large number of natural products, industrial chemicals and pharmaceuticals.¹ Additionally, aryl halides are important synthetic blocks to construct various compounds.² A series of cross-coupling reactions including the Heck reaction, Suzuki reaction, Ullmann reaction, Grignard reaction, Stille reaction, Sonogashira reaction, Negishi reaction, Kumada reaction, and Hiyama reaction can be conducted using aryl halides.

However, hazardous, toxic and corrosive molecular halogens are usually used as halogenating agents in the laboratory,³ *e.g.*, in bromination, where bromine is used as a direct reagent for the synthesis of bromoaromatic compounds, which causes environmental pollution and some undesirable side reactions such as the production of toxic HBr gas, uncontrolled polybromination and lower yields. Thus, many reagents have been developed to replace molecular halogens as the source of electrophilic halide cations. The most common alternative to Br₂ is NBS,⁴ which is used as a “Br” source *via* electrophilic substitution to obtain brominated compounds, which is an important way to produce bromides. Essentially, bromide anions were reacted with oxidants to generate Br⁺. Further, co-oxidants such

as PhI(OAc)₂,⁵ H₂O₂ (ref. 6) and metal oxidants⁷ were developed. Meanwhile, quaternary ammonium salts,⁸ pyridinium salts,⁹ 4-(dimethylamino)pyridine tribromide¹⁰ and *N,N*-dibromotosylamide (TsNBr₂)¹¹ were selected as bromination reagents. In recent years, Lewis or Brønsted acids and Lewis bases have been employed to boost the reactivity of bromination by different research groups.¹² Nevertheless, most of these methods suffer from limitations such as the requirement for essential transition-metal catalysts, inevitable operational complexity, uncommon bromine sources, and a narrow substrate range. Therefore, efficient preparation of aryl halides under mild and green reaction conditions is a continuing goal for chemists in organic synthesis and several other research fields.

In recent years, considerable attention has been paid to the development of a new route for the construction of halogenated scaffolds by utilizing safe and readily available halide sources such as alkali metal halides (halide = I, Br, and Cl).¹³ A combination of oxidants and bromides such as oxone/NaBr,¹⁴ CAN/KBr,¹⁵ CAN/LiBr,¹⁶ Selectfluor®/KBr,¹⁷ NaBrO₃-NaBr,¹⁸ and NaBr/NaNO₃/TFA¹⁹ has been employed in these bromination reactions. We also noted that Fe(NO₃)₃·9H₂O had relatively high Lewis acidity and great catalytic activity.²⁰ Meanwhile, Fe(NO₃)₃·9H₂O is a cheap, non-toxic and readily available inorganic oxidant and has been used as an efficient oxidant,²¹ nitro source²² and catalyst in cross-coupling reactions.²³ We also found that I₂ could be generated *in situ* from Fe(NO₃)₃·9H₂O/NaI in DMSO to catalyze the oxidation process.²⁴ Thus, we propose that Fe(NO₃)₃·9H₂O competes with alkali metal halides, showing potential to induce halogenation of arenes. In this study, it was found that Fe(NO₃)₃·9H₂O/KBr exhibits efficiency for the synthesis of *p*-bromoaromatic compounds at room temperature, while Fe(NO₃)₃·9H₂O/KI is efficient for the synthesis of *p*-iodoaromatic compounds. Compared with the previous reports, a Fe(NO₃)₃·9H₂O/alkali metal halide system could synthesize aryl halides at room temperature with high to

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5ra00837a>

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excellent yields for substrates with an electron-donating group and low to moderate yields for substrates with an electron-withdrawing group. In addition, this protocol was readily scaled up to 15 mmol level without any loss of efficiency.²⁵

Results and discussion

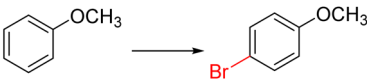
The initial step of the study was the optimization of reaction with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.625 mmol)/KBr (0.625 mmol), using anisole (0.5 mmol) as a model substrate in various solvents for 2 h at room temperature (Table 1, entries 1–11). To our delight, *para*-bromination of anisole proceeded smoothly in CH_3CN , giving the desired product in a high yield up to 99%. When the reaction was carried out in hexane, CH_2Cl_2 , and EA, the brominated product was obtained in high yields up to 67%, 98% and 89%, respectively. Then, other types of Br sources such as NaBr, LiBr, CuBr_2 or FeBr_3 could also be applied in this reaction to give excellent yields (Table 1, entries 12–15). This

indicated that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ combined with other bromine salts also successfully afforded 4-bromoanisole. In order to find the best method for the bromination of anisole, the reaction time and the ratio of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /KBr were determined, which indicated that the optimum conditions are $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.625 mmol)/KBr (0.625 mmol) and a reaction time of 2 h (Table 1, entries 16–24). In addition, the reaction did not occur without $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Table 1, entry 25). We also tested other types of Fe salts and nitrates, among which the desired product was offered by $\text{Cu}(\text{NO}_3)_2$ with 29% yield (Table 1, entries 26–31).

The obtained results for the reaction of *para*-bromination of anisole promoted our procedure to various anisole analogues (Table 2). Gratifyingly, the bromination of arenes containing electron-donating substituents such as alkoxy (Table 2, entries 1–5) and benzyloxy (Table 2, entry 6) proceeded smoothly to give the corresponding *para*-brominated products in good to excellent yields. Naphthyl substrates (Table 2, entries 7 and 8) were found to work well, giving the corresponding product in 86% and 97% yields. It is noteworthy that when 2-methoxynaphthalene reacted with multiple substrates under standard conditions but with the decreasing amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 0.25 mmol, the yield of desired product was increased to 87%. In addition, phenyl-, methyl-, and ethyl-substituted substrates also gave the corresponding products in high yields with monobromination at the *para* or *ortho* position with respect to the methoxyl substituent (Table 2, entries 9–13). Meanwhile, for weak electron-withdrawing substituted substrates, it offered the corresponding products in a relatively low yield, but when under adjusted conditions, the yield could be improved to a satisfactory value (Table 2, entries 14–19). However, for strong electron-withdrawing substituted substrates such as $-\text{CF}_3$ and $-\text{CN}$, the reaction did not occur (Table 2, entries 20 and 21).

Meanwhile, the strong electron-donating groups on anisole should be reacted under optimized conditions, that is, some bromination products or nitration products were obtained under standard conditions (Table 2, entries 22–26). For 1,2-dimethoxybenzene, the side product was a nitration product (15%). While the amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was decreased to 0.25 mmol, the yield of desired product was increased to 94%, and the yield of nitration product was decreased to 5% (Table 2, entry 22). For 1,3-dimethoxybenzene, the desired product was obtained in 99% yield at the ratio of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 mmol)/KBr (0.6 mmol) (Table 2, entry 23). For 1,4-dimethoxybenzene, the main product was a nitration product with 83% yield (Table 2, entry 24). In addition, for 1,2,3-trimethoxybenzene, the highly electron-rich substrate afforded the desired product in 90% yield with a $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /KBr ratio of 0.375 mmol/1.5 mmol. It should note that 2,3-dimethoxybenzaldehyde could offer 65% yield at a reaction temperature of 60 °C. Moreover, acetyl aniline and phenyl ester were also found to be compatible with this catalytic protocol with high yields (Table 2, entries 29 and 30). We also tested toluene, aniline and phenol, but unfortunately, the reaction was sluggish.

Table 1 Optimization of reaction conditions^a



Entry	Salt	Br-source	T/h	Solvent	Yield (%)
1	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	H_2O	7
2	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	DMSO	9
3	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	Acetone	<1
4	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	DMF	3
5	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	NMP	<1
6	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	Hexane	67
7	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_2Cl_2	98
8	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	EA	87
9	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	Methanol	<1
10	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	Ethanol	3
11	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	>99
12	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	NaBr	2 h	CH_3CN	98
13	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	LiBr	2 h	CH_3CN	95
14	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	CuBr_2	2 h	CH_3CN	96 ^b
15	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	FeBr_3	2 h	CH_3CN	95 ^c
16	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	1 h	CH_3CN	57
17	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	3 h	CH_3CN	97
18	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	4 h	CH_3CN	96
19	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	95 ^d
20	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	94 ^e
21	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	92 ^f
22	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	29 ^g
23	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	65 ^h
24	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	KBr	2 h	CH_3CN	64 ⁱ
25	—	KBr	2 h	CH_3CN	<1
26	FeCl_3	KBr	2 h	CH_3CN	<1
27	FeBr_3	KBr	2 h	CH_3CN	<1
28	$\text{Fe}_2(\text{SO}_4)_3$	KBr	2 h	CH_3CN	<1
29	$\text{Cu}(\text{NO}_3)_2$	KBr	2 h	CH_3CN	29
30	$\text{Co}(\text{NO}_3)_2$	KBr	2 h	CH_3CN	<1
31	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	KBr	2 h	CH_3CN	<1

^a Anisole (0.5 mmol), salt (0.625 mmol), Br-source (0.625 mmol), rt, GC yield. ^b CuBr_2 (0.313 mmol). ^c FeBr_3 (0.208 mmol). ^d $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.5 mmol). ^e $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.375 mmol). ^f $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 mmol). ^g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.125 mmol). ^h KBr (0.575 mmol). ⁱ KBr (0.525 mmol).



Table 2 Bromination of various substrates^a

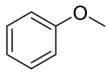
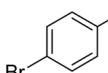
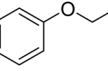
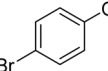
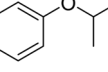
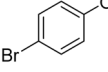
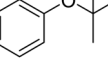
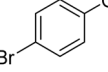
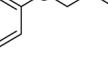
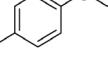
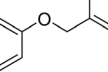
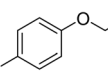
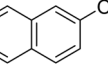
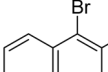
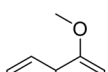
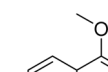
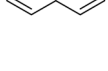
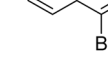
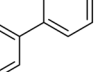
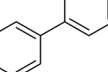
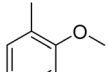
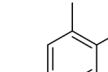
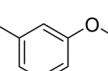
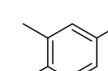
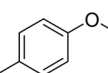
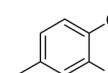
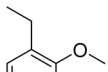
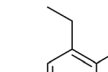
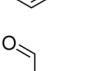
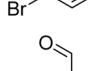
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3			90
4			83
5			89
6			85/99 ^b
7			97
8			86 ^c
9			71/91 ^b
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11			99
12			98
13			97
14			61/93 ^b
15			79/96 ^b

Table 2 (Contd.)

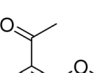
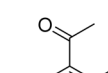
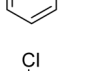
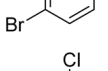
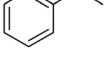
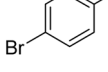
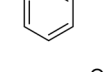
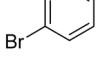
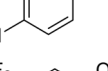
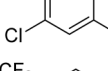
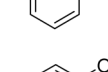
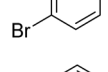
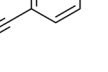
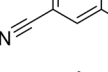
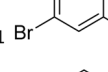

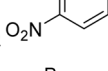
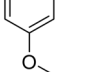
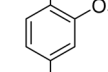
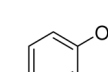
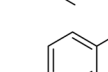
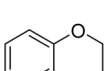
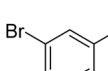
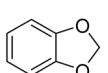
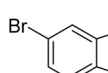
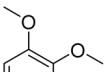
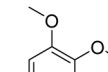
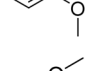
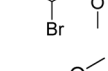
Entry	Substrate	Product	Yield/%
16			77/91 ^c
17			50/96 ^b
18			64/96 ^b
19			6/68 ^b
20			<1
21			<1
22		 	72/15 94 ^d /5 ^d
23			>99 ^e
24			84
25			82
26			79
27			90 ^f
28			33/65 ^b
29			<1



Table 2 (Contd.)

Entry	Substrate	Product	Yield/%
30			87

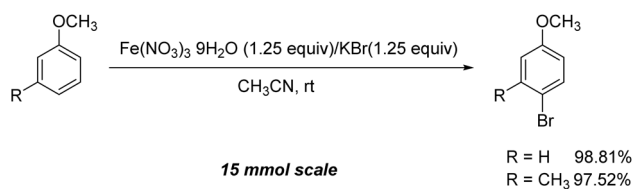
^a Anisole (0.5 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.625 mmol), KBr (0.625 mmol), rt, 2 h, GC yield. ^b 60 °C. ^c 4 h. ^d $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 mmol). ^e $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 mmol), KBr (0.6 mmol). ^f $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.375 mmol), KBr (1.5 mmol).

Furthermore, it is notable that the present bromination could be scaled up to gram level: excellent yields of the corresponding products were obtained in one batch from 15 mmol of anisole and 3-methylanisole by using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /KBr as an additive for 22 h (Scheme 1).

Inspired by the protocol of the bromination of anisole, the scope of the reaction was extended to iodination with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /NaI (Table S1†). The results are provided in Table 3, which indicate that this protocol is suitable for the iodination of anisole analogues by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /NaI with a ratio of 2 equiv./2 equiv. for 5 h at room temperature. In addition, the results were similar to those of the bromination process.

Moreover, possible mechanisms for the formation of the bromination are shown in Scheme 2. According to these results, that is, for 1,2-dimethoxybenzene, the side product was a nitro product (15%), and for 1,4-dimethoxybenzene, the main product was a nitration product with 83% yield. Meanwhile, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) are the generally accepted radical scavengers in organic chemistry. It was successfully found that the addition of TEMPO and BHT could influence the nitration process very significantly. For example, a low yield of 2 was obtained when TEMPO (2%, 0.5 equiv.) or BHT (7%, 0.25 equiv.) was added, and the bromination process was affected to a small extent under the reaction condition (Table 4).

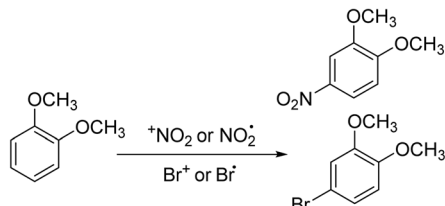
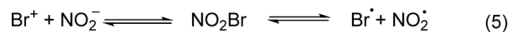
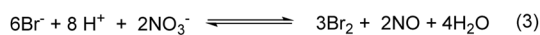
From these results, we propose a similar ionic pathway for our bromination process since our results are comparable with some of those works, 25a–c (Scheme 2). First, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was reacted with $\text{Fe}(\text{OH})_3$ and H^+ (eqn (1)), and then NO_3^- was converted into $^+\text{NO}_2$ (eqn (2)). The bromide ion (Br^-) from KBr would be reacted with $^-\text{NO}_3$ and H^+ to generate intermediate

Scheme 1 Scale-up of bromination by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /KBr.Table 3 Iodination of various substrates^a

Entry	Substrate	Product	Yield/%
1			>99
2			>99
3			>99
4			>99
5			>99
6			90
7			98
8			99
9			35 ^b
10			<1
11			73
			26
12			94
			93
13			93
14			41/69 ^b

^a Anisole (0.5 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.625 mmol), NaI (0.625 mmol), rt, 2 h, GC yield. ^b 60 °C.





Scheme 2 Possible mechanisms for bromination.

Table 4 Quenching experiments for the bromination process

Additive	Equiv.	Yield of 1 (%)	Yield of 2 (%)
TEMPO	0	72	16
TEMPO	0.5	69	2
TEMPO	0.25	60	13
BHT	0.25	72	7

Br_2 (eqn (3)). Then, unstable nitryl bromide (BrNO_2) was formed and depending on the substrate nature, it could act as electrophilic and radical species (eqn (4) and (5)). It was presumed that the bromination process involves typical electrophilic bromination to a large extent.

Conclusions

In conclusion, we have developed a simple, efficient and environmentally friendly methodology for the halogenation of anisole analogues using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{KBr}$ or NaI at room temperature. In this method, substrates with an electron-donating group afforded the corresponding product in good to excellent yields, while those with an electron-withdrawing group gave low to moderate yields. More importantly, this protocol is also applicable to gram-scale synthesis. It is hoped that this methodology will be very much useful in organic synthesis.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Author contributions

Conceptualization: Huanjun Xu and Yiying Li; methodology: Caicui Li, Yao Cheng and Fudan Pang; formal analysis: Xinmei Wang and Xiaodan Wang; investigation: Caicui Li, Xiushuo Yan, Zhengtao Huang and Yao Cheng; resources: Yiying Li, Huanjun Xu and Jinhui Wang; writing – original draft preparation: Xiaodan Wang and Huanjun Xu; writing – review and editing: Huanjun Xu and Jinhui Wang; supervision: Yiying Li and Huanjun Xu; project administration: Huanjun Xu; and funding acquisition: Yiying Li, Huanjun Xu and Jinhui Wang. All the authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Youth Project of Yazhou Bay Innovation Institute of Hainan Tropical Ocean University (No. 2022CXQNXM01), the National Natural Science Foundation of China (22165009), the Hainan Provincial Natural Science Foundation of China (821QN260), the Project of Hainan Association for Science and Technology of Youth Science and Talents (QCXM202023), and the National Science and Technology Major Project of the Ministry of Science and Technology of China (2018ZX09735005).

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