

A Green and Efficient Trinitration System for Aromatic Compounds with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/[\text{HMIM}]\text{ClO}_4$ as Catalyst in $\text{HNO}_3/\text{Ac}_2\text{O}$

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Abstract To investigate the green trinitration method of aromatic compounds, with Lewis acid/ionic liquid as catalyst and $\text{HNO}_3/\text{Ac}_2\text{O}$ as nitration reagent, a Lewis acid/ionic liquid/ $\text{HNO}_3/\text{Ac}_2\text{O}$ system was established. In various combinations of Lewis acids and ionic liquids, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/[\text{HMIM}]\text{ClO}_4$ proved to be a very efficient catalyst for the trinitration of activated aromatic compounds and reusable for 3 times. Reaction conditions for the trinitration were optimized and yields of the trinitro products were from mild to excellent. This sulfuric acid-free system has the advantages of strong trinitration ability, low environment pollution, low toxicity, low cost and high potential for industrial application.

Keywords Green trinitration; Aromatic compound; Lewis acid; Ionic liquid; Acetyl nitrate

1 Introduction

Trinitrated aromatic compounds are widely used as pharmaceuticals, dyes, pesticides, explosives, intermediates and other fine chemicals^[1]. Therefore, trinitration reaction of aromatic compounds has been a very important reaction in chemical industry. Traditional trinitration reaction is carried out with a mixture of sulfuric acid and nitric acid. Sulfuric acid can strongly promote the protonation of nitric acid to form nitronium ion, which is regarded as the nitrating species. This system is very efficient and has been widely utilized for many years^[2]. However, the mixed acid system has many notorious disadvantages, such as corrosion susceptibility, high acidic waste water pollutant generation, and low yields during production due to oxidative decompositions of substrates and products. In recent years, many environmental friendly nitration systems without sulfuric acid have been developed to overcome these problems, but most of them are selective for mononitration and hard to achieve trinitration^[3]. Because nitro-group's strong passivation effect can prevent further nitration of mononitration intermediates, much stronger reaction systems are needed for trinitration. Currently, only few studies about green trinitration of aromatic compounds have been done. Millar *et al.*^[4] used N_2O_5 as nitrating reagent to synthesize 2,4,6-trinitrotoluene (TNT), but sulfuric acid was still needed at the trinitration step. Iranpoor *et al.*^[5] reported that the ionic complexes of N_2O_4 and 18-crown-6/ $\text{Zn}(\text{NO}_3)_2$ could achieve trinitration of phenol. Crampton *et al.*^[6] reported that toluene could be trinitrated by N_2O_5 in perfluorocarbon solvents.

Yi *et al.*^[7] used ytterbium perfluorooctanesulfonate and perfluorooctanesulfonic acid as catalysts in fluoruous media, which showed efficient polynitration of aromatic compounds. However, these trinitration systems have many drawbacks including environmental pollution, low yields, or expensive solvents. In addition, industrial production of trinitroaromatic compounds still relies on mixed acid technology. Therefore, the research of a new green trinitration system is exigently needed.

To construct a sulfuric acid free nitration system, other types of acids or anhydrides should be used to form nitronium ion instead of sulfuric acid^[8]. Nitric acid/acetic anhydride system has a strong nitration capability and is easily recovered by distillation^[9]. Under appropriate catalytic conditions, $\text{HNO}_3/\text{Ac}_2\text{O}$ system can achieve dinitration^[10,11], so we used $\text{HNO}_3/\text{Ac}_2\text{O}$ system as a potential trinitration system for our study.

In order to achieve trinitration, catalyst is essential for $\text{HNO}_3/\text{Ac}_2\text{O}$ system. One option is Lewis acids (LAs), which are commonly used catalysts for many reactions. More importantly, some kinds of LAs can efficiently catalyze nitration reaction^[12], such as lanthanide metal salts^[13] and bismuth salt^[14,15] to form bidentate metal complexes with nitric acid to promote the nitration process. Another option is ionic liquids (ILs), which have been focused on in the recent years^[16–18]. ILs have high electric conductivity, wide electrochemical window, high thermal stability, extremely low volatility and special solubility. They are not only excellent substitutes for conventional solvents, but also potential catalysts for nitration reactions^[19–21]. There were several reports of using LA and IL

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simultaneously to facilitate Friedel-Crafts alkylation reaction^[22], cycloaddition reaction^[23] and mononitration reaction^[24], which produced high yields and enhanced selectivity. However, ILs are usually used as solvent rather than catalyst in most research and a large quantity is required. The cost greatly limits its applications. If just catalytic amounts of IL and LA are used simultaneously to enhance the nitration capability of HNO₃/Ac₂O system, trinitration may be achieved.

We used an LA/IL cooperating catalyst to catalyze the trinitration reaction of aromatic compounds. The goal of this study is to build a new, green and low-cost method of trinitration of aromatic compounds in HNO₃/Ac₂O/LA/IL system and investigate the catalytic mechanism of this cooperating catalyst.

2 Experimental

2.1 Reagents and Apparatuses

Chemicals were purchased from Sinopharm Chemical Reagent Ltd., Aladdin Reagent Ltd. or Shanghai Chengjie Chemical Reagent Ltd., and used without further purification. Thin layer chromatography(TLC) was performed on a silica gel plate purchased from Merck Ltd.(Darmstadt, Germany). Column chromatography was performed using silica gel(200—300 mesh) purchased from MeiGao Ltd.(Qingdao, China). Melting points were determined with an X-4 digital micro melting point tester(Taike Ltd., Beijing, China) and uncorrected. NMR spectra were recorded on a Bruker Avance III 600 MHz NMR Spectrometer.

2.2 General Procedure for Trinitration

To a solution of aromatic compound(3 mmol) and IL(5%, molar fraction, 0.15 mmol) was added LA at 0—5 °C. Then nitric acid(95%, mass fraction) was added dropwise. After the addition was completed, the mixture was stirred at a given temperature. After a given period of time, the solvent was removed under reduced pressure. Butyl acetate(5 mL×3) was added to the solid and the yellow organic phase was separated simply by decantation. The butyl acetate solution was concentrated and the residue was purified by recrystallization with

ethanol(30%, volume fraction) or silica-gel column chromatography to yield the product.

2.3 Recycling of the Catalyst

Following the extraction with butyl acetate, the remaining LA/IL was directly used for the next catalytic reaction after drying in a vacuum oven at 70 °C for 5 h.

3 Results and Discussion

First, the trinitration of anisole in HNO₃/Ac₂O/LA system was tested. Several kinds of LAs were chosen to test the catalytic activities using an activated aromatic compound anisole as substrate(Table 1). The results showed that without LAs, no trinitration product 2,4,6-trinitroanisole was detected in the system(Entry 1, Table 1). Only bismuth nitrate[Bi(NO₃)₃], lanthanum nitrate[La(NO₃)₃] and samarium nitrate[Sm(NO₃)₃] showed catalytic activities(Entries 2—7, Table 1) and the yield order was Bi(NO₃)₃(42.1%)>Sm(NO₃)₃(27.4%)>La(NO₃)₃(13.8%).

No trinitration product was detected with ZrO(NO₃)₂, Fe(NO₃)₃, Fe(NO₃)₃, Cu(NO₃)₂, Zn(NO₃)₂ and AlCl₃ as catalysts. That may be because that bismuth nitrate and lanthanide nitrates can form bidentate metal nitrates with nitric acid and liberate a proton(Eq.1). Then the proton reacts with another molecule of nitric acid to form a nitronium ion^[25]. Among these metal ions, bismuth(III) ion has the biggest charge-to-size ratio(*Z/r* ratio) and the strongest polarizability, which could enhance the nitrate anion binding and shift the equilibrium toward the right side^[26]. As a result, when Bi(NO₃)₃ was used as the catalyst, the highest yield was obtained. Furthermore, bismuth was widely regarded as a harmless, environment-friendly and green metal^[27], so we use Bi(NO₃)₃ as LA catalyst during future experiments.

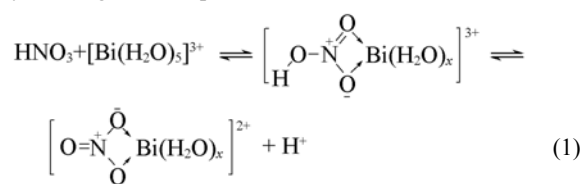
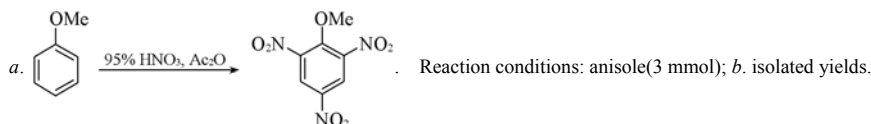


Table 1 Effect of LAs on the yield of 2,4,6-trinitroanisole^a

Entry	<i>n</i> (HNO ₃)/mmol	<i>n</i> (Ac ₂ O)/mmol	LA	<i>n</i> (LA)/mmol	Temperature/°C	Time/h	Yield ^b (%)
1	96	96	—		20	48	0
2	48	48	Bi(NO ₃) ₃ ·5H ₂ O	0.45	50	18	16.6
3	48	48	Bi(NO ₃) ₃ ·5H ₂ O	1.5	50	18	34.3
4	48	48	Bi(NO ₃) ₃ ·5H ₂ O	4.5	50	18	42.1
5	48	48	Bi(NO ₃) ₃ ·5H ₂ O	4.5	20	48	32.5
6	48	48	La(NO ₃) ₃ ·6H ₂ O	4.5	20	48	13.8
7	48	48	Sm(NO ₃) ₃ ·6H ₂ O	4.5	20	48	27.4
8	96	96	ZrO(NO ₃) ₂ ·2H ₂ O	4.5	20	48	0
9	96	96	Fe(NO ₃) ₃ ·9H ₂ O	4.5	20	48	0
10	96	96	Cu(NO ₃) ₂ ·3H ₂ O	4.5	20	48	0
11	96	96	Zn(NO ₃) ₂ ·6H ₂ O	4.5	20	48	0
12	96	96	AlCl ₃	4.5	20	48	0



Although trinitration can be achieved in $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LAs}$ system, the yields are very poor. Based on the previous studies of our team, we focused our attention on the catalytic activities of ILs. In many types of ILs, imidazolium ILs (Fig. 1) are widely applied in many reactions because of their high stability, solubility and ease to be synthesized. In this study, imidazolium ILs with different acidity and solubility were selected.

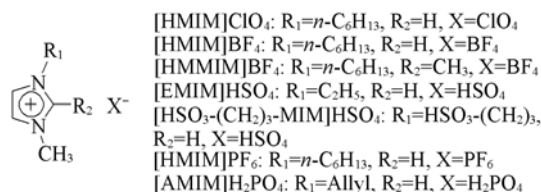
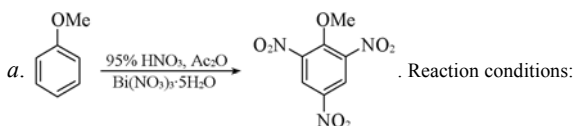


Fig.1 Chemical structure of the imidazolium ILs

To our surprise, all the ILs exhibited efficient catalytic activities (Table 2). In the presence of 48 mmol of HNO_3 , 48 mmol of Ac_2O , 4.5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.15 mmol of 1-hexyl-3-methylimidazolium perchlorate ($[\text{HMIM}]\text{ClO}_4$), the reaction engendered 2,4,6-trinitroanisole in a yield of 85.2% at 50 °C for 3 h (Entry 4, Table 2), while the yield was only 42.1% without ILs (Entry 4, Table 1).

Table 2 Effect of ILs on the yield of 2,4,6-trinitroanisole^a

Entry	$n[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ mmol	IL or inorganic salt (0.15 mmol)	Time/h	Yield ^b (%)
1	0	$[\text{HMIM}]\text{ClO}_4$	48	0
2	0.45	$[\text{HMIM}]\text{ClO}_4$	18	33.3
3	1.5	$[\text{HMIM}]\text{ClO}_4$	18	78.6
4	4.5	$[\text{HMIM}]\text{ClO}_4$	18	85.2
5	1.5	$[\text{HMIM}]\text{BF}_4$	18	75.8
6	1.5	$[\text{HMMIM}]\text{BF}_4$	18	75.0
7	1.5	$[\text{EMIM}]\text{HSO}_4$	18	49.5
8	1.5	$[\text{HSO}_3\text{-(CH}_2)_3\text{-MIM}]\text{HSO}_4$	18	46.7
9	1.5	$[\text{HMIM}]\text{PF}_6$	18	54.3
10	1.5	$[\text{AMIM}]\text{H}_2\text{PO}_4$	24	40.1
11	1.5	NaBF_4	24	25.0
12	1.5	NaClO_4	24	27.4
13	1.5	HClO_4	24	25.9
14 ^c	4.5	$[\text{HMIM}]\text{ClO}_4$	48	0
15 ^d	4.5	$[\text{HMIM}]\text{ClO}_4$	48	0

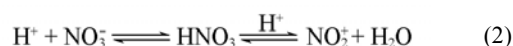


anisole (3 mmol), HNO_3 (48 mmol), Ac_2O (48 mmol), temperature (50 °C);
 b. isolated yields; c. CH_2Cl_2 (4 mL) was used as solvent instead of Ac_2O ;
 d. $[\text{HMIM}]\text{ClO}_4$ (1 g) was used as solvent instead of Ac_2O .

$[\text{HMIM}]\text{ClO}_4$ and 1-hexyl-3-methylimidazolium tetrafluoroborate ($[\text{HMIM}]\text{BF}_4$) proved to be most efficient for the trinitration of anisole, which significantly promoted the dissolution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to get homogeneous reaction systems. In the presence of 1.5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, the yields of 2,4,6-trinitroanisole increased from 34.3% to 78.6% and 75.8%, respectively (Entries 3 and 5, Table 2). In the experiments that 1-ethyl-3-methylimidazolium hydrosulfate ($[\text{EMIM}]\text{HSO}_4$), 1-(3-sulfonic acid)propyl-3-methylimidazolium hydrosulfate ($[\text{HSO}_3\text{-(CH}_2)_3\text{-MIM}]\text{HSO}_4$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[\text{HMIM}]\text{PF}_6$) or 1-allyl-3-methylimidazolium dihydric phosphate ($[\text{AMIM}]\text{H}_2\text{PO}_4$) was used, only a

part of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in these systems, and the yields were decreased to 40.1%—54.3% (Entries 7—10, Table 2). $[\text{HSO}_3\text{-(CH}_2)_3\text{-MIM}]\text{HSO}_4$ had the strongest acidity of these ILs, but it didn't show the highest activity (Entry 8, Table 2). These results indicated that the dissolving capacity of ILs played an important role in trinitration, and the acidity may not be an important factor. In order to prove this assumption, more experiments were conducted. Previous reports showed that $\text{C}_2\text{—H}$ of the imidazole ring could form hydrogen bond with nucleophilic groups to promote substitution reactions because of the acidity of imidazole ring^[17,28]. Therefore, a parallel experiment was carried out using 1-hexyl-2-methyl-3-methylimidazolium tetrafluoroborate ($[\text{HMMIM}]\text{BF}_4$), which has no $\text{C}_2\text{—H}$, instead of $[\text{HMIM}]\text{BF}_4$. However, no significant decrease in yield was observed, proving that the acidity of imidazole ring was not the major factor of trinitration (Entry 6, Table 2). Moreover, control experiments catalyzed by sodium fluoroborate, sodium perchlorate and perchloric acid were also carried out to test the function of acid radical ions and no improvements of the yields were observed (Entries 11—13, Table 2). Based on these results, it was apparent that the catalytic ability was not generated simply by imidazolium cations or acid radical ions, but the dissolving capacity of ILs.

Furthermore, Earle *et al.*^[29] reported that the anions of ILs were important for the nitration reaction. Halogen anion and mesylate anion can respectively cause halogenation and oxidation reaction rather than nitration. They pointed out that the acidity of anions' conjugate acids should be stronger or at least not weaker than HNO_3 , which would inhibit the acid ionization of HNO_3 and promote the base ionization to form NO_2^+ (Eq. 2). $[\text{AMIM}]\text{H}_2\text{PO}_4$ showing the lowest yield of 40.1% was consistent with this theory (Entry 10, Table 2).



In the absence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ or Ac_2O , trinitrated products were not detected, proving the LA and Ac_2O were indispensable to this reaction system (Entries 1, 14 and 15, Table 2).

Then we examined the trinitration in the $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LA}/\text{IL}$ system with a range of activated and deactivated aromatic substrates (Table 3). The results showed that the highly activated aromatic compounds could easily be trinitrated (Entries 1—3, Table 3); the weakly activated aromatic compound toluene was harder to be trinitrated (Entry 4, Table 3); the deactivated aromatic compound chlorobenzene failed to be trinitrated (Entry 5, Table 3). This system proved to be effective for trinitration of activated aromatics.

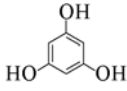
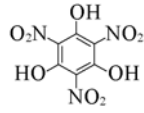

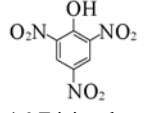
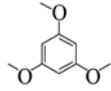
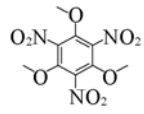

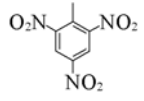

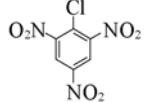
After the reaction, the product 2,4,6-trinitroanisole was extracted by butyl acetate and the catalyst remained was easily recovered by drying in a vacuum oven at 70 °C for 5 h. The recovered catalyst could be reused 3 times with the yields of 2,4,6-trinitroanisole decreasing slightly (Table 4).

To contrast the $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LA}/\text{IL}$ system with traditional nitro-sulfuric acid or nitrate-sulfuric acid systems, a comparison of the trinitration reaction of 1,3,5-trimethoxybenzene was performed (Scheme 1)^[30]. Rather than using a large amount of sulfuric acid, the $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LA}/\text{IL}$ system didn't generate

highly corrosive waste sulfuric acid and a higher yield was achieved. The existing green trinitration methods need expensive and poisonous reagents, such as perfluorocarbon solvents and crown ether solvents, pollute the environment and are too

costly for practical application in industry. The $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LA}/\text{IL}$ system can resolve these drawbacks by using low costly and low toxic reagents for industrialized application.

Table 3 Trinitration of aromatic compounds promoted by $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/[\text{HMIM}]\text{ClO}_4^a$

Entry	Substrate	Temperature/ $^{\circ}\text{C}$	Time/h	Trinitration product	Yield ^b (%)
1 ^c	 Phloroglucinol	20	0.25	 2,4,6-Trinitrophloroglucinol	94.7
2 ^c	 Phenol	20	1	 2,4,6-Trinitrophenol	86.0
3 ^c	 1,3,5-Trimethoxybenzene	35	3	 2,4,6-Trinitro-1,3,5-trimethoxybenzene	80.7
4	 Toluene	70	24	 2,4,6-Trinitrotoluene	31.6
5	 Chlorobenzene	70	24	 2,4,6-Trinitrochlorobenzene	0

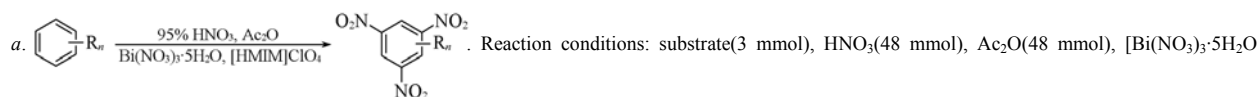
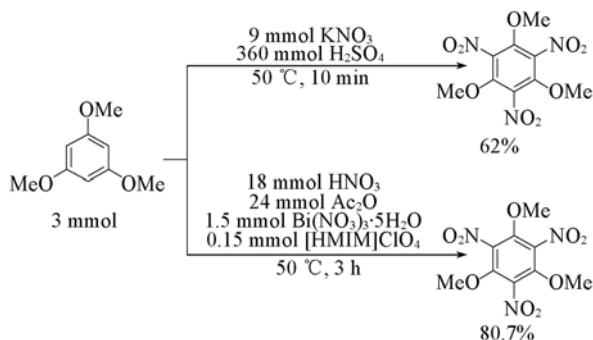


Table 4 Results of catalyst recycle studies^{*}

Run	Time/h	Yield of 2,4,6-trinitroanisole(%)
1	18	78.6
2	18	76.1
3	18	76.9
4	22	73.5

^{*} Reaction conditions: anisole(3 mmol), HNO_3 (48 mmol), Ac_2O (48 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.5 mmol), $[\text{HMIM}]\text{ClO}_4$ (0.15 mmol), temperature= 50°C .



Scheme 1 Comparison of the trinitration reaction of 1,3,5-trimethoxybenzene

4 Conclusions

In conclusion, a green and efficient $\text{HNO}_3/\text{Ac}_2\text{O}/\text{LA}/\text{IL}$

trinitration system of aromatic compounds was established, in which LA/IL was the catalyst and $\text{HNO}_3/\text{Ac}_2\text{O}$ was the nitration reagent. In various combinations of LAs and ILs, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/[\text{HMIM}]\text{ClO}_4$ proved to be a very efficient catalyst for the trinitration of activated aromatic compounds, which could be recycled and reused 3 times. The reaction conditions were optimized and the yields of the trinitro products were from mild(31.6%) to excellent(94.7%). Then a comparison of this method with other trinitration methods was made. Compared with the traditional nitro-sulfuric acid system, this sulfuric acid-free system has a comparable trinitration capability and much lower environment pollution. Compared with existing green trinitration systems, this system is lower costly, lower toxic and offers a high potential for industrial application.

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