

# An Efficient Method for the Nitration of Phenols with $\text{NaNO}_2$ in the Presence of 3-Methyl-1-Sulfonic Acid Imidazolium Chloride

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**Abstract.** Nitrophenols can be obtained in high yields via nitrosation-oxidation of phenols by 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} as a new Brønsted acidic ionic liquid and  $\text{NaNO}_2$  at room temperature. In situ generation of  $\text{HNO}_2$  and a radical-cation mechanism via the nitrous acid catalyzed pathway appear to be applicable to phenol nitration using this reagent system.

**Keywords:** 3-Methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}; Brønsted acidic ionic liquid; Nitrosation-oxidation; Nitration; Nitrophenols; Sodium nitrite ( $\text{NaNO}_2$ ).

## INTRODUCTION

Ambient temperature ionic liquids, especially those based on 1,3-dialkylimidazolium cations, have gained considerable interest as promising alternative green solvents in organic synthesis [1]. These ionic liquids have several interesting properties, such as excellent chemical and thermal stability, non-volatility, non-coordinating natures, safety, good solvating capability, a wide liquid range, and ease of recycling [1]. Furthermore, their hydrophobicity/hydrophilicity can be tuned by appropriate modification of the cations or anions [1]. Therefore, wide applications in catalytic and non-catalytic reactions have been found for room temperature ionic liquids [2-6]. In addition, the synthesis of task-specific ionic liquids which have a functional group in their framework may expand the applications of ionic liquids in organic chemistry [7,8]. Among ionic liquids, acidic ones have been successfully used in many organic transformations [7-10]. In continuation of our previous studies on the applications of acidic reagents and catalysts in organic synthesis [11,12], more recently, we have synthesized ionic liquid 3-methyl-1-

sulfonic acid imidazolium chloride {[Msim]Cl} as a new Brønsted acidic reagent from the simple reaction of 1-methylimidazole with chlorosulfonic acid at room temperature (Figure 1) [13]. We believe that this new ionic liquid can be applied as a reagent, as well as catalyst, for different organic transformations. Herein, we found that the acidity of this Brønsted acidic reagent was suitable for the in situ generation of  $\text{HNO}_2$ , when used in conjunction with  $\text{NaNO}_2$ , for the nitration of phenols.

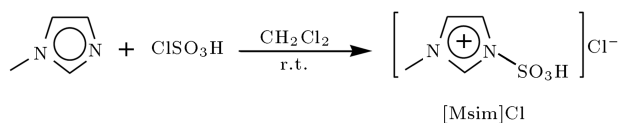
The nitration of organic compounds is a very active and rewarding area of research, being also the subject of a large body of literature [14]. Moreover, nitro-aromatic compounds have been extensively utilized as chemical feedstock for a wide range of useful materials, such as dyes, pharmaceuticals, perfumes and plastics [15]. The nitration of benzene and toluene is one of the most important routes to substituted aromatics in the production of chemical intermediates [16]. Nitration normally requires the use of a corrosive liquid phase nitric acid-sulfuric acid mixture, leading to an excessive waste stream. Furthermore, the nitration reactions are not usually regioselective and some over-nitration or competitive oxidation may occur [17]. The nitration of phenol, taken as a special case, has been achieved by several nitrating agents [18-27]. For example, some nitrating agents including sodium nitrite [18,19], concentrated nitric acid, acid anhydrides or triflates [20-22], peroxy nitrite [23], metal nitrates [24-26] and nitrogen oxides [27] have been utilized for this transformation. Although several

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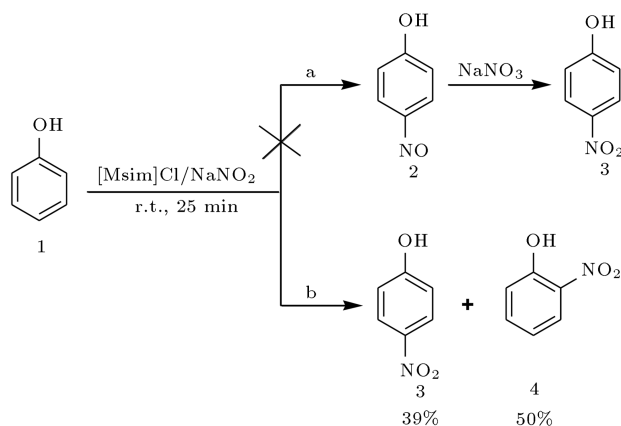


**Figure 1.** The synthesis of ionic liquid [Msim]Cl.

methods for the nitration of phenols are known, newer methods continue to attract attention for their experimental simplicity and effectiveness. In this work, we wish to use [Msim]Cl/NaNO<sub>2</sub> as a new and efficient reagent for the nitration of phenolic compounds to give the corresponding nitrated phenols at high yields and short reaction times.

## RESULTS AND DISCUSSION

During the course of our studies on the utilization of NO<sup>+</sup> in functional group transformations [28], we thought that phenol (**1**) could be converted to *p*-nitrosophenol (**2**), selectively, by a 3-methyl-1-sulfonic acid imidazolium chloride (3 eq)/NaNO<sub>2</sub> (1 eq) system (1 equivalent of [Msim]Cl is needed for the oxidation step). Moreover, phenol nitrosation is rapid and yields almost entirely the *para*-isomer which can be readily converted to *p*-nitrophenol via a mild oxidation with HNO<sub>3</sub> [29] etc. (Figure 2, path a). Therefore, we decided to produce *p*-nitrophenol via the nitrosation-oxidation strategy in a one-pot reaction under mild conditions [30]. We selected [Msim]Cl as the acid source (a proton source for the in situ generation of HNO<sub>2</sub> and NO<sup>+</sup> under mild conditions)/NaNO<sub>2</sub> system for the nitrosation of phenols (Figure 2, path b). In most reported methods for the nitration of phenols, NaNO<sub>3</sub> (1 eq) was needed for the second step; in situ generation of HNO<sub>3</sub> for the oxidation of *p*-nitrosophenol (Figure 2, path a). In contrast to the reported procedures in aqueous media [31], we observed that nitrosation and oxidation were occurred simultaneously using the [Msim]Cl/NaNO<sub>2</sub> system. Thus, in this reaction, mono-nitration was occurred,



**Figure 2.** The mono-nitration of phenol.

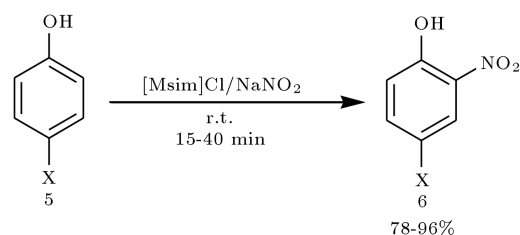
and *p*-nitrophenol (**3**) as well as *o*-nitrophenol (**4**) were obtained at 39% and 50%, respectively, after 25 min (Figure 2, path b).

A good range of 4-substituted phenols (**5**) was also subjected to the nitration reaction in the presence of 3-methyl-1-sulfonic acid imidazolium chloride and NaNO<sub>2</sub> at room temperature (Figure 3). The nitration reactions proceeded under mild conditions at room temperature and afforded the products at high yields and short reaction times (Figure 3 and Table 1). The presented nitration reactions were readily carried out by grinding the nitrating agents and phenols (**1** or **5**) in a mortar. The mono-nitrophenols were obtained by a simple workup.

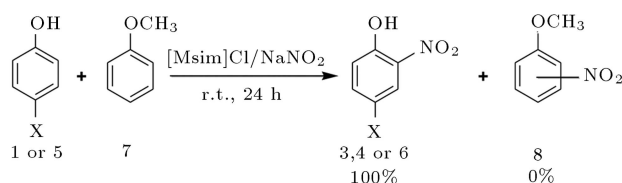
A competitive reaction was also performed between phenols and anisole. It was observed that exclusive phenol nitration proceeded; anisole remaining intact in the reaction mixtures after 24 hours (Figure 4). Selective mono-nitration of 4,4'-dihydroxydiphenyl (**5 k**) was also achieved by controlling the stoichiometric of the reagents (Table 1, entry 12).

The 3-Methyl-1-sulfonic acid imidazolium chloride/sodium nitrite system is similar to N<sub>2</sub>O<sub>4</sub> (N<sub>2</sub>O<sub>4</sub> ⇌ NO<sup>+</sup>NO<sub>3</sub><sup>-</sup>) in the case of generation of HNO<sub>2</sub> (eq 1) and NO<sup>+</sup> that work as a nitrosating agent (Figure 5, eq 2). Thus, on the basis of our observations, the previously reported results concerning the applications of N<sub>2</sub>O<sub>4</sub> [32] and metal nitrate dinitrogen tetroxide complexes [M(NO<sub>3</sub>)<sub>m</sub>.nN<sub>2</sub>O<sub>4</sub>] [27], and the reported mechanism for the nitration of phenols [33], the following reported nitrous acid catalyzed mechanism may be approved (Figure 5) [19,34].

In another study, the [Msim]Cl/NaNO<sub>2</sub> system was examined for di-nitration of phenols. For this purpose, 6.2 eq of [Msim]Cl and 2 eq of NaNO<sub>2</sub> were reacted with 1 eq of *p*-methoxyphenol. In this reaction,



**Figure 3.** The mono-nitration of phenols using [Msim]Cl/NaNO<sub>2</sub> system.



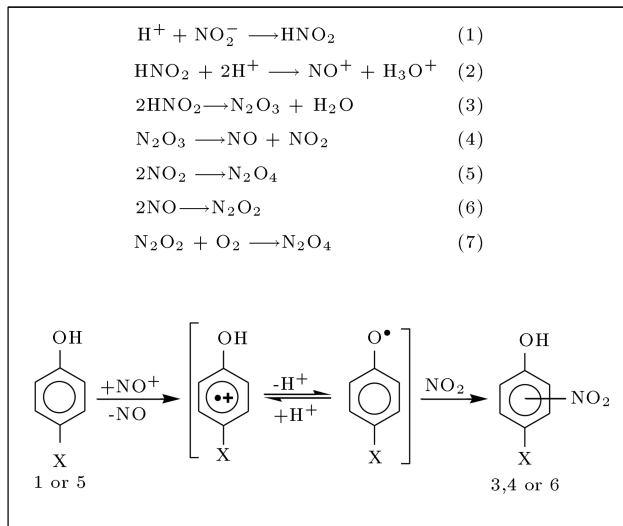
**Figure 4.** The competitive nitration reaction between phenols and anisole.

**Table 1.** Mono-nitration of phenols using [Msim]Cl/NaNO<sub>2</sub> system at room temperature.

5	a	b	c	d	e	f	g	h	i	j	k
X	F	Cl	Br	CN	Ph	CHO	OCH <sub>3</sub>	COCH <sub>3</sub>	CH <sub>2</sub> Ph	NHOAc	4-HOC <sub>6</sub> H <sub>4</sub> -
Entry	Substrate	Product	Time (min)	Yield <sup>a</sup> (%)	M.p.(°C)						
					Found	Reported					
1	1	3	25	39	111-114	115 [35]					
		4		50	44-46	44 [35]					
2	5a	6a	15	94	72-73	73-74 [36]					
3	5b	6b	15	96	89-90	91 [37]					
4	5c	6c	15	95	87-89	84 [37]					
5	5d	6d	20	93	139-142	145 [36]					
6	5e	6e	25	87	61-64	61-64 [38]					
7	5f	6f	25	91	139-141	140-142 [19]					
8	5g	6g	20	93	52-54	54-56 [38]					
9	5h	6h	35	90	121-123	123 [37]					
10	5i	6i	25	91	60-62	66 [19]					
11	5j	6j	30	89	177-180	180 [38]					
12	5k	6k	40	78	181-183	183-184 [19]					
13	1	3,4	24 h	— <sup>b</sup>	—	—					

a: Isolated yields.

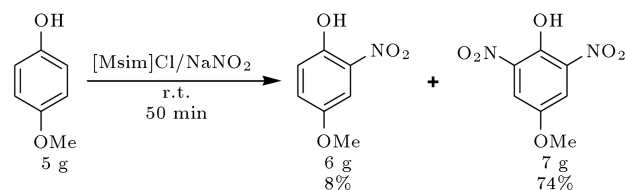
b: The reaction was not carried out in the absence of [Msim]Cl.


**Figure 5.** The proposed mechanism for the nitration of phenols.

mono- and di-nitrated products were obtained at 8% and 74% yields, respectively, within 50 min (Figure 6).

We also tried to use the [Msim]Cl/NaNO<sub>2</sub> system for the nitration of aniline; however, our attempt was not successful.

To compare the efficiency of the [Msim]Cl/NaNO<sub>2</sub> system for the nitration of phenols with the other systems, we have tabulated the results of the mono-nitration of *p*-bromophenol under different reaction


**Figure 6.** The di-nitration of *p*-methoxyphenol.

conditions in Table 2. As shown in Table 2, [Msim]Cl/NaNO<sub>2</sub> is superior to the previously reported reagent system.

## CONCLUSION

In summary, we have introduced 3-methyl-1-sulfonic acid imidazolium chloride/NaNO<sub>2</sub> as an efficient and novel reagent for the efficient nitration of phenols. The promising points of this method are the simple experimental procedure, mild reaction conditions, safety, high yields, short reaction times and the minimization of chemical waste, as compared to their liquid phase counterparts.

## EXPERIMENTAL

All Chemicals were purchased from the Merck or Fluka Chemical Company. The nitration products were characterized by comparison of their <sup>1</sup>H NMR, TLC and melting points with those in the authentic samples.

**Table 2.** Comparison of the results of nitration of *p*-boromophenol using different reagents.

Entry	Reagent System	Time (min)	Yield (%)	Ref.
1	Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> /Fe(NO <sub>3</sub> ) <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	360	98	[26]
2	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /Fe(NO <sub>3</sub> ) <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	390	97	[26]
3	NaHSO <sub>4</sub> .H <sub>2</sub> O/NaNO <sub>3</sub> /wet SiO <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub>	130	70	[39]
4	Mg(HSO <sub>4</sub> ) <sub>2</sub> /NaNO <sub>3</sub> /wet SiO <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub>	130	78	[39]
5	Silica sulfuric acid/NaNO <sub>2</sub> /wet SiO <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub>	120	90	[38]
6	Tribromoisocyanuric acid/NaNO <sub>2</sub> /wet SiO <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub>	60	92	[19]
7	[Msim]Cl/NaNO <sub>2</sub>	15	95	—

Melting points were recorded on a Stuart Scientific Apparatus SMP3 (UK) in open capillary tubes.

### Procedure for the Preparation of Ionic Liquid [Msim]Cl

A round-bottomed flask (100 mL) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and then chlorosulfonic acid (0.605 g, 5.2 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, stood for 5 min, and the CH<sub>2</sub>Cl<sub>2</sub> was decanted. The residue was washed with dry CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL) and dried under vacuum to give [Msim]Cl as a viscous colorless oil at 92% yield, 0.912 g [13].

### Typical Procedure for the Mono-Nitration of Phenol (1) Using [Msim]Cl/NaNO<sub>2</sub> System

A mixture of compounds consisting of phenol (0.094 g, 1 mmol), [Msim]Cl (0.616 g, 3.1 mmol) and NaNO<sub>2</sub> (0.069 g, 1 mmol) was ground vigorously in a mortar at room temperature. After completion of the reaction, as monitored by TLC, the reaction mixture was extracted with EtOAc (2 × 15 mL) and the organic extracts were combined. Anhydrous Na<sub>2</sub>SO<sub>4</sub> (0.5 g) was added to the extracts. After 3 min, the resulting mixture was filtered, and the solvent was evaporated. The residue was a mixture of *o*- and *p*-nitrophenol. Only *o*-nitrophenol (**4**) is soluble in *n*-pentane. *n*-Pentane was added to the mixture, stirred and filtered; the residue was *p*-nitrophenol (**3**, 39% yield). The solvent of the filtrate was evaporated to give *o*-nitrophenol in 50%.

### General Procedure for the Mono-Nitration of 4-Substituted Phenols Using [Msim]Cl/NaNO<sub>2</sub> System

A mixture of 4-substituted phenol (1 mmol), [Msim]Cl (0.616 g, 3.1 mmol) and NaNO<sub>2</sub> (0.069 g, 1 mmol) was ground vigorously in a mortar at room temperature. After completion of the reaction, as monitored by

TLC, the reaction mixture was extracted with EtOAc (2 × 15 mL) and the organic extracts were combined. Anhydrous Na<sub>2</sub>SO<sub>4</sub> (0.5 g) was added to the extracts. After 3 min, the resulting mixture was filtered, and the solvent was evaporated to give the pure product.

Notice: The reactions displayed in Figure 4, as well as entry 13 of Table 1, were performed in a 10 mL round-bottomed flask with magnetic stirring.

### Spectral Data of Ionic Liquid [Msim]Cl

Viscous colorless oil; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz): δ (ppm) 3.77 (s, 3H, CH<sub>3</sub>), 7.46 (s, 1H), 7.51 (s, 1H), 8.84 (s, 1H), 13.96 (s, 1H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz): δ (ppm) 36.5, 120.6, 124.2, 138.6; MS (m/z): 199 (M<sup>+</sup>+1), 198 (M<sup>+</sup>), 183 (M<sup>+</sup>-CH<sub>3</sub>), 163 (M<sup>+</sup>-Cl), 82 (M<sup>+</sup>-ClSO<sub>3</sub>H), 67 (M<sup>+</sup>-CH<sub>4</sub>ClSO<sub>3</sub>); Anal. Calcd. for C<sub>4</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>3</sub>S: C, 24.19; H, 3.55; N, 14.10. Found: C, 24.41; H, 3.69; N, 13.92 .

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