JOC The Journal of Organic Chemistry

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Design of Ionic Liquid 3-Methyl-1-sulfonic Acid Imidazolium Nitrate as Reagent for the Nitration of Aromatic Compounds by *in Situ* Generation of NO_2 in Acidic Media

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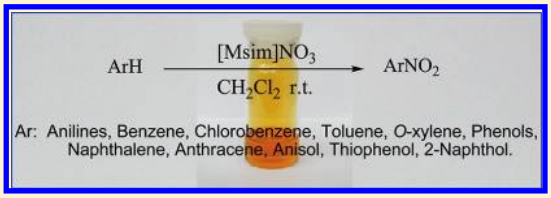
Supporting Information

ABSTRACT: 3-Methyl-1-sulfonic acid imidazolium nitrate ([Msim]-NO_3) as a new Brønsted acidic ionic liquid and nitrating agent was prepared and used for the efficient nitration of aromatic compounds (even aniline derivatives). The dramatic effect of this reagent by *in situ* generation of nitrogen dioxide as a radical on aromatic compounds to give nitroarenes has been studied.



Ionic liquids (ILs) have received considerable interest as eco-friendly solvents, catalysts, and reagents in the context of green synthesis because of their unique properties such as low volatility, nonflammability, high thermal stability, negligible vapor pressure, and ability to dissolve a wide range of materials.[1] In continuation of a project involving the production and applications of acidic ILs in organic synthesis, we have recently introduced a new category of ionic liquids, namely, sulfonic acid functionalized imidazolium salts (SAFIS).[2] These ILs were successfully employed as catalysts to prepare bis(indolyl)methans,[2a] *N*-sulfonyl imines,[2b] nitro phenolic compounds,[2c] 1-amidoalkyl-2-naphthols,[2d] and benzimidazoles.[2e] Herein, we report the novel ionic liquid 3-methyl-1-sulfonic acid imidazolium nitrate ([Msim]NO_3), which exhibits many interesting properties (Figure 1).

Figure 1. Structure and color of 3-methyl-1-sulfonic acid imidazolium nitrate.

The nitration of arenes is an interesting process, not only for the application of nitroarenes as explosives but also due the versatile use of nitroarenes as intermediates in various important functional group transformations.[3] Nitro-aromatic compounds are also extensively utilized as chemical feedstocks for a wide range of useful materials such as dyes, pharmaceuticals, perfumes, and plastics.[4a] Several reagents and catalysts have been employed for the nitration of aromatic compounds, such as sodium nitrite/[Msim]Cl,[2c] trichloroisocyanuric acid or silica sulfuric acid/$NaNO_2$/wet SiO_2,[4b,c] trimethylsilyl nitrate,[4d] *N*-nitropyridinium salts,[4e] nitrogen oxide,[4f] nitric acid/P_2O_5/silica gel,[4g] nitric acid/mixed metal oxides,[4h] nitric acid/lanthanide reagents,[4i] HNO_3–Ac_2O system in [bmpy][$N(Tf)_2$],[4j] HNO_3 in [bmim]Otf,[4k] [NO_2][BF_4] in [emim][X] (X = OTf^-, CF_3COO^-, and NO_3^-),[4l] NO_2/air-catalyzed by sulfonic acid functionalized ionic liquid,[4m] and a mixture of nitric acid and acetic anhydride in ionic liquid.[4n] There are rare nitrating agents in which both an acidic catalyst and a nitro group source are present and are simultaneously employed. Moreover, many of the reported methods are associated with one or more of the following drawbacks: (i) low yields, (ii) long reaction times, (iii) the use of a large catalyst load, (iv) the use of toxic or expensive catalysts, (v) low regioselectivity, (vi) over nitration, (vii) oxidation of reagents, and (viii) safety problems. Thus, the design of an efficient, inexpensive, nonpolluting, and versatile reagent for the nitration aromatic compounds is still of practical importance.

Recently, we have employed a mixture of 3-methyl-1-sulfonic acid imidazolium chloride (as a co-catalyst) and sodium nitrite (as nitrating agent) for the nitration of phenolic compounds.[2c] This combination was similar to N_2O_4 ($N_2O_4 \Leftrightarrow NO^+NO_3^-$) in the case of generation of HNO_2 and NO^+, which worked as a nitrosating agent. For that system,[2c] a nitrous acid catalyzed mechanism can be proposed.[2c,4b,c] Moreover, using 3-methyl-1-sulfonic acid imidazolium chloride/sodium nitrate, only phenolic compounds were nitrated, and the system did not work for the nitration of the other aromatic compounds. However, in the present investigation, [Msim]NO_3 by the *in situ* generation of NO_2 as a radical without any co-catalysts was

Received: January 22, 2012
Published: March 13, 2012

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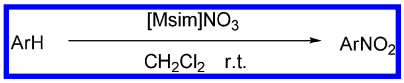
used to produce a wide range of aromatic compounds in high yields and very short reaction times. Direct nitration of aniline at room temperature is another highlight in this method.

With these issues in mind, we designed and synthesized the ionic liquid 3-methyl-1-sulfonic acid imidazolium nitrate ([Msim]NO_3) as a new SAFIS, a highly efficient and organic reagent without the need of a co-catalyst for the nitration of various aromatic compoundes (Scheme 1).

Scheme 1. Nitration of Aromatic Compounds Using [Msim]NO_3



After the preparation of [Msim]NO_3 *via* the reaction of [Msim]Cl with nitric acid (Scheme 2), its structure was identified by IR, ^{1}H and ^{13}C NMR, mass spectra, and CHN analysis.

The IR spectrum of the reagent shows two strong peaks at ca. 1354 and 1635 cm^{-1} that are typical of $\nu_{O-N=O}$ symmetric stretching vibration and $\nu_{O-N=O}$ asymmetric stretching vibration, respectively. Additionally, the two peaks observed at 1166 and 1309 cm^{-1} correspond to vibrational modes of the N−SO_2 bond. The ^{1}H NMR spectrum of [Msim]NO_3 shows the unmistaken acidic hydrogen (SO_3H) peak at 14.24 ppm. To confirm that this peak is really related to the hydrogen of SO_3H in the compound, we also acquired the ^{1}H NMR spectra of $ClSO_3H$, [Msim]Cl and 1-methylimidazolium chloride with HNO_3 in DMSO-d_6. In these spectra, the peaks of the acidic hydrogens of [Msim]NO_3, $ClSO_3H$, [Msim]Cl, and 1-methylimidazolium chloride with HNO_3 were observed at 14.24, 13.45, 13.96, 8.46, and 13.01 ppm, respectively. The rest of the NMR signals are provided in the Experimental Section. The mass spectrum of the compound gave the correct molecular ion peak at 225.

The thermogram (TG) of the reagent shows several weight losses. The loss of about 21% of weight from 60 to 160 °C appears to correspond to the loss of NO_2. The second weight loss occurs between 240 and 320 °C and the subsequent loss after 320 °C are related to molecular decomposition (Figure 2).

An experiment was performed to confirm the loss of nitrogen dioxide from [Msim]NO_3 (Figure 3). The gas (nitrogen dioxide) that was released from the reagent upon heating at about 60 °C was collected over a test tube and transferred to a round-bottomed flask in the presence of copper powder and ethyl acetate. NO_2 in equilibrium with dinitrogen tetroxide (N_2O_4)[5] reacts with copper metal to form $Cu(NO_3)_2$ at room temperature in 45 min. In this reaction, appearance of the blue color due to copper nitrate formation in anhydrous media is convincing evidence of the release of nitrogen dioxide.[6] Moreover, the excess copper powder residue turned black over time, suggesting that O_2 is produced from [Msim]NO_3 as well. Oxygen reacts with copper metal to form the black copper oxide as an insoluble residue (Scheme 3 and Figure 3).

The ^{1}H NMR spectrum of the ionic liquid that remained in the test tube after all the NO_2 and O_2 was driven off was determined. This spectrum showed the existence of the 1-methylimidazolium cation. It is also clear that [Msim]NO_3 even at room temperature led to the formation of NO_2, O_2, H_2O, and the zwitterionic salt. The latter is hydrolyzed by H_2O to give 1-methylimidazolium cation and hydrogen sulfate anion (Scheme 4), which was observed by NMR. The cation is then converted to the initial starting material (1-methylimidazole) upon neutralization with base, followed by regeneration of [Msim]NO_3 *via* [Msim]Cl (Scheme 8).

To confirm that [Msim]Cl was completely converted to [Msim]NO_3, a solution of $AgNO_3$ in distilled water was added to a solution of the reagent in distilled water. The absence of AgCl precipitate indicates complete conversion of the [Msim]Cl to [Msim]NO_3. Excess chlorosulfonic acid is removed through repeated washing of the IL with dichloromethane. Slight excess of HNO_3 did not influence the performance of the IL as a nitration agent.

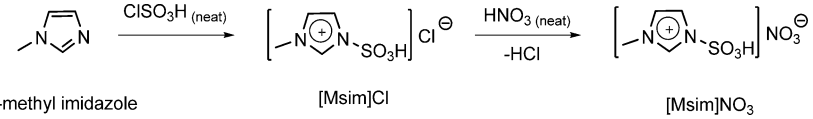
We have also investigated the potential of [Msim]NO_3 as a nitration agent on a model reaction with naphthalene. NO_2 exists in equilibrium with dinitrogen tetroxide (N_2O_4). Homolytic dissociation of dinitrogen tetroxide to form the NO_2 radical and heterolytic dissociation produces NO^+, NO_3^-, NO_2^-, and NO_2^+.[3] Therefore in this case, several intermediates of nitrogen oxides could be found. We investigated the effective application of NO_2 with iodine as a radical scavenger (Scheme 5).[7] In the presence of iodine; the yield of 1-nitro naphthalene was very low even after 24 h. Nitration of naphthalene was also examined in the presence of butylated hydroxytoluene (BHT) as a radical scavenger. In this reaction media, the nitration process was carried out slowly, and the yield of 1-nitro-naphthalene was decreased even after long reaction time. It can therefore be concluded that nitrogen dioxide in the radical form makes up the bulk of the active species under these reaction conditions. The results are presented in Table 1.

When our reagent was reacted with benzenethiol, the main product was 1,2-diphenyldisulfane. As shown in Scheme 6 benzenethiol is converted to the corresponded Ar-S$^\bullet$ radical in the presence of NO_2.[4a] Two of these radicals dimerize to form 1,2-diphenyldisulfane, and nitrous acid is a byproduct in this reaction (Scheme 6).

A plausible mechanism for the nitration of naphthalene involves the release of NO_2 from [Msim]NO_3 to produce the naphthalene radical and nitrous acid (HNO_2). A second NO_2 radical and the naphthalene radical react to form nitro naphthalene (Scheme 7).

In contrast to many previously reported procedures for the nitration of aniline, we have successfully nitrated aniline to produce 2-nitroaniline and 4-nitroaniline using [Msim]NO_3. In the existing methods, the nitrogen of aniline attracts H^+ in acidic media, thus deactivating the nitration process. The reaction proceeds *via* an ionic mechanism,[8] and the resulting product (3-nitroaniline) forms in low yield. In our method with [Msim]NO_3, the *in situ* generation of NO_2 via a radical

Scheme 2. Preparation of 3-Methyl-1-sulfonic Acid Imidazolium Nitrate, [Msim]NO_3



dx.doi.org/10.1021/jo300137w | J. Org. Chem. 2012, 77, 3640−3645

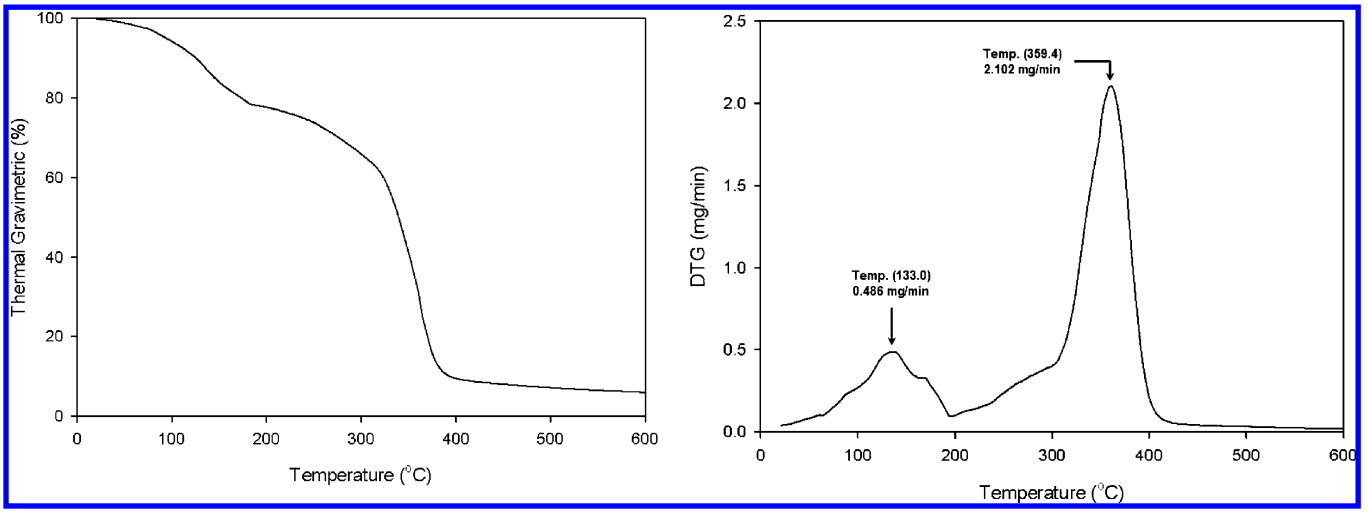


Figure 2. Thermal gravimetry (TG) and differential thermal gravimetry (DTG) of $[Msim]NO_3$.

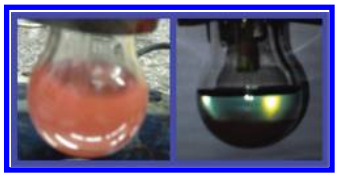
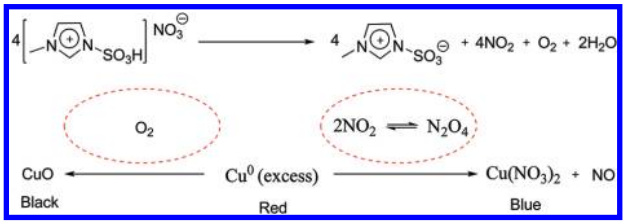
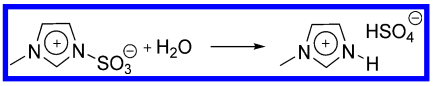


Figure 3. Preparation of copper nitrate (with blue color) from copper powder, evidence for the release of nitrogen dioxide.

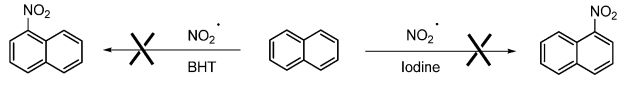
Scheme 3. Identification of Nitrogen Dioxide and Oxygen Using Copper Powder



Scheme 4. Production of 1-Methylimidazolium Cation *via* Hydrolizing Zwitterionic Salt by the Preduced H_2O in Reaction Media



Scheme 5. Trapping NO_2 Radical with Iodine and Butylated Hydroxytoluene (BHT)



mechanism facilitates the efficient nitration of aniline to form 2-nitroaniline and 4-nitroaniline in good yields and regioselectivity, despite the *in situ* formation of acid.

A wide range of aromatic compounds such as benzene, chlorobenzene, toluene, *o*-xylene, naphthalene, anthracene, phenols, anisol, thiophenol, 2-naphthol, and anilines were also nitrated with $[Msim]NO_3$ (Table 2).

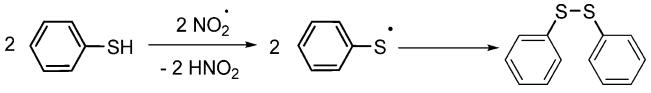
To maximize the unique advantages of this reagent, the scalability, recoverability, and reusability of 1-methylimidazole (the main starting material for the synthesis of the reagent) and regeneration of 3-methyl-1-sulfonic acid imidazolium nitrate

Table 1. Effect of Iodine and Butylated Hydroxytoluene as Radical Scavengers on the Nitration of Naphthalene (1 mmol) in the Presence of $[Msim]NO_3$ (1 mmol)

entry	radical scavenger (mmol)	time (min)	yield[a] (%)
1		immediately	84
2	I_2 (0.2)	1440	45
3	I_2 (0.5)	1440	30
4	I_2 (1)	1440	22
5	BHT (0.2)	1440	52
6	BHT (0.5)	1440	41
7	BHT (1)	1440	35

[a]Isolated yield of 1-nitronaphthalene.

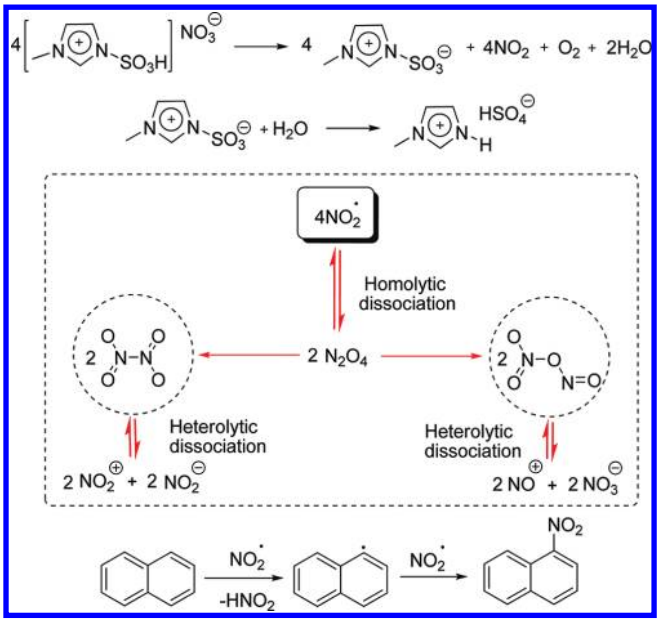
Scheme 6. Production of 1,2-Diphenyldisulfane Using $[Msim]NO_3$.



were studied. The reaction can easily be scaled up to 20 mmol quantities without significant changes in the yield and the reaction times. To study regeneration of the reagent, the reaction of naphthalene with $[Msim]NO_3$ was carried out several times, and the resulting IL phases (unreacted $[Msim]NO_3$, the zwitterionic salt, and 1-methylimidazolium salt) were combined. Water was added to the combined reaction mixtures, and the mixture was stirred for 5 min and filtered ($[Msim]NO_3$ and zwitterionic salt is miscible with water and separate from remained starting material and product.) $[Msim]NO_3$ and the zwitterionic salt were hydrolyzed in aqueous media. A solution of (10%) NaOH was then added to the reaction media, and the mixture was stirred for 5 min, resulting in the formation of 1-methylimidazole. The solution was extracted with ethyl acetate, washed with water, and dried. Evaporation of the solvent gave 1-methylimidazole (96% recovery). The recovered 1-methylimidazole was reacted with chlorosulfonic acid to give [Msim]Cl. Then, [Msim]Cl was again reacted with nitric acid (100%) to produce $[Msim]NO_3$. The activity of the reproduced $[Msim]NO_3$ as nitration agent was identical to before. The regeneration of this reagent is summarized in Scheme 8.

dx.doi.org/10.1021/jo300137w | J. Org. Chem. 2012, 77, 3640–3645

Scheme 7. Plausible Mechanism for the Nitration of Naphthalene Using [Msim]NO_3



In summary, we have introduced a novel SAFIS ([Msim]-NO_3) as a highly efficient reagent for the nitration of aromatic compounds. There are several attractive novelties about this nitration agent. The acidic reagent and the source of *in situ* NO_2 are present in a single compound that also serves as the ionic liquid.

EXPERIMENTAL SECTION

General Methods. The known products were identified by comparison of their physical and spectral data (IR, ^{1}H NMR, ^{13}C NMR, and mass) with those reported in the literature. Progress of the reactions was monitored by TLC.

General Procedure for the Preparation of the Ionic Liquid [Msim]NO_3. 1-Methylimidazole (0.410 g, 5 mmol) in dry dichloromethane (50 mL) was added to a round-bottomed flask (100 mL), and chlorosulfonic acid (0.605 g, 5.2 mmol) was then added dropwise over a period of 5 min at room temperature. The reaction mixture was then stirred for 20 min, and the dichloromethane was decanted after the reaction mixture was allowed to settle for 5 min. The residue was washed with dry dichloromethane (3 × 50 mL) to remove excess of chlorosulfonic acid and dried under vacuum to give [Msim]Cl as a viscous colorless oil.[2] Then, nitric acid 100% (0.315 g, 5 mmol) was dropwise added to [Msim]Cl (0.993 g, 5 mmol) over a period of 5 min at room temperature under a continuous flow of nitrogen to remove the HCl gas that is produced. The resulting mixture was stirred for 10 min under these conditions to give [Msim]NO_3 as a viscous yellow red oil in 99% (1.113 g) yield. IR (Nujol) 680, 1062, 1166, 1309, 1354, 1635, 2848, 2964, 3159, 3100−3400 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 3.85 (s, 3H, CH_3), 7.59 (s, 1H), 7.64 (s, 1H), 9.00 (s, 1H), 14.24 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 36.1, 120.5, 124.0, 136.6; MS m/z = 226 (M^+ + 1), 225 (M^+), 210 ($M^+ - CH_3$), 163 ($M^+ - NO_3$), 82 ($M^+ - NO_3SO_3H$), 67 ($M^+ - CH_4NO_3SO_3$). Anal. Calcd for $C_4H_7N_3O_6S$: C, 21.34; H, 3.13; N, 18.66. Found: C, 21.08; H, 3.24; N, 18.45.

General Procedure for the Nitration of Aromatic Compounds. To a round-bottomed flask (10 mL) was added 3-methyl-1-sulfonic acid imidazolium nitrate (0.225 g, 1 mmol, 0.128 mL) in dry dichloromethane (2 mL). The aromatic compound (1 mmol) was then added, and the mixture was stirred at room temperature the required short time (10−1800 min). After the reaction was completed (monitored with TLC), dichloromethane (5 mL) was added to the reaction mixture, and the mixture was stirred for 2 min and separated. The organic solvent was evaporated, and the product was easily purified by short column chromatography. **Note:** For the nitration of aniline and 4-methylaniline, after the reaction was completed, the reaction mixture was basified to pH 8 by the slow addition of 10% NaOH solution. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic solution was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a crude product, which was purified with short column chromatography.

General Procedure for the Use of Iodine or Butylated Hydroxytoluene (BHT) as Radical Scavengers. To a round-bottomed flask (10 mL) containing different amounts of iodine or butylated hydroxytoluene (BHT) as radical scavengers (0.2, 0.5, and 1 mmol) in dry dichloromethane (2 mL) was added 3-methyl-1-sulfonic

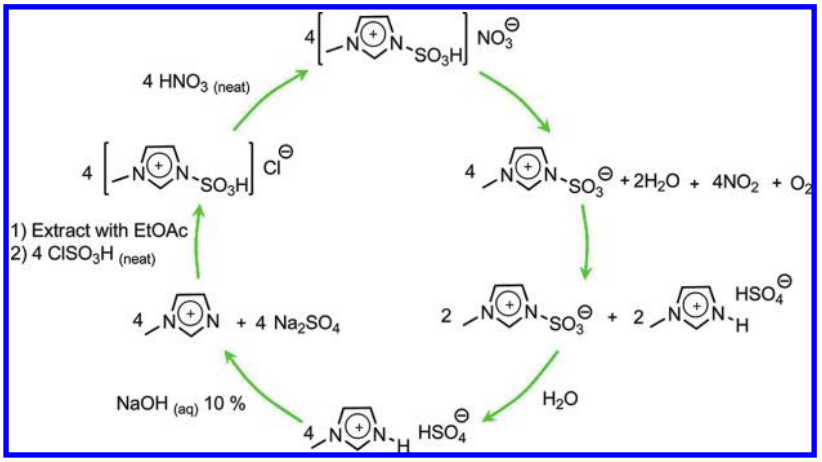
Table 2. Nitration of Aromatic Compounds Using [Msim]NO_3 at Room Temperature

substrate	product	time (min)	yield[a] (%)	mp/bp (°C) found	mp/bp (°C) reported [ref]
benzene	nitrobenzene (**1**)	2	82 (0.1009 g)	210−211	208−210 [4a]
toluene	4-nitrotoluene (**2**)	2	70 (0.0959 g)	52−54	53−55 [4a]
O-xylene	4-nitro-*o*-xylene (**3**)	1	89 (0.1345 g)	30−32	30−31 [4a]
naphthalene	1-nitronaphthalene (**4**)	immediately	84 (0.1455 g)	59−61	70−71 [4a]
anthracene	9-nitroanthracene (**5**)	immediately	80 (0.1785 g)	137−139	145−146 [9]
naphtalene-2-ol	1-nitronaphtalene −2-ol (**6**)	immediately	85 (0.1609 g)	100−103	103 [9]
phenol	2-nitrophenol (**7a**)	immediately	51 (0.0707 g)	43−47	44 [10]
	4-nitrophenol (**7b**)	immediately	42 (0.0582 g)	113−115	113−114 [4a]
biphenyl-4,4′-diol	3-nitrobiphenyl-4,4′-diol (**8**)	immediately	95 (0.2194 g)	180−182	180−184 [4c]
1-(4-hydroxyphenyl)ethanone	1-(4-hydroxy-3-nitrophenyl)ethanone (**9**)	immediately	90 (0.1632 g)	121−123	122−124 [4c]
anisol	4-nitroanisol (**10**)	1	92 (0.1406 g)	52−54	52−54 [4a]
4-bromophenol	4-bromo-2-nitrophenol (**11**)	immediately	90 (0.1960 g)	82−83	84 [4c]
benzenethiol	1,2-diphenyldisulfide (**12**)	5	75 (0.1634 g)	62−64	62−64 [4a]
aniline	2-nitroaniline (**13a**)	2	47 (0.0646 g)	71−73	69−72 [11]
	4-nitroaniline (**13b**)	2	39 (0.0541 g)	147−151	148 [12]
4-methylaniline	2-nitro-4-methylaniline (**14**)	15	81 (0.1231 g)	110−112	115−117 [13]
chlorobenzene[b]	1-chloro-4-nitrobenzene (**15**)	30	75 (0.1178 g)	82−84	82−83 [4a]

[a]Isolated yield was calculated on the basis of the reaction of aromatic compound (1 mmol) with [Msim]NO_3 (1 mmol). [b]This reaction was carried out in the absence of dichloromethane.

dx.doi.org/10.1021/jo300137w | J. Org. Chem. 2012, 77, 3640−3645

Scheme 8. Regeneration of $[Msim]NO_3$



acid imidazolium nitrate (0.225 g, 1 mmol, 0.128 mL). Naphthalene (0.128 g, 1 mmol) was then added, and the mixture was stirred at room temperature. After 24 h, dichloromethane (5 mL) was added to the reaction mixture, and the mixture was stirred for 2 min and separated. The organic solvent was evaporated, and the product was purified by short column chromatography.

Spectral Data of the Products. *Nitrobenzene (**1**).* Pale yellow oil; isolated yield 82% (0.1009 g). IR (Nujol) 704, 1348, 1590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.56 (t, J = 7.1 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), (dd, J = 8.3 Hz, 1.15 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 123.8, 129.7, 135.0, 158.5.

*1-Nitronaphthalene (**4**).* Yellow solid; isolated yield 84% (0.1455 g). IR (KBr) 653, 1336, 1519 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.72 (t, J = 6.9 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 8.23 (d, J = 7.5 Hz, 1H), 8.56 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)123.5, 124.4, 124.5, 125.5, 127.7, 129.0, 129.8, 134.7, 135.0.

*9-Nitroanthracene (**5**).* Yellow solid; isolated yield 80% (0.1785 g). IR (KBr) 692, 1369, 1517 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.59 (t, J = 5.7 Hz, 2H), 7.68 (t, J = 6.0 Hz, 2H), 7.98 (d, J = 6.0 Hz, 2H), 8.09 (d, J = 6.0 Hz, 2H), 8.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 121.8, 123.1, 126.6, 128.8, 129.3, 130.7, 131.2, 144.9.

*1-Nitronaphthalen-2-ol (**6**).* Yellow solid; isolated yield 85% (0.1609 g). IR (KBr) 717, 1373, 1539, 3150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.26 (t, J = 5.7 Hz, 1H), 7.50 (t, J = 6.9 Hz, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 8.0 (d, J = 9.0 Hz, 1H), 8.91 (d, J = 8.7 Hz, 1H), 12.23 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 119.3, 123.2, 125.6, 126.9, 128.6, 129.3, 131.0, 139.1, 139.2, 158.8. MS m/z = 190 (M^+ + 1), 189 (M^+), 143 ($M^+ - NO_2$).

*2-Nitrophenol (**7a**).* Yellow solid; isolated yield 51% (0.0707 g). IR (KBr) 748, 1373, 1533, 3230 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.01 (t, J = 8.5 Hz, 1H), 7.17 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 8.11 (dd, J = 6.9 Hz, 1.6 Hz, 1H), 10.59 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 120.3, 120.6, 125.4, 134.1, 137.9, 155.5.

*4-Nitrophenol (**7b**).* Yellow solid; isolated yield 42% (0.0582 g). IR (KBr) 846, 1338, 1494, 1346 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.17 (S, 1H, OH), 6.93 (d, J = 9.0 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 115.7, 126.3, 161.3. MS m/z = 140 (M^+ + 1), 139 (M^+), 93 ($M^+ - NO_2$).

*4-Bromo-2-nitrophenol (**11**).* Yellow solid; isolated yield 90% (0.1960 g). IR (KBr) 883, 970, 1313, 1527, 3273 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.07 (d, J = 8.7 Hz, 1H), 7.66 (dd, J = 8.7 Hz, 2.4 Hz, 1H), 8.24 (d, J = 2.1 Hz, 1H), 10.49 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 111.7, 121.7, 127.3, 140.3, 142.9, 154.1. MS m/z = 219 (M^+ + 1), 218 (M^+), 170 ($M^+ - NO_2$).

*1,2-Diphenyldisulfide (**12**).* White solid; isolated yield 75% (0.1634 g). IR (KBr) 510, 686, 1573 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.29−7.43 (m, 6H), 7.62- 7.64 (m, 4H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 127.3, 127.6, 129.2, 137.1.

*2-Nitroaniline (**13a**).* Orange solid; isolated yield 47% (0.0646 g). IR (KBr) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.13 (s, 2H, NH_2), 6.69 (t, J = 7.7 Hz, 1H), 6.8 (dd, J = 8.8 Hz, 0.9 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 8.10 (dd, J = 8.6 Hz, 1.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 117.3, 119.2, 126.5, 132.5, 136.1, 154.2.

*4-Nitroaniline (**13b**).* Yellow solid; isolated yield 39% (0.0541 g). IR (KBr) 840, 1298, 1587, 3360, 3481 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.60 (d, J = 9.1 Hz, 2H), 6.68 (s, 2H, NH_2), 7.94 (d, J = 9.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 113.2, 127.2, 136.5, 156.5.

*4-Methyl-2-nitroaniline (**14**).* Red-Brown solid; isolated yield 81% (0.1231 g). IR (KBr) 810, 867, 1382, 1508, 3016, 3043 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ (ppm) 2.20 (s, 3H), 7.04 (d, J = 6.0 Hz, 1H), 7.16 (t, J = 8.4 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 8.95 (s, 2H, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 20.9, 120.3, 122.3, 123.0, 130.1, 136.1. MS m/z = 153 (M^+ + 1), 152 (M^+), 106 ($M^+ - NO_2$).

*1-Chloro-4-nitrobenzene (**15**).* Yellow solid; isolated yield 75% (0.1178 g); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50 (d, J = 9.0 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 124.8, 129.5, 141.2, 146.5.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge partial support of this work by the Research Affairs Office of Bu-Ali Sina University (Grant Number 32-1716 entitled development of chemical methods, reagents and molecules), and Center of Excellence in Development of Chemical Method (CEDCM), Hamedan, I.R. Iran.

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