

Samarium-promoted Chemoselective Reduction of Aromatic Nitro Compounds in Ionic Liquid

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The differently substituted aromatic nitro compounds were chemoselectively reduced by Sm/HOAc system in an ionic liquid medium to afford aromatic amines. Under these conditions the other substituents, such as -X, -CHO, -COOH, -CN, -NHTos and -alkyl, remained intact. The notable advantages of this reaction are its mild conditions, simple operation, short reaction time, high yields and easy recycling of ionic liquid.

Keywords ionic liquid, samarium/HOAc system, chemoselective reduction, aromatic nitro compounds, aromatic amines

Aromatic amines were widely used as intermediates in the preparation of important chemicals, which are extensively distributed in nature with wide range of biological activity.¹ Up to now there have been many reduction methods for aromatic nitro groups, such as catalytic hydrogenation,² reduction with active metals in the presence of an acid,³ hydrazine reduction,⁴ TiCl₄-dialkyl telluride reduction,⁵ NaBH₄-NiCl₂ reduction,⁶ electrochemical⁷ or enzymatical reduction.⁸ Since introduced by Kagan and his group,⁹ samarium has been extensively investigated as a reductant in synthetic chemistry and is a metal with good reductive potential ($E_{\text{Sm}^{3+}/\text{Sm}^0}^0 = -2.41 \text{ V}$). It is not expensive and can be activated by catalyst I₂,¹⁰ Cp₂TiCl₂,^{11,12} TiCl₄,^{13,14} TMSCl,^{15,16} MCl_n etc. to form active species.

Recently Yu *et al.*¹⁷ reported a novel electron-transfer system for the chemoselective reduction of aromatic ni-

tro groups. Banik *et al.*¹⁸ reported a facile reduction of aromatic nitro compounds to aromatic amines by samarium/cat. I₂. Huang *et al.*¹⁹ reported a facile reduction procedure for nitroarenes with Cp₂TiCl₂/Sm system. Hou *et al.*²⁰ reported samarium metal promoted selective formation of azoxy compounds. Although these chemical methods have some advantages, they have always some drawbacks such as lack of the desired chemoselectivity over other functional groups that are often present in the substrate, time-consuming, inconvenient separation, comparatively low yields, or difficult to recycle the solvent. On the other hand, the developments of environmental protection and green chemistry are more and more important for the human being. Therefore, there is a need for the development of mild, convenient and environment-friendly methods for the selective reduction of aromatic nitro compounds.

Here, we wish to report that samarium/HOAc system chemoselectively reduces aromatic nitro compounds in an ionic liquid medium. Ionic liquids are a new class of solvents, which have attracted growing interest over the past years due to their unique physical and chemical properties.²¹ They usually consist of poorly coordinating ion pairs. A classical example is the readily accessible 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]⁺[BF₄]⁻ (Scheme 1), which is a colorless mobile but non-volatile liquid with no smell²¹ and easily dissolves metal salts, transition metal catalysts and many organic

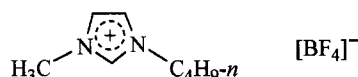
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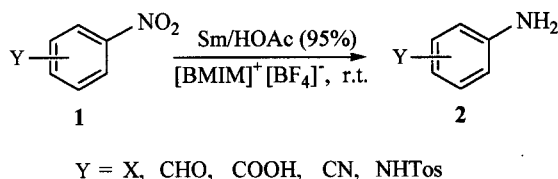
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compounds. In addition, $[\text{BMIM}]^+[\text{BF}_4]^-$ is capable of defending general redox agents, acids and bases.²¹ So $[\text{BMIM}]^+[\text{BF}_4]^-$ was used as the solvent. After the reaction completed, the ionic liquid was recycled and it was found that the chemoselectivity of the reaction was good, *i. e.*, the substituted groups ($-\text{X}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{CN}$, $-\text{NHTos}$) were intact. The time for a complete reaction was short. The yields were high, and the separation was simple. The reaction is shown in Scheme 2.

Scheme 1



Scheme 2



For different substituted aromatic nitro compounds the results are summarized in Table 1.

In short, it was found that in $[\text{BMIM}]^+[\text{BF}_4]^-$ the Sm/HOAc system is excellent for chemoselective reduction of aromatic nitro groups under mild conditions. The notable advantages of this method are recycling of the sol-

vent, high yielding and simple operation. At the same time the method is environment-friendly.

Experimental

Melting points were uncorrected. IR spectra were recorded on a Bruker Vector-22 infrared spectrometer. ¹H NMR spectra were obtained with a Bruker AC-400 MHz spectrometer in CDCl_3 or $\text{DMSO}-d_6$ solution using TMS as the internal standard. Mass spectra were recorded on an HP 5989B MS spectrometer. The reactions were performed in a Schlenk-type glass apparatus under a nitrogen atmosphere.

General procedure for the reduction reaction

Under an inert atmosphere of nitrogen, metallic samarium powder (0.3 g, 2.0 mmol), substrate (1.0 mmol) and $[\text{BMIM}]^+[\text{BF}_4]^-$ (3 mL) were placed in a two-necked reaction flask. Magnetically stirred at room temperature, 6.0 mmol of HOAc (95%) was added dropwise slowly within 60 min with a syringe. The mixture was stirred until the reaction was complete as monitored by TLC. Then diethyl ether (20 mL \times 2) was added, the mixture was stirred for 5 min, and left standing for 5 min. Then ether layer was transferred by a syringe. The mixed ether layer was washed with water (20 mL) and dried over anhydrous Na_2SO_4 . The solvent was

Table 1 Results of aromatic nitro compounds reduced by Sm/HOAc in $[\text{BMIM}]^+[\text{BF}_4]^-$

Entry	Compound	Substrate	Product	Reaction time (h)	Yield (%) ^a
1	1a	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{C}_6\text{H}_5\text{NH}_2$ (2a)	3	91
2	1b	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ (2b)	4	88
3	1c	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ (2c)	4	86
4	1d	<i>p</i> - $\text{ClC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{ClC}_6\text{H}_4\text{NH}_2$ (2d)	2.5	95
5	1e	<i>o</i> - $\text{ClC}_6\text{H}_4\text{NO}_2$	<i>o</i> - $\text{ClC}_6\text{H}_4\text{NH}_2$ (2e)	2.5	95
6	1f	<i>p</i> - $\text{BrC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{BrC}_6\text{H}_4\text{NH}_2$ (2f)	3	90
7	1g	<i>p</i> - $\text{IC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{IC}_6\text{H}_4\text{NH}_2$ (2g)	3.5	82
8	1h	<i>o</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{NO}_2$	<i>o</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2$ (2h)	4	80
9	1i	<i>p</i> - $\text{H}_2\text{NC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ (2i)	4	83
10	1j	<i>p</i> - $\text{HO}_2\text{CC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{HO}_2\text{CC}_6\text{H}_4\text{NH}_2$ (2j)	2	98
11	1k	<i>m</i> - $\text{HO}_2\text{CC}_6\text{H}_4\text{NO}_2$	<i>m</i> - $\text{HO}_2\text{CC}_6\text{H}_4\text{NH}_2$ (2k)	2	97
12	1l	<i>p</i> - $\text{TosHNC}_6\text{H}_4\text{NO}_2$	<i>p</i> - $\text{TosHNC}_6\text{H}_4\text{NH}_2$ (2l)	3	98
13	1m	<i>o</i> - $\text{CNC}_6\text{H}_4\text{NO}_2$	<i>o</i> - $\text{CNC}_6\text{H}_4\text{NH}_2$ (2m)	3	93
14	1n	α -Nitronaphthalene	α -Aminonaphthalene (2n)	3.5	87

^a Isolated yields.

removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel. On the other hand, dichloromethane (20 mL) was added to the ionic liquid containing residue, with stirring for 5 min, filtration and evaporation of dichloromethane afforded the recycled ionic liquid.

2a Oil (lit.²³); ¹H NMR (CDCl₃, 400 MHz) δ : 3.35 (s, 2H), 6.44 (d, $J = 7.62$ Hz, 2H), 6.99 (q, 2H), 6.59 (q, 1H); IR (KBr) ν : 3340, 3420, 3020, 1620, 1610, 1500, 1470 cm⁻¹; MS (70 eV) m/z (%): 93 (M⁺, 100).

2b M.p. 44–46 °C (lit.²² 41–46 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 3.45 (s, 2H), 6.33 (d, $J = 7.40$ Hz, 2H), 6.79 (d, $J = 7.40$ Hz, 2H), 2.18 (s, 3H); IR (KBr) ν : 3340, 3430, 3010, 2910, 2880, 1620, 1540, 1440 cm⁻¹.

2c Oil (lit.²³); ¹H NMR (CDCl₃, 400 MHz) δ : 2.24 (s, 3H), 3.27 (s, 2H), 6.30–7.22 (m, 4H); IR (KBr) ν : 3380, 3480, 3010, 2890, 2840, 1640, 1590, 1500, 1470 cm⁻¹; MS (70 eV) m/z (%): 107 (M⁺, 81), 106 (100).

2d M.p. 71–73 °C (lit.²² 68–71 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 5.01 (s, 2H), 6.66 (d, $J = 7.72$ Hz, 2H), 7.01 (d, $J = 7.72$ Hz, 2H); IR (KBr) ν : 3400, 3480, 1640, 1500, 1480 cm⁻¹.

2e Oil (lit.²³); ¹H NMR (CDCl₃, 400 MHz) δ : 3.86 (s, 2H), 6.40–7.30 (m, 4H); IR (KBr) ν : 3380, 3480, 3020, 3040, 1640, 1505, 1480 cm⁻¹; MS (70 eV) m/z (%): 127 (M⁺, 100), 129 (33).

2f M.p. 62–64 °C (lit.²² 62–64 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 3.58 (s, 2H), 6.57 (d, $J = 7.70$ Hz, 2H), 7.28 (d, $J = 7.70$ Hz, 2H); IR (KBr) ν : 3480, 3440, 3180, 1640, 1520, 1500, 1480 cm⁻¹.

2g M.p. 63–65 °C (lit.²² 63–65 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 3.56 (s, 2H), 6.39 (d, $J = 7.68$ Hz, 2H), 7.36 (d, $J = 7.68$ Hz, 2H); IR (KBr) ν : 3420, 3300, 3200, 3060, 3020, 1660, 1580, 1480, 1440 cm⁻¹.

2h Oil (lit.²³); ¹H NMR (CDCl₃, 400 MHz) δ : 3.60 (s, 2H), 3.66 (s, 3H), 6.54–6.60 (m, 4H); IR ν : 3380, 3440, 3020, 3220, 1640, 1580, 1520, 1400 cm⁻¹; MS (70 eV) m/z (%): 123 (M⁺, 84), 108 (100).

2i M.p. 139–141 °C (lit.²² 143–145 °C); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 4.00 (s, 4H),

6.48 (d, $J = 7.22$ Hz, 4H); IR (KBr) ν : 3380, 3300, 3200, 3000, 1680, 1540, 1450 cm⁻¹.

2j M.p. 187–188 °C (lit.²² 187–189 °C); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 6.61–6.68 (m, 3H), 6.78 (d, $J = 8.68$ Hz, 2H), 7.83 (d, $J = 8.68$ Hz, 2H); IR (KBr) ν : 3460, 3360, 1660, 1640, 1580 cm⁻¹.

2k M.p. 178–180 °C (lit.²² 178–180 °C); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 6.88–7.10 (m, 3H), 7.49–7.69 (m, 4H); IR (KBr) ν : 2960, 1660, 1560, 1490 cm⁻¹.

2l M.p. 184–180 °C (lit.¹⁷ 185–180 °C); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 2.32 (s, 3H), 9.41 (brs, 1H), 7.29 (d, $J = 8.40$ Hz, 2H), 6.67 (d, $J = 8.80$ Hz, 2H), 4.90 (s, 2H), 7.56 (d, $J = 8.0$ Hz, 2H); 6.39 (d, $J = 8.80$ Hz, 2H); IR (KBr) ν : 3670, 3480, 3420, 2988, 1640, 1625, 1580, 1474 cm⁻¹.

2m M.p. 49–52 °C (lit.²² 49–52 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 4.72 (s, 2H), 6.69 (d, $J = 8.40$ Hz, 1H), 6.66–6.82 (m, 1H), 7.26 (d, $J = 7.80$ Hz, 1H), 7.29 (d, $J = 8.40$ Hz, 1H); IR (KBr) ν : 3450, 3390, 1635, 1548, 1470 cm⁻¹.

2n M.p. 48–50 °C (lit.²² 48–50 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 3.81 (s, 2H), 6.59 (d, $J = 7.11$ Hz, 1H), 7.00–7.85 (m, 6H); IR (KBr) ν : 3380, 3440, 3020, 3220, 1640, 1580, 1520, 1400 cm⁻¹.

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