

Ionic liquid mediated efficient reduction of nitroarenes using stannous chloride under sonication

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Abstract—Nitroarenes were rapidly reduced to the corresponding aromatic amines using stannous chloride in ionic liquid as a safe and recyclable reaction medium under sonication. The method is environmentally benign and sensitive functional groups remain unaffected.

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Reduction of aromatic nitrocompounds to the corresponding amines is a synthetically important transformation,¹ both in industry and academic laboratories, particularly when a molecule has several other reducible functionalities. Therefore, numerous new reagents and methods have been developed for reduction of aromatic nitrocompounds,² some of which are incompatible with other substituents or unsafe in view of green chemistry.

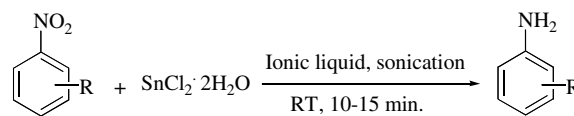
Room temperature ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-butyl-3-methylimidazolium triflate ([bmim][OTf]) are environmentally benign solvents due to their unique chemical and physical properties such as excellent chemical and thermal stability with ease of reuse, miniscule vapor pressure, unique miscibility and non-flammability.³ They behave like polar aprotic solvents and have been employed as green solvents for a vast array of organic and enzymatic transformations,^{4–6} in liquid–liquid separation,⁷ and recycling of organometallic catalysts.⁸ Further, ionic liquids have also been shown to enhance the rate of many transformations.⁹

Only two papers reported ionic liquid mediated reduction of nitroarenes using zinc in ammonium salts¹⁰ and samarium.¹¹ Stannous chloride is amongst the popular reducing agent used for reduction of aromatic nitrocompounds.¹² However, no other attempt has been made for the reduction of nitrocompounds either using stannous chloride with other additives except NaBH₄, which was reported by Satoh.^{12b} As safer and green technologies like recyclable media or catalysts are getting more importance in modern synthetic chemistry, we wish to report a novel use of ionic liquid for rapid reduction of nitroarenes under sonication.

Reaction of various aromatic nitrocompounds with stannous chloride in [bmim][BF₄] or [bmim][OTf] under sonication afforded corresponding amines in good to excellent yields (Scheme 1). The scope and generality of this method is illustrated with respect to various nitroarenes are summarized in Table 1. All reactions were carried out in ionic liquids [bmim][BF₄] and [bmim][OTf] under sonication for 10–15 min at room

Keywords: Ionic liquid; Reduction of nitroarene; Stannous chloride; Sonication.

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Scheme 1. Reduction of nitroarenes with stannous chloride in ionic liquid under sonication.

Table 1. Reduction of nitroarenes with stannous chloride in [bmim][BF₄] and [bmim][OTf] under sonication

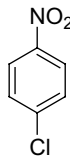
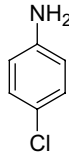
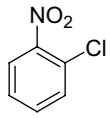
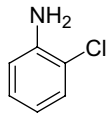
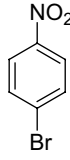
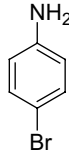
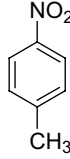
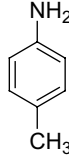
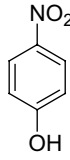
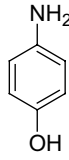
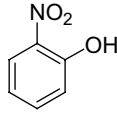
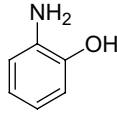
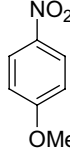
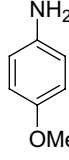
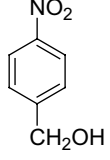
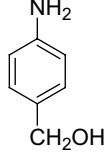
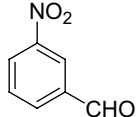
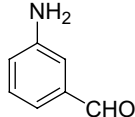
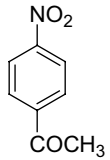
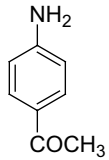
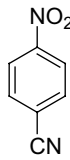
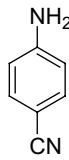
Entry	Reactant	Product ^a	% Yield ^b	
			[bmim][BF ₄]	[bmim][OTf]
1			87	96
2			84	90
3			98	97
4			92	89
5			91 ^c	89 ^c
6			86 ^c	87 ^c
7			87	89
8			80	80
9			47	62
10			83	89
11			99	86

Table 1 (continued)

Entry	Reactant	Product ^a	% Yield ^b	
			[bmim][BF ₄]	[bmim][OTf]
12			88 ^c	93 ^c
13			83 ^c	86 ^c
14			88 ^c	94 ^c
15			92 ^c	96 ^c

^a All products were characterized by proton NMR and LCMS analysis (compared with literature values).

^b Isolated yields of pure amines.

^c Product and ionic liquid were extracted in dichloromethane and separated by column.

temperature. As is evident, the ultrasound-assisted reduction of the aromatic nitrocompounds with stannous chloride proceeded smoothly at room temperature with complete conversion in a very short period (TLC and NMR show the absence of any starting or side products). We used sonication as a means to achieve efficient mixing and enhance the rate of conversion. Without sonication nitroreduction under stirring at room temperature even after 10 h was sluggish, as viscous reaction mixture makes mechanical or magnetic stirring inefficient. The rate enhancement under sonication in the present protocol may be attributed to cavity effect and formation of hot spots as reported for many other kinds of transformations in the literature.¹³ Sensitive functional groups like CHO, CN, CH₂OH, etc. remained unaffected. Low yield was observed for the reduction of *m*-nitrobenzaldehyde due to subsequent self-condensation leading to formation of higher oligomers. Further, nitroarenes like entries 14 and 15, which are insoluble or partially soluble in organic solvents, can also be reduced effectively in good yield. Nitroarenes were initially dissolved in ionic liquid and sonicated after adding stannous chloride. Products were extracted with ether and the remaining ionic liquid was recovered by extracting with dichloromethane. In case of ether-insoluble amines, both products and ionic liquid were extracted with dichloromethane and separated in a column using *n*-hexane/ethyl acetate solvent mixture (1:5). Completion of the reaction was monitored by TLC and products were characterized by proton NMR and LCMS data (compared with literature data). The reduction can also be performed upon heating the reaction mixture in ionic liquid for 100–120 °C. The transformation was observed to be faster in ionic liquid than in ethyl acetate or alcohol. In the reduction process, ionic liquid can be recovered in more than 90% yield after extracting the product with diethyl ether or dichloro-

methane, which can be reused for the same compounds to avoid cross contamination (trace amount of amine contaminant has been observed in some cases). The reduction of *p*-nitroacetophenone is representative: *p*-nitroacetophenone (165 mg, 1.00 mmol) and [bmim][BF₄] or [bmim][OTf] (1 mL) were placed in a 25 mL round-bottomed flask and sonicated to dissolve the compound. Stannous chloride (1.128 g, 5 mmol) was added and sonicated for 10 min (TLC showed the completion of the reaction). The reaction mixture was neutralized with sodium bicarbonate and extracted with ether (5 mL × 2). The combined extract was dried over anhydrous Na₂SO₄ and then the solvent was removed under reduced pressure to get pure *p*-aminoacetophenone. Ionic liquid was recovered by extracting with dichloromethane and can be reused for the same reduction.

In conclusion, we have found that ionic liquid is a good reaction medium for rapid reduction of aromatic nitrocompounds in good yield at room temperature under sonication. In addition, it can be reused for same reactions and convenient for the reduction of compounds, which are partially soluble or insoluble in common organic solvents. Further, this method is simple and safe from green chemistry point of view.

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