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Reduction of nitro compounds using copper as catalyst in dioxolane medium

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Reduction of aromatic nitro compounds using copper as catalyst is reported in this paper. This novel method is simple, ecofriendly and does not make use of any acidic/basic medium for the reduction. Water is added along with dioxalane solvent making it more suitable and versatile.

Keywords: Aromatic nitro compounds, copper, dioxolane, nitrophthalic acid.

INTRODUCTION

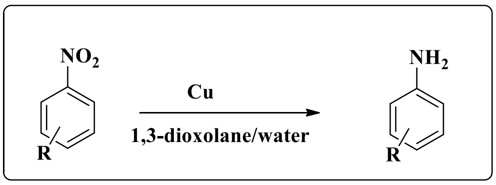
Reduction of aromatic nitro compounds into their respective amines is of great interest as they are being used as important scaffolds for the synthesis of biologically potent molecules [1]. They have also found applications in the preparation of agricultural chemicals and dyes. Various procedures have been reported in the literature; selective reduction is an extremely demanding task as the reduction sometimes stops at the formation of intermediate azoarenes, hydrazines and hydroxylamines [2]. Of late, few methods are reported involving metal nanoparticles of Ag in $NaBH_4$ [3], using coinage metal nanoparticles - Au, Ag. Cu/aqueous $NaBH_4$ [4], copper/cobalt phthalocyanines were used as catalysts for the reduction [5], gold nanoparticles supported on TiO_2 or Fe_2O_3/H_2 [6], carbon nanofiber held on platinum and palladium nanoparticles [7], bimetallic Pt–Ni nanoparticles [8], polymer-supported nanostructured platinum carbonyl clusters [9], copper nanoparticles along with ammonium formate in ethylene glycol [10], Ir, Pt, and Pd supported on carbon as catalysts [11], $Pt/CaCO_3$ or $Pt/C–H_3PO_4$ [12]. There have been reports for the use of copper for conjugate reduction [13], cationic copper/pybox catalyst for the reduction of secondary amides [14] using tetramethyldisiloxane (TMDS) in the presence of copper complexes [15], copper carbine complex for the conjugate reduction of α,β-unsaturated carbonyl compounds [16], nickel chloride supported on natural phosphate [17], copper nanoparticles under ultrasound and microwave irradiation [18].

The earlier reports of the aromatic nitro compounds using zinc and tin indicate that the reaction is dependent on pH of the reaction medium. Our research group has reported the use of iron [19] and zinc [20] in previous reports. Herein, we report a novel method for the reduction of aromatic nitro compounds using copper powder in 1,3-dioxolane in presence of water. The reaction is accomplished in neutral medium and proceeds with excellent chemoselectivity and yield. This reaction avoids the use of acids/acidic medium for the reduction of nitro compounds.

MATERIALS AND METHODS

All the reaction precursors, aromatic nitro compounds, copper turnings and solvents were obtained from SRL, India and were used without any further purification. The completion of reaction and formation of the products were monitored by thin layer chromatography (TLC) carried out on aluminium sheets coated in Merck Kieselgel silica gel 60, procured from Merck India. The boiling points and melting points of the formed products were determined by the boiling and melting point apparatus (Campbell Electronics, Mumbai, India). All the products formed are known and reported and their authenticity was confirmed and compared to authentic compounds obtained from Sigma-Aldrich, Mumbai. Purification was done by column chromatography carried out using silica gel (60–120 mesh) as the stationary phase.

And the temperatures which are mentioned in the procedure refer to the temperature of the oil bath used for heating.



Scheme 1. General procedure for reduction of aromatic nitro compounds to aromatic amines.

Aromatic nitro compound (1.0 g, 0.08 moles) was refluxed with copper (5.0 g, 0.08 moles) in dioxalane (7 mL) in the presence of catalytic amount of water (0.5 mL) for 15- 40h with different

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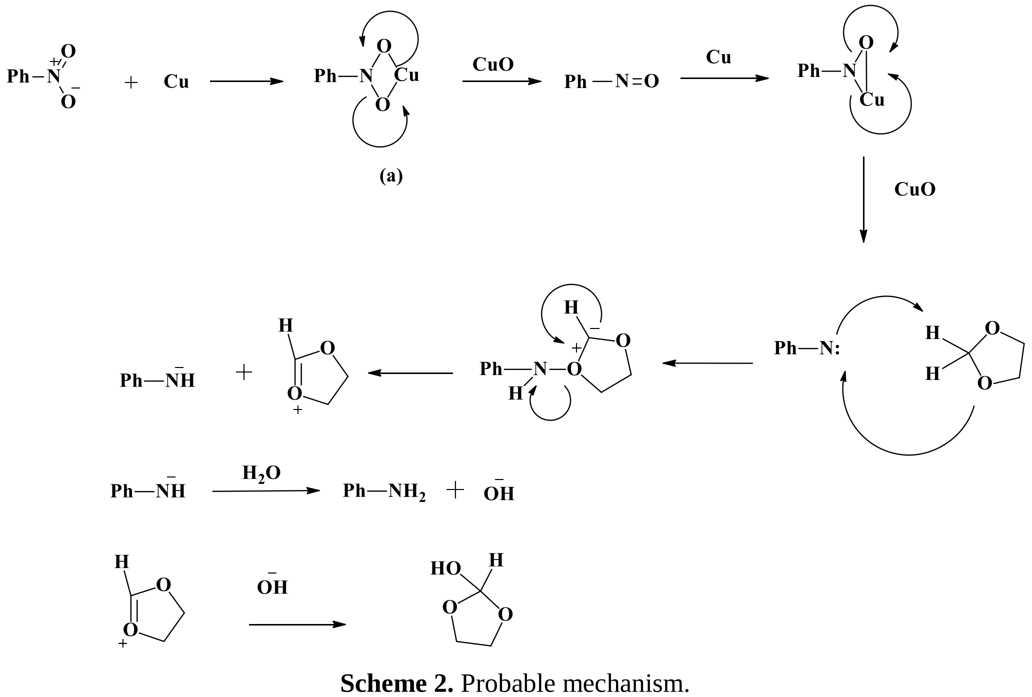
nitro compounds. The completion of the reaction was monitored using TLC. After the reaction was completed, the reaction mixture was filtered off to remove the residue (formed from catalyst). The filtrate was extracted with ether and acidified with 5% HCl and the aqueous layer was separated and neutralized with 5% NaOH. The reduced compound was then re-extracted with ether and was concentrated under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography. The pure product obtained was identified by TLC and was compared with the reported products.

RESULTS AND DISCUSSION

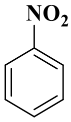
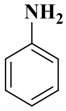
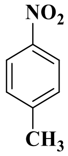
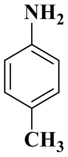
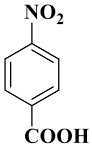
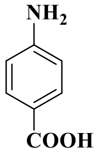
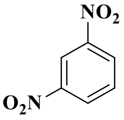
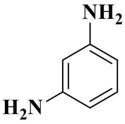
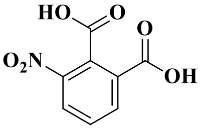
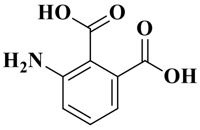
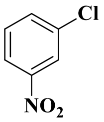
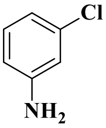
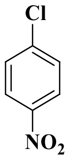
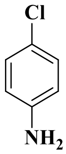
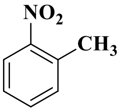
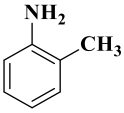
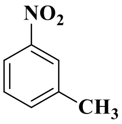
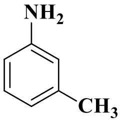
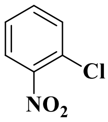
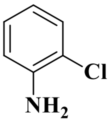
Reduction was carried out by reacting a mixture of aromatic nitro compound (1 mole) and copper (0.05-0.08 moles) in presence of 1,3-dioxolane-water, as a solvent under reflux temperature for 15 to 40 h. Copper (II) oxide which was formed as a valuable byproduct was separated by filtration. 1,3-dioxolane/water mixture was easily recovered by vacuum distillation and reused. In general, our desired product aromatic amines were obtained in 75-90% yield. We further observed that the reaction did not proceed in the absence of water. We also observed that, when 1,3-dioxolane was replaced by other water-miscible solvents like DMSO, acetonitrile, methanol, etc., the reaction was not activated. This method has several advantages like: the reduction avoids corrosive media, it makes use of an environmentally friendly solvent, and the most important benefit is, it selectively reduces nitro group in the presence of other reducible groups and it avoids the use of hydrogen under pressure and expensive catalysts. Recycling of solvents and easy work up makes it an ideal method for the reduction of aromatic nitro compounds. During the reduction, functional groups like methoxy, cyano, ester, chloro, amide, alkene and keto groups are tolerated.

Proposed mechanism for the reduction of nitro compounds to amines is given below in Scheme 2. First step involves the oxidative addition of metal to nitro compound leading to the formation of intermediate (**a**), which undergoes retrocycloaddition to form a nitroso derivative and one molecule of CuO. Further, another Cu atom adds to the nitroso derivative which eliminates a molecule of CuO to form the unstable nitrene intermediate. In presence of dioxolane, nitrene pulls out a proton as depicted in the scheme. The driving force for the reaction could be the coordination of 1,3-dioxolane with copper in oxidative addition intermediate (**a**). The formation of intermediate nitroso compound was detected by GC. GC also showed the formation of a minor amount of azoxy compounds probably by the reaction of nitrene with the nitroso derivative.



Scheme 2. Probable mechanism.

Table 1. Reduction of aromatic nitro compounds to corresponding amines

Entry	Nitro compound	Time (h)	Product	Yield %	B.p. (lit.) °C	B.p. (obs) °C	M.p. (lit.) °C	M.p. (obs.) °C
1		38		70	184.1	184	-	-
2		20		80	200	199.5	-	-
3		23		75	-	-	187	187
4		15		85	282	282	-	-
5		40		78	-	-	180	178
6		14		73	96	95.5	-	-
7		15		75	232	232.2	-	-
8		18		72	201	201.5	-	-
9		20		74	203	202.5	-	-
10		21		71	209	208.9	-	-

CONCLUSION

In conclusion, we have reported a novel method for the reduction of aromatic nitro compounds. The reported method has several advantages like: the reduction avoids corrosive media, it makes use of an environmentally friendly solvent, and the most important benefit is that, it selectively reduces nitro group in the presence of other reducible groups. The method avoids the use of hydrogen under pressure and expensive catalysts. Recycling of solvents and easy work up makes it an ideal method for the reduction of aromatic nitro compounds.

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