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PAPER

Zinc phthalocyanine with PEG-400 as a recyclable catalytic system for selective reduction of aromatic nitro compounds†‡

Upendra Sharma, Neeraj Kumar,* Praveen Kumar Verma, Vishal Kumar and Bikram Singh*

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Zinc phthalocyanine with PEG-400 was established as a catalytic system for chemo and regioselective reduction of aromatic nitro compounds to corresponding amines. A large range of reducible functional groups such as acid, amide, ester, halogen, lactone, nitrile, *N*-benzyl, *O*-benzyl, hydroxy and heterocycles were well tolerated. Direct synthesis of benzotriazole from *O*-dinitrobenzene was achieved for the first time. The present catalytic system was successfully employed for the reduction of carbonyl and ester compounds to corresponding alcohols and reductive amination of benzaldehydes with primary amines to form corresponding secondary amines. Remarkable advantages of the present catalytic method include low loading of metal, avoidance of toxic ligands and high isolated yields. The catalyst was recyclable up to four times without any loss of selectivity and activity.

Introduction

Functionalized anilines are industrially important intermediates for pharmaceuticals, polymers, herbicides and fine chemicals.[1] Reduction of nitro compounds is one of the fundamental processes for the synthesis of functionalized amines on laboratory as well as industrial scale. Catalytic hydrogenation,[2] sodium borohydride/catalyst,[3] hydrazine/catalyst[4] and a variety of other catalytic systems[5] have been developed for the reduction of aromatic nitro compounds. These methods require expensive metals, moisture-sensitive reagents and organic solvents.

Recently, the Matthias Beller group has employed abundant and low cost iron for nitroarene reduction, but the use of toxic ligand and organic solvent limit the scope.[6] Although, our group also reported selective iron-based catalytic systems, the desired selectivity was not observed with nitrostyrenes.[7] Our previous efforts have utilized Co and Cu phthalocyanines[8] and we further thought to employ abundant, cheap and less-toxic zinc for catalytic reduction of nitroarenes to corresponding amines. Although, zinc metal in different forms such as Zn–CH_3COOH, Zn–HCl, Zn–NaOH, Zn–NH_4Cl, Zn–$CaCl_2$, Zn–$(NH_4)_2HPO_3{\cdot}H_2O$ has been employed for reduction of aromatic nitro compounds,[9] most of these methods require organic solvents, acid or base for pre-activation of catalyst and lack the desired selectivity. In addition to this, little consideration was given to the environment, cost, safety, or simplicity of operation. Khan *et al.* successfully applied Zn/NH_4Cl and Zn/HCO_2NH_4 in [bmim]BF_4[10] for chemoselective reduction of aromatic nitro compounds at room temperature and overcame most of the above mentioned limitations. The use of excess zinc metal limits the scope of this method. Recently, with an objective to develop environmentally benign reaction conditions with excellent efficiency and selectivity, polyethylene glycol-400 (PEG-400) has been shown to be an useful solvent due to its non-toxicity, cost effectiveness and reusability.[11] Herein, we report zinc phthalocyanine (ZnPc) with PEG-400 as a recyclable green catalytic system for selective reduction of nitroarenes.

Results and discussion

Preliminary experiments were carried out with 4-nitrobenzonitrile as model substrate using different zinc-based catalysts, hydrogen sources and solvents. As expected, reduction was incomplete without catalyst even after prolonged heating for 24 h (Table 1, entry 15). No product was obtained with $ZnSO_4{\cdot}7H_2O$ and ZnI_2, while, moderate to good yields were recorded in the presence of $ZnCl_2$, $ZnBr_2$ and Zn dust (Table 1, entries 1–5). Very high yield with >99% selectivity was obtained in the presence of ZnPc (Table 1, entry 6). The use of different hydrogen sources revealed efficient reduction to 4-aminobenzonitrile (>99% yield) with hydrazine hydrate (Table 1, entry 6). Obviously, in the absence of a hydrogen source reduction was not observed (Table 1, entry 16). Starting substrate was not consumed completely in the case of ammonium acetate, sodium acetate and $NaBH_4$ (Table 1, entries 8, 9 and 13) while no conversion was observed with other hydrogen sources (Table 1, entries 10–12 and 14). The use of ammonium formate provided product in traces (Table 1, entry 7).

The effect of changing the solvent has also been studied. Very good yields were obtained in ethanol, [Bmim]BF_4, [Bmim]-HSO_4, ethylene glycol and PEG-400 (See ESI, Table S1, entries

Natural Plant Products Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh-176 061, India. E-mail: neerajnpp@rediffmail.com, bikram_npp@rediffmail.com; Fax: +91-1894-230433; Tel: +91-1894-230426

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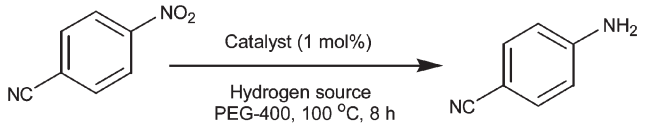
Table 1 Evaluation of different catalysts and hydrogen sources for reduction of 4-nitrobenzonitrile



Entry	Catalyst	Hydrogen source	Yield[a] (%)
1	$ZnSO_4·7H_2O$	$NH_2NH_2·H_2O$	No reaction[b]
2	$ZnCl_2$	$NH_2NH_2·H_2O$	89[b]
3	$ZnBr_2$	$NH_2NH_2·H_2O$	68[b]
4	ZnI_2	$NH_2NH_2·H_2O$	No reaction[b]
5	Zn dust	$NH_2NH_2·H_2O$	52[b]
6	ZnPc	$NH_2NH_2·H_2O$	99
7	ZnPc	Ammonium formate	<1
8	ZnPc	Ammonium acetate	23
9	ZnPc	Sodium acetate	15
10	ZnPc	Potassium formate	No reaction
11	ZnPc	Ammonium chloride	No reaction
12	ZnPc	Formic acid	No reaction
13	ZnPc	$NaBH_4$	42
14	ZnPc	Water	No reaction
15	Without catalyst	$NH_2NH_2·H_2O$	14 (56)[c]
16	ZnPc	Without hydrogen source	No reaction

[a] Yield was calculated on the basis of GC-MS analysis. [b] 5 mol% of the catalyst is used. [c] After 24 h.

2, 5, 6, 8 and 10‡). In other tested solvents such as water, THF, water–ethanol (1 : 1) and toluene, low yield was observed (Table S1, entries 1, 4, 7 and 9‡). No product was observed in ethyl acetate (Table S1, entry 3‡). Comparable yields were obtained in both [Bmim]BF_4 and PEG-400, however, PEG-400 is preferred over [Bmim]BF_4 because of its availability and non-toxicity. In addition to this, the environmental safety of ionic liquids is still debated.

To investigate the scope of the catalytic method, reduction of structurally diverse nitro compounds was carried out. The reduction of halogen-substituted nitrobenzenes proceeded without dehalogenation and the amines were obtained in high yields (Table 2, entries 2–7). In general, dehalogenation of halogen substituted aromatic nitro compounds takes place with earlier reported methods such as catalytic hydrogenation[2] or $Pd(OAc)_2$/PMHS[12] and S_8/mild base.[13] A series of aromatic nitro substrates containing functional groups such as methoxy, acid, nitrile, sulphonamide, methyl, hydroxyl and lactone were successfully reduced with >99% chemoselectivity and high conversion (Table 2, entries 8–11, 13–15 and 27). The selectivity and conversion were monitored by GC-MS analysis. The reduction of 4-nitrobenzamide was not observed at higher temperatures, however, at room temperature good yield and high selectivity was obtained (Table 2, entry 12). High chemoselectivity with moderate to good yields were observed in various ester-substituted nitroarenes (Table 2, entries 18–26). Various heterocyclic nitroarenes were converted to corresponding anilines without affecting heterocyclic ring (Table 2, entries 28–31). In the case of 1-nitronaphthalene, >99% selectivity and yield was obtained (Table 2, entry 32). 2-Nitrofluorene was selectively (>99%) reduced to the corresponding 2-aminofluorene with >99% yield which is higher than reported earlier (Table 2, entry 33).[6a,7,8] Reduction of nitroarenes with groups like $–OCH_2C_6H_5$ and $–NHCH_2C_6H_5$ were often not studied or affected by other methods.[6,14] Under the present reaction conditions, both these substrates were reduced successfully with high yield and selectivity (Table 2, entries 16 and 17). Another important finding was the tolerance of double bond in the case of 3-nitrostyrene, which had high selectivity (98%) and conversion (91%) and is higher than in our earlier reported methods (Table 2, entry 35).[7,8]

Regioselective reduction of a nitro group is always a challenging task. Here, in the case of 1,3 and 1,4 dinitro benzene only one nitro group was reduced selectively (Table 2, entries 37 and 38), however, reduction of 1,2-dinitrobenzene showed moderate conversion (58%) (Table 2, entry 36). In order to see the effect of hydrogen source on regioselectivity and conversion, the reduction of dinitrobenezenes was performed with excess hydrogen source *i.e.* 4 equiv. $N_2H_4·H_2O$. In the case of 1,3 and 1,4 dinitrobenzene, regioselectivity was not altered reflecting the specificity of the method, however, to our surprise exclusive formation of benzotriazole was observed in the case of 1,2 dinitrobenzene (Scheme 1). Benzotriazole derivatives possess important biological activities and have versatile utility in pharmaceutical industries.[15] To date, the common approach for the synthesis of benzotriazole includes diazotization of *o*-phenylenediamine which is operationally tedious and involves the use of toxic reagents.[16] Our method provides a useful new route to benzotriazoles starting from cheap 1,2-dinitrobenzene under environmentally friendly conditions. Also reduction of 2-nitrophenyl hydrazine resulted in the formation of benzotriazole (Scheme 1). In the case of substituted dinitrobenzene excellent chemo- and regioselectivity was observed (Table 2, entries 39 and 40).

The reusability study of the developed catalytic system on reduction of model substrate showed that it can be reused up to four cycles without any loss in catalytic activity (Table 3).

Additionally, the developed catalytic system was applied to carbonyl reduction. Hydrazine hydrate was replaced with sodium borohydride as hydrazine hydrate leads to hydrazone derivative formation. Nitro substituted carbonyl compounds were effectively reduced to alcohols without affecting the nitro group (Table 4, entries 1–8). In the absence of a catalyst, moderate reduction of 4-nitrobenzaldehyde (50% yield) was observed whereas the presence of ZnPc provided excellent yield (Table 4, entry 3). In the case of α,β-unsaturated compounds, double bond reduction was also observed (Table 4, entries 6 and 8). Important functional groups such as halide, hydroxyl, methoxy and cyano were well tolerated and good to excellent yield was obtained (Table 4, entries 9–16). Furthermore, nitro substituted esters were efficiently and selectively reduced to the corresponding benzyl alcohols (Scheme 2).

ZnPc was also employed for the chemoselective reductive amination of nitro substituted benzaldehydes in ethanol (Scheme 3).

Conclusions

In conclusion, an efficient and practical method employing ZnPc in PEG-400 was reported for the reduction of nitro and carbonyl

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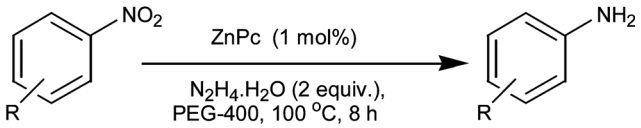
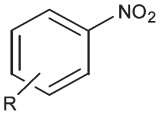
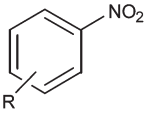
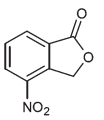
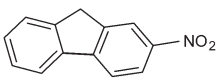
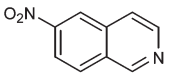
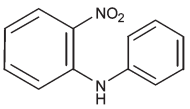
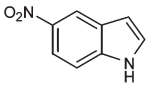
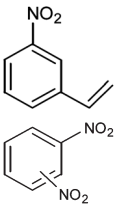
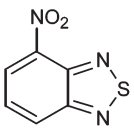
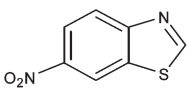
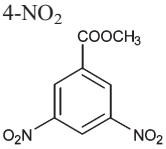
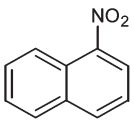
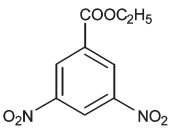
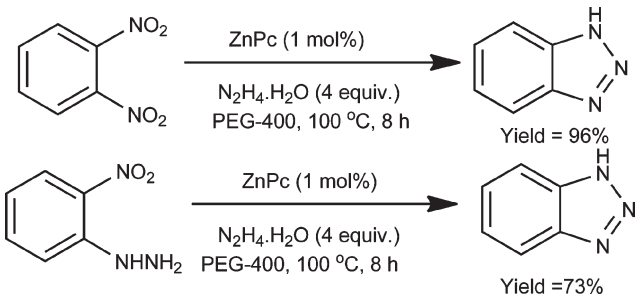
Table 2 ZnPc catalyzed reduction of nitroarenes to corresponding anilines



Entry	Substrate	Con./Sel.	Yield[a] [%]	Entry	Substrate	Con./Sel.	Yield[a] [%]
							
1	R = H	96/99	96[b]	14	R = 4-CH_3	97/99	97 (84)
2	R = 4-F	80/99	80 (69)	15	R = 4-OH	89/99	89 (72)[b]
3	R = 2-Cl	60/99	60[b]	16	R = 4-OBn	99/99	99 (89)
4	R = 4-Cl	98/99	98 (85)[b]	17	R = 4-NHBn	81/99	81
5	R = 3-Br	99/99	99 (89)[b]	18	R = 2-$COOCH_3$	46/99	46[b]
6	R = 4-Br	99/99	99 (86)	19	R = 3-$COOCH_3$	99/99	99 (91)[b]
7	R = 4-I	99/99	99 (93)	20	R = 4-$COOCH_3$	86/99	86
8	R = 4-OCH_3	68/99	68 (60)[b]	21	R = 4-$COOCH_2CH_3$	76/90	68
9	R = 4-COOH	98/99	98 (81)	22	R = 4-Cl, 6-$COOCH_3$	94/93	87
10	R = 3-CN	99/99	99 (90)[b]	23	R = 3-Cl, 6-$COOCH_3$,	95/95	90[b]
11	R = 4-CN	99/99	99 (93)	24	R = 4-Br, 5-$COOCH_3$,	76/66	50
12	R = 4-$CONH_2$	70/99	70[c]	25	R = 2-CH_3, 3-$COOCH_3$	77/90	69
13	R = 4-SO_2NH_2	99/99	99 (88)	26	R = 4-$NHCOCH_3$, 5-$COOCH_3$	94/58	54
27		99/99	99[b]	33		99/99	99 (91)
28		99/99	99 (95)	34		64/99	64 (63)
29		60/99	60[b]	35		91/98	89 (80)
30		99/99	99 (84)[b]	36	2-NO_2	58/99 90/95	58 85[d]
				37	3-NO_2	84/99 99/99	84 (71) 99 (89)[b]
				38	4-NO_2	97/99	97 (82)
31		99/99	99 (86)[b]	39		87/99 99/99	87 99[b]
32		99/99	99 (90)	40		81/99	81

[a] Time and temperature were not optimized separately for all reactions. Yield was calculated on the basis of GC-MS. Isolated yields are given in parenthesis after increasing substrate amount to 5 mmol. [b] Four equivalents of hydrazine hydrate were used. [c] Reaction carried out at room temperature for 10 h. [d] Phenyl hydrazine (2 equiv.) was used as the hydrogen source.

compounds. Excellent conversion and selectivity was observed for the reduction of nitro and carbonyl compounds. The merits of the current catalytic method include: (i) low loading of catalyst (up to 0.25 mol%), (ii) use of recyclable green solvent PEG-400 (iii) recyclability of the catalyst up to four times without any loss in activity and selectivity. The catalytic system



Scheme 1 Synthesis of triazole derivative from nitro compounds.

Table 3 Recyclability of the catalyst

Cycle	1st	2nd	3rd	4th	5th
Yield (%)[a]	>99	97	>99	>99	62

[a] GC-MS yield is reported.

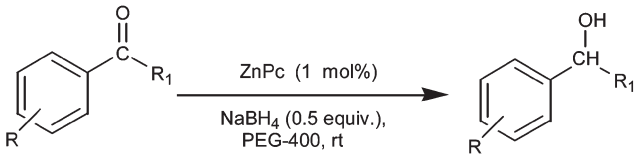
is also applicable for the selective reduction of esters to corresponding alcohols, reductive amination of nitro-substituted benzaldehyde and for the synthesis of biologically important benzotriazole. Further study on understanding the mechanism of the reaction and scope of ZnPc for synthesis of substituted benzotriazole is being carried out.

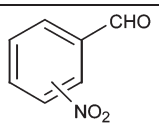
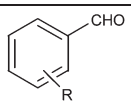
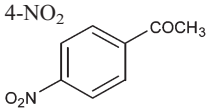
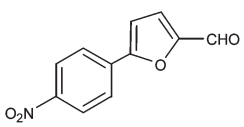
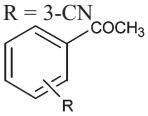
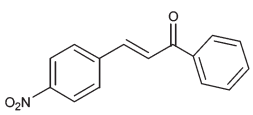
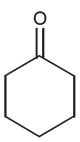
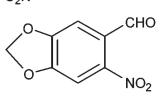
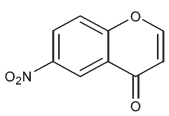
Experimental

Representative experimental procedure for reduction of nitro compounds

To a mixture of nitro compound (1.34 mmol) and catalyst (1 mol %) in PEG-400 (3 ml) was added hydrazine hydrate (2 equiv.). The reaction mixture was stirred at 100 °C for 8 h. Time was not optimized separately for all substrates. After completion of reaction as monitored by TLC (silica gel, hexane–ethyl acetate), the reaction mixture was cooled to ambient temperature and 20 ml of ethyl acetate was added. PEG-400 was removed by washing with distilled water and ethyl acetate layer was dried under

Table 4 ZnPc catalyzed reduction of carbonyl compounds to corresponding alcohols



Entry	Substrate	Time (h)	Yield[a] [%]	Entry	Substrate	Time (h)	Yield[a] [%]
							
				9	R = H	1	92
1	2-NO_2	2.5	81	10	R = 4-Br	2	89
2	3-NO_2	0.75	86	11	R = 3-OCH_3, 4-OH	2	83
3	4-NO_2	1.5	90	12	R = 2,3,4-OCH_3	1	79
4		4.5	90	13	R = 2-COOH	3	62[d]
				14	R = 3-CN	1.5	90
5		2	89				
				15	R = H	1.5	86
				16	R = Br	2	88
6		1	92[b]	17		4	81
7		1.5	90				
8		3	85[c]				

[a] Isolated yield. [b] Combined yield for saturated and unsaturated alcohol. [c] Both carbonyl and double bond were reduced completely. [d] Phthalide is formed.

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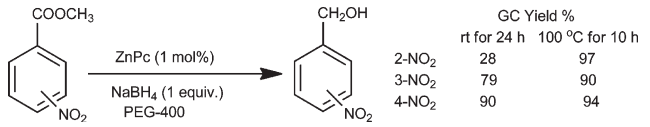
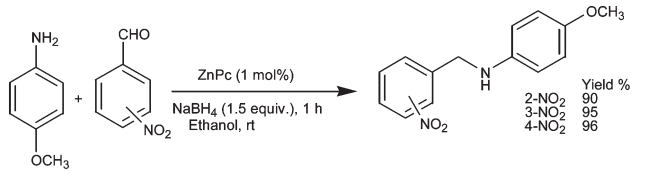


Scheme 2 Chemoselective reduction of nitro substituted methylbenzoate.



Scheme 3 Chemoselective reductive amination of nitro substituted benzaldehydes.

reduced pressure using a rotatory evaporator and analyzed by GC-MS. In some cases (Table 2, entries 9, 12, 15 and 32) where the products are partially soluble in water the reaction mixture was dissolved in ethyl acetate and directly analyzed by GC-MS. The initial temperature of the column was 70 °C held for 4 min and was programmed to 230 °C at 4 °C min^{-1}, then held for 15 min at 230 °C, the sample injection volume was 2 µl in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min^{-1} on split mode (1 : 50). Whenever necessary, crude products were purified by column chromatography (silica 230–400, *n*-hexane–ethyl acetate mixture).

Representative experimental procedure for reduction of carbonyl compounds

To a mixture of carbonyl compound (1.34 mmol) and catalyst (1 mol%) in PEG-400 (3 ml) was added sodium borohydride (0.5 equiv.). The reaction mixture was stirred at room temperature for the appropriate time. After completion of the reaction as monitored by TLC (silica gel, hexane–ethyl acetate) the crude product was extracted with diethyl ether (3 × 10 ml). Diethyl ether fractions were combined and dried under reduced pressure by using a rotatory evaporator. Crude products were purified by column chromatography (silica 60–120, *n*-hexane–ethyl acetate mixture).

Representative experimental procedure for reductive amination of nitro-substituted benzaldehydes

To a mixture of nitrobenzaldehyde (1 mmol), 4-methoxyaniline (1 mmol) and catalyst (1 mol%) in ethanol (5 ml) was added sodium borohydride (1.5 equiv.). The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction as monitored by TLC (silica gel, hexane–ethyl acetate) the reaction mixture was filtered and passed through anhydrous Na_2SO_4. The filtrate was dried under vacuum and the crude products obtained were purified by column chromatography (silica 60–120, *n*-hexane–ethyl acetate mixture).

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