Human Hair Catalyzed Selective Reduction of Nitroarenes to Amines

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Keywords: Human Hair, Catalyst, Reduction, Nitro, Amine

Abstract: Nowadays it is great challenge to use natural, cheap and biodegradable materials as catalyst in different organic reactions. In this work we use directly human hair dough as completely biodegradable, renewable, and available material in every locality for reduction of nitroarenes in aqueous media at 50 °C. Using this new catalyst, structurally different aromatic nitro compounds, as well as heterocyclic ones are reduced to corresponding amines in high to excellent yields. The presented catalytic system is applicable for large scale reduction of nitroarenes.

1. Introduction

Reduction of nitro group has emerged as the most promising synthetic route to production of amine derivatives, which are essential intermediates in dyes, pigments, pharmaceuticals and agrochemicals.^{1,2} Traditional approaches such as Béchamp reduction method, generates large amount of waste and requires mineral acids, which is not appropriate for acid sensitive functional groups.³ In recent years, an increasing attention has been paid to catalytic nitro reduction using transition metals such as Cu,^{4,5} Co,^{6,7} Pd,⁸⁻¹¹ Ni,^{12,13} Au¹⁴⁻¹⁷ and Zn^{18,19}. Along this line, due to the superior catalytic activity in bimetallic variants relative to their monometallic analogs, variety of bimetallic catalysts have been developed for organic reactions including the reduction of nitroarenes.²⁰⁻²⁶ However, it is still a great sustainable processes challenge to develop efficient, green and cheap catalysts for selective reduction of nitro group to amines.

Human hair is considered a minor excretory organ for trace elements such as Fe, Au, Cu, Mn, Mg and Cr, Co, Zn, Ni, etc.²⁷⁻³² The content of trace elements in hair depend on different factors such geographic residence, environmental characteristics, age,

sex, and color of hair. For example, red hair contains relatively high concentrations of iron while white hair has low concentrations of manganese.³³⁻³⁸

In the past decade, due to environmental issues and efforts for development of sustainable chemistry, attention to the use of hair in various sciences has increased. For instance, recently human hair is used as a support for stabilizing of different transition metal nanoparticles such as Ni,^{39,40} Ru,³⁹⁻⁴¹ Au,^{40,42} Ag,^{41,42} and Cu⁴⁰ resulting material have been applied as catalyst for various organic reactions. However, to the best of our knowledge, any report of using hair as a catalyst in any organic reaction has not been documented. Therefore, in continuation of our interest in development of abundant and naturally based catalysts,⁴³⁻⁴⁸ in this work for the first time we used human hair as catalyst for the reduction of structurally different nitroarenes in aqueous media under mild reaction conditions.

2. Experimental

2.1. General:

Reactions were monitored by gas chromatography (GC) and thin layer chromatography (TLC) using Merck silica gel 60F254 glass plate with 0.25 mm thickness. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively, on a Bruker Avance HD apparatus in $\text{DMSO-}d_6$ and CDCl_3 and chemical shifts are given on the δ -scale in ppm. The TEM and SEM images were captured with EOL JEM-2010 and JEOL JSM 840, respectively. XPS analyses were performed using a K-Alpha spectrometer. EDX results were obtained using a Carl Zeiss Sigma instrument.

2.2. General procedure for the hair catalyzed reduction of nitroarenes:

Initially, 2 g of human hair crushed into small pieces, washed with distilled water and then vacuum dried. Then, aqueous solution of NaOH (3.7 mmol in 3 mL H_2O) and 1 g of the crushed human hair was added to the reaction tube and stirred at 50 $^\circ\text{C}$ until dissolving the hair. Afterward nitroarenes (0.4 mmol), NaBH_4 (0.8 mmol,

30 mg) and EtOH (0.75 mL) were added and the reaction mixture was stirred for appropriate reaction time at 50 °C. Then, reaction mixture was washed with ethyl acetate (3×5 mL) and the organic phase was separated. Further purification of amine product was performed by plate or column chromatography using hexane and ethyl acetate as eluents.

3. Results and discussions

Initially, structure of fresh human hair was studied with energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. EDX analysis of hair showed different elements such as Na, Ca, C, O, N, Al, Si, S, and Ca (Fig. 1).

Fig. 1 EDX spectrum of human hair

The presence of C and N was further confirmed by XPS by showing peaks related to C 1s at 284.7, 285.5, 286.4, and 288.1 eV are assigned to C-C or C=C, C-N, C-O, and C=O ^{49,50} and a peak at 400 eV related to N 1s ⁵¹ (Fig. 2).

Fig. 2 XPS spectra of hair in A) C 1s and B) N 1s regions.

Also, SEM of hair (after and before) of the treatment with alkaline solution was studied. SEM images of hair before treating with NaOH showed the presence of very uniform hair strand (Fig. 3). However, SEM images after treating with alkaline media exhibited ununiformed broken hair particles (Fig. 4). Also, TEM images of hair, after treating with alkaline media, showed the presence of hair layers (Fig. 1 ESI).

Fig. 3 SEM images of human hair before treating with NaOH solution

Fig. 4 SEM images of human hair after treating with NaOH solution

In order to study the catalytic activity of hair, reduction of 4-nitrotoluene (**1a**) was selected as benchmark reaction and the effects of human hair amount, solvent, temperature, and reducing agent on the yield of reaction were investigated.

Initially effect of different hair amounts and solvents were evaluated. The study of the reaction in solvents such as EtOH, DMF, toluene, CH₃CN in the presence of 0.4 g of human hair, NaOH (3.7 mmol) and NaBH₄ (0.8 mmol) gave very poor yields during 6h (Table 1, entries 1-4). However, using solvents such as H₂O and H₂O:EtOH (1:0.25) in the presence NaOH (3.7 mmol) afforded 17% and 25% yields,

respectively (Table 1, entries 5 and 6). Selecting H₂O:EtOH (1:0.25) as a solvent and increasing the hair amounts, yields were improved and 80% yield was achieved using 1 g of the hair (Table 1, entry 9). Results indicated that with increasing reaction times, yields were further improved and quantitative yield was achieved after 12 h (Table 1, entry 12). It should be noted that with decreasing NaBH₄ amounts to 0.4 mmol, the yield of desired product was dropped to 67% (Table 1, entry 13). Also, the reactions in the absence of NaBH₄ and also in the absence of hair failed to proceed (Table 1, entries 14-16). For possibility of metal leaching from hair, we washed hair with EDTA (40 mL, 0.5 M) for 2 h and then used it for the reduction of 4-nitrotoluene under most optimized condition (Table 1, entry 12). Results indicated formation of desired product in 90% yield confirming lack of leaching of active catalysts in the presence of EDTA (Table 1, entry 17). Performing reaction using woman's brown hair gave also excellent yield (Table 1, entry 18). However, using dyed hair and natural white hair 20% and 46% yield was achieved, respectively (Table 1, entries 19 and 20). Finally, we tested cat's hair obtained from veterinary clinic in the reduction, but reaction did not proceed and starting material was intact (Table 1, entry 21).

Table 1 Optimization of the reaction conditions for the reduction of 4-nitrotoluene (**1a**).^a

Entry	Solvent	Time (h)	Hair (g)	Yield (%) ^b
1	EtOH	6	0.4	5
2	DMF	6	0.4	<2
3	Toluene	6	0.4	<1
4	CH ₃ CN	6	0.4	<1
5	H ₂ O	6	0.4	17
6	H ₂ O:EtOH	6	0.4	25
7	H ₂ O:EtOH	6	0.6	30
8	H ₂ O:EtOH	6	0.8	55
9	H ₂ O:EtOH	6	1	80
10	H ₂ O:EtOH	7	1	85
11	H ₂ O:EtOH	9	1	90
12	H ₂ O:EtOH	12	1	>99
13	H ₂ O:EtOH	12	1	67 ^c
14	H ₂ O:EtOH	12	-	<1 ^d

15	H ₂ O:EtOH	12	1	14 ^e
16	H ₂ O:EtOH	12	-	<1 ^f
17	H ₂ O:EtOH	12	1	90 ^g
18	H ₂ O:EtOH	12	1	>99 ^h
19	H ₂ O:EtOH	12	1	20 ⁱ
20	H ₂ O:EtOH	12	1	46 ^j
21	H ₂ O:EtOH	12	1	<1 ^k

^a Reaction condition: human hair dissolved in solution of NaOH (3.7 mmol in 3 mL solvent), 4-nitrotoluene (0.4 mmol) and NaBH₄ (0.8 mmol).

^b Yields determined by GC.

^c Using 0.4 mmol of NaBH₄

^d Reaction performed in the absence of hair and NaOH

^e Reaction performed in the absence of NaBH₄

^f Reaction performed in the absence of hair and in the presence 3.7 mmol NaOH and NaBH₄ (0.8 mmol).

^g Reaction performed using hair washed with EDTA

^h Reaction performed using woman's brown hair

ⁱ Reaction performed using yellow dyed hair

^j Reaction performed using natural white hair of old men.

^k Reaction performed using cat's hair

In Table 2 it is demonstrated that the efficiency of NaBH₄ is extremely high compared with other reducing agents tested such as formic acid, isopropyl alcohol, hydrazine, glycerol, and ascorbic acid.

Table 2 Study of the efficiency of different reducing agents in the reduction of 4-nitrotoluene (**1a**).^a

Entry	Reductant	Yield (%) ^b
1	Formic acid	20
2	Isopropyl Alcohol	23
3	Hydrazine	22
4	Glycerol	18
5	Ascorbic acid	28
6	Sodium borohydride	>99

^a Reaction condition: human hair (1 g) dissolved in aqueous solution of NaOH (3.7 mmol in 3 mL H₂O), 4-nitrotoluene (0.4 mmol), EtOH (0.75 mL) and reducing agent (0.8 mmol) at 50 °C.

^b Yields determined by GC.

Having optimized conditions in hand (Table 1, entry 12), we investigated the reduction reaction of variety of nitro compounds **1** (Scheme 1). Results indicated that reduction of aromatic nitro compounds bearing electron withdrawing groups in the **1c – 1e**, **1h**, **1m – 1o** and **1p**, as well as electron donating groups in the **1a**, **1b**,

1f, **1h**, **1j** – **1l** and **1q** – **1s** were proceeded very well and 80-99% yields were obtained (Table 3). It should be noted that in the case of nitro aromatic compounds having formyl group in the **1m** – **1o**, both carbonyl and nitro groups were reduced to alcohol and amine, respectively. while in the case methyl 4-nitrobenzoate (**1p**), nitro group was reduced to amine without reduction of ester group.

Scheme 1 Reduction of structurally different nitroarenes **1** to the amines counterpart **2** using human hair as a catalyst.

a R= H, R¹= H, R²= Me

b R= H, R¹= H, R²= OMe

c R= H, R¹= H, R²= Cl

d R= H, R¹= H, R²= Br

e R= H, R¹= NO₂, R²= Cl

f R= H, R¹= NH₂, R²= H

g R= NO₂, R¹= H, R²= H

h R= NO₂, R¹= H, R²= Cl

i R= H, R¹= H, R²= H

j R= CH₂OH, R¹= H, R²= H

k R= H, R¹= CH₂OH, R²= H

l R= H, R¹= H, R²= CH₂OH

m R= CHO, R¹= H, R²= H

n R= H, R¹= CHO, R²= H

o R= H, R¹= H, R²= CHO

a R= H, R¹= H, R²= Me

b R= H, R¹= H, R²= OMe

c R= H, R¹= H, R²= Cl

d R= H, R¹= H, R²= Br

e R= H, R¹= NH₂, R²= Cl

f R= H, R¹= NH₂, R²= H

g R= NH₂, R¹= H, R²= H

h R= NH₂, R¹= H, R²= Cl

i R= H, R¹= H, R²= H

j R= CH₂OH, R¹= H, R²= H

k R= H, R¹= CH₂OH, R²= H

l R= H, R¹= H, R²= CH₂OH

m R= CH₂OH, R¹= H, R²= H

n R= H, R¹= CH₂OH, R²= H

o R= H, R¹= H, R²= CH₂OH

p R= H, R ¹ = H, R ² = CO ₂ Me	p R= H, R ¹ = H, R ² = CO ₂ Me
q R= OH, R ¹ = H, R ² = H	q R= OH, R ¹ = H, R ² = H
r R= H, R ¹ = OH, R ² = H	r R= H, R ¹ = OH, R ² = H
s R= H, R ¹ = H, R ² = OH	s R= H, R ¹ = H, R ² = OH
t R= H, R ¹ = 2,5 dichloropyrimidin-4-amino, R ² = H	t R= H, R ¹ = 2,5 dichloropyrimidin-4-amino, R ² = H
u R= H, R ¹ = H, R ² = Ph	u R= H, R ¹ = H, R ² = Ph

Table 3 Reduction of structurally different nitroarenes **1** to the amines counterpart **2** using human hair as a catalyst, according to scheme 1.^a

Entry	Ar-NO ₂	Time (h)	Product	Yield (%) ^b
1	1a	12	2a	99 ^c
2	1b	12	2b	98 ^c
3	1c	10	2c	98 ^c
4	1d	10	2d	80 ^c
5	1e	10	2e	90 ^{d,e}
6	1f	9	2f	87 ^{c,e}
7	1g	10	2g	89 ^{d,e}
8	1h	9	2h	90 ^{c,e}
9	1i	8	2i	99 ^c
10	1j	11	2j	96 ^c
11	1k	12	2k	94 ^c
12	1l	10	2l	90 ^{c,e}
13	1m	11	2m	97 ^d

14	1n	12	2n	90 ^{d,e}
15	1o	10	2o	94 ^d
16	1p	12	2p	97 ^d
17	1q	10	2q	98 ^c
18	1r	12	2r	95 ^c
19	1s	9	2s	97 ^c
20	1t	24	2t	70 ^{d,e}
21	1u	12	2u	80 ^{c,e}

^a Reaction condition: human hair (1 g) dissolved in aqueous solution of NaOH (3.7 mmol in 3 mL H₂O), ArNO₂ (0.4 mmol), and EtOH (0.75 mL) at 50 °C.

^b Yields determined by GC.

^c Using 0.8 mmol NaBH₄

^d Using 1.6 mmol NaBH₄

^e Yields are isolated.

In order to show the features of the reaction for large-scale operation, we have scaled-up the reaction of 4-nitrotoluene (**1a**) to the 10 mmol, under optimized reaction conditions. Results indicated that reaction proceeded well and desired amine was obtained in 85% isolated yield (scheme 2).

Scheme 2 Reduction of 4-nitrotoluene (**1a**) in a large scale.

4. Conclusions

In conclusion, in this study we have presented a novel protocol in which human hair has been used as a catalyst for the important nitroarene reduction in aqueous media. By this method the structurally diverse nitroaromatic compounds have been reduced to corresponding amines in high to excellent yields under mild reaction condition. This method is applicable for large scale operation which is of interest for industrial purposes.

5. Acknowledgments

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council, Iran National Science Foundation (INSF-Grant number of 97021804) and the University of Alicante. We also thankful for financial support to the Spanish Ministerio de Econom_ a y Competitividad (MINECO; projects CTQ2013-43446-P and CTQ2014-51912-REDC), the Spanish Ministerio de Econom_ a, Industria y Competitividad, Agencia Estatal de Investigaci_ n (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU; projects CTQ2016-76782-P and CTQ2016-81797-REDC), the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante. Special

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Fig. 1. EDX spectrum of human hair.

Fig. 2. XPS spectra of hair in A) C 1s and B) N 1s regions.

Fig. 3. SEM images of human hair before treating with NaOH solution

Fig. 4. SEM images of human hair after treating with NaOH solution

Table 1. Optimization of the reaction conditions for the reduction of 4-nitrotoluene (**1a**).

Table 2. Study of the efficiency of different reducing agents in the reduction of 4-nitrotoluene (**1a**).

Scheme 1. Reduction of structurally different nitroarenes **1** to the amines counterpart **2** using human hair as a catalyst.

Table 3. Reduction of structurally different nitroarenes **1** to the amines counterpart **2** using human hair as a catalyst, according to scheme 1.

Scheme 2. Reduction of 4-nitrotoluene (**1a**) in a large scale.