

Fast and Efficient Protocol for Solvent-Free Reduction of Nitro Compounds to Amines with NaBH₄ in the Presence of Bis-Thiourea Complexes of Bivalent Cobalt Nickel, Copper and Zinc Chlorides

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(Received on 25th January 2016, accepted in revised form 13th May 2016)

Summary Reduction of nitro compounds to the corresponding amines has been carried out efficiently with NaBH₄ in the presence of bis-thiourea complexes of bivalent cobalt, nickel, copper and zinc chlorides, [M^{II}(tu)₂Cl₂]. The reactions were carried out under solvent-free conditions at room temperature to afford amines in high to excellent yields. Comparison of the results showed that the reducing capability of NaBH₄ was influenced with bis-thiourea complexes as: Co(tu)₂Cl₂> Ni(tu)₂Cl₂> Cu(tu)₂Cl₂> Zn(tu)₂Cl₂.

Keywords: Amines, Bis-thiourea, M^{II}(tu)₂Cl₂, NaBH₄, Nitro compounds, Reduction.

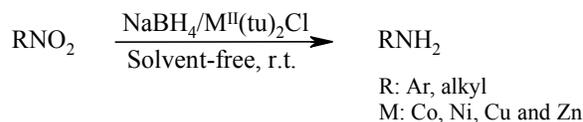
Introduction

Reduction of nitro compounds to the corresponding amines is one of the most important synthetic transformations in organic chemistry [1-4]. Aromatic amines can be easily transformed to other functional groups (H, F, Cl, Br, I, OH and etc.) via their diazonium salts [5]. In addition, structurally diverse arylamines constitute major building blocks, and they are used extensively as key intermediates for the preparation of pharmaceuticals, drugs, dyes, pigments and agrochemicals [6-9]. The literature review shows that though many synthetic routes have been reported for such achievement, however, the search for new facile, chemoselective and eco-friendly procedures that avoid using expensive and hazardous reagents/catalysts is the subject of interest and still is demanded.

During the past decades, NaBH₄ as a mild reducing agent has brought about revolutionary changes in the reduction of functional groups in modern organic synthesis [1-4]. It is well known that the alone NaBH₄ does not reduce nitro compounds under ordinary conditions. However, the reducing power of this reagent undergoes a drastic change towards reduction of nitro groups by the combination with metal halides or other promoters. NaBH₄ in the presence of NiCl₂ [10,11], CoCl₂ [12,13], CuCl₂ [14], ZrCl₄ [15], SnCl₂ [16], BiCl₃ [17], SbF₃ [18], CuSO₄ [19], Raney nickel [20], Ni₂B [21], nickel complexes of *o*-aminothiophenol Schiff base [22] and charcoal [23] are some of the combination systems which have been reported for reduction of nitro compounds to their corresponding amines.

In line with the outlined strategies, herein, we wish to introduce an easy, efficient and practical

protocol for solvent-free reduction of various aromatic and aliphatic nitro compounds to the corresponding amines with NaBH₄ in the presence of bis-thiourea complexes of bivalent cobalt, nickel, copper and zinc chlorides at room temperature (Scheme 1).



Scheme-1: Reduction of nitro compounds with NaBH₄/M^{II}(tu)₂Cl₂ system.

Experimental

General

All reagents and substrates were purchased from commercial sources with high quality and they were used without further purification. FT-IR and ¹H NMR spectra were recorded on Thermo Nicolet Nexus 670 and Bruker Avance spectrometers (300 MHz). The products are known and they were characterized by their ¹H NMR and FT-IR spectra followed by comparison with authentic data [21]. TLC was applied for the purity determination of substrates, products and the reaction monitoring over silica gel 60 F₂₅₄ aluminum sheet.

Preparation of Bis-thiourea Complexes of Bivalent Cobalt, Nickel, Copper and Zinc Chlorides, M(tu)₂Cl₂ [24]

In a round-bottom flask (50 mL) equipped with a magnetic stirrer, absolute ethanol (20 mL) and thiourea (0.02 mol, 1.52 g) were added. The flask

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was slightly warmed and stirred for complete dissolving of thiourea. Afterward, a solution of bivalent metal chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or ZnCl_2) (0.01 mol) in absolute ethanol (20 mL) was added and the mixture was continued to stirring for 4 h under reflux conditions. After completion of the reaction, the mixture was stand at room temperature for one week. During the time, ethanol was evaporated and the resulting solid complex was washed with absolute ethanol (10 ml). Drying the complex under air atmosphere affords the pure $\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ in 82-92% yields.

A Typical Procedure for Reduction of Nitrobenzene to Aniline with $\text{NaBH}_4/\text{Co}(\text{tu})_2\text{Cl}_2$ System

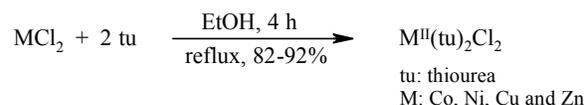
In a porcelain mortar, a mixture of nitrobenzene (0.123 g, 1 mmol) and $\text{Co}(\text{tu})_2\text{Cl}_2$ (0.141 g, 0.5 mmol) was ground by an agate at room temperature for 1 min. NaBH_4 (0.076 g, 2 mmol) was then added portion wisely and grinding the reaction mixture was continued for 2 min. During the reaction, heat was released and color of reaction was changed from blue to brown and finally black. In the case of $\text{Co}(\text{tu})_2\text{Cl}_2$ complex and due to its high reactivity relative to the complexes of Ni, Cu and Zn, grinding should be carried out with caution and in ice-bath. *Since the reaction may be associated with releasing smoke and little explosion/sparks.* TLC monitored the progress of the reaction (*n*-hexane/*EtOAc*: 5/2). After completion of the reaction, the mixture was dissolved in water and then extracted with *EtOAc* (2×5 mL). The organic layer was dried over anhydrous Na_2SO_4 . Evaporation of the solvent affords the pure liquid aniline in 96% yield (0.089 g, Table-3, entry 1).

Results and Discussion

Nowadays in organic synthesis, increasing attention is being focused on green chemistry using

environmentally benign reagents and conditions; specially using solvent-free conditions which often lead to clean and eco-friendly protocols through the simplified work-up procedures, energy saving, avoidance of solvent waste, dangers and toxicity [25]. Thus, performing the reactions in dry media has received many attentions over the solution phase. A literature review shows that though the application of NaBH_4 in the presence of various Lewis acids or promoters has been used for reduction of nitro compounds to amines, however, the combination system of bis-thiourea complexes of bivalent transition metal chlorides with NaBH_4 has not been investigated yet. This subject and continuation of our research program directed to the development of new protocols for NaBH_4 reduction of nitro compounds [18,21,23,26-29] encouraged us to investigate the facility of $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ systems (M: Co, Ni, Cu and Zn) for the titled transformation. In addition, we encouraged to examine the reactions under solvent-free conditions along the aims of green chemistry.

The study was started by the preparation of bis-thiourea complexes of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 as bivalent transition metal leaders of groups 9, 10, 11 and 12 (or VIII, IB and IIB) from Periodic Table (Scheme-2). The complexes were characterized by their physical data and then authorized with the reported data in literature (Table-1).



Scheme-2: Reaction of bivalent metal chlorides with thiourea.

Table-1: Physical and spectral data for $\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ complexes.

Entry	Physical Data	*	$\text{Co}(\text{tu})_2\text{Cl}_2$	$\text{Ni}(\text{tu})_2\text{Cl}_2$	$\text{Cu}(\text{tu})_2\text{Cl}_2$	$\text{Zn}(\text{tu})_2\text{Cl}_2$
	Color		Dark blue	Yellow	Light green	Colorless
	Yield (%)		90	86	92	82
1		Exp.	147	159	320	193
2	Melting Point (°C)	Lit.	148 [24]	163 [31]	>350 [32]	210 [32]
3		Exp.	3384	3373	3327	3205
4	$\nu(\text{N-H})(\text{Cm}^{-1})$	Lit.	3400 [30]	3013 [31]	3282 [33]	3366 [34]
5		Exp.	2659	2662	2687	2724
6	$\nu(\text{C-H})(\text{Cm}^{-1})$	Lit.	2670 [30]	2692 [31]	2767 [33]	2700 [32]
7		Exp.	1482	1496	1474	1445
8	$\nu(\text{C=N})(\text{Cm}^{-1})$	Lit.	1473 [30]	1634 [31]	1541 [33]	1483 [32]
9		Exp.	1388	1408	1395	1408
10	$\nu(\text{C=S})(\text{Cm}^{-1})$	Lit.	1414 [30]	1500 [31]	1174 [33]	1408 [32]
11		Exp.	499	576	475	478
12	$\nu(\text{M}^{\text{II}}-\text{S})(\text{Cm}^{-1})$	Lit.	500 [30]	507 [31]	474 [32]	476 [32]

*Exp: experimental, Lit.: literature

Promoter activity of the prepared complexes on reducing capability of NaBH_4 was then investigated by reduction of nitrobenzene as a model compound under different reaction conditions (Table-2). Observation of the results shows that reduction of nitrobenzene with $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ systems and inside various solvents did not have any efficiency, however, the effect of solvent-free condition on progress of the reaction is quite noteworthy. The examinations revealed that reduction of nitrobenzene (1 mmol) was carried out completely with 2:0.5 molar equivalents of NaBH_4 and $\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ complexes, respectively, within 2-8 min. In addition, the reactions were carried out at room temperature to afford aniline as a sole product. Entries 6, 12, 18 and 24 also show that although all of the complexes efficiently influenced the reducing capability of NaBH_4 , however, the rate enhancement and promoter activity of the complexes vary as $\text{Co}(\text{tu})_2\text{Cl}_2 > \text{Ni}(\text{tu})_2\text{Cl}_2 > \text{Cu}(\text{tu})_2\text{Cl}_2 > \text{Zn}(\text{tu})_2\text{Cl}_2$.

The scope and generality of this synthetic protocol was then studied through the reduction of structurally different aromatic nitro compounds at the optimized conditions. The summarized results in Table 3 show that reduction of nitroarenes having

electron-releasing or withdrawing functionalities was carried out successfully using 2-4 molar equivalents of NaBH_4 and 0.5-1.5 mmol of $\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ within 2-52 min under solvent-free conditions at room temperature. Molecules with the complexity of nitro and carbonyl groups did not show any selectivity and both of functional groups were reduced with the same reactivity. This fact was shown with the reduction of nitrobenzaldehydes and 3-nitroacetophenone to the corresponding amino alcohols (entries 9-13). It is notable that the complete reduction of nitroaldehydes and nitroketones required higher molar equivalents of NaBH_4 and bis-thiourea complexes. Further examinations resulted that the present method was also efficient for the reduction of 1,3-dinitrobenzene to the corresponding *m*-phenylenediamine using 4:1 molar equivalents of $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ under solvent-free conditions within 10-38 min (entry 15). Reducing capability of $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ system towards aliphatic nitro compounds was also studied by the reduction of 1-nitrohexane and 2-nitroheptane at the optimized reaction conditions. The results showed that as aromatic nitro compounds, this protocol was also efficient and the corresponding aliphatic amines were obtained efficiently within 3-15 min (entries 16, 17).

Table-2: Optimization experiments for reduction of nitrobenzene to aniline with NaBH_4 /bis-thiourea complexes

Entry	Metal Complex	Molar ratio (NaBH_4 /Complex)	Condition ^a	Time (h)	Conversion (%)
1	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:1	THF/reflux	2	5
2	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:1	$\text{CH}_3\text{CN}/\text{reflux}$	2	30
3	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:1	$\text{MeOH}/\text{reflux}$	1	5
4	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:1	<i>n</i> -Hexane/reflux	2	40
5	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:1	$\text{H}_2\text{O}/\text{reflux}$	30 min	60
6	$\text{Co}(\text{tu})_2\text{Cl}_2$	2:0.5	Solvent-free/r.t.	2 min	100
7	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	THF/reflux	2	5
8	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	$\text{CH}_3\text{CN}/\text{reflux}$	2	30
9	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	$\text{MeOH}/\text{reflux}$	1	<5
10	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	<i>n</i> -Hexane/reflux	2	10
11	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	$\text{H}_2\text{O}/\text{reflux}$	30 min	70
12	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:0.5	Solvent-free/r.t.	3 min	100
13	$\text{Ni}(\text{tu})_2\text{Cl}_2$	2:1	THF/reflux	2	<5
14	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	$\text{CH}_3\text{CN}/\text{reflux}$	2	5
15	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	$\text{MeOH}/\text{reflux}$	1	<5
16	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	<i>n</i> -Hexane/reflux	2	10
17	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	$\text{H}_2\text{O}/\text{reflux}$	1	20
18	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:0.5	Solvent-free/r.t.	4 min	100
19	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	THF/reflux	2	0
20	$\text{Cu}(\text{tu})_2\text{Cl}_2$	2:1	$\text{CH}_3\text{CN}/\text{reflux}$	2	<5
21	$\text{Zn}(\text{tu})_2\text{Cl}_2$	2:1	$\text{MeOH}/\text{reflux}$	2	0
22	$\text{Zn}(\text{tu})_2\text{Cl}_2$	2:1	<i>n</i> -Hexane/reflux	2	<5
23	$\text{Zn}(\text{tu})_2\text{Cl}_2$	2:1	$\text{H}_2\text{O}/\text{reflux}$	1	20
24	$\text{Zn}(\text{tu})_2\text{Cl}_2$	2:0.5	Solvent-free/r.t.	8 min	100

^aThe reactions were carried out in 1.5 mL solvent.

Table-3: Reduction of nitro compounds with $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$ systems.^a

Entry	Substrate	Product	$\text{Co}(\text{tu})_2\text{Cl}_2$		$\text{Ni}(\text{tu})_2\text{Cl}_2$		$\text{Cu}(\text{tu})_2\text{Cl}_2$		$\text{Zn}(\text{tu})_2\text{Cl}_2$					
			Molar ratio ^b	Time (min)	Yield (%)	Molar ratio ^b	Time (min)	Yield (%)	Molar ratio ^b	Time (min)	Yield (%)	Molar ratio ^b	Time (min)	Yield (%)
1			1:2:0.5	2	96	1:2:0.5	3	92	1:2:0.5	5	86	1:2:0.5	16	82
2			1:3:0.5	17	93	1:3:0.5	20	88	1:3:0.5	30	87	1:3:0.7	25	84
3			1:2:0.5	7	94	1:2:0.5	11	90	1:2:0.5	14	82	1:2:0.5	29	80
4			1:2:0.5	5	90	1:2:0.5	8	88	1:2:0.5	9	82	1:2:0.5	17	80
5			1:4:1.5	15	95	1:4:1.5	16	93	1:4:1.5	22	84	1:4:1.5	40	80
6			1:3:0.5	2	88	1:3:0.5	5	84	1:3:0.5	10	85	1:3:0.5	38	81
7			1:3:0.5	7	90	1:3:0.5	10	87	1:4:0.6	10	87	1:4:0.8	18	82
8			1:4:1.5	15	87	1:4:1.5	22	84	1:4:1.5	30	83	1:4:1.5	52	77
9			1:2.5:0.5	9	90	1:2.5:0.5	11	88	1:2.5:0.5	18	84	1:2.5:0.5	35	80
10			1:2.5:0.5	2	93	1:3:0.5	4	89	1:3:0.5	5	88	1:3:0.5	10	84
11			1:3:0.5	8	89	1:3:0.5	13	86	1:3:0.5	16	85	1:3:0.6	40	82
12			1:3:1	15	85	1:3:1	20	83	1:3:1	26	80	1:3.5:1	42	82
13			1:3:1	5	88	1:3:1	7	85	1:4:1.1	27	82	1:4:1.1	48	80
14			1:4:1	15	86	1:4:1	28	82	1:4:1	36	85	1:4:1.1	40	80
15			1:4:1	10	89	1:4:1	15	86	1:4:1	23	80	1:4:1	38	78
16	1-Nitrohexane	1-Hexylamine	1:2:0.5	3	84	1:2:0.5	5	86	1:2:0.5	8	81	1:2:0.5	10	85
17	2-Nitroheptane	2-Aminoheptane	1:2:0.5	7	86	1:2:0.5	10	84	1:2:0.5	14	80	1:2:0.5	15	82

^a NaBH_4 was added portion wisely within 20 sec. ^bMolar ratio as Subs./ $\text{NaBH}_4/\text{M}^{\text{II}}(\text{tu})_2\text{Cl}_2$

Conclusions

In summary, we have shown that NaBH₄ in the presence of bis-thiourea complexes of bivalent Co, Ni, Cu and Zn chlorides efficiently reduces verities of nitro compounds to the corresponding amines. Reduction reactions were carried out under solvent-free conditions at room temperature using the molar equivalents of 2-4 for NaBH₄ and 0.5-1.5 for M^{II}(tu)₂Cl₂ complexes. The product amines were obtained in high to excellent yields within 2-52 min. The complexes influenced the reducing capability of NaBH₄ as Co(tu)₂Cl₂ > Ni(tu)₂Cl₂ > Cu(tu)₂Cl₂ > Zn(tu)₂Cl₂. High yields, easy work-up procedure, ability to reduce aromatic and aliphatic nitro compounds as well as the benefits of using solvent-free conditions are the significant advantages that make this protocol a synthetically useful addition to the present methodologies.

Acknowledgements

The financial support of this work was gratefully acknowledged by the Research Council of Urmia University.

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