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Highly efficient method for oximation of aldehydes in the presence of bis-thiourea complexes of cobalt, nickel, copper and zinc chlorides

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CHRONICLE	ABSTRACT
	In this study, the selective oximation of structurally diverse aromatic aldehydes (versus ketones) to the corresponding aldoxime derivatives was investigated using the combination system of $NH_2OH \cdot HCl$ and bis-thiourea complexes of cobalt, nickel, copper and zinc chlorides, $M^{II}(tu)_2Cl_2$, in a mixture of CH_3CN-H_2O (1:1). All reactions were carried out successfully at room temperature within the immediate time up to 130 min giving the products in high yields. Investigation of the results exhibited that the applied bis-thiourea metal complexes represented the catalytic activity in order of $Co(tu)_2Cl_2$> $Ni(tu)_2Cl_2$> $Cu(tu)_2Cl_2$> $Zn(tu)_2Cl_2$ in their oximation reactions.

1. Introduction

Aldoximes and ketoximes are valuable chemical intermediates that are widely utilized in the chemical industry.[1,2] They are usually prepared by the reaction of carbonyl compounds and hydroxylamine hydrochloride in the presence of acids or bases including sulfuric acid[3], formic acid[4], pyridine[5], sodium acetate and sodium hydroxide.[6,7] Because of some limitations such as low yield of the products, long reaction times and the presence of acid or base sensitive functionalities in aldehyde or ketonic compounds, the classical methods usually are not suitable. In this context, several improvements such as using nano Fe_3O_4[8], Cu-SiO_2[9], $NH_2OH \cdot HCl/K_2CO_3$[10], Dowex 50WX4[11], hetero-geneous polyoxometalates[12,13], phase transfer catalysts[14], basic ionic liquid 1-butyl-3-methyl-imidazolium hydroxide[15], NH_3/oxidant/catalyst systems[16-21], wet basic Al_2O_3/microwave[22], SiO_2/ NH_2OH/microwave[23], absence of any catalyst and solvent[24], CaO/solvent-free[25], TiO_2/SO_4^{2-} solid super acid[26], ethylenediamine/oxone[27], Na_2SO_4/ultrasound[28], titanyl acetylacetonate/NH_2OH[29], Bi_2O_3/ $NH_2OH \cdot HCl$[30], clay-based titanium silicalite-1[31], host (dealuminated zeolite Y)-guest (12-molybdo-

phosphoric acid) nanocomposite[32] and organo-SOMO catalysis[33] have been reported for the preparation of oximes.

Among the documented catalyst systems for the formation of oximes, most studies are focused on the ammoximation of cyclohexanone and therefore a very limited range of substrates have been investigated. In this context, Sloboda-Rozner reported a sandwich-type polyoxometalate (POM) cluster, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$, which catalyzes the reaction of NH_3 and H_2O_2 to afford the *in situ* preparation of hydroxyl amine.[34] As well, the titled POM catalyst activates the nucleophilic surfaces of the resulting hydroxylamine to promote the oximation reaction. The bare Lewis base nucleophilic surfaces are resulted from the external oxygen atoms of W–O–W and W=O species. They act as nucleophilic sites as well as stabilizers of cationic intermediates.[35-38] In a case for using $NaZn_5W_{19}$, however, the oximation reaction was led to low yields of the corresponding aromatic aldoximes due formation of byproducts (amides and nitriles) and carboxylic acids while aliphatic aldehydes were used as substrates. In addition, the inherent acidity of the catalyst can causes the further transformation of the oximation products.[39-40] Therefore, improving of the selectivity in the oximation of aromatic aldehydes is a subject of more interests. From the industrial aspects, this method suffers from two major drawbacks: relatively high cost of hydroxylamine and the derived serious problems via disposing large amounts of inorganic salts which are co-produced in oximation reactions. Therefore, the requirement for decreasing the use of hydroxylamine in more than stoichio-metric amounts demands the environmental friendly and waste-free procedures as well as the *in situ* preparation of hydroxylamine for the oximation of aldehydes and ketones. Moreover, how to suppress the formation of by-products and increase the selectivity of oximation protocols are of the great significances. Consequently, the short lifetime, insufficient thermal stability and difficulty in recovery of the applied catalyst systems (because of their high solubility in water and polar organic solvents) are the issues which should be taken into account in the development and introduction of new oximation procedures.

In line with the outlined strategies and continuation of our research program directed to the application of bis-thiourea metal complexes of cobalt, nickel, copper and zinc chlorides, $M^{II}(tu)_2Cl_2$, as catalysts for reduction of nitro compounds[41] and silylation of alcohols[42], herein, we wish to introduce a new and highly efficient method for the selective oximation of structurally diverse aromatic and aliphatic aldehydes versus ketones using the combination system of $M^{II}(tu)_2Cl_2$/ $NH_2OH \cdot HCl$ in a mixture of CH_3CN-H_2O (1:1) at room temperature (Scheme 1).

M^{II}: Co(II), Ni(II), Cu(II) and Zn(II)
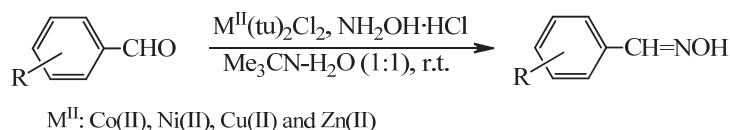
Scheme 1. Oximation of aldehydes with $M^{II}(tu)_2Cl_2/NH_2OH \cdot HCl$ system

2. Results and Discussion

The study was started by the preliminary preparation of bis-thiourea metal complexes of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ 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 the literature.[43]

tu: thiourea
M^{II}: Co(II), Ni(II), Cu(II) and Zn(II)
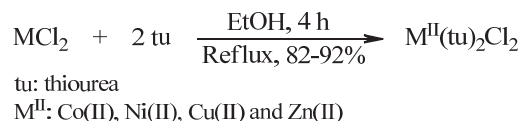
Scheme 2. Reaction of bivalent metal chlorides with thiourea

The promoter activity of the prepared complexes on the oximation of aldehyde was then investigated by the reaction of 4-chlorobenzaldehyde as a model compound with hydroxylamine hydrochloride in the absence and presence of $M^{II}(tu)_2Cl_2$ complexes at different conditions (Table 1). Observation of the results shows that in the absence of metal complexes, the oximation reactions did not has a reasonable efficiency. Whereas by using any of bis-thiourea metal complexes, the model reaction was carried out perfectly to afford 4-chlorobenzaldoxime as a sole product. Entries 6, 13, 20 and 27 (Table 1) exhibited that using a molar equivalent of $M^{II}(tu)_2Cl_2/NH_2OH\cdot HCl$ (0.2:1.2) per 1 mmol of 4-chlorobenzaldehyde was sufficient to complete the reaction in a perfect efficiency within the immediate time up to 15 sec. In addition, a mixture of CH_3CN-H_2O (1:1) was the best solvent of choice to progress of the reaction at room temperature. The results also represented that although all of the complexes influenced the oximation of 4-chlorobenz-aldehyde with hydroxylamine hydro-chloride, however, the rate enhancement and promoter activity of $Co(tu)_2Cl_2$ was greater than the other metal complexes. It is also notable that the oximation of 4-chlorobenzaldehyde with $NH_2OH\cdot HCl$, in the presence of $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$ and $ZnCl_2$ did not has any impressive results.

Table 1. Optimization experiments for oximation of 4-chlorobenzaldehyde to benzaldoxime with $NH_2OH\cdot HCl$/bis-thiourea metal chloride complexes

Entry	$NH_2OH\cdot HCl$ (mmol)	$M^{II}(tu)_2Cl_2$ (mmol)		Condition[a]	Time (min)	Conversion (%)
1	1.2	$Co(tu)_2Cl_2$	0.5	THF/reflux	30	95
2	1.2	$Co(tu)_2Cl_2$	0.5	n-Hexan/reflux	45	20
3	1.2	$Co(tu)_2Cl_2$	0.5	H_2O/reflux	15	95
4	1.2	$Co(tu)_2Cl_2$	0.5	EtOAc/reflux	35	40
5	1.2	$Co(tu)_2Cl_2$	0.5	CH_3CN/reflux	45	95
6	1.2	$Co(tu)_2Cl_2$	0.2	CH_3CN/H_2O (1:1)/r.t.	Immediate	95
7	1.2	$Co(tu)_2Cl_2$	0.5	EtOH/reflux	45	30
8	1.2	$Ni(tu)_2Cl_2$	0.5	THF/reflux	35	90
9	1.2	$Ni(tu)_2Cl_2$	0.5	n-Hexan/reflux	45	20
10	1.2	$Ni(tu)_2Cl_2$	0.5	H_2O/reflux	18	92
11	1.2	$Ni(tu)_2Cl_2$	0.5	EtOAc/reflux	45	25
12	1.2	$Ni(tu)_2Cl_2$	0.5	CH_3CN/reflux	45	90
13	1.2	$Ni(tu)_2Cl_2$	0.2	CH_3CN/H_2O (1:1)/r.t.	Immediate	90
14	1.2	$Ni(tu)_2Cl_2$	0.5	EtOH/reflux	45	25
15	1.2	$Cu(tu)_2Cl_2$	0.5	THF/reflux	45	85
16	1.2	$Cu(tu)_2Cl_2$	0.5	n-Hexan/reflux	45	15
17	1.2	$Cu(tu)_2Cl_2$	0.5	H_2O/reflux	20	90
18	1.2	$Cu(tu)_2Cl_2$	0.5	EtOAc/reflux	45	20
19	1.2	$Cu(tu)_2Cl_2$	0.5	CH_3CN/reflux	45	85
20	1.2	$Cu(tu)_2Cl_2$	0.2	CH_3CN/H_2O (1:1)/r.t.	15 sec	90
21	1.2	$Cu(tu)_2Cl_2$	0.5	EtOH/reflux	50	20
22	1.5	$Zn(tu)_2Cl_2$	0.5	THF/reflux	50	82
23	1.5	$Zn(tu)_2Cl_2$	0.5	n-Hexan/reflux	80	10
24	1.5	$Zn(tu)_2Cl_2$	0.5	H_2O/reflux	30	80
25	1.5	$Zn(tu)_2Cl_2$	0.5	EtOAc/reflux	80	20
26	1.5	$Zn(tu)_2Cl_2$	0.5	CH_3CN/reflux	30	75
27	1.4	$Zn(tu)_2Cl_2$	0.4	CH_3CN/H_2O (1:1)/r.t.	15 sec	80
28	1.5	$Zn(tu)_2Cl_2$	0.5	EtOH/reflux	90	0

[a]All reactions were carried out in 1.5 mL of the solvent.

The capability of $M^{II}(tu)_2Cl_2/NH_2OH\cdot HCl$ system for oximation of structurally diverse aromatic aldehydes was studied at the optimized reaction conditions. The results of this investigation are illustrated in Table 2. As seen, all reactions were carried out successfully at room temperature within the immediate time up to 65 min to afford aromatic aldoximes in high to excellent yields. The result shows that benzaldehyde can be converted to benzaldoxime in 96% yield (Table 2, entry 1). In the case of electron-releasing substitutions on aromatic rings such as methoxy, methyl and hydroxyl groups, the

corresponding aldoximes can be also obtained in high yields. As well, aromatic aldehydes with electron-withdrawing functionalities including 2-Cl, 4-Cl, 4-F, 3-NO$_2$ and 4-NO$_2$ were also successfully converted to the corresponding aldoximes in 82–98% yields using M^{II}(tu)$_2$Cl$_2$/NH$_2$OH·HCl system. Entry 17 represents that this synthetic method is also efficient for the oximation of aliphatic aldehydes via the transformation of citral to citral oxime. It is noteworthy that under the examined reaction conditions, all attempts for the oximation of acetophenone and 4-methoxy acetophenone as ketonic materials with M^{II}(tu)$_2$Cl$_2$/NH$_2$OH·HCl system were unsuccessful.

Investigation of the results (Table 2) exhibited that among the examined bis-thiourea metal complexes, cobalt chloride showed a higher catalytic activity than the other metal chlorides as Co(tu)$_2$Cl$_2$> Ni(tu)$_2$Cl$_2$> Cu(tu)$_2$Cl$_2$> Zn(tu)$_2$Cl$_2$. It was proposed that Lewis acid susceptibility of bivalent transition metal cations of first row of Periodic Table and relative stability of the prepared bis-thiourea complexes according to Irving-Williams series[44,45] maybe play a role in their catalytic activities. Co^{2+} with less stable bis-thiourea complex and more Lewis acidity can release thiourea and thus accept NH$_2$OH as a new ligand for participation in the formation of oximes. In this promotion, however, Zn^{2+} with more d-electrons behaves as less reactive bis-thiourea metal complex for thiourea/NH$_2$OH ligand displacement.

In order to highlight the promoter activity of M^{II}(tu)$_2$Cl$_2$/NH$_2$OH·HCl system, we therefore compared the oximation of 4-methoxybenzaldehyed with the current protocol and other reported methods. Investigation of the results (Table 3) shows that in view points of the short reaction times, mild reaction conditions, high yields, low loading amounts of NH$_2$OH·HCl and catalysts, cheapness and easy availability of the catalysts, the present method shows more or comparable efficiency than the other documented protocols.

Table 3. Comparison of the promoter activity of M^{II}(tu)$_2$Cl$_2$/NH$_2$OH·HCl system for oximation of 4-methoxybenzaldehyed with other reported protocols
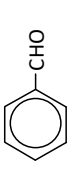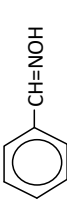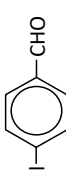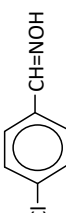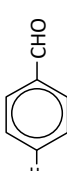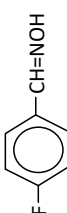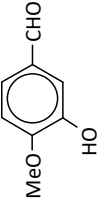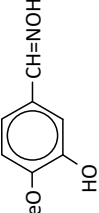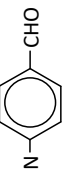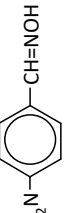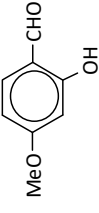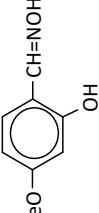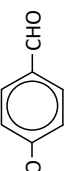
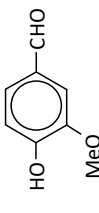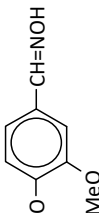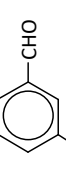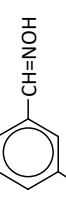| Entry	Catalyst (mol% or mg)	NH$_2$OH·HCl (mmol)	Condition	Time (min)	Yield (%)	Ref.
1	Co^{II}(tu)$_2$Cl$_2$ (20 mol%)	1.2	CH$_3$CN-H$_2$O (1:1)/r.t.	Immediate	90	*
2	DOWEX 50WX4 (1 g)	1.2	EtOH/r.t.	40	95	11
3	PMP-POM (400 mg)	1.5	Solvent-free/r.t.	10	100	13
4	KSF-POM (400 mg)	1.5	Solvent-free/r.t.	7.5	88	13
5	Al$_2$O$_3$-POM (400 mg)	1.5	Solvent-free/r.t.	10	81	13
6	SiO$_2$-POM (400 mg)	1.5	Solvent-free/r.t.	10	80	13
7	TiO$_2$-POM (400 mg)	1.5	Solvent-free/r.t.	9	86	13
8	ZrO$_2$-POM (400 mg)	1.5	Solvent-free/r.t.	10	94	13
9	K-La(PW11)$_2$ (25 mol%)		r.t.	6h	86	13
10	MPA-DAZY (0.6 g)	1.2	Solvent-free/r.t.	15	98	13
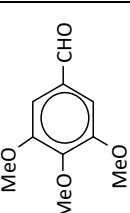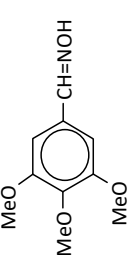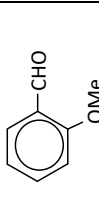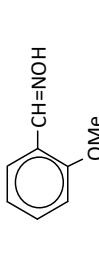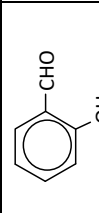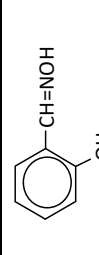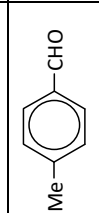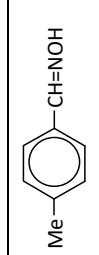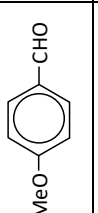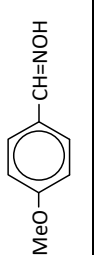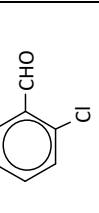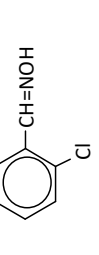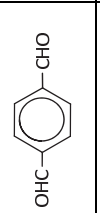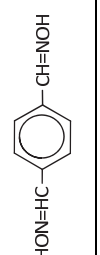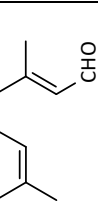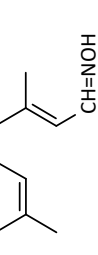
* Present work

3. Conclusions

In this study, bis-thiourea metal complexes of cobalt, nickel, copper and zinc chlorides were prepared and then utilized for the oximation of structurally diverse aromatic and aliphatic aldehydes with hydroxylamine hydrochloride successfully. All reactions were carried out in a mixture of CH$_3$CN-H$_2$O (1:1) at room temperature within the immediate time up to 65 min to afford aldoximes in high to excellent yields. The metal complexes showed a prominent catalytic activity as Co(tu)$_2$Cl$_2$> Ni(tu)$_2$Cl$_2$> Cu(tu)$_2$Cl$_2$> Zn(tu)$_2$Cl$_2$ in their oximation reactions. Short reaction times, high to excellent yield of the products, easy workup procedure as well as using the commercially available materials are the advantages which make this protocol a synthetically useful addition to the present methodologies.

Table 2. Oximation of aldehydes with $M^{II}(tu)_2Cl_2/NH_2OH \cdot HCl$ system[a–c]

Entry	Substrate	Product	Co(tu)₂Cl₂			Ni(tu)₂Cl₂			Cu(tu)₂Cl₂			Zn(tu)₂Cl₂			m.p.[Ref]
			Molar ratio	Time (sec)	Yield (%)	Molar ratio	Time (sec)	Yield (%)	Molar ratio	Time (sec)	Yield (%)	Molar ratio	Time (min)	Yield (%)	
1	C₆H₅–CHO	C₆H₅–CH=NOH	1:1.2:0.2	Im.	96	1:1.2:0.2	Im.	96	1:1.2:0.2	Im.	92	1:1.4:0.4	15 sec	80	31[46]
2	4-Cl-C₆H₄–CHO	4-Cl-C₆H₄–CH=NOH	1:1.2:0.2	Im.	95	1:1.2:0.2	Im.	90	1:1.2:0.2	15	90	1:1.4:0.4	15 sec	75	142–146[47]
3	4-F-C₆H₄–CHO	4-F-C₆H₄–CH=NOH	1:1.2:0.2	Im.	98	1:1.2:0.2	Im.	90	1:1.2:0.2	20	89	1:1.4:0.4	1	90	85[46]
4	3-MeO-4-HO-C₆H₃–CHO	3-MeO-4-HO-C₆H₃–CH=NOH	1:1.2:0.2	Im.	85	1:1.2:0.2	10	81	1:1.2:0.2	40	82	1:1.4:0.4	5	78	–
5	4-O₂N-C₆H₄–CHO	4-O₂N-C₆H₄–CH=NOH	1:1.2:0.2	3 min	82	1:1.2:0.2	5 min	82	1:1.2:0.2	6 min	85	1:1.4:0.4	12	80	128–132[48]
6	2-HO-4-MeO-C₆H₃–CHO	2-HO-4-MeO-C₆H₃–CH=NOH	1:1.2:0.2	10 min	89	1:1.2:0.2	13 min	88	1:1.2:0.2	14 min	85	1:1.4:0.4	22	80	–
7	4-HO-C₆H₄–CHO	4-HO-C₆H₄–CH=NOH	1:1.2:0.2	Im.	90	1:1.2:0.2	15	80	1:1.2:0.2	35	80	1:1.4:0.4	3	85	69–72[46]
8	4-HO-3-MeO-C₆H₃–CHO	4-HO-3-MeO-C₆H₃–CH=NOH	1:1.2:0.2	13 min	85	1:1.2:0.2	17 min	86	1:1.2:0.2	20 min	80	1:1.4:0.4	35	80	–
9	3-O₂N-C₆H₄–CHO	3-O₂N-C₆H₄–CH=NOH	1:1.2:0.2	3 min	88	1:1.2:0.2	4 min	80	1:1.2:0.2	6 min	75	1:1.4:0.4	24	78	121–122[49]

No.	Substrate	Product	Molar ratio[a]	Time	Yield (%)[c]	Molar ratio[a]	Time	Yield (%)[c]	Molar ratio[a]	Time	Yield (%)[c]	Molar ratio[a]	Time	Yield (%)[c]	mp (°C)
10	3,4,5-(MeO)$_3$C$_6$H$_2$CHO	3,4,5-(MeO)$_3$C$_6$H$_2$CH=NOH	1:1.2:0.2	2 min	85	1:1.2:0.2	2 min	78	1:1.2:0.2	5 min	80	1:1.4:0.4	35	80	180[46]
11	2-MeO-C$_6$H$_4$CHO	2-MeO-C$_6$H$_4$CH=NOH	1:1.2:0.2	Im.[b]	90	1:1.2:0.2	Im.[b]	84	1:1.2:0.2	10 min	82	1:1.4:0.4	2	82	85–89[46]
12	2-OH-C$_6$H$_4$CHO	2-OH-C$_6$H$_4$CH=NOH	1:1.2:0.2	15 min	82	1:1.2:0.2	18 min	79	1:1.2:0.2	21 min	85	1:1.4:0.4	45	78	58–63[46]
13	4-Me-C$_6$H$_4$CHO	4-Me-C$_6$H$_4$CH=NOH	1:1.2:0.2	6 min	80	1:1.2:0.2	10 min	80	1:1.2:0.2	10 min	80	1:1.4:0.4	65	80	81–84[46]
14	4-MeO-C$_6$H$_4$CHO	4-MeO-C$_6$H$_4$CH=NOH	1:1.2:0.2	Im.[b]	90	1:1.2:0.2	10	86	1:1.2:0.2	25	84	1:1.4:0.4	13	82	133–135[46]
15	2-Cl-C$_6$H$_4$CHO	2-Cl-C$_6$H$_4$CH=NOH	1:1.2:0.2[27]	Im.[b]	88	1:1.2:0.2	15	79	1:1.2:0.2	30	83	1:1.4:0.4	9	79	72–75[27]
16	OHC-C$_6$H$_4$-CHO	HON=HC-C$_6$H$_4$-CH=NOH	1:1.2:0.2	3 min	79	1:1.2:0.2	6 min	80	1:1.2:0.2	8 min	80	1:1.4:0.4	25	82	—
17	citral CHO	citral CH=NOH	1:1.2:0.2	60	80	1:1.2:0.2	2 min	78	1:1.2:0.2	3 min	75	1:1.4:0.4	20	78	—

[a]Molar ratio: Sub./NH$_2$OH·HCl/Cat. [b]Im. means immediately. [c]Yields refer to isolated pure product.

4. Experimental

4.1. General

All reagents and substrates were purchased from commercial sources with high quality and they were used without further purification. FT-IR and ^{1}H NMR spectra were recorded on Thermo Nicolet Nexus 670 and 300 MHz Bruker spectrometers, respectively. The products were characterized by their ^{1}H NMR and FT-IR spectra followed by comparison with the authentic ones. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

4.2. Preparation of bis-thiourea metal chloride complexes

To a round-bottom flask (100 mL) containing a magnetic stirrer and the solution of metal chloride ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, or $ZnCl_2$) (0.01 mol, in 20 mL EtOH), an ethanolic solution of thiourea (0.02 mol, 1.52 g in 20 mL) was added. The mixture was stirred under reflux conditions for 4 h. During the progress of the reaction, bis-thiourea metal complex was precipitated. The content of flask was transferred to a Petri-dish for evaporation of the solvent. The residue was washed with absolute ethanol to remove any contaminant. Drying the residue under air atmosphere affords $M^{II}(tu)_2Cl_2$ complex. It is notable that for dissolving thiourea in ethanol, slightly warming was required.

4.3. Typical procedure for oximation of 4-chlorobenzaldehyde with Co(tu)₂Cl₂/NH₂OH·HCl system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a solution of 4-chloro-benzaldehyde (1 mmol, 0.141 g) in a mixture of CH_3CN-H_2O (1:1) (1.5 mL) was prepared. After one min, hydroxylamine hydrochloride (1.2 mmol, 0.083 g) was added and the resulting solution was stirred at room temperature for 30 sec. To the prepared solution, $Co(tu)_2Cl_2$ (0.2 mmol, 0.0563 g) was added and stirring of the reaction mixture was continued for 5 sec at room temperature. Progress of the reaction was monitored by TLC (*n*-hexane/EtOAc: 5/2). After completion of the reaction, H_2O (3 mL) was added and the mixture was stirred for 5 min. The aldoxim product was extracted with EtOAc (2 × 4 mL) and the organic layer was then dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded the pure 4-chlorobenzaldoxime in 95% yield (Table 2, entry 2).

Acknowledgment

References

1. Roman, G., Comanita, E. & Comanita, B. (**2002**) Synthesis and reactivity of Mannich bases. Part 15: Synthesis of 3-(2-(1-pyrazolyl)ethyl)-1,2-benzisoxazoles. *Tetrahedron 58*, 1617−1622.
2. Xu, X., Henninger, T., Abbanat, D., Bush, K., Foleno, B., Hilliard, J. & Macielag, M. (**2005**) Synthesis and antibacterial activity of C2-fluoro, C6-carbamate ketolides, and their C9-oximes. *Bioorg. Med. Chem. Lett. 15*, 883−887
3. Gopalakrishnan, M., Thanusu J., & Kanagarajan, V. (**2009**) A facile solid-state synthesis and *in vitro* antimicrobial activities of some 2,6-diarylpiperidin/tetrahydrothiopyran and tetrahydropyran-4-one oximes. *J. Enzyme Inhib. Med. Chem. 24*, 669−675.
4. Li, J. T., Li, X. L. & Li, T. S. (**2006**) Synthesis of oximes under ultrasound irradiation. *Ultras. Sonochem. 13*, 200−202.

5. Ren, R. X. & Ou. W. (**2001**) Preparation of cyclic ketoximes using aqueous hydroxylamine in ionic liquids. *Tetrahedron Lett. 42*, 8445−8446.
6. Beckman, E. (**1890**) *Chem. Ber. 23*, 1680.
7. Beckman, E. (**1909**) *Lieb. Ann. Chem. 365*, 200.
8. Zeynizadeh, B. & Karimkoshteh, M. (**2013**) Magnetic Fe_3O_4 nanoparticles as recovery catalyst for preparation of oximes under solvent-free condition. *J. Nanostruct. Chem. 3*, 57−64.
9. Ramanjaneyulu, K., Rao, P. S., Rambabu, T., Jayarao, K., Devi, C. B. T. & Rao, B. V. (**2012**) Cupper supported silica promoted one-pot synthesis of aromatic oxime derivatives. *Der Pharma Chemica 4*, 473−478.
10. Bo, R. K, Gi, H. S, Jeum, J. K, Yong, J. Y. (**2013**) A development of rapid, practical and selective process for preparation of Z-oximes. *J Korean Chem. Soc. 57*, 295−299.
11. Setamdideh, D., Khezri, B. & Esmaeilzadeh, S. (**2012**) Synthesis of oximes with $NH_2OH \cdot HCl$/ DOWEX 50WX4 system. *J. Chin. Chem. Soc. 59*, 1119–1124.
12. Zaho, S. Huang, L. & Song, Y. F. (**2013**) Highly selective and efficient Lewis acid–base catalysts based on lanthanide-containing polyoxometalates for oximation of aldehydes and ketones. *Eur. J. Inorg. Chem. 2013*, 1659−1663.
13. Fazaeli, R., Tangestaninejad, S. & Aliyan, H. (**2007**) Solvent-free selective oximation of aldehydes using facile and reusable heterogeneous polyoxometalate. *Catal. Commun. 8*, 205−210.
14. Osadchenko, I. M. & Tomilov, A. P. (**2002**) Phase-transfer catalysis in synthesis of oximes. *Russ. J. Appl. Chem. 75*, 511–512.
15. Zang, H., Wang, M., Cheng, B. W. & Song, J. (**2009**) Ultrasound-promoted synthesis of oximes catalyzed by a basic ionic liquid [bmim]OH. *Ultrason. Sonochem. 16*, 301−303.
16. Mantegazza, M. A., Cesana, A. & Pastori, M. (**1996**) Ammoximation of Ketones on titanium silicalite. *Chem. Ind. 68*, 97−106.
17. Tvaruzkova, Z., Habersberger, K., Zilkovo, N. & Jiru, P. (**1991**) Role of surface complexes on titanium-silicate in the ammoximation of cyclohexanone with hydrogen peroxide. *Appl. Catal. 79,* 105−114.
18. Pertrini, G., Leofanti, G., Mantegazza, M. A. & Pignataro, F. (**1996**) Caprolactam via ammoximation. *ACS Symp. Ser. 626*, 33−48.
19. La Bars, J., Dakka, J. & Sheldon, R. A. (**1996**) Ammoximation of cyclohexanone and hydroxyaromatic ketones over titanium molecular sieves. *Appl. Catal. 36*, 69−80.
20. Armor, J. N. (**1980**) Ammoximation: direct synthesis of oximes from ammonia, oxygen and ketones. *J. Am. Chem. Soc. 102*, 1453−1454.
21. Raja, R., Sankar, G. & Thomas, N. M. (**2001**) Bifunctional molecular sieve catalysts for the benign ammoximation of cyclohexanone: one-step, solvent-free production of oxime and ε-caprolactam with a mixture of air and ammonia. *J. Am. Chem. Soc. 123*, 8153−8154.
22. Kad, G. L., Bhandari, M., Kaur, J., Rathee, R. & Singh, J. (**2001**) Solventless preparation of oximes in the solid state and via microwave irradiation. *Green Chem. 3*, 275−277.
23. Hajipour, A. R., Mallakpour, S. E. & Imanzadeh, G. (**1999**) A rapid and convenient synthesis of oximes in dry media under microwave irradiation. *J. Chem. Res*. 228−229.
24. Bandgar, B. P., Sadavarte, V. S., Uppalla, L. S. & Govande, R. (**2001**) Chemoselective preparation of oximes, semicarbazones, and tosylhydrazones without catalyst and solvent. *Monat. Chem. 132*, 403−406.
25. Sharghi, H. & Sarvari, M. H. (**2000**) A mild and versatile method for the preparation of oximes by use of calcium oxide. *J. Chem. Res*. 24−25.
26. Guo, J. J., Jin, T. S., Zhang, S. L. & Li, T. S. (**2001**) TiO_2/SO_4^{2-}: an efficient and convenient catalyst for preparation of aromatic oximes. *Green Chem. 3*, 193−195.
27. Xia, J. J. & Wang, G. W. (**2007**) Efficient preparation of aldoximes from arylaldehydes, ethylenediamine and oxone in water. *Molecules 12*, 231−236.
28. Li, J. T., Li, X. L., Li, T. S. (**2006**) Synthesis of oximes under ultrasound irradiation. *Ultrason. Sonochem. 13*, 200−202.

29. Zeynizadeh, B. & Amjadi, E. (**2009**) Facile oximation of carbonyl compounds with titanyl acetylacetonate/NH$_2$OH system. *Asian J. Chem*. *21*, 3611−3616.

30. Lakhinath, S., Baruah, J. M. & Thakur, A. J. (**2011**) A rapid, convenient, solventless green approach for the synthesis of oximes using grindstone chemistry. *Org. Med. Chem. Lett*. *1*, 12.

31. Yip, A. C. K. & Hu, X. (**2009**) Catalytic activity of clay-based titanium silicalite-1 composite in cyclohexanone ammoximation. *Ind. Eng. Chem. Res*. *48*, 8441–8450.

32. Moghadam, M., Tangestaninejad, S., Mirkhani, V., Mohammadpoor-Baltork, I. & Moosavifar, M. (**2009**) Host (nanocavity of dealuminated zeolite Y)–guest (12-molybdophosphoric acid) nanocomposite material: an efficient and reusable catalyst for oximation of aldehydes. *Appl. Catal. A Gen. 358*, 157–163.

33. Gentili, P. & Pedetti, S. (**2012**) A remarkably simple α-oximation of aldehydes via organo-SOMO catalysis. *Chem. Commun. 48*, 5358–5360.

34. Sloboda-Rozner, D. & Neumann, R. (**2006**) Aqueous biphasic catalysis with polyoxometalates: oximation of ketones and aldehydes with aqueous ammonia and hydrogen peroxide. *Green Chem*. *8*, 679–681.

35. Special issue on polyoxometalates (**1998**) *Chem. Rev. 98*, 1–390.

36. Neumann, R. (**1998**) Polyoxometalate complexes in organic oxidation chemistry. *Prog. Inorg. Chem. 47*, 317–370.

37. Kozhevnikov, I. V. (**2002**) Catalysis by Polyoxometalates. Volume 2, Wiley, Chichester.

38. Long, D. L., Tsunashima, R. & Cronin, L. (**2010**) Polyoxometallate als Bausteine für funktionelle nanosysteme. *Angew. Chem. 122*, 1780–1802.

39. Zhao, S., Liu, L. & Song, Y. F. (**2012**) Highly selective oximation of aldehydes by reusable heterogeneous sandwich-type polyoxometalate catalyst. *Dalton Trans. 41*, 9855–9858.

40. Xing, S., Han, Q., Shi, Z., Wang, S., Yang, P., Wu, Q. & Li, M. (**2017**) A hydrophilic inorganic framework based on a sandwich polyoxometalate: unusual chemoselectivity for aldehydes/ketones with in situ generated hydroxylamine. *Dalton Trans. 46*, 11537–11541.

41. Zeynizadeh, B. & Sorkhabi, S. (**2016**) Fast and efficient protocol for solvent-free reduction of nitro compounds to amines with NaBH$_4$ in the presence of bis-thiourea complexes of bivalent cobalt nickel, copper and zinc chlorides. *J. Chem. Soc. Pak. 38*, 679–684.

42. Zeynizadeh, B. & Sorkhabi, S. (**2018**) Fast and efficient method for silylation of alcohols and phenols with HMDS in the presence of bis-thiourea complexes of cobalt, nickel, copper and zinc chlorides. *Phosphorus, Sulfur, Silicon Relat. Elem. 193*, 127−135.

43. Parmar, S., Kumar, Y. & Mittal, A. (**2010**) Synthesis, spectroscopic and pharmacological studies of bivalent copper, zinc and mercury complexes of thiourea. *South Afr. J. Chem. 63*, 123–129.

44. https://en.wikipedia.org/wiki/Irving–Williams_series (accessed on Nov. 14, 2019).

45. Irving, H. M. N. H. & Williams, R. J. P. (**1953**) The stability of transition-metal complexes. *J. Chem. Soc*. 3192–3210.

46. Rappoport, Z. (**1966**) CRC Handbook of Tables for Organic Compound Identification, 3rd ed., Boca Raton.

47. Smolikova, J., Exner, O., Barbaro, G., Macciantelli, D. & Dondoni, A. (**1980**) Configuration and conformation of acyl derivatives of hydroxylamine. Part 22. Hydroxamoyl chlorides. A revision. *J. Chem. Soc. Perkin Trans. II*, 1051−1056.

48. Brehm, L. & Watson. J. (**1972**) The crystal structure of syn-*p*-nitrobenzaldoxime. *Acta Cryst. B 28*, 3646−3652.

49. Daltons, R. & Foley, H. G. (**1973**) O-carbamoyl oximes. *J. Org. Chem*. *38*, 4200−4203.