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Research Article

TRANSITION METAL COMPLEXES MEDIATED EFFICIENT AND FACILE CLEAVAGE OF OXIMES AND PHENYLHYDRAZONE TO CARBONYL COMPOUNDS

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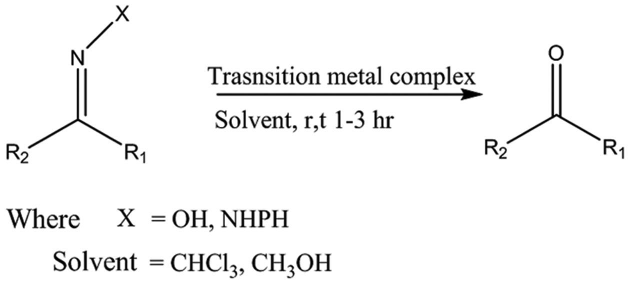
ABSTRACT

Graphical Abstract



Purpose: To report a new and efficient method for the regeneration of carbonyl compounds from their oximes and phenylhydrazones by employing transition metal complexes under mild conditions.

Methods: Different oxime and phenylhydrazone complexes have been examined for this regeneration process and found effective.

Results: A new method for the cleavage of oximes and phenylhydrazone into their corresponding carbonyl compounds has been done successfully.

Conclusion: The present method is of practical significance as it is rapid, high yielding, involves simple work-up under the very mild condition, and it applicable to both aldehydes and ketones. Thus, it is believed that the present method appears to be viable alternative to existing procedures.

Keywords: Regeneration, Carbonyl compounds, Oximes, Phenylhydrazones, Transition metal complexes.

INTRODUCTION

When a chemical reaction is to carried out selectively at one reactive site in a multifunctional molecule, the other reactive sites must be temporarily blocked. Many protecting groups have been and are being developed for this proposes [1]. Functional group protection and deprotection strategies are essential to target-oriented synthesis. In organic chemistry, carbonyl compounds can be protected as oximes, hydrazones or semicarbazones. Oximes are particularly useful as protecting group because of their stability. They can be prepared from non-carbonyl compounds (i.e., Barton reaction or nitrosation of alkenes and enols)[2] and therefore, deoximation of such oxime provides an alternative method for the synthesis of carbonyl compounds. Hence, it becomes evident that the importance of developing hydrazones and oximes cleavage techniques that encompass the desirable features of good yield, general applicability mildness, chemoselectivity, and environmental friendship.

The conversion of oximes and hydrazones into parent carbonyl compounds under mild conditions is an important process in organic chemistry. A number of methods have been reported for the cleavage of oximes and hydrazones [3-6]. However, many of the conventional procedure for the preparation of carbonyl compounds from their nitrogen derivatives have several limitations, i.e. the reagent used are often hazardous and expensive, long reaction times or reflux temperatures. Moreover, many of the methods cited in the literature do not describe the deoximation of aldoximes [7] give low yields of aldehydes. In order of circumvent some of the problems highlighted above, a mild and efficient method is still warranted for the regeneration of carbonyl compounds from oximes and phenylhydrazones. Recently cobalt (II) complex has been used in conjunction with hydrogen peroxide for oxidative deoximation of oximes [8]. Earlier it is found that transition metal complexes [9] are very efficient in the deprotection of N,N-dimethylhydrazones. In continuation of ongoing work on the application of transition metal complexes in organic synthesis, we reported that transition metals efficiently promote the nitration of aromatic compounds [10]. Herein, we report a facile method for the cleavage of oxime and phenylhydrazone into corresponding carbonyl compounds (Scheme 1).

Scheme 1

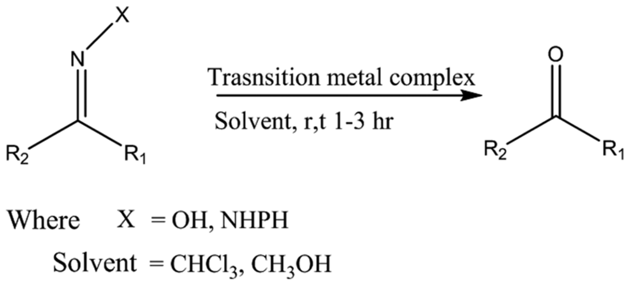


Table 1a: Cleavage of oximes with transition metal complex

Serial number	Oximes	Hg[Co(SCN)4]		[Ni(en)3S2)3]		Mn(acac)3	
		Time (h)	Yield (%)[ab]	Time (h)	Yield (%)[ab]	Time (h)	Yield (%)[ab]
1	Benzaldehyde	2	94	1	88	2	92
2	Anisaldehyde	3	80	3	88	3	90
3	4-Hydroxy-benzaldehyde	3	92	3	90	3	92
4	Acetophenone	1	92	1	90	1	92
5	4-Hydroxyaceto-phenone	1	94	1	92	1	90
6	4-Methoxyaceto-phenone	1	92	1	90	1	94
7	2-aminoacetophenone	1	94	1	92	1	92
8	Cyclohexanone	2	92	2	94	2	92
9	Benzophenone	2	90	2	92	2	94
10	Propiophenone	1	90	1	88	1	86

[a]*Isolated Yield, [b]*All products are characterized by comparison of their m.p., IR, 1H-NMR, and mass spectra with those of the authentic samples, C reflux, IR: Infrared, NMR: Nuclear magnetic resonance

Table 1b: Cleavage of oximes with transition metal complex

Serial number	Oximes	$[Cu(NH3)4]SO_4$		$[Co(NH3)5Cl]Cl_2$		$[Ni(NH3)6]Cl_2$	
		Time (hr)	Yield (%)[ab]	Time (hr)	Yield (%)[ab]	Time (hr)	Yield (%)[ab]
1	Benzaldehyde	2	92	1	88	2	92
2	Anisaldehyde	1	80	1	88	1	90
3	4-Hydroxy-benzaldehyde	3	90	3	88	3	90
4	Acetophenone	1	92	1	90	1	90
5	4-Hydroxyaceto-phenone	1	90	1	90	1	88
6	4-Methoxyaceto-phenone	1	92	1	90	1	90
7	2-amino-acetophenone	1	88	1	86	1	86
8	Cyclohexanone	2	90	2	90	2	88
9	Benzophenone	2	92	2	90	2	90
10	Propiophenone	1	90	1	88	1	86

[a]*Isolated Yield, [b]*All products are characterized by comparison of their m.p., IR, 1H-NMR, and mass spectra with those of the authentic samples. C reflux, IR: Infrared, NMR: Nuclear magnetic resonance

Table 2a: Cleavage of phenylhydrazones with transition metal complex

Serial number	Phenylhydrazones	$Hg[Co(SCN)_4]$		$[Ni(en)3S2)_3]$		Mn (acac)3	
		Time (hr)	Yield (%) [ab]	Time (hr)	Yield (%) [ab]	Time (hr)	Yield (%) [ab]
1	Benzaldehyde	2	92	2	90	2	92
2	Anisaldehyde	3	84	3	82	3	88
3	3,4,5-Trimethoxy-benzaldehyde	3	88	3	86	3	88c
4	4-Hydroxy-benzaldehyde	3	92	3	90	3	92
5	Acetophenone	1	90	1	88	1	90
6	4-Hydroxyacetophenone	1	92	1	90	1	90
7	4-Methoxyaceto-phenone	1	92	1	88	1	92
8	2-aminoacetophenone	1	90	1	88	1	90
9	Cyclohexanone	2	92	2	94	2	92c
10	Benzophenone	2	88	2	86	2	90

[a]*Isolated yield, [b]*All products are characterized by comparison of their m.p., IR, 1H-NMR, and mass spectra with those of the authentic samples, C reflux, IR: Infrared, NMR: Nuclear magnetic resonance

Experimental section

General method for oximes cleavage

To a solution of oximes (10 mmol) taken in chloroform (20 ml) moist [Ni(en) 3] S2O3 complex (5 mmol) is added and stirred at room temperature for 5-10 minutes. On completion of the reaction (change of pink color to colorless is observed), the mixture is filtered through a pad of celite and the filtrate is washed with water, dried over anhydrous sodium sulfate. After evaporation under reduced pressure, the product thus obtained is further purified by column chromatography.

General method for phenylhydrazone cleavage

To a solution of the phenylhydrazone (10 mmol) taken in methanol (20 ml), moist Hg[Co(SCN) 4] complex (5 mmol) is added, and stirred at room temperature for 5-10 minutes. On completion of the reaction (change of blue color to light blue color is observed), the mixture is filtered through a pad of celite and filtrate is washed with water, dried over anhydrous sodium sulfate. After evaporation under reduced pressure the product thus obtained is further purified by column chromatography.

RESULT AND DISCUSSIONS

The results of oximes cleavage are summarized in Table 1a and b. The reaction was tested in methanol, acetonitrile, and chloroform as solvent and chloroform is found to be best solvent. The yields for oxime cleavage were good (80-90%). Furthermore, aldoximes are deoximated under reflux condition. It is also observed that 3,4,5-trimethoxybenzaldoxime did not deprotected even under reflux condition for 24 hrs.

The cleavage of C=N of phenylhydrazone (Table 2a and b) also proceeded efficiently. It is noteworthy to note that the cleavage phenylhydrazone C=N bond is works well when methanol, used as a solvent giving

Table 2b: Cleavage of phenylhydrazones with transition metal complex

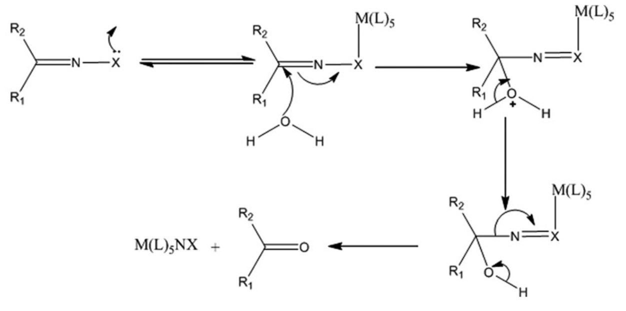
Serial number	Phenylhydrazones	$[Cu(NH3)4]SO_4$		$[Co(NH3)5Cl]Cl_2$		$[Ni(NH3)6]Cl_2$	
		Time (hr)	Yield (%) [ab]	Time (hr)	Yield (%) [ab]	Time (hr)	Yield (%) [ab]
1	Benzaldehyde	2	90	1	86	2	90
2	Anisaldehyde	1	80	1	88	1	90
3	3,4,5-Trimethoxy-benzaldehyde	1	90	1	88	1	86
4	4-Hydroxy-benzaldehyde	3	90	3	86	3	88
5	Acetophenone	1	90	1	88	1	90
6	4-Hydroxyaceto-phenone	1	92	1	90	1	90
7	4-Methoxyaceto-phenone	1	90	1	88	1	88
8	2-amino-acetophenone	1	90	1	88	1	90
9	Cyclohexanone	2	90	2	88	2	92
10	Benzophenone	2	90	2	88	2	90

[a]*Isolated yield, [b]*All products are characterized by comparison of their m.p., IR, 1H-NMR, and mass spectra with those of the authentic samples, IR: Infrared, NMR: Nuclear magnetic resonance

yields higher than 80% in most if the substrates tested. It is found that cyclohexanone, trimethoxybenzaldehyde, phenylhydrazone require refluxing condition with Mn(acac) 3 is used as transition metal complex.

Furthermore, it is noteworthy to note that over oxidation of resulted aldehydes and ketones were not observed. Earlier some studies [11] have indicated that copper II ion forms monocyclic chelates with semicarbazones and semicarbazides through the imino/terminal amino nitrogen and carbonyl oxygen. Thus is view of the above results and results obtained in the present study it is believed that the transition metal ion of metal complexes due to chelation exert a favorable effect on the hydrolysis of oximes and hydrazones at the imino bond making it more electrophilic as well as stabilizing the leaving group in the transition state. A tentative mechanism for C=N cleavage is depicted in Scheme 2.

Scheme 2



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