

Short communication

Transition Metal Free Oxidation of Alcohols to Carbonyl Compounds Using Hydrogen Peroxide Catalyzed with LiCl on Montmorillonite K10

Bagher Eftekhari-Sis, Behzad Khalili, Amir Abdollahifar
and Mohammed M. Hashemi*

Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran.

* Corresponding author: E-mail: mhashemi@sharif.edu

Received: 12-04-2006

Abstract

Alcohols have been successfully converted into their corresponding carbonyl compounds using hydrogen peroxide catalyzed by lithium chloride on montmorillonite K10. Clay supported lithium chloride can be recovered after using as catalyst for oxidation of alcohols. The future runs according to this procedure showed no considerable decrease in the reaction yield and catalyst effect.

Keywords: Oxidation, hydrogen peroxide, alcohols, lithium chloride, montmorillonite K10

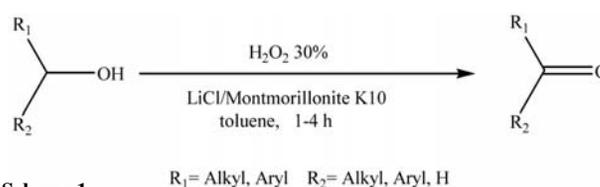
1. Introduction

Aldehydes and ketones are important precursors and intermediates for many drugs, vitamins and fragrances.^{1,2} Oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis and several methods are known for this particular conversion.^{3–8} However, different reagents used have various degree of success as well as limitations due to the strongly basic or acidic conditions. Most of the reagents involve heavy metal ions that are not ecofriendly. Oxidation of organic compounds with hydrogen peroxide is one of the most important step in synthetic organic chemistry for both environmental and economical reasons.^{9,10} Furthermore, lithium chloride is already used as the catalyst in some organic reactions.^{11–14}

Chemists have been using highly dispersed mineral solids with extensive specific areas, for a considerable time. Many organic reactions have been devised in which the reagents are deposited on various inorganic solid supports. These novel reagents have advantages over the conventional homogeneous solution techniques, such as: easy set-up and work-up, mild experimental conditions, and high yields and selectivity.^{15,16} Montmorillonite K10 has a great impact in organic synthesis and offer major breakthrough for the fine chemicals manufacturing industries.^{17,18}

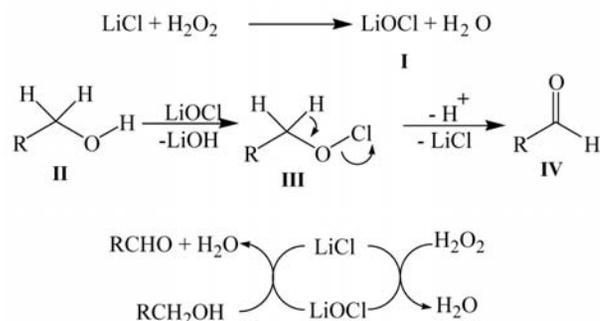
As a part of our systematic study on the development of supported reagents and catalysts for the organic transformations,^{19–25} we report herein an oxidation of

alcohols to carbonyl compounds with hydrogen peroxide catalyzed by lithium chloride supported on montmorillonite K10. Different types of alcohols (primary, secondary) were subjected to the oxidation by hydrogen peroxide on the clay supported lithium chloride. The overall reaction is best formulated as is shown in the Scheme 1.



Scheme 1

The proposed mechanism involves the attack of in-situ generated LiOCl (**I**) onto the alcohol (**II**) as shown in Scheme 2. Then HCl was eliminated from **III** to afford carbonyl compound (**IV**).²⁶



Scheme 2

2. Results and Discussion

As shown in Table 1, the various solvent such as dichloromethane, acetonitril, water, and toluene were examined in this work for oxidation of alcohols and toluene was found to be very good solvent in this oxidation method. The various lithium salts were examined for oxidation of alcohols, as shown in Table 2. High yield in relatively short reaction time was obtained using LiCl and LiBr supported on montmorillonite K10.

Table 1: Solvent effect on the oxidation of benzyl alcohol

Entry	Solvent	Time (h)	Yield (%)
1	CH ₂ Cl ₂	4	35
2	CH ₃ CN	4	50
3	H ₂ O	4	40
4	Ph-CH ₃	1.5	93

Table 2: The effect of various supported lithium salts on montmorillonite K10 for oxidation of benzyl alcohol.

Entry	Salt	Time (h)	Yield (%)
1	LiCl	1.5	93
2	LiBr	2	89
3	LiOH	4	73
4	Li ₂ CO ₃	4	71
5	Li ₂ SO ₄	5	56

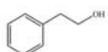
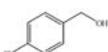
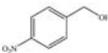
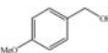
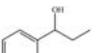
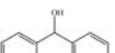
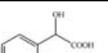
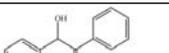
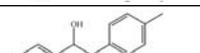
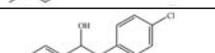
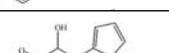
The effect of catalyst on the reaction (time/yield) was investigated using benzyl alcohol, as shown in Table 3. Association of catalyst with oxidant resulted in increased yield and in decreasing of reaction time. Using of K10 (Table 3, entry 2) and LiCl (Table 3, entry 5) lead to increasing in yield by 13% and 19% respectively, in comparison with Table 3, entry 1. However, using of LiCl in combination with K10 leads to 63% increasing in yield (Table 3, entry 4).

Table 3: The effect of catalyst (amount of K10/LiCl) on time and yield of oxidation of benzyl alcohol in toluene.

Entry	K 10 (g)	LiCl (g)	Time (h)	Yield (%)
1	0	0	2	30
2	0.2	0	2	43
3	0.2	0.03	2	84
4	0.2	0.05	1.5	93
5	0	0.05	2	49

Lithium chloride was supported on montmorillonite K10 (20% w/w) and used for the oxidation of alcohols to carbonyl compounds. It can be prepared by mixing lithium chloride and montmorillonite K10 as the support. The catalyst can be used several times. In this method work-up is carried out simply by separation of heterogeneous supported catalysts by filtrations and removal of the solvent followed by purification of the residue using short column

Table 4: Oxidation of alcohols with hydrogen peroxide catalyzed by lithium chloride on montmorillonite K10.

Entry	Alcohol	Time (h)	Yield (%) ^a
1		4	80
2		4.5	71
3		4	78
4		3.5	85
5		4	80
6		3.5	87
7		1.5	93, 89, 86 ^b
8		1.5	87
9		1.5	90
10		2	76
11		1	95
12		1.5	85
13		1.5	92
14		2	95
15		1.25	96 ^c
16		1.5	89
17		1	91
18		1.5	86
19		1.5	89

^a Yields refer to isolated products. ^b Catalyst was used over three runs. ^c Benzaldehyde is the sole product.

chromatography to give pure products. The results are summarized in Table 4.

In the case of mandelic acid (Table 4, Entry 15) oxidation with hydrogen peroxide in the presence of LiCl leads to benzaldehyde production in which CO₂ is released in the reaction. Montmorillonite K10 supported lithium chloride after using as catalyst for oxidation of alcohols can be recovered. In a typical procedure catalyst was recovered after the first use by washing with dichloromethane and n-hexane (2 × 15 ml), followed by drying at 100 °C for 3h and then reused for the oxidation of benzyl alcohol. The second and third runs, according to this procedure, showed no considerable decrease in the reaction yield (Table 4, Entry 7).

3. Conclusion

In conclusion montmorillonite K10 supported lithium chloride can be used as an efficient and recoverable catalyst for oxidation of alcohols to their carbonyl compounds. High yields, easy work-up and reusability of the catalyst are the most significant advantage of this method.

4. Experimental

All products are known compounds and were characterized by comparison of their physical and spectroscopic data with those of authentic samples. IR and ¹H-NMR spectra were recorded on Perkin Elmer 781 and Bruker DPX500 instruments. The progress of reaction was monitored by thin-layer chromatography (TLC) on silica gel.

Procedure for catalyst preparation: Lithium chloride (2 g) is added to deionized water (100 ml) and the mixture was stirred for 5 min until complete dissolution of the lithium chloride. Clay (montmorillonite K10) (8 g) is then added. The resulting suspension was refluxed and stirred vigorously for 2h and the solvent was evaporated. The dry solid residue was placed in oven at 120 °C for 24 hours.

Typical procedure for the oxidation of alcohols: Alcohol (1 mmol) was dissolved in toluene (15 ml), then 0.25 g of catalysts (K 10: 0.2 g, LiCl: 0.05 g) and hydrogen peroxide (30%, 5 ml) was added and the mixture was refluxed with stirring. The progress of the reaction was monitored by TLC (ethyl acetate:petroleum ether, 1:4), and after the completion of the reaction, mixture was filtered and the residue was washed with dichloromethane (2 × 10 ml). The combined filtrates were evaporated, and the residue was passed through a short column of silica gel to obtain pure carbonyl compound.

5. References

1. R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press: New York, **1981**.
2. M. Hudlicky, *Oxidation in Organic Chemistry*, American Chemical Society: Washington, D. C., **1990**.
3. B. M. Trost, I. Fleming, M. F. Semmelhack, In *Comprehensive Organic Synthesis*, Pergamon: New York, **1991**.
4. R. C. Larock, *Comprehensive Organic Transformations*, Wiley: New York, **1999**.
5. E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, *20*, 399–402.
6. A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165–185.
7. D. B. Dess, J. C. Martin, *J. Org. Chem.* **1983**, *48*, 4155–4156.
8. R. A. Sheldon, I. W. C. E. Arends, A. Dijkman, *Catal. Today* **2000**, *57*, 157.
9. A. Corma, V. Fomes, S. Iborra, M. Mifusd, M. Renz, *Journal of Catalysis* **2004**, *221*, 67.
10. A. O. Terentev, A. V. Kutkin, M. M. Platonov, Y. N. Ogibin, G. I. Nikishin, *Tetrahedron Lett.* **2003**, *44*, 7359–63.
11. H. Ren, A. Krasovskiy, P. Knochel, *Org. Lett.* **2004**, *6*, 4215–4217.
12. K. S. Roberts, N. S. Sampson, *J. Org. Chem.* **2003**, *68*, 2020–2023.
13. J. H. Smitrovich, L. DiMichele, C. Qu, G. N. Boice, T. D. Nelson, M. A. Huffman, J. Murry, *J. Org. Chem.* **2004**, *69*, 1903–1908.
14. A. Krasovskiy, P. Knochel, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 3333–3336.
15. G. H. Posner, *Angew. Chem.* **1978**, *90*, 527–536.
16. A. McKillop, D. W. Young, *Synthesis* **1979**, 481–500.
17. Balogh, P. Laszlo, *Chemistry Using Clays*, Springer-Verlag: Berlin, **1993**.
18. O. Sieskind, P. Alberch, *Tetrahedron Lett* **1993**, *34*, 1197–1200.
19. M. M. Hashemi, B. Eftekhari-Sis, B. Khalili, Z. Karimi-Jaberi, *J. Braz. Chem. Soc.* **2005**, *16*, 1082–1084.
20. M. M. Hashemi, B. Eftekhari-Sis, A. Abdollahifar, B. Khalili, *Tetrahedron* **2006**, *62*, 672–677.
21. B. Eftekhari-Sis, A. Abdollahifar, M. M. Hashemi, M. Zirak, *Eur. J. Org. Chem.* **2006**, 5152–5157.
22. M. M. Hashemi, A. Rahimi, Y. Ahmadibeni, *Acta Chem. Slov.* **2004**, *51*, 333–336.
23. M. M. Hashemi, D. Ghazanfari, *Acta Chem. Slov.* **2004**, *51*, 337–342.
24. M. M. Hashemi, A. Rahimi, Z. Karimi-Jaberi, Y. Ahmadibeni, *Acta Chem. Slov.* **2005**, *52*, 86–87.
25. M. M. Hashemi, B. Khalili, B. Eftekhari-Sis, *J. Chem. Res.* **2005**, 484–485.
26. V. B. Sharma, S. L. Jain, B. Sain, *Synlett* **2005**, 173–175.

Povzetek

V prispevku je predstavljena oksidacija alkoholov do ustreznih karbonilnih spojin z uporabo vodikovega peroksida in litijevega klorida kot katalizatorja, vezanega na montmorilonit K10. Litijev klorid, vezan na glino lahko po uporabi regeneriramo. Nadaljne ponovitve postopka ne kažejo znatnega zmanjšanja izkoristka reakcije in učinkovitosti katalizatorja.