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Efficient Oxidation of Alcohols with Potassium Permanganate Adsorbed on Aluminum Silicate Reagent

Ji-Dong Lou*, **Li-Yun Zhu,** and **Lan-Zhou Wang**

College of Life Sciences, China Institute of Metrology, Hangzhou, Zhejiang 310034, China

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Summary. A new reagent, potassium permanganate adsorbed on aluminum silicate, suitable for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is described.

Keywords. Oxidation; Alcohols; Potassium permanganate; Aluminum silicate.

Introduction

The oxidation of alcohols to carbonyl compounds is an important reaction in synthetic organic chemistry. Potassium permanganate ($KMnO_4$), an oxidizing agent used in organic chemistry for over a century, is one of the most versatile and vigorous ones of the commonly used oxidants for the above transformation. It is generally accepted that, in acidic, basic, or neutral media, permanganate ion oxidizes primary alcohols to aldehydes or acids, and secondary alcohols to ketones [1, 2].

The concept of utilizing reagents adsorbed on, or intercalated in, insoluble inorganic supports for organic synthesis has been employed. Some important methods have been reviewed [3, 4]. The classical methods for the oxidation of alcohols with $KMnO_4$ have now also been supplemented by using solid supports, such as molecular sieve [5], copper sulfate pentahydrate [6], bentonite [7], kieselguhr [8], zeolite [9], and zirconyl chloride octahydrate [10]. These supported reagents have achieved milder reaction conditions, simpler processing, and often higher selectivity. However, little of the above supported $KMnO_4$ reagents, for instance, $KMnO_4$-molecular sieve, $KMnO_4$-kieselguhr, and $KMnO_4$-zirconyl chloride octahydrate reagents, have been applied in the selective oxidation of primary alcohols to the corresponding aldehydes, and the rest are used only for the oxidation of secondary alcohols to ketones.

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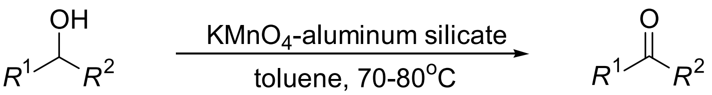
* Corresponding author. E-mail: lou@cim.edu.cn

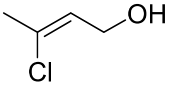
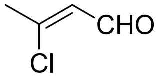
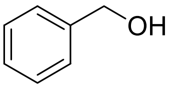
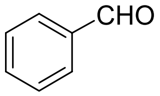
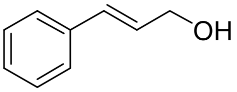
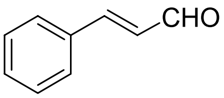
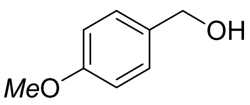
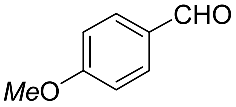
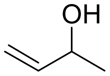
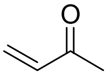
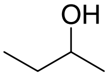
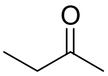
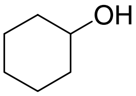
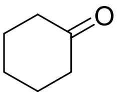
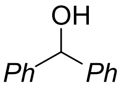
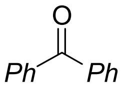
Results and Discussion

We now report that $KMnO_4$ adsorbed on aluminum silicate is a new reagent suitable for the selective oxidation of primary alcohols to the corresponding aldehydes, and it also can successfully oxidize secondary alcohols to ketones (Scheme 1). Therefore it compares favourably with those reagents reported only for oxidizing secondary alcohols. In addition, comparing with supported $KMnO_4$ reagents oxidizing primary alcohols, the present reagent has some extra advantages, such as shorter reaction times than those using $KMnO_4$-molecular sieve, $KMnO_4$-kieselguhr, and $KMnO_4$-



Scheme 1

Table 1. Oxidation of alcohols with $KMnO_4$-aluminum silicate reagent

Substrate	Product[a]	Yield[b, c]/%
		90
		97
		94
		97
		95
		85
		96
		96

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[a] All the aldehydes and ketones have been described previously in literature and were identified by their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones; [b] all products were distilled with a short *Vigreux* column under reduced pressure; [c] in case the boiling point of the products were higher than that of toluene, the work-up was according to procedure **A**; in case the boiling point of the products were lower than that of toluene, the work-up was according to procedure **B** (see Experimental)

zirconyl chloride octahydrate reagents, and higher yields than by using the $KMnO_4$-kieselguhr reagent. On the other hand, the present solid support is much cheaper than molecular sieve and zirconyl chloride octahydrate. Thus the present work not only is a new extension of reported supported $KMnO_4$ reagents, but also offers special promise for the oxidation of alcohols to the corresponding aldehydes or ketones with supported $KMnO_4$ reagents.

The $KMnO_4$-aluminum silicate reagent is prepared by addition of a weighed amount of aluminum silicate to a solution of $KMnO_4$ in water and evaporating to dryness. After contacting of the alcohols with $KMnO_4$-aluminum silicate reagent in toluene and filtration of the reaction mixture, the corresponding aldehydes or ketones are obtained by evaporation or distillation of the solvent. Further purification is accomplished by distillation. The results, which are given in Table 1, show that the reagent is generally applicable to a range of alcohols, and gives the corresponding products in good yields. Meantime, we have observed that aliphatic alcohols such as 1-hexanol or 1-octyl alcohol are not efficiently oxidised under these conditions.

Experimental

Preparation of $KMnO_4$-Aluminum Silicate Reagent

A 500 cm^3 round-bottomed flask is charged with 150 cm^3 of 0.1 *M* aqueous $KMnO_4$ and 10 g of aluminum silicate is added to it in one portion. The flask is then transferred to a rotary evaporator and water is removed under reduced pressure. The coated residues are separated physically and dried under vacuum to afford about 12 g of the $KMnO_4$-aluminum silicate reagent.

*Oxidation of Benzyl Alcohol to Benzaldehyde, Procedure **A***

The above reagent (700 mg) is placed in a flask together with 15 cm^3 of toluene and the mixture is magnetically stirred. A solution of 32.4 mg of benzyl alcohol (0.3 mmol) in 3 cm^3 of toluene is added and after 30 min at 70–80°C the solid is filtered and washed with 3×5 cm^3 of toluene. The combined filtrates are evaporated to give crude product, which is purified by distillation with a short *Vigreux* column under reduced pressure to afford 31 mg (97%) of benzaldehyde.

*Oxidation of 2-Butanol to 2-Butanone, Procedure **B***

The above reagent (700 mg) is placed in a flask together with 15 cm^3 of toluene and the mixture is magnetically stirred. A solution of 22 mg of 2-butanol (0.3 mmol) in 2 cm^3 of toluene is added and after 30 min at 70–80°C the solid is filtered off and washed with 3×5 cm^3 of toluene. The crude product is distilled carefully from the combined filtrates, which is then purified by re-distillation with a short *Vigreux* column under reduced pressure to give 18 mg (85%) of 2-butanone.

Acknowledgements

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References

[1] Fatiadi AJ (1987) Synthesis: 85
[2] Fieser LF, Fieser M (1967) Reagents for Organic Synthesis, vol 1. John Wiley & Sons, New York, pp 942–952 and subsequent volumes in the series

[3] Laszlo P (1987) Preparative Chemistry Using Supported Reagents. Academic Press, San Diego, CA
[4] Mckillop A, Young DW (1979) Synthesis: 401; 481
[5] Regen SL, Koteel CJ (1997) J Am Chem Soc **99**: 3837
[6] Menger FM, Lee CJ (1979) J Org Chem **44**: 3446
[7] Noureldin NA, Lee DG (1981) Tetrahedron Lett **22**: 4889
[8] Lou JD, Lou WX (1997) Synth Commun **27**: 3697
[9] Sreekumar R, Padmakumar R (1997) Tetrahedron Lett **38**: 5143
[10] Firouzabadi H, Fakoorpour M, Hazarkhani H (2001) Synth Commun **31**: 3859