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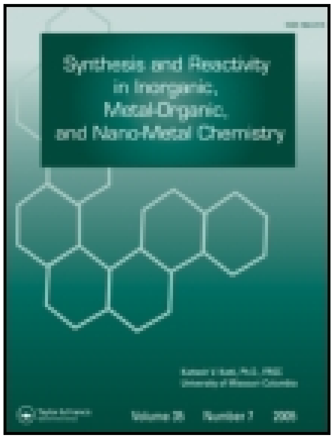

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

A Mild and Environmentally Benign Procedure for the Oxidative Cleavage of Oximes with Potassium Permanganate Supported on Kieselguhr

Ji-Dong Lou [a] [b] , Fang Lin [a] , Lihong Huang [a] & Xiao-Nan Zou [a]
[a] College of Life Sciences , China Jiliang University , Hangzhou , Zhejiang , 310018 , China
[b] Sirnaomics, Inc., 401 Professional Drive , Gaithersburg , MD , 20879 , USA

Accepted author version posted online: 14 May 2012.Published online: 06 Aug 2012.

To cite this article: Ji-Dong Lou , Fang Lin , Lihong Huang & Xiao-Nan Zou (2012) A Mild and Environmentally Benign Procedure for the Oxidative Cleavage of Oximes with Potassium Permanganate Supported on Kieselguhr, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:7, 1027-1029, DOI: 10.1080/15533174.2012.680148

To link to this article: http://dx.doi.org/10.1080/15533174.2012.680148

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:1027–1029, 2012

ISSN: 1553-3174 print / 1553-3182 online
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A Mild and Environmentally Benign Procedure for the Oxidative Cleavage of Oximes with Potassium Permanganate Supported on Kieselguhr

Ji-Dong Lou,[1,2] Fang Lin,[1] Lihong Huang,[1] and Xiao-Nan Zou[1]
[1]*College of Life Sciences, China Jiliang University, Hangzhou, Zhejiang 310018, China*
[2]*Sirnaomics, Inc., 401 Professional Drive, Gaithersburg, MD 20879, USA*

A facile, mild, and relative environmentally friendly procedure for the regeneration of aldehydes and ketones from their oximes with potassium permanganate supported on kieselguhr reagent at room temperature under heterogeneous conditions in the yield between 82–96% is described.

Keywords: carbonyl compounds, kieselguhr, oxidation, oximes, potassium permanganate

INTRODUCTION

Oximes of the aldehydes and ketones serve a number of useful purposes in organic synthesis. Aldehydes and ketones protected as oximes can later be removed to expose the original carbonyl functional group in the synthesis of complex organic molecules. Unstable carbonyl compounds are often converted to crystalline oximes for purification and characterization.[1,2] Since oximes can be prepared from non-carbonyl compounds, their deoximation provides an alternative pathway to the aldehydes and ketones.

For the deoximation, three major procedures have been employed, such as hydrolytic, reductive, and oxidative reactions, and the deoximation process can be undertaken in both homogeneous and heterogeneous conditions.[3–5] The most important procedure for this transformation are the oxidative cleavage of oximes and the oxidation methods used are mainly concentrated on chromium reagents, potassium permanganate, manganese triacetate, N-bromosuccinimide, dinitrogen tetroxide, sodium periodate, and tert-butylhydroperoxide.[6] However, although some of the reported methods are carried out under mild reaction conditions, most of them require drastic conditions, for instance, high temperature, long reaction times, toxic reagents, and tedious work-up procedures. Therefore, there has been considerable interest in the development of mild techniques for the conversion of oximes into their corresponding carbonyl compounds.

RESULTS AND DISCUSSION

It is well known that the use of solid supports has become popular due to their characteristic properties such as enhanced selectivity and reactivity, straightforward work-up procedure, milder reaction conditions and associated ease of manipulation.[7] Potassium permanganate, a relative environmentally friendly and inexpensive reagent, is one of the important oxidants employed in the deoximation. Adsorption of potassium permanganate on the surface of solid supports changes the selectivity and reactivity in various reactions. To the best of our knowledge, several supported potassium permanganate reagents have been reported in the oxidative cleavage of oximes to their parent carbonyl compounds, for instance, potassium permanganate-manganese(II) sulfate,[8] potassium permanganate-manganese dioxide,[8] potassium permanganate-wet silica gel,[9] potassium permanganate-montmorillonite K-10,[10] potassium permanganate-alumina,[11,12] and potassium permanganate-zeolite.[13] Two of them are carried out under heterogeneous conditions[12,13] and the rest are performed under solvent-free conditions,[8–11] all of which have achieved good results.

We previously reported that potassium permanganate supported on kieselguhr is a good reagent for the oxidation of alcohols to aldehydes and ketones under heterogeneous conditions[14] and solvent-free conditions,[15] respectively. In continuation of our ongoing program to develop environmentally benign methods, we now report that this reagent can be successfully employed in the oxidative cleavage of oximes (**1**) to the corresponding aldehydes and ketones (**2**) in high yields at room temperature under heterogeneous conditions (Scheme 1).

In the present procedure, the mixture of oximes and potassium permanganate supported on kieselguhr reagent is stirred in dichloromethane at room temperature, and a 1 to 2 molar ratio of the substrate to the oxidant is employed. The progress

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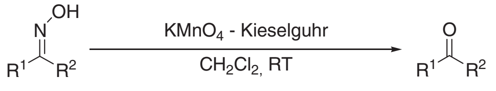
Received 17 September 2011; accepted 4 January 2012.
Address correspondence to Ji-Dong Lou, College of Life Sciences, China Jiliang University, Hangzhou, Zhejiang 310018, China. E-mail: lou@cjlu.edu.cn

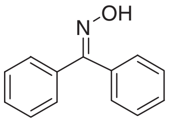
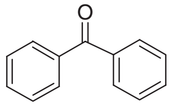
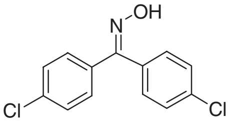
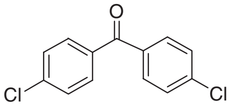
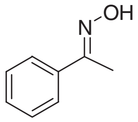
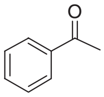
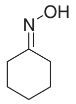
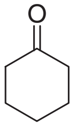
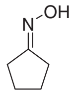
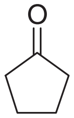
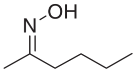
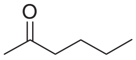
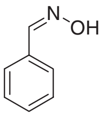
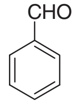
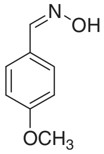
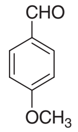
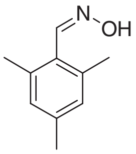
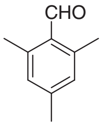
of the reaction is monitored with TLC, and the corresponding aldehydes and ketones is purified by preparative TLC in good yields. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples. Our results are listed in the Table 1.



(1) (2)

SCH. 1.

TABLE 1
Oxidative cleavage of oximes to their corresponding carbonyl compounds with potassium permanganate supported on kieselguhr reagent.

Entry	Oxime	Time (min)	Product[a]	Yield[b] (%)
1		20		92
2		20		90
3		20		92
4		20		96
5		20		86
6		20		82
7		20		86
8		20		84
9		20		82

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples.
[b]Isolated yields.

Comparing with the deoximation using supported potassium permanganate reagents under heterogeneous conditions previously reported, the present reagent has some advantages, such as for most products shorter reaction times and higher yields. The current method avoids the use of toxic reagents like chrominum compounds and therefore it may be carried out on a large scale.

EXPERIMENTAL

Oxidative cleavage of benzophenone oxime to benzophenone: Typical Procedure

The potassium permanganate-kieselguhr reagent[14] (1500 mg) is placed in a flask together with dichloromethane (30 mL) and the mixture is magnetically stirred. A solution of benzophenone oxime (197 mg, 1 mmol) in dichloromethane (5 mL) is added, and after 30 min at RT the solid is filtered and washed with dichloromethane (3 × 5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane:ethyl acetate (7:3) to afford 167 mg (92%) benzophenone.

CONCLUSION

In conclusion, a facile and mild procedure for the regeneration of aldehydes and ketones from their oximes is described. The method offers several advantages including short reaction times and high yields of the products, cleaner reactions, and a non-toxic and inexpensive reagent which makes the reaction process convenient, and it is more economic and environmentally benign.

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