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An environmentally benign method for oxidation of oximes with potassium permanganate supported on kieselguhr under solvent-free conditions

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Abstract A rapid and highly efficient procedure for oxidative cleavage of oximes to their parent aldehydes and ketones by grinding with potassium permanganate supported on kieselguhr at room temperature under solvent-free conditions with yields between 82 and 96 % is described. This method has advantages over previous methods used with potassium permanganate oxidation.

Keywords Kieselguhr · Oxidation · Oximes · Potassium permanganate · Solvent-free

Introduction

Oximes are useful as protecting groups in organic syntheses [1] and have found extensive application in the isolation, purification, and characterization of carbonyl compounds [2, 3]. Oximes have been used as intermediates for many synthetic products and have been also proved to be important and useful reagents in organic synthesis [4–6]. Several procedures, for example, hydrolytic [7], oxidative [7–12],

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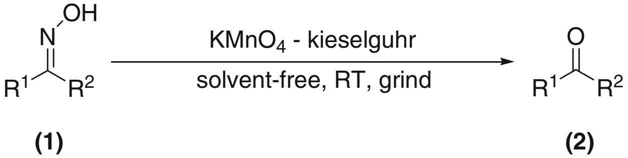
and reductive [13–15] reactions, have been reported for regeneration of carbonyl compounds, for example, aldehydes and ketones, from their corresponding oximes. Sometimes the deoximation process can be undertaken under both homogeneous and heterogeneous conditions. Oxidative cleavage is one of the most important reactions for this transformation in synthetic organic chemistry. Although some of the known methods or reagents are used under mild reaction conditions, most require drastic conditions, high temperature, long reaction times, reagents that are not readily available, and tedious work-up procedures. Therefore, the development of mild and efficient methods for selective cleavage of derivatives containing carbon–nitrogen double bonds, such as oximes, to afford carbonyl compounds continues to be a significant aspect of organic chemistry.

Results and discussion

Several potassium permanganate or potassium permanganate-based reagents have been used as oxidants for deoximation, for example, potassium permanganate–manganese(II) sulfate [16], potassium permanganate–manganese dioxide [16], potassium permanganate–wet silica gel [17], potassium permanganate–montmorillonite K-10 [18], potassium permanganate–alumina [19, 20], potassium permanganate–zeolite [21], potassium permanganate–graphite [22, 23], potassium permanganate–kieselguhr [24], and potassium permanganate–silica gel [25], all of which have achieved good results.

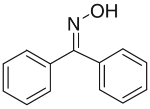
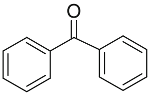
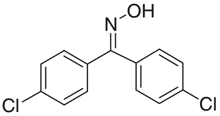
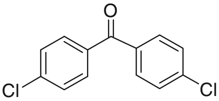
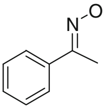
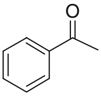
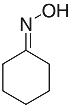
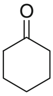
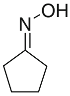
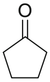
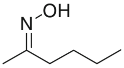
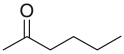
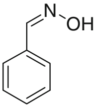
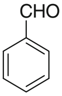
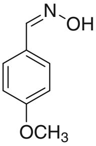
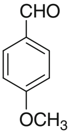
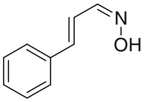
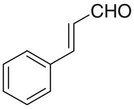
Because potassium permanganate is a relatively environmentally friendly agent [26, 27], we are interested in seeking newer or improved procedures with this reagent for oxidative cleavage of oximes to their parent aldehydes and ketones. We recently reported this oxidative transformation with potassium permanganate adsorbed on inorganic solids, for instance, graphite [22], kieselguhr [24], and silica gel [25] under heterogeneous conditions. In continuation of previous investigations, we now report here a rapid and highly efficient procedure for oxidation of oximes (**1**) to the corresponding aldehydes and ketones (**2**) with potassium permanganate supported on kieselguhr under solvent-free conditions at room temperature (Scheme 1). It is well known that the main advantages of organic reactions performed with solid-supported reagents [28–30] and under solvent-free conditions [31–33] are enhanced selectivity, milder reaction conditions, much improved reaction rates, formation of cleaner products, and associated ease of manipulation.

In this procedure the finely powdered oximes were converted to the corresponding carbonyl compounds in a mortar with grinding by a pestle in the presence of



Scheme 1 Oxidation of oximes

Table 1 Oxidative cleavage of oximes to their corresponding carbonyl compounds with potassium permanganate supported on kieselguhr under solvent-free conditions

Entry	Oxime	Time (min)	Product[a]	Yield[b] (%)
1		5		90
2		5		92
3		10		90
4		10		86
5		10		82
6		10		82
7		5		92
8		5		96
9		10		84

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

[b] Isolated yields

potassium permanganate supported on kieselguhr at room temperature under solvent-free conditions. In our experiments, a 1:1.2 molar ratio of substrate to the oxidant was used. The progress of the reaction was monitored with TLC, and the corresponding aldehydes and ketones were purified by preparative TLC. The oxidized products are all known compounds and were identified by comparison of spectra with those of authentic samples. Our results are listed in the Table 1. It is noteworthy that in the absence of kieselguhr the reactions are slow, substantial amounts of the starting materials are recovered unchanged from the reaction mixture, and the work-up of the reaction mixture is rather difficult.

Data for oxidation of benzaldehyde oxime to benzaldehyde with potassium permanganate or supported potassium permanganate reagents under different reaction conditions are listed in Table 2. It can be seen from this table that when potassium permanganate supported on kieselguhr under solvent-free conditions at room temperature was used the time required for completion of the oxidation was only 5 min and the yield was 92 % (entry 1); under heterogeneous conditions, however, it was completed in 20 min and the yield was 86 % (entry 4). In addition, comparison of this procedure with the others (Table 2) reveals the amount of manganese dioxide used is reduced (entries 2–5), the reactions are milder (entry 3), or the time required for oxidation is shorter (entries 3–5). Therefore, this method has benefits over previous potassium permanganate oxidation methods.

Experimental

Oxidation of benzaldehyde oxime to benzaldehyde: typical procedure

Potassium permanganate (190 mg, 1.2 mmol) and kieselguhr (570 mg, purchased from Tianjin Fu Chen Chemical Reagent Factory) were mixed with a pestle and mortar. Benzaldehyde oxime (121 mg, 1 mmol) was added. The reaction mixture was well ground at room temperature by use of a pestle. The progress of the reaction was monitored by TLC (silica gel GF_{254}) using hexane–ethyl acetate (7:3) as eluent. After 5 min the reaction was complete. The solid was isolated by filtration and

Table 2 Comparison of methods for oxidation of benzaldehyde oxime to benzaldehyde with potassium permanganate under different reaction conditions

Entry	Support	Reaction conditions	Molar ratio substrate to potassium permanganate	Reaction time	Yield (%)	Ref.
1	Kieselguhr	Solvent-free/RT/grind	1:1.2	5 min	92	This work
2	Montmorillonite K-10	Solvent-free/RT/grind	1:2	5 min	85	[18]
3	Alumina	Solvent-free/50 °C/grind	1:1.4	40 min	78	[19]
4	Kieselguhr	CH_2Cl_2/RT	1:2	20 min	86	[24]
5	Silica gel	CH_2Cl_2/RT	1:2	1 h	92	[25]

washed with dichloromethane (3 × 5 mL). The combined filtrates were evaporated to give the crude product, which was purified by preparative TLC (silica gel GF_{254}) with hexane–ethyl acetate (7:3) to afford 100 mg (92 %) benzaldehyde.

Conclusion

A rapid and highly efficient procedure for oxidative cleavage of oximes to their parent aldehydes and ketones by grinding with potassium permanganate supported on kieselguhr at room temperature under solvent-free conditions with yields between 82 and 96 % is described. Comparison of this procedure with others reveals that the amount of manganese dioxide used is reduced, the reaction conditions are milder, or the time required for oxidation is shorter. Therefore, this method has benefits over previous methods used with potassium permanganate oxidation.

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