ISSN 1070-4272, Russian Journal of Applied Chemistry, 2017, Vol. 90, No. 8, pp. 1326−1329. © Pleiades Publishing, Ltd., 2017.

VARIOUS TECHNOLOGICAL PROCESSES

Regeneration of Aldehydes and Ketones by the Oxidation of Oximes Using Potassium Permanganate-Graphite with Grinding under Solvent-Free Conditions[1]

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Received April 19, 2017

Abstract—A facile and efficient procedure for the oxidative cleavage of oximes to their parent aldehydes and ketones by grinding with potassium permanganate-graphite at room temperature under solvent-free conditions in the yields between 80 and 94% is described. All reactions are complete in 5 min.

DOI: 10.1134/S1070427217080225

AIMS AND BACKGROUND

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]. Likewise, 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]. Regeneration of carbonyl compounds, such as aldehydes and ketones, from the oxime derivatives is an important process in synthetic organic chemistry, for instance, regeneration by the way of hydrolytic, reductive, and oxidative reactions [7]. However, only a limited number of methods or reagents are available for the conversion of oximes to the corresponding carbonyl compounds under mild reaction conditions. Therefore, there has been considerable interest in the development of mild techniques for this transformation.

[1] The text was submitted by the authors in English.

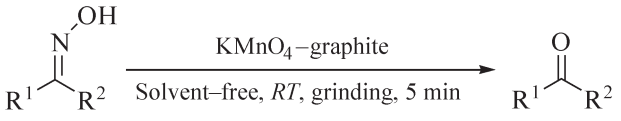
EXPERIMENTAL

Oxidation of benzaldehyde oxime to benzaldehyde: (typical procedure). Potassium permanganate (190 mg, 1.2 mmol) and graphite (760 mg) were mixed with a pestle and mortar. Benzaldehyde oxime (121 mg, 1 mmol) was added. The reaction mixture was well ground at room temperature using a pestle. The progress of the reaction was monitored by TLC (Aluminum-backed silica gel GF254) using hexane : ethyl acetate (7 : 3) as eluent. After 5 min the reaction was complete. The solid was filtered and washed with dichloromethane (3 × 5 mL). The combined filtrates were evaporated to give crude product, which was purified by preparative TLC (silica gel GF254) with hexane : ethyl acetate (7 : 3) to afford 102 mg (94%) benzaldehyde.

RESULTS AND DISCUSSION

The oxidative cleavage reaction is one of the most important procedures for regeneration of carbonyl

Scheme 1. Oxidation of oximes.



1 **2**

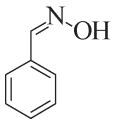
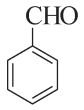
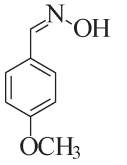
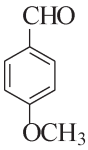
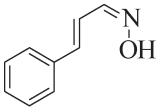
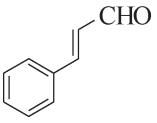
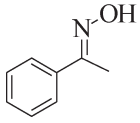
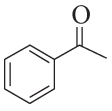
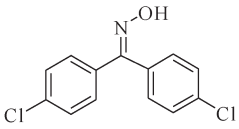
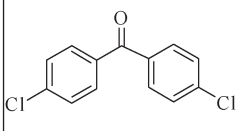
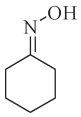
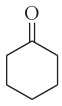
compounds from oximes. So far, several potassium permanganate ($KMnO_4$) or potassium permanganate-based reagents have been used as oxidants for deoximation, for example, potassium permanganate-manganese(II) sulphate [8], potassium permanganate-manganese dioxide [8], potassium permanganate-wet silica gel [9], potassium permanganate-montmorillonite K-10 [10], potassium permanganate-alumina [11, 12], potassium permanganate-zeolite [13], potassium permanganate-graphite [14, 15], potassium permanganate-kieselguhr [16, 17], potassium permanganate-silica gel [18], and potassium permanganate-aluminum silicate [19], etc. most of which have achieved good results.

Potassium permanganate-based reagents have been extensively used as oxidants for the oxidation of a variety of organic functional groups, either in aqueous or non-aqueous media [20, 21]. Because potassium permanganate is a relatively environmentally friendly agent, we are interested in seeking newer or improved procedures with this reagent for oxidative cleavage of oximes to their parent aldehydes and ketones. We have reported this oxidative transformation using potassium permanganate assisted with inorganic solids, for instance, graphite [14, 15], kieselguhr [16, 17], silica gel [18], and aluminum silicate [19], under heterogeneous conditions or under solvent-free conditions.

In continuation of previous investigations [14–19], we now report here a facile and efficient procedure for the oxidation of oximes (**1**) to the corresponding aldehydes and ketones (**2**) using potassium permanganate-graphite at room temperature under solvent-free conditions with grinding (Scheme 1).

In this procedure the oximes are converted to the corresponding carbonyl compounds in a mortar with grinding by a pestle in the presence of potassium permanganate-graphite at room temperature under solvent-free conditions. Under our experiments, a 1 to 1.2 molar ratio of the substrate to the oxidant is employed. The progress of the reaction is monitored with TLC, and the corresponding aldehydes and ketones is purified by preparative TLC. All reactions are complete in 5 min.

Table 1. Oxidative cleavage of oximes to their corresponding carbonyl compounds with potassium permanganate-graphite under solvent-free conditions

Entry	Oxime	Product[a]	Yield[b], %
1			94
2			84
3			86
4			90
5			94
6			80

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

The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples. Our results are listed in the Table 1.

Because the present reaction is performed under solvent-free conditions with solid-supported reagents, the main advantages of the present oxidation are of enhanced selectivity and reactivity, mild reaction conditions, and straightforward work-up procedure [22–27]. Furthermore, since the present method avoids the use of toxic reagents such as hexavalent chromium derivatives, it may be carried out on a large scale.

Some data for the oxidation of benzaldehyde oxime to benzaldehyde with supported potassium permanganate reagents under different reaction conditions are

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

Entry	Supports	Reaction conditions	Molar ratio substrate to potassium permanganate	Reaction time	Yield, %	References
1	Graphite	Solvent-free/RT/grind	1 : 1.2	5 min	94	Present work
2	Kieselguhr	Solvent-free/RT/grind	1 : 1.2	5 min	92	17
3	Montmorillonite K-10	Solvent-free/RT/grind	1 : 2	5 min	85	10
4	Alumina	Solvent-free/50OC/grind	1 : 1.4	40 min	78	11
5	Kieselguhr	CH_2Cl_2/RT	1 : 2	20 min	86	16
6	Silica gel	CH_2Cl_2/RT	1 : 2	1 h	92	18

listed in Table 2. By comparing the current procedure with the most of others (Table 2), the amount of potassium permanganate used is decreased, the reactions are milder, or the time of the oxidation is shorter. Therefore, the advantages of the present route are over most of those of previous potassium permanganate oxidation methods.

CONCLUSIONS

A facile and efficient procedure for oxidative cleavage of oximes to their parent aldehydes and ketones by grinding with potassium permanganate-graphite at room temperature under solvent-free conditions in the yields between 80 and 94% is described. All reactions are complete in 5 min. The main advantages of the present oxidation are of enhanced selectivity and reactivity, mild reaction conditions, and straightforward work-up procedure.

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