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Solid State Cleavage of Oximes with Potassium Permanganate Supported on Alumina

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ABSTRACT

A manipulatively simple and rapid method for conversion of oximes to the corresponding carbonyl compounds is described. The reaction is conducted under solvent-less conditions using alumina-supported permanganate. According to the reaction system and conditions used, different ketones and aldehydes are obtained in moderate and good yields.

735

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736

Imanzadeh, Hajipour, and Mallakpour

Oxidation of organic compounds in organic solvents under mild conditions is very important in organic synthesis.^[1,5] Over the last 15 years, several new oxidizing reagents have been reported for oxidation of organic compounds. Unfortunately, most of these reagents suffer at least one of the following disadvantages: (i) cost of preparation, (ii) longer reaction time, (iii) no selectivity, (iv) tedious work up procedure.

In recent years, the use of solid supports in synthetic organic chemistry has become more popular.^[6,7] The advantages of this method over conventional homogeneous reactions are that they provide high selectivity, enhanced reaction rate, and cleaner product.^[6,7]

Oximes are very useful for protecting groups in organic synthesis.^[8] These highly crystalline compounds can be prepared from carbonyl and non carbonyl compounds.^[9] Deoximation of such oximes provide an alternative method for the synthesis of carbonyl compounds. The classical method for cleavage of oximes to aldehydes and ketones includes acid hydrolysis which is not suitable for acid sensitive compounds.^[10] Several oxidative deoximation methods have been developed which have found some advantages over the classical hydrolysis method.^[11–15]

In continuation of our ongoing program to develop environmentally benign methods using solid supports,^[16–21] we now wish to report an excellent rapid and selective deoximation method by the KMnO₄–Al₂O₃ an inexpensive oxidant. In this simple and efficient method the finely powdered oximes are converted to the corresponding carbonyl compounds in a mortar with grinding by a pestle in the presence of supported permanganate on alumina. The reaction has been proceeded under solvent-free conditions for the time and at the temperature being specified in Table 1. Interestingly in this method no over oxidation to carboxylic acid was observed (Table 1, oxime 1).

In order to evaluate the effect of alumina in this reaction, we tried the reaction of benzophenone oxime with $KMnO_4$ without using alumina. The reaction was unsuccessful and benzophenone oxime was recovered after 40 min grinding in a mortar at 50°C. We also observed that in α , β -unsaturated oxime, only C=NOH group was selectively oxidized to corresponding carbonyl compounds and the reagent was ineffective in oxidizing double bond (Table 1, oxime 12)

Another noteworthy advantage of the reagent lies exclusive cleavage of ketoxime irrespective of the presence of aldoxime. When a mixture of finely powdered benzophenone oxime and benzaldehyde oxime was ground at 50° C for 30 min, only benzophenone oxime was selectively converted to benzophenone, and benzaldehyde oxime did not react at all (Sch. 1).

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Solid State Cleavage of Oximes

737

Table 1. Cleavage of oximes with supported permanganate on alumina.

		H MnO ₄ \Al ₂ O ₃	R_1	>==0	
Entry	R ₁	R ₂	Time (min)	Temperature (°C)	Yields ^a (%)
1	Ph	Н	40	50	78
2	Ph	CH ₂	20	50	94
3	Ph	Ph	15	50	99
4	$2-ClC_6H_4$	CH ₃	10	50	80
5	$3,4,5(MeO)_{3}C_{6}H_{2}$	H	40	50	88
6	4-MeOC ₆ H ₄	CH_3	15	50	84
7	$4-ClC_6H_4$	Н	40	50	80
8	$3,4(MeO)_2C_6H_3$	Н	40	50	73
9	$3,4(MeO)_2C_6H_3$	CH_3	15	50	93
10	$2-MeC_6H_4$	Н	40	50	90
11	$4-MeC_6H_4$	CH_3	15	50	93
12	PhCH=CH	Н	40	50	90
13	PhCH=CH	Ph	10	50	91
14	PhCH=CH	CH_3	10	50	87
15	2-naph	CH_3	15	50	95
16	2-naph	CH_3CH_2	25	50	92
17	4-NO ₂ C ₆ H ₃ CH=CH	Η	40	50	84
18	Ph	PhCO	30	50	97
19			10	50	91
20			15	50	87

^aYields refer to isolated products.

Pyridinium chlorochromate (PCC) is a reagent that converts the oximes to carbonyl compounds.^[22] In Table 2 some of the results of our experiments are compared with those reported with PCC. The results show that rate and the yields of reactions are higher with $KMnO_4-Al_2O_3$ than those reported with PCC. In addition, in our method the reactions took place under solvent-free conditions, therefore is cheaper and safer than PCC method.

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Table 2. Comparison of oxidation of some oximes with $KMnO_4$ -Al₂O₃ and PCC.

		KMnO ₄ -Al ₂ O ₃	PCC ^[22]
Substrate	Product	Yield (min)	Yield (h)
Cyclohexanone oxime Cyclopentanone oxime Acetophenone oxime Benzaloxime	Cyclohexanone Cyclopentanone Acetophenone Benzaldehyde	91 (10) 87 (15) 94 (20) 78 (40)	47 (18) 28 (18) 61 (15) 56 (15)

In conclusion, in this study, we introduced a new method for regeneration of carbonyl compounds from oximes using inexpensive alumina supported potassium permanganate. Aldehydes were in high yields without further oxidation to acid. Our method is simple, safe, low cost, and rapid.

All yields refer to isolated product. Thin layer chromatography (TLC) was carried out using glass sheets precoated with silica gel 60F. Melting points were determined on an Electro thermal Gallen Kamp apparatus and uncorrected. ¹H NMR spectra were recorded on a

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Solid State Cleavage of Oximes

739

Varian EM-390 (60 MHz). Infrared spectra were obtained using a Shimadzu IR-435 spectrometer. The purity of products was determined by GC and ¹H NMR spectroscopy, and comparing with authentic samples.

DEOXIMATION WITH ALUMINA SUPPORTED PERMANGANATE

General Procedure

Dry powder of benzophenone oxime (1 mmol, 0.197 g) was added to $KMnO_4-Al_2O_3$ (1.4 mmol, 1.0 g),^[16] and the mixture was ground with a pestle in a mortar at 50°C for 15 min. After completion of reaction (monitored by TLC), acetone (15 mL) was added to the reaction mixture and after vigorous stirring (5 min at room temperature), the mixture was filtered and acetone was evaporated by rotary evaporator. The residue was dissolved in the ether (20 mL). The organic layer was washed with 10% HCl (10 mL) and dried (MgSO₄). Evaporation of the solvent under vacuum gave the benzophenone in pure form (99%). M.p. 47–48°C, lit.^[3] 48°C.

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740

Imanzadeh, Hajipour, and Mallakpour

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