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A Facile, Mild, and Environmentally Benign Procedure for the Cleavage of Carbon–Nitrogen Double Bonds Using $KMnO_4$ in the Presence of Montmorillonite K-10 Under Solvent-Free Conditions

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Summary. An efficient and environmentally benign method for the conversion of oximes, semicarbazones, phenylhydrazones, and azines to their corresponding carbonyl compounds using $KMnO_4$/montmorillonite K-10 as a commercially available, non-toxic, stable, and inexpensive reagent is reported.

Keywords. Oximes; Semicarbazones; Phenylhydrazones; Azines; Montmorillonite K-10.

Introduction

Nitrogen derivatives of carbonyl compounds such as oximes, semicarbazones, phenylhydrazones, and azines are important in organic chemistry. These compounds are highly crystalline and used not only for the isolation and characterization but also for the protection of carbonyl compounds during synthesis [1]. One of the best methods for purifying aldehydes and ketones involves converting them to the above mentioned derivatives followed by regenerating the starting carbonyl compounds. Many methods and reagents have been developed for the cleavage of $C=N$ bonds [2–21]. However, some of the reported methods suffer from one or more of the following disadvantages, availability and preparation of the

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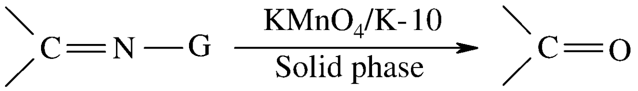
reagents, long reaction times, low yields of the products, use of toxic or expensive reagents, overoxidation of the products, and tedious workup. Therefore, introduction of a milder, non-toxic, and inexpensive reagent is desirable.

Results and Discussion

In recent years, the organic reactions on solid supports and under solvent-free conditions have attracted attention because of their enhanced selectivity, milder reaction conditions, much improved reaction rates, formation of cleaner products, and associated ease of manipulation [22]. In the course of our work on the development of environmentally benign methods using solid supports [23], we now report a convenient and inexpensive procedure for the regeneration of carbonyl compounds from oximes, semicarbazones, phenylhydrazones, and azines using $KMnO_4$/montmorillonite K-10 under solid phase conditions (Scheme 1).

As shown in Table 1, treatment of a variety of oximes with $KMnO_4$ in the presence of montmorillonite K-10 afforded the corresponding aldehydes and



G = OH, $NHCONH_2$, NHPh, N = CHAr

Scheme 1

Table 1. Regeneration of aldehydes and ketones from oximes, semicarbazones, phenylhydrazones, and azines using $KMnO_4$ in the presence of montmorillonite K-10

Entry	Substrate	Product[a]	t/min	Yield/%[b]
1	Benzaldoxime	Benzaldehyde	5	85
2	2-Methoxybenzaldoxime	2-Methoxybenzaldehyde	10	96
3	2-Nitrobenzaldoxime	2-Nitrobenzaldehyde	60	86
4	3-Nitrobenzaldoxime	3-Nitrobenzaldehyde	60	88
5	4-Nitrobenzaldoxime	4-Nitrobenzaldehyde	60	88
6	4-Benzyloxybenzaldoxime	4-Benzyloxybenzaldhyde	25	94
7	Decanaldoxime	Decanal	50	93
8	Acetophenone oxime	Acetophenone	10	93
9	4-Bromoacetophenone oxime	4-Bromoacetophenone	30	94
10	4-Chloroacetophenone oxime	4-Chloroacetophenone	25	92
11	4-Methylacetophenone oxime	4-Methylacetophenone	15	95
12	Benzophenone oxime	Benzophenone	20	97
13	1-Acetonaphthone oxime	1-Acetonaphthone	20	93
14	Cyclododecanone oxime	Cyclododecanone	45	89
15	Benzaldehyde semicarbazone	Benzaldehyde	15	80
16	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	20	94

(*continued*)

Table 1 (*continued*)

Entry	Substrate	Product[a]	t/min	Yield/%[b]
17	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	15	93
18	4-Methy1benzaldehyde semicarbazone	4-Methy1benzaldehyde	15	94
19	4-Chlorobenzaldehyde semicarbazone	4-Chlorobenzaldehyde	15	94
20	2,4-Dimethoxybenzaldehyde semicarbazone	2,4-Dimethoxybenzaldehyde	15	96
21	Acetophenone semicarbazone	Acetophenone	10	93
22	4-Methylacetophenone semicarbazone	4-Methylacetophenone	10	95
23	4-Chloroacetophenone semicarbazone	4-Chloroacetophenone	10	95
24	Benzophenone semicarbazone	Benzophenone	20	94
25	Benzaldehyde phenylhydrazone	Benzaldehyde	15	82
26	3-Nitrobenzaldehyde phenylhydrazone	3-Nitrobenzaldehyde	20	94
27	4-Methoxybenzaldehyde phenylhydrazone	4-Methoxybenzaldehyde	10	92
28	4-Methylbenzaldehyde phenylhydrazone	4-Methylbenzaldehyde	10	91
29	4-Chlorobenzaldehyde phenylhydrazone	4-Chlorobenzaldehyde	10	95
30	2,4-Dimethoxybenzaldehyde phenylhydrazone	2,4-Dimethoxybenzaldehyde	15	96
31	Acetophenone phenylhydrazone	Acetophenone	10	90
32	4-Methylacetophenone phenylhydrazone	4-Methylacetophenone	10	92
33	4-Chloroacetophenone phenylhydrazone	4-Chloroacetophenone	10	94
34	Benzophenone phenylhydrazone	Benzophenone	20	95
35	Benzaldehyde azine	Benzaldehyde	25	83
36	4-Chlorobenzaldehyde azine	4-Chlorobenzaldehyde	25	86
37	Acetophenone azine	Acetophenone	30	88
38	Benzophenone azine	Benzophenone	30	90
39	4-Methoxybenzaldehyde-2,4-*DNPH*[c]	4-Methoxybenzaldehyde	30	0
40	Acetophenone-2,4-*DNPH*[c]	Acetophenone	30	0

[a] All products were identified by comparison of their physical and spectral data with those of authentic samples; [b] Isolated yields; [c] 2,4-*DNPH* represents 2,4-dinitrophenylhydrazone

ketones in 85–97% yields (entries 1–14). Semicarbazones, phenylhydrazones, and azines were also transformed to their carbonyl compounds in 80–96% yields (entries 15–38). However, 2,4-dinitrophenylhydrazones are resistant to this reagent system and remained intact in the reaction mixture (entries 39, 40). The regenerated aldehydes did not undergo further oxidation to their carboxylic acids under the reaction conditions. It is noteworthy that in the absence of montmorillonite K-10, the reactions are slow and considerable amounts of the starting materials are recovered unchanged from the reaction mixture. Furthermore, workup of the reaction mixture is rather difficult in this case.

In conclusion, the paper describes a facile and mild procedure for the regeneration of aldehydes and ketones from their oximes, semicarbazones, phenylhydrazones, and azines. The method offers several advantages including short reaction times, 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.

Experimental

General Procedure for the Conversion of Oximes, Semicarbazones, Phenylhydrazones, and Azines to their Carbonyl Compounds

A mixture of 1 mmol of substrate, 2 mmol of $KMnO_4$ and 300 mg of montmorillonite K-10 was ground in a mortar with a pestle for the time specified in Table 1. The progress of the reaction was monitored by TLC. The mixture was extracted with CH_2Cl_2. Evaporation of the solvent followed by chromatography on silica gel afforded the pure carbonyl compounds in 80–97% yields (Table 1). In the case of azines 3 mmol of $KMnO_4$ and 500 mg of montmorillonite K-10 were used.

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