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A mild and efficient method for cleavage of C=N using $Mg(HSO_4)_2$ in the presence of wet SiO_2

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Abstract—$Mg(HSO_4)_2$ in the presence of wet SiO_2 was reacted with oximes, hydrazones and semicarbazones and converts them to the corresponding carbonyl compounds in good to high yields under mild and heterogeneous conditions. © 2002 Elsevier Science Ltd. All rights reserved.

Oximes, hydrazones and semicarbazones are used not only for isolation, purification and characterization but also for protection of carbonyl compounds.[1,2] Since oximes can be prepared from non-carbonyl compounds,[3–8] the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. Some of the methods of generating carbonyl compounds from oximes [9–11] involve reagents that are often hazardous or very toxic, expensive, or not readily available, they need to be freshly prepared or the reactions require drastic conditions, long reaction times and tedious work-up. Thus, a milder, selective, non-hazardous and inexpensive reagent is still in demand. Little attention has been paid to the cleavage of the carbon–nitrogen double bonds of hydrazones and semicarbazones, and only a few reports are available dealing with the conversion of these derivatives into their corresponding carbonyl compounds.[12,13]

We now report a convenient method for the cleavage of the carbon–nitrogen double bonds of oximes, hydrazones and semicarbazones using $Mg(HSO_4)_2$ in the presence of wet SiO_2.

The results of the conversions of various oximes, hydrazones and semicarbazones to their corresponding carbonyl compounds are presented in Table 1. The products of the reaction with $Mg(HSO_4)_2$ in the presence of wet SiO_2 were isolated simply by filtering the mixture and evaporating the solvent from the filtrate. The method has advantages in terms of yield, heterogeneous nature, cheapness and availability of the reagents, short reaction times and easy work-up.

The oximes, hydrazones and semicarbazones were prepared by standard procedures.[14,15] The purity of the compounds was checked by TLC. A mixture of the substrate (1 mmol), *n*-hexane (5 mL), $Mg(HSO_4)_2$[16] (3 mmol) and wet SiO_2 [(SiO_2/H_2O: 50% w/w), 0.1 g] was stirred at room temperature for the specified time (Table 1). The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid residue was washed with *n*-hexane (9 mL). Evaporation of the solvent, followed by column chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yields.

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Table 1. Deoximation, dehydrazonation and desemicarbazonation with $Mg(HSO_4)_2$ in the presence of wet SiO_2 at room temperature

Entry	Substrate	Product	Time (min)	Yield[a,b] (%)
1	Benzaldehyde semicarbazone	Benzaldehyde	30	94
2	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	15	92
3	3-Methoxybenzaldehyde semicarbazone	3-Methoxybenzaldehyde	10	75
4	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	15	72
5	Acetophenone semicarbazone	Acetophenone	10	85
6	Salicylaldehyde semicarbazone	Salicylaldehyde	15	90
7	Cyclohexanone semicarbazone	Cyclohexanone	60	80
8	4-Phenylcyclohexanone semicarbazone	4-Phenylcyclohexanone	10	95
9	1-Naphthaldehyde semicarbazone	1-Naphthaldehyde	30	92
10	5-Methyl-2-furaldehyde semicarbazone	5-Methyl-2-furaldehyde	10	87
11	1-Tetralone semicarbazone	1-Tetralone	45	90
12	4-Methylbenzaldehyde-4-nitrophenylhydrazone	4-Methylbenzaldehyde	10	90
13	3-Nitrobenzaldehyde-4-nitrophenylhydrazone	3-Nitrobenzaldehyde	60	88
14	4-Chlorobenzaldehyde phenylhydrazone	4-Chlorobenzaldehyde	10	95[c]
15	4-Phenylacetophenone phenylhydrazone	4-Phenylacetophenone	15	92[c]
16	2-Nitrobenzaldehyde phenylhydrazone	2-Nitrobenzaldehyde	20	90[c]
17	3-Methylacetophenone oxime	3-Methylacetophenone	30	95[c]
18	Acetophenone oxime	Acetophenone	90	90[c]
19	Benzophenone oxime	Benzophenone	300	96[c]
20	4-Bromobenzaldehyde oxime	4-Bromobenzaldehyde	180	95[c]
21	Camphor oxime	Camphor	30	93[c]

[a] Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.

[b] Isolated yields.

[c] Under reflux conditions.

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16. Preparation of $Mg(HSO_4)_2$: A 500 mL suction flask was equipped with a constant-pressure dropping funnel. A gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Anhydrous magnesium chloride (47.6 g, 0.5 mol) was charged into the flask and concentrated sulfuric acid (98.07 g, 1 mol) was added dropwise over a period of 30 min at room temperature. HCl gas was evolved immediately. After completion of the addition of the H_2SO_4, the mixture was shaken for 30 min; meanwhile, the residual HCl was exhausted by suction. A white solid material was thus obtained (108.5 g).