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Regeneration of carbonyl compounds by cleavage of C=N bonds under mild and completely heterogeneous conditions

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Abstract—Oximes, hydrazones, semicarbazones and azines are converted to the corresponding carbonyl compounds using a combination of $Zr(HSO_4)_4$ and wet SiO_2 in good to high yields under completely heterogeneous conditions.

The regeneration of carbonyl compounds from stable and readily prepared oximes, hydrazones, semicarbazones and azines has received considerable attention in recent years.[1–4] Since many valuable reactions have been developed to prepare oximes,[5–8] an efficient deoximation could lead to new methods of preparing carbonyl compounds as well.[9] Some of the reported methods of generating carbonyl compounds from oximes invariably require long reaction times, expensive or hazardous reagents and the formation of over-oxidized products leading to low yields.[10–12] Little attention has been paid to the conversion of hydrazones, semicarbazones and azines to the corresponding carbonyl compounds, and only a few reports are available dealing with these reactions.[13–16]

In continuation of our studies on the development of new methods for cleavage of carbon–nitrogen double bonds,[15–17] we wish to report that $Zr(HSO_4)_4$[18] in the presence of wet SiO_2, can be used for the efficient conversion of oximes, hydrazones, semicarbazones and azines to the corresponding carbonyl compounds. All reactions were performed under mild and completely heterogeneous conditions in good to high yields (Table 1).[19]

It should be noted that the above-mentioned reactions did not proceed using $Zr(HSO_4)_4$ or wet SiO_2 alone, even after prolonged heating.

As shown in Table 1, desemicarbazonation reactions using this method proceed at room temperature and in the presence of 0.25 mmol of $Zr(HSO_4)_4$, while other reactions proceed using higher amounts of the reagent under reflux conditions. Therefore, this methodology can be used for the selective regeneration of carbonyl compounds from semicarbazones in the presence of oximes, hydrazones and azines at room temperature. This is exemplified by competitive reactions between 4-phenylacetophenone semicarbazone and 4-chloroacetophenone oxime and between acetophenone semicarbazone and 3-acetylpyridine phenylhydrazone (Table 1, entries 26, 27).

The mildness of the reaction conditions, high efficiency, selectivity, reasonable yields of products, simple and clean work-up and heterogeneous reaction conditions are among the advantages of this new method.

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Keywords: oximes; hydrazones; semicarbazones; azines; heterogeneous conditions.

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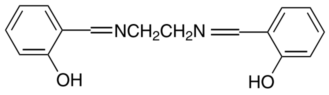
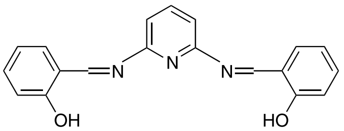
Table 1. Regeneration of carbonyl compounds from their corresponding oximes, hydrazones, semicarbazones and azines[a]

Entry	Substrate	Product	$Zr(HSO_4)_4$/ substrate	Conditions	Time (h)	Yield (%)[b]
1	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	0.25	rt	0.03	90
2	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	0.25	rt	0.07	85
3	Acetophenone semicarbazone	Acetophenone	0.25	rt	0.25	90
4	4-Bromoacetophenone semicarbazone	4-Bromoacetophenone	0.25	rt	0.12	82
5	4-Phenylacetophenone semicarbazone	4-Phenylacetophenone	0.25	rt	0.13	90
6	5-Methyl-2-furaldehyde semicarbazone	5-Methyl-2-furaldehyde	0.25	rt	0.2	90
7	Cyclopentanone semicarbazone	Cyclopentanone	0.25	rt	0.42	85
8	Cyclohexanone semicarbazone	Cyclohexanone	0.25	rt	0.3	92
9	4-Chlorobenzaldehyde oxime	4-Chlorobenzaldehyde	0.75	Reflux	0.75	80
10	3-Nitrosalicylaldehyde oxime	3-Nitrosalicylaldehyde	0.75	Reflux	4.5	85
11	4-Chloroacetophenone oxime	4-Chloroacetophenone	0.75	Reflux	1	80
12	2,4′-Dibromoacetophenone oxime	2,4′-Dibromoacetophenone	0.75	Reflux	0.25	90
13	1-Naphthaldehyde oxime	1-Naphthaldehyde	0.75	Reflux	2.2	80
14	4-Acetylpyridine oxime	4-Acetylpyridine	0.75	Reflux	0.25	85
15	α-Tetralone oxime	α-Tetralone	0.75	Reflux	0.3	82
16	Camphor oxime	Camphor	0.75	Reflux	0.75	90
17	Cyclohexanone oxime	Cyclohexanone	0.75	Reflux	0.8	85
18	4-Methylbenzaldehyde-4-nitro-phenylhydrazone	4-Methylbenzaldehyde	1.5	Reflux	1.5	90
19	4-Acetylpyridine phenylhydrazone	4-Acetylpyridine	1.5	Reflux	2.8	85
20	Cyclopentanone phenylhydrazone	Cyclopentanone	1.5	Reflux	1.5	90
21	Benzaldehyde azine	Benzaldehyde	1.5	Reflux	3.75	89
22	4-Hydroxybenzaldehyde azine	4-Hydroxybenzaldehyde	1.5	Reflux	3.25	85
23	2-Ethoxybenzaldehyde azine	2-Ethoxybenzaldehyde	1.5	Reflux	1.25	85
24		Salicylaldehyde	1.5	Reflux	2.8	84
25		Salicylaldehyde	1.5	Reflux	1	80
26	4-Phenylacetophenone semicarbazone+4-chloro-acetophenone oxime	4-Phenylacetophenone +4-chloroacetophenone	0.25	rt	0.13	100[c]+5[c]
27	Acetophenone semicarbazone+3-acetylpyridine phenylhydrazone	Acetophenone+3-acetylpyridine	0.25	rt	0.25	100[c]+0[c]

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

[b] Isolated yield.

[c] GC yield.

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18. *Preparation of $Zr(HSO_4)_4$*: A 500 mL suction flask was equipped with a constant-pressure dropping funnel. A gas outlet was connected to a vacuum system through an absorbing solution (water) and an alkali trap. Anhydrous $ZrCl_4$ (116.5 g, 0.5 mol) was charged into the flask and concentrated sulfuric acid (196.1 g, 2 mol) was added dropwise over a period of 40 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 (232.5 g).
19. *General procedure*: A mixture of the substrate (1 mmol), *n*-hexane (5 mL), $Zr(HSO_4)_4$ (0.25–1.5 mmol) and wet SiO_2 (50% w/w, 0.05 g) was stirred at room temperature or under reflux conditions, 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 (10 mL). Evaporation of the solvent followed by column chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yield.