

Efficient Cleavage of C=N Under Heterogeneous and Non-aqueous Conditions

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Regeneration of carbonyl compounds from stable and readily prepared oximes, hydrazones and semicarbazones has received a considerable attention in recent years.¹⁻⁴ Since many valuable reactions have been developed to prepare oximes,⁵⁻⁸ an efficient deoxygenation 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 time, 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 and semicarbazones to their corresponding carbonyl compounds, and only a few reports are available dealing with these reactions.^{3,11,13,14}

In continuation of our studies in development of new reagents of Cr(IV), supported on inert media,¹⁵ we wish to report that prolinium chlorochromate supported on silica gel¹⁶ as a new and efficient reagent for the cleavage of carbon-nitrogen double bonds of oximes, hydrazones and semicarbazones in refluxing hexane (Table 1, Scheme 1). The amine part of this reagent was selected on the basis of low toxicity and easy handling of the amine to the most related secondary amines such as pyrrolidine.

Our experiments show that the above mentioned conversions are occurred in completely heterogeneous and non-aqueous conditions, and the carbonyl compounds are obtained from good to high yields. It should be noted that these deoxygenation, dehydrazonation and desemicarbazonation reactions did not proceed well, using unsupported prolinium chlorochromate even after prolonged heating.

In order to show the ability of this method we have compared some of our results with those reported in the literature (Table 2).^{1,11,13,18}

In summary silica supported prolinium chlorochromate can serve as an efficient reagent for cleavage of carbon-

nitrogen double bonds of oximes, hydrazones and semicarbazones. The yields are almost quantitative and the work-up procedure is simple and convenient.

The synthesis and evaluation of oxidative potential of other Cr(VI) based reagents with secondary and tertiary amines in our laboratory is under way.

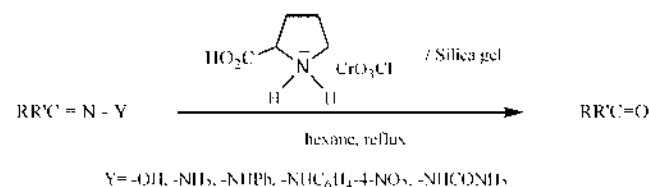
Experimental Section

General: Chemicals were purchased from Merck, Fluka, BDH and Aldrich Chemical Companies. Products were separated and purified by different chromatography techniques, and were identified by the comparison of their mp, bp, IR, NMR and refractive index with those reported for the authentic samples. All yields refer to the isolated products. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on Merck kieselgel 60H.

Preparation of silica supported prolinium chlorochromate: Chromium trioxide (5 g, 50 mmol) was added to a magnetically stirred solution of 6 N HCl (9.2 mL, 55 mmol) at room temperature. The homogeneous solution was cooled to 5 °C, proline (5.75 g, 50 mmol) was added over 10 min, and stirred for 6 h at -6 °C. A brown color solution was obtained which was concentrated under vacuum to provide prolinium chlorochromate (11.8 g, 47 mmol) as a dark brown solid in 94% yield. mp >270 °C; ¹H NMR (D₂O): δ 2.8 (t, *J* = 6 Hz, 1H), 2.1 (t, *J* = 6 Hz, 2H), 1.4 (m, 4H) ppm; IR (KBr): 3200 (vs), 1690 (s), 1600 (s), 1440 (s), 1040 (w), 950 (s), 760 (m) cm⁻¹.

Prolinium chlorochromate (1.25 g, 5 mmol) was added to a suspension of silica gel (5 g) in water (5 mL) and stirred until a homogeneous mixture was obtained. The solvent was evaporated under high vacuum (0.01 mmHg) for prolonged time (24 h) at 40 °C to produce the desired silica supported reagent.

General procedure: A solution of the substrate (1 mmol) in hexane (5 mL) was treated with 3.75 g of the solid supported reagent and the reaction mixture was magnetically stirred under reflux condition for the specified time (Table 1). The reaction was monitored by TLC (CCl₄/Et₂O: 6/1). After completion of the reaction the mixture was filtered and the solid residue was washed with hexane (10 mL). Evaporation of the solvent followed by column chromatography on



Scheme 1

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Table 1. Regeneration of aldehydes and ketones from corresponding oximes, hydrazones and semicarbazones

Entry	Substrate	Product	Time(h)	Yield % ^a
1	Acetophenone oxime	Acetophenone	6	94
2	4-Nitroacetophenone oxime	4-Nitroacetophenone	2.2	95
3	4-Methylacetophenone oxime	4-Methylacetophenone	7	95
4	3-Nitrobenzaldehyde oxime	3-Nitrobenzaldehyde	5.5	95
5	2,4-Dinitroacetophenone oxime	2,4-Dinitroacetophenone	0.5	97
6	Benzophenone oxime	Benzophenone	2	96
7	Cyclohexanone oxime	Cyclohexanone	1.5	93
8	Champhor oxime	Champhor	2	87
9	Benzaldehyde semicarbazone	Benzaldehyde	0.17	98
10	2-Hydroxybenzaldehyde semicarbazone	2-Hydroxybenzaldehyde	0.08	95
11	1-Naphthaldehyde semicarbazone	1-Naphthaldehyde	0.17	92
12	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	0.75	90
13	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	0.5	95
14	Acetophenone semicarbazone	Acetophenone	0.25	97
15	1-Tetralone semicarbazone	1-Tetralone	0.3	92
16	Cyclohexanone semicarbazone	Cyclohexanone	1	90
17	4-Phenylcyclohexanone semicarbazone	4-Phenylcyclohexanone	1	90
18	3-Nitrobenzaldehyde hydrazone	3-Nitrobenzaldehyde	4	95
19	4-Methylacetophenone hydrazone	4-Methylacetophenone	3.5	93
20	4-Methoxybenzaldehyde phenylhydrazone	4-Methoxybenzaldehyde	5	90
21	4-Chlorobenzaldehyde phenylhydrazone	4-Chlorobenzaldehyde	0.5	98
22	3-Nitrobenzaldehyde phenylhydrazone	3-Nitrobenzaldehyde	4.5	90
23	4-Phenylacetophenone phenylhydrazone	4-Phenylacetophenone	0.5	95
24	Benzaldehyde-4-nitrophenylhydrazone	Benzaldehyde	4.5	90
25	4-Methylbenzaldehyde-4-nitrophenylhydrazone	4-Methylbenzaldehyde	3	92
26	3-Nitrobenzaldehyde-4-nitrophenylhydrazone	3-Nitrobenzaldehyde	4.5	90

^aIsolated yield.**Table 2.** Comparison of some of the results obtained by our method (1) with some of those reported with chlorotrimethylsilane-sodium nitrate (2),¹ sodium perborate (3),¹¹ methyl ammonium chlorochromate adsorbed on alumina (4)¹⁷ and ozone (5)¹⁸

Entry	Substrate	Product	Yield %				
			(1)	(2)	(3)	(4)	(5)
1	Acetophenone oxime	Acetophenone	94	—	88	76	96
2	Benzophenone oxime	Benzophenone	96	—	87	61	95
3	Acetophenone semicarbazone	Acetophenone	97	80	—	—	—

silica gel gave the corresponding carbonyl compounds in excellent yields.

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