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Gui-Sheng Zhang <sup>a</sup> & Bing Chai <sup>a</sup>

<sup>a</sup> Department of Chemistry, Henan Normal University Xinxiang, 453002, Henan, P.R., China Published online: 04 Dec 2007.

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## METHYLAMMONIUM CHLOROCHROMATE ADSORBED ON SILICA GEL FOR REGENERATION OF CARBONYL COMPOUNDS FROM THEIR NITROGEN-CONTAINING DERIVATIVES UNDER MILD AND NON-AQUEOUS CONDITIONS

Gui-Sheng Zhang\*, Bing Chai

Department of Chemistry, Henan Normal University, Xinxiang 453002, Henan, P.R.China

Abstract: Oximes, p-nitrophenylhydrazones, 4-phenylsemicarbazones and semicarbazones are converted to their corresponding carbonyl compounds in good yields using methylammonium chlorochromate adsorbed on silica gel(MCC/SiO<sub>2</sub>) under mild and non-aqueous conditions.

Semicarbazones are preferred over oximes and hydrazones for isolation and purification of carbonyl compounds<sup>1</sup>. Semicarbazones are also used as protecting carbonyl compounds in synthesis<sup>2</sup>. Not only semicarbazones but also oximes and

<sup>\*</sup>To whom correspondence should be addressed

p-nitrophenylhydrazones which have carbon-nitrogen double bonds play an important role in the protecting and deprotecting of carbonyl compounds. Furthermore, being derivatives of carbonyl compounds, oximes, semicarbazones, and p-nitrophenylhydrazones can be generated from some non-carbonyl compounds. Thus, the cleavage of carbon-nitrogen double bonds is also a good method of preparing some aldehydes and ketones. Regeneration of the carbonyl compounds from carbon-nitrogen double bonds is an important step in these applications of oximes, p-nitrophenylhydrazones and semicarbazones. Although, several methods for the regeneration of carbonyl compounds from oximes and hydrazones<sup>2a.3</sup>, have been reported, such as copper chloride<sup>4a</sup>, cation exchange resin Dowex-50<sup>4b</sup>, clayfen<sup>4c</sup>, potassium bromate<sup>4d</sup>, and zirconium sulfophenyl phosphonate<sup>ce</sup>, these methods invariably require higher temperatures<sup>4a,4b</sup>, longer reaction times and involve toxic metal ions<sup>4e 4g</sup> as catalysts which are detrimental to the environment. Therefore, there is value in finding a good method and a readily available and safer reagent for the regeneration of carbonyl compounds.

We have previously reported that methylammonium chlorochromate adsorbed on silica gel (MCC/SiO<sub>2</sub>) is a convenient reagent for oxidation of hydroxy compounds to the corresponding carbonyl compounds.<sup>5</sup> This reagent is stable and easily prepared by the addition of a weighed amount of silica gel to a solution of methylammonium chlorochromate in water and rotary evaporation to dryness. In the course of further exploration on the application of MCC/SiO<sub>2</sub> in synthetic organic chemistry, it has been investigated as a convenient, non-hazardous and inexpensive reagent for the

oxidative cleavage of carbon-nitrogen double bonds to their parent carbonyl compounds.

The reaction is performed by simple magnetic stirring of a mixture of the oxidant and substrate in a suitable solvent depending on the solubility. The results show that the derivatives are converted to their corresponding aldehydes and ketones in good yields. Further oxidation of aldehydes to their carboxylic acids is not observed. 2,4-Dinitrophenylhydrazones remain intact in the reaction mixture under the same reaction condition.





In summary, MCC/SiO<sub>2</sub> is effective in converting oximes, pnitrophenylhydrazones, semicarbazones and 4-phenylsemicarbazones to their corresponding carbonyl compounds with the advantages of mild reaction conditions, ease of work-up and better yields. The results of the oxidation are reported in Table.

### Experimental

Mps were determined on a micro-melting point apparatus and are uncorrected.

Substrate	Solvent(mL) CH <sub>2</sub> Cl <sub>2</sub> : ether	Time (h)	m.p.°C(liter.) <sup>6</sup> of 2,4-DNP	Yield (%) <sup>b</sup>
acetophenoneoxime	1:2 (20)	4	236-237 (237)	81.9
cyclohexanoneoxime	1:2 (20)	0.5	159-160.5 (160)	59.4
benzophenoneoxime	1:2 (20)	5	237-239 (238)	65.1
3-pentanoneoxime	1:2 (20)	2	153-156 (156)	61.8
benzaldoxime	CH <sub>2</sub> Cl <sub>2</sub> (20)	0.5	235-236.5 (237)	86.2
furfuraldoxime	I:1 (20)	0.5	200-202 (202)	49.6
p-methoxybenzaldoxime	1:2 (20)	0.25	252-255 (254)	74.6
3-phenylacrylicaldoxime	1:1 (20)	0.5	210-212 (200.5-201.5)	52.2
p-bromabenzaldoxime	1:1 (20)	3	188-191 (- <sup>c</sup> )	69.4
acetophenone 4-NPH <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub> (20)	0.5	236-237 (237)	79.0
3-pentanone 4-NPH	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.5	153-156 (156)	56.8
heptaldehyde 4-NPH	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.3	105-107.5 (107)	57.6
benzaldehyde 4-NPH	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.3	235-236.5 (237)	70.6
p-methoxybenzaldehyde 4-NPH	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.3	252-255 (254)	80.4
3-phenylacrylicaldehyde 4-NPH	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.3	210-212 (200.5-201.5)	76.0
acetophenone 4-PSC <sup>°</sup>	CH <sub>2</sub> Cl <sub>2</sub> (55)	0.5	236-237 (237)	92.8
cyclohexanone 4-PSC	1:2 (30)	6	159-160.5 (160)	46.8
3-pentanone 4-PSC	1:2 (25)	0.5	153-156 (156)	60.2
heptaldehyde 4-PSC	CH <sub>2</sub> Cl <sub>2</sub> (20)	0.25	105-107.5 (107)	51.3

Table. Oxidative Cleavage of Carbon-Nitrogen Double Bonds with MCC/silica gel.\*

(continued)

benzaldehyde 4-PSC	CH <sub>2</sub> Cl <sub>2</sub> (15)	0.5	235-236.5 (237)	50.1
3-phenylacrylicaldehyde 4-PSC	CH <sub>2</sub> Cl <sub>2</sub> (25)	1	210-212 (200.5-201.5)	43.2
acetophenone semicarbazone	CH <sub>2</sub> Cl <sub>2</sub> (10)	0.5	236-237 (237)	98.5
cyclohexanone semicarbazone	CH <sub>2</sub> Cl <sub>2</sub> (10)	0.5	159-160.5 (160)	45.1
3-pentanone semicarbazone	1:2 (20)	0.5	153-156 (156)	65.2
heptaldehyde semicarbazone	1:2 (20)	0.15	105-107.5 (107)	40.4
benzaldehyde semicarbazone	1:2 (20)	0.15	235-236.5 (237)	58.1
p-methoxybenzaldehyde semicarbazone	CH <sub>2</sub> Cl <sub>2</sub> (10)	0.3	252-255 (254)	58.6
3-phenylacrylicaldehyde semicarbazone	1:2 (20)	0.15	210-212 (200.5-201.5)	60.5

**Table Continued** 

a. The reaction was carried out with 1.5 equiv of MCC/Silica gel under reflux.

b. Yields were based on 2,4-dinitrophenylhydrazone derivatives identified by comparison of mps and spectra characteristics with those of the corresponding authentic samples, independently prepared.

- d. 4-NPH means p-nitrophenylhydrazone
- e. 4-PSC means 4-phenylsemicarbazone

IR spectra were measured on a Nicolet FT-IR spectrometer. The <sup>1</sup>H NMR spectra were obtained on a Varian EM-360A (60MHz) spectrometer in CDCl<sub>3</sub> with TMS as the internal standard. The elemental analyses were measured on a Perkin-Elmer 2400 spectrometer.

c. Calc. for C<sub>13</sub>H<sub>9</sub>N<sub>4</sub>O<sub>4</sub>Br: C 42.76, H 2.48, N 15.34; Found C 42.81, H 2.50, N 15.41.

**General Procedure:** In a round-bottomed flask (100ml) equipped with a condenser and a magnetic stirrer, a solution of the substrate (1mmol) in the suitable solvent depending on the solubility was prepared. To the solution the oxidant (1.5mmol) was added with stirring, and the flask was heated in a water bath (38-40<sup>o</sup>C). The mixture was stirred for the time indicated in the Table. The progress of the reaction was monitored by TLC. The reaction mixture was filtered, and the solid material was washed with certain solvent several times. The combined filtrate was evaporated to furnish the product which was isolated as 2,4-dinitrophenylhydrazone.

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