Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

# Trimethylammonium Chlorochromate Adsorbed on Alumina: An Efficient and Convenient Reagent for the Oxidative Cleavage of 4-Phenylsemicarbazones and Semicarbazones to Their Parent Carbonyl Compounds

Hui Gong [a] & Gui-Sheng Zhang [a]

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

To cite this article: Hui Gong & Gui-Sheng Zhang (1999) Trimethylammonium Chlorochromate Adsorbed on Alumina: An Efficient and Convenient Reagent for the Oxidative Cleavage of 4-Phenylsemicarbazones and Semicarbazones to Their Parent Carbonyl Compounds, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:15, 2591-2596, DOI: 10.1080/00397919908086418

To link to this article: http://dx.doi.org/10.1080/00397919908086418

SYNTHETIC COMMUNICATIONS, 29(15), 2591-2596 (1999)

# TRIMETHYLAMMONIUM CHLOROCHROMATE ADSORBED ON ALUMINA : AN EFFICIENT AND CONVENIENT REAGENT FOR THE OXIDATIVE CLEAVAGE OF 4-PHENYLSEMICARBAZONES AND SEMICARBAZONES TO THEIR PARENT CARBONYL COMPOUNDS

Hui Gong, Gui-Sheng Zhang*

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

**ABSTRACT**: Deprotection of 4-phenylsemicarbazones and semicarbazones to their parent aldehydes and ketones in high yields has been carried out by using trimethylammonium chlorochromate adsorbed on alumina as selective oxidant under mild conditions.

Derivatives of carbonyl compounds such as oximes, p-nitrophenylhydrazones and semicarbazones not only are used for the characterization and purification of carbonyl compounds but also play an important role in the protection of carbonyl compounds, as they are highly crystalline and stable compounds. Thus, the regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in organic synthetic chemistry.

---

*To whom correspondence should be addressed.

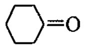
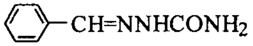
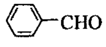
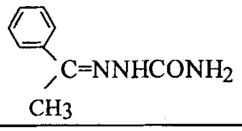
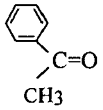
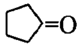
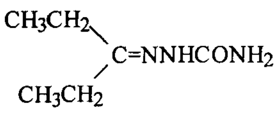
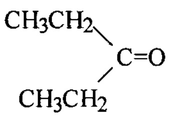
The classical methods for the cleavage of these kinds of derivetives include acid hydrolysis which is not suitable for acid sensitive compounds[1]. Several oxidative methods for these derivatives have been developed with some advantages over the classical hydrolysis method[2-17].But among them, little work has been done on the oxidative cleavage of semicarbazones and 4-phenylsemicarbazones and only few reports are available on the use of this method for the conversion of these derivatives to the corresponding carbonyl compounds.[13,14]

We have previously reported that trimethylammonium chlorochromate adsorbed on alumina (TMCC/alumina) as an efficient reagent for the oxidation of oximes and p-nitrophenylhydrazones to corresponding carbonyl compounds under non-aqueous conditions.[18] Herein, we wish to report a mild and convenient method for the oxidative deprotection of 4-phenylsemicarbazones and semicarbazones in high yields by using the same oxidizing reagent. TMCC/alumina is stable and easily preparative. It was synthesized by adding a weighed amount of alumina to a solution of trimethylammonium chlorochromate in water and rotary evaporation to dryness.The oxidative reaction is easily performed by simple stirring of a mixture of the oxidant and substrate in a suitable solvent at a reflux temperature in a water bath. Our experiments show that 4-phenylsemicarbazones and semicarbazones are converted to their corresponding aldehydes and ketones in suitable solvent depending on the solubility. Further oxidation of aldehydes to their carboxylic acids is not observed. A summary of the results shows that TMCC/alumina is a convenient reagent for oxidation of 4-phenylsemicarbazones and semicarbazones to their parent carbonyl compounds with the advantages of mild reaction conditions, ease of work-up and high yields.

**Scheme 1**

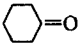
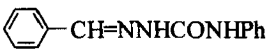
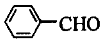
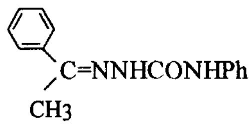
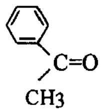
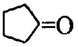
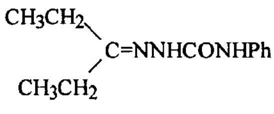
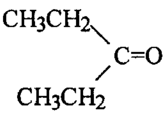
X = H, Ph

**Table 1. Oxidative Deprotection of semicarbazones 4-phenylsemicarbazones with TMCC/alumina [a]**

| Substrate | Product | Solvent (mL) | Time (min) | Yield [b] (%) |
|---|---|---|---|---|
|  |  | Ether (15) | 30 | 87 |
|  |  | $CH_2Cl_2$ (40) | 10 | 75 |
|  |  | $CH_2Cl_2$(30) | 30 | 76 |
|  |  | $CH_2Cl_2$ (30) | 30 | 93 |
|  |  | Ether (15) | 30 | 86 |
| $CH_3(CH_2)_5CH=NNHCONH_2$ | $CH_3(CH_2)_5CH=O$ | Ether (15) | 10 | 79 |

*(continued)*

Table 1. Continued

| | | | | |
|---|---|---|---|---|
|  |  | $CH_2Cl_2$ (30) | 30 | 94 |
|  |  | $CH_2Cl_2$(30) | 10 | 99 |
|  |  | $CH_2Cl_2$ (30) | 30 | 84 |
|  |  | $CH_2Cl_2$ (30) | 30 | 71 |
|  $(CH_3CH_2)_2C=NNHCONHPh$ |  $(CH_3CH_2)_2C=O$ | $CH_2Cl_2$ (30) | 30 | 70 |
| $CH_3(CH_2)_5CH=NNHCONHPh$ | $CH_3(CH_2)_5CH=O$ | $CH_2Cl_2$ (30) | 10 | 61 |

a. The reaction was carried out with 1.5 equiv of TMCC/alumina at reflux temperature.

b. Yields were based on 2,4-dinitrophenylhydrazone derivatives[19] identified by melting points and the spectra characteristics with the corresponding authentic samples.

## Experimental Section

IR spectra were determined on a BIO-RAD FTS-40 instrument. $^1H$ NMR spectra were recorded with a HITACHI R-24B (60MHz) spectrometer. Solvent was freshly distilled. Semicarbazones and 4-phenylsemicarbazones were prepared by reaction of semicarbazide hydrochloride and 4-phenylsemicarbazide hydrochloride with corresponding ketones or aldehydes and identified by their melting points, IR and $^1H$ NMR. TMCC/alumina was prepared according to literature.[18]

**General Procedure for the Regeneration of Carbonyl Compounds from Semicarbazones and 4-phenylsemicarbazones** In a round-bottomed flask

(100ml) equipped with a condenser and a magnetic stirrer, a mixture of the substrate (1mmol) and a suitable amount of solvent was added. To this solution the oxidant (1.5mmol) was added. The mixture was stirred and refluxed in a water bath for 10-30 min. The solid material was filtered and washed with ether several times. The combined filtrate was evaporated to furnish the product that was isolated as 2,4-dinitrophenylhydrazones.

**Acknowledgment** Project 29577273 Supported by National Science Foundation of China and Science and Technology Commission of Henan Province.

**References**

1. Hershberg E. B., *J. Org. Chem.*, **1948**,*13*,542.
2. Kirk D. N. and Slade C. J., *Tetrahedron Lett.*, **1980**,*21*,651.
3. McGuckin W. F. and Kendall E. C., *J. Am. Chem. Soc.*, **1952**,*74*,5811.
4. Gillam A. E. and West T. F., *J. Chem. Soc.*, **1945**,95.
5. Eisenbraum E. J., Wesley R. P., Budhram R. S. and Dewprasad B., *Chem. Ind.(London)* **1989**,549.
6. Ram R. N. and Varsha K., *Tetrahedron Lett.*, **1991**,*32*,5829.
7. Ranu B. C. and Sarkar D. C., *J. Org. Chem.*, **1988**,*53*,878.
8. Laszlo P. and Polla E., *Synthesis* **1985**,439.
9. Narayanan S. and Srinivasan V. S., *J. Chem. Soc., Perkin Trans.2* **1986**,1557.
10. Curini M., Rosati O., Pisani E. and Costantino U., *Synlett*, **1996**, 333.

11. Butler R. N., Morris G. J. and O'Donohue A. M., *J. Chem. Res.(S)* **1981**,61.

12. Salmon M., Miranda R. and Angeles E., *Synth. Commun.*, **1986**,*16*,1827.

13. Baltork I. M., and Pouranshirvani Sh. *Synth. Commun.*, **1996**,*26*,1.

14. Firouzabadi H., Seddighi M., Ahmadi Z. A. and Sardarian A. R. *Synth. Commun.*, **1989**,*19*,3385.

15. Zhang G. S., Yang D. H., Chen M. F., Cai K. *Synth. Commun.* **1998**,*28*,2221.

16. Zhang G. S., Yang D. H., Chen M. F. *Synth. Commun.***1998**, *28*, 3721.

17. Zhang G. S., Yang D. H., Chen M. F., Cai K. *Synth. Commun.***1998**, *28*, 607.

18.Zhang G. S., Yang D. H., and Chen M. F. *Organic Preparation and Procedure International* **1998**,*30*, in press.

19. The formation of 2,4-dinitrophenylhydrazone is described as follows: To the oxidative crude product, a solution of 0.3g (1.5mmol) of 2,4-dinitrophenylhydrazine, 0.8g $H_2SO_4$, and 4.3mL of EtOH was added. The mixture was stirred for 10 minutes, then kept for several hours at room temperature. The solid was filtered, washed with alcohol and water.

Accepted 12-12-1998