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

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

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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.

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The classical methods for the cleavage of these kinds of derivetives include acid hydrolysis which is not suitable for acid sensitive compounds¹. Several oxidative methods for these derivatives have been developed with some advantages over the classical hydrolysis method²⁻¹⁷.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 oxidative deprotection of 4-phenylsemicarbazones and method for the 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 4phenylsemicarbazones and semicarbazones to their parent carbonyl compounds with the advantages of mild reaction conditions, ease of work-up and high yields.

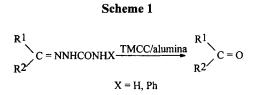


Table 1. Oxidative Deprotection of semicarbazones

| 4-phenylsemicarbazones with TMCC/alumina a | | | | | | |
|--|---|--------------------------------------|-------|--------------------|--|--|
| Substrate | Product | Solvent | Time | Yield ^b | | |
| | | (mL) | (min) | (%) | | |
| \bigcirc =NNHCONH ₂ | ○ =0 | Ether (15) | 30 | 87 | | |
| CH=NNHCONH ₂ | С⊢сно | CH ₂ Cl ₂ (40) | 10 | 75 | | |
| C=NNHCONH ₂ CH ₃ | C=O CH3 | CH ₂ Cl ₂ (30) | 30 | 76 | | |
| =NNHCONH ₂ | 0= | CH ₂ Cl ₂ (30) | 30 | 93 | | |
| CH ₃ CH ₂ C=NNHCONH ₂ CH ₃ CH ₂ | CH ₃ CH ₂ C=O CH ₃ CH ₂ | Ether (15) | 30 | 86 | | |
| CH3(CH2)5CH=NNHCONH2 | CH ₃ (CH ₂) ₅ CH=O | Ether (15) | 10 | 79 | | |

4-phenylsemicarbazones with TMCC/alumina ^a

(continued)

| = NNHCONHPh | ○= 0 | CH ₂ Cl ₂ (30) | 30 | 94 |
|---|---|--------------------------------------|----|----|
| CH=NNHCONHPh | Сно | CH ₂ Cl ₂ (30) | 10 | 99 |
| C=NNHCONHPh CH3 | C=O CH3 | CH ₂ Cl ₂ (30) | 30 | 84 |
| -NNHCONHPh | [)=0 | CH ₂ Cl ₂ (30) | 30 | 71 |
| CH ₃ CH ₂ C=NNHCONHPh CH ₃ CH ₂ | CH ₃ CH ₂ C=O CH ₃ CH ₂ | CH ₂ Cl ₂ (30) | 30 | 70 |
| CH3(CH2)5CH≕NNHCONHPh | CH3(CH2)5CH=O | CH ₂ Cl ₂ (30) | 10 | 61 |

Table 1. Continued

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

b. Yields were based on 2,4-dinitrophenylhydrazone derivatives¹⁹ 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.

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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 H₂SO₄, 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.

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