Monatshefte für Chemie 130, 581–583 (1999)

Monatshefte für Chemie
Chemical Monthly

Ammonium Chlorochromate Adsorbed on Montmorillonite K-10: A New Reagent for the Oxidation of Alcohols to the Corresponding Carbonyl Compounds under Non-Aqueous Conditions

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Summary. A variety of alcohols were oxidized to the corresponding carbonyl compounds by reaction of ammonium chlorochromate adsorbed on montmorillonite K-10 in dichloromethane at room temperature in excellent yields.

Keywords. Ammonium chlorochromate; Montmorillonite; Oxidation; Alcohol; Carbonyl compounds.

An Montmorillonit-K-10 adsorbiertes Ammoniumchlorochromat: Ein neues Reagens zur Oxidation von Alkoholen zu Carbonylverbindungen unter nichtwäßrigen Bedingungen

Zusammenfassung. Eine Reihe von Alkoholen wurden mittels an Montmorillonit-K-10 adsorbierten Ammoniumchlorochromats in Dichlormethan bei Raumtemperatur in ausgezeichneten Ausbeuten zu den entsprechenden Carbonylverbindungen oxidiert.

Introduction

The oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis [1]. Although a large number of reagents are known in the literature [2], there still appears a need either to improve the existing oxidation methods [3] or to introduce novel reagents [4] to permit better selectivity under milder conditions and with easy work-up procedures. Among the various methods available, chromium reagent based oxidations are very popular.

The concept of utilizing reagents adsorbed on inert inorganic supports for organic synthesis has been reported and applied especially to chromium compounds [6]. We have reported that *bis*(trimethylsilyl) chromate supported on montmorillonite K-10 [7, 8] and 3-carboxypyridinium chlorochromate supported on alumina [9, 10] oxidize alcohols to the corresponding carbonyl compounds.

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Analogously, ammonium chlorochromate (*ACC*) adsorbed on montmorillonite K-10 is a new reagent suitable for the oxidation of alcohols.

Results and Discussion

Heating chromium trioxide and ammonium chloride in water at 40°C results in a nearly homogeneous solution [11]. *ACC* supported on montmorillonite was conveniently prepared simply by adding montmorillonite K-10 into such a solution. An orange free flowing solid was obtained after evaporation of the solvent.

The oxidation reactions were carried out by adding 1–2 equivalents of *ACC* supported on montmorillonite K-10 to the stirred solution of an alcohol in dichloromethane at room temperature. For example, benzyl alcohol was oxidized to benzaldehyde in almost quantitative yield. Other benzylic alcohols were similarly oxidized within 2 h at room temperature. Primary benzylic alcohols were oxidized to the corresponding aldehydes, and over-oxidation to the corresponding acids was not observed even after prolonged heating with an excess of supported *ACC*.

Aliphatic primary alcohols were successfully oxidized to the corresponding aldehydes, aliphatic secondary alcohols to the corresponding ketones. The results are summarized in Table 1. The oxidation of aryl substituted unsaturated alcohols proceeded less satisfactorily. Cinnamaldehyde, for example, was obtained in only 61% yield along with 39% of benzaldehyde demonstrating that carbon-carbon double bonds are prone to cleavage with the reagent.

In conclusion, ammonium chlorochromate adsorbed on montmorillonite K-10 can be easily prepared and may serve as an excellent oxidant for the oxidation of various types of alcohols. The products can be isolated by simple filtration of the reaction mixture without aqueous work-up. The high reactivity and selectivity of the supported reagent avoids the use of a larger excess of oxidant which often causes over-oxidation.

Table 1. Oxidation of alcohols to carbonyl compounds by means of ammonium chlorochromate supported montmorillonite K-10

Alcohol	Reaction time (h)	Product	Yield (%)
Benzyl	1	Benzaldehyde	97 (92)
4-Methylbenzyl	1	4-Methylbenzaldehyde	95 (90)
5-Methyl-2-nitrobenzyl	2	2-Methyl-5-nitrobenzylaldehyde	88 (78)
4-Nitrobenzyl	1.5	4-Nitrobenzaldehyde	92 (80)
Salicyl	2	Salicylaldehyde	90 (80)
1-Octanol	2	Octanal	85 (74)
2-Ethylhexanol	2	2-Ethylhexanal	92 (85)
Cyclohexanol	1	Cyclohexanone	88 (80)
2-Methylcyclohexanol	1	2-Methylcyclohexanone	82 (75)
(−)-Menthol	1.5	(−)-Menthone	92 (85)
Benzhydrol	2	Benzophenone	88 (81)
Benzoin	2	Benzil	85 (75)

Yields determined by GLC; numbers in parentheses refer to yields of isolated products

Experimental

Products were characterized by GLC and by direct comparison with authentic samples. Yields are based on GLC analysis and isolated products. Montmorillonite K-10 was dried and simultaneously activated in a microwave oven for 5 min at 900 W prior to use.

Preparation of ACC/montmorillonite K-10

To a solution of 5 g chromium trioxide (0.05 mol) in 10 ml H_2O 10.70 g NH_4Cl (0.1 mol) are added within 15 min at 40°C. The mixture is cooled until a yellow-orange solid forms. Reheating to 40°C gives a solution. Montmorillonite K-10 (20 g) is then added to the solution with stirring at 40°C. After evaporation under reduced pressure, the orange solid is dried in vacuum for 1 h at 80°C. The reagent can be kept for at least 3 months in air at room temperature without losing its activity.

Oxidation of alcohols

The above reagent (1.7 g, 2.6 mmol) was placed in a round bottomed flask and covered with 10 ml CH_2Cl_2. To the stirred mixture, 1.6 mmol of alcohol were added. After the indicated time (Table 1), the solid was filtered and washed with three 20 ml portion of CH_2Cl_2. The combined filtrates were evaporated, and the residue was passed through a small bed of silica gel to afford the corresponding carbonyl compounds after removing the solvent.

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Received June 8, 1998. Accepted (revised) August 10, 1998