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Oxidation of Alcohols by Montmorillonite K-10 Supported *Bis*(trimethylsilyl)chromate

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Summary. *Bis*(trimethylsilyl)chromate generated from chromic anhydride and hexamethyldisiloxane in dichloromethane was applied onto a montmorillonite K-10 surface. This reagent proved to be suitable for oxidizing alcohols of various types to the corresponding carbonyl compounds.

Keywords. Oxidation; Montmorillonite; Carbonyl compounds; Supported chromium oxidant.

Oxidation von Alkoholen mit an Montmorillonit K-10 adsorbiertem *Bis*(trimethylsilyl)chromat

Zusammenfassung. *Bis*(trimethylsilyl)chromat, dargestellt aus Chromsäureanhydrid und Hexamethyldisiloxan in Dichlormethan, wurde an Montmorillonit K10 adsorbiert. Mit diesem Reagens werden unterschiedliche Alkohole in sehr guten Ausbeuten zu den entsprechenden Carbonylverbindungen oxidiert.

Introduction

Oxidation under mild and heterogenous conditions in organic media is important in organic synthesis. Recently, attention has been paid to the preparation of new reagents suitable for such purposes [1–16]. The most important synthetic application of chromium oxidants is the oxidation of alcoholes to carbonyl compounds [17]. Pyridinium dichromate [18] and chlorochromate [19] have often been used for this purpose because of mild reaction condition and high yields. Chromium oxidants adsorbed on solid supports, such as pyridinium chlorochromate on alumina [20], chromic acid on silica [21], and chromyl chloride on silica/alumina [22] have reported to give better yields under milder conditions than the corresponding parent oxidants [23].

Chromic anhydride mixed with trimethylsilyl chloride has been used for the oxidation of several functional groups [24, 25]. *Bis*(triphenylsilyl)chromate [26] and *bis*(trimethylsilyl)chromate (*BTSC*, [27]) have also been used. Unfortunately, oxidation with these reagents suffers from various disadvantages, notably homogenous conditions and moderate yields.

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Here we report that *BTSC* supported on montmorillonite K-10 can efficiently oxidize various types of alcohols to the corresponding carbonyl compounds in high to excellent yields.

Results and Discussion

Heating chromic anhydride with a slight excess of hexamethyldisiloxane in dichloromethane produces a nearly homogeneous solution. *BTSC* supported on montmorillonite K-10 was then prepared by addition of montmorillonite K-10 the vigorously stirred solution. A dark brown free-flowing solid was obtained upon evaporation of volatile materials. It can be stored in a dark brown bottle without appreciable loss of reactivity at least for 3 months. When a variety of alcohols were treated with 1.2 equivalents of *BTSC* supported on montmorillonite K-10, the corresponding carbonyl compounds were obtained in high to excellent yields.

The results are summarized in Table 1. No overoxidation to carboxylic acids was observed in the case of primary alcohols, even after prolonged heating with an excess of reagent. Cinnamyl alcohol was successfully oxidized to the corresponding α,β-unsaturated aldehyde. Use of excess oxidant was avoided in order to prevent further oxidation. In this reaction, no trace of benzaldehyde could be detected. Obviously, the oxidant cannot cleave the double bond of cinnamyl alcohol.

In conclusion, *bis*(trimethylsilyl)chromate supported on montmorillonite K-10 can be easily prepared and acts as an excellent reagent for the oxidation of a variety of alcohols at room temperature. The products can easily be separated by simple filtration and evaporation of the solvent; therefore, no aqueous work-up is needed. The high reactivity of the supported reagent makes the use of a larger excess of oxidant, which often causes over-oxidation and other side reactions, unnecessary.

Table 1. Oxidation of Alcohols to carbonyl compounds by *bis*(trimethylsilyl)chromate supported on Montmorillonite K-10[a]

Alcohol	Temperature (°C)	Time (min)	Product	Yield (%)
Benzyl alcohol	25	10	Benzaldehyde	99
4-Methyl-benzyl alcohol	25	10	4-Methyl-benzaldehyde	98
4-Methyl-2-nitro benzyl alcohol	25	10	4-Methyl-2-nitrobenzaldehyde	98
Cinnamyl alcohol	25	10	Cinnamaldehye	99
1-Octanol	25	20	Octanal	98
Dodecanol	50	20	Dodecanal	98
2-Octanol	25	20	2-Octanone	99
2-Ethylhexanol	25	20	2-Ethylhexanal	87
Cyclohexanol	25	10	Cyclohexanone	97
Menthol	50	20	Menthone	96
3-Morpholino-1-propanol	25	10	3-Morpholino-propanal	98

[a] 1–1.2 equivalents of chromium oxidant in dichloromethane; reactions using chromium oxidant stored for 3 months proceeded slightly slower than those conducted with freshly prepared reagents

Experimental

Products were characterized by GLC and by direct comparison with authentic samples. Yields are based on GLC analysis. Montmorillonite K-10 was dried and simultaneously activated in a microwave oven for 3 min at 780 W prior to use.

Preparation of bis(trimethylsilyl)chromate supported on montmorillonite K-10

To a solution of 6.4 ml hexamethylsiloxane (0.03 mol) in 20 ml of CH_2Cl_2, chromic anhydride (0.03 mol) was added. The reaction mixture was stirred at 50°C for 5 h. The CrO_3 dissolved, and the dark red mixture became homogeneous. Montmorillonite K-10 (13 g, pre-dried for 12 h at 120°C and activated in a microwave oven for 3 min) was added, and the resulting mixture was stirred for further 5 h. The solvent and other volatile components were distilled off under reduced pressure to afford 19 g of the supported chromium oxidant. The calculated 1.59 mmol of this typical batch of the reagent were regarded as the effective chromium concentration.

Oxidation of cyclohexanol, general procedure

Montmorillonite K-10 (0.75 g, equivalent to 1.2 mmol of chromium(VI) oxidant) was placed in a round bottom flask and covered with 5 ml of CH_2Cl_2. Cyclohexanol (1.04 mmol) was added, and after stirring the reaction mixture at room temperature for 10 min it was filtered and washed with 10 ml of CH_2Cl_2. Evaporation of the solvent afforded 99 mg of cyclohexanone (97.6%). GC analysis showed the presence of negligible amounts of impurities.

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