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3-Carboxypyridinium Chlorochromate Adsorbed on Alumina as a Selective Oxidant for Primary and Secondary Alcohols

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Summary. A Simple and efficient method for the oxidation of alcohols to carbonyl compounds under non-aqueous conditions employing 3-carboxypyridinium chlorochromate adsorbed on alumina is described.

Keywords. Oxidation; Alcohols; Carbonyl compounds; 3-Carboxypyridinium chlorochromate; Adsorbed reagent; Alumina.

An Aluminiumoxid adsorbiertes 3-Carboxypyridiniumchlorochromat als selektives Oxidationsmittel für primäre und sekundäre Alkohole

Zusammenfassung. Eine einfache und effiziente Methode für die Oxidation von Alkoholen zu Carbonylverbindungen unter nichtwäßrigen Bedingungen wird beschrieben, welche auf der Verwendung von an Aluminiumoxid adsorbiertem 3-Carboxypyridiniumchlorochromat beruht.

Introduction

The oxidation of alcohols to carbonyl compounds is an important transformation in organic chemistry attracting much interest [1–4]. The utility of chromium(VI) reagents in the oxidative transformation is hampered due to inherent toxicity, cumbersome preparation, and potential danger (ignition or explosion) as well as by difficulties in terms of product isolation and waste disposal [5]. Pyridinium chlorochromate oxidizes a wide variety of alcohols to carbonyl compounds in dichloromethane solution with high efficiency, but working up of the reaction mixture is cumbersome.

3-Carboxypyridinium chlorochromate has been recently introduced as an efficient reagent for the cleavage of carbon-nitrogen double bonds [7] and the oxidative deprotection of trimethylsilyl ethers and tetrahydropyranyl ethers [8]. In continuation of our investigations utilizing reagents adsorbed on supports [4, 9, 10], we wish to report a facile oxidation of primary and secondary alcohols to the

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corresponding carbonyl compounds using 3-carboxypyridinium chlorochromate supported on alumina.

Results and Discussion

3-Carboxypyridinium chlorochromate (*CPCC*) is a stable yellow-orange solid. It can easily and cheaply be prepared by the reaction of nicotinic acid with chromium trioxide in 6*N* hydrochloric acid [7]. Although oxidation of benzyl alcohol to benzaldehyde smoothly proceeded using this reagent in CH_2Cl_2, the oxidation of other benzylic alcohols did not occur in good yield. For example, when 4-methylbenzyl alcohol was subjected to oxidation with *CPCC*, only 20% of 4-methylbenzaldehyde were obtained even after refluxing for a long period. Other primary and secondary alcohols did not give considerable amounts of the corresponding carbonyl compounds.

Since organic synthesis by solid phase methods is a powerful tool [11] and chromium oxidants like pyridinium chlorochromate adsorbed on alumina [12], chromic acid on silica [13], and chromyl chloride on silica-alumina have been reported to give better yields under milder conditions as compared to the parent oxidants, we tried to follow this road for *CPCC*.

Thus, *CPCC* adsorbed on alumina was prepared by adding alumina to a solution of *CPCC* in CH_2Cl_2 and evaporating to dryness. The yellow-orange solid was kept in vacuum at room temperature and stored in the dark before use. A variety of alcohols dissolved in CH_2Cl_2 were subjected to oxidation using 1.2–2 mmol of the reagent. We found the adsorbed reagent to be remarkably effective in oxidizing primary and secondary alcohols to aldehydes and ketones in high to excellent yields. No indications of overoxidation could be observed in the case of primary alcohols.

Interestingly, cinnamyl alcohol gave only 65% of cinnamaldehyde and 35% of benzaldehyde, demonstrating carbon-carbon double bonds being prone to cleavage by the above reagent. The results obtained from the oxidation of 10 alcohols are reported in Table 1.

Table 1. Oxidation of alcohols to carbonyl compounds by *CPCC* on alumina in CH_2Cl_2

Alcohol	Reaction time (h)	Product	Yield[a] (%)
Benzyl	1	Benzaldehyde	98 (92)
4-Methylbenzyl	1	4-Methylbenzaldehyde	95 (90)
5-Methyl-2-nitrobenzyl	2	5-Methyl-2-nitrobenzylaldehyde	92 (85)
4-Nitrobenzyl	8	4-Nitrobenzaldehyde	90 (86)
Cinnamyl alcohol	3.5	Cinnamaldehyde	65 (60)
Cyclohexanol	6	Cyclohexanone	88 (80)
2-Methylcyclohexanol	7	2-Methlcyclohexanone	80 (70)
1-Octanol	7	1-Octanal	85 (72)
Benzhydrol	2	Benzophenone	90 (82)
(−)-Menthol	8	(−)-Menthone	95 (90)

[a] Yields determined by GLC numbers in parentheses: yields of isolated products; all compounds isolated had identical physical data with corresponding authentic samples

In conclusion, *CPCC* adsorbed on alumina can be easily prepared and serves as an excellent oxidizing agent for various types of alcohols under non-aqueous conditions at ambient temperature, work-up consisting of a mere filtration.

Experimental

Products were characterized by GLC and by direct comparison with authentic samples. Yields are based on GLC analysis and isolated products.

Carboxypyridinium chlorochromate adsorbed on alumina

To a solution of 10 g chromium trioxide (0.1 mol) in 18 ml 6*N* hydrochloric acid, 12.3 g nicotinic acid (0.1 mol) were added within 5 min at 2–5°C. The mixture was stirred at ambient temperature until a yellow-orange solid formed. Reheating to 40°C gave a solution. Alumina (60 g) was then added to the solution with stirring at 40°C. After evaporation in a rotary evaporator, the orange solid is dried in vacuum for 2 h at room temperature. The reagent could be kept for several weeks under vaccum in the dark without losing its activity.

Oxidation of alcohols to carbonyl compounds

The above reagent (5 g, 5 mmol) was added to a solution of 2.52 mmol alcohol in 10 ml CH_2Cl_2. After stirring for the time given in Table 1, the solid was filtered and washed with three 10 ml portions of CH_2Cl_2. The combined filtrates were evaporated. The residue was passed through a small silica gel pad (eluent: petroleum ether:EtOAc = 8:2) to give the pure carbonyl compounds (Table 1).

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