Monatshefte für Chemie 135, 793–797 (2004)
DOI 10.1007/s00706-003-0129-7

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Oxidation of Alcohols with 4-Aminopyridinium Chlorochromate Supported on Silica Gel

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Received August 15, 2003; accepted (revised) October 16, 2003

Summary. 4-Aminopyridinium chlorochromate supported on silica gel was found to be an efficient reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds.

Keywords. Alcohol; Oxidation; 4-Aminopyridinium chlorochromate; Silica gel.

Introduction

Solid phase organic synthesis for preparation of various compounds has provided an attractive option for organic synthesis [1–3]. Micro porous solids such as silica gel offer a wide range of active sites for the supported reagents. Silica gel as an inorganic support has been used in various chemical reactions, however, there are few examples using supported organic molecules on silica gel as oxidizing agents [4–7].

Oxidation of alcohols to the carbonyl compounds is an important transformation in organic synthesis and because of its significance and in spite of the availability of plethora of methods to accomplish this objectives [8–10], a practically simple procedure is yet to be desired.

Pyridinium chlorochromate is used for oxidation of organic compounds consistently [11–13]. Chromium oxidants, such as pyridinium chlorochromate adsorbed on alumina [14, 15], on silica [16], chromic acid on silica [17], ammonium chlorochromate on silica [18] and chromyl chloride on silica–alumina [19] have

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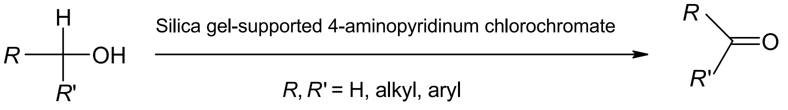


Scheme 1

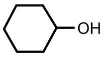
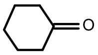
been reported to give better yields under milder conditions as compared to the unsupported oxidants. During the course of our systematic study on the development of supported reagents and catalysts for the oxidation of organic compounds [20–30], we are reporting a novel heterogeneous oxidant based on 4-aminopyridinium chlorochromate supported on silica gel as an efficient and convenient method for the oxidation of alcohols to the corresponding carbonyl compounds in high yields (Scheme 1).

Results and Discussions

Silica gel supported 4-aminopyridinium chlorochromate is a stable solid. It can be prepared from the reaction of 4-aminopyridine with activated silica gel (Si–NH pyridine bond formation), which is then reacted with a solution of chromium trioxide in hydrochloric acid.

The oxidation of alcohols is performed in dichloromethane as solvent and work up is simply by separation of the heterogeneous supported oxidant by filtration and removal of the solvent followed by purification of the residue using column chromatography to give aldehydes and ketones in high yields. The results are summarized in the Table 1.

Table 1. Oxidation of primary and secondary alcohols with silica gel supported 4-aminopyridinium chlorochromate

Entry	Substrate	Time	Product[a]	Yield[b]	Mp or Bp (°C)	
		h		%	Found	Reported [31]
1[c]	$C_6H_5CH_2OH$	2	C_6H_5CHO	97	180	179
2[c]	p-$CH_3C_6H_4CH_2OH$	2	p-$CH_3C_6H_4CHO$	97	202	204
3[c]	p-$CH_3OC_6H_4CH_2OH$	1.5	p-$CH_3OC_6H_4CHO$	100	248	247
4[c]	p-$O_2NC_6H_4CH_2OH$	4	p-$O_2NC_6H_4CHO$	93	106	106
5	$C_6H_5CH(OH)CH_3$	3	$C_6H_5COCH_3$	92	202	200
6	$C_6H_5CH(OH)C_6H_5$	3	$C_6H_5COC_6H_5$	95	48	48
7	$C_6H_5CH(OH)COC_6H_5$	3	$C_6H_5COCOC_6H_5$	97	95	95
8		6		85	135	135
9[c]	$CH_3(CH_2)_4CH_2OH$	6	$CH_3(CH_2)_4CHO$	85	128	128
10[c]	$CH_3(CH_2)_6CH_2OH$	6	$CH_3(CH_2)_6CHO$	83	172	171

[a] All compounds were fully characterized by their mp or bp, IR and ^1H NMR spectra; [b] yields refer to pure isolated products; [c] no indications of over-oxidation could be observed in the case of primary alcohols

Table 2. Reusability of silica gel supported 4-aminopyridinium chlorochromate*

Experimental trail	Substrate	Product	Yield (%)
1st	$C_6H_5CH_2OH$	C_6H_5CHO	97
2nd	$C_6H_5CH_2OH$	C_6H_5CHO	94
3rd	$C_6H_5CH_2OH$	C_6H_5CHO	92
4th	$C_6H_5CH_2OH$	C_6H_5CHO	92

* All reactions were carried out according to the typical procedure

Reusability of Silica Gel Supported 4-Aminopyridinium Chlorochromate

Silica gel supported 4-aminopyridinium chlorochromate after using as oxidant for the oxidation of alcohols can be re-converted to corresponding chlorochromate salt by treatment by a solution of chromium trioxide in hydrochloric acid. In a typical procedure silica gel supported 4-aminopyridinium chlorochromate after the first use for the oxidation of benzyl alcohol to benzaldehyde was re-converted to chlorochromate salt by a solution of chromium trioxide in hydrochloric acid according to the mentioned procedure for the preparation of silica gel 4-aminopyridinium chlorochromate and then it was re-used for the oxidation of benzyl alcohol to benzaldehyde. The second, third, and fourth run according to this procedure showed no considerable decrease in the reaction yields (Table 2).

The silica gel supported 4-aminopyridine was recovered quantitatively after each experiment. The IR spectrum of the recovered reagent exhibited signals at $\bar{\nu} = 890$ and $1563\,\mathrm{cm}^{-1}$ corresponding to Si–N stretching.

In conclusion, silica gel supported 4-aminopyridinium chlorochromate can be used as an efficient and recoverable oxidant for controlled oxidation of primary and secondary alcohols to their corresponding carbonyl compounds. Mild reaction conditions, high yields, easy work up, and reusability of the supported reagent are the most significant aspects of this method.

Experimental

Chemicals were purchased from Merck, Aldrich, and Riedel-de Haen AG and were used without further purification. IR spectra were recorded on a FT-IR Unicam Mattson 1000 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-80 (80 MHz) spectrometer in $CDCl_3$. All products are known compounds and they were identified by their melting and boiling points, IR and ^1H NMR spectra [31]. All yields refer to pure isolated products.

Activation of Silica Gel

Chromatography grade silica gel (10 g, 70–230 mesh) was heated in an electric furnace at 700°C for 3 h. Then it was cooled to room temperature to obtain activated silica gel (9.3 g).

Supporting of 4-Aminopyridine on Activated Silica Gel

To a stirred solution of 4-aminopyridine (3 g, 30 mmol) in 70 ml of ethyl acetate activated silica gel (9.3 g) was added and the mixture was refluxed for 9 h. Then it was cooled to room temperature and filtered. The solid matter was continuously extracted with ethyl acetate in a *Soxhlet* apparatus for 12 h to remove unreacted 4-aminopyridine. It was filtered and dried in an oven at 70°C for 3 h to yield silica gel supported 4-aminopyridine (11.2 g), which contained 1.9 g (20 mmol) of 4-aminopyridine on activated silica gel (9.3 g).

Preparation of Silica Gel Supported 4-Aminopyridinium Chlorochromate

To a fresh solution of 2 g of chromium trioxide (20 mmol) in 4 cm^3 of 6 N hydrochloric acid, silica gel supported 4-aminopyridine (11.2 g, contain 20 mmol of 4-aminopyridine) was added within 3 min at 7–12°C, and the mixture was stirred at ambient temperature for 30 min until a lemon solid was formed. After evaporation of the solvent, the solid was dried at 50°C for 2 h. The supported reagent can be kept for weeks in the dark without losing its activity.

Typical Procedure for the Oxidation of Benzyl Alcohol to Benzaldehyde

Benzyl alcohol (1.1 g, 10 mmol) was dissolved in 50 cm^3 of dichloromethane. Then silica gel supported 4-aminopyridinium chlorochromate (8.4 g, containing 15 mmol of 4-aminopyridinium chlorochromate) was added and the mixture was stirred at ambient temperature for 2 h, during which the progress of the reaction was monitored by TLC. The reaction mixture was filtered and the residue was washed with two 10 ml portions of dichloromethane. The combined filtrates were evaporated, and the residue was passed through a short silica gel pad (eluent: petroleum ether:ethyl acetate = 4:1) to obtain 1.05 g (97%) of pure benzaldehyde.

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