



Silica chloride/ Hydrogen peroxide: Heterogeneous system for oxidation alcohols to corresponding carbonyl compounds

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ABSTRACT

Primary and secondary benzylic alcohols are converted to their corresponding carbonyl compounds efficiently using heterogeneous system "silica chloride/ hydrogen peroxide". In these reactions, further oxidation of the aldehyde to corresponding carboxylic acids was not observed.

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KEYWORDS

Heterogeneous system;
Silica chloride;
Hydrogen peroxide;
Oxidation;
Carbonyl compounds.

INTRODUCTION

Solid supports have found wide applications in organic reactions from different views^[1]. They mostly facilitate the work-up of the reaction mixtures and usually high selectivity accompanied with high yields of the products is observed. Silica gel is one of the extensively used supports for different purposes in organic chemistry^[2]. Modified silica supports for functional group transformation is also interest.

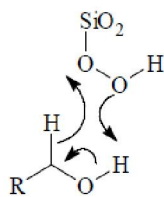
Silica chloride is an important modified silica gel that its preparation and applications has been under attention in recent years. Hojo et al. have prepared SiO₂-Cl by dropwise addition of SOCl₂ to the well-stirred mixture of silica gel in CH₂Cl₂ at room temperature. Then they have removed solvent to dryness under reduced pressure. The SiO₂-Cl was used as an effective catalyst for thioacetalization of carbonyl functions to 1,3-dithiolanes and dithianes^[3].

Very recently, Firouzabadi et al. have modified the

preparation of silica chloride in order to increase the capacity of the reagent^[4]. According to this modification; the reagent can be prepared by the reaction of thionyl chloride (SOCl₂) and silica gel under reflux conditions for 48h in a quantitative yield. SiO₂-Cl is a grayish and stable powder that should be stored in the absence of moisture. Nevertheless, a literature survey shows that less attention has been paid to solid silica chloride as a potential heterogeneous inorganic reagent in organic synthesis.

There are explored new applications of solid silica chloride as a catalyst for trans thioacetalization of acetals and transformation of acylals into the 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes^[5], Modified swern oxidation using dimethyl sulfoxide (DMSO) for selective oxidation of benzylic alcohols^[6], deprotection of thioacetals and silyl and tetrahydropyranyl ethers into their corresponding carbonyl compounds^[7].

Full Paper



Scheme 1

EXPERIMENTAL

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. IR spectral were recorded as neat films or as KBr pellets on a Shimadzu model 8300 FT-IR spectrophotometer. ¹HNMR spectra were recorded on a Bruker DPX-100 instrument with CDCl₃ as solvent and Me₄Si as an internal standard.

General Procedure for Preparation of Chlorinated Silica Gel (SiO₂-Cl)

To an oven dried (120°C, vacuum) silica gel (10 g) in a round bottom flask (250 mL) equipped with a condenser and a drying tube, thionyl chloride (40 mL) was added and refluxed for 48 h. The unreacted thionyl chloride was distilled off. The resulting white-grayish powder was flame-dried and stored in a tightly capped bottle. This silica chloride can be used for months without losing its activity.

General Procedure for Oxidation of Alcohols by using heterogeneous system silica chloride/ hydrogen peroxide

Dichloromethane (10 mL) and SiO₂-Cl (1g) were placed in a 100 mL flask equipped with a magnetic stirrer. 0.5 mL H₂O₂ 30% was added to the stirred solution. Stirring was continued at room temperature for 20 min. To the resulting mixture, alcohol (1mmol) was added. After completion of the reaction which was monitored by TLC 0.5 g of silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was applied on a silica gel pad (2 cm thick). The filter cake was washed with petroleum ether/ethyl acetate (5:1)(50 ml) and the solvent was evaporated to afford carbonyl compounds in

TABLE 1 : Oxidation of alcohol to carbonyl compound by Silica chloride/ Hydrogen peroxide

Yield%	Time (min)	Substrate	Entry
90	30		1
93	30		2
90	20		3
90	120		4
85	12(h)		5
93	30		6
92	60		7
90	40		8
85	120		9
No Reaction			10
No Reaction			11
No Reaction			12

high yields

RESULTS AND DISCUSSION

In this study, oxidation of alcohols using hydrogen peroxide (H_2O_2) in the presence of solid silica chloride is described. As shown in the TABLE, the rate of oxidation and yield of products depended on the nature of the substrate. Oxidations of benzylic alcohols with electron releasing groups (Entry 2-4) are faster than those with electron withdrawing group (Entry 5). 4-nitro benzyl alcohol oxidizes to its corresponding aldehyde at higher time and 85% yield. Cinnamyl alcohol was converted to cinnamaldehyde in a high yield without cleavage of benzylic double bond (Entry 9). Primary and secondary aliphatic alcohols (entry 10-12) did not oxidize under these conditions.

CONCLUSIONS

The reactions are relatively clean with no tar formation and no over oxidation to carboxylic acids. This reaction has several interesting features: 1) Yields are satisfactory. 2) The reaction is specific, avoiding over oxidation of aromatic aldehyde into acid. 3) The reagent is cheap and easy to prepare. 4) The experimental set-up and work-up are exceedingly simple.

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