

Selective Oxidation of Benzylic and Allylic Alcohols with NaOCl/Silica Gel System

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(Received 9 May 2008, Accepted 22 May 2008)

Sodium hypochlorite, a cheap and readily available compound, when supported on silica gel can selectively oxidize benzylic and allylic alcohols to their carbonyl compounds in the presence of catalytic amount of DMSO.

Keywords: Sodium hypochlorite, Oxidation, Alcohol, Catalyst, DMSO

INTRODUCTION

The supported reagent technique has received increasing attention and metallic salts impregnated on clay are most popular reagents for oxidation of organic substrate [1,2]. However, from both economic and environmental viewpoints, there is an urgent demand for greener, more atom efficient methods that employ clean oxidants such as molecular oxygen [3-8], hydrogen peroxide [9] and sodium hypochlorite [10]. These oxidants are highly attractive since they are cheap and produce no toxic waste products in contrast to many commonly employed agents. Aqueous sodium hypochlorite is easy to prepare and has a high percentage of available oxygen. Although it is frequently used reagent, but there are some limitations such as lack of selectivity, over oxidation of alcohols to carboxylic acids and immiscible in organic solvents [11-13]. Therefore, design of new and less polluting oxidation procedures has become a priority for the new chemistry.

EXPERIMENTAL

All the alcohols were purchased from Fluka and Merck companies. The reactions were monitored by TLC using silica

gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230-400 mesh) and were identified by comparison of their spectra and physical data with those of the authentic samples. ¹H NMR spectra were recorded at 300 MHz on a JEOL spectrometer with tetramethylsilane (Me₄Si) as an internal reference and CDCl₃ as the solvent. IR spectra were recorded on a Pye-Unicam SP 1100 spectrophotometer. Elemental analysis was performed on a LECO 250 instrument.

Preparation of NaOCl/SiO₂ as an Oxidizing Agent

To a round bottomed flask (200 ml) was added 20 g silica gel (60-200 mesh) and a solution of 6% NaOCl (50 ml). The suspension was mixed thoroughly and then dried by freeze dryer apparatus. The reagent at this point is a homogeneous, free flowing white powder, which is not sensitive to moisture and light. Storage under an inert dry atmosphere and in a brown bottle appears to greatly increase the shelf time of reagent. Prolonged heating under vacuum produced a powder of no or low utility for the reaction. Potentiometric measurement of NaOCl content in the reagent was found to be 17 mmol NaOCl per 10 g reagent.

Oxidation of 4-Chlorobenzyl Alcohol as a Typical Procedure

NaOCl/SiO₂ (17 mmol, 10 g), 4-chlorobenzyl alcohol (10

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mmol, 1.44 g) and DMSO (2.25 mol%) were added to 25 ml of CH_2Cl_2 . The mixture was refluxed for 5 min and progress of the reaction was monitored by GC. After completion of the reaction, the mixture was filtered and the solvent was removed under reduced pressure. The crude 4-chlorobenzaldehyde was purified using column chromatography (1.39 g, 98 %).

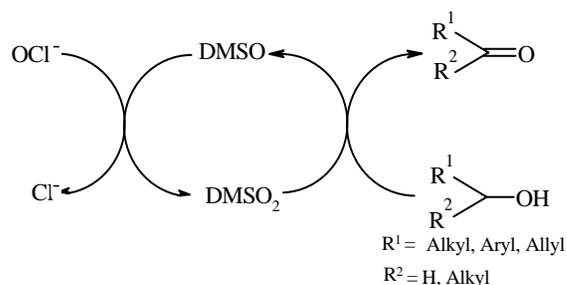
RESULTS AND DISCUSSION

In our on going program to find new procedures for the oxidation of organic compounds [14,15], we have found that sodium hypochlorite in combination with a silica gel in the presence of catalytic amount of DMSO can selectively oxidize benzylic and allylic alcohols and hydroquinone. To start our investigation on the oxidation of organic substrates with sodium hypochlorite/silica gel in nonaqueous media, we have selected benzyl alcohol as a probe substrate. Our attempts failed and only a little amount of benzaldehyde was obtained after even long period of time at refluxing in CH_2Cl_2 . Regarding to previous reports on the use of sodium hypochlorite [16], we found that dimethyl sulfoxide (DMSO) could be used to catalyze the oxidation reaction. In numerous procedures such as the Swern procedure, DMSO in the presence of thionyl chloride [17], sulfur trioxide/Py [18] and acetic anhydride [19] can be used for the oxidation of alcohols.

Recently, Firouzabadi *et al.* reported Swern oxidation for the conversion of alcohols into their corresponding carbonyl compounds using DMSO in the presence of silica chloride [20]. More recently, Miller, *et al.* reported the oxidation of organic substrates using commercial bleach in the presence of Ni catalyst at low temperature (0 °C). This system showed no selectivity in the oxidation of aliphatic and benzylic alcohols and oxidizes primary alcohols to their corresponding carboxylic acids [21].

As such, a mild, efficient and selective method that can be used to promote the transformation of hydroxyl groups into carbonyls by commercial reagent is of increasing important. In this article, we have presented a new method in which traces of DMSO in the presence of NaOCl/silica gel conducts selective oxidation of alcohols to the corresponding aldehydes or ketones (Scheme 1).

In order to find the optimum conditions for oxidation



Scheme 1. Selective oxidation of alcohols to the corresponding aldehydes or ketones using NaOCl/silica gel in the presence of trace of DMSO

reaction, we treated 1:1.7 mole ratios of 4-chlorobenzyl alcohol and NaOCl/silica gel in the presence of trace of DMSO in CH_2Cl_2 , and an excellent yield of 4-chlorobenzaldehyde was obtained after 5 min. To show the generality of this method, we oxidized a variety of benzylic alcohols bearing both electron releasing and electron withdrawing groups on the aromatic ring under optimum reaction conditions and good yields of the corresponding aldehydes and ketones was achieved. The results are shown in Table 1.

As indicated in this Table, primary benzylic alcohols having both electron releasing (Table 1, entry 6) and electron withdrawing groups (Table 1, entries 2-5 and entries 8 and 9) afforded the corresponding carbonyl compounds in good to excellent yields in 5-80 min. Primary benzylic diol also converted to the corresponding dialdehyde in 65% yield (Table 1, entry 10). Cinnamyl alcohol as a representation of primary α,β -unsaturated alcohol is selectively oxidized to the corresponding α,β -unsaturated aldehyde in 70% yield after 40 min (Table 1, entry 11). 2-t-Butyl hydroquinone efficiently converted to 2-t-butyl benzoquinone in high yield after 30 min (Table 1, entry 7). On the contrary, aliphatic alcohols are not oxidized under the same reaction conditions. Even secondary benzylic and secondary α,β -unsaturated alcohols (Table 1, entries 13-15) are oxidized in low yields after 70 min. This observation suggested a possible chemoselective oxidation of primary alcohols in the presence of secondary ones.

In this respect, when we treated an equimolar amount of benzyl alcohol and 1-phenylethanol with one equivalent of NaOCl/Silica gel, after 7 min benzaldehyde was formed in 95% yield and virtually no ketone could be detected by GC (Table 2, entry 1). An even more difficult problem of

Selective Oxidation of Benzylic and Allylic Alcohols

Table 1. Oxidation of Primary and Secondary Alcohols Using NaOCl/Silica Gel^a

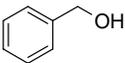
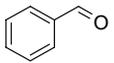
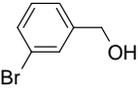
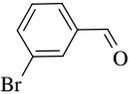
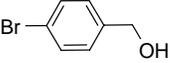
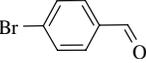
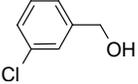
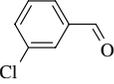
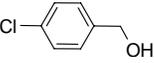
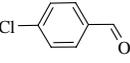
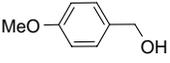
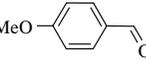
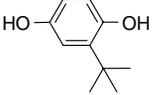
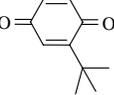
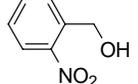
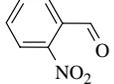
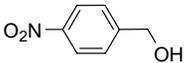
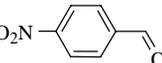
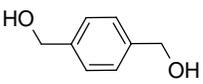
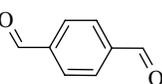
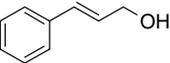
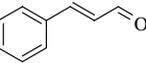
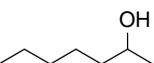
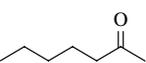
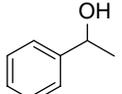
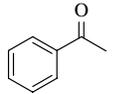
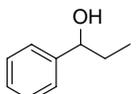
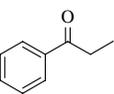
Entry	Substrate	Product ^b	Time (min)	Yield (%) ^c
1			7	98
2			7	94
3			8	91
4			7	94
5			5	98
6			6	90
7			30	80
8			80	75
9			60	80
10			40	65
11			40	70
12			120	n.r.
13			70	30
14			70	25

Table 1. Continued

15			70	20
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^aStandard reaction conditions: 2.25 mol% of DMSO, 10 mmol alcohol, 17 mmol NaOCl/SiO₂, 25 ml of CH₂Cl₂, reflux temperature. ^bStructures are confirmed by IR, ¹H NMR, ¹³C NMR, m.p or b.p. ^cThe isolated products were at least 97% pure.

Table 2. Inter and Intramolecular Selective Oxidation of Primary and Secondary Alcohols^a

Entry	Substrate	Product	Time (min)	Yield (%) ^b
1			7	95
				0
2			55	60
				7
3			40	70
				8
				0.5
4			50	75
				10
				0.5

^aStandard reaction conditions: 2.25 mol% of DMSO, 10 mmol alcohol, 17 mmol NaOCl/SiO₂, 25 ml of CH₂Cl₂, reflux temperature. ^bYields refer to GC yield, and *n*-octane use as a internal standard.

selectivity is that of primary vs. secondary allylic alcohols which gives a 60:7 ratio of aldehyde to ketone in this case (Table 2, entry 2). We next turned to the synthetically more useful case of intramolecular competition between primary and secondary benzylic positions (Table 2, entry 3, 4), which proved to be successful in the oxidation of primary benzylic position.

In conclusion, we have demonstrated a very effective, practical, inexpensive, selective and catalytic method for the oxidation of alcohols with readily available silica gel and commercial bleach. This simple system is stable and safe, and can be handled without any special care. Selective oxidation of benzyl alcohols over aliphatic alcohols, chemoselective oxidation of primary α,β -unsaturated alcohols to the corresponding α,β -unsaturated aldehydes and intramolecular selective oxidation of primary benzylic alcohol in the presence of secondary benzylic alcohol are advantages of this system.

ACKNOWLEDGMENTS

Financial support of this work from the Research Council of Mazandaran University is gratefully acknowledged.

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