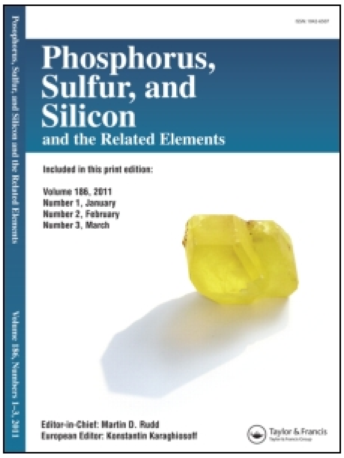

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Heterogeneous Swern Oxidation. Selective Oxidation of Alcohols by DMSO/SiO 2 -Cl System

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HETEROGENEOUS SWERN OXIDATION. SELECTIVE OXIDATION OF ALCOHOLS BY DMSO/SiO_2-Cl SYSTEM

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Dimethyl sulfoxide in the presence of solid SiO_2-Cl in CH_2Cl_2 at $-60^\circ C$ rapidly converts benzyl alcohols to their corresponding carbonyl compounds in high yields.

Keywords: Alcohols; carbonyl compound; dimethyl sulfoxide; oxidation; silica chloride; swern oxidation

INTRODUCTION

Oxidation of primary and secondary alcohols to the corresponding carbonyl compounds using dimethyl sulfoxide (DMSO) is widely used in organic synthesis.[1] The first procedure for alcohol oxidation using DMSO is reported by Pfitzner and Moffatt, and involves activation of the DMSO by dicyclohexylcarbodiimide (DCC).[2] In the Swern procedure, dimethyl sulfoxide (DMSO) in the presence of oxalyl chloride,[3,4] thionyl chloride,[4] trifluoro acetic anhydride,[5] sulfur trioxide/Py,[6] and acetic anhydride[7] can be used for the oxidation of alcohols. Handling of oxalyl chloride, thionyl chloride, and acid anhydrides especially for the large-scale operations is hazardous and not so easy. The dimethyl sulfoxide/acetic anhydride procedure needs long reaction times (18–48 h) and is usually contaminated with thiomethyl ethers as by products.[7,8] In order to reduce the hazards and also to improve the selectivity of Swern oxidation, in this article, we have presented a new method in which DMSO in the presence of solid silica chloride conducts selective oxidation of benzyl alcohols.

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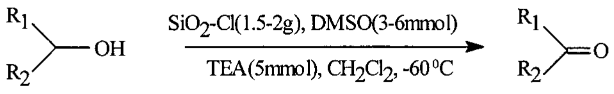
RESULTS AND DISCUSSION

Silica chloride has been prepared from the reaction of silica gel with thionyl chloride and reported to be an efficient reagent for the selective thioacetalization of carbonyl compounds and transformation of sulfoxides to the thioethers.[9] Very recently, we have modified the preparation of silica chloride in order to increase the capacity of the reagent.[10] According to this modification, the reagent can be prepared by the reaction of thionyl chloride ($SOCl_2$) and silica gel under reflux conditions for 48 h in a quantitative yield. SiO_2-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.

We have explored new applications of solid silica chloride as a catalyst for transthioacetalization of acetals and transformation of acylals into the 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes.[10] Now, we report a modified Swern oxidation using dimethyl sulfoxide (DMSO) in the presence of solid silica chloride for the selective oxidation of benzylic alcohols. The handling and storage of solid silica chloride is much easier than oxalyl chloride; thionyl chloride, trifluoro acetic anhydride, sulfur trioxide/Py, and acetic anhydride that are corrosive liquids with high vapor pressures. Solid silica chloride also is a suitable reagent for the large-scale operations.

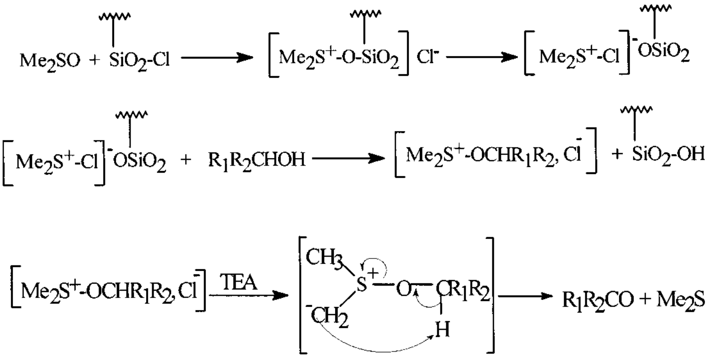
A solution of DMSO in dry CH_2Cl_2 was added dropwise to the previously cooled SiO_2—Cl (−60°C) and then a solution of an alcohol in CH_2Cl_2 was added to the mixture of DMSO/SiO_2—Cl while the temperature was kept at −60°C. By the addition of triethylamine (TEA) to the mixture and raising the temperature to 25°C the desired carbonyl compounds were produced in high yields (Scheme 1 and Table I). We also have proposed a mechanism (Scheme 2) for this system in which the role of solid silica chloride is clarified.



R_1= alkyl, aryl, cinammyl
R_2= H, alkyl, aryl

SCHEME 1

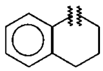
As shown in Table I, various types of benzylic alcohols with electron-releasing and electron-withdrawing groups were converted efficiently to their corresponding carbonyl compounds in 85–93% yields. Cinnamyl



SCHEME 2

alcohol was converted to cinnamaldehyde in a high yield without the cleavage of the benzylic double bond. Surprisingly, 3-phenyl-1-propanol (Table I, entry 14) was converted to the corresponding carbonyl compound in 80% yield whereas, 2-phenylethanol remained almost intact. We do not have any reasonable explanation for this result.

TABLE I Oxidation of Alcohols by DMSO/-SiO_2Cl in CH_2Cl_2 at −60°C

			Conversion[a]			
Entry	R_1	R_2	RCH_2OH	RCHO	-SiO_2-Cl (gr)	Yield[b,c,d] (%)
1	Ph	H	0	100	1.5	85
2	4-$(CH_3O)C_6H_4$	H	0	100	1.5	88
3	4-$(CH_3)C_6H_4$	H	0	100	2	90
4	4-$(Cl)C_6H_4$	H	0	100	2	90
5	4-$(NO_2)C_6H_4$	H	5	95	2	90
6	2-$(NO_2)C_6H_4$	H	7	93	2	85
7	Ph	Ph	0	100	2	93
8	Ph	CH_3	0	100	2	92
9	PhCO	Ph	0	100	2	90
10	PhCH=CH	H	7	93	2	90
11			5	95	2	85
12	$CH_3(CH_2)_5CH_2$	H	50	50	2	35
13	$CH_3(CH_2)_4CH_2$	CH_3	70	30	2	25
14	$PhCH_2CH_2$	H	15	85	2	80
15	$PhCH_2$	H	85	15	2	5

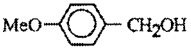
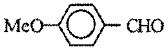
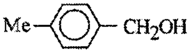
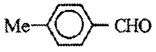
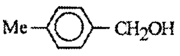
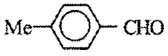
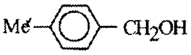
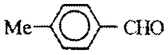
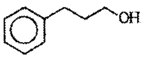
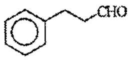
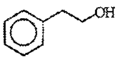
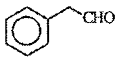
[a] Conversion was determined by GC and NMR.

[b] Yields refer to isolated products.

[c] Structures are confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, mp/bp.

[d] Benzaldehyde was isolated as its 2,4-dinitrophenyl-hydrazine derivative.

TABLE II Selective Oxidation of Alcohols by DMSO/-SiO_2Cl in CH_2Cl_2 at −60°C

Entry	Substrate	Product	Yield[a]
1			100
	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	0
2			100
	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	0
3			100
	$CH_3(CH_2)_5CH(OH)CH_3$	$CH_3(CH_2)_5COCH_3$	0
4			90
	$Ph(CH_2)_2CH_2OH$	$Ph(CH_2)_2CHO$	10
5	$Ph(CH_2)_2CH_2OH$	$Ph(CH_2)_2CHO$	80
	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	5
6			80
			0

[a]GC yield.

In order to show the chemoselectivity of the method for the oxidation of different alcohols, we have performed a number of competitive reactions and their results are tabulated in Table II. These results clearly show that the presented method is potentially applicable for the chemoselective oxidation of benzylic alcohols versus saturated alcohols (Table II, entries 1–4). 3-phenyl-1-propanol was easily converted to the corresponding aldehyde in a good yield in the presence of 1-octanol (Table II, entry 5). 3-Phenyl-1-propanol in the presence of 2-phenylethanol was oxidized with high selectivity in 80% yield whereas, 2-phenylethanol remained intact (Table II, entry 6).

EXPERIMENTAL SECTION

General Procedure

Methylene chloride (10 ml) and SiO_2-Cl (1.5–2 g) were placed in a 100 ml flask equipped with a magnetic stirrer. The contents of the flask were cooled below −60°C and DMSO (3–5 mmol) in CH_2Cl_2 (5 ml) was added dropwise to the stirred cold solution in 5 min. Steering was continued at −60°C for 20 min. To the resulting mixture, a solution of an alcohol (1 mmol) in CH_2Cl_2 (5–10 ml) was added dropwise in 5 min. The mixture was stirred at −60°C for 10 min followed by the dropwise addition of TEA (5 ml) in CH_2Cl_2 for 5 min. The reaction mixture was allowed to warm up to room temperature and then H_2O (50 ml) was added to the mixture. The aqueous layer was separated and extracted with another portion of CH_2Cl_2 (50 ml). The organic extracts were combined and washed with dilute aqueous solution of HCl (1%, 50 ml), H_2O (50 ml), dilute aqueous solution of $NaHCO_3$ (5%, 50 ml) and H_2O (50 ml). The resulting organic solution was evaporated to dryness to give the highly pure corresponding carbonyl compound (Table I).

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