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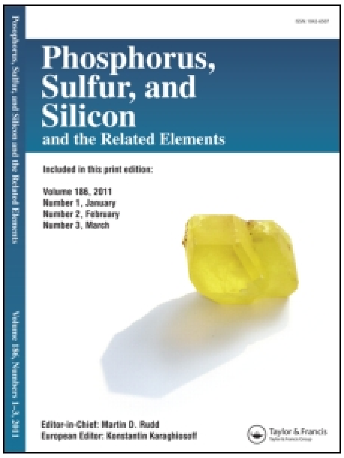

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Silica Chloride/Wet SiO_2 as a Novel Heterogeneous System for the Deprotection of Acetals Under Mild Conditions

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SILICA CHLORIDE/WET SiO_2 AS A NOVEL HETEROGENEOUS SYSTEM FOR THE DEPROTECTION OF ACETALS UNDER MILD CONDITIONS

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Tehran, Iran;[b] *Bu-Ali Sina University, Hamadan, Iran;*[c]
and Kashan University, Kashan, Iran[d]

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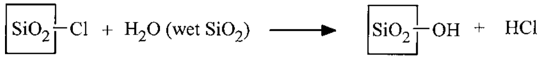
A combination of silica chloride and wet SiO_2 was used as an effective deacetalizating agent for the conversion of acetals to their corresponding carbonyl derivatives under mild and heterogeneous condition.

Keywords: Deacetalization; silica chloride

There is current general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.[1] In continuation of our studies on the application of heterogeneous systems[2] we found that silica chloride[3,4] (**I**) is an excellent source for generation of HCl. It is interesting to note that the addition of wet SiO_2 to the reaction mixture containing silica chloride generates HCl in situ (Scheme 1). Therefore, we used it for a different purposes.[4] We also were interested in using reagent (**I**) for the conversion of acetals to their corresponding carbonyl derivatives. We report on a simple



I

SCHEME 1

Financial support for this work by Research Affairs, Yazd University, Yazd, Iran and Bu-Ali Sina University, Hamadan, Iran, is gratefully acknowledged.

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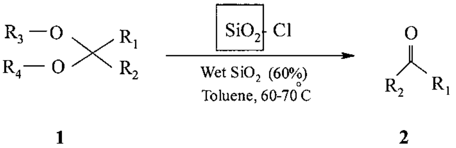
method for the effective conversion of acetals to their corresponding carbonyl derivatives under mild and heterogeneous condition. (Scheme 2 and Table I).



SCHEME 2

Acetals are widely used as protecting groups in organic synthesis and, as a consequence, many methods have been examined for both their formation and removal.[6,7] Typically, deprotection of acetals requires the use of protic[8] or Lewis acids,[9] iodotrimethylsilane,[10] cobalt, or manganese salts in the presence of air or O_2,[11] pyridinium tosylate,[12] montmorillonite K10,[13] ceric ammonium nitrate (CAN),[14] etc.

We hoped that the silica chloride (**I**)/wet SiO_2 system would be a superior proton source to all of the reported acidic solid supports or acidic resins such as polystyrene sulfonic acid and Nafion-H[15] for running reactions under heterogeneous conditions. Here, we report on a convenient method for the deacetalization of acetals by using silica chloride (**I**) and wet SiO_2 (**II**) under heterogeneous conditions (Scheme 2).

Different types of acetals (**I**) were subjected to the deacetalization reaction in the presence of silica chloride and wet SiO_2 (60% *w*/*w*) under mild and heterogeneous condition with quantitative yields. we used toluene as a solvent at 60–70°C. The results of deacetalization were shown in Table I.

In conclusion, a cost-effective and easy procedure for the effective conversion of acetals to their corresponding carbonyl derivatives has been achieved. The low cost and availability of the reagents, easy procedure, and work-up make this method attractive for organic chemists.

EXPERIMENTAL SECTION

General

Chemicals such as carbonyl compounds, ethylene glycol, thionyl chloride, and silica gel were purchased from the chemicals companies Fluka, Merck, and Aldrich. Acetals and 5-norbornene-2,2-dimethyl-1-ol were synthesized according to the our previously reported procedure.[6] Silica chloride was synthesized according to the reported procedure.[3,4]

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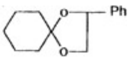
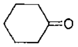
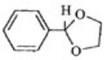
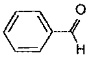
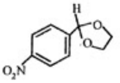
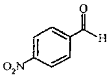
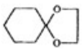
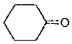
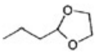
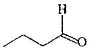
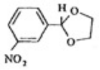
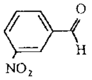
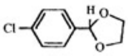
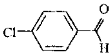
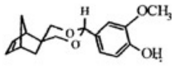
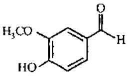
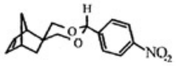
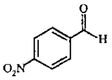
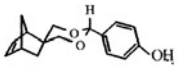
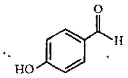
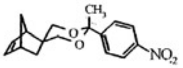
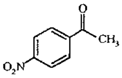
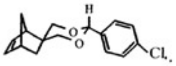
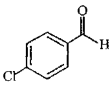
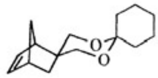
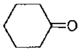
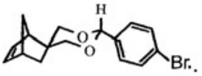
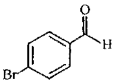
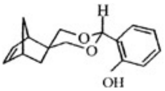
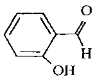
TABLE I Deprotection of Acetals by Silica Chloride (**I**) and Wet SiO_2 (**II**) in Toluene at 60–70°C

Entry	Substrate	$Substrate_{(mmol)}$/ $I_{(g)}/II_{(g)}$	Time (min)	$Yield_{(\%)}$	Product
1a		0.25/0.4/0.5	90	85^a	
1b		0.25/0.3/0.5	60	92^a	
1c		0.25/0.3/0.5	60	94	
1d		0.25/0.35/0.5	90	80^a	
1e		0.25/0.3/0.5	60	75^a	
1f		0.25/0.3/0.5	60	90	
1g		0.25/0.3/0.5	60	92	
1h		0.25/0.4/0.6	70	92	
1i		0.25/0.4/0.5	45	95	
1j		0.25/0.45/0.5	60	90	
1k		0.25/0.45/0.5	80	93	
1l		0.25/0.4/0.5	60	90	
1m		0.25/0.4/0.5	90	82^a	
1n		0.25/0.4/0.5	60	92	
10		0.25/0.45/0.5	70	93	

[a]The isolated yields are based on weight of 2,4-Dinitro phenyl hydrazone derivative.

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The deacetalization products were characterized by comparison of their spectral (IR, ^{1}H-NMR), TLC, and physical data with that of authentic samples.

Deacetalization of (1i) to the Corresponding Aldehyde (2i). A Typical Procedure

A mixture of **1i** (0.07 g, 0.25 mmol), silica chloride (**I**) (0.4 g) and wet SiO_2 (**II**) (60% w/w, 0.5 g) in toluene (3 mL) was heated at 60–70°C for 45 min. Then the solvent was removed under reduced pressure. By addition of ethanol and water, 4-nitrobenzaldehyde (**2i**) was obtained in quantitative yield.

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