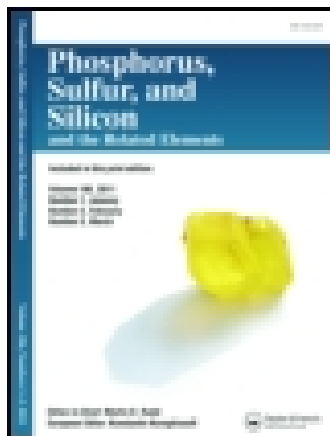


This article was downloaded by: [Imperial College London Library]

On: 08 October 2014, At: 01:18

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

### Silica Chloride/Wet SiO<sub>2</sub> as a Novel Heterogeneous System for the Deprotection of Acetals Under Mild Conditions

BiBi Fatemeh Mirjalili<sup>a</sup>, Ali Pourjavadi<sup>b</sup>, Mohammad Ali Zolfigol<sup>c</sup> & Abdolhamid Bamoniri<sup>d</sup>

<sup>a</sup> Yazd University, Yazd, Iran

<sup>b</sup> Sharif University of Technology, Tehran, Iran

<sup>c</sup> Bu-Ali Sina University, Hamadan, Iran

<sup>d</sup> Kashan University, Kashan, Iran

Published online: 18 Jun 2010.

To cite this article: BiBi Fatemeh Mirjalili, Ali Pourjavadi, Mohammad Ali Zolfigol & Abdolhamid Bamoniri (2003) Silica Chloride/Wet SiO<sub>2</sub> as a Novel Heterogeneous System for the Deprotection of Acetals Under Mild Conditions, Phosphorus, Sulfur, and Silicon and the Related Elements, 178:12, 2667-2670, DOI: [10.1080/714040981](https://doi.org/10.1080/714040981)

To link to this article: <http://dx.doi.org/10.1080/714040981>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

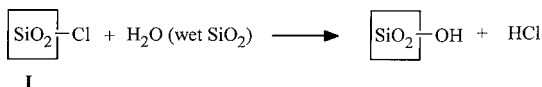
## SILICA CHLORIDE/WET SiO<sub>2</sub> AS A NOVEL HETEROGENEOUS SYSTEM FOR THE DEPROTECTION OF ACETALS UNDER MILD CONDITIONS

*BiBi Fatemeh Mirjalili,<sup>a</sup> Ali Pourjavadi,<sup>b</sup>  
Mohammad Ali Zolfigol,<sup>c</sup> and Abdolhamid Bamoniri<sup>d</sup>  
Yazd University, Yazd, Iran,<sup>a</sup> Sharif University of Technology,  
Tehran, Iran,<sup>b</sup> Bu-Ali Sina University, Hamadan, Iran,<sup>c</sup>  
and Kashan University, Kashan, Iran<sup>d</sup>*

*A combination of silica chloride and wet SiO<sub>2</sub> was used as an effective deacetalizing 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.<sup>1</sup> In continuation of our studies on the application of heterogeneous systems<sup>2</sup> we found that silica chloride<sup>3,4</sup> (**I**) is an excellent source for generation of HCl. It is interesting to note that the addition of wet SiO<sub>2</sub> to the reaction mixture containing silica chloride generates HCl in situ (Scheme 1). Therefore, we used it for a different purposes.<sup>4</sup> We also were interested in using reagent (**I**) for the conversion of acetals to their corresponding carbonyl derivatives. We report on a simple

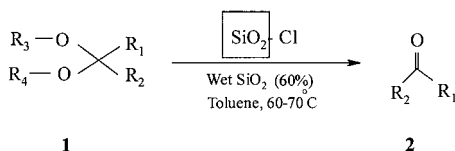


**SCHEME 1**

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

Address correspondence to Mohammad Ali Zolfigol, Department of Chemistry, Bu-Ali Sina University, PO Box 4135, Hamadan 65174, Iran. E-mail: Zolfi@basu.ac.ir

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.<sup>6,7</sup> Typically, deprotection of acetals requires the use of protic<sup>8</sup> or Lewis acids,<sup>9</sup> iodotrimethylsilane,<sup>10</sup> cobalt, or manganese salts in the presence of air or O<sub>2</sub>,<sup>11</sup> pyridinium tosylate,<sup>12</sup> montmorillonite K10,<sup>13</sup> ceric ammonium nitrate (CAN),<sup>14</sup> etc.

We hoped that the silica chloride (I)/wet SiO<sub>2</sub> 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<sup>15</sup> 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<sub>2</sub> (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<sub>2</sub> (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.<sup>6</sup> Silica chloride was synthesized according to the reported procedure.<sup>3,4</sup>

**TABLE I** Deprotection of Acetals by Silica Chloride (I) and Wet SiO<sub>2</sub> (II) in Toluene at 60–70°C

Entry	Substrate	Substrate <sub>(mmol)</sub> / I <sub>(g)</sub> /II <sub>(g)</sub>	Time (min)	Yield(%)	Product
1a		0.25/0.4/0.5	90	85 <sup>a</sup>	
1b		0.25/0.3/0.5	60	92 <sup>a</sup>	
1c		0.25/0.3/0.5	60	94	
1d		0.25/0.35/0.5	90	80 <sup>a</sup>	
1e		0.25/0.3/0.5	60	75 <sup>a</sup>	
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 <sup>a</sup>	
1n		0.25/0.4/0.5	60	92	
1o		0.25/0.45/0.5	70	93	

<sup>a</sup>The isolated yields are based on weight of 2,4-Dinitro phenyl hydrazone derivative.

The deacetalization products were characterized by comparison of their spectral (IR,  $^1\text{H-NMR}$ ), 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  $\text{SiO}_2$  (**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.

### REFERENCES

- [1] a) I. M. Riego, Z. Sedin, J. M. Zaldivar, N. C. Marziano, and C. Tortato, *Tetrahedron Lett.*, **37**, 513 (1996); b) N. J. Turro, *Tetrahedron*, **43**, 1589 (1987).
- [2] M. A. Zolfigol, *Tetrahedron*, **57**, 9509 (2001).
- [3] F. Mohanazadeh, A. R. Momeni, and Y. Rangbar, *Tetrahedron Lett.*, **33**, 6127 (1994).
- [4] H. Firouzabadi, N. Iranpoor, B. Karimi, and H. Hazarkhani, *Synlett*, 263 (2000).
- [5] a) M. A. Zolfigol, M. Torabi, and S. E. Mallakpour, *Tetrahedron*, **57**, 8381 (2001); b) M. A. Zolfigol, F. Shirini, and A. Ghorbani Choghamarani, *Synth. Commun.*, **32**, 1809 (2002).
- [6] A. Pourjavadi and B. F. Mirjalili, *J. Chem. Research (S)*, 562 (1999).
- [7] a) H. Firouzabadi, N. Iranpour, and M. A. Zolfigol, *Bull. Chem. Soc. Jap.*, **71**, 2169 (1998); b) B. F. Mirjalili, M. A. Zolfigol, and A. H. Bamoniri, *J. Korean Chem. Soc.*, **45**, 546 (2001).
- [8] T. W. Green and P. G. M. Wuts, *Protective Groups in Organic Synthesis* (John Wiley and Sons, Inc. New York, 1991).
- [9] S. E. Sen, S. L. Roach, J. K. Boggs, G. J. Ewing, and J. Magrath, *J. Org. Chem.*, **62**, 6684 (1997).
- [10] D. N. Butler, B. Halton, and R. N. Warrener, *Aus. J. Chem.*, **53**, 561 (2000).
- [11] M. M. Hashemi and F. Kalantari, *Synth. Commun.*, **30**, 1857 (2000).
- [12] R. Sterzycki, *Synthesis*, 724 (1979).
- [13] E. G. L. Gautier, A. E. Graham, A. Mckillop, S. P. Standen, and R. J. K. Taylor, *Tetrahedron Lett.*, **38**, 1881 (1997).
- [14] A. Ates, A. Gautier, B. Leroy, J. M. Plancher, Y. Quesnel, and I. E. Marko, *Tetrahedron Lett.*, **40**, 1799 (1999).
- [15] G. A. Olah, R. Molhotra, and S. C. Narang, *J. Org. Chem.*, **43**, 4628 (1978).