

Acetalization of Carbonyl Compounds by Using Silica-bound Sulfuric Acid under Green Condition

Bi Bi Fatemeh Mirjalili,^{*} Mohammad Ali Zolfigol,^{*} Abdolhamid Bamoniri,[‡] and Azizeh Hazar

Department of Chemistry, College of Science, Yazd University, P.O. Box 89195-741, Yazd, Iran

[‡]Department of Chemistry, College of Science, Bu-Ali Sina University, P.O. Box 4135, Hamadan 65174, Iran

^{*}Department of Chemistry, College of Science, Kashan University, Kashan 51167, Iran

Received October 24, 2003

Aldehydes and ketones were converted to their corresponding acetals in the presence of silica-bound sulfuric acid in *n*-hexane under mild and heterogeneous conditions with excellent yields.

Key Words : Acetalization, Silica-bound sulfuric acid, Heterogeneous conditions

Introduction

The protection of aldehydes and ketones by the formation of acetals or ketals is important in the preparation of a variety of multi functional organic molecules. Acetals as a functional group which is stable under neutral and basic conditions are not only the most widely used protecting groups but are also efficient chiral auxiliary groups for enantioselective synthesis.^{1,2} Numerous procedures have described the formation of acetals under acidic conditions. Protic acid such as polyaniline-supported sulfuric acid,³ pyridinium salts,⁴ Lewis acids such as SbCl₃,⁵ WCl₆,⁶ ZrCl₄,⁷ DDQ,⁸ NBS,⁹ Envirocat EPZG,¹⁰ iodine,¹¹ ion exchange resins such as titanium cation- exchange montmorillonite,¹² transition metal complexes such as rhodium, ruthenium and iridium complexes¹³ have been developed for the acetalization of carbonyl compounds. From the standpoint of environmental demand for chemical processes, much attention has been paid to development of solid reagents for acetal formations. On the other hand, any reduction in the amount of sulfuric acid needed and /or any simplification in handling procedures is required for risk reduction, economic advantage and environmental protection.

Some heterogeneous methods for organic synthesis have been described either a solid acid as catalyst or a supported catalyst. These solids are readily separable from the product by simple filtration and they are recyclable. In addition there is a current research and general interest in heterogeneous systems in industry and in developing technologies.

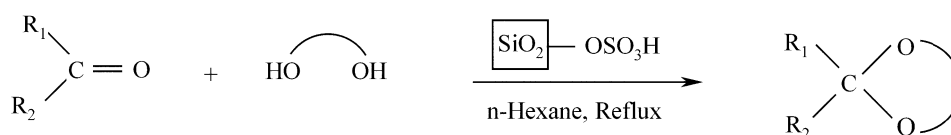
Results and Discussion

Recently, we have reported the preparation of silica-bound sulfuric acid as a stable acidic reagent (solid acid) and showed its catalytic activity in synthetic methodology.¹⁴ The acidity of the prepared silica-bound sulfuric acid is 2.6 mmole H⁺g⁻¹. In continuation of our studies in this regard, here we wish to report another application of silica-bound sulfuric acid, for the acetalization of carbonyl compounds under mild and heterogeneous condition. Different kinds of diols and carbonyl compounds were subjected to the acetalization reaction in the presence of silica-bound sulfuric acid in *n*-hexane under reflux condition (Scheme 1 and Table 1). After completion of the reaction, the heterogeneous mixture was filtered and the solid residue was washed with dichloromethane. The solid residue is silica-bound sulfuric acid, which was recycled easily. Running the reactions with recycled silica-bound sulfuric acid for three times show that no decrease in the yield was observed. This means that silica-bound sulfuric acid can be reused for several times.

We hoped that the silica-bound sulfuric acid would be a superior reagent to some of the older reported procedures for running acetalization reaction under heterogeneous conditions.

Conclusion

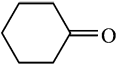
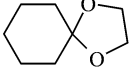
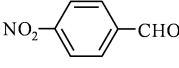
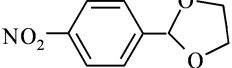
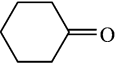
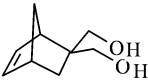
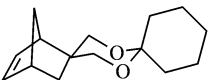
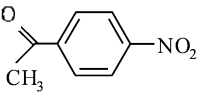
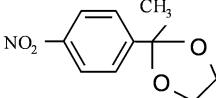
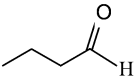
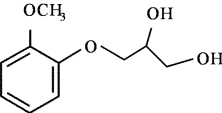
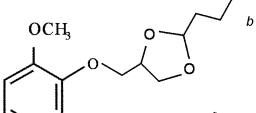
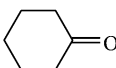
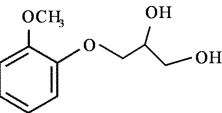
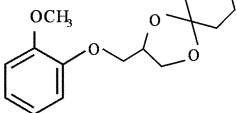
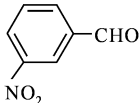
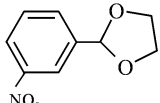
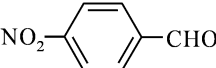
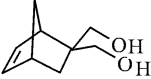
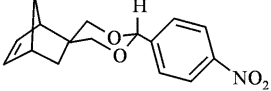
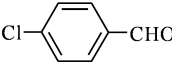
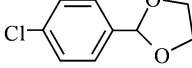
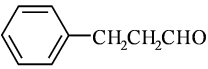
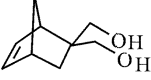
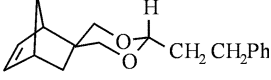
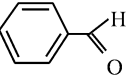
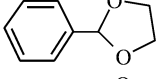
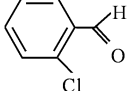
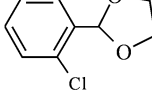
Silica-bound sulfuric acid can serve as an efficient catalyst for the acetalization of carbonyl compounds under mild and heterogeneous conditions. The yields are good to excellent and the procedure is simple and convenient. Moreover, the



Scheme 1

^{*}Corresponding Author. e-mail: fmirjalili@yazduni.ac.ir

Table 1. acetalization of carbonyl compounds with various diols by using Silica bound sulfuric acid under heterogeneous condition^a

Entry	Carbonyl compound (I)	Diol (II)	Product (III)	Time (min)	Yield (%)
a		HOCH ₂ CH ₂ OH		60	85
b		HOCH ₂ CH ₂ OH		60	90
c				60	75
d		HOCH ₂ CH ₂ OH		140	85
e				60	85
f				60	75
g		HOCH ₂ CH ₂ OH		60	88
h				60	92
i		HOCH ₂ CH ₂ OH		60	85
j				60	80
k		HOCH ₂ CH ₂ OH		60	58
l		HOCH ₂ CH ₂ OH		60	85

^aReaction condition: I (1 mmole), II (1 mmole), Silica-bound sulfuric acid (0.2 gr) and *n*-Hexan (5 ml.), reflux for 60-140 min. ^bthis compound is a mixture of two diastereomeric forms.

new element here is that the reaction is heterogeneous and this could be worthwhile in an industrial setting for innovative green chemical manufacturing in the future.¹⁵

The availability of the reagent, easy and clean work-up and high yield make this method attractive for organic synthesis.

Experimental Section

General. Chemicals such as carbonyl compounds, ethylene glycol, and guaiacol glyceryl ether were purchased from

Fluka, Merck and Aldrich chemical companies. Silica-bound sulfuric acid^{14a} and 5-Norbornene-2,2-dimethylol¹⁰ were synthesized according to our previous reported procedure. The acetalization products were characterized by comparison of their spectral (IR, ¹H-NMR), TLC and physical data with the authentic samples.

General procedure for the preparation of acetals or ketals. A suspension of carbonyl compound, diol and silica-bound sulfuric acid in *n*-hexane were stirred under reflux condition for 60-140 minutes (Table 1). The progress of the reaction was followed by TLC. After completion of the

Table 2. Spectral data of the acetals and ketals

Product No.	Structure of Product	IR v. cm ⁻¹ , KBr pellets	¹ H-NMR ^a δ, ppm, CDCl ₃
IIIa		2980 (C-H), 1460 (CH ₂), 1375 (CH ₂), 1100 (C-O)	1.4 (m, 10H, CH ₂), 3.8 (s, 4H, CH ₂ O)
IIIb		1530 (N=O), 1350 (N=O), 1100 (C-O)	3.8 (s, 4H, CH ₂ O), 5.5 (1H, s, O-CH-O), 7.4 (d, 2H, Ar-H), 7.9 (d, 2H, Ar-H)
IIIc		1650 (=CH), 1461 (CH ₂), 1375 (CH ₂), 1100 (C-O)	0.78 (dbr, 1H), 1.3 (dd, 1H), 1.4-1.7 (m, 12H), 2.7 (s, 1H), 2.9 (s, 1H), 3.4-3.7 (m, 4H), 6 (sbr, 2H)
IIIc ^b		1460 (CH ₂), 1376 (CH ₃), 1100 (C-O)	Diastereomer A: 0.9 (t, J = 7.5 Hz, 3H), 1.4 (m, 2H), 1.7 (m, 2H), 3.84 (s, OCH ₃), 3.9 (dd, J = 9.5 and 7 Hz, 1H), 4 (dd, J = 5.2 and 9.5 Hz, 1H), 4.15 (dd, J = 5.2 and 10 Hz, 1H), 4.25 (dd, J = 8 and 7 Hz, 1H), 4.5 (m, 1H), 5 (t, J = 4.8 Hz, 1H), 6.9 (m, 4H) Diastereomer B: 0.9 (t, J = 7.5 Hz, 3H), 1.4 (m, 2H), 1.7 (m, 2H), 3.8 (t, J = 8 Hz, 1H), 3.84 (s, OCH ₃), 3.99 (m, 2H), 4.09 (dd, J = 5.2 and 9.5 Hz, 1H), 4.5 (m, 1H), 4.93 (t, J = 4.8 Hz, 1H), 6.9 (m, 4H)
IIIf		1500, 1600 (C=C), 1450 (CH ₂), 1375 (CH ₃), 1100-1250 (C-O)	1.4 (m, 2H), 1.6 (m, 8H), 3.8 (s, OCH ₃), 3.9 (m, 2H), 4.1 (m, 2H), 4.5 (m, 1H), 7 (m, 4H)
IIIg		3100 (=CH), 1500, 1600 (C=C), 1530 (N=O), 1350 (N=O), 1100 (C-O)	3.9 (m, 4H), 5.6 (s, 1H), 7.3-8 (m, 4H)
IIIh		3100 (=CH), 1607 (C=C), 1523 (N=O), 1353 (N=O), 1115 and 1038 (C-O)	0.6 (dbr, J = 12 Hz, 1H), 1.15 (dd, J = 12 and 3.6 Hz, 1H), 1.5 (sbr, 2H), 2.8 (sbr, 1H), 3.2 (sbr, 1H), 3.6 (d, J = 12 Hz, 1H), 3.9 (d, J = 12 Hz, 1H), 4 (d, J = 12 Hz, 1H), 4.1 (d, J = 12 Hz, 1H), 5.5 (s, 1H), 6.2 (sbr, 1H), 6.25 (sbr, 1H), 7.7 (d, J = 8.6 Hz, 2H), 8.2 (d, J = 8.6 Hz, 2H)
IIIi		3050 (=CH), 1500 and 1600 (C=C), 1100-1300 (C-O)	3.8 (s, 4H), 5.6 (s, 1H), 7.3 (d, 2H), 7.5 (d, 2H)
IIIj		3050 (=CH), 1453 (CH ₂), 1030 and 1238 (C-O)	0.4 (dbr, J = 12 Hz, 1H), 1 (dd, J = 12 and 3.6 Hz, 1H), 1.4 (m, 2H), 1.9 (m, 2H), 2.1 (sbr, 1H), 2.7 (td, 2H), 3.2 (sbr, 1H), 3.5 (m, 2H), 3.7 (m, 2H), 4.3 (t, 1H), 6.1 (m, 2H), 7.2 (m, 5H)

^aH-NMR spectra were recorded on FT-NMR (90 MHz). ^bthis compound is a mixture of two diastereomer and ¹H-NMR spectra was recorded on FT-NMR (500 MHz)

reaction, the heterogeneous mixture was filtered and washed with dichloromethane. Then the solvent was removed under reduced pressure and crude product was isolated. After purification, the structure of products were characterized by their spectral (IR, ¹H-NMR) data. (Table 2).

Preparation of acetal (IIIh) from *p*-Nitrobenzaldehyde.

A mixture of *p*-nitrobenzaldehyde (0.15 g, 1 mmole), 5-norbornene-2,2- dimethylol, (0.15 g, 1 mmole), silica-bound sulfuric acid (0.2 g) and *n*-hexane (5 mL) were heated under reflux condition for 60 minutes. Then the heterogeneous mixture was filtered and washed with dichloromethane. The solvent was removed under reduced pressure. After addition of ethanol and water, the acetal as pure solid was obtained. Yield: 0.25 g, 90%, m.p: 123-125 °C. [Lit¹⁶ m.p: 124 °C].

Acknowledgment. Financial support for this work by the research affairs, Yazd University, Bu-Ali Sina University, Kashan University, are gratefully acknowledged and also Mr. F. Fallah and Mr.H. Babazadeh for their helps.

References

- Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
- Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd Ed.; John Wiley: New York, U. S. A., 1999; p 293.
- Palaniappan, S.; Narender, P.; Saravanan, C.; Rao, V.-J. *Synlett* **2003**, *12*, 1793.
- Sterzycki, R. *Synthesis* **1979**, 724.
- Wang, W.-B.; Shi, L.-L.; Huang, Y.-Z. *Tetrahedron* **1990**, *46*, 3315.
- Firouzabadi, H.; Iranpoor, N.; Kamiri, B. *Synth. Commun.* **1999**, *29*, 2255.

7. Firouzabadi, H.; Iranpoor, N.; Kamiri, B. *Synlett* **1999**, 321.
 8. Karimi, B.; Ashtiani, A. *Chem. Lett.* **1999**, 28, 1199.
 9. Karimi, B.; Seradj, H.; Ebrahimian, G. R. *Synlett* **1999**, 1456.
 10. Bandgar, B. P.; Gaikwad, N. B. *Monsh. Chem.* **1998**, 129, 719.
 11. Tomonori, K.; Tomoo, M.; Kohki, E. *Tetrahedron Lett.* **2001**, 42, 8329.
 12. Basu, M. K.; Samajdar, S.; Becker, F. F.; Banik, B. K. *Synlett* **2002**, 319.
 13. (a) Ott, J.; Tombo, G. M.; Ramos, S. B.; Venanzi, L. M.; Wang, G.; Ward, T. R. *Tetrahedron Lett.* **1989**, 30, 6151. (b) Sueiue, M.; Venanzi, L. M. *Helv. Chem. Acta* **2001**, 84, 898.
 14. (a) Zolfigol, M. A. *Tetrahedron* **2001**, 57, 9509. (b) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A. *J. Korean Chem. Soc.* **2001**, 45, 546. (c) Zolfigol, M. A.; Bamoniri, A. *Synlett* **2002**, 1621. (d) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A. *Molecules* **2002**, 7, 751. (e) Zolfigol, M. A.; Ghaemi, E.; Madrakian, E. *Molecules* **2002**, 7, 734. (e) Zolfigol, M. A.; Shirini, F.; Ghorbani-Choghamarani, A.; Mohammadpoor-Baltork, I. *Green Chem.* **2002**, 4, 562. (f) Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Bodaghi-fard, M. A. *Tetrahedron Lett.* **2003**, 44, 2889. (g) Zolfigol, M. A.; Chehardoli, G. A.; Mallakpour, S. E. *Synth. Commun.* **2003**, 33, 833.
 15. Clark, J. H. *Acc. Chem. Res.* **2002**, 35, 791.
 16. Pourjavadi, A.; Mirjalili, B. B. F. *J. Chem. Resesrch(S)* **1999**, 562.
-