Silica Sulfuric Acid: An Efficient Catalyst for the Direct Conversion of **Primary and Secondary Trimethylsilyl Ethers to their Corresponding Ethers** under Mild and Heterogeneous Conditions

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conditions

Abstract: Primary and secondary trimethylsilyl ethers were converted to their corresponding ethers in the presence silica sulfuric acid with good to excellent yields under mild and heterogeneous conditions.

1 Scheme 1 Keywords: silica sulfuric acid, silyl ethers, ethers, heterogeneous

Symmetrical and unsymmetrical alkyl/aryl ether formation is an important reaction in organic synthesis and has generated significant interest in recent years.¹⁻⁸ Methods to effect this transformation include the classic Williamson procedure, the Mitsunobu reaction, and the Ullmann condensation. Rearrangement and elimination of alkyl alcohols that are sterically hindered is the major disadvantage of older reported procedures for ether synthesis. This problem is amplified when the alcohols are immobilized on solid supports and their activated species become the limiting reagent.⁴ The alcohol-sulfuric acid reaction is most often used for the conversion of simple primary alcohols in to symmetrical ethers. Secondary and tertiary alcohols undergo predominantly dehydration when subjected to these conditions. Occasionally a small amount of the symmetrical ether is formed as a by-product in the case of secondary alcohols.9

Recently, we have reported the preparation of silica sulfuric acid I (Figure 1) as a stable acidic reagent (solid acid) and showed its catalytic activity in synthetic methodology.¹⁰ In continuation of our studies in this regard, we have found that trimethylsilyl ethers can be converted to their corresponding ethers in the presence silica sulfuric acid I. Therefore, we decided to apply this reagent for ether synthesis. Here we wish to report the first example of direct conversion of primary and secondary trimethylsilyl ethers into the related ethers with good to excellent yields under mild and heterogeneous conditions (Scheme 1).

R¹ R² R³COTMS

n-Hexane, r.t.

A mixture of the substrate 1 (4 mmol), *n*-hexane (20 mL) and silica sulfuric acid I (1 g) was stirred at room temperature for the specified time (Table 1).^{11,12} The reaction was monitored by TLC. After completion of the reaction the mixture was filtered and the solid residue was washed with *n*-hexane. Evaporation of the solvent followed by column chromatography on silica gel gave highly pure ethers with good to excellent yields. The solid residue is silica sulfuric acid, which was recycled easily. Running the reactions with recycled silica sulfuric acid for three times show that no decrease in the yield was observed. This means that silica sulfuric acid can be reused for several times.10g

 $(R^{1}R^{2}R^{3}C)_{2}O$

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In conclusion, silica sulfuric acid can serve as an efficient catalyst for the direct conversion of primary and secondary trimethylsilyl ethers into the corresponding ethers under mild and heterogeneous conditions. The yields are almost good to excellent and the procedure is simple and convenient. Rearrangement, elimination and ether cleavage bond were not observed. Moreover, the 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.¹⁴

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Table 1Direct Conversion Trimethylsilyl Ether 1 to their Corresponding Ethers 2 in the Presence of Silica Sulfuric Acid (I) in n-Hexane at Room Temperature^a

Entry	Substrates	1	Products ^b	2	Time (min)	Yield (%) ^c
1	4-CH ₃ °C ₆ H ₄ CH ₂ OTMS	а	$4-CH_3OC_6H_4CH_2)_2O$	a	15	95
2	4-(CH ₃) ₂ CHC ₆ H ₄ CH ₂ OTMS	b	4-(CH ₃) ₂ CHC ₆ H ₄ CH ₂) ₂ O	b	15	95
3	4-(CH ₃) ₃ CC ₆ H ₄ CH ₂ OTMS	с	4-(CH ₃) ₃ CC ₆ H ₄ CH ₂) ₂ O	с	15	95
4	2-ClC ₆ H ₄ CH ₂ OTMS	d	(2-ClC ₆ H ₄ CH ₂) ₂ O	d	40	80
5	4-ClC ₆ H ₄ CH ₂ OTMS	e	$(4-ClC_6H_4CH_2)_2O$	e	40	85
6	2,4-Cl ₂ C ₆ H ₃ CH ₂ OTMS	f	(2,4-Cl ₂ C ₆ H ₃ CH ₂) ₂ O	f	45	80
7	2-BrC ₆ H ₄ CH ₂ OTMS	g	(2-BrC ₆ H ₄ CH ₂) ₂ O	g	45	80
8	2-O ₂ NC ₆ H ₄ CH ₂ OTMS	h	$(2-O_2NC_6H_4CH_2)_2O$	h	35	80
9	3-O ₂ NC ₆ H ₄ CH ₂ OTMS	i	$(3-O_2NC_6H_4CH_2)_2O$	i	45	85
10	4-O ₂ NC ₆ H ₄ CH ₂ OTMS	j	$(4-O_2NC_6H_4CH_2)_2O$	j	30	90
11	C ₆ H ₅ CHCH ₃ CH ₂ OTMS	k	(C ₆ H ₅ CHCH ₃ CH ₂) ₂ O	k	20	92
12	C ₆ H ₅ CH=CHCH ₂ OTMS	1	(C ₆ H ₅ CH=CHCH ₂) ₂ O	1	27	90
13	СН2ОТМЗ	m	CH ₂) ₂ O	m	30	90
14	CH2OTMS	n	((CH ₂) ₂ O	n	30	80
15	CH ₂ OTMS	0	CCH ₂) ₂ O	0	25	80
16	<i>n</i> -C ₇ H ₁₅ OTMS	р	$n - (C_7 H_{15})_2 O$	р	15	80
17	<i>n</i> -C ₈ H ₁₇ OTMS	q	$n - (C_8 H_{17})_2 O$	q	15	80
18	CH ₂ OTMS	r	(CH ₂) ₂ O	r	15	85
19	CH ₂ OTMS	S	-CH ₂)20	S	15	82
20	3-CH ₃ OC ₆ H ₄ CH ₂ OTMS	t	$(3-CH_3OC_6H_4CH_2)_2O$	t	15	90
21	2-CH ₃ OC ₆ H ₄ CH ₂ OTMS	u	(2-CH ₃ OC ₆ H ₄ CH ₂) ₂ O	u	15	90
22	4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CH ₂ OTMS	v	$(4-C_6H_5CH_2OC_6H_4CH_2)_2O$	V	15	85
23	(C ₆ H ₅) ₂ CHOTMS	W	(C ₆ H ₅) ₂ CH) ₂ O	W	35	80
24	4-ClC ₆ H ₄ CHCH ₃ OTMS	x	(4-ClC ₆ H ₄ CHCH ₃) ₂ O	X	45	70
25	C ₆ H ₅ CH ₃ CHOTMS	у	(C ₆ H ₅ CH ₃ CH) ₂ O	у	35	75

^a Silica sulfuric acid/silyl ether (0.25 g:1 mmol).

^b All of the isolated products are known and their spectra and physical data have been reported in the literature.

^c Isolated yields.

- (1) Quach, T. D.; Batey, R. A. Org. Lett. 2003, 5, 1381.
- (2) Buck, E.; Song, Z. J.; Tschaen, D.; Dormer, P. G.; Valante, R. P.; Reider, P. J. Org. Lett. 2002, 4, 1623.
- (3) Busch-Petersen, J.; Corey, E. J. Org. Lett. 2000, 2, 1641.
- (4) Xiao, X. Y.; Li, R.; Hurst, D.; Zhuang, H.; Shuhao, S.;
 Czarnik, A. W.; Robichaud, A. J.; Wacker, D. A.; Robertson, D. W. J. Comb. Chem. 2002, 4, 536.
- (5) Wang, S.; Guin, J. A. Chem. Commun. 2000, 2499.
- (6) Bagnell, L.; Cablewski, T.; Strauss, C. R. Chem. Commun. 1999, 283.
- (7) Lu, B.; Li, L. J.; Li, T. S.; Li, J. T. J. Chem. Res., Synop. 1998, 604.
- (8) Verhoef, M. J.; Creyghton, E. J.; Peters, J. A.; Bekkum, H. V. Chem. Commun. 1997, 1989.
- (9) Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. Introduction to Organic Chemistry, 4th ed.; Macmillan Publishing Company: New York, 1992, 233.
- (10) (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.
 (f) Zolfigol, M. A.; Shirini, F.; Ghorbani-Choghamarani, A.;

Mohammadpoor-Baltork, I. *Green Chem.* **2002**, *4*, 562. (g) Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Bodaghi-fard, M. A. *Tetrahedron Lett.* **2003**, *44*, 2889. (h) Zolfigol, M. A.; Chehardoli, G. A.; Mallakpour, S. E. *Synth. Commun.* **2003**, *33*, 833. (i) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A.; Zarei, A. *Bull. Korean Chem. Soc.* **2003**, *24*, 400.

- (11) Chemicals were purchased from Fluka, Merck and Aldrich chemicals companies. The products were characterized by comparison of their spectral (IR, ¹H NMR), TLC and physical data with the authentic samples. Silica sulfuric acid was synthesized according to the our previously reported procedure. ^{10a} All silyl ethers were synthesized according to the reported procedure. ¹³
- (12) **Preparation of Silica Sulfuric Acid:** A 500 mL suction flask was used. It was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and gas inlet tube for conducting HCl gas over an adsorbing solution i. e. H_2O . Into it were charged 60.0 g of silica gel. Chlorosulfonic acid was added dropwise over a period of 30 min at r.t. HCl gas evolved from the reaction vessel immediately. After the addition was complete the mixture was shaken for 30 min. A white solid (silica sulfuric acid) 76.0 g was obtained.^{10a}
- (13) Firouzabadi, H.; Karimi, B. Synth. Commun. 1993, 23, 1633.
- (14) Clark, J. H. Acc. Chem. Res. 2002, 35, 791.