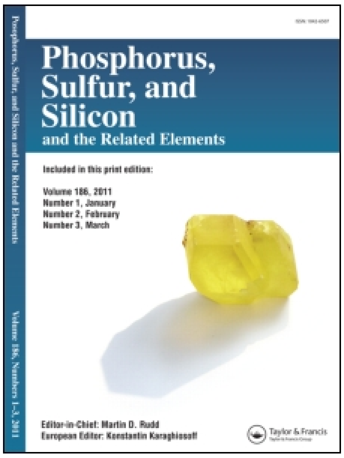

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Silica Triflate as a New, Mild and Efficient Catalyst for Tetrahydropyranylation of Alcohols and Deprotection of Tetrahydropyranyl Ethers

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Silica triflate, a new stable derivative of silica gel, is easily prepared by the reaction of silica gel with trifluoromethanesulfonyl chloride. Silica triflate acts as a highly effective and reusable catalyst for tetrahydropyranylation of alcohols and deprotection of tetrahydropyranyl ethers under mild and completely heterogeneous reaction conditions.

Keywords Alcohols; silica gel; silica triflate; tetrahydropyranylation; trifluoromethanesulfonyl chloride

INTRODUCTION

Due to the remarkable stability of tetrahydropyranyl ethers towards a variety of reaction conditions such as strongly basic media, Grignard reagents, oxidizing and reducing agents, alkylation and acylation reactions, and because of their easy removal under mild acidic conditions, tetrahydropyranylation is considered as one of the most

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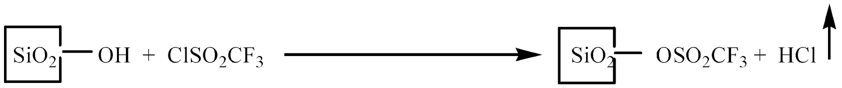
important methods for the protection of alcoholic hydroxyl groups. A variety of reagents have been used for tetrahydropyranylation and detetrahydropyranylation, e. g., $ZrCl_4$,[1] I_2,[2] LiBr,[3] $PdCl_2(CH_3CN)_2$,[4] Wells-Dawson heteropolyacid,[5] $Fe(ClO_4)_3$,[6] sulfuric acid supported on silica gel,[7] potassium dodecatungstocobaltate trihydrate,[8] DDQ,[9] PPh_3Br_2,[10] ion exchange resins,[11] $BF_3.OEt_2$,[12] acetyltriphenylphosphonium bromide,[13] and electrogenerated acid.[14] More recently, $Sc(OTf)_3$,[15] $[Ru(CH_3)_3(triphos)](OTf)_2$,[16] LiOTf,[17] $In(OTf)_3$[18] and $Bi(OTf)_3$[19] have also been employed for this purpose. Although these methods are satisfactory for many molecules, some have limitations, such as the use of expensive and toxic reagents, high temperature, long reaction times, incompatibility with other acid-sensitive functional groups, and non-reusability. Therefore, there is a need to develop an alternative method for tetrahydropyranylation as well as detetrahydropyranylation under mild reaction conditions.

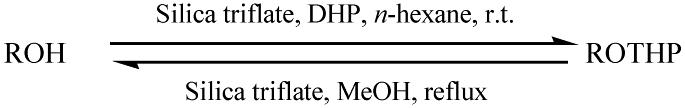
In continuation of our studies on the preparation of new derivatives of silica gel and their applications in functional group transformations,[20–22] we have found that trifluoromethanesulfonyl chloride reacts with silica gel to give silica triflate (**I**) as a white stable powder. It is interesting to note, that the reaction is easy and clean without any work-up procedure because HCl gas is evolved from the reaction vessel immediately (Scheme 1).



(I)

SCHEME 1

We anticipated that silica triflate (**I**) would be more efficient for running reactions under mild and heterogeneous conditions as compared to most of the reported triflates. Therefore, we were interested in using this reagent for the promotion of tetrahydropyranylation of alcohols and deprotection of tetrahydropyranyl ethers (Scheme 2).



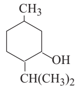
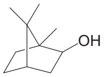
SCHEME 2

Optimization of the reaction conditions is carried out by the tetrahydropyranylation of 2-bromobenzyl alcohol with 3,4-dihydro-2*H*-pyran (DHP) in the presence of silica triflate. The best result was achieved by carring out the reaction with 1.2 equiv. of DHP in the presence of 0.03 g of silica triflate at room temperature for 3 min in *n*-hexane (Table I).

In order to extend the scope of this method, a variety of alcohols (primary, secondary, tertiary, benzylic, and allylic alcohols) were used applying the same reaction conditions (Table I). All reactions were performed under mild and completely heterogeneous reaction conditions in good to high yields. It is interesting, that dehydration products of secondary and tertiary alcohols were not observed during the course of the reaction (Table I). In addition, the double bond of cinnamyl alcohol, as an example of an allylic alcohol, was not affected using this method (Table I).

Deprotection of THP ethers can also be carried out by using similar amounts of silica triflate in refluxing methanol. The results of the deprotection reactions are also summarized in Table I.

TABLE I Tetrahydropyranylation and Detetrahydropyranylation of Alcohols in the Presence of Silica Triflate[a,b]

	Protection in *n*-hexane		Deprotection in methanol	
Substrate	Time (min)	Yield (%)	Time (min)	Yield (%)
2-$BrC_6H_4CH_2$ OH	3	90	5	92
2-$ClC_6H_4CH_2$ OH	6	92	4	90
4-$ClC_6H_4CH_2$ OH	3	90	8	90
2-$NO_2C_6H_4CH_2$ OH	12	85	10	90
3-$NO_2C_6H_4CH_2$ OH	6	90	8	95
4-$NO_2C_6H_4CH_2$ OH	6	95	8	90
2-$MeC_6H_4CH_2$ OH	4	90	5	87
4-$MeOC_6H_4CH_2OH$	2	92	8	90
4-$PhCH_2OC_6H_4CH_2OH$	2	85	6	95
Ph_2CHOH	5	95	20	87
$C_6H_5CH_2CH_2CH_2OH$	1	90	12	90
$C_6H_5CH(Me)CH_2OH$	3	95	9	92
$C_6H_5CH_2CH(OH)CH_3$	4	90	10	95
	21	80	25	90
	19	95	20	93
$(CH_3)_3COH$	2	90	8	90
$C_6H_5CH{=}CHCH_2OH$	3	90	3	90

[a] Products were characterized by their physical constants, comparison with authentic samples, and IR and NMR spectroscopy; [b] Isolated yield.

TABLE II Comparison of Some of our Results, with Some of Those Reported in the Literature[1,6,17]

		(min)(Yield %)			
Substrate	Product	Silica triflate	$ZrCl_4$	$Fe(ClO_4)_3$	LiOTf
Ph_2CHOH	$Ph_2CHOTHP$	(5)(95)	(180)(90)	(150)(75)	(240)(86)
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCH_2OTHP$	(3)(90)	(120)(98)	—	—
$(CH_3)_3COH$	$(CH_3)_3COTHP$	(2)(90)	(120)(87)	(180)(92.5)	—

We have found that silica triflate is a reusable catalyst and even after three runs for tetrahydropyranylation of alcohols with DHP and deprotection of THP ethers, the catalytic activity of the reagent was almost the same as that of the freshly used catalyst. No change in the IR spectrum of the catalyst before and after the reaction was observed, which demonstrates the stability of the reagent.

A comparison of some of the results with some of those reported in the literature[1,6,17] (Table II) shows the efficiency of the presented method.

Mildness of the reaction conditions, short reaction times, high efficiency, reasonable yields, simple and clean work-up, reusability of the catalyst, and heterogeneous reaction conditions are important advantages of this new method.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV254 plates. The FT-IR spectra were recorded on Schimadzu model 8300 instrument. The ^1H NMR spectra were recorded on a Bruker Advance DPX 250 MHz spectrometer.

Preparation of Silica Triflate

A 500 mL suction flask, charged with 18.0 g silica gel (type 60,15–40 μm), was equipped with a constant pressure dropping funnel containing trifluoromethanesulfonyl chloride (8.4 g, 0.05 mol), and a gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., water. Trifluoromethanesulfonyl chloride was added dropwise over a period of 30 min and the reaction mixture was slowly stirred at room temperature for further 30 min. The mixture was then heated to 60°C with stirring for 1 h to remove all HCl and excess amounts of trifluoromethanesulfonyl chloride. The reaction mixture was washed with 50 mL of dry CH_2Cl_2 and dried under vacuum. Silica triflate was obtained as a white solid (20.38–20.62 g), which was stored in a capped bottle; IR (KBr): 1255, 1230, 1130, 1010, 955, 820, 650, 530, 500 cm^{-1}.

Protection of Alcohols Catalyzed by Silica Triflate

A mixture of the respective alcohol (1 mmol), DHP (0.1008 g, 1.2 mmol) and silica triflate (0.03 g) in *n*-hexane (4 mL) was stirred at room temperature. The progress of the reaction was monitored by GC or TLC. After completion of the reaction, the reaction mixture was filtered through a silica-gel pad, and the solid residue was washed with *n*-hexane (5 mL). Evaporation of the solvent gave the respective THP ethers in good to high yields (Table I).

Deprotection of THP Ethers Catalyzed by Silica Triflate

A mixture of the respective THP ether (1 mmol) and silica triflate (0.03 g) in methanol (4 mL) was stirred at reflux conditions. The progress of the reaction was monitored by GC or TLC. After completion of the reaction the mixture was filtered and the solid residue was washed with methanol (5 mL). Evaporation of the solvent under reduced pressure gave almost pure alcohol (Table I). Further purification was carried out by column chromatography on silica gel to afford the pure alcohol.

REFERENCES

[1] N. Rezai, F. Meybodi, and P. Salehi, *Synth. Commun.*, **30,** 1799 (2000).

[2] N. Deka and J. C. Sarma, *Synth. Commun.*, **30,** 4435 (2000).

[3] M. A. Reddy, L. R. Reddy, N. Bhanumathi, and K. R. Rao, *Synth. Commun.*, **30,** 4323 (2000).

[4] Y.-G. Wang, X.-X. Wu, and Z.-Y. Jiang, *Tetrahedron Lett.*, **45,** 2973 (2004).

[5] G. P. Romanelli, G. Baronetti, H. J. Thomas, and J. C. Autino, *Tetrahedron Lett.*, **43,** 7589 (2002).

[6] M. M. Heravi, F. K. Behbahani, H. A. Oskooi, and R. H. Shoar, *Tetrahedron Lett.*, **46,** 2546 (2005).

[7] M. M. Heravi, D. Ajami, and M. Ghasemzadeh, *Synth. Commun.*, **29,** 1013 (1999).

[8] M. H. Habbi, S. Tangestaninejad, I. Mohammadpoor-Baltork, V. Mirkhani, and B. Yadollahi, *Tetrahedron Lett.*, **42,** 2851 (2001).

[9] K. Tanemura, T. Haroguchi, and T. Suzuki, *Bull. Chem. Soc. Jpn.*, **65,** 304 (1992).

[10] A. Wagner, M.-P. Heitz, and C. Mioskovski, *J. Chem. Soc., Chem. Commun.*, 1619 (1989).

[11] G. A. Olah, A. Husain, and B. P. Singh, *Synthesis*, 892 (1983).

[12] A. Srikrishna, J. A. Sattigeri, R. Viswajanani, and C. V. Yelmaggad, *J. Org. Chem.*, **60,** 2260 (1995).

[13] Y.-S. Hon and C.-F. Lee, *Tetrahedron Lett.*, **40,** 2389 (1999).

[14] S. Torri, T. Inokuchi, K. Kondo, and H. Ito, *Bull. Chem. Soc. Jpn.*, **58,** 1347 (1985).

[15] T. Oriyama, T. Watahiki, Y. Kobayashi, H. Hirano, and T. Suzuki, *Synth. Commun.*, **31,** 2305 (2001).

[16] S. Ma and L. M. Venanzi, *Tetrahedron Lett.*, **34,** 5269 (1993).

[17] B. Karimi and J. Mleki, *Tetrahedron Lett.*, **43,** 5353 (2002).

[18] T. Mineno, *Tetrahedron Lett.*, **43,** 7975 (2002).

[19] J. R. Stephens, P. L. Butler, C. H. Clow, M. C. Ostwald, R. C. Smith, and R. S. Mohan, *Eur. J. Org. Chem.*, 3827 (2003).

[20] F. Shirini, M. A. Zolfigol, M. Khaleghi, and I. Mohammadpoor-Baltork, *Synth. Commun.*, **33,** 1839 (2003).

[21] M. A. Zolfigol, F. Shirini, A. Ghorbani Choghamarani, and I. Mohammadpoor-Baltork, *Green Chem.*, **4,** 562 (2002).

[22] F. Shirini, M. A. Zolfigol, and K. Mohammadi, *Bull. Korean Chem. Soc.*, **24,** 519 (2003).