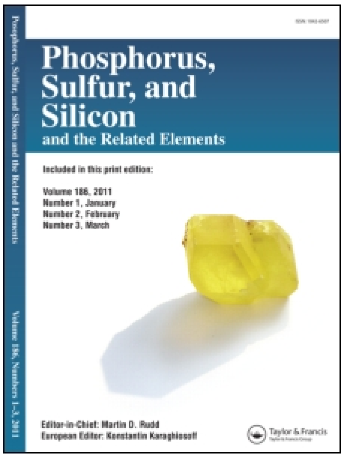

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE USE OF NAFION-H® AS AN EFFICIENT CATALYST FOR THE DEPROTECTION OF TRIMETHYLSILYL ETHERS TO THEIR CORRESPONDING ALCOHOLS UNDER MILD AND HETEROGENEOUS CONDITIONS

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Online publication date: 16 August 2010

To cite this Article Zolfigol, Mohammad Ali , Mohammadpoor-Baltork, Iraj , Habibi, Davood , Mirjalili, BiBi Fatemeh and Bamoniri, Abdolhamid(2004) 'THE USE OF NAFION-H® AS AN EFFICIENT CATALYST FOR THE DEPROTECTION OF TRIMETHYLSILYL ETHERS TO THEIR CORRESPONDING ALCOHOLS UNDER MILD AND HETEROGENEOUS CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 11, 2189 — 2193

To link to this Article: DOI: 10.1080/10426500490474996

URL: http://dx.doi.org/10.1080/10426500490474996

Phosphorus, Sulfur, and Silicon, 179:2189–2193, 2004

ISSN: 1042-6507 print / 1563-5325 online
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(Received March 23, 2004; accepted March 26, 2004)

Trimethylsilyl ethers were converted to their corresponding alcohols in the presence Nafion-H® and wet SiO_2 with good-to-excellent yields under mild and heterogeneous conditions.

Keywords: Heterogeneous conditions; Nafion-H®; trimethylsilyl ethers

Silyl protecting groups have played increasingly important roles in the synthesis of complicated molecules, specially for the synthesis of biologically significant products.[1–5] Although there have been many new reports for protection and deprotection of silyl groups,[1–17] the removal of silyl group under mild conditions with easy workup procedure is important.

The development of environmentally benign technologies is the most challenging goal of contemporary chemistry and chemical engineering. Environmentally friendly chemical processes should be designed to use environmentally benign feeds and solvents, and utilize efficient

Financial support for this work by the research affairs, Bu-Ali Sina University, Hamadan, Iran, and also Isfahan University, Isfahan, Iran (as a common project) is gratefully acknowledged.

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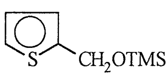
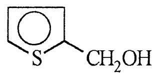
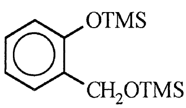
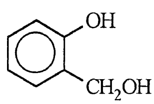
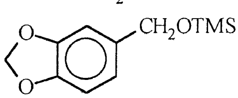
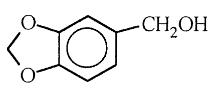
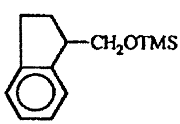
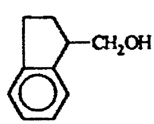
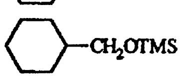
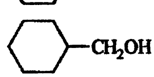
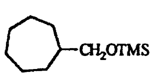
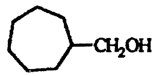
reagent or catalyst recycling systems.[18] In the development of industrial processes, separation is very important. Efficient separation of reagents and catalysts to enable their reuse for subsequent cycles of reactions are also key challenges. Especially in the stream of green chemistry, separation protocols that allow for effective recovery of reagents and catalysts have been increasingly appreciated.[19] Perfluorinated solvents are immiscible with conventional organic solvents at ambient temperature (at 20°C) but become miscible at 36°C.[20] Compounds functionalized with perfluorinated groups often dissolve preferentially in fluorous solvents.[21] Based on this fact, in the search for chemical transformations integrating innovative workup procedures fluorous techniques (fluorous biphasic chemistry[18] and fluorous triphasic reactions[22]) are becoming increasingly popular in organic synthesis for the separation of temporarily fluorous labeled from fluorous non–labeled compounds. Consequently, if one or more of the components of a reaction mixture, e.g., homogeneous catalysts, reagents, or products, are equipped with a perfluorinated auxiliary, the organic and the fluorous components can be separated easily by either liquid–liquid extraction, solid–liquid extraction, or fluorous chromatography.[23]

On the other hand, acids are widely used as catalysts in industry, producing more than 1×10^8 mt/year of products. The most commonly used acids are HF, H_2SO_4, $HClO_4$, and H_3PO_4 (in liquid form or supported on Kieselguhr). Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and environmentally safe disposal.[24–16] There is much current research and general interest in heterogeneous systems[27] because of the importance that such systems have in industry and in developing technologies.[28,29] Among reported solid acids, Nafion-H® has been used for a wide variety of reactions ranging from alkylation with olefins, reaction of alkyl halides and alkyl esters, isomerization, transalkylation, acylation and nitration reactions and ether and ester synthesis, and acetal formation and rearrangements.[30] Very recently, we have reported the use of Nafion-H® as an excellent solid acid for the nitrosation of secondary amines and also synthesis of ethers under mild and heterogeneous conditions.[31] Therefore, we decided to apply this perfluorinated catalyst for the conversion of trimethylsilyl ethers to the corresponding alcohols in the presence wet SiO_2 at room temperature. Here we wish to report an efficient procedure for the conversion of trimethylsilyl ethers into alcohols with good-to-excellent yields under mild and heterogeneous conditions (Scheme 1). This system can be combined with perfluorinated solvents and used for biphasic and triphasic fluorous systems for different acid-catalyzed reactions.

$$\underset{\mathbf{1}}{\text{ROTMS}} \xrightarrow[n\text{-Hexane, rt.}]{\text{Nafion-H}} \underset{\mathbf{2}}{\text{ROH}}$$

SCHEME 1

TABLE I The Direct Conversion of Trimethylsilyl Ethers **1** to the Corresponding Alcohols **2** in the Presence of Nafion-H® and Wet SiO_2 in *n*-hexane at Room Temperature[a]

Entry	Substrates	**1**	Products[b]	**2**	Time (Min)	Yield[c] (%)
1	$4\text{-}CH_3OC_6H_4CH_2OTMS$	**a**	$4\text{-}CH_3OC_6H_4CH_2OH$	**a**	15	98
2	$C_6H_5CH(OTMS)CH_2OTMS$	**b**	$C_6H_5CH(OH)CH_2OH$	**b**	30	95
3	$4\text{-}(CH_3)_2CHC_6H_4CH_2OTMS$	**c**	$4\text{-}(CH_3)_2CHC_6H_4CH_2OH$	**c**	20	98
4	$4\text{-}(CH_3)_3CC_6H_4CH_2OTMS$	**d**	$4\text{-}(CH_3)_3CC_6H_4CH_2OH$	**d**	20	98
5	$2\text{-}ClC_6H_4CH_2OTMS$	**e**	$2\text{-}ClC_6H_4CH_2OH$	**e**	40	95
6	$4\text{-}ClC_6H_4CH_2OTMS$	**f**	$4\text{-}ClC_6H_4CH_2OH$	**f**	30	90
7	$2,4\text{-}Cl_2C_6H_3CH_2OTMS$	**g**	$2,4\text{-}Cl_2C_6H_3CH_2OH$	**g**	45	90
8	$2\text{-}BrC_6H_4CH_2OTMS$	**h**	$2\text{-}BrC_6H_4CH_2OH$	**h**	40	90
9	$2\text{-}O_2NC_6H_4CH_2OTMS$	**i**	$2\text{-}O_2NC_6H_4CH_2OH$	**i**	40	90
10	$3\text{-}O_2NC_6H_4CH_2OTMS$	**j**	$3\text{-}O_2NC_6H_4CH_2OH$	**j**	40	90
11	$4\text{-}O_2NC_6H_4CH_2OTMS$	**k**	$4\text{-}O_2NC_6H_4CH_2OH$	**k**	30	90
12	$C_6H_5CHCH_3CH_2OTMS$	**l**	$C_6H_5CHCH_3CH_2OH$	**l**	30	98
13	$C_6H_5CH{=}CHCH_2OTMS$	**m**	$C_6H_5CH{=}CHCH_2OH$	**m**	25	95
14	$n\text{-}C_7H_{15}OTMS$	**n**	$n\text{-}C_7H_{15}OH$	**n**	25	90
15	$n\text{-}C_8H_{17}OTMS$	**o**	$n\text{-}C_8H_{17}OH$	**o**	25	90
16		**p**		**p**	40	95
17		**q**		**q**	30	95
18		**r**		**r**	30	95
19		**s**		**s**	30	90
20		**t**		**t**	20	90
21		**u**		**u**	25	90

[a]Nafion-H®/wet SiO_2/trimethylsilyl ether (0.05 g: 0.05 g: 1 mmol).
[b]All of the alcohols are known.
[c]Isolated yields.

A mixture of the substrate **1** (1 mmol), *n*-hexane (5 ml), Nafion-H® (0.05 g), and wet SiO_2 (0.2 g) was stirred at room temperature for the specified time (Table I). 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 gave pure ethers in good-to-excellent yields.*

In conclusion, Nafion-H® can serve as an efficient catalyst for the conversion trimethylsilyl ethers into the corresponding alcohols under mild and heterogeneous conditions. The yields are good to excellent and the procedure is simple and convenient. This system can be combined with perfluorinated solvents and used for biphasic and triphasic fluorous systems for *any acid-catalyzed reactions*. We believed that Nafion-H® can be recycled by applying fluorous biphasic system and then be reused several times. Moreover, reaction is heterogeneous and may be useful industrially.[34,35]

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*Chemicals were purchased from Fluka, Merck, and Aldrich chemicals companies. The products were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC, and physical data with the authentic samples. All silyl ethers were synthesized according to the reported procedure.[32]

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