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The use of Nafion-H® as 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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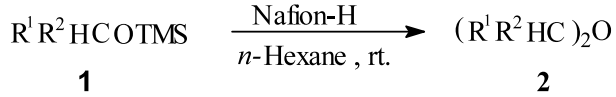
Abstract—Primary and secondary trimethylsilyl ethers were converted to their corresponding ethers in the presence Nafion-H® with good to excellent yields under mild and heterogeneous conditions.

Symmetrical and unsymmetrical alkyl/aryl ether formation is an important reaction in organic synthesis and has generated significant interest in recent years.[1–18] Methods to effect this transformation include the classic Williamson procedure, the Mitsunobu reaction, and the Ullmann condensation. Ion-exchange resin and heteroploy acid catalyzed etherification have also been reported.[15–18] Rearrangement and elimination of alkyl alcohols that are sterically hindered is the major disadvantage of the older procedures for ether synthesis. This problem is amplified when the alcohols are immobilized on solid supports and the activated species becomes the limiting reagent.[4] The alcohol–sulfuric acid reaction is most often used for the conversion of simple primary alcohols into 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.[19] In 1987, Olah's group reported a facile procedure for the synthesis of symmetrical and unsymmetrical ethers via reductive coupling of carbonyl compounds under mild acid-free conditions.[20]

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.[18,21–23] There is a great deal of current research and general interest in heterogeneous systems[24] because of the importance such systems have in industry and in developing technologies.[25] 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, acetal formation and rearrangements.[26] Very recently, we have reported the use of Nafion-H® as an excellent solid acid for the nitrosation of secondary amines under mild and heterogeneous conditions.[27] In continuation of our studies, we have found that trimethylsilyl ethers can be converted to the corresponding ethers in the presence Nafion-H®. Therefore,



1 **2**

Scheme 1.

Keywords: Nafion-H®; trimethylsilyl ethers; ethers; heterogeneous conditions.
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0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
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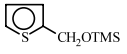
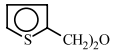
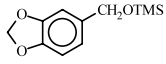
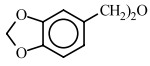
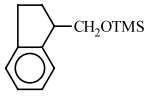
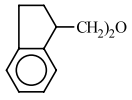
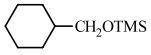
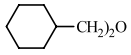
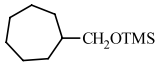
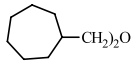
Table 1. The direct conversion of primary and secondary trimethylsilyl ethers **1** to the corresponding symmetrical ethers (**2**) in the presence of Nafion-H® in *n*-hexane at room temperature[a]

Entry	Substrates	1	Products[b]	2	Time (Min)	Yield[c] (%)
1	4-$CH_3OC_6H_4CH_2OTMS$	**a**	4-$CH_3OC_6H_4CH_2)_2O$	**a**	15	90
2	3-$CH_3OC_6H_4CH_2OTMS$	**b**	3-$CH_3OC_6H_4CH_2)_2O$	**b**	15	85
3	2-$CH_3OC_6H_4CH_2OTMS$	**c**	2-$CH_3OC_6H_4CH_2)_2O$	**c**	15	85
4	4-$(CH_3)_2CHC_6H_4CH_2OTMS$	**d**	4-$(CH_3)_2CHC_6H_4CH_2)_2O$	**d**	15	90
5	4-$(CH_3)_3CC_6H_4CH_2OTMS$	**e**	4-$(CH_3)_3CC_6H_4CH_2)_2O$	**e**	15	90
6	2-$ClC_6H_4CH_2OTMS$	**f**	2-$ClC_6H_4CH_2)_2O$	**f**	45	80
7	4-$ClC_6H_4CH_2OTMS$	**g**	4-$ClC_6H_4CH_2)_2O$	**g**	45	85
8	2,4-$Cl_2C_6H_3CH_2OTMS$	**h**	2,4-$Cl_2C_6H_3CH_2)_2O$	**h**	45	70
9	2-$BrC_6H_4CH_2OTMS$	**i**	2-$BrC_6H_4CH_2)_2O$	**i**	45	70
10	2-$O_2NC_6H_4CH_2OTMS$	**j**	2-$O_2NC_6H_4CH_2)_2O$	**j**	40	75
11	3-$O_2NC_6H_4CH_2OTMS$	**k**	3-$O_2NC_6H_4CH_2)_2O$	**k**	45	70
12	4-$O_2NC_6H_4CH_2OTMS$	**l**	4-$O_2NC_6H_4CH_2)_2O$	**l**	40	85
13	$C_6H_5CHCH_3CH_2OTMS$	**m**	$C_6H_5CHCH_3CH_2)_2O$	**m**	20	85
14	$C_6H_5CH{=}CHCH_2OTMS$	**n**	$C_6H_5CH{=}CHCH_2)_2O$	**n**	25	85
15	4-$C_6H_5CH_2OC_6H_4CH_2OTMS$	**o**	4--$C_6H_5CH_2OC_6H_4CH_2)_2O$	**o**	20	85
16	*n*-$C_7H_{15}OTMS$	**p**	*n*-$C_7H_{15})_2O$	**p**	20	80
17	*n*-$C_8H_{17}OTMS$	**q**	*n*-$C_8H_{17})_2O$	**q**	20	80
18		**r**		**r**	25	70
19		**s**		**s**	30	75
20		**t**		**t**	25	80
21		**u**		**u**	20	80
22		**v**		**v**	20	80
23	$(C_6H_5)_2CHOTMS$	**w**	$(C_6H_5)_2CH)_2O$	**w**	35	70
24	4-$ClC_6H_4CHCH_3OTMS$	**x**	4-$ClC_6H_4CHCH_3)_2O$	**x**	60	70
25	$C_6H_5CH_3CHOTMS$	**y**	$C_6H_5CH_3CH)_2O$	**y**	35	70

[a]Nafion-H®/trimethylsilyl ether (0.25 g : 1 mmol). [b]All of the products are known and their spectra and physical data obtained match those reported in the literature. [c]Isolated yields.

we decided to apply this reagent for ether synthesis. Here we wish to report the first examples of the direct conversion of primary and secondary trimethylsilyl ethers into ethers with good to excellent yields under mild and heterogeneous conditions (Scheme 1).

A mixture of the substrate **1** (4 mmol), *n*-hexane (20 ml) and Nafion-H® (1 g) was stirred at room temperature for the specified time (Table 1).[28] 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 pure ethers in good to excellent yields.

In conclusion, Nafion-H® can serve as an efficient catalyst for the direct conversion of primary (entries 1–22) and secondary (entries 23–25) trimethylsilyl ethers into the corresponding ethers under mild and heterogeneous conditions. The yields are good to excellent and the procedure is simple and convenient. Rearrangement, elimination and ether cleavage reactions were not observed. Moreover, reaction is heterogeneous and may be useful industrially.[30]

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