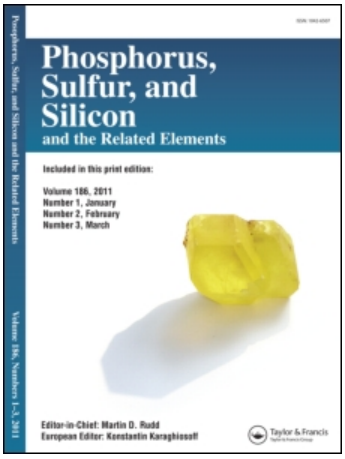

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A Novel Efficient Method for the Silylation of Alcohols Using Hexamethyldisilazane in an Ionic Liquid

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A Novel Efficient Method for the Silylation of Alcohols Using Hexamethyldisilazane in an Ionic Liquid

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Benzylic and primary alcohols were protected by hexamethyldisilazane in good to excellent yields at r.t. in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) ionic liquid. In addition, the ionic liquid was recovered quantitatively and reused efficiently in the next reactions. The protocol was successfully applied to the protection of phenols.

Keywords Silyl ethers; HMDS; ionic liquid; alcohols

Protected hydroxyl groups are very important for their organic[1] and analytical chemistry[2] applications. Many organic transformations require at least one step of alcohol group protection.[3,4] One of the most popular methods for this purpose is to convert alcohols into their corresponding silyl ethers.[5,6] However, some of the reported procedures suffer from drawbacks, such as a limited reactivity and a cumbersome removal of byproducts. Hexamethyldisilazane (HMDS) is a cheap and commercially available reagent frequently used for the trimethylsilylation of hydroxyl groups, giving ammonia as the only byproduct.[7] However, poor silylation power is a main limitation for the application of HMDS.[8] Various catalytic systems have been developed to ease these processes.[9–20] Although these methods improve reaction conditions and shorten the reaction time, in many cases, drastic conditions still are necessary for the completion of the process.

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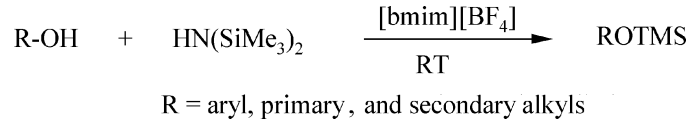
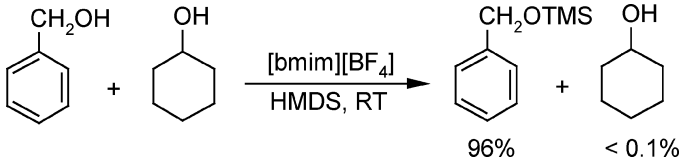
Ionic liquids have been studied extensively as a clean solvent for a wide range of chemical transformations.[21] In view of the emerging importance of ionic liquids as novel reaction media and in continuation of our previous experiences on the protection of hydroxyl groups,[11] here we report a mild and highly efficient method for the protection of alcohols using HMDS in [bmim][BF_4] (Scheme 1).



SCHEME 1

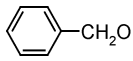
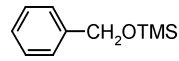
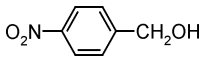
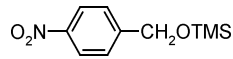
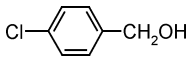
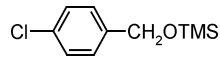
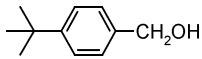
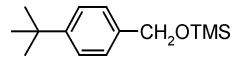
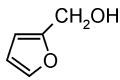
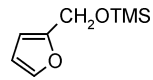
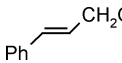
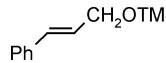
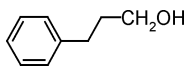
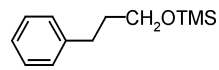
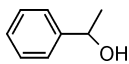
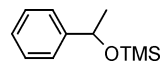
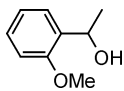
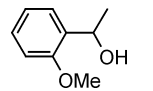
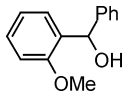
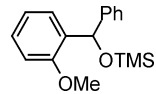
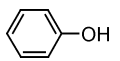
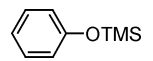
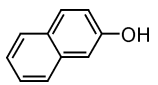
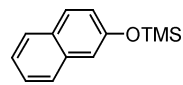
The treatment of benzyl alcohol with HMDS in [bmim][BF_4] at r.t. afforded the corresponding trimethylsilyl derivative of the alcohol within 30 minutes in a 96% yield (Table I, entry 1). The product was extracted by diethyl ether from the reaction medium. A variety of benzylic and primary alcohols were converted to their corresponding TMS ethers by using the same procedure (entries 2–13). The reactions were complete in less than 60 min for benzylic alcohols and in less than 120 min for other primary alcohols, and yields were 75–96%. The chemoselectivity of the protocol was demonstrated using an equimolar mixture of benzyl alcohol, cyclohexanol, and HMDS (Scheme 2). After 30 min, benzyl alcohol was converted to trimethylsilylbenzylether quantitatively, and no formation of trimethylsilylcyclohexylether was detected. This chemoselectivity was further confirmed using *tert*-butyl alcohol. The subjection of tertiarybutylalcohol to the same conditions expectedly resulted in the formation of <10% of the corresponding silyl ether after 4 h. The results are summarized in Table I.



SCHEME 2

In summary, the present protocol involves mild reaction conditions at an ambient temperature with high yields of isolated products in short reaction times. The silyl ether products were easily separable from the reaction mixture by a simple extraction with diethyl ether. The use of ionic liquid as a novel reaction medium for the transformation of alcohols to silyl ethers is another advantage of the procedure, which eases the reaction conditions. The ionic liquid can be recovered easily

TABLE I The Silylation of Alcohols Using HMDS in [bmim][BF_4]

			RT in [bmin][BF_4]		Reflux in CH_2Cl_2	
Entry	Substrate	Product	Time (min)	Yield (%)[a,b]	Time (h)	Yield (%)[b,c]
1			30	96	24	55
2			60	90	24	42
3			30	95	24	35
4			45	95	24	50
5			60	92	24	43
6			60	95	24	22
7			120	75	24	10
8	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CH_2OTMS$	120	75	24	12
9	$CH_3(CH_2)_4CH_2OH$	$CH_3(CH_2)_4CH_2OTMS$	120	75	24	10
10	$CH_3(CH_2)_8CH_2OH$	$CH_3(CH_2)_8CH_2OTMS$	120	85	24	10
11			45	92	24	10
12			45	96	24	12
13			60	87	24	15
14			90	95	24	11
15			90	97	24	18

[a]Isolated yields.

[b]Reactions were monitored by TLC, and products were identified by GC-Mass (GC-Mass Analysis: A Fisons Instruments gas chromatograph 8000 equipped with mass detector (Trio 1000) with 70 ev were used).

[c]GC yields.

after the completion of the reaction and reused in at least 10 subsequent experiments.

GENERAL PROCEDURE FOR THE PREPARATION OF TRIMETHYLSILYLETHERS

A mixture of alcohol (2 mmol) and hexamethyldisilazane (2 mmol) in 2 mL of [bmim][BF_4] was stirred at an ambient temperature for an appropriate length of time (Table I). The course of the reaction was monitored by thin layer chromatography (TLC) or gas chromatography (GC). The reaction mixture was extracted twice by 10-mL portions of diethyl ether. Combined ethereal phases were washed with water and dried over anhydrous calcium chloride. Products were obtained after evaporation of the volatile portion and were purified with a bulb-to-bulb distillation unit.

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