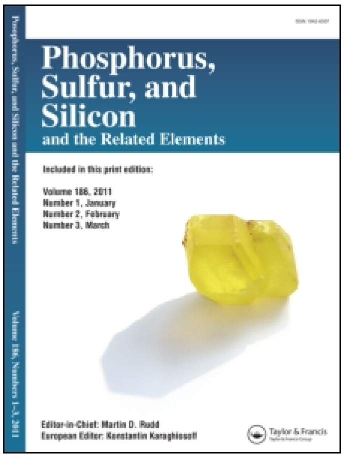

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Trimethylsilylation of Alcohols and Phenols, and Direct Acetylation of Silyl Ethers Catalyzed by $Fe(ClO_4)_3.6H_2O$

Hossein A. Oskooie[a]; Majid M. Heravi[a]; Maryam H. Tehrani[a]; Farahnaz K. Behbahani[a]; Omid M. Heravi[a]
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Trimethylsilylation of Alcohols and Phenols, and Direct Acetylation of Silyl Ethers Catalyzed by $Fe(ClO_4)_3.6H_2O$

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In this article, a mild and efficient protocol for the trimethylsilylation of various aliphatic and benzylic alcohols and phenols with trimethylsilyl chloride using a catalytic amount of ferric perchlorate at room temperature and relatively short reaction times in good to excellent yields is reported. Direct acetylation of trimethylsilyl ethers catalyzed with $Fe(ClO_4)_3.6H_2O$(0.02 mmol) / $Fe(ClO_4)_3SiO_2$(0.2 g) using acetic anhydride at ambient temperature is also reported.

Keywords Acetylation; alcohols; $Fe(ClO_4)_3.6H_2O$; phenols; trimethylsilylation

INTRODUCTION

Lately, several transformations in organic synthesis have been catalyzed using ferric perchlorate, such as protection of alcohols and deprotection of tetrahydropyranyl ethers,[1] acetylation of alcohols and phenols,[2] aromatization of Hantzsch 1,4-dihydropyridines,[3] and synthesis of 1,5-bezodiazepine derivatives.[4] In addition, ferric perchlorate has been utilized to catalyze the acetylation of THP ethers[5] and the conversion of oximes to aryl- and alkyl hydrazones.[6]

On the other hand, the protection of alcohol functions by trimethylsilyl group has been frequently and widely used in organic synthesis[7] and even more often used in analytical chemistry to prepare silyl ethers as volatile derivatives of alcohols and phenols.[8]

Several methods have been developed for this conversion, including trimethylsilyl halides/tertiary amine[9] allylsilanes/p-toluenesulfonic acid,[10] iodine,[11] trifluoromethanesulfonic acid,[12] $Sc(OTf)_3$,[13] zinc

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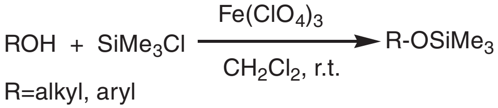
Address correspondence to Majid M. Heravi, Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran. E-mail: mmh1331@yahoo.com chloride,[14] trimethylsilyl azide,[15] tungstophosphoric acid,[16] and lithium perchlorate dispread in silica gel.[17]

During the multistep synthesis of natural products, the efficiency of the synthetic protocol employed often depends largely on the protection and the deprotection of the functional groups involved. To this end, protecting groups have played a crucial role during the synthesis of complex natural products. Therefore, protection and deprotection of alcohols play essential roles in synthetic strategies.[18]

There are several methods for the deprotection of silyl ethers, such as HF–MeCN,[19] KF–Crown ether,[20] $BF_3 \cdot Et_2O$–$CHCl_3$,[21] NBS,[22] $CF_3SO_3SiMe_3$–CH_2Cl_2,[23] NH_4F–MeOH,[24] SiF_4–MeCN,[25] aqueous acid,[26] tetrabutylammonium fluoride (TBAF),[27] K_2CO_3,[28] Lewis acids,[29] neutral alumina,[30] $K_2S_2O_8$,[31] oxidative cleavage of trimethylsilyl ethers to the corresponding carbonyl compounds,[32] and the conversion of alcohols into acetates.[33] The methods for the direct conversion of silyl ethers to acetate are limited, and even those suffer from serious drawbacks. Therefore, the introduction of new and economic methods using a catalytic amount of reagent for such functional group transformations is still in demand.

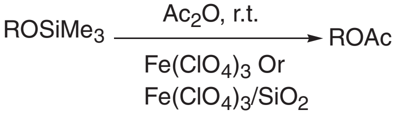
Due to the importance of the protection–deprotection protocol, the advantages of one-pot reactions, and our continuous interest in catalytic reactions,[34] in this article, we wish to report that ferric perchlorate, in a catalytic amount, can protect aliphatic and benzylic alcohols and phenols to silyl ethers. It also converts silyl ethers directly to the corresponding acetates in excellent yields in a one-pot reaction using acetic anhydride at ambient temperature (Schemes 1 and 2).



$$ROH + SiMe_3Cl \xrightarrow[CH_2Cl_2,\ r.t.]{Fe(ClO_4)_3} R\text{-}OSiMe_3$$

R=alkyl, aryl

SCHEME 1 Trimethylsilylation of alcohols and phenols by $Fe(ClO_4)_3.6H_2O$.



$$ROSiMe_3 \xrightarrow[Fe(ClO_4)_3 \text{ Or } Fe(ClO_4)_3/SiO_2]{Ac_2O,\ r.t.} ROAc$$

R=alkyl, aryl

SCHEME 2 Direct acetylation of silyl ethers by $Fe(ClO_4)_3.6H_2O$.

RESULTS AND DISCUSSION

Many silylating agents, such as chlorotrimethylsilane, 3,4-hexamethy ldisiloxane, N,O-bis(trimethylsilyl)acetamide, hexamethyldisilazane (HMDS), and ethyl(trimethylsilyl) acetate, have been used for the introduction of a trimethylsilyl group onto a variety of alcohols. Trimethylsilyl chloride is a cheap and commercially available compound that can be used for the preparation of trimethylsilyl ethers from hydroxy compounds. Its handling does not require special precautions, and the work-up is not time consuming, as the by-product of the reaction is hydrochloric acid, which is simple to remove from the reaction medium. At first, we tried to work with benzyl alcohol as a reagent and trimethylsilyl chloride as a silylating agent without a catalyst under solvent-free conditions for a long period of time, which gave no product. When we used 0.02 mmol of $Fe(Clo_4)_3.6H_2O$ as a catalyst under the same reaction conditions, benzyl trimethylsilyl ether was obtained in 98% yields after 25 min.

To investigate the merit and generality of this procedure, a variety of primary benzyl alcohols bearing electron-withdrawing groups (chloro, nitro; Table I, entries 8 and 9) and electron-releasing groups(methoxy, hydroxyl, methyl; Table I, entries 6 and 7) were used. In all cases, the formation of substituted benzyl trimethyl silylethers in high yields and short reaction times using alcohols with electron–releasing groups were observed, while alcohols with electron-withdrawing groups produced trimethylsilyl ethers with significantly longer reaction times(Table I, entry 8) or did not give any product at all (Table I, entry 9). It is likely that electron-withdrawing groups decrease the nucleophilicity of the hydroxyl group.

In order to evaluate the steric effect on the formation of the silyl ether, a reaction with methyl-1-phenyl ethanol was attempted. The reaction carried out, and silyl ether was obtained without any by-product such as alkene from the elimination reaction (Table I, entry 10). In addition, aliphatic aldehydes were used, and the results were obtained as well as for benzylic alcohols (Table I, entries 1, 2, and 4). Finally, it was interesting to attempt this procedure with other hydroxyl compounds such as phenols. Unfortunately, phenols, and particularly phenols bearing electron-withdrawing groups, did not react (Table I, entries 12–16).

Trimethylsilyl ether compounds were then used in direct acetylation reaction with $Fe(ClO_4)_3.6H_2O$ and $Fe(ClO_4)_3$-SiO_2. The reactions carried out using trimethylsilyl ethers and acetic anhydride at ambient temperature obtained products in high yields and short reaction times (Table II). The results of using both $Fe(ClO_4)_3.6H_2O$ and $Fe(ClO_4)_3$-SiO_2 were the same. However it is better to use $Fe(ClO_4)_3$-SiO_2 instead

TABLE I Protection of Alcohols and Phenols Catalyzed Using $Fe(ClO_4)_3$ in the Presence of Trimethyl Silyl Chloride

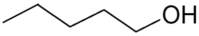
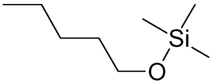
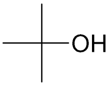
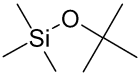
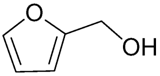
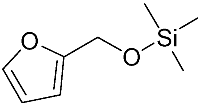
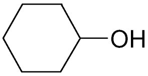
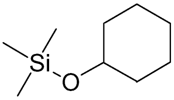
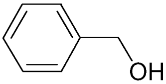
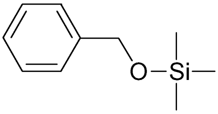
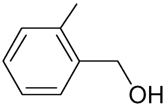
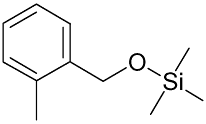
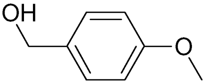
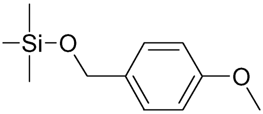
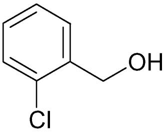
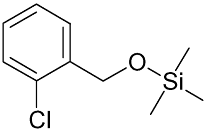
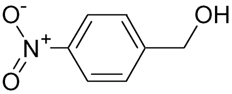
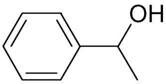
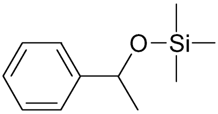
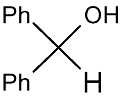
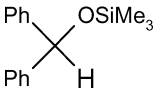
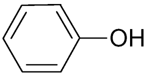
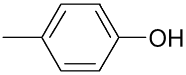
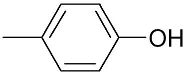
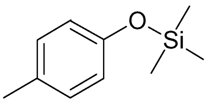
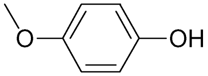
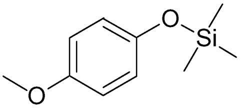
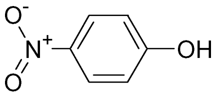
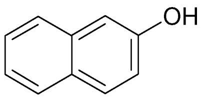
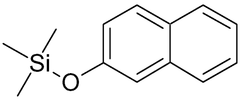
Entry	Substrate	Time(min)	Product	Yield%
1		75		95
2		95		93
3		30		98
4		80		97
5		25		98
6		45		94
7		2		96
8		50		95
9		500	—	—
10		40		98
11		45		97

TABLE I Protection of Alcohols and Phenols Catalyzed Using $Fe(ClO_4)_3$ in the Presence of Trimethyl Silyl Chloride *(Continued)*

Entry	Substrate	Time(min)	Product	Yield%
12		180		—
13		200		—
14		180		60
15		60		64
16		250		-
17		60		20

of $Fe(ClO_4)_3.6H_2O$. $Fe(ClO_4)_3$ $.6H_2O$ is a hygroscopic compound, and this property limits its use in reactions and it also needs special precaution. The reaction using $Fe(ClO_4)_3$-SiO_2 as a catalyst has all the heterogenous catalysis advantages.

CONCLUSION

In summary, $Fe(ClO_4)_3.6H_2O$ and $Fe(ClO_4)_3$–SiO_2, are found as a mild, efficient, and novel catalyst for the silylation of various hydroxy substrates with trimethylsilyl chloride under mild and neutral conditions. This procedure provides a novel, efficient, and general methodology for the preparation of trimethylsilyl ether in high yields. It is noteworthy to mention that $Fe(ClO_4)_3.6H_2O$ is a high hygroscopic compound, which is readily prepared by the reaction of ferric hydroxide and can be stored for a long time in desiccators. It is neither toxic, expensive, nor explosive, even when heated in solution. In addition, $Fe(ClO_4)_3$–SiO_2

TABLE II Fe(ClO_4)$_3$.6H_2O-Catalyzed Direct Conversion of Silyl Ethers to Acetate

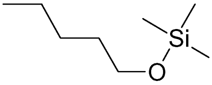
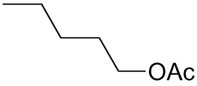
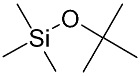
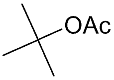
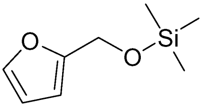
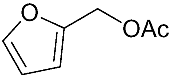
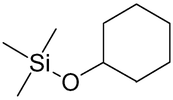
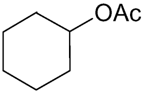
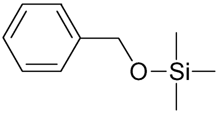
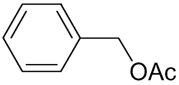
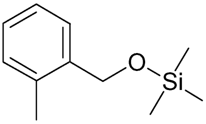
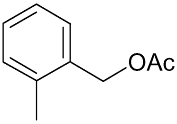
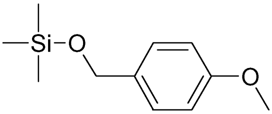
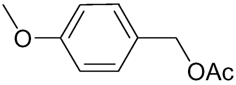
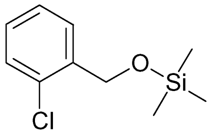
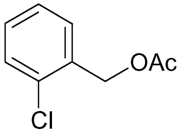
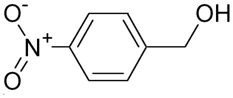
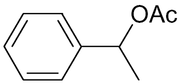
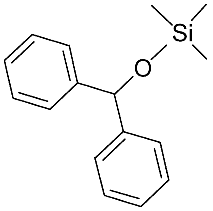
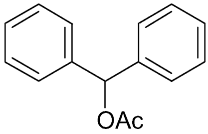
Entry	Substrate	Time(min)/Yield% Fe(ClO_4)$_3$.6H_2O (0.02 mmol)/Fe (ClO_4)$_3$ /SiO_2(0.2 g)	Product
1		40/94//20/94	
2		55/93//40/93	
3		20/97//13/97	
4		50/95//35/95	
5		15/98//8/98	
6		30/96//15/96	
7		10/97//7/97	

TABLE II $Fe(ClO_4)_3.6H_2O$-Catalyzed Direct Conversion of Silyl Ethers to Acetate *(Continued)*

Entry	Substrate	Time(min)/Yield%	Product
8		20/98//10/98	
9		30/98//15/98	
10		10/97//7/97	

is cheap, stable, easy to handle, and nontoxic catalyst. When used, the work-up procedure is very simple, consisting only of filtration and removal of the solvent.

EXPERIMENTAL

Preparation of Trimethylsilyl Ethers Using $Fe(ClO4)_3.6H_2O$: Typical Procedure

A mixture of benzyl alcohol (0.54 g, 5 mmol), $Fe(ClO4)_3.6H_2O$ (0.05 g, 0.1 mmol), trimethylsilyl chloride (0.815 g, 7.5 mmol), and dichloromethane (5 mL) was stirred at an ambient temperature. The progress of the reaction was monitored by TLC (eluent, n-hexane:diethyl ether, 4:1). After the completion of the reaction, water was added to the mixture to the mixture (15 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was separated and evaporated to dryness under reduced pressure to give the product (Table I).

Acetylation of Trimethylsilyl Ethers Using $Fe(ClO4)_3$ as Catalyst

The trimethyl silyl ethers were prepared according to the above procedure.

General Procedure

In a 10 mL flask, trimethyl silyl ether (1 mmol), acetic anhydride (1.5 mmol), and $Fe(ClO_4)_3$ (0.02 g, 1 mol%) were added and stirred at room temperature for the indicated times in Table II. After the completion of the reaction (monitored by TLC, eluent, n-hexane:diethyl ether, 4:1), dichloromethane (20 mL) was added and $Fe(ClO_4)_3/SiO_2$ filtrated. The filtrate was neutralized with sodium bicarbonate (10%). Then the organic layer was separated from the aqueous phase by separatory funnel. The organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the pure product was obtained in high yield (Table II).

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