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Polyvinylpolypyrrolidoniume tribromide as new and metal-free catalyst for the formylation and trimethylsilylation of hydroxyl group

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Abstract

Trimethylsilylation of alcohols was achieved using 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as silylating agent, in the presence of polyvinylpolypyrrolidoniume tribromide in acetonitrile at room temperature. Also a variety of alcohols were converted into alkyl formates by ethyl formate and a catalytic amount of polyvinylpolypyrrolidoniume tribromide under solvent free conditions at room temperature.

Keywords: Polyvinylpolypyrrolidone; Polyvinylpolypyrrolidoniume tribromide; Formylation; Silylation; Ethyl format; 1,1,1,3,3,3-Hexamethyldisilazane (HMDS)

Finding molecules, which are able to catalyze the reaction between others, is an important contribution of molecular chemists to increase the efficiency of chemical reactions whereby our daily life based on consumption of chemicals is shifted closer to an ecologically and economically tolerable equilibrium with our environment [1]. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research mainly because the reactions are carried out under mild conditions and the organic products are easily isolated from the reaction media. The protection–deprotection steps of active protic functional groups are frequently required in multistep synthesis to prevent their interference while modifying other functional groups in the same molecule [2]. Trimethylsilylation of organic compounds including labile hydrogen atoms find increasing use in analytical and in preparative organic chemistry [3]. Silyl ethers are one of the most popular protecting groups of hydroxyl moiety in synthetic organic chemistry and a various types of silyl ethers have been reported in the last decade [4–6]. Also *O*-formylation might be the method of choice for protecting a hydroxyl group in a complex synthetic sequence because deformylation can be occurred selectively in the presence of acetate or other ester groups.

1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is one of the most common silylating agent for silylation of hydroxyl group [7–10,6]. Also there are several reports on the formylation of alcohols by ethyl formate as cheap and non-toxic formylating reagent [11–14]. Their handling does not require special precautions, and the workup is not time-

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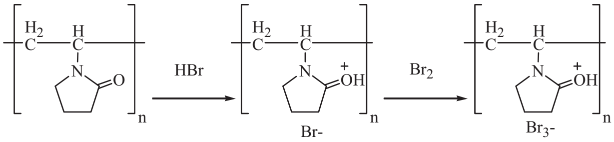

Scheme 1.

consuming, because the by-product of the reaction is ammonia and ethanol, which is simple to remove from the reaction media. However, the low activity of these reagents is the main drawback to their applications. Therefore, an appropriate catalyst should be used to activate these reagents.

In continuation of our ongoing efforts to develop new procedures for the protection and deprotection of organic functional groups [15–21], we decided to use polyvinylpolypyrrolidoniume tribromide as new and efficient catalyst for the preparation of trimethylsilyl ethers and alkyl formates.

Polyvinylpolypyrrolidoniume tribromide was prepared *via* reaction of polyvinylpolypyrrolidone with hydrobromic acid (HBr); then combination of resulting salt with bromine (Br_2).

Initially, in order to find appropriate conditions for the trimethylsilylation and formylation reactions, different solvents were screened. After solvents screening, we found that solvent-free conditions is the best choice for the preparation of alkyl formates, and acetonitrile is the appropriate solvent for the trimethylsilylation reaction.

Consequently, herein we disclosed a new catalytic protocol for the trimethylsilylation of primary, secondary and tertiary alcohols to produce the corresponding trimethylsilyl ethers using 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and a catalytic amount of polyvinylpolypyrrolidoniume tribromide in acetonitrile, (as solvent), at room temperature (Scheme 1 and Table 1).

Trimethylsilylation was carried out heterogeneously under mild and neutral conditions. Trimethylsilyl ethers easily obtained by mixing 1 mmol of alcohols, 0.8 mmol of 1,1,1,3,3,3-hexamethyldisilazane and 0.02 g of polyvinylpolypyrrolidoniume tribromide; then stirring of the resulting mixture at room temperature. After completion, reaction was quenched with water and the pure product was easily obtained by evaporation of solvent.

Table 1

Trimethylsilylation of hydroxyl groups using hexamethyldisilazane (HMDS) in the presence of a catalytic amount of polyvinylpolypyrrolidoniume tribromide in acetonitrile at room temperature.[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1	2-Chlorobenzyl alcohol	2-Chlorobenzyl trimethylsilyl ether	5	99
2	**4-Nitrobenzyl alcohol**	**4-Nitrobenzyl trimethylsilyl ether**	**60**	**90**
3	3-Flourobenzyl alcohol	3-Flourobenzyl trimethylsilyl ether	8	98
4	4-Bromobenzyl alcohol	4-Bromobenzyl trimethylsilyl ether	15	94
5	4-Chlorobenzyl alcohol	4-Chlorobenzyl trimethylsilyl ether	5	90
6	4-*iso*-Propylbenzyl alcohol	4-*iso*-Propylbenzyl trimethylsilyl ether	5	99
7	4-*tert*-Butylbenzyl alcohol	4-*tert*-Butylbenzyl trimethylsilyl ether	10	99
8	Pentaflourobenzyl alcohol	Pentaflourobenzyl trimethylsilyl ether	11	92
9	2-Phenyl ethanol	2-Phenyl ethyl trimethylsilyl ether	2	90
10	2-hydroxy-1,2-diphenylethanone	2-Oxo-1,2-diphenylethyl trimethylsilyl ether	10	82
11	**Cholesterol**	**Cholesterol trimethylsilyl ether**	**25**	**99**
12	2-Admantanol	2-Admantyl trimethylsilyl ether	5	96
13	1-Phenyl-1-propanol	1-Phenylpropyl trimethylsilyl ether	7	98
14	2-Phenylpropan-1-ol	2-Phenylpropyl trimethylsilyl ether	2	85
15	1-Heptanol	1-Heptyl trimethylsilyl ether	5	94
16	Pyridin-3-ylmethanol	Pyridin-3-ylmethyl trimethylsilyl ether	15	60
17	Furan-2-ylmethanol	Furan-2-ylmethyl trimethylsilyl ether	2	91
18	2-Methyl-1-phenyl-2-propanol	2-Methyl-1-phenyl-2-propyl trimethylsilyl ether	90	80
19	1-Admantanol	1-Admantyl trimethylsilyl ether	9	95
20	(4-Chlorophenyl)(phenyl)methanol	(4-Chlorophenyl)(phenyl)methyl trimethylsilyl ether	85	98
21	*p*-Cresol	*p*-Tolyl trimethylsilyl ether	2	97

[a] Substrate/HMDS/catalyst = 1 mmol/0.8 mmol/0.02 g.

[b] Isolated yield.