Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5005-5010

An Efficient and Convenient Method for Desilylation-Acetylation of Trimethylsiyl Ethers Catalyzed by Silica Sulfuric Acid

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An efficient and convenient method for desilylation-acetylation of trimethylsiyl ethers with acetic anhydride using silica sulfuric acid as catalyst under mild conditions is described.

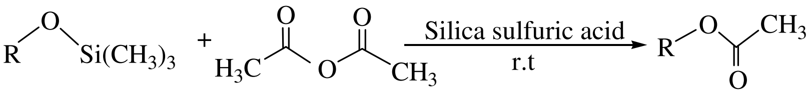
Key Words: Trimethylsilyl ether, Desilylation, Acetylation, Silica sulfuric acid.

INTRODUCTION

Aliphatic, aromatic and aryl substituted aliphatic carboxylic esters are very important compounds in industry and commerce. They can be extensively used as solvents, plasticizers, antiseptic substances, pesticides and as starting materials for synthesis of valuable medicines. They are synthesized by several methods. For example, esterification of carboxylic acids and alcohols[1] transesterification[2] alkylation of carboxylate anions[3,4] and acylation of alcohols or phenols[5,6]. On the other hand, ethers are also changed into esters by acylation using acylating agents such as acyl and aroyl halides (including sulfacyl halides) and anhydrides of carboxylic acids[7,8]. Ganem and Small[8] reported a dual mechanism involvting O-acylation of the ether followed by dissociation to the more stable carbonium ion or nucleophilic displacement (S_N^1 or S_N^2) at the oxonium by acetate.

Trimethylsilyl (TMS) ethers can be converted into the corresponding acetates using acetyl chloride and zinc chloride in acetonitrile[9] and acetic anhydride and montmorillonite[10] K-10. These methods have their own merits. But some methods have not been entirely satisfactory with drawbacks such as long reaction times (up to 24 h in the case of α-naphthyl trimethylsilyl ether)[10], low yields, tedious work-up, the emerging problem of corrosivity, effluent pollution and expensive, non-recoverable and unavailable catalysts.

Silica sulfuric acid is a kind of new type of solid acid, which has been extensively used in organic synthesis[11-20] due to its strong acidity, cheap, non-corrosive nature, reusability and non-polluting nature. Therefore, we are interested in using this inorganic acidic salts as a new sulfuric acid function. The work-up of the reactions is very simple, usually only removal of the catalyst by filtration and evaporation of the solvent are involved. In connection with our continued work on silica sulfuric acid, herein the desilylation-acetylation of trimethylsilyl ethers with acetic anhydride catalyzed by silica sulfuric acid is reported (**Scheme-I**).



1 **2** **3**

Scheme-I

EXPERIMENTAL

Trimethylsilyl ethers were prepared by reported procedure[21,22]. Silica sulfuric acid was prepared by reported procedure[14-18]. ^{1}H NMR spectra were measured on a Bruker Avance 400 (400 MHz) spectrometer using tetramethylsilane (TMS) as internal reference and $CDCl_3$ or CCl_4 as solvent. Boiling points and melting points are uncorrected. The products were characterized by comparison of their melting or boiling points with handbook[23-26] and literature values[27].

Conversion of the trimethylisilyl ethers into the corres-ponding acetates: A mixture of the trimethylisilyl ether (**1**) (2 mmol) and acetic anhydride (**2**) (5 mmol) in dry dichloromethane (5 mL) (except for those in absence of solvent) was stirred in the presence of silica sulfuric acid (800 mg) at room temperature for the length of time as indicated in Table-1. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the catalyst was washed with dichloromethane (2 × 5 mL). The filtrate was washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure furnished the essentially pure product **3**. Further purification was achieved by column chromatography on silica gel using petroleum ether and diethyl ether as eluent. Data of some compounds are shown below.

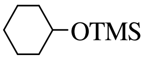
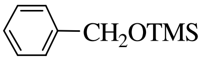
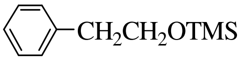
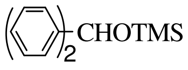
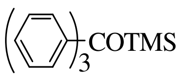
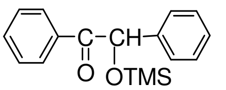
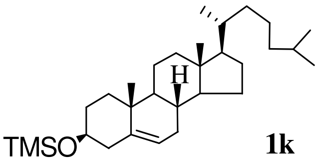
3k: m.p. 112-114 °C (lit.[23] 114-115 °C). ^{1}H NMR: $\delta = 0.71$ (s, 3H, 18-CH_3), 0.88 (d, 6H, $J = 6.4$ Hz, 26, 27-CH_3), 0.95 (d, 3H, $J = 6.4$ Hz, 21-CH_3), 1.04 (s, 3H, 19-CH_3), 2.06 (s, 3H, 3-$OCOCH_3$), 4.64 (m, 1H, 3α-H), 5.40 (d, 1H, $J = 4.4$ Hz, 6-H).

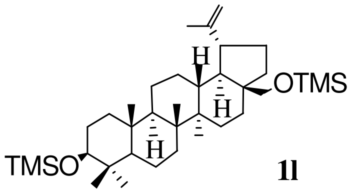
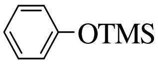
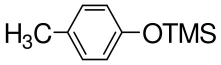
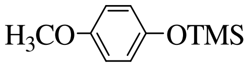
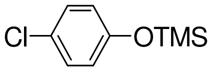
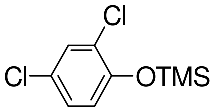
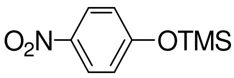
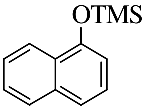
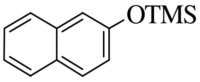
3l: m.p. 220-222 °C (lit.[25] 218-220 °C). ^{1}H NMR: $\delta = 0.84$, 0.88, 1.00, 1.04, 1.40 (s, 15H, 5 × CH_3), 1.06-1.68 (complex, CH_2, CH), 1.70 (s, 3H, 30-CH_3), 2.06 (s, 3H, 22-$OCOCH_3$), 2.08 (s, 3H, 3-$OCOCH_3$), 2.32 (m, 1H, 3-H), 3.86 (d, 1H, *J* = 11.2 Hz, 28-H'), 4.28 (d, 1H, *J* = 11.2 Hz, 28-H), 4.60 (s, 1H, 29-H'), 4.70 (s, 1H, 29-H).

RESULTS AND DISCUSSION

It is found that in the absence of catalyst no product was obtained. In the presence of silica sulfuric acid, treatment of a variety of silylated alcohols or phenols (**1**) with acetic anhydride (**2**) in dichloromethane (except for those in absence of solvent) at room temperature gave the corresponding acetates (**3**) in good yields. The results are shown in Table-1.

TABLE-1
DESILYLATION-ACETYLATION OF TRIMETHYLSIYL ETHERS WITH ACETIC ANHYDRIDE CATALYZED BY SILICA SULFURIC ACID

Entry	Substrate	Solvent	Time (min)	Yield (%)
1	$CH_3(CH_2)_3OTMS$ **1a**	None	25	91
2	$CH_3(CH_2)_6OTMS$ **1b**	None	30	90
3	$CH_3(CH_2)_8CH_2OTMS$ **1c**	None	30	88
4	 **1d**	None	45	76
5	 **1e**	None	20	92
6	 **1f**	None	30	86
7	 **1g**	None	35	84
8	 **1h**	CH_2Cl_2	55	68
9	 **1i**	CH_2Cl_2	180	28
10	 **1j**	CH_2Cl_2	60	66
11	 **1k**	CH_2Cl_2	50	77

Entry	Substrate	Solvent	Time (min)	Yield (%)
12	 **1l**	CH_2Cl_2	45	82
13	 **1m**	None	30	84
14	 **1n**	None	25	92
15	 **1o**	None	25	93
16	 **1p**	CH_2Cl_2	35	82
17	 **1q**	CH_2Cl_2	40	80
18	 **1r**	CH_2Cl_2	45	78
19	 **1s**	CH_2Cl_2	60	82
20	 **1t**	CH_2Cl_2	70	72

As for alcoholic trimethylsilyl ethers, primary (**1a**, **1b**, **1c**, **1e**, **1f**, **1g** and **1l**) and secondary (**1d**, **1h**, **1j**, **1k** and **1l**) alcoholic trimethylsilyl ethers can be more easily acetylated at room temperature. However, the hindered tertiary alcoholic trimethylsilyl ether shows the lowest activity. For example, triphenylmethanolic trimethylsilyl ether (**1i**) is acetylated with acetic anhydride in the presence of silica sulfuric acid at room temperature for 3 h, only afforded **3i** in 82 % yield. Therefore, primary and secondary alcoholic trimethylsilyl ether can be acetylated more easily than tertiary alcoholic trimethylsilyl ether.

As for phenolic trimethylsilyl ethers, electron-donating groups in aromatic ring have increased the reaction speed as well as reaction yields (**1n** and **1o**). On the other hand, electron-withdrawing groups in aromatic ring have decreased yields and increased reaction time (**1p**, **1q** and **1r**).

The yields and reaction conditions of present method comparing with actual figures for other methods have also been studied. The present procedure gives relatively better yields and needs much shorter reaction times than the reaction with a montmorillonite K-10 catalyst[10]. For example, α-naphthyl acetate (**3s**) was obtained in 32 % yield with montmorillonite K-10 catalyst after 24 h at room temperature. However, present procedure with silica sulfuric acid catalyst after only 1 h gave α-naphthyl acetate (**3s**) in 82 % yield at room temperature. Hence, the silica sulfuric acid would be the better catalyst to this kind of reaction.

The catalyst were easily regenerated washing with dichloromethane, followed in a desiccator drying at room temperature for 4 h. The catalyst could be reused six times for the synthesis of **3e** without significant loss of activity.

In conclusion, a desilylation-acetylation reaction of trimethylsilyl ethers is developed with the advantages of operational simplicity, higher yields, shorter reaction times and a recyclable and environmentally-friendly catalyst.

ACKNOWLEDGEMENTS

This project was supported by the National Natural Science Foundation of China, Educational Ministry of China, Science and Technology Commission of Hebei Province.

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(*Received*: 1 February 2007; *Accepted*: 1 April 2008) AJC-6494