SHORT PAPER

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Phosphomolybdic acid, an efficient and practical reagent for the oxidative deprotection of trimethylsilyl ethers to corresponding carbonyl compounds[†]

Tong-Shou Jin*, Yan-Wei Li, Guang Sun, Xin-Ru Song and Tong-Shuang Li

Department of Chemistry, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China

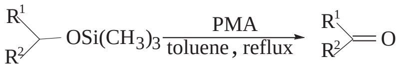
The oxidative deprotection of trimethylsilyl ethers to corresponding carbonyl compounds with phosphomolybdic acid (PMA) in refluxing toluene gives excellent yields.

Keywords: oxidative, deprotection, trimethylsilyl ethers, phosphomolybdic acid, heteropoly acid

The alcohol function is one of the most versatile group in organic chemistry and its controlled manipulation during synthesis is of great value to synthetic organic chemists. The protection of hydroxyl groups by means of silyl ethers has been extensively used in organic synthesis.[1] Hexamethyldisilazane (HMDS) has been found to be a convenient reagent for converting alcohols to their trimethylsilyl derivates.[2-5]

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years. However, some of the reported methods show limitations such as the requirement for aqueous reaction conditions,[6,7] use of expensive reagents,[8-10] long reaction times,[11,12] low yields of the products[13] and tedious workup.[7] Therefore introduction of new methods and inexpensive reagents for such function group transformation is still in demand.

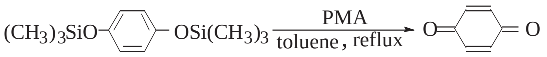
In recent years, phosphomolybdic acid (PMA), a kind of heteropoly acid (HPA) has been found to be useful catalyst in a variety of organic reactions.[14-18] HPA is superior to common inorganic acids. Furthermore, HPA can be used not only as an acid catalyst, but also as an oxidative and bifuntional catalyst. Herein we report a new and convenient method for the oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds in high yields using PMA. This oxidation is rather rare in the literature (Scheme 1).



1 **2**

(R^1, R^2 = H, aryl or alkyl)

Scheme 1



3 **4**

Scheme 2

In the presence of PMA, treatment of a variety of trimethylsilyl ethers in toluene refluxing gave the corresponding carbonyl compounds in good to excellent yields. The results are shown in Table 1. The present procedure needs much shorter reaction time than with potassium ferrate supported on to montmorillonite K-10.[19] For example, with potassium ferrate supported onto montmorillonite K-10 for 10 hours in refluxing acetonitrile, 4-chlorobenzyl aldehyde (**2g**) was obtained in 95% yield, but our procedure with PMA for 3.5 hours in refluxing toluene gave 4-chlorobenzyl aldehyde (**2g**) in the same yield.

As shown in Table 1, we found that a variety of trimethylsilylated benzylic alcohols with electron donating and electron withdrawing groups were converted to their corresponding aldehydes in good to excellent yields. Trimethylsilylated benzylic alcohols with electron donating could be easily converted into aldehydes in excellent yields. For example, trimethylsilylated *p*-methylbenzalcohol (**1d**) and *p*-methoxybenzalcohol (**1e**) required short reaction times (10 min and 12 min respectively) and gave products (**2d** and **2e**) with a excellent yields (97% and 96%). Trimethylsilylated benzylic alcohols with electron withdrawing groups showed lower activity, they need longer reaction times and gave secondary yields. For example, trimethylsilylated *p*-nitrobenzalcohol (**1f**) required a longer reaction time (45min) and gave product (**2f**) with a lower yield (85%). Therefore, trimethylsilylated benzylic alcohols with electron donating groups could be oxidated more easily than trimethylsilylated benzylic alcohols with eletron withdrawing groups.

Trimethylsilylated phenol was oxidated by PMA. For example, trimethylsilylated hydroquinone (**3j**) was oxidated with PMA for 10 min and gave 92% yield.

In a word, we have developed a new method and practical reagent for the direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds with the advantages of operational simplicity, high yields and short reaction times.

Experimental

All compounds used are known their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Trimethylsilyl ethers were prepared by reported procedure.[21,22]

General procedure for the oxidative deprotection of trimethylsilyl ethers to corresponding carbonyl compounds: In a round-bottomed flask (50ml) equipped with a magnetic stirrer and a condenser, a solution of trimethylsilyl ether (3mmol) in toluene (5ml) was prepared. Phosphomolybdic acid (0.3mmol) was added to the solution and refluxed for the length of time indicated in Table 1. The progress of reaction was monitored by TLC (eluent: petroleum/ether = 2:1). After completion of the reaction, the mixture was cooled to room temperature, then filtered and the filtrate was washed with saturated aqueous $NaHCO_3$ (2 × 10ml) and brine water (2 × 10ml), dried (Na_2SO_4) and evaporated. Further purification was achieved by distillation or column chromatograph on silica gel with light petroleum (b.p. 60–90°C) as eluent wherever necessary. Products were characterised by their melting points or boiling points.

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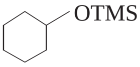
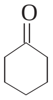
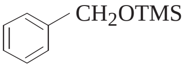
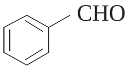
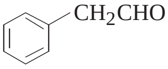
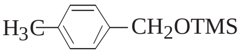
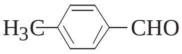
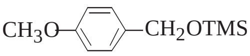
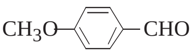
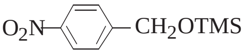
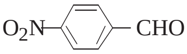
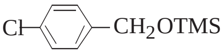
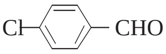
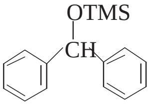
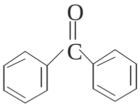
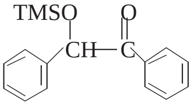
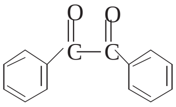
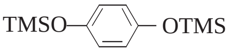
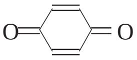
* To receive any correspondence. E-mail: orgsyn@mail.hbu.edu.cn

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Oxidative deprotection of trimethlsilyl ethers with PMA to carbonyl compounds in refluxing toluene

Entry	Substrate	Reaction time min/(h)	Product	Yields /%[a]	B.p./torr. or m.p./°C	
					Rep.[20]	Found
1	 **1a**	(1.2)	 **2a**	90	155/760	58–60/30
2	 **1b**	20	 **2b**	95	178–179/760	76–78/20
3	 **1c**	50	 **2c**	90	195/760	80-82/20
4	 **1d**	10	 **2d**	97	204–205/760	95–97/20
5	 **1e**	12	 **2e**	96	248/760	125–126/20
6	 **1f**	45	 **2f**	85	105–108	106–108
7	 **1g**	(3.5)	 **2g**	90	47–50	48–50
8	 **1h**	12	 **2h**	95	48–49	49–50
9	 **1i**	(1)	 **2i**	89	94–95	95–96
10	 **3j**	10	 **4j**	92	113–115	114–115

[a] Yields refer to isolated products.

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