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Direct Oxidative Deprotection using Montmorillonite Supported Bis(trimethylsilyl)chromate†

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Direct oxidative deprotection of different trimethylsilyl ethers to their corresponding carbonyl compounds has been achieved using montmorillonite K-10 supported bis(trimethylsilyl)chromate in dichloromethane.

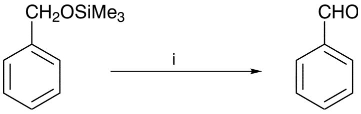
The protection of functional groups is a useful and important method in organic synthesis. Hydroxy groups are one of the most abundant functional groups in organic molecules and its controlled manipulation is very important in multistep synthesis. One of the most useful and convenient methods for protection of hydroxy groups is their transformation to trialkylsilyl ethers.[1,2]

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has recently found much attention.[3] However some of the reported methods show limitations such as the requirement for aqueous reaction conditions,[4,5] use of expensive reagents,[6–8] long reaction times, tedious work-up[5] and low yields of products.[9] Therefore introduction of new methods and inexpensive reagents for such functional group transformations is still in much demand.

Recently we have demonstrated the use of bis(trimethylsilyl)chromate supported on silica gel and montmorillonite K-10 as an efficient and mild oxidizing agent under classical heating[10,11] or microwave irradiation.[11,12] Now we wish to report a new and efficient method for the oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds using bis(trimethylsilyl)chromate supported on montmorillonite K-10 in dichloromethane at room temperature.

Heating chromic anhydride under reflux with a slight excess of hexamethyldisoloxane in dichloromethane produces a nearly homogeneous solution. BTSC supported on montmorillonite K-10 is conveniently prepared simply by adding montmorillonite K-10 to a vigorously stirred solution of BTSC.[10,11] A dark brown free-flowing solid was obtained on evaporation of volatiles. This reagent can be stored in a dark brown bottle without appreciable loss of reactivity for at least three months.

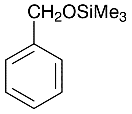
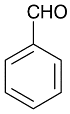
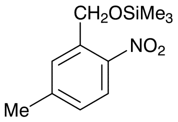
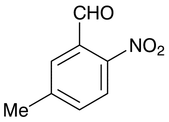
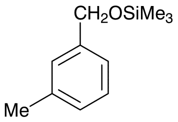
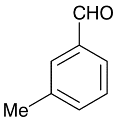
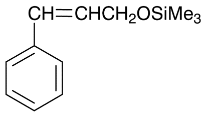
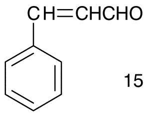
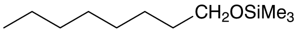
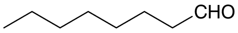
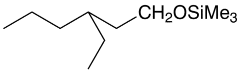
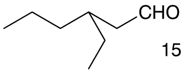
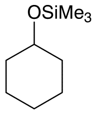
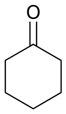
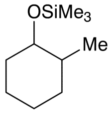
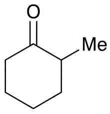
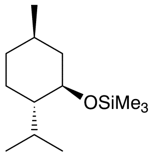
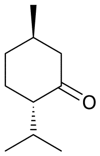
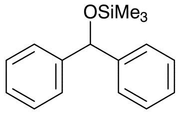
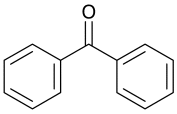
In a typical reaction 2–2.2 equiv. of BTSC supported on montmorillonite K-10 was added to a stirred solution of a trimethylsilyl ether in dry CH_2Cl_2 (Scheme 1). The reaction mixture was stirred at room temperature until the reaction was complete, then it was filtered and washed with dichloromethane. Evaporation of the solvent gave the corresponding carbonyl compounds. Different types of trimethylsilyl ethers were converted to their corresponding carbonyl compounds in high yield. For example benzyl trimethylsilyl ether (Table 1, entry 1) was oxidized to benzaldehyde in excellent yield.



Scheme 1 *Reagents and conditions*: i, CrO_3, TMSOTMS, montmorillonite K-10, CH_2Cl_2, 25 °C, 25 min

Substituted benzyl trimethylsilyl ethers (entries 2 and 3) were similarly oxidized to their corresponding aldehydes under the same conditions. No traces of benzoic acid were observed even after prolonged reflux of benzaldehyde with excess supported BTSC. Cinnamyl trimethylsilyl ether (entry 4) was also oxidatively deprotected to cinnamyl aldehyde in

Table 1 Oxidative deprotection of trimethylsilyl ethers with BTSC supported on montmorillonite K10

Entry	Alcohol	Carbonyl compound	Reaction time/min	Yield (%)
1			10	93
2			15	91
3			10	93
4			15	90
5			15	88
6			15	82
7			20	90
8			20	89
9			30	88
10			20	92

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

high yield. No benzaldehyde was detected in this reaction, showing that benzylic double bonds are not prone to cleavage by this method.

In conclusion, BTSC supported onto montmorillonite K-10 is a simple and inexpensive reagent for one-pot oxidative deprotection of trimethylsilyl ethers.

Experimental

All products were known compounds and identified by comparison with authentic samples. Yields refer to GC analysis. Trimethylsilyl ethers were synthesized according to the reported procedure.[13] BTSC supported on montmorillonite K-10 was also prepared according to a reported procedure.[10–12]

Oxidative Deprotection of Trimethylsilyl Ethers, a Typical Procedure.—In a round bottomed flask (50 ml) equipped with a magnetic stirrer and a condenser a solution of trimethylsilyl benzyl ether (180 mg, 1 mmol) in CH_2Cl_2 (20 ml) was prepared. To this solution pre-made BTSC supported onto montmorillonite K-10 (1.66 g equiv. to 2.4 mmol of CrO_3) was added. The reaction mixture was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC [eluent: light petroleum–ethyl acetate (8:2)]. The mixture was filtered and the solid material was washed with CH_2Cl_2 (20 ml). The filtrate was evaporated to dryness under reduced pressure and the resulting crude material was purified on a silica gel pad. After evaporation of solvent pure benzaldehyde was obtained in 93% yield (Table 1).

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12 *Preparation of Bis(trimethylsilyl)chromate Supported on Montmorillonite K-10*.—To a solution of hexamethyldisiloxane (6.4 ml, 0.03 mol) in 20 ml of dry dichloromethane was added chromic anhydride (3 g, 0.03 mol). The reaction mixture was stirred in an oil-bath at 50 °C for 5 h. Solid chromic anhydride dissolved and the dark red mixture became a homogeneous solution. Montmorillonite K-10 (13 g) pre-dried in a 120 °C oven overnight and activated in a microwave oven for 3 min was added to the warm reaction mixture and the resulting mixture was stirred for a further 5 h. The solvent and other volatile components were distilled under reduced pressure to afford 19 g of supported chromium oxidant.
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