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Direct Oxidative Deprotection of Trimethylsilyl Ethers to their Corresponding Carbonyl Compounds with Bis (trimethylsilyl) Chromate Supported onto Silica Gel in Aprotic Solvent.

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Abstract :

Primary and secondary trimethylsilyl ethers are converted to their carbonyl compounds effeciently using bis (Trimethylsilyl) chromate supported on silica gel in dichloromethane. Benzylic double bonds are not prone to cleavage reactions with this method.

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years¹⁻¹⁵. However some the reported methods show limitations such as the requirment for aqueous reaction conditions^{4,7} use of expensive reagents^{9,13,14}, long reaction times^{6,8}, low yields of products¹² and tedious work up⁷. Therefore introduction of new mild methods, inexpensive and common reagents for such functional group transformations is still in demand.

Recently we have reported oxidation of primary and secondary alcohols to the corresponding carbonyl compounds using bis (trimethylsilyl)chromate supported onto silica gel under microwave irradiation¹⁶ and supported onto montmorillonite K-10 under classical heating⁷ or microwave irradiation¹⁸.

Now in this communication we report that bis (trimethylsilyI) chromate supported onto silica gel, a previously reported oxidizing agent²⁰ is able to oxidatively deprotect trimethylsilyI ethers to their corresponding carbonyI compounds.

In a typical reaction 2-2.4 equivalents of BTSC supported onto silica gel was added to the stirring solution of a trimethylsilyl ether in dichloromethane. The reaction mixture was stirred at room temperature until the reaction was complete, then it was filtered and washed with dichloromethane. Evaporation of solvent gave the corresponding carbonyl compounds. Different types of trimethyl silyl ethers were converted to their corresponding carbonyl compounds by this procedure in high yield.

For example trimethylsilyl benzyl ether (entry 1) was deprotected oxidatively by this method to benzaldehyde in almost quantitative yield after 20 min stirring in dichloromethane at room temperature (Table)



Substituted trimethylsilyl benzyl ethers (Entries 2 and 3) were similarly oxidized to their corresponding aldehydes under above condition. No trace of benzoic acid was observed even after prolonged reflux of benzaldehyde with excess supported BTSC. Trimethylsilyl cinnamyl ether (Entry 4) was also oxidatively deprotected to cinnamyl aldehyde in high yields. Benzaldehyde (28%) was detected in this reaction showing benzylic double bonds are prone to cleavage reaction with this method.

In conclusion BTSC supported onto silica gel presents a simple and inexpensive reagent for one pot oxidative deprotection of trimethylsilyl ethers. Due to the simplicity of the method and inexpensive reagents being used this methodology should find utility in organic synthesis.

Experimental

All chemicals used were of the high commercially available purity and none required further purification. All products were identified with their NMR and IR spectroscopic data. The yields reported in table are based on isolated products BTSC supported on silica gel and trimethylsilyl ethers were prepared according to reported procedures respectively^{19,20}.

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 silica gel (1.66g equivalent to 2.4 mmol of chromium (VI) oxide) was added. The reaction mixture was stirred at room temperature for 25 min. The progress of reaction was monitored by TLC (eluent pet ether: 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

Entry	Alcohol	Carbonyl Compound	Reaction Time(min)	Yield %
1	CH ₂ OSi(Me) 3	СНО	25	95%
2 Me	CH ₂ OSi(Me) ₃ NO ₂ CH ₂ OSi(Me) ₃	Me ÇHO	15	93%
3 Me ⁻		Me	15	94%
4	CH=CHCH ₂ OSI(Me) ₃	сн=снсно	20	71%
5 -		е)3 Сно	20	89%
6 -	CH ₂ OSi(Me) ₃	СНО	20	78%
7	OSi(Me) ₃ OSi(Me) ₃		25	89%
8			25	88%
9	OSI(Me) 3		25	89%
10			25	92%

Table.Oxidative Deprotection Of Trimethylsilyl Ethers With BTSC Supported onto Silica Gel

resulting crude material was purified on silica gel pad. After evaporation of solvent pure benzaldehyde was obtained in 95% yield. (Table).

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