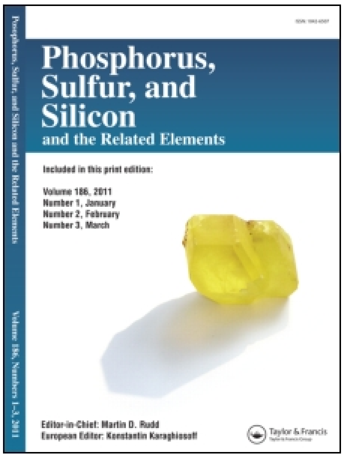

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Tajbakhsh, Mahmoud , Alinezhad, Heshmatollah and Urimi, Azade Geran(2008) 'Oxidative Deprotection of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds Using Cetyltrimethylammonium Peroxodisulfate', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 6, 1447 — 1454

To link to this Article: DOI: 10.1080/10426500701672200

URL: http://dx.doi.org/10.1080/10426500701672200

Phosphorus, Sulfur, and Silicon, 183:1447–1454, 2008

ISSN: 1042-6507 print / 1563-5325 online
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Oxidative Deprotection of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds Using Cetyltrimethylammonium Peroxodisulfate

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Cetyltrimethylammonium peroxodisulfate $(CTA)_2S_2O_8$ *was quantitatively prepared and used for the oxidation and deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds in acetonitrile. Selective oxidation of allylic or benzylic trimethylsilyl ethers in the presence of saturated alkyl trimethylsilyl ethers were also achieved. This new reagent is more efficient and has several advantages over similar oxidants in terms of the amount of oxidant, short reaction time, simple work up, and high yield.*

Keywords Cetyltrimethylammonium peroxodisulfate; deprotection; oxidation; trimethylsilyl ethers

INTRODUCTION

The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in synthetic organic chemistry of polyfunctional molecules, including the total synthesis of natural products. Thus, a large number of protective groups have been developed along with numerous methods for their removal.[1–5]

Conversion of the hydroxy group to a trimethylsilyl ether moiety is one of the most useful and convenient methods for the protection of this functional group.[6] Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has attracted considerable attention during recent years.[7–15] However, some of the reported methods show limitations because of the use of expensive reagents, long reaction time, low yields of the products or tedious work-up. Therefore, the

Received 24 July 2007; accepted 9 September 2007.
Financial support from the Research Council of Mazandaran University is gratefully acknowledged.

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introduction of new methods and inexpensive reagents for such transformations is still in a challenge.

$(CTA)_2S_2O_8$ is easily prepared by addition of an aqueous solution of cetyltrimethylammonium chloride to a solution of potassium peroxodisulfate in water.[16] The isolated $(CTA)_2S_2O_8$ was characterized by its spectroscopical and physical data.

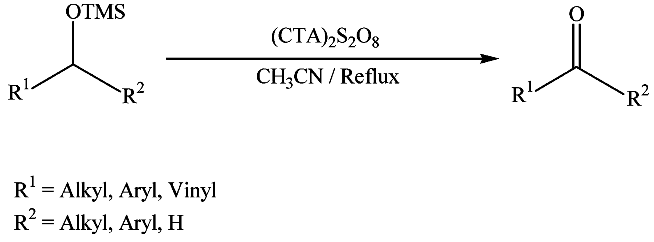
In our ongoing program to find new oxidizing agents[17] for organic substrates we have found that $(CTA)_2S_2O_8$ is an efficient oxidant for benzylic, allylic, and aliphatic trimethylsilyl ethers and hydroquinone trimethylsilyl ethers.

RESULTS AND DISCUSSION

In order to find the optimum conditions for the oxidation and deprotection of trimethylsilyl ethers with $(CTA)_2S_2O_8$, we have chosen 4-chlorobenzyltrimethylsilyl ether as a model substrate. First, we have performed the oxidation and deprotection in different solvents such as hexane, chloroform, dichloromethane, THF, acetone, and acetonitril. Our results showed that acetonitril was the best solvent to give the highest yield of 4-chlorobenzaldehyde (Table I).

We have also carried out the oxidation and deprotection reaction at different temperatures. The results indicated that refluxing in acetonitril gave the highest yield of 4-chlorobenzaldehyde. Different mole ratios of oxidant to substrate were also examined; a 1:1 molar ratio of oxidant to substrate resulted in the highest yield of 4-chlorobenzaldehyde. In order to show the applicability and generality of this method we have examined the reaction of benzylic, allylic and aliphatic trimethylsilyl ethers with $(CTA)_2S_2O_8$ in refluxing acetonitril (Scheme 1). The results are shown in Table II.

In this procedure, the oxidant is carefully added to the substrate and the mixture is refluxed until TLC analysis indicates a complete reaction.



SCHEME 1

TABLE I Deprotection of 4-Chlorobenzyltrimethylsilyl Ether in Different Solvents Using $(CTA)_2S_2O_8$ at Reflux Temperature

Solvent	Reaction time (min)	Yield (%) [a]
CH_3CN	2	95
C_3H_6O	10	90
THF	60	75
CH_2Cl_2	60	50
$CHCl_3$	60	30
n-C_6H_{12}	60	10

[a] Yields refer to isolated products.

Trimethylsilyl ethers were converted to the corresponding aldehydes and ketones in good to excellent yields and no significant side reactions, such as overoxidation to the respective carboxylic acids or oxidation of double bonds were observed.

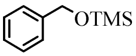
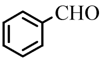
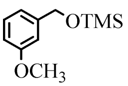
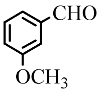
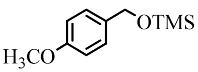
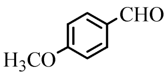
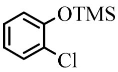
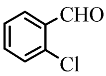
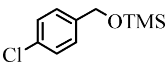
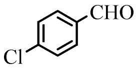
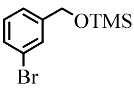
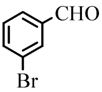
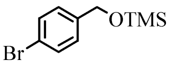
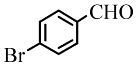
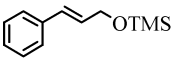
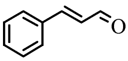
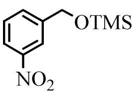
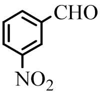
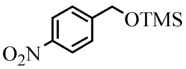
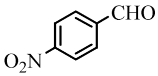
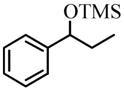
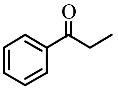
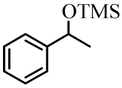
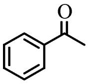
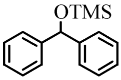
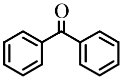
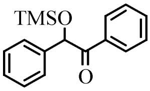
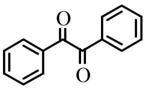
As indicated in Table II, benzylic trimethylsilyl ethers with different substituents at the phenyl ring when treated with $(CTA)_2S_2O_8$ in refluxing acetonitrile afforded the corresponding aldehydes and ketones in excellent yields and short reaction time. Benzoin under the reaction conditions required a longer reaction time and gave a lower yield. Benzylic trimethylsilyl ethers bearing a strongly electron withdrawing group such as NO_2 gave lower yield and required also a longer reaction time. Primary and secondary aliphatic as well as allylic trimethylsilyl ethers needed longer reaction time and afforded the corresponding aldehydes and ketones in lower yield. A higher molar ratio of oxidant to substrate did not improve the yield of the reaction.

Similarly, trimethylsilyl ethers of hydroquinones when treated with $(CTA)_2S_2O_8$ under the same reaction conditions gave the corresponding benzoquinones in excellent yields (Table II).

In order to determine the chemoselectivity the oxidation reaction was carried out with a mixture of allylic (or benzylic) and saturated trimethylsilyl ethers under the same reaction conditions; the results are shown in Table III.

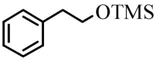
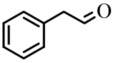
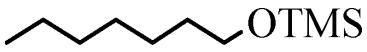
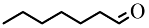
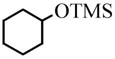
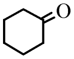
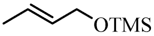
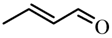
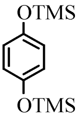
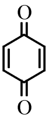
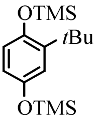
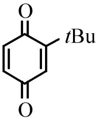
As shown in Table III, when an equimolar amount of benzyl trimethylsilyl ether and 2-phenyl-1-ethyltrimethylsilyl ether were treated with one equivalent of $(CTA)_2S_2O_8$ in refluxing acetonitrile for 8 min only benzyl trimethylsilyl ether was oxidized, while 2-phenyl-1-ethyltrimethylsilyl ether remained unchanged. Similarly, cinamyl trimethylsilyl ether was selectively oxidized in the presence of 2-phenyl-1-ethyltrimethylsilyl ether and 1-phenyl-1-ethyltrimethylsilyl ether gave exclusively acetophenone in the presence

TABLE II Oxidative Deprotection of Trimethylsilyl Ethers with $(CTA)_2S_2O_8$

Substrate	Product	Time (min)	Yield (%) [a,b]
		8	97
		15	94
		8	95
		15	94
		10	95
		12	93
		10	95
		20	90
		60	70
		60	75
		17	93
		20	95
		20	92
		60	80

(Continued on next page)

TABLE II Oxidative Deprotection of Trimethylsilyl Ethers with $(CTA)_2S_2O_8$ (Continued)

Substrate	Product	Time (min)	Yield (%) [a,b]
		60	80
		60	75
		60	75
		60	80
		15	95
		25	97

[a] Products were characterized by their physical constants, spectroscopic data (IR, ^1H NMR), GC, and comparison with authentic samples; [b] yield of isolated pure carbonyl compounds.

of cyclohexyltrimethylsilyl ether. Hydroquinone trimethylsilyl ether was also oxidized quantitatively in the presence of 1-heptyl trimethylsilyl ether after 15 min (Table III).

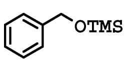
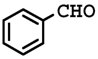
In order to show the advantages and drawbacks of our reagent we have compared some of our results with those reported in the literature (Table IV). As indicated in Table IV $(CTA)_2S_2O_8$ has certain advantages over similar oxidizing agents in terms of amounts of oxidant, short reaction times, higher yield of the product, and especially milder reaction conditions.

EXPERIMENTAL

Preparation of Cetyltrimethylammonium Peroxodisulfate, $(CTA)_2S_2O_8$

To a solution of hexadecyl trimethylammonium bromide (3.7 g, 10 mmol) in 75 mL of water $K_2S_2O_8$(1.3 g, 5 mmol) in 100 mL of water was added dropwise and the reaction mixture was stirred for 20 min at room temperature. A white solid was formed. The precipitate was

TABLE III Chemoselective Oxidative Deprotection of Trimethylsilyl Ethers with $(CTA)_2S_2O_8$

Substrate	Product	Time (min)	Yield (%)[a]
		8	97
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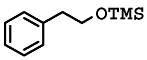
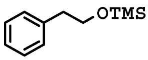
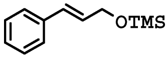
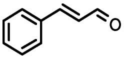
			0
			90
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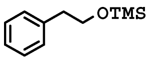
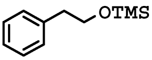
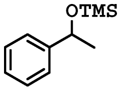
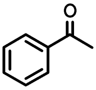
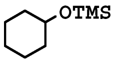
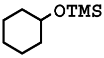
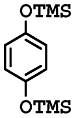
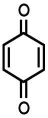
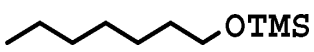
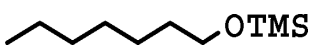
		20	0
			95
+	+		
		20	0
			95
+	+		
		15	0

[a] Yield was determined by ^{1}H NMR.

filtered, washed with cold distilled water (50 mL) and dried in a desiccator under vacuum over calcium chloride to afford a white powder. The yield of $(CTA)_2S_2O_8$ was 92%; it decomposes at 125°C to a light brown material.

General Procedure for the Conversion of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds

To a solution of the substrate (1 mmol) in MeCN (15 mL) was added $(CTA)_2S_2O_8$ (0.76 g, 1 mmol) and the mixture was magnetically stirred under reflux conditions for 8-60 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane / EtOAc, 10:1). The reaction mixture was cooled to room temperature and filtered. The solid material

TABLE IV Comparison of Some of the Results Obtained by the Oxidative Deprotection of Trimethylsilyl Ethers Using $(CTA)_2S_2O_8$ with those Using Other Oxidants

Reagent	Substrate	Reagent/ Substrate	Time (min)	Reaction Conditions	Yield (%)	Ref
2,6-DCPFC[a]	p-$MeOC_6H_4CH_2OSiMe_3$	1:1	6	CH_3CN,	96	17e
	$(C_6H_5)_2CHOSiMe_3$		5	r. t.	100	
QFC[b]	p-$MeOC_6H_4CH_2OSiMe_3$	1:1	30	CH_3CN,	94	17c
	$(C_6H_5)_2CHOSiMe_3$		96	r. t.	93	
BTPPC[d]	p-$MeOC_6H_4CH_2OSiMe_3$	1:1	300	CH_3CN,	90	17g
	$(C_6H_5)_2CHOSiMe_3$		18	reflux	95	
3-CPCC[c]	p-$MeOC_6H_4CH_2OSiMe_3$	2:1	45	CH_2Cl_2,	93	17h
	$(C_6H_5)_2CHOSiMe_3$		120	reflux.	80	
[BTPPPODS]	p-$MeOC_6H_4CH_2OSiMe_3$	1:1	5	CH_3CN,	94	17d
	$(C_6H_5)_2CHOSiMe_3$		7	reflux	95	
ATPPD[e]	p-$MeOC_6H_4CH_2OSiMe_3$	1.15:1	15	CH_3CN,	92	17f
	$(C_6H_5)_2CHOSiMe_3$		20	reflux	95	

[a]2,6-Dicarboxypyridinium fluorochromate; [b] quinolinium fluorochromate; [c]3-carboxypyridinium chlorochromate; [d]benzyltriphenylphosphonium peroxodisulfate; and [e]allyltriphenylphosphonium peroxodisulfate.

was washed with MeCN (20 mL). The filtrates were combined and the solvent was evaporated. The resulting crude material was purified by chromatography using silica gel and an appropriate eluent (n-hexane / EtOAc, 10:1). The pure carbonyl compounds were obtained in 70–97% yields (Tables II and III).

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