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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>

A Mild and Efficient Method for Oxidative Deprotection of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds Using



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To cite this Article Ghasemnejad-Bosra, Hassan , Tajbakhsh, Mahmood , Ramzanian-Lehmali, Farhad , Shabani-Mahali, Majid and Khalilzadeh, Mohammad A.(2008) 'A Mild and Efficient Method for Oxidative Deprotection of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds Using $[\text{PhCH}_2\text{NMe}_2\text{Ph}]_2\text{S}_2\text{O}_8$ ', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 6, 1496 — 1500

To link to this Article: DOI: 10.1080/10426500701688214

URL: <http://dx.doi.org/10.1080/10426500701688214>

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A Mild and Efficient Method for Oxidative Deprotection of Trimethylsilyl Ethers to the Corresponding Carbonyl Compounds Using $[\text{PhCH}_2\text{NMe}_2\text{Ph}]_2\text{S}_2\text{O}_8$

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Deprotection of trimethylsilyl ethers to the parent aldehydes and ketones in high yields has been carried out under mild conditions using N-benzyl N,N-dimethyl anilinium peroxodisulfate.

Keywords Deprotection; N-benzyl N,N-dimethyl anilinium peroxodisulfate; oxidation; trimethylsilyl ethers

INTRODUCTION

The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in the 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 method for their removal.^{1–4}

Conversion of the hydroxy group to trimethylsilyl ether is one of the most useful and convenient methods for the protection of this functional group. Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years.^{5–14}

Received 6 August 2007; accepted 16 September 2007.

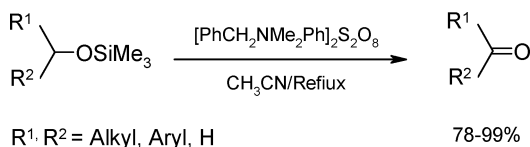
We are thankful to the Azad University of Medical Sciences of Babol and Mazandaran University Research Council for partial support of this work.

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However, some of the reported methods show limitations such as the use of expensive reagents, long reaction times, low yields of the products, and tedious work-up. Therefore, the introduction of new methods and inexpensive reagents for the transformation of this functional group is still in demand.

RESULTS AND DISCUSSION

As a part of our investigations to develop new oxidation methods, we report here a new, simple, and general procedure that can be used for the oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds under non-aqueous conditions.¹⁵ We have found *N*-benzyl *N,N*-dimethyl anilinium peroxodisulfate to be a new, rapid and efficient reagent for this purpose (Scheme 1).



SCHEME 1

N-Benzyl *N,N*-dimethyl anilinium peroxodisulfate ($[\text{PhCH}_2\text{NMe}_2\text{Ph}_2\text{S}_2\text{O}_8]$) is a mild, efficient, stable and cheap reagent, which was used for our studies under non-aqueous conditions. This reagent is a white powder and is prepared by dropwise addition of an aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ to an aqueous solution of *N*-benzyl *N,N*-dimethyl anilinium bromide at room temperature. Filtration and drying of the precipitate produced a white powder, which could be stored for months without losing its oxidation ability. It was characterized by ^1H MNR spectroscopy and elemental analysis.

To find the optimum conditions for the oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds we have chosen benzyl trimethylsilyl ether as a model compound.

The effect of the solvent in the oxidation reaction was evaluated by carrying out the oxidation in a series of solvents with varying polarity. Deprotection of benzyl trimethylsilyl ether with the equimolar amount of the peroxodisulfate was carried out in dichloromethane, chloroform, tetrahydrofuran, *n*-hexane and acetonitrile at reflux temperature. The results are presented in Table I.

As indicated in Table I a 1:1 molar ratio of the trimethylsilyl ether and the oxidant in refluxing acetonitrile gives benzaldehyde in excellent yield.

TABLE I Deprotection of Benzyl Trimethylsilyl Ether in Different Solvents using $[\text{PhCH}_2\text{NMe}_2\text{Ph}]_2\text{S}_2\text{O}_8$ at Reflux Temperature

Solvent	Reaction period (min)	Yield (%) ^a
CH_3CN	5	99
CHCl_3	90	70
CH_2Cl_2	96	74
$n\text{-C}_6\text{H}_{12}$	100	15
THF	95	35

^aYields refer to isolated products.

In order to evaluate the general applicability of this method we have oxidized benzylic, allylic and aliphatic trimethylsilyl ethers to the corresponding carbonyl compounds with *N*-benzyl *N*, *N*-dimethyl anilinium peroxodisulfate in acetonitrile. The results are shown in Table II. It becomes clear from Table II that benzylic trimethylsilyl ethers are oxidized in excellent yield under the reaction conditions. The strong electron withdrawing nitro group retards the reaction and also aliphatic silylethers need longer reaction time for oxidation.

TABLE II Oxidative Deprotection of Trimethylsilyl Ethers with $[\text{PhCH}_2\text{NMe}_2\text{Ph}]_2\text{S}_2\text{O}_8$ in CH_3CN at Reflux Temperature

Substrate	Time (min)	Product ^a	Yield (%) ^{b,c}
$\text{C}_6\text{H}_5\text{CH}_2\text{OSiMe}_3$	5	$\text{C}_6\text{H}_5\text{CHO}$	99
$(\text{C}_6\text{H}_5)_2\text{CHOSiMe}_3$	8	$(\text{C}_6\text{H}_5)_2\text{CO}$	97
<i>o</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	7	<i>o</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	98
<i>p</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	6	<i>p</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	97
<i>p</i> - $\text{ClC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{OSiMe}_3$	7	<i>p</i> - $\text{ClC}_6\text{H}_4\text{COCH}_3$	92
<i>m</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	7	<i>m</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	95
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	6	<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	96
<i>p</i> - $\text{MeC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	12	<i>p</i> - $\text{MeC}_6\text{H}_4\text{CHO}$	94
<i>o</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	9	<i>o</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	96
<i>p</i> - $\text{MeC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{OSiMe}_3$	10	<i>p</i> - $\text{MeC}_6\text{H}_4\text{C}(\text{CH}_3)\text{O}$	96
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	45	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	78
$\text{C}_6\text{H}_5\text{CH}(\text{p-ClC}_6\text{H}_4)\text{OSiMe}_3$	7	$\text{C}_6\text{H}_5\text{C}(\text{p-ClC}_6\text{H}_4)\text{O}$	95
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$	25	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$	86
$\text{CH}_3(\text{CH}_2)_7\text{OSiMe}_3$	40	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	82
α -tetralol trimethylsilyl ether	11	A-tetralon	94
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OSiMe}_3$	7	Cinnamaldehyde	93

^aAll of the products were characterized by comparing their IR and ^1H NMR data with those of authentic samples; ^bYields refer to isolated products; and ^cEluent: EtOAc/*n*-hexane (1:10).

It is noteworthy that, unlike other oxidative hydrolytic methods, the major drawback of overoxidation of the resulting aldehydes is not observed under the reaction conditions. α,β -Unsaturated derivatives are oxidized very efficiently without affecting the olefinic bond and the reaction is essentially chemoselective. Furthermore, functional groups such as chloro, methoxy, nitro, and alkyl groups were also inert to this reagent and no byproduct formation was observed (Table II).

In conclusion, *N*-benzyl *N,N*-dimethyl anilinium peroxodisulfate is a mild, efficient, and inexpensive reagent for the one-pot oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds in non-aqueous conditions.

EXPERIMENTAL

All products were isolated and identified by comparison of their physical data with those of authentic samples. ^1H NMR spectra were measured at 90 MHz with a JEOL JNM-EX 90 spectrometer with tetramethylsilane as an internal reference and DMSO- d_6 as solvent. IR spectra were recorded with a Pye-unicam SP 1100 spectrophotometer. Elemental analyses were performed on a LECO 250 instrument. Melting points were determined with an Electro Thermal 9100 apparatus. All solvent were freshly distilled before use. The trimethylsilyl ethers were prepared according to a published procedure.¹⁰

Preparation of *N*-Benzyl, *N,N*-Dimethyl Anilinium Peroxodisulfate [$\text{PhCH}_2\text{NMe}_2\text{Ph}$] $_2\text{S}_2\text{O}_8$

To a solution of *N,N*-dimethyl anilinium bromide (14.60 g, 50 mmol) in water (100 mL) was added dropwise $\text{K}_2\text{S}_2\text{O}_8$ (13.51 g, 50 mmol) in water (100 mL) and the reaction mixture was stirred for 0.5 h at room temperature. The precipitate formed was filtered, washed with cooled distilled water (50 mL), and dried in a desiccator under vacuum over calcium chloride to afford a white powder (92%), which decomposes at 181–183°C to a dark brown material. ^1H NMR (DMSO): δ 8.2–6.9 (m, 10H, C_6H_5), 5.80 (s, 2H, CH_2), 3.95 (s, 6H, CH_3). Analysis: for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_8\text{S}_2$ Calcd. C, 58.43%; H, 5.87%; N, 4.54%, Found: C, 58.46%; H, 5.89%; N, 4.56%.

General Procedure for the Oxidative Deprotection of Trimethylsilyl Ethers with *N*-Benzyl, *N,N*-Dimethyl Anilinium Peroxodisulfate

In a round bottomed flask (50 mL) equipped with a magnetic stirrer a mixture of the substrate (1 mmol) in CH_3CN (5 mL) and *N*-benzyl

N,N-dimethyl anilinium peroxodisulfate (1 mmol) was placed. The reaction mixture was stirred at reflux temperature for the specified time (Table II). The progress of the reaction was monitored by TLC. After the reaction was completed, the mixture was filtered and the solid material was washed with diethyl ether (2×10 mL). From the combined filtrates, the solvent was evaporated under reduced pressure to afford pure carbonyl compound in 78–99%. If necessary, the products were further purified by column chromatography on a silica gel using an appropriate eluent (EtOAc/*n*-hexane, 15:85).

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