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Mild and Efficient Method for Oxidative Deprotection of Trimethylsilyl Ethers Mediated by Tetraethylammonium Superoxide

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Abstract: Oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds has been achieved under the mild reaction conditions of *in situ* generated tetraethylammonium superoxide.

Keywords: deprotection, phase-transfer catalyst, superoxide ion, trimethylsilyl ether

The selective introduction and removal of protecting groups is very important in synthetic organic chemistry.^[1,2] Trimethylsilylation of hydroxyl groups has been recognized as a useful method for the protection of alcohols. The cleavage of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years.^[3–11] In continuation of our research program on superoxide research,^[12] we describe herein our results on the reactivity of *in situ* generated tetraethylammonium superoxide (Et₄NO₂) with different trimethylsilyl ethers under nonaqueous conditions at room temperature, affording the corresponding carbonyl compounds (Scheme 1).

As an outcome, trimethylsilyl ethers (1a-j) were readily deprotected to their corresponding carbonyl compounds (2a-j). However, the substrates (1f-j) invariably provided a little amount of corresponding carboxylic acids (3f-j) along with the carbonyl compounds (2f-j).

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The reactions were accomplished by using a 2.0-fold molar excess of KO_2 with respect to substrate (1) in anhydrous DMF. Generally, the substrate trimethylsilyl ether was allowed to react with *in situ* generated superoxide ion for 2–5 h at room temperature. The reaction was then quenched with cold brine solution and worked up to afford the products in excellent yield (Table 1). The total disappearance of the starting material was checked by thin-layer chromatography (TLC). All the oxidation products are known compounds and are identified by the comparison of their physical data and IR and NMR spectra with those of the authentic samples.

In conclusion, a mild and convenient method for the oxidative removal of the trimethylsilyl protecting group, using *in situ* generated tetraethylammonium superoxide, has been described.

EXPERIMENTAL

Melting points were measured in open capillaries and are uncorrected. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer. ¹H NMR

Table 1. Oxidative deprotection of trimethylsilyl (TMS) ethers with *in situ* generated tetraethylammonium superoxide

Entry	Substrate	Product(s)	Yield (%)
a	Ph ₂ CHOTMS (1a)	Ph ₂ CO (2a)	87
b	PhCH(Me)OTMS (1b)	PhCOMe (2b)	85
с	$c-C_6H_{11}OTMS$ (1c)	Cyclohexanone (2c)	82
d	$4-ClC_6H_4CH(Me)OTMS$ (1d)	$4-ClC_6H_4COMe$ (2d)	76
e	$4-PhC_6H_4CH(Me)OTMS$ (1e)	$4-PhC_6H_4COMe$ (2e)	85
f	PhCH ₂ OTMS ($1f$)	PhCHO (2f)	80
		PhCOOH (3f)	11
g	$2-MeOC_6H_4CH_2OTMS$ (1g)	$2-MeOC_6H_4CHO(2g)$	76
		$2-\text{MeOC}_6\text{H}_4\text{COOH}(3\text{g})$	12
h	$3-MeOC_6H_4CH_2OTMS$ (1h)	$3-\text{MeOC}_6\text{H}_4\text{CHO}(2\mathbf{h})$	73
		$3-\text{MeOC}_6\text{H}_4\text{COOH}$ (3h)	12
i	$4-MeOC_6H_4CH_2OTMS$ (1i)	$4-MeOC_6H_4CHO$ (2i)	73
		$4-\text{MeOC}_6\text{H}_4\text{COOH}(3i)$	14
j	$2-NO_2C_6H_4CH_2OTMS$ (1j)	$2-NO_2C_6H_4CH_2OH(2j)$	72
		$2-NO_2C_6H_4COOH(3j)$	14

Oxidative Deprotection of Trimethylsilyl Ethers

spectra were run on a Jeol AL300 FTNMR spectrometer (chemical shift in δ ppm, relative to TMS as internal reference). Potassium superoxide and tetraethylammonium bromide were procured from E. Merck, Germany and were used as received. Dry N,N-dimethylformamide (DMF) from Aldrich, USA, was stored over molecular sieves (4 Å) prior to use. Trimethylsilyl ethers were prepared according to a literature procedure.^[13]

Oxidative Deprotection of Trimethylsilyl Ethers by *in situ* Generated Tetraethylammonium Superoxide Ion: General Procedure

A mixture of potassium superoxide (1.13 g, 16 millimol) and tetraethylammonium bromide (1.68 g, 8 millemol) (weighted under nitrogen atmosphere using an atmosbag) in dry dimethylformamide (25 ml) was stirred for 15 min, and then trimethylsilyl ether 1a-j (8 millimol) was added. After the reaction was completed (2–5 h) as indicated by TLC, brine solution (20 ml) was introduced followed by saturated sodium hydrogen carbonate solution (20 ml). The reaction mixture was extracted with diethyl ether or dichloromethane (3 × 20 ml). The combined organic extract was washed with water, dried over anhydrous Na₂SO₄, filtered, and evaporated to give the product (2a-j). The aqueous phase was acidified with hydrochloric acid and extracted with diethyl ether or dichloromethane (3 × 20 ml) to isolate the acidic product (3f-j).

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