

Research Article

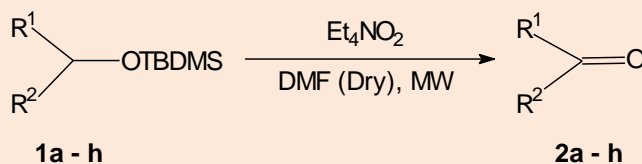
One-Pot Oxidative Deprotection of Aliphatic *tert*-Butyldimethylsilyl Ethers using Tetraethylammonium Superoxide under Microwave IrradiationSurabhi Pandey¹, Balmukund Yadav¹, Ajay K. Shukla² and Raghvendra S. Raghuvanshi^{1*}¹Department of Chemistry, Faculty of Science, Udai Pratap (Autonomous) College, Varanasi 221002, India²Department of Chemistry, T.D.P.G. College, Jaunpur 222002, India**Abstract**

Oxidative deprotection of *tert*-butyldimethylsilyl ethers to their corresponding carbonyl compounds has been achieved using *in situ* generated tetraethylammonium superoxide under microwave irradiation.

Keywords: Deprotection, superoxide, TBDMS, microwave irradiation

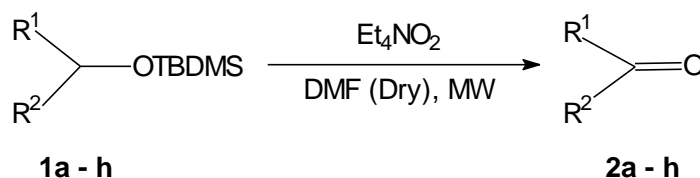
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**Introduction**

The protection of hydroxyl functions as *tert*-butyldimethylsilyl (TBDMS) ethers has been recognized as one of the most useful protecting methods in organic synthesis because of the ease in which it can be introduced to and removed from alcohols [1, 2]. Though a large number of reagents have been used to remove the TBDMS group [2], however, there are very few procedures for one step removal and oxidation [3-13]. Often these procedures utilize hazardous reagents, high acidic medium and prolonged reaction times.

In the view of the above and as a part of our ongoing research program on superoxide chemistry [14, 15], we describe herein our results on the reactivity of *in situ* generated tetraethylammonium superoxide (Et_4NO_2) with different *tert*-butyldimethylsilyl ethers in dry DMF under microwave irradiation, affording corresponding carbonyl compounds (**Scheme 1**).



Scheme 1. Preparation of carbonyl compounds.

Experimental Procedure

Potassium superoxide and tetraethylammonium bromide were procured from E. Merck, Germany and were used as received. Dry DMF of Aldrich, USA was stored over molecular sieves (4Å) prior to use. The substrate *tert*-butyldimethylsilyl ethers were prepared according to a literature procedure [16]. A Kenstar digital microwave oven at full power (800 W) was used.

General procedure for the oxidative deprotection of *tert*-butyldimethylsilyl ethers

A mixture of potassium superoxide (0.43g; 0.006 mol) and tetraethylammonium bromide (0.63g; 0.003 mol) were weighed under nitrogen atmosphere using an atmospag and were transferred into the two-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and a Liebig condenser protected by calcium chloride drying tube. Dry dimethylformamide (15 ml) was added to it and the mixture was agitated magnetically for 15 min to facilitate the formation of tetraethylammonium superoxide. The substrate *tert*-butyldimethylsilyl ethers **1a-h** (0.003 mol) was finally introduced and the contents of vessel were subjected to microwave irradiation for the specified time (**Table 1**).

The reaction mixture was poured into a beaker containing brine solution (15 mL) and cold water (15 mL). Sodium hydrogen carbonate solution (15 mL) was added to it then extracted with diethyl ether (3 x 20 mL). The combined organic extract was dried over Na₂SO₄ (anhyd.), filter and evaporated to give the products **2a-h**.

Results and Discussion

In the course of reaction, (Et₄N)O₂ was generated *in situ* by the phase transfer reaction of KO₂ and Et₄NBr in dry DMF was subsequently allowed to react with *tert*-butyldimethylsilyl ether, under microwave irradiation. As an outcome, *tert*-butyldimethylsilyl ethers **1a-h** were readily deprotected to their corresponding carbonyl compounds **2a-h** (Table 1).

Table 1 Oxidative deprotection of *tert*-butyldimethylsilyl (TBDMS) ethers with tetraethylammonium superoxide/microwave.

Entry	Substrate	Product	Time MW/min	Yield (%)
a	PhCH ₂ OTBDMS (1a)	PhCHO (2a)	2.0	81
b	4-MeOC ₆ H ₄ CH ₂ OTBDMS (1b)	4-MeOC ₆ H ₄ CHO (2b)	2.0	78
c	4-NO ₂ C ₆ H ₄ CH ₂ OTBDMS (1c)	4-NO ₂ C ₆ H ₄ CHO (2c)	2.0	77
d	4-ClC ₆ H ₄ CH ₂ OTBDMS (1d)	4-ClC ₆ H ₄ CHO (2d)	2.0	74
e	PhCH(Me)OTBDMS (1e)	PhCOMe (2e)	2.5	85
f	Ph ₂ CHOTBDMS (1f)	Ph ₂ CO (2f)	2.5	88
g	<i>c</i> -C ₆ H ₁₁ OTBDMS (1g)	Cyclohexanone (2g)	2.5	81
h	4-PhC ₆ H ₄ CH(Me)OTBDMS (1h)	4-PhC ₆ H ₄ COMe (2h)	3.0	84

The reactions were accomplished by using 2.0-fold molar excess of KO₂ with respect to substrate (**1**) in anhydrous DMF. Generally, the substrate *tert*-butyl dimethylsilyl ether was allowed to react with *in situ* generated tetraethylammonium superoxide for 2-3 minutes under microwave irradiation. The reaction was then quenched with cold brine solution and then worked up to afford the products. The total disappearance of the starting material was checked by TLC. All the oxidation products are known compounds and are identified by the comparison of their physical data, IR and ¹H NMR spectra with those of the authentic samples.

Conclusion

In conclusion, a mild and efficient method for the oxidative removal of *tert*-butyldimethylsilyl protecting group, using *in situ* generated tetraethylammonium superoxide under microwave irradiation, has been described.

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