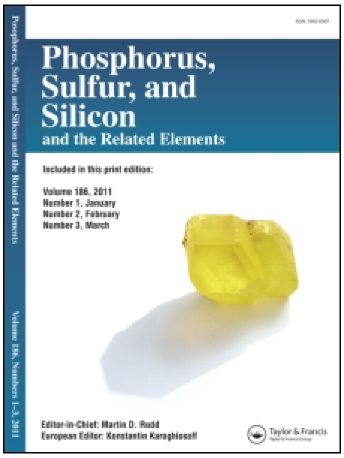

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An Efficient and Mild Deprotection of 1,3-Oxathiolanes to Carbonyl Compounds Using the Superoxide Ion

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An Efficient and Mild Deprotection of 1,3-Oxathiolanes to Carbonyl Compounds Using the Superoxide Ion

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An efficient deprotection of 1,3-oxathiolanes to carbonyl compounds has been achieved under the mild reaction conditions of tetraethylammonium superoxide in an aprotic medium at room temperature.

Keywords Deprotection; 1,3-oxathiolane; phase-transfer catalyst; superoxide ion

INTRODUCTION

Protection and deprotection are common features of multistep organic synthesis. Among the various functional groups, the protection of the carbonyl group using 1,3-oxathiolanes has attracted a great deal of interest owing to their remarkable applications. They can be used as acyl carbanion equivalents[1] for carbon–carbon bond forming reactions. The utility of chiral 1,3-oxathiolanes for the synthesis of optically active tertiary alcohols having a carbonyl functionality at the α-position has been nicely demonstrated in organic synthesis.[2,3] Moreover, the use of oxathiolanes is much more convenient than O,O-acetals or S,S-acetals. Although a large number of methods has been reported for the deprotection of 1,3-dithiolanes,[4] only a few are known for the deprotection of 1,3-oxathiolanes.[5] Usual and current methods for the deprotection of 1,3-oxathiolanes employ ammonium tribromide,[6] IBX-β-cyclodextrin,[7] BNBTS,[8] isoamylnitrite,[9] chloramine-T,[10] TMSOTf,[11] NCS-$AgNO_{3,}$[12] NBS,[13] and Amberlys-15/glyoxylic acid.[14]

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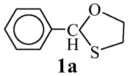
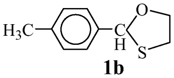
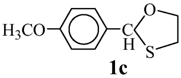
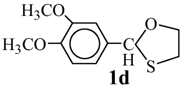
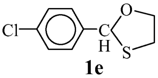
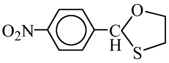
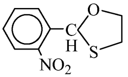
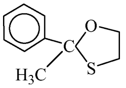
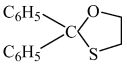
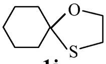
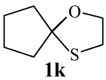
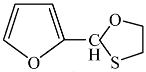
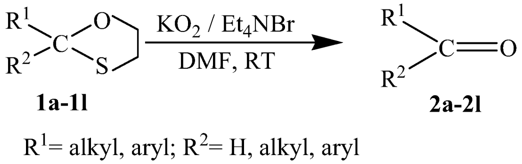
TABLE I Deprotection of 1,3-Oxathiolanes with *In Situ* Generated Tetraethylammonium Superoxide

Entry	Substrate	Time (h)	Yield (%)[a]
1	 **1a**	1.5	83
2	 **1b**	2.0	81
3	 **1c**	2.0	79
4	 **1d**	2.5	77
5	 **1e**	2.0	80
6	 **1f**	2.5	76
7	 **1g**	2.5	73
8	 **1h**	2.75	84
9	 **1i**	3.0	91
10	 **1j**	3.0	90
11	 **1k**	3.0	88
12	 **1l**	3.0	65

[a] Yields are pure isolated product.



SCHEME 1 Superoxide-induced deprotection of 1,3-oxathiolanes.

RESULTS AND DISCUSSION

In light of the above, and as a part of our ongoing research on the use of the superoxide ion[15] in organic synthesis, we report herein a mild and efficient method to restore carbonyl compounds from 1,3-oxathiolanes using in situ generated tetraethylammonium superoxide in dry DMF at room temperature (Scheme 1).

A wide variety of structurally different 1,3-oxathiolanes (**1a–1l**) were prepared by the reaction of the appropriate carbonyl compound with 2-mercaptoethanol in the presence of Montmorillonite K-10 clay[16] (**1a–1d, 1f, 1j–1l**) and PAS[17] (**1e, 1g, 1h, 1i**) as a catalyst in dichloromethane. The reaction conditions were then optimized for the transformation of 1,3-oxathiolanes to the parent carbonyl compounds. As an outcome, a mixture of substrate, potassium superoxide, and tetraethylammonium bromide in the molar ratio 1:2:1 in dry DMF was found to give the best result. Subsequently various 1,3-oxathiolanes (**1a–1l**) were smoothly converted to their parent carbonyl compounds (**2a–2l**) under the optimized conditions at room temperature (Table I). The products **2a–2h** were accompanied by the formation of the corresponding acids, albeit in low yield (10–15%).

CONCLUSION

The present findings demonstrate the role of the superoxide ion as a convenient and safe deprotecting agent for 1,3-oxathiolanes to the parent carbonyl compounds.

EXPERIMENTAL

Potassium superoxide and tetraethylammonium bromide were produced from E. Merck, Germany and were used as received. Dry *N,N*-dimethylformamide (DMF), from Aldrich, USA, was stored over molecular sieves (4Å) prior to use. The other reagents and solvents were of A.R. grade. All the protected and deprotected compounds were fully characterized by their IR, ^{1}H NMR, and ^{13}C NMR spectra. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. NMR spectra were run on a JEOL AL300 FTNMR spectrometer; chemical shifts are given in δ ppm, relative to TMS as the internal reference. All the products were purified by column chromatography.

REACTION OF IN SITU GENERATED TETRAETHYLAMMONIUM SUPEROXIDE WITH 1,3-OXATHIOLANES (1a–1l): GENERAL PROCEDURE

A mixture of potassium superoxide (1.13 g, 16 mmol) and tetraethylammonium bromide (1.68 g, 8 mmol) (weight under a nitrogen atmosphere using an atmosbag) in dry DMF (25 mL) was stirred for 15 min, and then the substrate 1,3-oxathiolane (**1a-1l**) (8 mmol) was added. After the reaction was over (1.5 to 3 h) as indicated by TLC, a cold brine solution (10 mL) was introduced to decompose the unreacted potassium superoxide, followed by the addition of saturated sodium hydrogen carbonate solution (10 mL). The reaction mixture was extracted with diethyl ether (3 × 15 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered, and evaporated to give the crude product (**2a-2l**), which was purified by column chromatography on silica gel using *n*-hexane:ethyl acetate (9:1) as an eluent. The aqueous phase was acidified with hydrochloric acid and extracted with diethyl ether (3 × 10 mL) to isolate the acidic product.

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