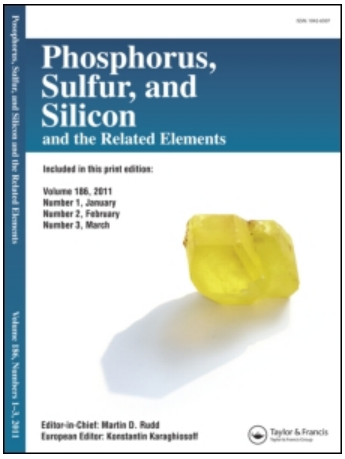

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Online publication date: 16 August 2010

To cite this Article Ghorbani-Vaghei, Ramin and Khazaei, Ardeshir(2004) 'FACILE AND EFFICIENT METHOD FOR DEPROTECTION OF 1,3-OXATHIOLANES WITH *N,N'*-DIBROMO-*N,N'*-1,2-ETHANEDIYLBIS(*p*-TOLUENESULPHONAMIDE)', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 9, 1787 — 1791
To link to this Article: DOI: 10.1080/10426500490466508
URL: http://dx.doi.org/10.1080/10426500490466508

Phosphorus, Sulfur, and Silicon, 179:1787–1791, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490466508

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FACILE AND EFFICIENT METHOD FOR DEPROTECTION OF 1,3-OXATHIOLANES WITH *N*,*N*′-DIBROMO-*N*,*N*′-1,2-ETHANEDIYLBIS(*P*-TOLUENESULPHONAMIDE)

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(Received January 6, 2004; accepted January 8, 2004)

Aliphatic and aromatic 1,3-oxathiolanes are readily oxidized to aldehydes and ketones in good yields under mild conditions by N,N′*-dibromo-*N,N′*-1,2-ethanediylbis(*p*-toluenesulphonamide) [**BNBTS**].*

Keywords: **BNBTS**; deprotection; oxathiolanes; oxidation

INTRODUCTION

The electrophilic nature of the carbonyl groups is a dominant feature of their extensive chemistry. One of the major challenging problems during many multistep syntheses is how to protect a carbonyl from nucleophilic attack until its electrophilic properties can be exploited. For this reason, deprotection of the carbonyl groups remains a crucial challenge to organic chemists. Among various functional groups, protection of the carbonyl groups as a 1,3-oxathiolane is important for the following reasons: they can be used as acyl carbanion equivalents[1a,b,c] for C—C bond formation; the chiral 1,3-oxathiolanes are valuable for synthesis of α-hydroxyaldehydes;[1a] and 1,3-oxathiolanes are comparatively more stable than *O*,*O*-acetals in acidic conditions, and much easier to remove than *S*,*S*-acetals and as protecting groups of carbonyl compounds.[2] A variety of methods for the deprotection of oxathiolanes are reported employing isoamylnitrite,[3] chloramine-T,[4] TMSOTf alone[5] or in the presence of *p*-nitrobenzaldehyde,[6] polymer-supported *p*-nitrobenzaldehyde,[7] NCS-$AgNO_3$,[8] I_2-$AgNO_3$,[9]

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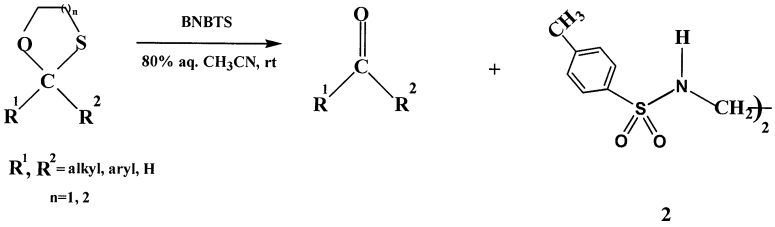
NBS in acetone,[10] glyoxylic acid in the presence of Amberlyst 15 in a microwave oven[11] and ammonium tribromide.[12] However, these methods suffer from drawbacks such as the difficulty of removing the byproduct oxathioacetals derived from *p*-nitrobenzaldehyde,[6] the use of expensive polymer-supported reagent,[7] on the requirement of a large molar excess of reagents such as expensive silver salts.[8,9] Consequently, it seems that there is still a need for development of newer methods that can proceed under mild and economically appropriate conditions. Therefore, we decided to study the application of *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis(*p*-toluenesulphonamide) [**BNBTS**],[13] which is relatively easy to make.

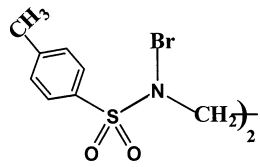
RESULTS AND DISCUSSION

We now report a convenient method for conversion of 1,3-oxathiolanes to aldehydes and ketones using **BNBTS** (Figure 1).

Aliphatic and aromatic 1,3-oxathiolanes were found to be oxidized to aldehydes and ketones using **BNBTS** in aqueous acetonitrile at room temperature (Scheme 1).



SCHEME 1



1 BNBTS

FIGURE 1 Since **BNBTS** contain two bromine atoms that are attached to nitrogen atoms it is very possible that this reagent releases Br^+ which can act as an electrophilic species,[13] in situ.

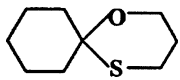
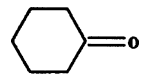
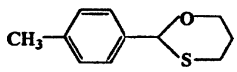
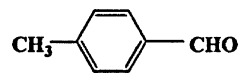
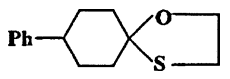
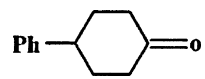
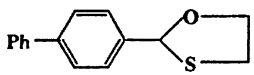
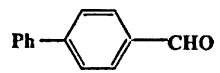
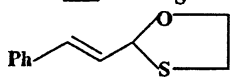
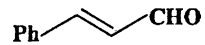
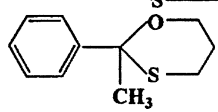
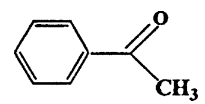
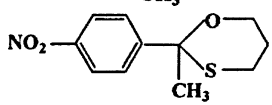
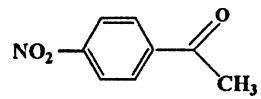
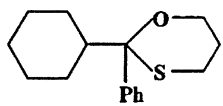
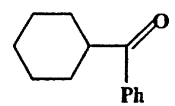
The advantages of **BNBTS** are as follows:

1. The preparation of **BNBTS** is easy.
2. **BNBTS** is stable in atmospheric conditions for two months.
3. After completion of the reaction and evaporation of solvent, the sulphonamide is recovered and can be reused many times without decreasing the yield.

The results of the conversion of various 1,3-oxathiolanes to aldehydes and ketones are presented in Table I.

Since **BNBTS** contains two bromine atoms that are attached to nitrogen atoms, it is very possible that this reagent releases Br^+ which can act as an electrophilic species,[13] in situ. The products of reaction

TABLE I Deprotection of 1,3-Oxathiolanes with **BNBTS** in Aqueous Acetonitrile at Room Temperature

Entry	Substrate	Product[a]	Time [min]/h	Yield (%)
1			4	90
2			[30]	93
3			2.5	84
4			[60]	89
5			[90]	92
6			[20]	82
7			7	85
8			10	90

[a]Products were characterized by their physical properties, comparison with authentic samples, and by spectroscopic methods.

with **BNBTS** were isolated simply by filtering off the sulfonamide **2** and evaporating the solvent from the filtrate. The method has advantages in terms of yields, simplicity of reaction conditions, short reaction times, and lack of side products. The recovered starting material **2** was rebrominated and used many times without reducing the yield.

CONCLUSION

From the results obtained, we find that the described procedure and the reaction conditions are simple. The new reagent (**BNBTS**) is stable and the recovered reagent can be reused.

Infrared (IR) and nuclear magnetic resonance (NMR) spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively.

GENERAL PROCEDURE FOR DEPROTECTION OF 1,3-OXATHIOLANES USING BNBTS

A solution of the 1,3-oxathiolane (1.0 mmol) in acetonitrile (2 ml) was added quickly to a well-stirred solution of **BNBTS** (4 mmol) in aqueous 80% acetonitrile (10 ml) at room temperature. The mixture was stirred for the specified time (Table I). After completion of the reaction, the insoluble sulphonamide **2** was removed by filteration and washed with cold acetonitrile (5 ml). The solvent was then evaporated and ether was added. The ethereal phase was washed with saturated aqueous sodium carbonate and water and then was dried with $MgSO_4$ and evaporated to give the product.

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