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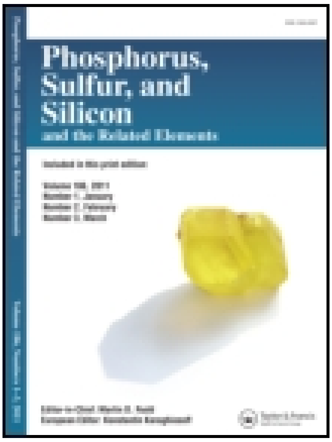

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An Efficient and Selective Oxidation of Sulfides and Thiols with Silica-Supported 1,1,3,3-Tetramethylguanidine/Br_2 Complex

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AN EFFICIENT AND SELECTIVE OXIDATION OF SULFIDES AND THIOLS WITH SILICA-SUPPORTED 1,1,3,3-TETRAMETHYLGUANIDINE/Br_2 COMPLEX

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Silica-supported 1,1,3,3-tetramethylguanidine/Br_2 complex is an efficient reagent for the selective oxidation of aliphatic and aromatic sulfides to the corresponding sulfoxides and the oxidative coupling of thiols to disulfides in aqueous solution at room temperature in a short reaction time.

Keywords Oxidation; silica-supported 1,1,3,3-tetramethylguanidine/Br_2 complex; sulfide; thiol

INTRODUCTION

Selective oxidative coupling of thiols to disulfides and oxidation of sulfides to sulfoxides are of interest from both biological and synthetic chemistry points of view.[1–10] Although a large number of oxidizing agents can affect the conversion of sulfides to sulfoxides and the oxidative coupling of thiols to disulfides,[11–24] the susceptibility of sulfoxides and disulfides to further oxidation narrows the choice of reagents for these processes. Therefore, the development of new oxidants for the selective transformation of sulfides to sulfoxides and thiols to disulfides is of importance in synthetic organic chemistry.

The use of molecular bromine for the oxidation of sulfides and thiols is restricted because the formation of HBr (as a reduction product) can affect the selectivity of the reaction. Under acidic conditions, the main product becomes contaminated by the formation of side products such as sulfonic acids, sulfinic acids, and bromo-substituted sulfides and sulfoxides.[25] Therefore, if bromine is to be used as an oxidant, it is necessary that these problems be circumvented by carrying out the reactions under conditions where HBr is not released as a free acid.

A number of amine-based complexes of bromine have been reported in the literature,[26] in which amine acts as a HBr acceptor. However, as indicated in Scheme 1, the amine part of the complex is only able to neutralize 1 mol of HBr being produced in the oxidation process. Therefore the reaction media is still acidic from the remaining 1 mol of HBr.

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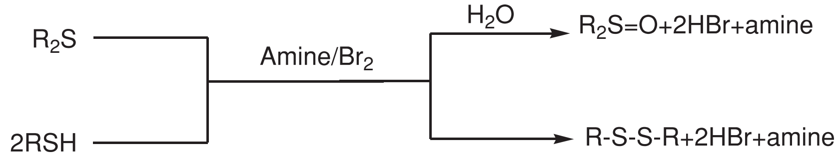
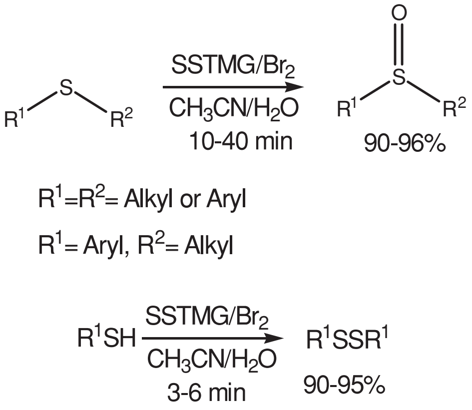


Scheme 1

RESULTS AND DISCUSSION

This article reports the oxidation of sulfides and thiols to the corresponding sulfoxides and disulfides utilizing 1,1,3,3-tetramethylguanidine/Br_2 on hydrated silica gel (Scheme 2).

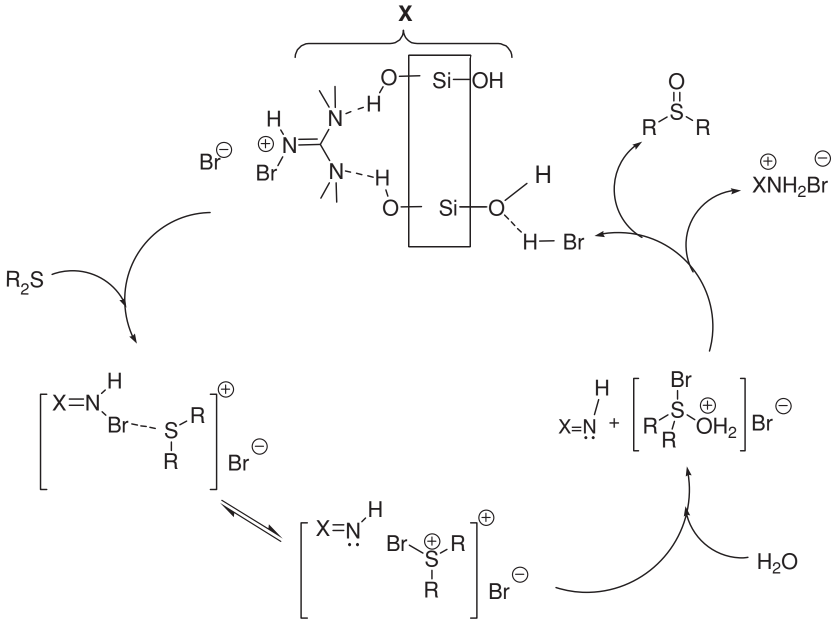


Scheme 2

This silica-supported 1,1,3,3-tetramethylguanidine/Br_2 (SSTMG/Br_2) oxidant is not only safe to handle owing to full chemisorption of the toxic bromine complex, but both the 1,1,3,3-tetramethylguanidine and silica gel act as a HBr scavenger and prevent the solution from becoming acidic (Scheme 3).

The silica-supported 1,1,3,3-tetramethylguanidine/Br_2 complex was readily prepared by adding bromine to a magnetically stirred slurried mixture of silica in an *n*-hexane solution of 1,1,3,3-tetramethylguanidine. The mixture was filtered, washed with *n*-hexane, and dried at room temperature. This yellow-orange, non-hygroscopic, homogenous solid is very stable at room temperature and is not affected by ordinary exposure to light, air, or water and has none of the offensive odor of bromine or amine. Easy workup and the stability of the reagent make it a safe and convenient source of active bromine.

This method offers a simple, general, selective, and highly efficient route for converting sulfides and thiols to their corresponding sulfoxides and disulfides without overoxidation. As shown in Table I, the reaction time for oxidation is relatively short, and the generality of the method was examined using alkyl, aryl, dialkyl, diaryl, and cyclic sulfides as well as alkyl and aryl thiols. It was discovered that a wide variety of sulfides and thiols can be selectively oxidized by this inexpensive reagent under mild reaction conditions.



Scheme 3

The possible mechanism for the oxidation of sulfides to the corresponding sulfoxides using silica-supported 1,1,3,3-tetramethylguanidine/Br_2 complex is outlined in Scheme 3.

In conclusion, we report an easy and versatile method for the selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides without any over-oxidation. The amine and silica parts of the complex act as HBr acceptors, preventing the solution from becoming acidic. The formation of 1,1,3,3-tetramethylguanidine/hydrobromide as the reaction proceeds seems to accelerate the rate of oxidation possibly by increasing the ionic strength of the solution.

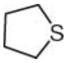
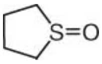
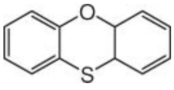
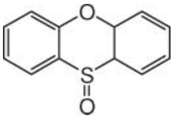
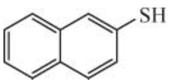
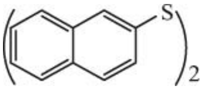
EXPERIMENTAL

Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H NMR spectra were obtained on solutions in $CDCl_3$ and DMSO-d_6. All reaction products were known and characterized by IR and ^{1}H NMR spectra and melting points as compared with those obtained from authentic samples. All chemical reagents were purchased from Fluka and Merck and were used without purification.

Preparation of Silica-Supported 1,1,3,3-Tetramethylguanidine/Br_2

A solution of bromine (3.84 g, 24 mmol) in *n*-hexane (20 mL) was added to a magnetically stirred slurry mixture of silica gel (16.00 g) in *n*-hexane (100 mL) solution of 1,1,3,3-tetramethylguanidine (2.76 g, 24 mmol). The mixture was stirred for an additional 1 h, and then the product was collected by vacuum filtration as yellow solid; yield 20.88 g.

Table I Oxidation of sulfides and thiols with the silica-supported 1,1,3,3-tetramethylguanidine/Br_2 complex

Entry	Reductant	Product	Time (min)	Yield (%)	M p or Bp (°C) Found (Reported) [ref.]
1	$(CH_3(CH_2)_3)_2S$	$(CH_3(CH_2)_3)_2SO$	15	94	27–29 (29–31.6)[a] [27]
2			10	92	232–234 (235–237)[b] [27]
3	$PhSCH_3$	$PhSOCH_3$	30	96	31–33 (33–34)[a] [28]
4	p-$BrC_6H_4SCH_3$	p-$BrC_6H_4SOCH_3$	15	90	73–75 (74–76)[a] [28]
5	p-$O_2NC_6H_4S\ CH_3$	p-$O_2NC_6H_4SOCH_3$	20	91	139–141(140–142)[a] [28]
6	$PhSCH_2CH_3$	$PhSOCH_2CH_3$	10	95	141–144 (146)[a] [28]
7	$PhCH_2SCH_2Ph$	$PhCH_2SOCH_2Ph$	10	93	129–132 (133–135)[a] [28]
8	$PhCH_2SPh$	$PhCH_2SOPh$	25	92	120–122 (123–124)[a] [28]
9	PhSPh	PhSOPh	20	94	68–70 (70.5)[a] [29]
10			40	93	150–153 (53–155)[a] [30]
11	$CH_3(CH_2)_2SH$	$(CH_3(CH_2)_2S)_2$	3	90	193–194 (193)[b] [31]
12	$CH_3(CH_2)_3SH$	$(CH_3(CH_2)_3S)_2$	4	92	190–191 (192)[b] [31]
13	$CH_3(CH_2)_7SH$	$(CH_3(CH_2)_7S)_2$	5	91	72–75 (74–75)[a] [28]
14	$C_6H_{11}SH$	$(C_6H_{11}S)_2$	5	94	120–123 (125–130)[a] [29]
15	$PhCH_2SH$	$(PhCH_2S)_2$	3	95	67–71 (69–72)[a] [29]
16	PhSH	$(PhS)_2$	6	93	57–59 (61–62)[a] [29]
17	p-$CH_3C_6H_4SH$	(p-$CH_3C_6H_4S)_2$	5	95	44–46 (45–46)[a] [32]
18	o-ClC_6H_4SH	(o-$ClC_6H_4S)_2$	5	92	84–86 (87–88)[a] [30]
19			3	95	135–137 (139)[a] [33]

[a] Melting point.
[b] Boiling point.

Oxidation of Sulfides

In a typical reaction, methyl phenyl sulfide (0.124 g, 1 mmol) was added to the mixture of silica-supported 1,1,3,3-tetramethylguanidine/Br_2 (1 g) in aqueous acetonitrile (CH_3CN:H_2O; 3:1 v/v, 20 mL). The mixture was stirred at room temperature for 30 min, while the progress of the reaction was followed by TLC (n-hexane:ethylacetate 7:1). The product was extracted into CH_2Cl_2 (2 × 10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a product (0.134 g, 96%) of sufficient purity for most purposes; Mp 31–33°C (ref.[28]: 33–34°C).

Oxidation of Thiols

In a typical procedure, *p*-methyl thiophenol (0.124 g, 1 mmol) was added to a mixture of silica-supported 1,1,3,3-tetramethylguanidine/Br_2 (0.5 g) in aqueous acetonitrile (CH_3CN:H_2O; 3:1 v/v, 20 mL). The mixture was stirred at room temperature for 3 min, while the progress of the reaction was followed by TLC (*n*-hexane:ethylacetate 7:1). The product was extracted into CH_2Cl_2 (2 × 10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a product (0.118 g, 96%) of sufficient purity for most purposes; Mp 44–46°C (ref.[32]: 45–46°C).

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