

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### An Efficient and Selective Oxidation of Sulfides and Thiols with Silica-Supported 1,1,3,3-Tetramethylguanidine/Br<sub>2</sub> Complex

Ahmad Shaabani<sup>a</sup>; Elham Farhangi<sup>a</sup>; Abbas Rahmati<sup>a</sup>

<sup>a</sup> Department of Chemistry, Shahid Beheshti University, Tehran, Iran

Online publication date: 03 February 2010

**To cite this Article** Shaabani, Ahmad , Farhangi, Elham and Rahmati, Abbas(2010) 'An Efficient and Selective Oxidation of Sulfides and Thiols with Silica-Supported 1,1,3,3-Tetramethylguanidine/Br<sub>2</sub> Complex', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 185: 2, 463 — 468

**To link to this Article:** DOI: 10.1080/10426500902814031

**URL:** <http://dx.doi.org/10.1080/10426500902814031>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## AN EFFICIENT AND SELECTIVE OXIDATION OF SULFIDES AND THIOLS WITH SILICA-SUPPORTED 1,1,3,3-TETRAMETHYLGUANIDINE/Br<sub>2</sub> COMPLEX

Ahmad Shaabani, Elham Farhangi, and Abbas Rahmati

Department of Chemistry, Shahid Beheshti University, Tehran, Iran

*Silica-supported 1,1,3,3-tetramethylguanidine/Br<sub>2</sub> 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<sub>2</sub> 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.<sup>1–10</sup> Although a large number of oxidizing agents can affect the conversion of sulfides to sulfoxides and the oxidative coupling of thiols to disulfides,<sup>11–24</sup> 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.

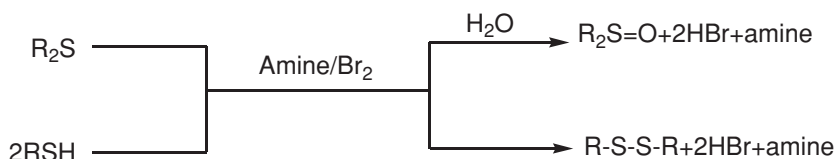
The use of molecular bromine for the oxidation of sulfides and thiols is restricted because the formation of HBr (as a reduction product) can affect the selectivity of the reaction. Under acidic conditions, the main product becomes contaminated by the formation of side products such as sulfonic acids, sulfinic acids, and bromo-substituted sulfides and sulfoxides.<sup>25</sup> 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,<sup>26</sup> 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.

Received 16 December 2008; accepted 11 February 2009.

Financial assistance from the Research Council of Shahid Beheshti University of Iran is gratefully acknowledged.

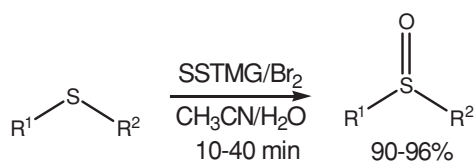
Address correspondence to Ahmad Shaabani, Department of Chemistry, Shahid Beheshti University, P. O. Box 19396-4716, Tehran, Iran. E-mail: a-shaabani@cc.sbu.ac.ir



Scheme 1

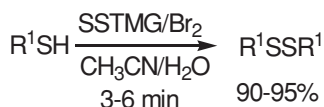
## RESULTS AND DISCUSSION

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



R<sup>1</sup>=R<sup>2</sup>= Alkyl or Aryl

R<sup>1</sup>= Aryl, R<sup>2</sup>= Alkyl

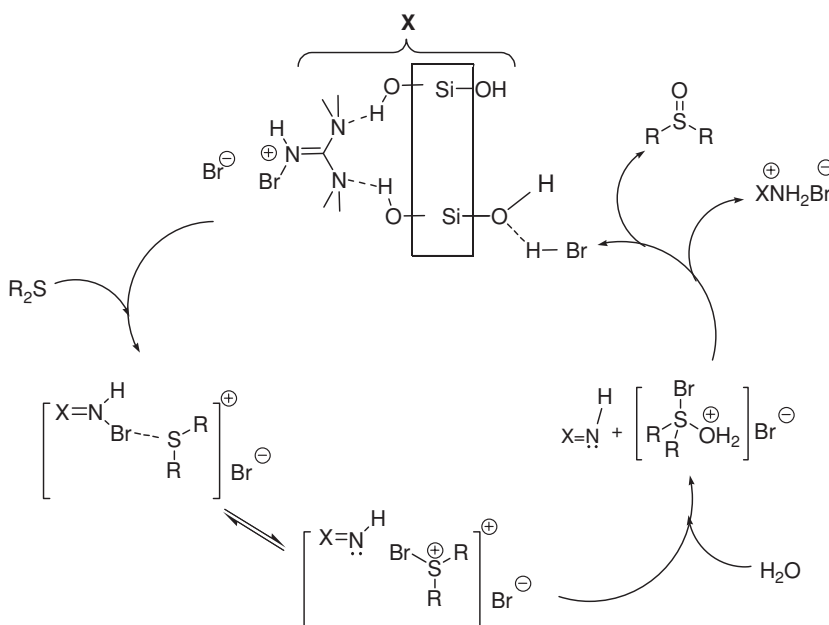


Scheme 2

This silica-supported 1,1,3,3-tetramethylguanidine/Br<sub>2</sub> (SSTMG/Br<sub>2</sub>) 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<sub>2</sub> 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 over-oxidation. 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.



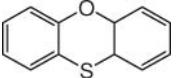
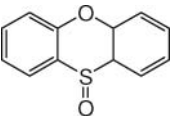
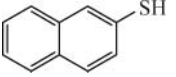
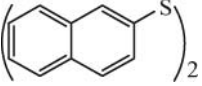
## EXPERIMENTAL

Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer.  $^1H$  NMR spectra were obtained on solutions in  $CDCl_3$  and  $DMSO-d_6$ . All reaction products were known and characterized by IR and  $^1H$  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/ $\text{Br}_2$  complex

Entry	Reductant	Product	Time (min)	Yield (%)	M p or Bp ( $^{\circ}\text{C}$ ) Found (Reported) [ref.]
1	$(\text{CH}_3(\text{CH}_2)_3)_2\text{S}$	$(\text{CH}_3(\text{CH}_2)_3)_2\text{SO}$	15	94	27–29 (29–31.6) <sup>a</sup> [27]
2			10	92	232–234 (235–237) <sup>b</sup> [27]
3	$\text{PhSCH}_3$	$\text{PhSOCH}_3$	30	96	31–33 (33–34) <sup>a</sup> [28]
4	$p\text{-BrC}_6\text{H}_4\text{SCH}_3$	$p\text{-BrC}_6\text{H}_4\text{SOCH}_3$	15	90	73–75 (74–76) <sup>a</sup> [28]
5	$p\text{-O}_2\text{NC}_6\text{H}_4\text{SCH}_3$	$p\text{-O}_2\text{NC}_6\text{H}_4\text{SOCH}_3$	20	91	139–141 (140–142) <sup>a</sup> [28]
6	$\text{PhSCH}_2\text{CH}_3$	$\text{PhSOCH}_2\text{CH}_3$	10	95	141–144 (146) <sup>a</sup> [28]
7	$\text{PhCH}_2\text{SCH}_2\text{Ph}$	$\text{PhCH}_2\text{SOCH}_2\text{Ph}$	10	93	129–132 (133–135) <sup>a</sup> [28]
8	$\text{PhCH}_2\text{SPh}$	$\text{PhCH}_2\text{SOPh}$	25	92	120–122 (123–124) <sup>a</sup> [28]
9	$\text{PhSPh}$	$\text{PhSOPh}$	20	94	68–70 (70.5) <sup>a</sup> [29]
10			40	93	150–153 (153–155) <sup>a</sup> [30]
11	$\text{CH}_3(\text{CH}_2)_2\text{SH}$	$(\text{CH}_3(\text{CH}_2)_2)_2\text{S}$	3	90	193–194 (193) <sup>b</sup> [31]
12	$\text{CH}_3(\text{CH}_2)_3\text{SH}$	$(\text{CH}_3(\text{CH}_2)_3)_2\text{S}$	4	92	190–191 (192) <sup>b</sup> [31]
13	$\text{CH}_3(\text{CH}_2)_7\text{SH}$	$(\text{CH}_3(\text{CH}_2)_7)_2\text{S}$	5	91	72–75 (74–75) <sup>a</sup> [28]
14	$\text{C}_6\text{H}_{11}\text{SH}$	$(\text{C}_6\text{H}_{11})_2\text{S}$	5	94	120–123 (125–130) <sup>a</sup> [29]
15	$\text{PhCH}_2\text{SH}$	$(\text{PhCH}_2)_2\text{S}$	3	95	67–71 (69–72) <sup>a</sup> [29]
16	$\text{PhSH}$	$(\text{Ph})_2\text{S}$	6	93	57–59 (61–62) <sup>a</sup> [29]
17	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$	$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{S}$	5	95	44–46 (45–46) <sup>a</sup> [32]
18	$o\text{-ClC}_6\text{H}_4\text{SH}$	$(o\text{-ClC}_6\text{H}_4)_2\text{S}$	5	92	84–86 (87–88) <sup>a</sup> [30]
19			3	95	135–137 (139) <sup>a</sup> [33]

<sup>a</sup>Melting point.<sup>b</sup>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/ $\text{Br}_2$  (1 g) in aqueous acetonitrile ( $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ ; 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  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  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 $^{\circ}\text{C}$  (ref.<sup>28</sup>: 33–34 $^{\circ}\text{C}$ ).

### 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/ $\text{Br}_2$  (0.5 g) in aqueous acetonitrile ( $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ ; 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  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  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.<sup>32</sup>; 45–46°C).

## REFERENCES

1. M. C. Carreno, *Chem. Rev.*, **95**, 1717 (1995).
2. A. Ogawa, T. Nishiyama, N. Kambe, S. Murai, and N. Sonada, *Tetrahedron Lett.*, **28**, 3271 (1987).
3. J. R. Johnson, W. F. Bruce, and J. D. Dutcher, *J. Am. Chem. Soc.*, **65**, 2005 (1943).
4. R. J. Cremllyn, *An Introduction to Organosulfur Chemistry* (Wiley & Sons, New York, 1996).
5. S. Oae, *Organic Sulfur Chemistry: Structure and Mechanism* (CRC Press: Boca Raton, FL, 1991).
6. G. Capozzi and G. Modena, In *The Chemistry of Thiol Group Part 2*, S. Patai, Ed., (Wiley, New York, 1974), p. 785.
7. B. M. Trost, *Acc. Chem. Res.*, **11**, 453 (1978).
8. T. Durst, In *Comprehensive Organic Chemistry*, D. Barton and W. D. Ollis, Eds., (Pergamon, Oxford, 1979), vol. 3.
9. P. Kowalski, K. Mitka, K. Ossowska, and Z. Kolarska, *Tetrahedron*, **61**, 1933 (2005).
10. K. Kaczorowska, Z. Kolarska, K. Mitka, and P. Kowalski, *Tetrahedron*, **61**, 8315 (2005).
11. M. Madesclaire, *Tetrahedron*, **42**, 5459 (1986).
12. Z.-G. Xiong, J. Zhang, and X.-M. Hu, *Appl. Catal. A: Gen.*, **334**, 44 (2008).
13. M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, and A. A. Abbasi-Larki, *Appl. Catal. A: Gen.*, **349**, 177 (2008).
14. S. M. Bonesi, E. Carbonell, H. Garcia, M. Fagnoni, and A. Albini, *Appl. Catal. B: Envir.*, **79**, 368 (2008).
15. A. R. Supale and G. S. Gokavi, *Catal. Lett.*, **124**, 284 (2008).
16. B. Sreedhar, P. Radhika, B. Neelima, N. Hebalkar, and A. K. Mishra, *Catal. Commun.*, **10**, 39 (2008).
17. M. Bagherzadeh, R. Latifi, L. Tahsini, and M. Amini, *Catal. Commun.*, **10**, 196 (2008).
18. F. Gregori, I. Nobili, F. Bigi, R. Maggia, G. Predieri, and G. Sartori, *J. Mol. Catal. A: Chem.*, **286**, 124 (2008).
19. C. Pinedo-Rivilla, J. Aleu, and I. G. Collado, *J. Mol. Catal. B: Enz.*, **49**, 18 (2007).
20. J. N. Moorthy, N. Singhal, and K. Senapati, *Tetrahedron Lett.*, **49**, 80 (2008).
21. A. G. Sathicq, G. P. Romanelli, V. Palermo, P. G. Vázquez, and H. J. Thomas, *Tetrahedron Lett.*, **49**, 1441 (2008).
22. F. P. Ballistreri, G. A. Tomaselli, and R. M. Toscano, *Tetrahedron Lett.*, **49**, 3291 (2008).
23. C. A. Gamelas, T. Lourenço, A. P. da Costa, A. L. Simplicio, B. Royo, and C. C. Romão, *Tetrahedron Lett.*, **49**, 4708 (2008).
24. L. Palombi, C. Bocchino, T. Caruso, R. Villano, and A. Scettri, *Tetrahedron Lett.*, **49**, 5611 (2008).
25. A. Bravo, B. Dordi, F. Fontana, and F. Minisci, *J. Org. Chem.*, **66**, 3232 (2001).
26. (a) J. A. Struss, W. D. Barnhart, and M. R. Velasco, *Tetrahedron Lett.*, **47**, 6635 (2006). (b) G. Kar, A. K. Saikia, U. Bora, S. K. Dehury, and M. K. Chaudhuri, *Tetrahedron Lett.*, **44**, 4503 (2003). (c) M. H. Ali and M. McDermott, *Tetrahedron Lett.*, **43**, 6271 (2002). (d) M. H. Ali and G. J. Bohnert, *Synthesis*, 1238 (199). (e) A. Shaabani, A. Rahmati, and E. Farhangi, *J. Sulfur Chem.*, **27**, 287 (2006). (f) A. Shaabani, M. B. Teimouri, and H. R. Safaei, *Synth. Commun.*, **30**, 265 (2000).
27. S. J. Searles and H. Y. Hays, *J. Org. Chem.*, **23**, 2028 (1958).
28. *Dictionary of Organic Compounds*, 6th ed. (Chapman and Hall, London, 1996).
29. K. Orito, T. Hatakeyama, M. Takeo, and H. Sugimoto, *Synthesis*, 1357 (1995).

30. T.-L. Ho and C. M. Wong, *Synthesis*, 561 (1972).
31. N. Iranpoor, H. Firouzabadi, and M. A. Zolfigol, *Synth. Commun.*, **28**, 367 (1998).
32. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 74th ed. (CRC Press, Ann Arbor, MI, 1993).
33. T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).