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SHORT COMMUNICATION

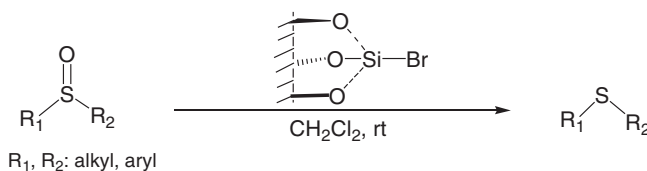
A very useful and mild method for the deoxygenation of sulfoxide to sulfide with silica bromide as heterogeneous promoter

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Silica bromide (SB) as heterogeneous reagent and promoter is prepared from reaction of silica gel with PBr_3 as a non-hygroscopic, filterable, cheap, and stable yellowish powder that can be stored for months. The results show that the SB is suitable and efficient reagent for deoxygenation of sulfoxides to the corresponding sulfides under mild conditions at room temperature. The easy availability of this reagent makes this simple procedure attractive and a practical alternative to the existing methods.



Keywords: silica bromide; sulfoxides; sulfides; deoxygenation; heterogeneous

1. Introduction

Deoxygenation of sulfoxides is a repeating theme in organic chemistry because of its use in various synthetic transformations and considerable utility in biochemical reactions.[1] Many specific advantages of using insoluble resins as supports, reagents, or catalysts have been reviewed,[2, 3] these include the simulation of high-dilution [4, 5] or pseudodilution [6] conditions, the fishhook and concentration principle,[7] selective intrapolymeric reactions,[8] bulk and steric effects of the polymer backbone in asymmetric synthesis,[9] the stabilization of reactive substances,[10, 11] and the elimination of volatile malodorous reagents.[12, 13]

In the recent years, reagents such as lithium alanate/titanium (IV) chloride,[14] titanium (II) chloride,[15] titanium (IV) chloride/sodium iodide,[16] chromium (II) chloride,[17]

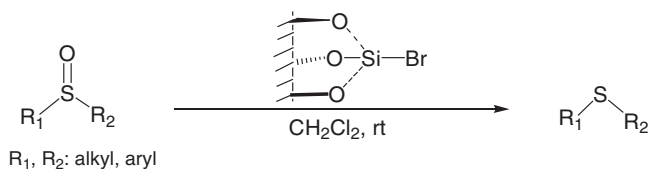
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molybdenum (III)/vanadium,[18] tungsten hexachloride,[19] catecholborane,[20] molybdenum (V)/indium,[21] iodide ion,[22] sodium hydrogen sulfite,[23] hydrochloric acid/potassium iodide,[24] 1,3-dithiane/N-Bromosuccinimide/Br₂,[25] silane/dichlorodioxomolybdenum (VI),[26] dimethyl sulfoxide reductase,[27] triphenyl phosphine/bromine/cuprous bromide,[28] indium/pivaloyl chloride,[29] triflic anhydride/potassium iodide,[30] zinc/acetic acid,[31] Mo(CO)₆,[32] gallium/MoCl₅,[33] triphenylphosphine/TiCl₄,[34] iodine/pyridine/sulfur dioxide,[35] acetyl chloride/potassium iodide,[36] trimethylsilyl iodide and trimethylsilyl bromide,[37] ZrCl₄/NaI and ZrOCl₂·8H₂O/NaI,[38] I₂/thioacetic acid,[39] and silica chloride (for review see [40]) have been reported for deoxygenation of sulfoxides to sulfides.

Another approach to the deoxygenation of sulfoxides is the use of sulfur compounds, *e.g.* thiols,[41] hydrogen sulfide,[42] carbodithionic acids,[43] thiophosphinic, thiophosphonic, thiophosphoric acid,[44] sulsulfides,[45, 46], sulfenyl, sulfonyl, and sulfonyl chlorides,[47] disulfides,[48] and elemental sulfur (S₈).[49]

2. Result and discussions

Inspired by our results using the silica bromide (SB) for the mild and selective bromination of alcohols under mild conditions,[50] we report here SB as a heterogeneous promoter for the efficient conversion of sulfoxides to their corresponding sulfides in CH₂Cl₂ at room temperature (Scheme 1).



Scheme 1. Conversion of sulfoxides to their corresponding sulfides in the presence of silica bromide.

SB is obtained from reaction of silica gel (Art 7734 for column chromatography from Merck) and phosphorus tribromide in refluxing toluene (Scheme 1). The amount of bromosilyl group (2.2 mmole of Br/g silica) is determined by a standard method.[51] The resulting yellowish powder is kept in a dessicator. The reagent (SB, 2.2 mmole of Br/g silica) which was applied to converted diphenyl sulfoxide to diphenyl sulfide quantitatively after 5 min in CH₂Cl₂ at room temperature.

Since the introduced filterable SB showed an excellent reactivity for the conversion of diphenyl sulfoxide to diphenyl sulfide and provided very simple and practical isolation of the product, we decided to study its applicability as a general reagent for the conversion of different classes of sulfoxides into sulfides. We optimized the conditions for the conversion of diphenyl sulfoxide to diphenyl sulfide using different molar ratios of SB (Table 1).

We then applied the optimized conditions for the reaction of structurally different sulfoxides, and found that they can be conveniently reduced to the corresponding sulfides under effective and mild conditions. Deoxygenation of both alkyl and aryl sulfoxides takes place very smoothly without any side product formation. As shown in Table 2, the sulfoxides were reduced in excellent yields. This reagent is suitable for the deoxygenation of aromatic and aliphatic sulfoxides. The functional group entries which show that chloro, methoxy, aldehyde, phenol, carboxylic acid, esters, and vinyl functionalities are intact under the reaction conditions.

Table 1. Conversion of diphenyl sulfoxide (1 mmol) to diphenyl sulfide with SB in CH₂Cl₂ at room temperature.

Entry	Molar equivalent of SB	Yield of product (%)
1	1	43
2	2	73
3	3	89
4	3.5	93
5	4	98
6	4.5	98
7	5	98

A comparison of the results presented in this article with that reported earlier [45] clearly indicates that brominated silica is a more effective reagent than iodotrimethylsilane and bromotrimethylsilane. For example, the reaction time for deoxygenation of phenyl sulfoxide is 3 min (99%). This time for iodotrimethylsilane and bromotrimethylsilane is, respectively, 2 h (73%) and 48 h (reflux, mixture of products).

3. Conclusion

In conclusion, we have shown that SB can promote the deoxygenation of sulfoxides to the corresponding sulfides in high yield. Although the literature reports a number of procedures for the deoxygenation of sulfoxides, the excellent yields, heterogeneous conditions, simplicity, good availability of starting materials, compatibility with a variety of functionalities, and ease of isolation of the products make our procedure a practical alternative.

4. Experimental

Chemicals were obtained from Merck, Aldrich and Fluka chemical companies. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advanced DPX-250 MHz spectrometer using tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The silica gel used for the preparation of SB was art 7734 for column chromatography from Merck.

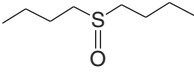
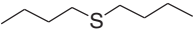
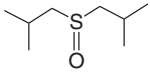
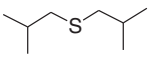


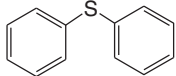
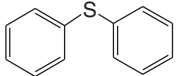
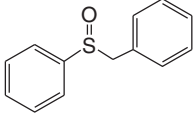
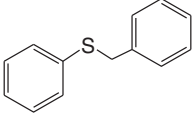
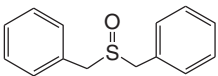
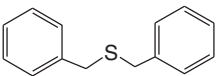
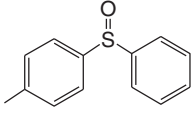
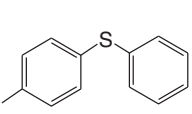
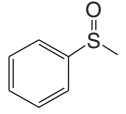
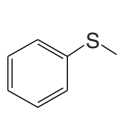
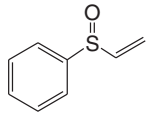
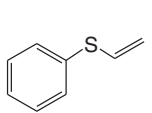
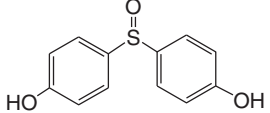
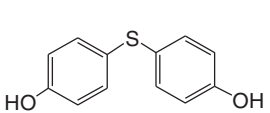
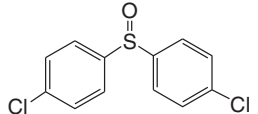
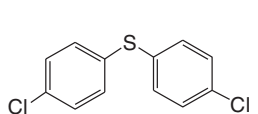
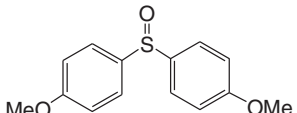
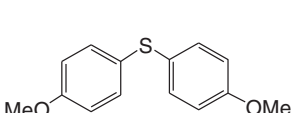
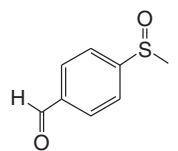
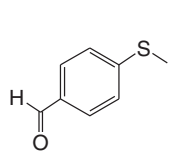
4.1. Procedure for preparation of SB

To silica gel (40 g) and dry toluene (80 mL) in a round bottomed flask equipped with a condenser and a drying tube was added phosphorus tribromide (75 g, 0.21 mol) and refluxed for 18 h. After cooling, the product was filtered and washed, first, with dry 1,4-dioxane (2 × 20 mL) and then with dichloromethane (2 × 20 mL). The yellowish product was kept in dessicator. The amount of bromosilyl group (2.2 mmole of Br/g silica) is determined by a standard method [39].

4.2. Deoxygenation of diphenyl sulfoxide to diphenylsulfide

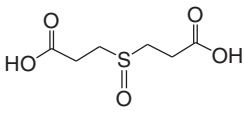
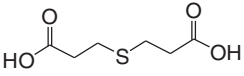
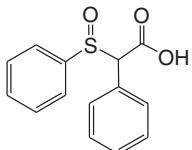
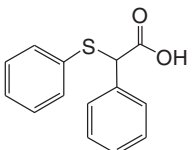
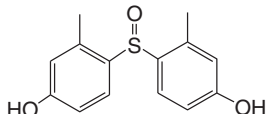
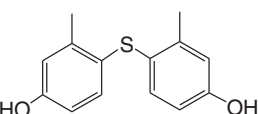
In a typical procedure, diphenyl sulfoxide (2.2 g, 0.01 mol) and brominated silica (18.18 g, 40 mmole Br/g silica) are mixed in an aprotic solvent, *e.g.* dichloromethane (2 mL) or carbon tetrachloride, at room temperature with exclusion of atmospheric moisture, for 5 min. Diphenyl sulfide is isolated in pure state by simple filtration and evaporation of the solvent (1.84, 99%).

Table 2. Conversion of sulfoxides to sulfides.

Entry	Substrate	Product	Time ^a (min)	Yield ^b (%)
1			10	91
2			10	91
3			10	92
4			3	99
5			5	98
6			7	96
7			5	92
8			7	94
9			7	89
10			5	91
11			7	94
12			7	89
13			10	92

(Continued)

Table 2. Continued.

Entry	Substrate	Product	Time ^a (min)	Yield ^b (%)
14			10	94
15			5	95
16			10	96

Notes: ^aThe course of reaction was checked by thin-layer chromatography or gas chromatography. ^bYield of isolated pure sulfide.

4.3. ¹H NMR data for selected compounds

Product (Table 2, Entry 1): ¹H NMR (200 MHz, CDCl₃): δ 0.93–0.96 (t, 6H), 1.40–1.47 (m, 4H).

Product (Table 2, Entry 5): ¹H NMR (200 MHz, CDCl₃): δ 4.77 (s, 2H), 6.54–7.04 (m, 10H).

Product (Table 2, Entry 15): ¹H NMR (200 MHz, CDCl₃): δ 4.92 (s, 2H), 1.40–1.47 (m, 4H), 1.56–1.63 (m, 4H), 2.52–2.55 (t, 4H).

References

- [1] Black S, Harte EM, Hudson B, Wartofsky L. A specific enzymatic reduction of L-(–)methionine sulfoxide and a related nonspecific reduction of disulfides. *J Biol Chem.* 1960;235:2910–2916.
- [2] Mathur NK, Williams RE. Organic syntheses using polymeric supports, polymeric reagents, and polymeric catalysts. *J Macromol Sci Rev Macromol Chem C.* 1976;15:117–125.
- [3] Leznoff CC. The use of insoluble polymer supports in organic chemical synthesis. *Chem Soc Rev.* 1974;3:65–85.
- [4] Fridkin M, Patchornik A, Katchalski A. A synthesis of cyclic peptides utilizing high molecular weight carriers. *J Am Chem Soc.* 1965; 87:4646–4648.
- [5] Grubbs RH, Gibbons C, Kroll LC, Bonds WD Jr, Brubaker CH Jr. Activation of homogeneous catalysts by polymer attachment. *J Am Chem Soc.* 1973;95:2373–2375.
- [6] Jayalekshmy P, Mazur S. Pseudodilution, the solid-phase immobilization of Benzylne. *J Am Chem Soc.* 1976;98:6710–6711.
- [7] Harrison IT, Harrison S. Synthesis of a stable complex of a macrocycle and a threaded chain. *J Am Chem Soc.* 1967;89:5723–5724.
- [8] Kraus MK, Patchornik A. Directed mixed ester condensation of two acids bound to a common polymer backbone. *J Am Chem Soc.* 1971;93:7325–7327.
- [9] Kawama M, Emoto S. Asymmetric synthesis on an insoluble polymer support. *Tetrahedron Lett.* 1972;13:4855–4858.
- [10] Fyles TM, Leznoff CC. The use of polymer supports in organic synthesis. V. The preparation of monoacetates of symmetrical diols. *Can J Chem.* 1976;54:935–942.
- [11] Letsinger L, Kornet LMJ, Mahadevan V, Jerina DM. Reactions on polymer supports. *J Am Chem Soc.* 1964;86:5163–5165.
- [12] Crosby GA, Weinshenker NM, Uh HS. Polymeric reagents. III. Synthesis of an insoluble polymeric thioanisole and its utilization for the oxidation of alcohols. *J Am Chem Soc.* 1975;97:2232–2235.
- [13] Michels R, Kato M, Heitz W. Polymere reagenzien, polymere selenreagenzien. *Makromol Chem.* 1976;177:2311–2318.
- [14] Drabowicz J, Mikolajczyk M. A mild and efficient reduction of sulphoxides by means of lithium alanate and titanium(IV) chloride. *Synthesis.* 1976;8:526–527.
- [15] Drabowicz J, Mikolajczyk M. A rapid and mild reduction of sulphoxides with titanium(II) chloride. *Synthesis.* 1978;2:138–139.

- [16] Baliki R. Mild and efficient deoxygenation of sulfoxides with titanium(IV) chloride/sodium iodide reagent system *Synthesis*. 1991;2:155–157.
- [17] Akita T, Inaba M, Uchida H, Ohta A. Reduction of some nitro compounds and sulfoxides with chromium(II) chloride. *Synthesis*. 1977;11:792–794.
- [18] Olah GA, Surya Prakash GK, Ho TL. Synthetic methods and reactions; XXVI. Efficient deoxygenation of sulfoxides with molybdenum(III) and vanadium(II) reagents. *Synthesis*. 1976;12:810–811.
- [19] Firouzabadi H, Karimi B. Efficient deoxygenation of sulfoxides to thioethers and reductive coupling of sulfonyl chlorides to disulfides with tungsten hexachloride. *Synthesis*. 1999;3:500–504.
- [20] Harrison DJ, Tam NC, Vogels CM, Thomas Baker LR, Decken A, Westcott SA. A gentle and efficient route for the deoxygenation of sulfoxides using catecholborane (HBCat; cat = 1,2-O₂C₆H₄). *Tetrahedron Lett*. 2004;45:8493–8496.
- [21] Yoo BW, Song MS, Park MC. Mild and efficient deoxygenation of sulfoxides with MoCl₅/Indium system. *Synth Commun*. 2007;37:3089–3093.
- [22] Strecker RA, Anderson KK. Reduction of alkyl aryl sulfoxides by iodide ions in acid solutions. *J Org Chem*. 1968;33:2234–2237.
- [23] Johnson CR, Bacon CC, Rigau JJ. Chemistry of sulfoxides and related compounds. XXXVII. Reduction of sulfoxides with sodium hydrogen sulfite. *J Org Chem*. 1972;37:919–920.
- [24] Chasar DW, Shockcor JP. The deoxygenation of sulfoxides with anhydrous HCl/KI. Phosphorus, Sulfur, Silicon *Relat Elem*. 1980;8:187–188.
- [25] Iranpoor N, Firouzabadi H, Shaterian HR. A new approach to the reduction of sulfoxides to sulfides with 1,3-dithianes in the presence of electrophilic bromine as Catalyst. *J Org Chem*. 2002;67:2826–2830.
- [26] Fernandes AC, Ramao C. A novel method for the reduction of sulfoxides and pyridine N-oxides with the system silane/MoO₂Cl₂. *Tetrahedron*. 2006;62:9650–9654.
- [27] Hanlon SP, Graham DL, Hogan PJ, Holt RA, Reeve CD, Slaw AL, McEwan AG. Asymmetric reduction of racemic sulfoxides by dimethyl sulfoxide reductases from *Rhodobacter capsulatus*, *Escherichia coli* and *Proteus* species. *Microbiology*. 1988;144:2247–2253.
- [28] Bahrami K, Khodaei MM, Khedri M. A novel method for the deoxygenation of sulfoxides with PPh₃/ Br₂/ CuBr. *Chem Lett*. 2007;36:1324–1325.
- [29] Park ES, Hwan S, Lee LJH, Rhee HJ, Toon CM. Deoxygenation of sulfoxide and aza-aromatic N-oxide using a protocol of indium and acyl Chloride. *Synthesis*. 2005;20:3499–3501.
- [30] Bahrami K, Khodaei MM, Karimi A. Mild and efficient deoxygenation of sulfoxides to sulfides with triflic anhydride/Potassium iodide reagent system. *Synthesis*. 2008;16:2543–2546.
- [31] Shockvavi A, Rostami E, Hiedarian D, Fattahi H. Microwave assisted rapid, efficient and chemoselective deoxygenation of sulfoxides to thioethers using Zn/AcOH on silica gel. *Iranian J Chem Eng*. 2008;27:129–134.
- [32] Yoo BW, Song MS, Park MC. Bull. A facile and efficient deoxygenation of sulfoxides with Mo(CO)₆. *Korean Chem Soc*. 2007;28:171–172.
- [33] Yoo BW, Park MC, Shin J. Rapid and mild deoxygenation of sulfoxides with MoCl₅/Gallium system under ultrasonication. *Bull Korean Chem Soc*. 2009;30:1927–1928.
- [34] Kikuchi S, Konishi H, Hashimoto Y. The deoxygenation of sulfoxide mediated by the Ph₃P/Lewis acid combination and the application to the kinetic resolution of racemic phosphines using optically active sulfoxide. *Tetrahedron*. 2005;61:3587–3591.
- [35] Nojima M, Nagata T, Tokura N. Deoxygenation of sulfoxides to sulfides in an iodine-pyridine-sulfur dioxide system. *Bull Chem Soc Jpn*. 1975;48:1343–1344.
- [36] Temois J, Guillen F, Piacenza G, Rose S, Plaquevent JC, Coquerel G. Towards a robust and reliable method for the reduction of functionalized sulfoxides. *Org Process Res Dev*. 2008;12:614–617.
- [37] Olah GH, Gupta BGB, Narang SC. Synthetic methods and reactions; deoxygenation of sulfoxides with alkylhalosilane reagents. *Synthesis*. 1977;5:583–584.
- [38] Firouzabadi H, Iranpoor N, Jafarpour M. ZrCl₄/NaI and ZrOCl₂ · 8H₂O/NaI as effective systems for reductive coupling of sulfonyl chlorides and chemoselective deoxygenation of sulfoxides. *J Sulfur Chem*. 2005;26:313–324.
- [39] Jabari A, Zarei M, Jamaledini A. I₂ as a mild and efficient catalyst in deoxygenation of sulfoxides with thioacetic acid. *J Sulfur Chem*. 2012;33:413–418.
- [40] Larock RC. *Comprehensive organic transformations*. 2nd ed. New York: Wiley; 1999. p. 689–702.
- [41] Wallace TJ, Mahon J. Reactions of thiols with sulfoxides. III. Catalysis by acids and bases. *J Org Chem*. 1965;30:1502–1506.
- [42] Mehmet Y, Hyne JB. The reaction of hydrogen sulfide with sulfoxides. *Phosphorous Sulfur*. 1976;1:47–54.
- [43] Mikolajczyk M. Entschwefelung von thioäuren mit dimethylsulfid. *Angew Chem*. 1966;78:393–395.
- [44] Oae S, Nakanishi A, Tsujimoto T. The reduction of semipolar linkages by O,O-dialkyl dithiophosphoric acid. *Tetrahedron*. 1972;28:2981–2990.
- [45] Bordwell FG, Pitt BM. The formation of α-chloro sulfides from sulfides and from sulfoxides. *J Am Chem Soc*. 1955;77:572–577.
- [46] Tanikaga R, Nakayama K, Tanaka K, Kaji A. Rapid reaction between sulfonium ion and sulfur. Preparative reduction of sulfoxide. *Chem Lett*. 1977;34:395–396.
- [47] Fukamiya N, Okano M, Arantani T. Deoxygenation reaction of sulphoxide using trifluoromethanesulphonyl chloride. *Chem Ind. (London)* 1982;13:199–201.

- [48] Oae S, Tsuchida Y, Nakai M. The tracer study of the reactions of diphenyl sulfone and diphenyl sulfoxide with diphenyl disulfide. *Bull Chem Soc Jpn.* 1971;44:451–454.
- [49] Oae S, Kawamura S. The tracer study of the reactions of diphenyl sulfone and diphenyl sulfoxide with sulfur. *Bull. Chem Soc Jpn.* 1963;36:163–167.
- [50] Mohanazadeh F, Zolfigol MA, Sedrpoushan A, Veisi H. Synthesis of silica bromide as heterogeneous reagent and its application to conversion of alcohols to alkyl bromides. *Lett Org Chem.* 2012;9:598–603.
- [51] Jeffery GH, Bassett J, Mendham J, Denney RC. *Vogel's textbook of quantitative chemical analysis.* 5th ed. New York: Wiley; 1989. p. 339.