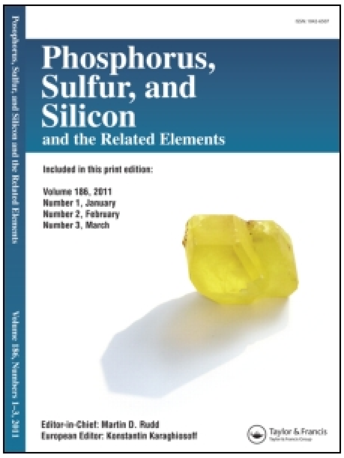

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# A Simple and Efficient Method for Reduction of Sulfoxide Under Solvent-Free Conditions

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# A SIMPLE AND EFFICIENT METHOD FOR REDUCTION OF SULFOXIDE UNDER SOLVENT-FREE CONDITIONS

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***Benzyl DABCO bromide was found to be an efficient and mild reagent for the reduction of sulfoxides to the corresponding sulfide using sulfuric acid adsorbed silica gel under solvent-free conditions at room temperature.***

**Keywords** Reduction; solvent free conditions; sulfoxide; sulfuric acid adsorbed silica gel

## INTRODUCTION

Sulfoxides are important reagents in the application of organosulfur compounds in organic synthesis.[1] The reduction (or deoxygenation) of sulfoxides to the corresponding sulfides is an important organic and biological reaction.[2,3] Over the years, several methods have been developed to reduce sulfoxides.[4–11] However, many of these transformations are limited by side reactions, low yields, lack of chemoselectivity, or harsh conditions and involve reagents that are strong nucleophiles or very reactive species such as carbenes.[12] Consequently, it is desirable to develop alternative methods for the reduction of sulfoxides using mild conditions.

Recently, the use of catalysts and reagents supported on solid supports and solvent-free conditions was developed because such reagents not only simplify the purification processes but also help to prevent the release of toxic reaction residues into the environment.[13–17]

In continuation of our investigations on organic reactions in solventless systems and discovering new applications of supported acids,[18,19] we report in this article an extremely convenient, mild, and efficient procedure for the reduction of sulfoxides to their corresponding sulfides using benzyl DABCO bromide and sulfuric acid adsorbed silica gel ($H_2SO_4$-silica) under solvent free conditions.

## RESULTS AND DISCUSSION

Reactions under solvent-free conditions have received increasing attention in recent years. The advantage of these methods over conventional homogenous reactions is that they

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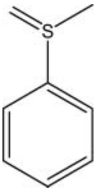
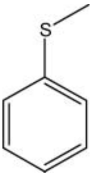
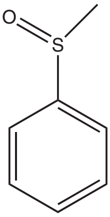
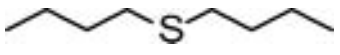
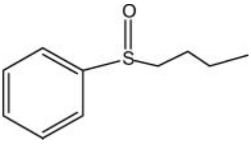
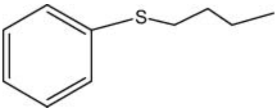
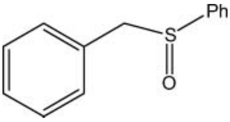
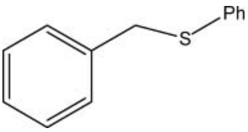
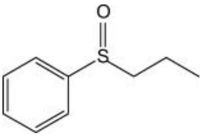
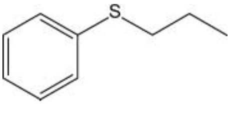
provide greater selectivity, proceed with enhanced reaction rates, give cleaner products, and involve simple manipulation.

During the course of our studies on the oxidation of sulfides with benzyl DABCO tribromide,[20] we observed that methyl phenyl sulfoxide was reduced to methyl phenyl sulfide. This finding and the recent reports on the use of $H_2SO_4$-silica in various organic reactions[21] have encouraged us to develop a simple method for the reduction of sulfoxides to their corresponding sulfides using benzyl DABCO bromide and $H_2SO_4$-silica. First, the $H_2SO_4$-silica was prepared by creating a mixture of $H_2SO_4$ (98%) and silica gel (0.063–0.2 mm) according to the previously reported method.[22] This reagent is stable and can be kept at room temperature for months without losing its activity. Then, we attempted the reduction of methyl phenyl sulfoxide by benzyl DABCO bromide in the presence of $H_2SO_4$-silica. The treatment of 1 mmol of methyl phenyl sulfoxide with 2 mmol of benzyl DABCO bromide in the presence of $H_2SO_4$-silica (4 mmol $H_2SO_4$ in 1.18 g $H_2SO_4$-silica) afforded the corresponding sulfide in a short time in almost quantitative yield. In a

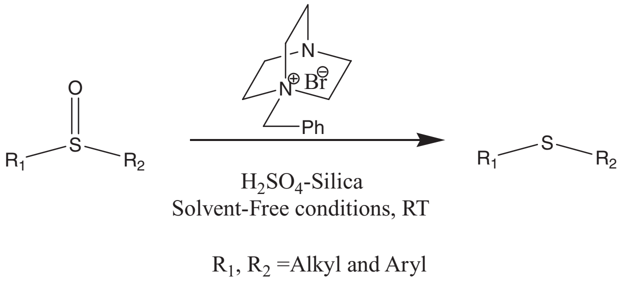
**Table I** Reduction of sulfoxides with benzyl DABCO bromide and $H_2SO_4$-silica under solvent free conditions at RT [a,b,c]

| Substrate | Product | Time (min) | Yield |
|---|---|---|---|
|  |  | 7 | 92 |
|  |  | 5 | 95 |
|  |  | 7 | 91 |
|  |  | 10 | 45 |
|  |  | 6 | 93 |

[a] Yield refers to isolated pure products.

[b] Sulfoxide/benzyl DABCO bromide/$H_2SO_4$-silica (1:2:4 mmol).

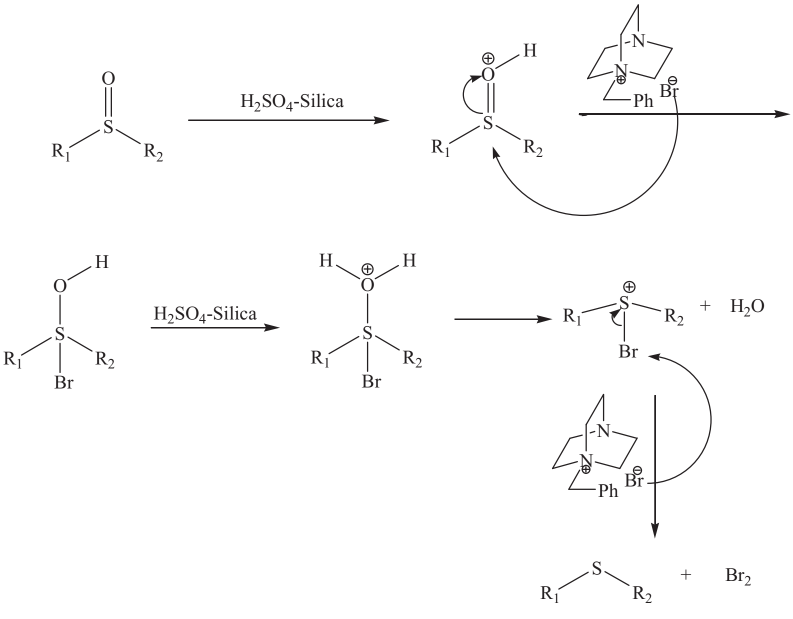
[c] The products were characterized from their spectral (IR and $^1H$ NMR) and comparison to authentic samples.



Scheme 1

controlled experiment, we observed that the reaction does not take place in the absence of $H_2SO_4$-silica. Therefore, we employed the above conditions for the conversion of various sulfoxides to the corresponding sulfides under solvent-free conditions (Scheme 1, Table I).

The possible mechanism of the reaction is shown in Scheme 2; initially $H_2SO_4$-silica reacted with sulfoxide to generate protonated sulfoxide, then the reduction occurs via a halosulfonium ion subsequently reduced to a sulfide by a second halide ion.



Scheme 2

The activity of benzyl DABCO bromide/$H_2SO_4$-silica seems to be higher than other known catalysts for the reduction of sulfoxides because of the shorter reaction time and high yield (Table II). In addition, the simple experimental procedure, mild reaction conditions, and solvent-free conditions are the advantages of the present protocol.

In conclusion, we have developed an efficient method for the reduction of sulfoxide to the corresponding sulfides using benzyl DABCO bromide in the presence of $H_2SO_4$-silica with advantages such as the following: a) The reagent is inexpensive and easily handed, and can be stored on the shelf for months without losing its activity. b) The procedure is

**Table II** A comparative study of various systems for reduction of methyl phenyl sulfoxide

| Entry | Reagent | Conditions | Time | Yield$^{(Ref)}$ |
|---|---|---|---|---|
| 1 | Benzyl DABCO bromide/$H_2SO_4$-silica | Solvent-free /RT | 7 min | 92 |
| 2 | Silane/$MoO_2Cl_2$[a] | THF/Reflux | 2 h | 100[23] |
| | | THF/RT | 20 h | 66[23] |
| 3 | Catecholborane/$MoO_2Cl_2(H_2O)_2$[b] | THF/Reflux | 15 min | 94[24] |
| | | THF/RT | 16 h | 88[24] |
| 4 | $BH_3$ THF/$MoO_2Cl_2$[c] | THF/Reflux | 10 min | 93[24] |
| 5 | TABCO/1,3-dithiane[d] | $CHCl_3$/RT | 15 min | 94[25] |

[a] The reaction was carried out with 100 mol% of $PhSiH_3$ and with 0.3 mol% of PMHS and 5mol% of $MoO_2Cl_2$.

[b] The reaction was carried out with 1.0 mmol of sulfoxide, 2 mmol of catecholborane, and 5 mol% of $MoO_2Cl_2(H_2O)_2$.

[c] The reaction was carried out with 1.0 mmol of sulfoxide, 2.0 mmol of $BH_3$-THF, and 5 mol% of $MoO_2Cl_2$.

[d] The ratio of sulfoxide:1,3-dithiane:TABCO (2,4,4,6-tetrabromo-2,5-cyclohexadienone) is 1:1.1:0.2.

simple and occurs under solvent free conditions. c) The yield of sulfide is good to high, and the reaction time is short. d) The isolation of product is straightforward. In conclusion, this method can be a useful alternative to the traditional methods for the reduction of sulfoxides

## EXPERIMENTAL

$H_2SO_4$-silica,[22] benzyl DABCO bromide,[26] and all sulfoxides[20] were prepared according to the reported methods. Yields refer to isolated pure products. The products were characterized by comparison with authentic samples (IR, $^1$H NMR spectrum). All $^1$H NMR spectra were recorded at 300 MHz in $CDCl_3$ relative to TMS (0.00 ppm). IR spectra were recorded with a Perkin Elmer RXI spectrophotometer. Spectra of solids were recorded using KBr pellets.

### General Procedure for Reduction of Sulfoxide

In a mortar, a mixture of sulfoxide (1 mmol), benzyl DABCO bromide (2 mmol), and $H_2SO_4$-silica (4 mmol $H_2SO_4$ in 1.18 g $H_2SO_4$-silica) was ground with a pestle for the time specified in Table I. The progress of the reaction was followed by TLC. $CH_2Cl_2$ (5 mL) was added to the reaction mixture, and the solid material was separated by filtration. The filter cake was washed with $CH_2Cl_2$ (2 × 5 mL), and the filtrates were combined. Evaporation of the solvent resulted in a highly pure product.

## REFERENCES

1. J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed. (Wiley, New York, 1992).
2. (a) J. Drabowicz, B. Dudzinski, and M. Mikolajczyk, *Synlett*, 252 (1992); (b) F. Mohanazadeh, A . R. Momeni, and Y. Ranjbar, *Tetrahedron Lett.*, **35,** 6127 (1994); (c) E. Nicolas, M. Vilaseca, and E. Giralt, *Tetrahedron*, **51,** 5701 (1995); (d) K. Fujiki, S. Kurita, and E. Yoshida, *Synth. Commun.*, **19,** 3619 (1996); (e) Y. Wang and M. Koreeda, *Synlett*, 885 (1996).
3. S. Black, E. M. Harte, B. Hudson, and L. Wartofsky, *J. Biol. Chem.*, **235,** 2910 (1960).
4. M. Madesclaire, *Tetrahedron*, **44,** 6537 (1988).
5. V. Y. Kukushkin, *Coord. Chem. Rev.*, **139,** 375 (1995).

6. J. H. Espenson, *Coord. Chem. Rev.*, **249,** 329 (2005).
7. B. R. Raju, G. Devi, Y. S. Nongpluh, and A. K. Saikia, *Synlett*, 358 (2005).
8. R. Sanz, J. Escribano, Y. Fernandez, R. Aguado, M. R. Pedrosa, and F. J. Arnaiz, *Synthesis*, 1629 (2004).
9. D. J. Harrison, N. C. Tam, C. M. Vogels, R. F. Langler, R. T. Baker, A. Decken, and S. A. Westcott, *Tetrahedron Lett.*, **45,** 8493 (2004).
10. B. W. Yoo, K. H. Choi, D. Y. Kim, K. I. Choi, and J. H. Kim, *Synth. Commun.*, **33,** 53 (2003).
11. K. C. Nicolaou, A. E. Koumbis, S. A. Snyder, and K. B. Simonsen, *Angew. Chem., Int. Ed.*, **39,** 2529 (2000).
12. J. Drabowicz, H. Togo, M. Mikolajczyk, and S. Oae, *Org. Prep. Proc. Int.*, **16,** 171 (1984).
13. A. Loupy, F. Maurel, and A. Sabatie-Gogova, *Tetrahedron*, **60,** 1683 (2004).
14. B. K. Pchelka, A. Loupy, and A. Petit, *Tetrahedron*, **62,** 10968 (2006).
15. R. S. Varma, A. K. Chatterjee, M. Varma, *Tetrahedron Lett.*, **34,** 3207 (1993).
16. D. Kumar, M. S. Sundaree, G. Patel, V. S. Rao, and R. S. Varma, *Tetrahedron Lett.*, **47,** 8239 (2006).
17. D. Kumar, S. Sundaree, V. S. Rao, and R. S. Varma, *Tetrahedron Lett.*, **47,** 4197 (2006).
18. A. R. Hajipour, S. A. Pourmousavi, and A. E. Rouho, *Phosphorus, Sulfur, and Silicon*, **182,** 921 (2007).
19. A. R. Hajipour, A. Zarei, L. Khazdooz, L. S. A. Pourmousavi, S. Zahmatkesh, and A. E. Ruoho, *J. Sulfur Chem.*, **25,** 389 (2004).
20. S. A. Pourmousavi and P. Salehi, *Bull. Korean Chem. Soc.*, **29,** 1332 (2008).
21. (a) B. Mukhopadhyay, *Tetrahedron Lett.*, **47,** 4337 (2006); (b) V. K. Rajput, B. Roy, and B. Mukhopadhyay, *Tetrahedron Lett.*, **47,** 6987 (2006); (c) V. K. Rajput, and B. Mukhopadhyay, *Tetrahedron Lett.*, **47,** 5939 (2006).
22. H. Firouzabadi and M. Abbasi, *Synth Commun.*, **29,** 14 (1999).
23. A. C. Fernandes and C. C. Romao, *Tetrahedron*, **62,** 9650 (2006).
24. A. C. Fernandes and C. C. Romao, *Tetrahedron Lett.*, **48,** 9176 (2007).
25. N. Iranpoor, H. Firouzabadi, and H. R. Shaterian, *J. Org. Chem.*, **67,** 2826 (2002).
26. A. R. Hajipour and N. Mahboubghah, *J. Chem. Res., (S)*, 122 (1998).