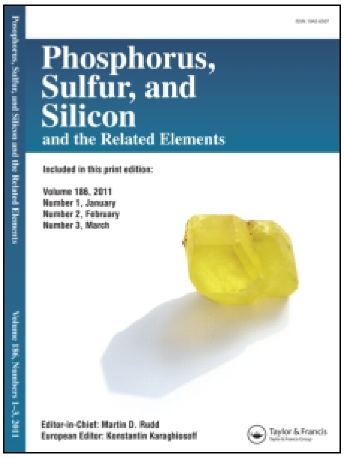

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$(PhCH_2PPh_3)^+Br_3^-$: A Versatile Reagent for the Chemoselective Oxidation of Sulfides to Sulfoxides

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$(PhCH_2PPh_3)^+Br_3^-$: A VERSATILE REAGENT FOR THE CHEMOSELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES

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Benzyltriphenylphosphonium tribromide (BTPTB), as a stable solid reagent, is easily prepared by the reaction of benzyltriphenylphosphonium bromide with Br_2. This reagent can be used as an efficient reagent for the chemoselective oxidation of dialkyl and aryl-alkyl sulfides to their corresponding sulfoxides in the presence of diaryl sulfides and primary alcohols. All reactions were performed in a refluxing mixture of methanol and water in very short reaction times.

Keywords Benzyltriphenylphosphonium bromide; benzyltriphenylphosphonium tribromide; chemoselective oxidation; sulfides; sulfoxides

Sulfoxides, as useful synthetic intermediates which are used for the construction of various chemically and biologically significant molecules,[1] are usefully prepared by the oxidation of sulfides. Various methods are available for the oxidation of sulfides to sulfoxides.[2–19] However, some of these methods suffer from drawbacks such as low yields of the products, long reaction times, low selectivity, overoxidation of sulfoxides to sulfones, the use of expensive reagents, and the use of corrosive acids and hazardous peracids. Consequently, introduction of new methods and procedures to circumvent these problems is still in demand.

Very recently, benzyltriphenylphosphonium tribromide (BTPTB) was used in the tetrahydropyranylation of alcohols[20] as well as the thioacetalization of carbonyl compounds.[21] In continuation of our ongoing research program on the development of new methods for the oxidation of organic compounds,[22–26] in this article, in addition to the introduction of a new and high yielding method for the preparation of BTPTB, we report the applicability of this reagent in the chemoselective oxidation of dialkyl and aryl-alkyl sulfides to their corresponding sulfoxides (Scheme 1).

We carried out our initial studies with dibenzyl sulfide to find the optimal reaction conditions. These studies showed that the best result was obtained in a refluxing mixture

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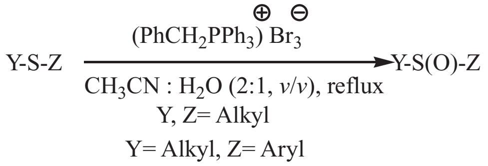
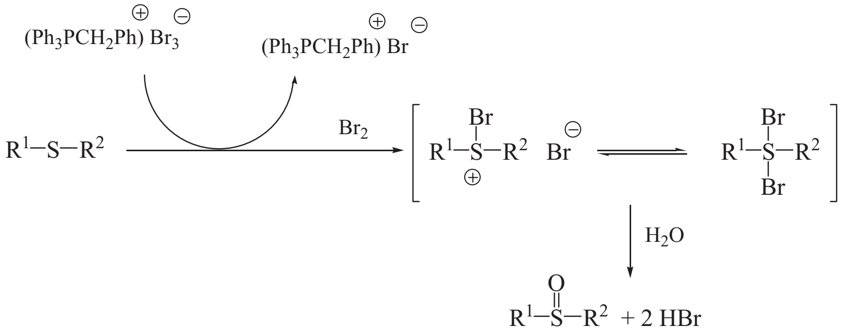


$$\text{Y-S-Z} \xrightarrow[\substack{\text{CH}_3\text{CN : H}_2\text{O (2:1, } v/v\text{), reflux} \\ \text{Y, Z= Alkyl} \\ \text{Y= Alkyl, Z= Aryl}}]{\overset{\oplus}{(\text{PhCH}_2\text{PPh}_3)}\,\overset{\ominus}{\text{Br}_3}} \text{Y-S(O)-Z}$$

Scheme 1

of $CH_3CN:H_2O$ (2:1, *v/v*) when the relative ratio of BTPTB to substrate was 2:1. After optimization of the reaction conditions, different types of dialkyl and aryl-alkyl sulfides were subjected to oxidation under the determined conditions. As shown in Table I, the corresponding sulfoxides were obtained in very short reaction times in high yields. Our investigations clarified that primary alcohols are resistant to the oxidation under the selected conditions, and diaryl sulfides are oxidized slower than the other sulfides using this method, and the reaction is incomplete in most cases (Table I, entries 7, 9, 10). Therefore this methodology can be used for the selective oxidation of dialkyl and aryl-alkyl sulfides in the presence of primary alcohols and diaryl sulfides (Table I, entries 7 and 11). It is important to note that results show no sulfone formation using this method, even after prolonged heating.

A plausible mechanism of this oxidation is shown in Scheme 2 based on reported pathway in literature,[11] our observations, and obtained results.

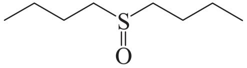
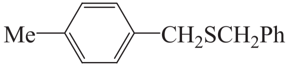
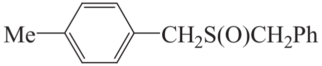
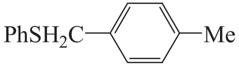
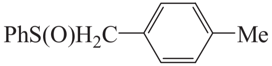
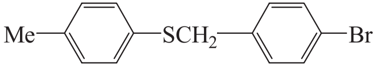
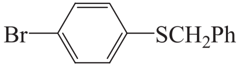
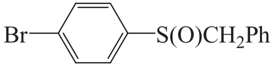
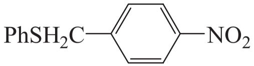
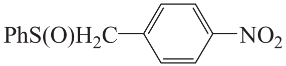
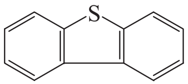
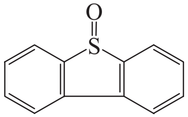


Scheme 2

Table II, which is used for the comparison of the efficiency of our method with some of those reported in the literature, shows that the current method is simpler, more efficient, and less time consuming.

In conclusion, we have reported the application of benzyltriphenylphosphonium tribromide in efficient oxidation of dialkyl and aryl-alkyl sulfides. Very short reaction times, high yields of the products, simple procedure, and easy and clean work-up are important advantages of this method. The chemoselective oxidation of the above-mentioned substrates in the presence of diaryl sulfides and primary alcohols, as one of the most important advantages, make this method attractive for the chemists. We believe that the present method could be an important addition to the existing methodologies.

Table I Oxidation of sulfides to sulfoxides[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)[Ref]
1			Immediately	95[5]
2	$(PhCH_2)_2S$	$(PhCH_2)_2SO$	"	92[5]
3			"	89[12]
4			"	92[4]
5			"	91[4]
6			"	89[4]
7	$PhSCH_2CH_2OH$	$PhS(O)CH_2CH_2OH$	"	91[5]
8			5	85[4]
9			60	Trace
10	PhSPh	PhS(O)Ph	60	Trace
11	$(PhCH_2)_2S + PhSPh$	$(PhCH_2)_2SO + PhS(O)Ph$	Immediately	$100^c + 0^c$

[a] Products were characterized by their physical data, comparison with authentic samples, and IR and NMR spectroscopy.

[b] Isolated yield.

[c] Conversion.

Table II Comparison of efficiency of various reagents in the oxidation of dibenzyl sulfide

Entry	Reagent	Time (min)	Yield (%)	Reference
1	HIO_3/wet SiO_2	170	92	5
2	H_2O_2/Mn(III)-Schiff base complex	100	95	7
3		24 (h)	10	14
4	3-Carboxypyridinium chlorochromate/$AlCl_3$	20	87	12
5	H_2O_2/MoO_3	14	96	13
6	Cetyltrimethylammonium tribromide	120	92	11
7	H_2O_2/NBS	11 (h)	90	17
8	PVP-HNO_3/KBr	15	98	15
9	BTPTB	Immediately	92	This work

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka, and Aldrich Chemical Companies. Products were separated and identified by the comparison of their mp, IR, NMR, and bp with those reported for the authentic samples. ^1H NMR spectra were recorded on JNM-EX 90A or Bruker-DRX MH2 NMR spectrometers.

Preparation of BTPTB

A 0.5 M solution (1 mL) of Br_2 in MeOH was added dropwise to a stirring solution of benzyltriphenylphosphonium bromide (0.3 mmol, 0.13 g) in EtOH (5 mL) in an ice bath, and the mixture ws stirred for 1 h, then filtered. The yellow solid residue was washed with distilled water and dried at room temperature and recrystallized from CH_3CN to give BTPTB in 85% yield. (According to the previously reported method, BTPTB was prepared in 70% yield.[21])

Oxidation of Sulfides Using BTPTB

BTPTB (2 mmol, 1.2 g) was added to a solution of the substrate (1 mmol) in MeCN-H_2O (2:1, *v/v*) (3 mL). The mixture was stirred at reflux temperature. After completion of the reaction, most of the solvent was evaporated, and Et_2O (5 mL) was added. The mixture was filtered, and the solid residue was washed with Et_2O (5 mL). The filtrate was washed with a saturated solution of $NaHCO_3$ and H_2O and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding sulfoxides in high yields.

REFERENCES

1. S. Patai, Z. Roppoprt, and C. Stirling, *The Chemistry of Sulfones and Sulfoxides* (John Wiley, Chichester, UK 1988).
2. D. A. Peak and T. I. Watkins, *J. Chem. Soc.*, 445 (1950).
3. C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75,** 4250 (1953).
4. V. Mirkhani, S. Tangestaninejad, M. Moghadam, I. Mohammadpoor-Baltork, and H. Kargar, *J. Mol. Catal. A: Chem.*, **242,** 251 (2005).
5. M. M. Lakouraj, M. Tajbakhsh, F. Shirini, and M. V. Asady Tamami, *Synth. Commun.*, **35,** 775 (2005).

6. M. Al-Hashemi, E. Fisset, A. C. Sulivan, and J. R. H. Wilson, *Tetrahedron Lett.*, **47,** 8017 (2006).
7. F. Hosseinpoor and H. Golchoubian, *Tetrahedron Lett.*, **47,** 5195 (2006).
8. K. Kaczorowska, Z. Kolarska, K. Mitka, and P. Kowalski, *Tetrahedron*, **61,** 8315 (2005).
9. A. R. Hajipour, S. E. Mallakpour, and H. Adibi, *J. Org. Chem.*, **67,** 8666 (2002).
10. H. Firouzabadi, N. Iranpoor, and M. A. Zolfigol, *Synth. Commun.*, **28,** 1179 (1998).
11. G. Kar, A. K. Saikia, U. Bora, S. K. Dehury, and M. K. Chaudhuri, *Tetrahedron Lett.*, **44,** 4503 (2003).
12. I. Mohammadpoor-Baltork, H. R. Memarian, and K. Bahrami, *Can. J. Chem.*, **83,** 115 (2005).
13. M. M. Khodaei, K. Bahrami, and M. Khedri, *Can. J. Chem.*, **85,** 7 (2007).
14. R. S. Varma and D. R. Dahiya, *Synth. Commun.*, **28,** 4087 (1998).
15. M. A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi, and S. Jafari, *Catal. Commun.*, **9,** 1739 (2008).
16. M. A. Zolfigol, K. Amani, M. Hajjami, and A. Ghorbani-Choghamarani, *Monatsh. Chem.*, **139,** 895 (2008).
17. B. Karimi and D. Zareyee, *J. Iran. Chem. Soc.*, **5,** S103 (2008).
18. K. Surendra, N. S. Krishnaveni, V. P. Kumar, R. Sridhar, and K. R. Rao, *Tetrahedron Lett.*, **46,** 4581 (2005).
19. A. Bravo, B. Dordi, F. Fontana, and F. Minisci, *J. Org. Chem.*, **66,** 3232 (2001).
20. A. R. Hajipour, S. A. Pourmousavi, and A. E. Ruoho, *Synth. Commun.*, **35,** 2895 (2005).
21. A. R. Hajipour, S. A. Pourmousavi, and A. E. Ruoho, *Synth. Commun.*, **38,** 2548 (2008).
22. P. Salehi, M. A. Zolfigol, F. Shirini, and M. Baghbanzadeh, *Current Org. Chem.*, **10,** 2171 (2006).
23. F. Shirini, M. A. Zolfigol, P. Salehi, and M. Abedini, *Current Org. Chem.*, **12,** 183 (2008).
24. F. Shirini, M. A. Zolfigol, and A. Shahriari, *J. Iranian Chem. Soc.*, **5,** 420 (2008).
25. F. Shirini, M. A. Zolfigol, and A. R. Abri, *ARKIVOC*, 14 (2008).
26. M. A. Zolfigol, F. Shirini, G. Chehardoli, and E. Kolvari, *J. Mol. Catal. A: Chem.*, **265,** 272 (2007).