Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

p-Toluenesulfonic Acid Catalyzed Hypervalent Oxidation of Sulfides to Sulfoxides

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To cite this article: Rui-Yang Yang & Li-Xing Dai (1994) p-Toluenesulfonic Acid Catalyzed Hypervalent Oxidation of Sulfides to Sulfoxides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:16, 2229-2236, DOI: 10.1080/00397919408019047

To link to this article: http://dx.doi.org/10.1080/00397919408019047

SYNTHETIC COMMUNICATIONS, 24(16), 2229-2236 (1994)

p-TOLUENESULFONIC ACID CATALYZED HYPERVALENT OXIDATION OF SULFIDES TO SULFOXIDES

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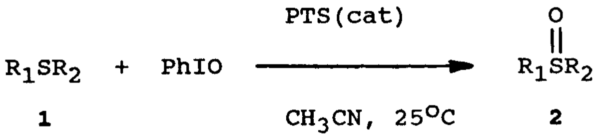
Sulfoxides can be obtained in excellent yields via iodosobenzene oxidation of sulfides in the presence of catalytic amount of p-toluenesufonic acid in acetonitrile under mild conditions.

Sulfoxides are very important intermediates in organic synthesis.[1] They are generally synthesized via oxidation of sulfides, and many methods have been appeared in literatures.[2-8] However, all these exsisting methods either employ highly toxic materials or give further oxidation of sulfoxides to sufones or even both, and therefore careful control of reaction temperature and the quantity of oxidants are necessary. Thus, new efficient methods for selective oxidation of sulfides to sufoxides have to be developed.

During the last decade, hypervalent iodine compounds have been widely used as oxidants in organic synthesis due to their unique oxidizing abilities to organic substrates.[9] It was found that Fe or Mn phorphyrin complexes[7] could catalyze iodosobenzene to oxidize sulfides to sulfoxides. Recently, Kim[8] reported that benzeneseleninic acid could also activate iodosobenzene to oxidize sulfides to sulfoxides selectively. The carboxylic acids with similar acidity to that of the benzene seleninic acid such as benzoic acid and acetic acid have also been used by Kim but none of them could catalyze this reaction. However, both the metal phorphyrin complexes and benzeneseleninic acid are precious and the latter is highly toxic. In continuation of our study on the application of hypervalent iodine compounds in organic synthesis,[10] we reported here a practical method for the synthesis of sulfoxides via p-toluenesulfonic acid(PTS) catalyzed iodosobenzene oxidation of sulfides.

In the presence of catalyzed amount of PTS, sulfides can be readily oxidized to sufoxides in acetonitrile at room temperature in excellent yields(eq.1). The results are summarized in the Table. This reaction is applicable to various sulfides such as dialkylsufides (**1g**), alkylarylsulfides (**1a-f**) and even diarylsulfide (**1h**). The sulfide with a strong electron withdrawing group like NO_2 (**1f**) can also react readily to give the corresponding sulfoxide in excellent yield.



$$\underset{\mathbf{1}}{R_1SR_2} + PhIO \xrightarrow[CH_3CN,\ 25^oC]{PTS(cat)} \underset{\mathbf{2}}{R_1\overset{O}{\overset{\|}{S}}R_2} \qquad \text{eq. 1}$$

1,2	R_1	R_2	**1,2**	R_1	R_4
a	Ph	Me	**e**	p-ClC_6H_4	Me
b	Ph	Et	**f**	p-$O_2NC_6H_4$	Me
c	Ph	Bn	**g**	Bn	Bn
d	p-$CH_3C_6H_4$	Me	**h**	Ph	Ph

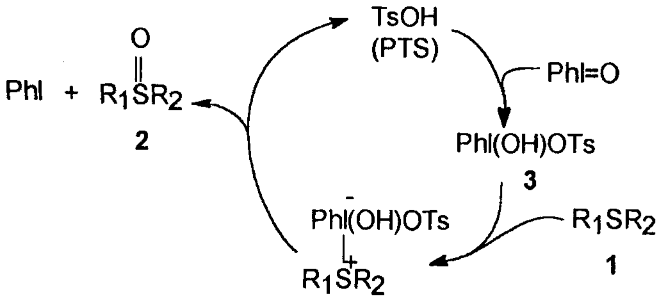
This PTS catalyzed reaction obviously undergoes in the following way(scheme): First, PTS reacts with iodosobenzene to form toluenesulfonyloxyhydroxyiodobenzene **3**, then **3** oxidizes sulfides to give sulfoxides, iodobenzene and PTS.[11]

Table. Compounds **2a-h** Prepared

Product	Yield[a] (%)	mp(^{o}C) found	mp(^{o}C) reported	IR[b] ν(cm^{-1})	^{1}H NMR(CDCl$_3$/TMS) δ, J (Hz)
2a	82	oil	28-30[5]	1480,1450,1420, 1090,1030,960, 750,695	2.52(s,3H), 7.40(m,5H)
2b	81	oil	oil[5]	2950,1480,1440, 1410,1080,1040, 1020,960,745, 690	1.03(t,3H, J=8),2.40-2.90(m,2H), 7.33(m,5H)
2c	96	121-123	122-123[13]	1490,1440,1410, 1080,1030,995, 910,890,740, 690	3.03(s,2H), 7.33-7.60 (m,10H)
2d	81	41-43	41-43[5]	2900,1490,1440, 1405,1295,1085, 1030,1010,950, 810	2.30(s,3H), 2.47(s,3H), 6.97-7.50 (m,4H)
2e	80	45-47	44-46[14]	3050,1570,1480, 1420,1390,1290, 1090,1040,1005, 955,820,740,680	2.53(s,3H), 7.36(s,4H)
2f	99	150-151	151-152[15]	1600,1580,1490, 1420,1340,1080, 1040,1000,960, 860,740,720,680	2.78(s,3H), 7.69-8.56 (m,4H)
2g	91	131-133	132-134[5]	1490,1450,1410, 1290,1070,1120, 915,885,775, 700	3.90(s,4H), 7.31(s,10H)
2h	92	68-70	69-71[5]	1070,1000,910, 750,730,700	7.15-7.67 (m,10H)

a.Isolated yield. b.KCl discs for solids, neat for oil.

Scheme



In summary, an efficient method for the synthesis of sulfoxides is described via PTS catalyzed iodosobenzene oxidation of sulfides in acetonitrile. This reaction is noteworthy for its mild reaction conditions, high yield, no toxicity and lack of over-oxidation.

All melting points were uncorrected. ^{1}H NMR were recorded on a Varian EM-60A (60 MHz) spectrometer using TMS as internal standard or external standard. IR were obtained on a Shimadzu 440 spectrometer. Iodosobenzene was prepared according to literature procedure.[12]

Sulfoxide 2; General Procedure:

Iodosobenzene (220 mg, 1.0 mmol) was added to a solution of sulfide (1.0 mmol) and PTS (19 mg, 0.10 mmol) in acetonitrile (3 mL). The mixture was stirred for about 1 h at r.t. The acetonitrile was evaporated and the crude product obtained was purified by prparative TLC or chromatography on silica gel (eluenet: PE/Et_2O, 1:4) to give **2**. The products were identified by comparison of melting points with literature values and by IR and ^1H NMR (Table).

We thank the Chinese Academy of Sciences and the National Natural Science Foundation for financial support.

References:

1. Solladie,G. In "Comprehensive Organic Synthesis", ed. Trost, B.M. and Fleming,I., Vol.6, p148, Pergamon, Oxaford, 1991.
2. Uemura,S. in "Comprehensive Organic Synthesis", ed. Trost,B.M. and Fleming,I., Vol.7, p762, Pergamon, Oxaford, 1991.
3. Reich,H.J.; Chow,F.; Peake,S.L. Synthesis **1978**,299.
4. Davis,F.A.; Jenkins,R.Jr.; Yocklovich,S.G. Tetrahedron Lett. **1978**, 5171.
5. Drabowicz,J.; Midura,W.; Mikolajczyk,M. Synthesis **1979**,39.
6. Kim,Y.H.; Yoon,D.C. Tetrahedron Lett. **1988**, 29, 6453.
7. Pautet,F.; Daudon,M. Tetrahedron Lett. **1991**, 32, 1457 and references cited therein.
8. Roh,K.R.; Kim,K.S.; Kim,Y.H. Tetrahedron Lett. **1991**,32,793.

9. Varvoglis,A. Chem.Soc.Rev. **1981**,10,377.
Varvoglis,A. Synthesis **1984**,709.
Moriarty,R.M.; Prakash,O. Acc.Chem.Res. **1986**,19, 244.
Merkushev,E.B. Russ.Chem.Rev.(Engl.Transl.) **1987**, 56,826.
Ochia,M. Rev.Heteroat.Chem. **1989**,2,92.
Maletina,I.I.; Orda,V.V.; Yagupolskii,L.M. Russ.Chem.Rev.(Engl. Transl.) **1989**,58,544.
Moriarty,R.M.; Vaid,R.K.; Koser,G.F. Synlett **1990**, 365.
Moriarty,R.M.; Vaid,R.K. Synthesis **1990**,431.
Stang,P.J. Angew.Chem., Int.Ed.Engl. **1992**,31,274.
Koser,G.F. In The Chemistry of Functional Groups, Supplement D; Patai,S.; Rappoport,Z. Eds.; Wiley: New York, 1983; Chapter 18, pp 774-806.

10. Yang,R.-Y.; Dai,L.-X. Synthesis **1993**,481.
Yang,R.-Y.; Dai,L.-X. J.Org.Chem. **1993**,58,3381 and references cited therein.

11. Koser,G.F.; Kokil,P.B.; Shah,M. Tetrahedron Lett. **1987**, 5431.

12. Saltzman,H.; Sharefkin,J.G. Org.Synth. Col.Vol.V, Wiley,New York, N.Y., 1973, p658.

13. Auret,B.J.; Boyd,D.R.; Henbest,H.B.; Ross,S. J.Chem.Soc.(C) **1968**, 2371.

14. Goetz,H.; Klabuhn,B.; Marschner,F.; Hohberg,H.; Skuballa,W. Tetrahedron **1971**,27,999.

15. Leandri,G.; Mangini,A.; Passerini,R. J.Chem.Soc. **1957**,1386.

(Received in the UK 10 February 1994)