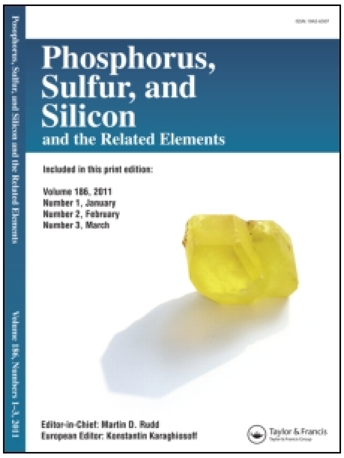


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Selective and Efficient Oxidation of Sulfides to Sulfoxides Using Ceric Ammonium Nitrate (CAN)/Brönsted Acidic Ionic Liquid

Abdol R. Hajipour[a,b]; Leila Khazdooz[b]; Arnold E. Ruoho[a]
[a] Dept. of Pharmacology, Medical School, University of Wisconsin, Madison, Wisconsin, USA [b] Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, Iran

To cite this Article Hajipour, Abdol R. , Khazdooz, Leila and Ruoho, Arnold E.(2009) 'Selective and Efficient Oxidation of Sulfides to Sulfoxides Using Ceric Ammonium Nitrate (CAN)/Brönsted Acidic Ionic Liquid', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 3, 705 — 711

To link to this Article: DOI: 10.1080/10426500802266233

URL: http://dx.doi.org/10.1080/10426500802266233

Phosphorus, Sulfur, and Silicon, 184:705–711, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802266233

Taylor & Francis
Taylor & Francis Group

Selective and Efficient Oxidation of Sulfides to Sulfoxides Using Ceric Ammonium Nitrate (CAN)/Brönsted Acidic Ionic Liquid

Abdol R. Hajipour,[1,2] Leila Khazdooz,[2]
and Arnold E. Ruoho[1]
[1]Dept. of Pharmacology, University of Wisconsin, Medical School, Madison, Wisconsin, USA
[2]Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, Iran

A selective and efficient procedure for the oxidation of sulfides to the corresponding sulfoxides is reported using ceric ammonium nitrate in the presence of methylimidazolium hydrogensulfate as Brönsted acidic ionic liquid ([Hmim]HSO_4) as the solvent under mild conditions. The use of nontoxic and inexpensive materials, straightforward procedure, short reaction times, and good yields of the products are the major advantages of this method.

Keywords Brönsted acidic ionic liquid; ceric ammonium nitrate; methylimidazolium hydrogen sulfate; sulfide; sulfoxide

INTRODUCTION

Ionic liquids (IL) have frequently been used as an alternative for classical organic solvents in modern synthetic chemistry.[1–5] Ionic liquids are superior to conventional organic solvents due to their extremely low vapor pressure, excellent thermal stability, reusability, and ability to dissolve many organic and inorganic substrates.[6] The application of ionic liquids as solvents and catalysts has been reported for a variety of functional group transformations, but their use as acid catalysts under solvent-free conditions requires more

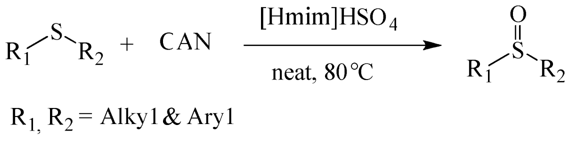
Received 14 May 2008; accepted 11 June 2008.

We gratefully acknowledge the funding support received for this project from the Isfahan University of Technology (IUT), IR Iran. Further financial support from the Center of Excellence in Sensor Research (IUT) is gratefully acknowledged.

Address correspondence to Abdol R. Hajipour, Dept. of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, WI 53706-1532, USA. E-mail: arhajipour@wisc.edu

attention.[7] Brönsted acidic ionic liquids combining the advantageous characteristics of solid acids and mineral acids are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid, in chemical processes.[8] Ionic liquids with Brönsted acidic counter ions such as 1-hexyl-3-methylimidazolium bisulfate ([hmim][HSO_4]),[9] 1-butyl-3-methylimidazolium dihyrogen phosphate ([bmim][H_2PO_4]),[9] 1-[2-(2-hydroxy-ethoxy)ethyl]-3-methylmidazolium bisulfate ([heemim][HSO_4]),[9] 1-butyl-3-methylimidazolium chloroaluminate ([bmim]Cl.2$AlCl_3$),[10] 1-butyl-3-methylimidazolium bisulfate ([bmim][HSO_4]),[11] and methylimidazolium hydrogensulfate [Hmim]HSO_4[12] have been used as acid catalysts and provide a useful medium under solvent-free conditions because of their polar nature.

The selective oxidation of sulfides to sulfoxides is an attractive and important method, because sulfoxides have been utilized extensively in carbon–carbon bond formation reactions and as versatile building blocks in organic synthesis.[13] Oxidation of sulfides is a very useful route for preparation of sulfoxides. Several methods are available for conversion of sulfides to sulfoxides.[14–22] However, some of the existing methods use expensive, toxic, or rare oxidizing reagents that are difficult to prepare. Many of these procedures also suffer from poor selectivity and also often suffer from lack of generality and economic applicability. Therefore, there is a need for a simple, less expensive, general, and safer method for conversion of sulfides to sulfoxides. In continuation of our ongoing program to develop efficient reagents for oxidizing organic compounds,[23–27] we now wish to report a facile and selective method for oxidation of sulfides to their corresponding sulfoxides with ammonium cerium (IV) nitrate in the presence of ([Hmim]HSO_4) as a Brönsted acidic ionic liquid under solvent-free conditions (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

With thioanisole as the model compound, the effects of reaction conditions on the sulfoxidation with other metal nitrates and various non-nitrates oxidants using Brönsted acidic ionic liquid ([*Hmim*]HSO_4) at 80°C have been investigated; the results are listed in Table I. The

TABLE I Sulfoxidation of Thioanisole Using Various Metal Nitrates and Oxidants in the Presence of Brönsted Acidic Ionic Liquid ([*Hmim*]HSO_4) at 80°C[a]

Entry	Metal nitrate	Yield (%)	Time (min)
1	$NaNO_3$	70	240
2	NH_4NO_3	10	105
8	$Ca(OCl)_2$	Trace	60
9	KIO_4	0	60
10	$KBrO_3$	5	60
11	$K_2S_2O_8$	40	45
12	CAN	94	5

[a] Reaction conditions: metal nitrates or oxidants (1 mmol), [*Hmim*]HSO_4 (2 mmol) and thioanisole (1 mmol) were mixed and stirred at 80°C.

results show that most of these metal nitrates are not effective oxidants for this transformation under the mentioned conditions, and ceric ammonium nitrate (CAN) is the best oxidant under these conditions.

The generality of the method was examined using alkyl aryl, dialkyl, diaryl, and cyclic sulfides, and also aryl disulfides. It was discovered that a wide variety of sulfides can be selectively oxidized by this inexpensive reagent under mild conditions (Table II). The rate of the reactions of arylalkyl and diaryl sulfides is not dependent on the substituents of the aromatic ring.

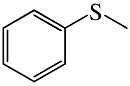
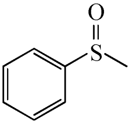
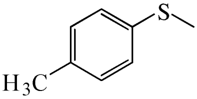
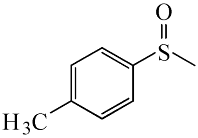
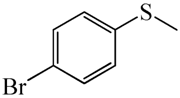
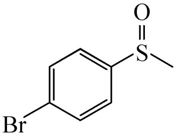
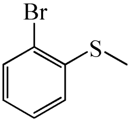
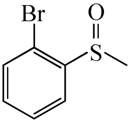
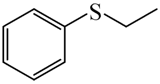
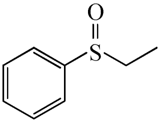
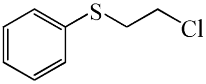
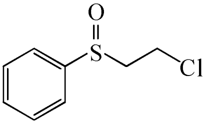
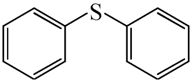
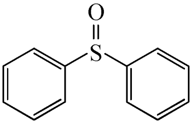
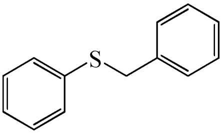
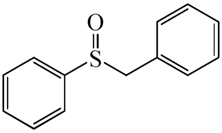
The oxidation of various sulfides gave the corresponding sulfoxides in high yields and short to moderate reaction times. The products were obtained by simple extraction with ethylacetate. By using this method, we did not observe any by-products such as over-oxidation to sulfon or nitration of aromatic rings.

In conclusion, we have introduced a straightforward and efficient method for selective oxidation of sulfides to their sulfoxides using ceric ammonium nitrate in the presence of Brönsted acidic ionic liquid ([*Hmim*]HSO_4^-) at 80°C. The use of non-toxic and inexpensive materials, stability of the oxidation system, simple method, short reaction times, good yields of the products, mild reaction conditions, and the straightforward method of the isolation of the product are the advantages of this method.

EXPERIMENTAL

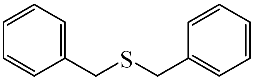
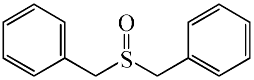
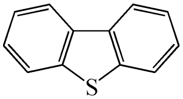
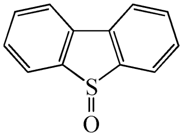
Products were characterized by comparison of authentic samples (IR, ^{1}HNMR spectrum, melting point, mixed melting point, and co-TLC

TABLE II Oxidation of Sulfide to Sulfoxide Using CAN/[*Hmim*]HSO_4 at 80°C[a,b]

Entry	Substrate	Product	Time (Min)	Yield (%)
1			5	94
2			7	94
3			10	93
4			10	89
5			3	93
6			6	92
7			10	92
8			8	88

(*Continued on next page*)

TABLE II Oxidation of Sulfide to Sulfoxide Using CAN/[*Hmim*]HSO_4 at 80°C[a,b] (*Continued*)

Entry	Substrate	Product	Time (Min)	Yield (%)
9			7	81
10			20	75

[a] The yields refer to the isolated products after purification.

analysis) with those obtained by literature methods[15] or alternative methods of synthesis. All melting points were taken on a Gallenkamp melting apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian 250 NMR Spectrometer operating at 250 MHz. The spectra were measured in CCl_4 and $CDCl_3$ relative to TMS (0.00 ppm). GC analysis was run with Shimadzu GC-14A. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. Spectra of solids were performed using KBr pellets. [Hmim]HSO_4 was prepared according to a previously reported method.[28]

General Procedure for the Sulfoxidation of Thioanisole Using Various Metal Nitrates or Oxidants/[Hmim]HSO_4

In a round-bottomed flask, thioanisole (1 mmol), metal nitrates or oxidants (1 mmol), and methylimidazolium hydrogensulfate [*Hmim*]HSO_4(2 mmol) were mixed. The reaction mixture was warmed to 80°C in an oil bath and stirred for the time specified in (Table I). The reaction progress was followed by TLC (EtOAc–cyclohexane, 20:80), and the product was extracted with ethylacetate (2 × 5 mL) and washed with water. The ethylacetate mixture was dried with magnesium sulfate. The solvent was evaporated under reduced pressure to give the corresponding products. Purification of the residue using flash column chromatography (silica gel, EtOAc–cyclohexane, 20:80) provided the pure methyl phenyl sulfoxide.

General Procedure for the Oxidation of Sulfide Using CAN/[Hmim]HSO_4

Sulfide (1 mmol), ceric ammonium nitrate (1 mmol), and methylimidazolium hydrogensulfate [*Hmim*]HSO_4(2 mmol) were added to a round-bottomed flask. The reaction mixture was placed in an oil bath at 80°C and stirred for the time specified in Table II. The reaction was followed by TLC (EtOAc–cyclohexane, 20:80). After completion of the reaction, the product was extracted with ethylacetate (2 × 5 mL) and washed with water. The ethylacetate mixture was dried with magnesium sulfate. The solvent was evaporated under reduced pressure to give the corresponding products. Purification of the residue using flash column chromatography (silica gel, EtOAc–cyclohexane, 20:80) provided the pure sulfoxide.

Methyl Phenyl Sulfoxide (1)

^{1}H NMR ($CDCl_3$), δ ppm 2.72 (s, 3H), 7.50–7.55 (m, 3H), 7.64–7.68 (m, 2H). IR (KBr) 3055, 2996, 2911, 1476, 1443, 1089, 1048, 956, 750 cm^{-1}.

4-Bromophenyl Methyl Sulfoxide (3)

^{1}H NMR ($CDCl_3$), δ ppm 2.70 (s, 3H). 7.52 (d, $J = 9$ Hz, 2H), 7.65 (d, $J = 9$ Hz, 2H). IR (KBr) 3010, 2989, 2910, 1420, 1384, 1042, 1005, 816 cm^{-1}.

Ethyl Phenyl Sulfoxide (5)

^{1}H NMR ($CDCl_3$), δ ppm 1.25 (t, $J = 8.0$ Hz, 3H), 2.09–3.18 (q, $J = 8.0$ Hz, 2H), 7.55–7.7 (m, 3H), 7.9–7.95 (m, 2H). IR (KBr) 3107, 3056, 2978, 2934, 1478, 1443, 1086, 1044, 749 cm^{-1}.

Diphenyl Sulfoxide (7)

^{1}H NMR ($CDCl_3$), δ ppm 7.2–7.35 (m, 6H), 7.45–7.55 (m, 4H). IR (KBr): 3047, 1475, 1440, 1087, 1036, 736 cm^{-1}.

REFERENCES

[1] T. Welton, *Chem. Rev.,* **99,** 2071 (1999).

[2] R. Sheldon, *Chem. Commun*., 2399, (2001).

[3] J. D. Holbrey and K. R. Seddon, *Clean Prod. Process.,* **1,** 223 (1999).

[4] A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, and J. H. Davis Jr., *J. Am. Chem. Soc.,* **124,** 5962 (2002).

[5] D. W. Morrison, D. C. Forbes, and J. H. Davis Jr., *Tetrahedron Lett.,* **42,** 6053 (2001).

[6] J. Kwan and M.-J. Kim, *J. Org. Chem.,* **67,** 6845 (2002).

[7] T.-S. Li, Z.-H. Zhang, F. Yang, and C.-G. Fu, *J. Chem. Res.,* **1,** 38 (1998).

[8] (a) J. S. Wilkes, *J. Mo1. Catal. A*: *Chem*., **214,** 11 (2004); (b) D. Fang, X. L. Zhou, Z. W. Ye, and Z. L. Liu, *Ind. Eng. Chem. Res.,* **45,** 7982 (2006).

[9] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J. P. Bazureau, and J. Hamelin, *Catal. Commun.,* **3,** 185 (2002).

[10] M. K. Potdar, S. S. Mohile, and M. M. Salunkhe, *Tetrahedron Lett.,* **42,** 9285 (2001).

[11] V. Singh, S. Kaur, V. Sapehiyia, J. Singh, and G. L. Kad, *Catal. Commun.,* **6,** 57 (2005).

[12] A. R. Hajipour, L. Khazdooz, and A. E. Ruoho,*Catal. Commun.,* **9,** 89 (2008).

[13] (a) G. H. Posner, M. Weitzberg, T. G. Hamill, E. Asirvatham, H. Cun-Heng, and J. Clardy, *Tetrahedron,* **42,** 2919 (1986); (b) M. Zahouily, M. Journet, and M. Malacria, *Synlett,* 366 (1994); (c) S. G. Pyne and A. R. Hajipour, *Tetrahedron,* **48,** 9385 (1992); (d) J. M. Khurana, A. K. Pand, and A. Gogia, *Org. Prep. Proc. Int.,* **28,** 234 (1996); (e) A. R. Hajipour, *Synthetic Comm*., **26,** 3627 (1996).

[14] M. Tajbakhsh, R. Hosseinzadeh, and A. Shakoori, *Tetrahedron Lett*., **45,** 1889 (2004).

[15] S. E. Martin and L. I. Rossi, *Tetrahedron Lett*., **42,** 7147 (2001).

[16] Y. J. Chen and Y. P. Huang, *Tetrahedron Lett.,* **41,** 5233 (2000).

[17] Y. J. Chen and J. Y. Shen, *Tetrahedron Lett*., **46,** 4205 (2005).

[18] X. T. Zhou, H. B. Ji, Z. Cheng, J. C. Xu, L. X. Pei, and L. F. Wang, *Bioorg. Med. Chem. Lett.,* **17,** 4650 (2007).

[19] K. Surendra, N. S. Krishnaveni, V. P. Kumar, R. Sridhar, and K. R. Rao, *Tetrahedron Lett.,* **46,** 4581 (2005).

[20] A. O. Beaudenon and S. Quideau, *Tetrahedron Lett*., **47,** 5869 (2006).

[21] Y. Peng, X. Feng, X. Cui, Y.Jiang, M. C. K. Choi, and A. S. C. Chan, *Synthetic Comm.,* **33,** 2793 (2003).

[22] A. Shaabani, A. Bazgir, K. Soleimani, and P. Salehi, *Synthetic Comm.,* **33,** 2935 (2003).

[23] A. R. Hajipour, B. Kooshki, and A. E. Ruoho, *Tetrahedron Lett.,* **46,** 5503 (2005).

[24] A. R. Hajipour, H. Bagheri, and A. E.Ruoho, *Phosphorus, Sulfur, and Silicon,* **178,** 2441 (2003).

[25] A. R. Hajipour and A. E. Ruoho, *Phosphorus Sulfur, and Silicon,* **26,** 83 (2003).

[26] A. R. Hajipour, S. Mallakpour, and H. Adibi, *Sulfur Letters,* **25,** 155 (2002).

[27] A. R. Hajipour and N. Mahboubghah, *Indian J. Chem. B,* **37,** 1041 (1998).

[28] A. R. Hajipour, F. Rafiee, and A. E. Ruoho, *Synlett,* 1118 (2007).