The highly selective metal-free oxidation of sulfides, tellurides and phosphines using sodium bromate in the presence of recyclable ionic liquid [bmim]HSO₄, at 80 °C

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The metal-free oxidation of sulfides to sulfones using sodium bromate (NaBrO₃) in [bmim]HSO₄:H₂O (3:1, v/v) at 80 °C is reported. Phenylalkyl, phenylbenzyl, diaryl and heteroaryl sulfides were transformed to the corresponding sulfones. Aryl tellurides and phosphines were oxidised to the corresponding telluroxides and phosphine oxides. All the reactions proceeded smoothly and gave high yields in 20–55 min. The ionic liquid [bmim]HSO₄ was easily recovered and recycled.

Keywords: oxidation, sodium bromate, [bmim]HSO₄, sulfones, telluroxides and phosphine oxides

Sulfones are used extensively for the preparation of a variety of fine chemicals or speciality chemicals. Sulfones are useful reagents in organic synthesis, particularly in asymmetric organocatalysis¹ and are also important building blocks for the synthesis of various biologically active molecules (Fig. 1).²

Therefore, the synthesis of functionalised sulfones is of considerable interest. A variety of oxidising agents have been used for the synthesis of sulfones. Transition metal-based catalysts such as Si-V10-2(silica-vanadia),³ MeO₃Re,⁴ Mn(III)Schiff-base,⁵ Ti(O₁Pr)₄.⁶ [$(n-C_4H_9)_4N$]₄(α -Mo₈O₂₆)⁷ and SiO₂-W₂-imidazole⁸ have been used for the preparation of sulfones in organic solvents. Other oxidising agents include polyvalent iodine,⁹ oxone,¹⁰ ozone,¹¹ aqueous NaOCl,¹² oxygen,¹³ NaIO₄¹⁴ and IBX.¹⁵ However, some of these are expensive, require excessive use of oxidants and are difficult to prepare.

Sodium bromate is an inexpensive important oxy-halo oxidant which has proved to be a versatile reagent in effecting a variety of oxidation reactions,¹⁶ and for the oxidative cleavage of alkyl and trimethylsilyl ethers and ethylene acetals to the corresponding carbonyl compounds.^{17,18} Imidazolium cation based ionic liquids have received considerable attention in recent years¹⁹ because of their unique physical and chemical properties such as thermal stability, recyclability and ability to dissolve a large range of organic and inorganic compounds.²⁰

In continuation of our interest in exploring oxidation reactions in ionic liquids,²¹ we decided to explore the oxidation of sulfides, selenides, tellurides and phosphines with sodium bromate in the Brønsted acidic ionic liquid [bmim]HSO₄ under appropriate conditions.

Result and discussion

In this paper, we report the successful oxidation of sulfides to the corresponding sulfones, tellurides to telluroxides and phosphines to phosphine oxides using a 1:3 molar ratio of substrate:sodium bromate in the presence of the ionic liquid [bmim]HSO₄:H₂O (3:1, v/v) at 80 °C.

The optimum reaction conditions were identified by examining reactions using diphenyl sulfide (1a) as a model



Used as fungicide

Analogue of thrombocytopenia inhibitor

Fig. 1 Sufones are important building blocks in the synthesis of various biologically active molecules.

substrate. Reactions were studied by varying the molar ratio of substrate to oxidant (NaBrO₃) and also using water as a co-solvent. Initially, a reaction of diphenyl sulfide (**1a**) was examined with sodium bromate: **1a** using 1:1 molar ratio in the presence of ionic liquid [bmim]HSO₄ at room temperature. There was no reaction even after 3 h, as revealed by TLC (petroleum ether:ethyl acetate, 85:15, v/v). The starting material was isolated (Table 1, entry 1). The same reaction was then attempted at 80 °C under otherwise identical conditions. The reaction was incomplete after 2 h but yielded 43% of **2a** after separation by column chromatography (Table 1, entry 2).

The same reaction, was carried out using a 1:2 molar ratio of substrate (1a):NaBrO₃ in presence of [bmim]HSO₄ at 80 °C, yielded 63% of 2a in 90 min (Table 1, entry 3). The same reaction was then carried out using 1:3 molar ratio of 1a:NaBrO, in the presence of [bmim]HSO₄ at 80 °C and yielded 71% of 2a in 90 min (Table 1, entry 4). The best yield of 2a corresponding to 89% was obtained when the reaction was attempted using 1:3 ratio of substrate (1a):NaBrO₃ in [bmim]HSO:H₂O (3:1, v/v) at 80 °C. The reaction was complete in 30 min as revealed by TLC using petroleum ether:ethyl acetate (85:15, v/v) (Table 1, entry 5). The addition of water as co-solvent appeared to enhance the rate of reaction. While reactions carried out at a higher temperature (entry 6) did not affect the yield, reactions carried out using a higher amount of water as solvent, reduced the yields (entries 7-8). It can be concluded that 1:3 molar ratio of substrate (1a):NaBrO₂ in [bmim]HSO₄:H₂O (3:1 mL, v/v) at 80 °C is the optimum condition for the oxidation of sulfides to sulfones. The generality of the procedure was examined for a variety of sulfides containing aromatic and aliphatic groups under the optimum reaction conditions. All the reactions

Table 1 Optimisation for the oxidation of diphenylsulfide (1a) with sodium bromate (NaBrO₃) in [bmim]HSO₄ under different conditions

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Entry	Substrate: Oxidant	IL:H ₂ 0	Temperature/ °C	Time/ min	Yield/ %
1	1:1	[bmim]HS0 ₄ :H ₂ 0 (4:0)	r.t.	180	_ a
2	1:1	[bmim]HS0 ₄ :H ₂ 0 (4:0)	80	120	43
3	1:2	[bmim]HS0 ₄ :H ₂ 0 (4:0)	80	90	63
4	1:3	[bmim]HS0 ₄ :H ₂ 0 (4:0)	80	90	71
5	1:3	[bmim]HS0 ₄ :H ₂ 0 (3:1)	80	30	89
6	1:3	[bmim]HS0 ₄ :H ₂ 0 (3:1)	100	30	90
7	1:3	[bmim]HS0 ₄ :H ₂ 0 (1:1)	80	50	82
8	1:3	[bmim]HS0,:H,0 (1:3)	80	90	75

^aNo reaction

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1a–l

Scheme 1 Oxidation of sulfides to sulfones.

Table 2 Reaction of sulfides with sodium bromate (1:3 ratio) in [bmim]HSO	,:H,O (3:1, v/v) at 80 °C
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S No	Reactant		Product (2) ^b	Time/min	Viold/0%a
5. NU	R	R'		11116/11111	
1	C ₆ H ₅	C ₆ H ₅	Diphenyl sulfone	30	89
2	4-CIC ₆ H ₄	4-CIC ₆ H ₄	Di(4-chlorophenyl) sulfone	30	92
3	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	Dibenzyl sulfone	35	82
4	4-CIC ₆ H ₄	C ₆ H ₅	4-Chlorophenyl phenyl sulfone	20	84
5	4-BrC ₆ H ₄	C ₆ H ₅	4-Bromophenyl phenyl sulfone	30	88
6	4-(H ₃ C)C ₆ H ₄	C_6H_5	4-Methylphenyl phenyl sulfone	25	90
7	C ₆ H ₅ CH ₂	C_6H_5	Benzyl phenyl sulfone	30	87
8	C_6H_5	<i>n</i> -C ₃ H ₇	Phenyl <i>n</i> -propyl sulfone	20	91
9	<i>n</i> -C ₅ H ₂₅	C_6H_5	n-Dodecyl phenyl sulfone	35	89
10	3-Bromothiophene		3-Bromothiophene-1,1-dioxide	30	83
11	2H-Benzo[e][1,2]thiazin-3	(4 <i>H</i>)-one	2H-1,4-Benzothiazine-3(4H)-one, 1,1-dioxide	55	85
12	9 <i>H</i> -Thioxanthene		9H-Thioxanthene-9-one-10,10-dioxide	45	92

^a% of yield.

^bLiterature melting points and reported melting points are given in the ESI file.

proceeded smoothly and gave the corresponding sulfones in high yields. The results are summarised in Scheme 1, (Table 2, entries 1–12). Both cyclic and acyclic sulfides gave sulfones in high yield.

The oxidation of diphenyl selenide was attempted under a variety of conditions by changing the molar ratio of substrate to NaBrO₃, the ratio of the ionic liquid:H₂O and the temperature. However, all the reactions resulted into mixtures and did not give either diphenyl selenoxide or diphenyl selenone in high yields. Interestingly, we observed that diaryl tellurides gave the corresponding telluroxides, using 1:3 ratio of substrate:NaBrO₃ and 3:1 ratio of [bmim]HSO₄:H₂O at 80 °C (Eqn 1). Triaryl and trialkyl phosphines also underwent oxidation under these conditions to give the corresponding phosphine oxides (Eqn 2). All the products were characterised by IR, NMR and by comparison of their melting points with the literature data. These results are listed in Table 3 and in the ESI.

The recyclability of $[bmim]HSO_4$ was investigated in the reaction of diphenyl sulfide with sodium bromate under the same experimental conditions. The aqueous medium along with $[bmim]HSO_4$ obtained after separation of the product was reused again. Comparable yields of the product were obtained even after reusing the recovered medium for three times as shown in Fig. 2.

Experimental

The products were identified by m.p. and mixed m.p. (wherever applicable) on Buchi melting point apparatus M-560, IR and NMR spectra (see ESI). IR spectra were recorded in chloroform on Table 3 Oxidation of tellurides and phosphines with sodium bromate (1:3 molar ratio) in [bmim]HSO_4:H_2O (3:1, v/v) at 80 $^\circ C$

$$\begin{array}{ccc} Ar - Te - Ar' & \underline{NaBrO_3, 80 \ ^\circ C} & Ar - \underline{Te} - Ar' \\ 3a - d & [bmim]HSO_4:H_2O & 4a - d \end{array}$$
(1)

$$\begin{array}{ccc} R_{3}P & \xrightarrow{\text{NaBrO}_{3}, \ 80 \ ^{\circ}\text{C}} & R_{3}P=0 \\ \textbf{5a-c} & \text{[bmim]HSO}_{4}:H_{2}O & \textbf{6a-c} \end{array}$$
(2)

R = Aryl, Alkyl

S. No	Reactant	Product (4, 6) ^b	Time/min	Yield/% ^a
13	(C ₆ H ₅) ₂ Te	$(C_{6}H_{5})_{2}$ Te=0	30	85
14	[3-(CH ₃ 0)C ₆ H ₄] ₂ Te	[3-(CH ₃ 0)C ₆ H ₄] ₂ Te=0	55	79
15	[4-(CH ₃ 0)C ₆ H ₄] ₂ Te	$[4-(CH_{3}0)C_{6}H_{4}]_{2}$ Te=0	35	89
16	[4-(H ₃ C)C ₆ H ₄] ₂ Te	$[4-(H_{3}C)C_{6}H_{4}]_{2}$ Te=0	30	92
17	(C ₆ H ₅) ₃ P	$(C_6H_5)_3P=0$	25	95
18	$(C_{6}H_{11})_{3}P$	$(C_6H_{11})_3P=0$	25	82
19	(<i>n</i> -C ₄ H ₉) ₃ P	$(n-C_4H_9)_3P=0$	30	85

^a% of yield.

^bLiterature melting points and reported melting points are given in the ESI file.

PerkinElmer FTIR Spectrum-2000. ¹H NMR spectra were recorded on a Hitachi FT-NMR model R-600 (60 MHz) with CDCl₃ or DMSO as solvent and TMS as internal standard. All phosphine compounds were purchased from Spectrochem and Sigma Aldrich and used as such. The ionic liquid was prepared by reported procedure.²² All the sulfides²³ and tellurides²⁴ were prepared by the reported literature.



Fig. 2 Recyclability of ionic liquid [bmim]HSO,.

Oxidation of sulfides, tellurides and phosphines; general procedure

A mixture of sodium bromate (3.12 mmol), and substrate 1 or 3 or 5 (1.04 mmol) in 4 mL of [bmim]HSO₄:H₂O (3:1, v/v) was placed in a 50 mL round-bottomed flask mounted over a magnetic stirrer and fitted with an air condenser. The contents were heated in an oil-bath maintained at 80 °C for the time specified in Table 2 and 3. The progress of the reaction was monitored by TLC using ethyl acetate:petroleum ether (50:50, v/v) as eluent. After completion of the reaction, the contents were allowed to cool to room temperature. A saturated solution of sodium thiosulfate (~5 mL) was added into the reaction mixture in order to remove excess unreacted bromine. The mixture was poured into a beaker containing ice cold water (~30 mL) and stirred well. The solid product was filtered under suction pump and recrystallised. The products were characterised by its m.p., IR and NMR spectra.

Conclusion

In conclusion, we have developed a metal-free oxidation of sulfides to sulfones using sodium bromate (NaBrO₃) in [bmim] HSO_4 :H₂O (3:1, v/v) at 80 °C. Structurally diverse phenyl alkyl, phenyl benzyl, diaryl, and heteroaryl sulfides were transformed to corresponding sulfones. Tellurides and phosphines are oxidised to corresponding telluroxides and phosphine oxides. All the reactions proceeded smoothly and gave high yields in 20–55 min.

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Electronic Supplementary Information

Melting points and spectral data are available through: stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

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