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Graphical Abstract

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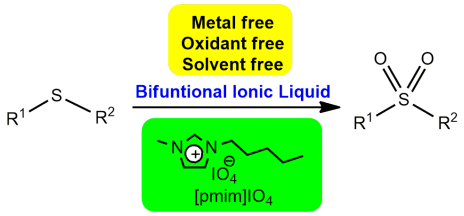

Metal and solvent free selective oxidation of sulfides to sulfone using bifunctional ionic liquid [pmim]IO_4

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ABSTRACT: The oxidation of organo-sulfides to sulfones has been accomplished using an easily accessible bifunctional ionic liquid, [pmim]IO_4 in the absence of any other oxidants, metal and organic solvent at ambient temperature. A variety of sulfides including dialkyl, aryl-alkyl, diaryl, aryl-hetero aryl have been oxidized to the corresponding functionalized sulfones in high yields by this procedure.

Keywords*: Ionic liquid, Suifide, Sulfone, organic solvent free,oxidation*

The selective oxidation of sulfide to sulfone has considerable significance in biology and pharmaceutical industry.[1] The derivatives of heteroaryl sulfones constitute core units of many potent molecules which were used as drugs and potential precursors (Figure 1).[2] Sulfones are very useful reagents in organic synthesis particularly in asymmetric organocatalysis.[3] In addition, polymeric sulfones are attractive functional materials having excellent thermal stability and good electrical properties.[4] Moreover, oxidative desulfurization processes for obtaining ultra low sulfur fuels involve oxidation of sulfides to sulfones.[5]

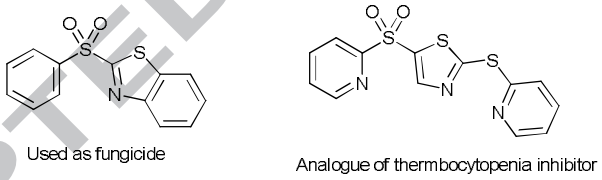
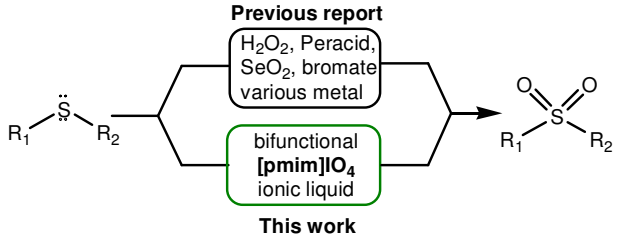


Figure 1. Biologically active sulfone and its analogue

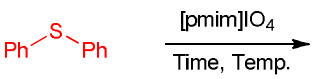
Oxidation of organo-sulfur compound also finds application in the removal of sulfur-containing pollutants during air and waste water treatment.[6] Thus, synthesis of functionalized sulfones is of considerable interest. A variety of oxidizing agents have been used for the oxidation of sulfides to sulfones. H_2O_2 in combination with various metal salts has been widely used.[7] Some of the other oxidizing agents include polyvalent iodine,[8] oxone,[9] ozone,[10] aqueous NaOCl,[11] oxygen,[12] $NaIO_4$[13] and others.[14] The oxidations were carried out in different organic solvents, supercritical carbon dioxide[15] and ionic liquid.[16] Ionic liquids have received much attention due to their negligible volatility, and other advantageous properties.[17] We report here a novel approach using a bifunctional ionic liquid [pmim]IO_4[18] for the selective oxidation of organosulfides to sulfones in neat in absence of any solvent, metal and co-oxidant (Scheme 1).



Scheme 1. Oxidation of sulfide using oxidative ionic liquid

To standardize the reaction conditions a series of experiments were performed with the variation of amount of IL, reaction temperature and time for a representative oxidation of diphenyl sulfide using [pmim]IO_4. The reaction produced either sulphoxide or a mixture of sulphoxide and sulfone at varying amounts (Table 1, entries 1-4). Best result leading to

Table 1. Optimization of reaction conditions



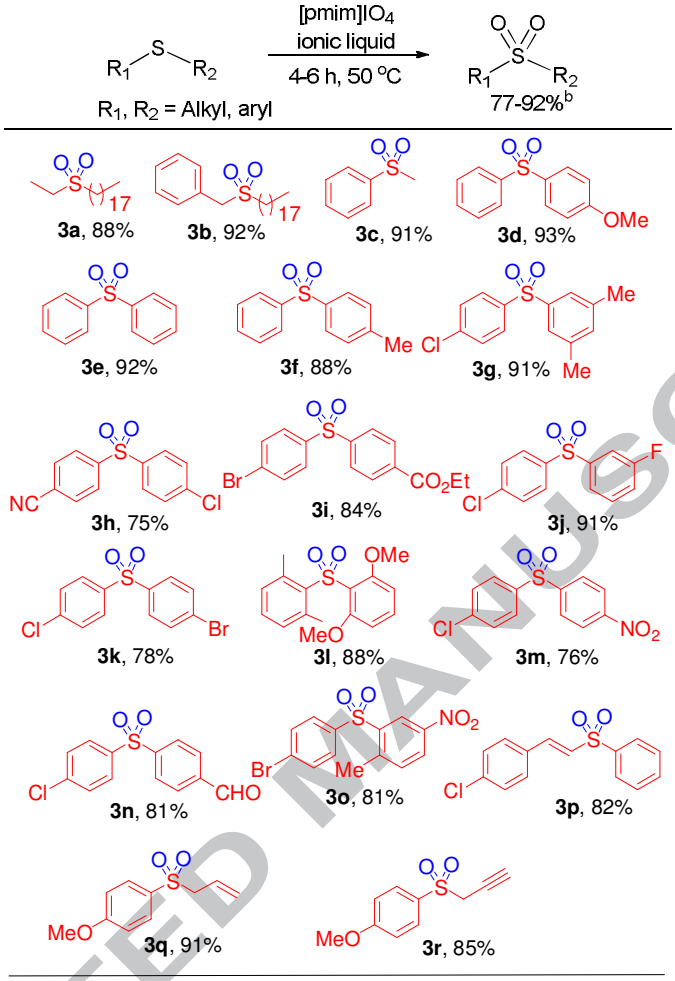
Entry	IL (equiv.)	Temp.(^{o}C)	Time (h)	Yield (%)[a]
1	2	rt	4	18
2	3	rt	4	23
3	3	rt	6	28
4	4	rt	6	56
5	4	50	5	81
6	4	50	4	92
7	5	rt	4	52
8	5	50	5	
9	5	50	4	88
10		80	8	25[b]
11		80	8	11[c]

[a]Yields refer to those of purified products characterized by IR and ^{1}H and ^{13}C NMR spectroscopic data.[b]$NaIO_4$ (3 equiv.) as additive and H_2O as a solvent used.[c] $NaIO_4$ (3 equiv.) as an additive and DMF as a solvent used.

selective oxidation to sulfone was achieved using 4 equivalents of ionic liquid at 50 ^{o}C for 4 h (Table 1, entry 6). When we carried out a blank reaction in water and DMF separately using $NaIO_4$ as an oxidizing agent in absence of IL, the reaction did not go well even after prolonged heating (80 ^{o}C, 8 h) (Table 1, entries 10 and 11). Thus it is likely that ionic liquid has an effect on the activation of IO_4^- ion in the oxidation of sulfide.

A series of diversely substituted sulfides were subjected to oxidation by the standardized reaction conditions. The results are summarized in Table 2. Both aliphatic and aromatic sulfides were efficiently converted into their respective sulfones with excellent chemoselectivity although aliphatic sulfides took longer time than aromatic ones. Several functional groups and moieties such as -Me, -OMe, -Br, -Cl, -F, - COMe, -NO_2, -CN, double bond, triple bond were compatible with this procedure. Even, an easily oxidizable –CHO group survives under these reaction conditions using [pmim]IO_4 (Table 2, **3n**). It is noteworthy that the aryl sulfides substituted with electron-donating groups gave higher yields compared to those bearing electron-withdrawing substituents. The hindered (2,6-dimethoxyphenyl)(2,6-dimethylphenyl)sulfane (Table 2, **3l**) underwent facile oxidation with [pmim]IO_4 to produce corresponding sulfone without any difficulty. Several

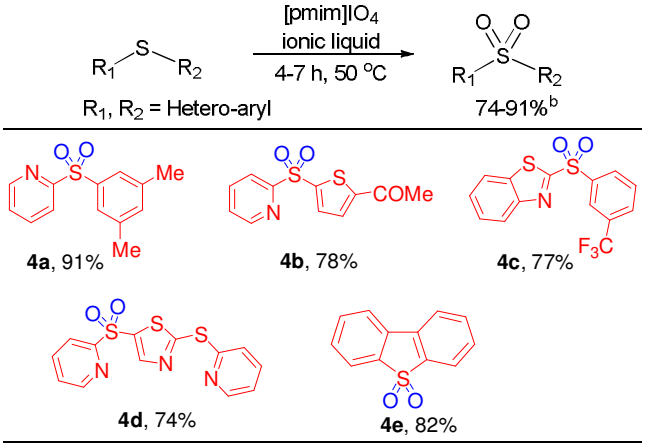
Table 2. Oxidation of sulfides to sulfone using [pmim]IO_4 ionic liquid[a]



[a]Reaction condition: diphenyl sulphide (1 mmol), [pmim]IO_4 ionic liquid (4 equiv.).

[b] Yields refer to those of purified products characterized by IR and ^{1}H and ^{13}C NMR spectroscopic data

Table 3. Synthesis of heterocyclic sulfone[a]

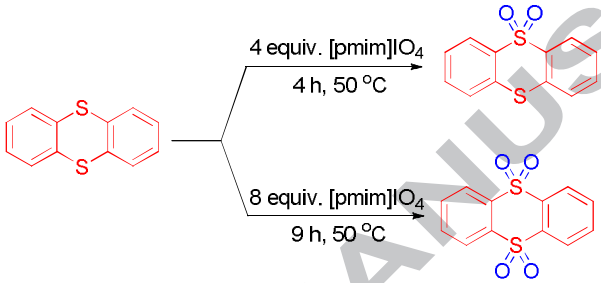


[a]Reaction condition: diphenyl sulphide (1 mmol), [pmim]IO_4 ionic liquid (4 equiv.).

[b] Yields refer to those of purified products characterized by IR and ^{1}H and ^{13}C NMR spectroscopic data.

unsymmetrical heteroaryl-heteroaryl sulfides containing thiophenyl, pyridinyl, thiazolyl, benzothiazolyl, dibenzothiophenyl moieties underwent oxidation to produce the corresponding sulfones (Table 3). Thus, this procedure is efficient enough for the oxidation of heteroaryl sulfides, which was not addressed earlier. The reduction is uniform with *o*-, *m*-, *p*- substituted aryl sulfides. We also investigated the oxidation of a disulfide, thianthrene (Scheme 2). We observed that use of 4 equiv. of ionic liquid led to the oxidation of one sulfide moiety keeping another unchanged. However use of excess ionic liquid (8 equiv.) makes both sulfide moieties to disulfone.

We assume that the oxidation is mediated by the IO_4 counter ion of the ionic liquid following the standard reaction path way.[19]



Scheme 2. Mono and di-oxidation of thianthrene.

A highly chemo-selective and efficient method for the oxidation of sulfides to the corresponding sulfones using an oxidizing [pmim]IO_4 ionic liquid in absence of any solvent, catalyst or external oxidising agent has been developed.[20] The simplicity in operation, general applicability, mild conditions and wide substrate scope make this procedure more attractive. We believe, this will find useful applications in organic synthesis.

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20. *Representative experimental procedure for the oxidation of diphenylsulfide to the corresponding sulfone (Table 2,* ***3e****):* A mixture of diphenyl sulphide (1 mmol) and [pmim]IO_4 ionic liquid[18] (prepared by the reaction of [pmim]BF_4 and $NaIO_4$) (4 equiv.) was vigorously stirred under air at 50 ^oC for 4 hours (TLC). The reaction mixture was extracted with ethyl acetate (3 X 7 cm^3) and the extract was washed with brine and dried over Na_2SO_4. Evaporation of organic solvent left the crude product which was recrystalised from ethanol to provide the corresponding sulfone as a white solid , mp 123 ^oC; IR (KBr) ν_{max}= 3080, 3066, 2781, 2459, 2330, 1969, 1898, 1770, 1579, 1475, 1448, 1309, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.5 Hz, 4H), 7.56 (t, *J* = 7 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.8 (4C), 129.4 (4C), 133.3 (2C), 141.8 (2C).

    This procedure was followed for all the reactions listed in Table 2 and Table 3. Although this procedure was described with a 1 mmol scale, 10 mmol scale reactions also provided uniform results. All of these products listed in Table 2 are known except five (Table 2, **3b**, **3g**, **3j**, **3l** and **3o**). The all heterocyclic sulfones in Table 3 are new except one (Table 3, **4e**). These known compounds were identified by comparison of their spectral data (^1H NMR and ^{13}C NMR) with those reported (**3a**,[21a] **3c**,[21b] **3d**,[21b] **3e**,[21c] **3f**,[21c] **3h**,[21d] **3i**,[21e] **3k**,[21f] **3m**,[21g] **3n**,[21f] **3p**,[21i] **3q**,[21j] **3r**,[21j] **4e**,[21b]). The new compounds were properly characterized by their IR, ^1H NMR, ^{13}C NMR, and HRMS spectroscopic data which were provided below.

    ((Octadecylsulfonyl)methyl)benzene (Table 2, 3b). Colourless liquid; IR (neat) ν_{max}= 2966, 2914, 1921, 1871, 1344, 1275, 1193 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.5 Hz, 3H), 1.25-1.29 (m, 25 H), 1.34-1.37 (m, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 4.21 (s, 2H), 7.40 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 21.9 (2C), 22.8, 29.2 (2C), 29.4 (2C), 29.5 (2C), 29.6 (2C), 29.7, 29.8, 32.1,

51.3, 59.6, 128.4, 129.1 (2C), 129.2 (2C), 130.7 (2C); Anal Calcd for $C_{25}H_{44}O_2S$: C, 73.47; H 10.85; Found: C, 73.44; H 11.01%.

1-(4-Chlorophenylsulfonyl)-3,5-dimethylbenzene (Table 2, 3g). White solid; mp 137-139 ^oC; IR (KBr) ν_{max}= 3084, 2955, 2916, 1908, 1764, 1607, 1578, 1472, 1391, 1321, 1151, 1084 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.26 (s, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 2H), 7.94 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4 (2C), 125.3 (2C), 129.2 (2C), 129.7 (2C), 135.3 (2C), 139.6, 139.8, 140.6, 141.0; Anal Calcd for $C_{14}H_{13}ClO_2S$: C, 59.89; H 4.67; Found: C, 60.02; H 4.51%.

1-(4-Chlorophenylsulfonyl)-3-fluorobenzene (Table 2, 3j). White solid; mp 128-131 ^oC; IR (KBr) ν_{max}= 2966, 2938, 2846, 1581, 1463, 1417, 1329, 1291cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.30 (m, 1H), 7.48-7.53 (m, 3H), 7.62-7.64 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.15 (d, *J* = 23.7 Hz, 1C), 118.6 (d, *J* =21.2 Hz, 1C), 123.6 (d, *J* = 3.7 Hz, 1C), 129.4 (2C), 129.9 (2C), 131.4 (d, *J* = 8.7 Hz, 1C), 139.6, 140.5, 143.5, 162.3 (d, *J* = 251.2 Hz, 1C); HRMS Calcd for $C_{12}H_8ClFO_2S$ $[M+H]^+$: 270.9996; Found: 270.9989.

2-(2,6-Dimethylphenylsulfonyl)-1,3-dimethoxybenzene (Table 2, 3l). White solid; mp 153-155 ^oC; IR (KBr) ν_{max}= 2972, 2941, 2837, 1584, 1474, 1429, 1310, 1254, 1155, 1107, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 6H), 3.69 (s, 6H), 6.55 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7 (2C), 56.4 (2C), 105.3 (2C), 130.7 (2C), 131.3 (2C), 134.5 (2C), 139.1 (2C), 159.4 (2C); HRMS Calcd for $C_{16}H_{18}O_4S$ $[M+Na]^+$: 329.0823; Found: 329.0821.

2-(4-Bromophenylsulfonyl)-1-methyl-3-nitrobenzene (Table 2, 3o). White solid; mp 190-192 ^oC; IR (KBr) ν_{max}= 3091, 2951, 2879, 1933, 1568, 1535, 1475, 1389, 1358, 1313, 1153, 1066, 887 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.56 (s, 3H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.68-7.71 (m, 3H), 7.83 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 125.4, 129.2, 130.0 (2C), 132.1 (2C), 132.5 (2C), 134.4, 135.1, 140.0, 144.5; HRMS Calcd for $C_{13}H_{10}BrNO_4S$ $[M+H]^+$: 355.9592; Found: 355.9581.

2-(3,5-Dimethylphenylsulfonyl)pyridine (Table 3, 4a). White solid; mp 143-147 ^oC; IR (KBr) ν_{max}= 3053, 2953, 1607, 1574, 1454, 1323, 1271, 1165, 1149, 1120, 987 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 6H), 7.20 (s, 1H), 7.26-7.46 (m, 1H), 7.66 (s, 2H), 7.90-7.93 (m, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.68 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3 (2C), 122.3, 126.5, 126.9, 135.7, 138.2, 138.8, 138.3, 139.4, 150.6 (2C), 158.3; HRMS Calcd for $C_{13}H_{13}NO_2S$ $[M+Na]^+$: 270.0565; Found: 270.0566.

1-(5-(Pyridin-3-ylsulfonyl)thiophen-2-yl)ethanone (Table 3, 4b). White solid; mp 149-150 ^oC; IR (KBr) ν_{max}= 2998, 1975, 1684, 1601, 1568, 1422, 1357, 1258, 1178 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.51-7.53 (m, 1H), 7.62 (d, *J* = 3.5 Hz, 1H), 7.83 (d, *J* = 4.5 Hz, 1H), 7.95-7.98 (m, 1H), 8.20 (d, *J* = 8 Hz, 1H), 8.71 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.1, 122.2, 127.6, 131.2, 135.1, 138.5, 146.2, 150.7, 151.6, 158.2, 190.4; HRMS Calcd for $C_{11}H_9NO_3S_2$ $[M+H]^+$: 268.0102; Found: 268.0098.

2-(3-(Trifluoromethyl)phenylsulfonyl)benzo[d]thiazole (Table 3, 4c). White solid; mp 135-136 ^oC; IR (KBr) ν_{max}= 2965, 2923, 2841, 1588, 1481, 1447, 1309, 1263, 1158, 1127cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 121.1, 122.5, 125.0, 126.5, 126.9, 127.0, 130.4, 131.4, 131.5, 131.8, 132.6, 135.9, 138.0, 153.8, 166.7; HRMS Calcd for $C_{12}H_8ClFO_2S$ $[M+H]^+$: 270.9996; Found: 270.9989.

2-(5-(Pyridin-2-ylsulfonyl)thiazol-2-ylthio)pyridine (Table 3, 4d). Light yellow solid; mp 128-131 ^oC; IR (KBr) ν_{max}= 2986, 2931, 2852, 1571, 1484, 1441, 1319, 1272, 1164, 1097 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.18-7.24 (m, 1H), 7.25-7.26 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.48-7.50 (m, 1H), 7.68-7.71 (m, 1H), 7.92-7.99 (m, 1H), 8.18 (t, *J* = 8.5 Hz, 1H), 8.33 (s, 1H), 8.65(s, 1H), 8.71 (s, 1H); 13C NMR (125 MHz, $CDCl_3$) δ 121.7, 122.4, 123.5, 127.4, 134.8, 137.5, 138.5, 148.2, 149.3, 150.6, 152.3, 158.6, 170.7; HRMS calcd for $C_{13}H_9N_3O_2S_3$ $[M+Na]^+$: 357.9755; Found: 357.9751.

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Supplementary Material

Supplementary material (Scanned copies of ^{1}H and ^{13}C NMR spectral data) associated with this article can be found, in the online version, at http://