Res Chem Intermed
DOI 10.1007/s11164-017-3026-0

Catalyst-free oxidation of sulfides to sulfoxides and diethylamine-catalyzed oxidation of sulfides to sulfones using Oxone as an oxidant

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Received: 19 March 2017 / Accepted: 26 June 2017

Abstract We describe here our journey from the failure of our attempts in controlled oxidation of sulfides to sulfoxides using an Oxone®–KBr combination to our success in the development of a catalyst-free protocol for the oxidation of sulfides to sulfoxides using Oxone as an oxidant. We also describe the failure of our attempts at the oxidation of sulfides to sulfones using an excess of Oxone–KBr as well as Oxone, and our success towards the development of a rapid, scalable and chromatography-free protocol for the oxidation of sulfides to sulfones using diethylamine–Oxone as an unprecedented catalyst–oxidant combination.

Graphical Abstract

Catalyst-free oxidation of sulfides to sulfoxides and diethylamine catalyzed oxidation of sulfides to sulfones using Oxone as an oxidant: A journey from illogical failure to pursued success

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Electronic supplementary material The online version of this article (doi:10.1007/s11164-017-3026-0) contains supplementary material, which is available to authorized users.

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Published online: 07 July 2017

Keywords Oxone · Oxidation · Sulfoxides · Sulfones · Organocatalysis · Diethylamine

Introduction

Modern chemistry has been invariably linked with sustainable chemistry, and, in an over-polluted world, its implementation has become a practical need both from socio and economic points of view. Consequently, in recent years, the development of sustainable, atom-economical, operationally simple, scalable, and catalyst-free protocols for the synthesis of pivotal intermediates useful in chemistry as well as biology has become the focal point of research. However, when catalyst-free conditions are unable to offer the aforesaid benefits, exploration of a commercially available, inexpensive, environmentally benign and easy to handle catalyst in organic synthesis is the most practical and logical alternative. Sulfoxides and sulfones are two important classes of compounds which find wide applications as intermediates in chemistry as well as biology. Among these, sulfoxides serve as valuable synthons in C–C bond forming reactions, [1–4] Diels–Alder reactions, [5, 6] as chiral auxiliaries [7], and in medicinal chemistry as anti-ulcer, antihypertensive, cardiotonic agents, and CNS stimulants as well as vasodilators [8]. They are also known to play an important role in enzyme activation [9], while a few sulfoxides find application in the separation of radioactive and less common metals [10]. Similarly sulfoxides and sulfones are also known to play a prominent role in the field of organic synthesis, pharmaceuticals, and agrochemicals as well as polymers [11–15].

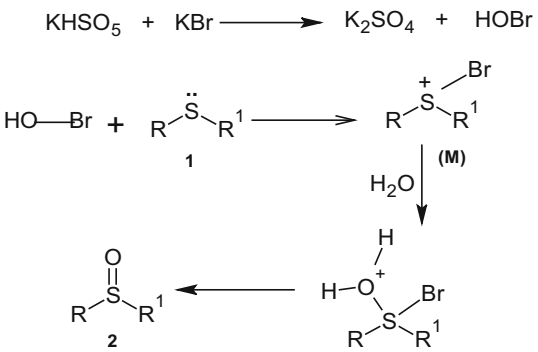
Controlled and chemoselective oxidation of sulfides is one of the rational pathways for the synthesis of sulfoxides and a great number of oxidizing agents, such as halogens [16, 17], N_2O_4/PVP [18], TEMPO-linked metalloporphirines [19], $NaIO_4$, [20] hypervalent iodine reagents [21–23], H_2O_2 [24–33], TBHP [34], Oxone® [35–38], etc., have been reported to effect the selective oxidation of sulfides to sulfoxides. Our interest in studies on the oxidation of sulfides stems from our earlier experiences in Oxone chemistry [39–42].

It is well known that Oxone is a stable 2:1:1 ternary composite of $KHSO_5$, K_2SO_4 and $KHSO_4$, and its use in various organic transformations is well documented [43]. We have reported earlier on the use of Oxone in oxidation of hydrazides to diacylhydrazines [39], and have also demonstrated that Oxone–KBr combination serves as an eco-safe source of bromonium ions. Thus, we exploited this oxidant–reagent combination in the bromination of activated arenes, in the oxidation of alkylcyanohydrazines to azo-*bis*-i*so*-butyronitriles, and in chemoselective deprotection of dithioacetals to carbonyls [40–42]. A literature survey within the framework of the use of Oxone and an Oxone–KBr combination in the oxidation of sulfides revealed that, Oxone supported on alumina or silica gel under the influence of thermal or MW activation [35, 36], has been reported to effect oxidation of sulfides to sulfoxides. However, the essentiality in the use of more than stoichiometric amounts of Oxone, inorganic supports and the necessity of

thermal/MW activation make these protocols less attractive in practice. Yu et al. have recently described a solvent-dependent protocol in the chemoselective oxidation of sulfides to sulfoxides using Oxone as an oxidant [37]. This protocol also suffers from the drawbacks of thermal activation (reflux in ethanol) and very long reaction times (12 h). Hajipour et al. [38], on the other hand, have reported an organic solvent-soluble derivative of Oxone, i.e., benzyltriphenylphosphonium peroxymonosulfate (BTPP), in selective oxidation of sulfides to sulfoxides. However, its very high molecular weight and consequently the cost of BTPP restricts the practical applicability of the developed protocol in the synthesis of sulfoxides. With this literature survey, with our experiences in Oxone chemistry, and with our aim to make chemistry simple and easily adaptable, we set out to develop an alternate pathway in the chemoselective oxidation of sulfides to sulfoxides using Oxone as an oxidant. In this regard, taking recourse to our earlier reported concept on the generation of Br^+ ions using the Oxone–KBr combination [40–42], we surmised that sulfur, as a soft nucleophile, Br^+ generated in situ using the Oxone–KBr combination would chemoselectively attack sulfur in thioether, **1**, to yield sulfenyl bromide, **M**, which on subsequent reaction with water would furnish the corresponding sulfoxide, **2** (Scheme 1).

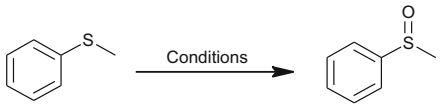
Results and discussion

To check the feasibility of the planned protocol, a model reaction was carried out using thioanisole, Oxone and potassium bromide as the substrates. Thus, to an equimolar solution of thioanisole, **1a**, and potassium bromide (1 mmol, each) in aqueous acetonitrile (3:1, 4 mL) was added dropwise an aqueous solution of Oxone (1 equiv., 6 mL). It was noticed that oxidation of thioanisole to the corresponding sulfoxide results in a very short time (10 min, TLC). However,the resulting sulfoxide continues to undergo overoxidation to furnish the corresponding sulfone as the major product (TLC, NMR) (Table 1, entry 1). In ordert to control the reaction at the sulfoxide stage, the same reaction was then carried out at 273 K.



Scheme 1 Planned oxidation of sulfides to sulfoxides using an Oxone–KBr combination

Table 1 Optimization of reaction conditions for the controlled oxidation of thioanisole, **1a**



No.	Oxone:KBr (euivq.)	Time (min)	Yield (%)[a]	
			Sulfoxide	Sulfone
1	1.0:1.0	10, 30, 90	70, 15, 15	30, 85, 85
2[b]	1.0:1.0	10, 30, 90	60, 20, 20	40, 80, 80
3	0.75:1.0	15	60	30
4	0.50:1.0	15	50	30
5	1.0:0.75	10, 30	60, 40	40, 60
6	1.0:0.5	10, 30	70, 50	30, 50
7	1.0:0.2	15, 30	90, 80	10, 20
8	1.0:-	15, 60	90, 70	10, 30
9	0.8:-	15, 60	92, 85	Traces, 15
10	0.7:-	10, 60	92, 90	Traces, 10

[a] Isolated yields

[b] At 0 °C

However; we did not observe any pronounced change in the behavior of the sulfoxide towards its overoxidation (Table 1, entry 2). These two interesting results prompted us to pursue this reaction further.

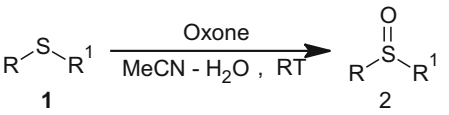
A set of experiments were then carried out using the same model substrate and different proportions of Oxone as well as potassium bromide. It was observed that, even with the decrease in the proportion of Oxone, the reaction furnished a mixture of sulfoxide and sulfone along with minor amounts of unreacted starting material (TLC) (Table 1, entries 3, 4). It was further observed that, with the decrease in the proportion of potassium bromide, oxidation of thioanisole to corresponding sulfoxide requires nearly the same time period (10–15 min). However, its overoxidation to sulfone needs a slightly longer time (Table 1, entries 5–7), and, in the absence of potassium bromide, oxidation of the initially formed sulfoxide takes an appreciably longer time (Table 1, entry 8). Further optimization of the reaction conditions was focused on the proportion of Oxone. Interestingly, using less than a stoichiometric amount of Oxone, conversion of sulfide to the corresponding sulfoxide proceeds smoothly in nearly the same time span (Table 1, entries 9, 10), and, happily enough, its overoxidation to sulfone requires a very long time. This particular aspect of the reaction allows executing the chemoselective oxidation of sulfide to the corresponding sulfoxide.

After establishing the correct reaction conditions, we next planned to explore the generality as well as the scope of the reaction conditions. Initially, various substituted thioethers bearing methyl, nitro, bromo, and *iso*-propyl as well as

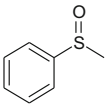
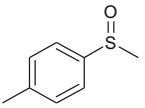
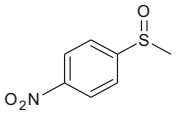
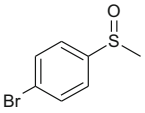
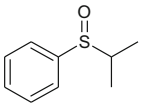
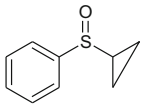
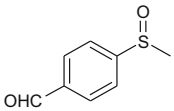
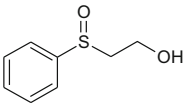
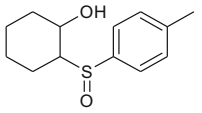
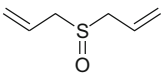
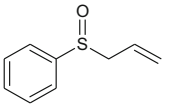
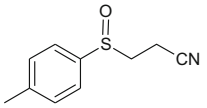
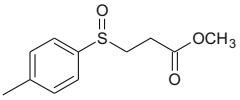
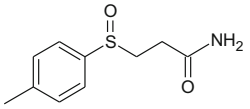
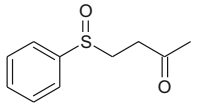
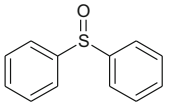
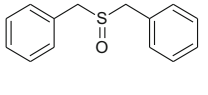
cyclopropyl groups were subjected to oxidation. In all the cases, the corresponding sulfoxides were obtained in excellent yield (Table 2, entries **2b**–**2f**). We next turned our attention to check the chemoselectivity in this oxidation process. Accordingly, sulfides containing aldehyde and primary as well as secondary alcoholic groups were selected as substrates. In all these cases, chemoselective oxidation of sulfide to sulfoxide was observed (Table 2, entries **2g**–**2i**). During oxidation of diallyl sulfide and allyl phenyl sulfide, chemoselective oxidation of sulfides to corresponding sulfoxides was also observed (Table 2, entries **2j**, **2k**). So as to explore the functional group compatibility, sulfides containing nitrile and ester amide as well as a keto group were subjected to oxidation under the established reaction conditions. In all these cases, corresponding sulfoxides (Table 2, **2l**–**2o**) resulted in excellent isolated yields. Finally, the reaction was extended towards the oxidation of diaryl and dibenzyl sulfides. In these cases too, corresponding sulfoxides (Table 2, **2p**–**2q**) were obtained in excellent yields. So as to check the practical utility of the developed protocol, oxidation of dibenzyl sulfide was carried out on 50-mmol scales when the corresponding sulfoxide was obtained as the sole product in excellent yield (94%) in a very short time (10 min). Most gratifyingly, after isolation of the product as a colorless solid, it did not require any further purification.

During optimization of the reaction conditions for the oxidation of sulfides to sulfoxides, we had noticed that (1) with the choice of equimolar quantities of thioanisole, Oxone and KBr, the initially formed sulfoxide continues to undergo overoxidation to yield the corresponding sulfone as the major product; however, even after prolonged stirring at room temperature, its oxidation to sulfone does not go to completion, and, consequently, the final product is a mixture of sulfoxide and sulfone, later being the major product (Table 1, entry 1,) and (2), with the choice of more than the optimized amount of Oxone (Table 1, entry 8), the resulting oxidation product is also a mixture of sulfoxide and sulfone. In this case, the former compound is obtained as the major product. Based upon these two observations, we surmised that, with the choice of either more than stoichiometric quantities of Oxone–KBr or of Oxone, the oxidation of sulfide to sulfone could be easily achieved. These two important observations prompted us to extend this oxidative protocol towards the oxidation of sulfides to sulfones. A variety of reagents within the range of the experimental conditions has recently been reported for the oxidation of sulfides to sulfones [44–52]. However, we were interested in exploring the use of Oxone or the Oxone–KBr combination in this oxidation. Thus, we initially attempted the oxidation of thioanisole, **1a**, to the corresponding sulfone, **3a**, using Oxone and KBr in different proportions (Table 3). However, the resultant product was noticed to be a mixture of sulfoxide and sulfone (Table 3, entries 1–3). After this failure, we undertook an uncatalyzed oxidation of thioanisole using different proportions of Oxone (Table 3, entries 4–6). Once again, in all the cases, the resultant product was noticed to be a mixture of sulfoxide, **2a**, and sulfone, **3a**, later being obtained as the major but not the sole product. In the light of our earlier studies (Table 1) on the oxidation of sulfides to sulfoxides, the results obtained during these oxidation studies were surprising, and we do not have any logical explanation for this behaviour. Hence, we became more determined to develop a protocol for obtaining sulfone as the sole product using Oxone as an oxidant.

Table 2 Chemoselective oxidation of sulfides to sulfoxides

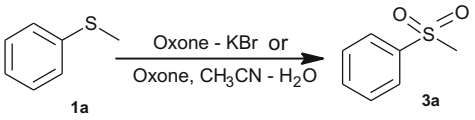


1 2

		
2a	**2b**	**2c**
15 / 92	**15 / 90**	**15 / 95**
		
2d	**2e**	**2f**
15/ 92	**15/ 90**	**15/ 89**
		
2g	**2h**	**2i**
20 / 89	**15 / 85**	**20 / 95**
		
2j	**2k**	**2l**
15 / 92	**10 / 96**	**10 / 93**
		
2m	**2n**	**2o**
20 / 90	**20 / 90**	**15 / 89**
		**2q** (on 50 mmol scale)
2p	**2q**	**10 / 94**
10 / 88	**10 / 92**	

Reaction conditions: Sulfide (1 mmol), acetonitrile - water (1:3, v / v, 4 mL), aqueous Oxone (0.7 mmol in 6 mL H_2O), RT; b: all compounds gave satisfactory spectral (IR, NMR) analysis

Table 3 Optimization of reaction conditions for oxidation of thioanisole, **1a**, to the corresponding sulfone, **3a**



No.	Oxone (euqiv.)	KBr (equi.v)	Time (min)	Yield (%)[a]	
				Sulfoxide	Sulfone
1	1.5	1.5	90	10	90
2	2.0	2.0	90	10	90
3	2.0	1.0	90	20	80
4	1.5	–	90	15	85
5	2.0	–	90	10	90
6	2.5	–	90	10	90

[a] Isolated yields

A literature survey as regards the use of Oxone inthe oxidation of sulfides to sulfones revealed that there are only few earlier reports on this oxidative transformation. Trost et al. and Morimoto et al. have reported, respectively, the use of Oxone and a clay mineral–Oxone combination for this oxidation [53, 54]. However, apart from the mineral support, both these protocols require the use of Oxone in excess. Yu et al. have reported an Oxone-mediated, catalyst-free protocol for the oxidation of sulfides to sulfones [37]. However this protocol suffers from drawbacks regarding the very long reaction times and elevated temperature (reflux, 12 h). Web et al. have also reported the use of Oxone in the direct oxidation of sulfides to sulfones [55]. Their protocol necessitates the use Oxone as a solution in EDTA as solvent and the control of pH between 7.5–8.0 by using sodium carbonate buffer. During the literature search, one report attracted our attention: Ceccherelli et al. have reported the use of a base–Oxone combination in an oxidative Nef reaction [56]. After this report, to our knowledge, there are no reports on the use of a base–Oxone combination in other oxidative transformations. This interesting observation coupled with our continued interest in the development of ecobenign methodologies using basic catalysts [57–62], meant that we became interested in investigating the use ofa base–Oxone combination in the oxidation of sulfides.

A few model reactions were carried out initially. Thus, to a well-stirred mixture of thioanisole, **1a** (1 mmol), and a selected base catalyst (0.2 mmol) in acetonitrile (2 mL) was added the solution of Oxone (2 mmol) in water (4 mL). Each reaction was monitored by TLC. It was observed that, with the choice of inorganic base catalysts, the oxidation of sulfide, **1a**, to the corresponding sulfone, **3a**, does not go to completion (Table 4, entries 1, 2). On the other hand, with the choice of organobasic catalysts like DBU, DABCO, piperidine, diethylamine, and DMAP, as well as triethylamine, thioanisole directly undergoes oxidation to cthe orresponding sulfone (Table 4, entries 3–8). Each model reaction was exothermic, fast and, most

Table 4 Optimization of reaction conditions for base-catalyzed oxidation of thioanisole, **1a**, to the corresponding sulfone, **3a**

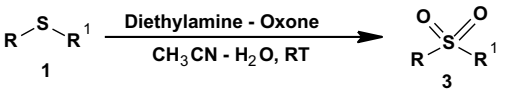
No.	Oxone (equiv.)	Catalyst (20 mol%)	Time (min)	Yield (%)[a]	
				Sulfoxide	Sulfone
1	2.0	K_3PO4	60	20	80
2	2.0	K_2CO3	120	50	50
3	2.0	DABCO	5	–	85
4	2.0	DBU	5	–	90
5	2.0	Piperidine	5	–	90
6	2.0	Triethylamine	30	–	82
7	2.0	DMAP	30	–	85
8	2.0	DEA	5	–	97
9	1.5	DEA	5	–	96[b]

[a] Isolated yields; *DEA* diethylamine

interestingly, in none of the organic base catalyzed reactions did we notice the presence of sulfoxide in the final product (TLC). Among the catalysts screened, based upon the parameters of cost, commercial availability, ease of handling and easy removal from the reaction mixture during work-up, diethylamine was noticed to be the best-suited catalyst. During further optimization of the reaction conditions, it was noticed that, with the use of 1.5 equiv. of Oxone, cthe onversion of thioanisole to the corresponding sulfone takes place in nearly the same time and yield (Table 4, entry 9).

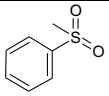
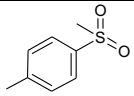
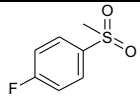
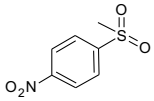
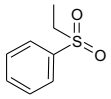
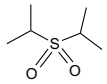
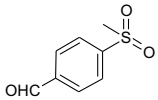
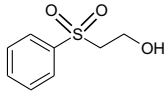
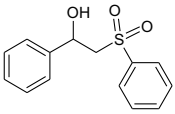
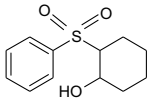
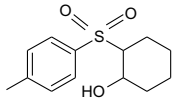
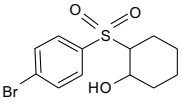
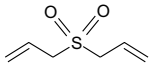
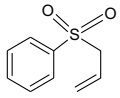
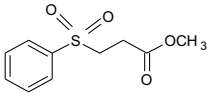
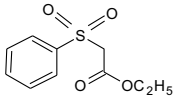
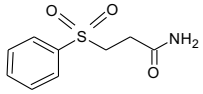
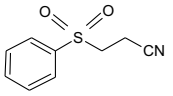
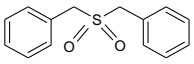
Employing the optimized reaction conditions, initially, various substituted thioanisoles were subjected to oxidation, when the corresponding sulfones were obtained in almost quantitative yields (Table 5, entries **3a**–**3e**). Subsequently, an array of structurally diverse thioethers containing easily oxidizable substituents like aldehyde as well as a secondary alcoholic group were subjected to oxidation under the same reaction conditions. Once again, the corresponding sulfones resulted in excellent yield (Table 5, entries **3h**–**3m**). During screening of functional group compatibility in this oxidation protocol, sulfides containing allyl, ester, and amide as well as nitrile functions were subjected to oxidation. The protocol was noticed to be functional grou- compatible (Table 5, **3n**–**3s**). In most cases, the resultant sulfone being a solid product and its isolation proved to be very easy. Thus, simply upon dilution of the reaction mixture with water followed by filtration of the resultant solid, the corresponding sulfone was obtained. Most gratifyingly,the resulting sulfone did not require any further purification. On the other hand, when the sulfone was obtained as a liquid, simple filtration through a short column of silica gel yielded the pure product.

Table 5 Diethylamine catalyzed, chemoselective oxidation of sulfides to sulfones

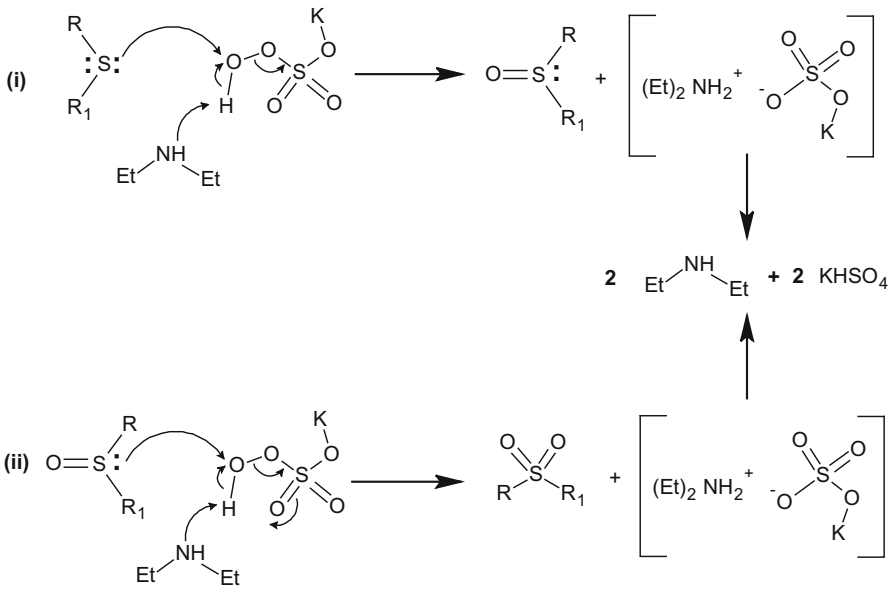


1 → 3

Time (min.) / Yield (%)

 **3a** 5 / 98	 **3b** 5 / 98	 **3c** 5 / 99
 **3d** 5 / 97	 **3e** 5 / 91	 **3f** 5 / 90
 **3g** 5 / 98	 **3h** 10 / 88	 **3i** 5 / 88
 **3j** 10 / 90	 **3k** 15 / 95	 **3l** 15 / 90
 **3m** 15 / 90	 **3n** 10 / 88	 **3o** 5 / 99
 **3p** 10 / 96	 **3q** 10 / 90	 **3r** 10 / 99
 **3s** 5 / 97	 **3t** 10 / 95	**3t** (on 50 mmol scale) **10 / 94**

Reaction conditions: sulfide (1 mmol), acetonitrile (1mL), diethylamine (20 mol %), Oxone [1.5 mmol in water (4 mL)], RT;



Scheme 2 Plausible mechanism for diethylamine-catalyzed oxidation of sulfides to sulfones

Encouraged by this success in the development of a high-yielding and operationally simple protocol in the oxidation of sulfides to sulfones, we next planned to explorethe scalability of the developed protocol. In this regard, dibenzylsulfide was once a gain selected as a model substrate. Under the established reaction conditions, the oxidation of dibenzylsulfide was performed on a 50-mmol scale. Most gratifyingly, the corresponding sulfone, i.e., dibenzylsulfone, was obtained as a colorless solid in almost quantitative yield and, after isolation, it did not require any further purification.

Plausible mechanism of diethylamine catalyzed oxidation of sulfides to sulfones is depicted in Scheme 2.

Conclusion

In conclusion, we have developed an ecobenign, catalyst-free, and scalable protocol for the chemoselective oxidation of sulfides to sulfoxides using commercially available Oxone as an oxidant. We have also developed a chemoselective, chromatography-free and scalable protocol for the oxidation of sulfides to sulfones using diethylamine–Oxone as a unique catalyst–oxidant combination. To the best of our knowledge, the literature to date contains no precedent for such a simple, energy-efficient and scalable protocol for the oxidation of sulfides to sulfoxides and sulfones.

Experimental

General

Simple substituted thioethers were procured from commercial sources and were used as received. Functionalized thioethers essential for the synthesis of sulfoxides/sulfones (**2l–2o/3p–3s**) were prepared by potassium phosphate-catalyzed Michael addition of thiols to acrylonitrile, methyl acrylate, acrylamide or methyl vinyl ketone, respectively (see supplementary information). Thioethers, essential for the synthesis of sulfoxide, **2i**, and β-hydroxy sulfones (**3j–3m**) were prepared by potassium phosphate-catalyzed, regioselective opening of respective epoxides with thiol [63; see supplementary information]. Melting points were recorded using a Kumar melting point apparatus. IR spectra were recorded using a Perkin Elmer Spectrum 1 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance-II (300 MHz) spectrometer. High-resolution mass spectra (HRMS) were recorded using a Thermo-Scientific-Q-Exactive, Accela 1250 pump instrument.

Representative procedure for the oxidation of sulfides to sulfoxides

To a well-stirred solution of thioether (1 mmol) in aqueous-acetonitrile (3:1, 4 mL) was added dropwise a solution of Oxone (0.7 mmol) in water (6 mL). Stirring was continued and the reaction was monitored by TLC. Upon completion of the reaction, the mixture was diluted with chilled water. The resultant sulfoxide, if solid, was filtered, washed with water and dried, or otherwise the reaction mixture was extracted with ethyl acetate. The organic extract was washed with water, dried over anhydrous sodium sulfate and the solvent was removed. The resultant residue was filtered through a short column of silica gel. Elution with petroleum ether–ethyl acetate (98:2%, v/v) afforded the pure sulfoxide.

Representative procedure for the oxidation of sulfides to sulfones

To a well-stirred solution of thioether (1 mmol) and diethylamine (0.2 mmol) in acetonitrile (2 mL) was added the solution of Oxone (1.5 mmol) in water (4 mL). Stirring was continued and the reaction was monitored by TLC. Upon completion of the reaction, the mixture was diluted with chilled water. In most of the cases, sulfones were obtained as pure solid products. Thus, they were isolated by simple filtration. However, when the resulting sulfone was a liquid, the product was extracted with ethyl acetate. The organic extract was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed. The resultant residue on filtration through a short column of silica gel afforded pure sulfone.

Spectral data of new compounds is summarized below (For original spectra of all the synthesized compounds, please see supporting information)

*(Prop-2-ene-1-sulfinyl) Benzene, (**2l**)* Colorless oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.55–7.53 (m, 2H, ArH), 7.52–7.42 (m, 3H, ArH), 5.60–5.50 (m, 1H, = CH), 5.27–5.23 (m, 1H, = CH*H*), 5.15–5.09 (m, 1H, = CH*H*), 3.55–3.40 (m, 2H, SCH2); ^{13}C- NMR (CDCl3, 75 MHz): δ = 142.84, 131.06, 129.00, 125.21, 124.27, 123.80, 60.74 ppm.

*3-[(4-methyl phenyl) sulfinyl] propane nitrile (**2m**)* White solid; Mp 47–49 °C; ^{1}H-NMR (DMSO, 300 MHz): δ = 7.52 (d, 2H, J = 7.8 Hz, 2H, ArH), 7.31 (d, J = 8.1 Hz, 2H, ArH), 3.32–3.23 (m, 1H, SCH*H*), 3.05–2.97 (m, 1H, SCH*H*), 2.89–2.79 (m, 1H, SCH*H*), 2.68–2.63 (m, 1H, SCH*H*), 2.29 (s, 3H, $ArCH_3$); ^{13}C-NMR (DMSO, 75 MHz): δ = 141.91, 138.99, 10.16, 130.29, 124.38, 118.50, 50.17, 21.36 ppm.

*Methyl 3-[(4 methyl phenyl) sulfinyl] propanoate (**2n**)* Pale yellow oil; ^{1}H-NMR (DMSO, 300 MHz): δ = 7.46 (d, J = 7.5 Hz, 2H, ArH), 7.29 (d, J = 7.5 Hz, ArH), 3.66 (s, 3H, OCH_3), 3.29–3.11 (m, 1H, SCH*H*), 2.96–2.87 (m, 1H, SCH*H*)), 2.71–2.63 (m, 1H, CH*H*)), 2.46–2.38 (m, 1H, CH*H*)), 2.33 (s, 3H, $ArCH_3$); ^{13}C-NMR (DMSO, 75 MHz): δ = 171.58, 141.49, 139.79, 130.07, 124.23, 52.01, 50.72, 25.88, 21.33 ppm.

*3-[4-(Methylphenyl) sulfinyl] propanamide (**2o**)* White solid; Mp 142–144 °C; ^{1}H-NMR (DMSO, 300 MHz): δ = 7.56–7.45 (m, 2H, ArH), 7.37–7.31 (m, 2H, ArH), 6.90 (s, 1H, NH_2), 3.14–3.04 (m, 1H, SCH*H*), 2.94–2.85 (m, 1H, SCH*H*), 2.51–2.37(m, 1H, CH*H*), 2.33(3H, s), 2.29–2.18 (m, 1H, SCH*H*); ^{13}C- NMR (DMSO, 75 MHz): δ = 173.31, 142.05, 139.36, 130.39, 124.56, 51.46, 27.45, 21.28 ppm.

*1-Phenyl-2-(phenyl sulfonyl) ethanol, (**3j**)* White solid. Mp 108–110 °C; IR (KBr, cm^{-1}): 3365, 3094, 3085, 2962, 2944, 2935, 2922, 1690, 1463, 1431, 1338, 935, 960, 690; ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.33–3.38 (1H, m), 3.49–3.57 (1H, m), 3.70 (1H, d), 5.28 (1H, d), 7.28–7.33 (5H, m), 7.61(2H, t, J = 8.1 Hz), 7.69–7.71 (1H,m), 7.79 (2H, d, J = 8.1 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz):63.97, 68.47, 125.66, 128.00, 128.38, 128.80, 129.49, 134.14, 139.21, 140.63; HRMS: mass calculated for $C_{14}H_{15}O_3S$ $(M + H)^+$: 263.0736; Observed mass: 263.0733.

*2-[4-(Bromophenyl) sulfonyl] Cyclohexanol (**3m**)* White solid. Mp 138–141 °C, IR (KBr, cm^{-1}): 3345, 2990, 2966, 1478, 1461, 1307, 1203, 938, 730, 670, 590; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.23–1.38 (4H, m), 1.75 (2H, d, J = 6.0 Hz), 1.92 (1H, d, J = 12.6 Hz), 2.36 (1H, t, J = 11.4 Hz), 2.95–3.03 (1H, m), 3.46 (1H, broad doublet), 3.87–3.95 (1H, Sextet, J = 5.1 Hz), 7.73–7.76 (4H, d), ^{13}C-NMR ($CDCl_3$, 75 MHz):23.54, 24.52, 25.70, 34.23, 68.28, 69.13, 129.62, 130.52, 132.59, 135.98; HRMS: mass calculated for $C_{12}H_{16}O_3^{79}BrS$ $(M + H)^+$: 318.9998; Observed mass: 318.9996.

*3-(Phenyl sulfonyl) propanamide (**3r**)* White solid; Mp 136–138 °C; IR (KBr, cm^{-1}): 3384, 3235, 2975, 2934, 2901,1635, 1312, 1104, 920, 750; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.75 (2H, t, J = 7.5 Hz), 3.47 (2H, t, J = 7.5 Hz), 5.62 (1H, broad singlet), 5.89 (1H, broad singlet), 7.58–7.63 (2H, m), 7.67–7.72 (1H, m), 7.92–7.95 (2H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz): 28.20, 51.74, 128.01, 129.44, 134.04, 138.80, 170.84; HRMS: mass calculated for $C_9H_{12}O_3NS$ $(M + H)^+$: 214.0532; Observed mass: 214.0531.

*3-(Phenyl sulfonyl) propanenitrile (**3s**)* White solid; yield: 193 mg (99%); Mp 93–94 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 7.94$ (d, $J = 7.5$ Hz, 2H, ArH), 7.74 (t, $J = 7.2$ Hz, 1H, ArH), 7.64 (t, $J = 7.5$ Hz, 2H, ArH), 3.41 (t, $J = 7.5$ Hz, 2H, SCH2), 2.83 (t, $J = 7.5$ Hz, 2H, CH2); ^{13}C-NMR (CDCl3, 300 MHz): $\delta = 137.54$, 134.71, 129.77, 128.25, 116.30, 50.98, 12.00; HRMS (ESI): *m/z* [M + H] + calcd for $C_9H_{10}O_2NS$: 196.0427; found mass: 196.0427.

Acknowledgements Authors UVD and SSK thank UGC New Delhi for the financial support [F. 43 - 221/2014 (SR)]. We are also grateful to the Department of Science & Technology (DST), New Delhi, for financial assistance to the Department of Chemistry, Shivaji University Kolhapur, under the DST–FIST program.

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