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Selective Oxidation of Organosulphides using *m*-CPBA as oxidant

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ABSTRACT

*An alternative approach for the oxidation of organosulfides**7** to corresponding organosulfones**8**and organosulfides**9** is described using m-CPBA as oxidant under mild reactions. The oxidation reactions were carried out at 35 ^{o}C and 0 ^{o}C, oxidation products were isolated as organosulfones**8**andorganosulfoxides**9** respectively. The oxidation products **8** and **9** were isolated in high yields.*

Key words: oxidation reaction, *m*-chloroperbenzoic acid, organosulfides, organosulfones and organosulfoxides

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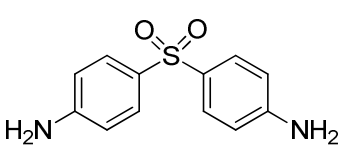
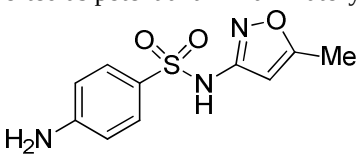
INTRODUCTION

Sulphur chemistry is developed as well established research area of organic chemistry [1].Organosulfones are important reaction intermediates forthe synthesis of various compounds for synthetic and medicinal purposes [2,3]. In addition, sulfonefunctionality is common structural motif found in various biological active compounds **1**-**6**(Figure 1). Dapsone**1**is identified as potent antibiotic agent and used for the treatment of leprosy [4]. Sulfamethoxazole**2** was reported as antibiotic agent and used for the treatment of urinary infections [5]. Carbutamide**3**was introduced as first oral antidiabetic agent thatacts by blocking KATP channels of β-cells in pancreas [6].Glyburide**4**was developed as second generation sulfonylureas for enhancing the insulinsecretion [7]. Both valdecoxib**5** and rofecoxib**4**were reported as potent anti-inflammatory drugs [8,9].



1: Dapsone



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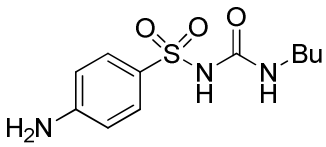
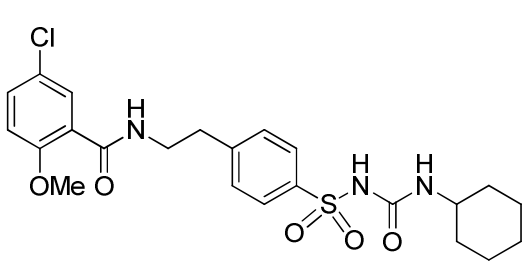
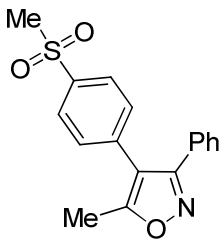


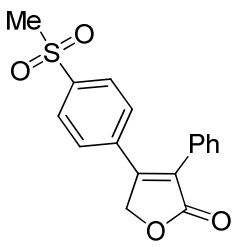
3:Carbutamide



4: Glyburide



5: Valdecoxib



6: Rofecoxib

Figure 1 Biologically active molecules 1-6 having sulfone functionality

MATERIALS AND METHODS

Melting points were obtained in open capillary tubes. ^{1}H NMR and ^{13}C NMR spectra were recorded on a AV-400 Bruker using the solvents indicated with 400 and 100 MHz, respectively, also a DRX-500 Bruker was used in the some cases for ^{1}H (500 MHz) and ^{13}C (125 MHz). Mass spectra (*m*/*z*) were recorded under the conditions of electron impact (EI) and electrospray (ES) and chemical ionization (CI). All reactions were monitored by thin-layer chromatography that was performed on pre-coated sheets of silica gel 60, and column chromatography was performed with silica gel 60 (Avra synthesis, 100–200 mesh). Eluting solvents are indicated in the text. Dry THF was used from a solvent purification system while acetonitrile of HPLC grade was used and dried with molecular sieves (4 Å). All other purchased chemicals were used without further purification.

Procedure for the Synthesis of arylthioethers7a-d: Thiophenol (5.0 mmol, 0.51 mL) was added to the mixture of glacial acetic acid (7.5 mL), 70% perchloric acid (1.6 mL) and acetic anhydride (1.3 mL) at 0 ^{o}C.After that, *tert*-butanol (10 mmol, 0.95 mL) was added at same temperature and reaction mixture was stirred for 12 h. The progress of reaction was monitored by TLC. After the completion of reaction, water (10 mL) was added and reaction mixture was extracted with EtOAc (3 X 10 mL) and the combined organic layerwas washed with 20% aqueous sodium hydroxide solution (2 X 10 mL). The organic layerwas dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude products were characterized as arylalkylsulfides**7** and directly used in oxidation reactions without any further purification.

Tert-butylphenylsulfide**7a**[10]
Yellow oil; yield: 91%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 9H, 3Me), 7.30-7.54 (m, 3H, ArH), 7.53-7.62 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 30.9, 58.8, 128.4, 128.6, 132.8, 137.5; IR(film): ν = 2956, 1471, 1166, 893, 748, 692, 509 cm^{-1}; GC-MS: (%) 166 (87), 109 (100), 65(90), 51(30), 41(60).
Tert-butyl-4-methoxyphenylsulfide**7b** [10]

Colourless oil; yield: 75%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9H, 3Me), 3.80 (s, 3H, OMe), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 7.07-7.14 (m, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 1H, ArH).

Tert-butyl-4-chlorophenylsulfide**7c**[10]
Colourless oil;yield: 84%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H, 3Me), 7.29 (d, *J* = 7.2 Hz, 2H, ArH), 7.45 (d, *J* = 7.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.8, 46.0, 55.6, 128.6, 131.2, 135.1, 138.6; GC-MS: (%) 184 (50), 143 (73), 108 (80), 57 (100), 41 (66).

[(1-methylethyl)thio]Benzene**7d** [11]
Yellow oil;yield: 82%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, *J* = 4.8 Hz, 6H, 2Me), 3.18-3.29 (m, 1H, CH), 7.31-7.37 (m, 3H, ArH), 7.44-7.49 (m, 2H, ArH); GC-MS (%) 152 (95), 109 (100), 90 (80), 72 (30), 45 (65).

Procedure for the Synthesis of arylsulfones8a-d: The mixture of arylbutylsulfide**7** (1.0 mmol, 1.0 equiv) and *m*-CPBA (2.0 mmol, 2.0 equiv) in THF (5.0 mL) was stirred at 35 ^{o}C for 20-50 minutes. The progress of reaction was monitored by TLC. After the completion of reaction, THF was removed under vacuum and water (5.0 mL) was added. The reaction mixture was extracted with EtOAc (3 X 5 mL) and the combined organic layerwas dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude products were purified by column chromatography using 5% EtOAc in hexane as eluent and isolated products were characterized as arylalkylsulfones**8**.

[(1,1-dimethylethyl)sulfonyl]benzene**8a** [12]
Colourless oil; yield: 87%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 9H, 3Me), 7.40-7.44 (m, 3H, ArH), 7.50-7.54 (m, 2H, ArH); IR (film): ν = 2951, 1659, 1458, 1257, 1013, 801, 745cm^{-1}; GC-MS: (%) 197 (100), 122 (40), 105 (70), 77 (65), 44 (45).

1-[(1,1-dimethylethyl)sulfonyl]-3-methoxybenzene **8b** [13]
White solid; mp: 104-106 ^{o}C; yield: 90%;^{1}H NMR (400 MHz, $CDCl_3$):δ = 1.13 (s, 9H, 3Me), 3.79 (s, 3H, OMe), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 7.02-7.06 (m, 1H, ArH), 7.11-7.15 (m, 1H, ArH), 7.29-7.34 (m, 1H, ArH); GC-MS: (%) 251 (M + Na).

1-Chloro-4[(1-methylethyl)sulfinyl]benzene **8c** [14]
Whitesolid; mp: 76-78 ^{o}C; yield: 83%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H, 3Me), 7.47 (d, *J* = 7.6 Hz, 2H, ArH), 7.75 (d, *J* = 7.6 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.6, 67.6, 129.0, 131.8, 133.3, 140.4; GC-MS: (%) 216 (80), 123 (100), 83 (85), 70 (40), 60 (63).

[(1-Methylethyl)sulfonyl]benzene **8d** [12]
Colourless oil; yield: 78%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20(d, *J* = 5.2 Hz, 6H, 2Me), 3.00-3.16 (m, 1H, CH), 7.33-7.38 (m, 3H, ArH), 7.63-7.66 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 45.8, 128.4, 128.7, 132.7, 137.4; IR(film): ν = 2873, 1393, 1220, 882, 670, 577, 512 cm^{-1}; GC-MS (%) 184 (77), 120 (55), 100 (97), 86 (90), 64 (35).

Procedure for the Synthesis of arylsulfones9a-d: The mixture of arylbutylsulfide**7** (1.0 mmol, 1.0 equiv) and *m*-CPBA (1.2 mmol, 1.2 equiv) in THF (5.0 mL) was stirred at 0^{o}Cfor 40-60 minutes. The progress of reaction was monitored by TLC. After the completion of reaction, THF was removed under vacuum and water (5.0 mL) was added. The reaction mixture was extracted with EtOAc (3 X 5 mL) and the combined organic layerwas driedover anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude products were purified by column chromatography using 2% EtOAc in hexane as eluent and isolated products were characterized as arylalkylsulfoxide**9**.

[(1,1-dimethylethyl)sulfinyl]benzene**9a** [15]
White solid; mp: 62-64 ^{o}C; yield: 82%;^{1}H NMR(400 MHz, $CDCl_3$): δ = 1.21 (s, 9H, 3Me), 7.18-7.34 (m, 5H, ArH); IR(film): ν = 2960, 1391, 1180, 898, 659, 628, 512 cm^{-1}; GC-MS: (%) 182 (90), 125 (100), 90 (82), 81 (40), 50 (30), 41 (70).

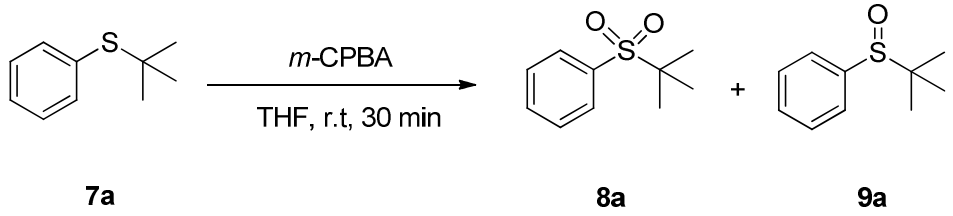
1-[(1,1-dimethylethyl)sulfinyl]-3-methoxybenzene**9b** [15]
White solid; mp: 96-98 ^{o}C; yield: 78%;^{1}H NMR (400 MHz, $CDCl_3$):δ = 1.15 (s, 9H, 3Me), 3.82 (s, 3H, OMe), 6.06-7.01 (m, 1H, ArH), (7.04-7.09 (m, 1H, ArH), 7.14-7.17 (m, 2H, ArH); ESI (MS): (%) 235 (M + Na).

1-Chloro-4-[(1,1-dimethylethyl)sulfinyl]benzene**9c** [15]
White solid; mp: 84-86 ^{o}C; yield: 80%;^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H, 3Me), 7.31 (d, *J* = 7.4 Hz, 2H, ArH), 7.73 (d, *J* = 7.4 Hz, 2H, ArH); IR(film): ν = 2964, 1471, 1294, 1076, 977, 825, 754, 653cm^{-1}; GC-MS: (%) 200 (93), 155 (70), 114 (80), 75 (45), 55 (63).

[(1-methylethyl)sulfinyl]benzene**9d** [16]
Colourless oil;yield: 76%;^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.45 (d, *J* = 6.0 Hz, 6H, CH_3), 3.09-3.25 (m, 1H, CH), 7.20-7.25 (m, 3H, ArH), 7.43-7.47 (m, 2H, ArH); IR(film): ν = 2865, 1382, 1210, 878, 660, 620, 522 cm^{-1}; GC-MS (%) 168 (87), 110 (95), 89 (87), 75 (100), 53 (55).

RESULTS AND DISCUSSION

Numerous approaches have been reported for the oxidation of aryl alkyl thioethers using various oxidants including oxone [11,17], DMP [18], hydrogen peroxide [19], sodium meta perborate [20],cumene peroxide [21] and $NaIO_4$[22]. Some of the oxidation reactions of sulphides have been achieved using metal complexes specially transition metal complexes [23]. In addition, some acid or metal catalyzed oxidation reactions of sulphides also exist in the literature [21,24]. Most of the oxidation approaches provide sulfones or mixture of sulfones with sulfoxides.
Herein, we report a temperature-dictated approach for the oxidation of a series of sulfides**8** to the corresponding sulfones**8** and sulfoxides**9**using *m*-CPBA as oxidant under mild reactions. The synthesis of precursors **7** was achieved by reaction of thiophenols with $HClO_4$ and *tert*-butanol in glacial acetic acid at room temperature [22]. Initially, optimal reaction conditions and solvents for the oxidation reaction were established using phenylbutylthioether**7a** as model substrate. The oxidation reaction was performed in dichloromethane using 2.0 equivalent of *m*-CPBA at room temperature under oxygen atmosphere for 30 min. The major product **8a** was characterized as phenylbutylsulfonewhile minor product **9a**was characterized asphenylbutylsulfoxide(Scheme 1).



7a **8a** **9a**

Scheme 1 Oxidation of sulphide 7a using *m*-CPBA as oxidant

In order to find optimal reaction condition, the same reaction was attempted with different solvents (Table 1). The oxidation reaction proceeded well in chlorinated solvents such as dichloromethane and chloroform (Table 1, entries 1 and 2) and reaction product **8a** was isolated in 81% and 74% yield respectively. In acetonitrile, the oxidation

reaction was also proceeded well and **8a** was isolated in 69% yield (Table 1, entries 3). Furthermore, the reaction was tested in methanol and oxidation product **8a** was isolated in 45% yield (Table 1, entry 4). In THF, the reaction was completed in 30 minutes and product **8a** was isolated in 87% (Table 1, entry 5). After getting promising result in THF, the same reaction was attempted in the mixture of THF and water (1:1) but this solvent combination could not facilitate the reaction efficiently (Table 1, entry 6). In addition, the same oxidation reaction was tested in polar solvent DMSO and oxidation product was isolated in 80% (Table 1, entry 7).

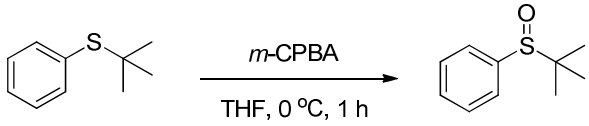
Table 1. Different solvents for the oxidation of 7ato 8ausing *m*-CPBA oxidant

Entry	Solvent	Time (min)	**8a**Yield (%)
1	DCM	0.5	81
2	$CHCl_3$	0.5	74
3	MeCN	4	69
4	MeOH	4	45
5	THF	0.5	87
6	THF:H_2O(1:1)	4	10[a]
7	DMSO	4	80

[a]*Yield was reported on the basis of ^{1}H NMR.*

Furthermore, our efforts were directed to see the course of reaction at lower temperature. The similar oxidation reaction of **7a** was performed in THF at 0 ^oC using two equivalents of *m*-CPBA. The reaction was completed in 1 h but the spectroscopic analysis of isolated product could not match with expected product **8a**. Finally, it was characterized as (*tert*-butylsulfinyl)benzene**9a**and obtained in 84% yield. After the knowing the structure of compound **9a**, the same reaction was optimized with different stoichiometry of *m*-CPBA at same temperature (Table 2).

Table 2Optimization of stoichiometry of *m*-CPBA for the oxidation of 7a to 9a using *m*-CPBA oxidant



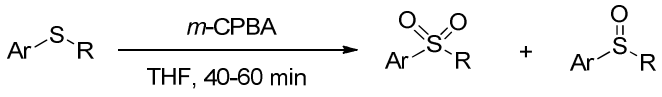
7a **9a**

Entry	Amount of *m*-CPBA (equiv)	**9a**Yield (%)
1	2.0	84
2	1.5	85
3	1.2	83
4	1.0	77[a]

[a]*Starting material was also observed*

Initially, 2.0 equivalent of *m*-CPBA was used and compound **9a** was isolated in 84% yield (Table 2, entry 1). Furthermore, reactions were performed with 1.5 and 1.2 equivalent of *m*-CPBA but not much difference was observed in yields (Table 2, entries 2 and 3). In addition, the same reaction was used with 1.0 equivalent of *m*-CPBA and reaction product **9a** was observed in 77% yield along with some starting material. After getting the best reactions for synthesis of both organosulfone**8a** and sulfoxide**9a**, the scope of reaction was extended with different substrates **7**(Table 3). All the oxidation reactions of sulphides **7** to corresponding sulfoxides**9** were carried out with 1.2 equivalent of *m*-CPBA in THF at 0 ^oC. Both electron withdrawing and donating groups on aromatic were used and reaction was working more efficiently with electron donating group than electron withdrawing group (Table 3, entries 3, 4, 5 and 6).

Table 3 The scope of oxidation reaction with various organosulfides7 using *m*-CPBA oxidant



7 **8** **9**

Entry	Ar	R	Time (min)	Temperature (^oC)	Yield (%)	
					8	**9**
1	**7a:**Ar = Ph	^{t}Bu	30	35	87**(8a)**	8 **(9a)**
2	**7a:**Ar = Ph	^{t}Bu	60	0	-	82 **(9a)**
3	**7b:**Ar = 3-OMeC_6H_4	^{t}Bu	50	35	90 **(8b)**	trace
4	**7b:**Ar = 3-OMeC_6H_4	^{t}Bu	60	0	-	78 **(9b)**
5	**7c:**Ar = 4-ClC_6H_4	^{t}Bu	20	35	83 **(8c)**	
6	**7c:**Ar = 4-ClC_6H_4	^{t}Bu	40	0	-	80 **(9c)**
7	**7d:**Ar = Ph	^{i}Pr	25	35	78 **(8d)**	10 **(9d)**
8	**7d:**Ar = Ph	^{i}Pr	50	0	-	76 **(9d)**

CONCLUSION

In summary, we have demonstrated an alternative approach for the oxidation of organosulfides to corresponding organosulfones and organosulfides under mild reactions. The oxidation approach was dictated by temperature and organosulfones were synthesized at 35 ^{o}C while organosulfoxides were obtained at 0 ^{o}C. Our method to oxidize organosulfides is very simple, economical and metal-free. Research studies about the wider scope of this approach are currently in progress.

Acknowledgements
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