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Facile Preparation of Indolyl-2/3-methylsulfoxides Using HF/H_2O_2

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Abstract: A variety of indolyl-2/3-methylsulfides tethered with sensitive functionalities were oxidized to the corresponding sulfoxides using a hitherto unexplored HF/H_2O_2 system.

Keywords: HF/H_2O_2, indolyl-2/3-methylsulfide, indolyl-2/3-methylsulfoxide

INTRODUCTION

In general, the preparation of sulfoxides could be easily achieved via the oxidation of the corresponding sulfide using oxidizing agents.[1] However, careful quantitative control of the oxidizing reagent is most essential to prevent the overoxidation of the sulfoxide to the corresponding sulfone. During the past 25 years, arylmethylsulfoxides and arylmethylsulfones tethered with functional groups have been exploited as bidentate synthons for the synthesis of naturally occurring aromatic/heteroaromatic polycycles.[2] The sulfide/sulfoxide/sulfones units attached to the indole skeleton have been explored as reverse transcriptase[3] as well as tubulin polymerase[4] inhibitors. Recently, several methods have been developed for the oxidation of sulfides using H_2O_2/heteropolyacids,[5] $H_2O_2/ZrCl_2$[6] and H_2O_2/MoO_2Cl_2.[7] Very recently, KF/*m*-3-chloroperbenzoic

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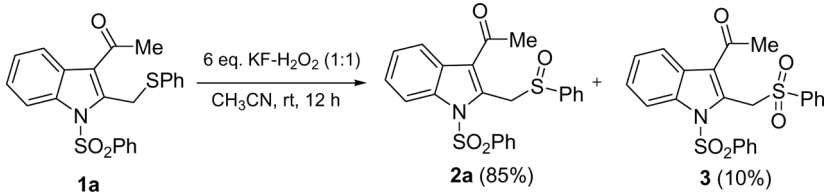
acid (CPBA) has been employed for the preparation of indlolylmethyl sulfoxides[8] as well as glycosyl sulfoxides.[9] However, the oxidation of sulfide with $HOF \cdot CH_3CN$ led to the formation of corresponding sulfones.[10]

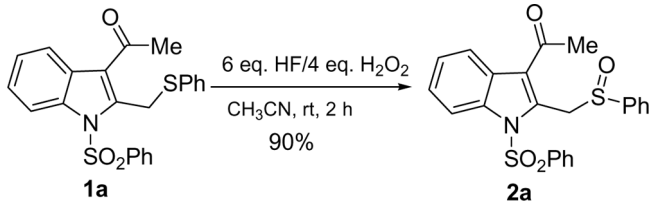
RESULTS AND DISCUSSION

In continuation of our work on the synthesis of carbazole alkaloids,[11] we required different types of indolyl-2/3-methylsulfoxide containing functional groups such as ester, ketone, and cyanide for annelation studies.[12] The synthetic utility as well as biological potency of indolylmethylsulfoxides prompted us to develop a simple and economically viable route for the smooth oxidation of indolyl-2/3-methylsulfides into the corresponding sulfoxides. Accordingly, the oxidation of the sulfide **1a** was planned using 50% H_2O_2 as an oxidizing agent. Because KF/*m*-CPBA has efficiently transformed indolylmethylsulfide into the corresponding sulfoxide,[8] initially the oxidation of the sulfide **1a** was performed using 6 equivalents of KF/H_2O_2 (1:1) in acetonitrile at room temperature for 12 h. Contrary to our expectation, the workup of the reaction led to the isolation of sulfone **3** and sulfoxide **2a** in 85% and 10% yields, respectively (Scheme 1).

Using the similar conditions, when the oxidation of sulfide **1a** was performed at room temperature using 6 equivalents HF/H_2O_2 (1:1) for 1 h, the required sulfoxide **2a** could be isolated in the major portion along with minor amount of sulfone **3** (15% yield). It should be noted that the oxidation of sulfide **1a** using 6 equivalents of H_2O_2 in the absence of HF led to the isolation of sulfone **3** as an exclusive product. Encouraged by this result, we carried out the oxidation of sulfide **1a** using varying proportions of 50% H_2O_2 and 40% aq. HF. Finally, using H_2O_2 and aq. HF in the ratio of 4:6 led to the formation of sulfoxide **2a**. Thus, the interaction of 40% aq. HF and 50% H_2O_2 (4:6) in acetonitrile at room temperature for 30 min followed by addition of the sulfide **1a** led to the isolation of sulfoxide **2a** in 90% yield, (Scheme 2).



Scheme 1. Oxidation of sulfide **1a** using KF/H_2O_2.



Scheme 2. Preparation of sulfoxide **2a** using HF/H_2O_2.

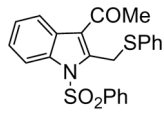
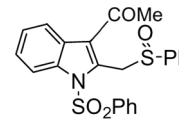
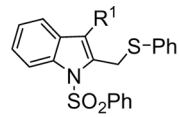
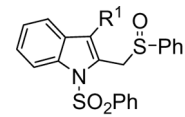
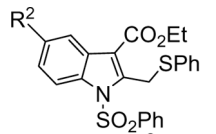
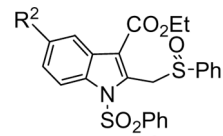
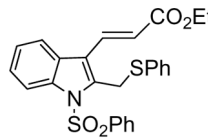
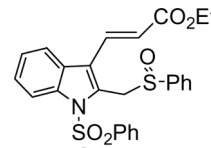
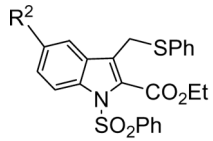
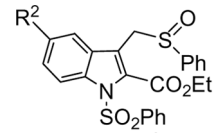
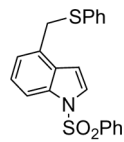
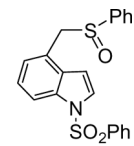
Further oxidation of the sulfoxide **2a** to the corresponding sulfone **3** was not observed under this condition. The applicability of the HF/H_2O_2 (6:4) system for the sulfoxidation of variety of indolyl-2/3-methylsulfides was then examined in acetonitrile at room temperature. A ratio of 1:4:6 sulfide/H_2O_2/HF was found to be the optimum for the smooth transformation of the sulfides **1a–o** into the corresponding sulfoxides **2a–o**. The structures of different types of sulfoxides **2a–o** prepared using HF/H_2O_2 along with their respective yields are presented in Table 1. In all these cases, the sulfoxides are isolated in good yields (80–92%) without any trace of sulfones. The indolyl-2-methylsulfoxides **2a–g** could be regarded as bidentate synthons (entries 1–4), and they may be utilized as crucial intermediates for the synthesis of carbazole derivatives via base-mediated Michael addition followed by intramolecular cyclization.[12] The isomeric indolyl-3-methylsulfoxides **2 h** and **2i** could also be prepared in excellent yields (entry 5). The HF/H_2O_2 methodology was also applied to the synthesis bis- as well as tris-sulfoxides **2l–o** (entries 8–10).

In conclusion, we have synthesized several indolylmethylsulfoxides via sulfoxidation using a combination of 40% aq. HF and 50% H_2O_2 in acetonitrile with excellent selectivity. The methodology reported herein is simple, clean, and economically viable for the sulfoxidation of arylmethyl as well as hetero-arylmethylsulfides.

EXPERIMENTAL

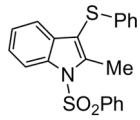
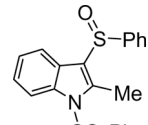
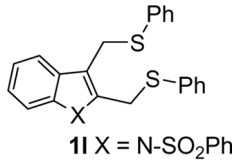
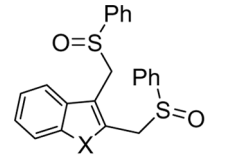
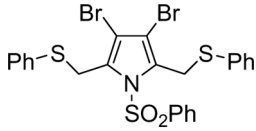
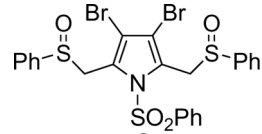
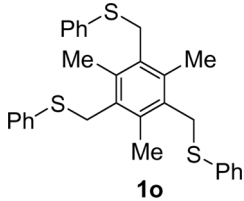
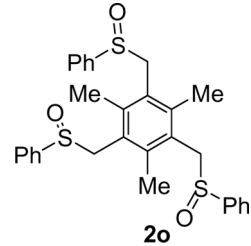
All melting points were uncorrected. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Column chromatography was carried out on silica gel (grade 60, mesh size 230–400, Merck). Infrared (IR) spectra were recorded on a Shimadzu Fourier transform infrared (FT-IR) 8300 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard on Jeol GSX 400 and Bruker-300 spectrometers. Chemical shift values were quoted in parts

Table 1. Preparation of indolylmethylsulfoxides using $HF–H_2O_2$

Entry	Sulfide	Sulfoxide	Yield (%)[a]
1	 **1a**	 **2a**	90
2	 **1b** R^1 = CN **1c** R^1 = Br **1d** R^1 = Me	 **2b** R^1 = CN **2c** R^1 = Br **2d** R^1 = Me	89 82 81
3	 **1e** R^2 = H **1f** R^2 = OMe	 **2e** R^2 = H **2f** R^2 = OMe	80 85
4	 **1g**	 **2g**	80
5	 **1h** R^2 = H **1i** R^2 = OMe	 **2h** R^2 = H **2i** R^2 = OMe	85 90
6	 **1j**	 **2j**	85

(*Continued*)

Table 1. Continued

Entry	Sulfide	Sulfoxide	Yield (%)[a]
7	 **1k**	 **2k**	90
8	 **1l** X = N-SO_2Ph **1m** X = S	 **2l** X = N-SO_2Ph **2m** X = S	85 80
9	 **1n**	 **2n**	85
10	 **1o**	 **2o**	80

[a]Isolated yield after column chromatography.

per million (ppm) and coupling constants were quoted in hertz (Hz). Chemical shift multiplicities were reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Mass spectra were recorded on a Jeol DX 303 HF spectrometer. Elemental analysis were carried out on Vario EL III (CDRI, Lucknow) equipment. The required sulfides **1a–o** were prepared from the corresponding bromomethyl compounds using NaH/HSPh condition in dry tetrahydrofuran (THF).

Representative Procedure for the Preparation of 1-Phenylsulfonyl-2-phenylsulfinylmethyl-3-acetylindole (2a)

To a solution of 50% H_2O_2 (0.32 mL, 4.73 mmol) in acetonitrile (5 mL), 40% aq. HF (0.35 mL, 7.11 mmol) was added and stirred for 30 min at room temperature. To the reaction mixture, a solution of sulfide **2a** (0.5 g, 1.18 mmol) in acetonitrile (5 mL) was added, and stirring was continued for another 2 h. After the sulfide **1a** was consumed (monitored by thin-layer chromatography, TLC), the reaction mixture was quenched with ice water (15 mL), extracted with ethyl acetate (2× 10 mL), and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (hexane–EA; 7:3) afforded **2a** as a colorless solid (0.47 g, 90%). Mp: 130–131 °C. IR (KBr): 1080 (SO), 1182 (SO_2), 1370 (SO_2), 1676 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.63 (s, 3H, $-CH_3$), 5.03 (d, $J = 13.2$ Hz, 1H, –CH), 5.27 (d, $J = 12.9$ Hz, 1H, –CH), 7.32–7.42 (m, 2H, Ar-H), 7.44–7.58 (m, 6H, Ar-H), 7.66–7.69 (m, 2H, Ar-H), 7.78–7.81 (m, 1H, Ar-H), 7.86 (d, $J = 7.5$ Hz, 2H, Ar-H), 8.09–8.12 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.21, 55.17, 115.0, 121.08, 124.31, 124.82, 125.86, 126.66, 126.79, 127.01, 129.20, 129.56, 131.41, 134.01, 134.54, 136.30, 138.10, 143.64, 196.40. Anal. calcd. for $C_{23}H_{19}NO_4S_2$: C, 63.14; H, 4.38; N, 3.20; S, 14.66%. Found: C, 63.30; H, 4.09; N, 3.46; S, 14.49%.

Preparation of 1-Phenylsulfonyl-3-cyano-2-phenylsulfinyl methylindole (2b)

The procedure was similar to that of **2a.** Yield: 0.15 g (89%). Mp: 140–142 °C. IR (KBr): 1083 (SO), 1181 (SO_2), 1380 (SO_2), 2221 (CN) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.71 (s, 2H), 7.26 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.47–7.54 (m, 8H, Ar-H), 7.65 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.88 (d, $J = 8.0$ Hz, 2H, Ar # H), 8.07 (d, $J = 8.0$ Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 57.83, 99.44, 112.83, 114.86, 120.00, 124.21, 125.42, 126.87, 127.20, 129.54, 129.85, 132.02, 135.11, 135.75, 137.52, 137.72, 143.09. Mass (m/z) %: 405 (M # 16, 9%), 231 (35), 154 (39), 141 (28). Anal. calcd. for $C_{22}H_{16}N_2O_3S_2$: C, 62.84; H, 3.84; N 6.66, S, 15.25%. Found: C, 62.83: H, 3.98; N, 6.51; S, 15.17%.

Preparation of 1-Phenylsulfonyl-2-phenylsulfinylmethyl-3-bromoindole (2c)

The procedure was similar to that of **2a.** Yield: 0.15 g (82%). Mp: 140–142 °C. IR (KBr): 1080 (SO), 1185 (SO_2), 1378 (SO_2) cm^{-1}. ^1H NMR

($CDCl_3$, 300 MHz): δ 4.59 (d, $J = 12.7$ Hz, 1H, –CH), 4.76 (d, $J = 12.7$ Hz, 1H, –CH), 7.30–7.56 (m, 9H, Ar-H), 7.62 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.78 (d, $J = 7.3$ Hz, 2H, Ar-H), 8.12 (d, $J = 8.2$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): 57.33, 114.9, 115.49, 120.38, 124.27, 124.76, 126.59, 126.65, 126.78, 126.96, 128.93, 129.17, 129.27, 129.48, 131.44, 134.08, 134.34. Anal. calcd. for $C_{21}H_{16}NO_3S_2Br$: C, 53.17; H, 3.40; N, 2.95; S, 13.52%. Found: C, 53.40; H, 3.27; N, 3.21; S, 13.38%.

Preparation of 1-Phenylsulfonyl-3-methyl-2-phenylsulfinyl methylindole (2d)

The procedure was similar to that of **2a.** Yield: 0.58 g (81%). Mp: 141–142 °C. IR (KBr): 1083 (SO), 1172 (SO_2), 1387 (SO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.94 (s, 3H, –CH_3), 4.48 (d, $J = 13.2$ Hz, 1H, –CH), 4.56 (d, $J = 13.2$ Hz, 1H, –CH), 7.25–7.29 (m, 2H, Ar-H), 7.33–7.40 (m, 4H, Ar-H), 7.45–7.53 (m, 3H, Ar-H), 7.62–7.64 (m, 2H, Ar-H), 7.72–7.75 (m, 2H, Ar-H), 8.13 (d, $J = 8.0$ Hz, 1H, Ar-H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 9.04, 57.39, 114.98, 119.48, 123.97, 124.10, 125.63, 125.75, 126.37, 129.11, 129.28, 130.71, 131.20, 133.89, 136.68, 138.38, 143.86. Mass (m/z) %: 393 (M^+−16, 65), 378 (34). Anal. calcd. for $C_{22}H_{19}NO_3S_2$: C, 64.52; H, 4.68; N, 3.42; S, 15.66%. Found: C, 64.68; H, 4.42; N, 3.27; S, 15.49%.

Preparation of Ethyl-1-phenylsulfonyl-2-phenylsulfinylmethylindole-3-carboxylate (2e)

The procedure was similar to that of **2a.** Yield: 0.12 g (80%). Mp: 110–112 °C. IR (KBr): 1074 (SO), 1180 (SO_2), 1368 (SO_2), 1728 (CO) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (t, $J = 7.3$ Hz, 3H, –CH_3), 4.30 (q, $J = 7.2$ Hz, 2H, –CH_2), 5.13 (d, $J = 12.7$ Hz, 1H, –CH), 5.43 (d, $J = 12.2$ Hz, 1H, –CH), 7.30–7.36 (m, 2H, Ar-H), 7.38–7.48 (m, 2H, Ar-H), 7.50–7.58 (m, 4H, Ar-H), 7.62 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.86 (d, $J = 8.3$ Hz, 2H, Ar-H), 8.07 (d, $J = 6.8$ Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.22, 55.26, 60.89, 114.55 (2C), 114.60, 122.43, 122.47, 124.29, 124.79, 125.97, 126.76, 128.96, 129.48, 131.27, 134.45, 136.15, 136.20, 138.14, 143.66, 163.99. Mass (m/z) %: 451 (M^+, 24), 311 (24). Anal. calcd. for $C_{24}H_{21}NO_5S_2$: C, 61.65; H, 4.53; N, 3.00; S, 13.72%. Found: C, 61.49; H, 4.39; N, 3.24; S, 13.91%.

Preparation of Ethyl-1-phenysulfonyl-5-methoxy-2-phenylsulfinylmethylindole-3-carboxylate (2f)

The procedure was similar to that of **2a.** Yield: 0.3 g (85%). Mp: 93–94 °C. IR (KBr): 1079 (SO), 1181 (SO_2), 1362 (SO_2), 1702 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.39 (t, $J = 7.2$ Hz, 3H, $-CH_3$), 3.83 (s, 3H, $-CH_3$), 4.29 (q, $J = 7.2$ Hz, 2H, $-CH_2$), 5.11 (d, $J = 12.3$ Hz, 1H, –CH), 5.39 (d, $J = 12.3$ Hz, 1H, –CH), 6.97 (dd, $J = 2.7$ & 9.3 Hz, 1H, Ar-H), 7.40–7.61 (m, 9H, Ar-H), 7.81 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.99 (d, $J = 9.3$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.21, 55.39, 55.52, 60.87, 104.45, 115.31, 115.49, 124.30, 126.43, 126.64, 128.32, 128.97, 129.13, 130.80, 131.30, 134.43, 136.33, 138.13, 143.62, 157.30, 163.98. Anal. calcd. for $C_{25}H_{23}NO_6S_2$: C, 60.35; H, 4.66; N, 2.81%. Found: C, 60.13; H, 4.65; N, 2.60%.

Preparation of Ethyl-3-[2-(phenylthiomethyl)-1-(phenylsulfonyl)-indol-3-yl]acrylate (2g)

The procedure was similar to that of **2a**. Yield: 0.25 g (80%). Mp: 118 °C. IR (KBr): 1040 (SO), 1162 (SO_2), 1360 (SO_2), 1690 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.27 (t, $J = 7.1$ Hz, 3H, $-CH_3$), 4.19 (q, $J = 7.2$ Hz, 2H, $-CH_2$), 4.54 (d, $J = 13.2$ Hz, 1H, –CH), 4.70 (d, $J = 13.2$ Hz, 1H, –CH), 6.36 (d, $J = 15.9$ Hz, 1H, –CH), 7.19–7.27 (m, 2H, Ar-H), 7.29–7.33 (m, 6H, Ar-H), 7.34–7.41 (m, 3H, Ar-H), 7.46-7.49 (m, 3H, Ar-H), 7.70 (d, $J = 7.8$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.43, 54.04, 60.15, 111.94, 113.38, 115.30, 120.63, 121.72, 124.10, 125.06, 128.07, 128.28, 129.38, 134.32, 134.58, 136.56, 136.85, 167.50. Mass (m/z) %: 477 (M^+-16, 46%), 336 (27).

Preparation of Ethyl-1-phenylsulfonyl-3-phenylsulfinylmethylindole-2-carboxylate (2h)

The procedure was similar to that of **2a**. Yield: 0.15 g (85%). Mp: 118–120 °C. IR (KBr): 1082 (SO), 1190 (SO_2), 1370 (SO_2), 1720 (CO) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 1.28 (t, $J = 7.2$ Hz, 3H, $-CH_3$), 4.01–4.37 (m, 4H, $-CH_2$), 7.04–7.32 (m, 8H, Ar-H), 7.38 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.49 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.84 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.94 (d, $J = 8.3$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.95, 53.64, 62.41, 115.29, 115.42, 117.94, 120.72, 124.10, 124.35, 127.16, 127.35, 128.86, 129.02, 130.82, 131.40, 134.00, 136.75, 137.88, 142.83, 161.11. Anal. calcd. for $C_{24}H_{21}NO_5S_2$: C, 61.65; H, 4.53; N, 3.00; S, 13.72%. Found: C, 61.39; H, 4.79; N, 3.25; S, 13.58%.

Preparation of Ethyl-5-methoxy-1-phenylsulfonyl-3-phenylsulfinylmethylindole-2-carboxylate (2i)

The procedure was similar to that of **2a**. Yield: 0.27 g (90%). Mp: 92–93 °C. IR (KBr): 1078 (SO), 1187 (SO_2), 1373 (SO_2), 1720 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.37 (t, $J = 7.1$ Hz, 3H, $-CH_3$), 3.69 (s, 3H, $-CH_3$), 4.23–4.42 (m, 4H, $-CH_2$), 6.52 (d, $J = 2.4$ Hz, 1H, –CH), 6.97 (dd, $J = 2.4$ & 6.9 Hz, 1H, –CH), 7.24–7.40 (m, 5H, Ar-H), 7.45 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.56 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.83–7.91 (m, 3H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.96, 53.72, 55.55, 62.39, 102.11, 116.43, 117.12, 118.20, 124.17, 127.12, 128.97, 130.02, 131.29, 131.37, 131.49, 133.95, 137.53, 143.00, 157.03, 161.10. Anal. calcd. for $C_{25}H_{23}NO_6S_2$: C, 60.35; H, 4.66; N, 2.81; S, 12.89%. Found: C, 60.10; H, 4.89; N, 3.04; S, 12.66%.

Preparation of 1-Phenylsulfonyl-4-phenylsulfinylmethylindole (2j)

The procedure was similar to that of **2a**. Yield: 0.13 g (85%). Mp: 131–132 °C. IR (KBr): 1073 (SO), 1180 (SO_2), 1376 (SO_2) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.14 (d, $J = 12.2$ Hz, 1H, –CH), 4.34 (d, $J = 12.7$ Hz, 1H, –CH), 6.37 (d, $J = 3.9$ Hz, 1H, Ar-H), 6.90 (d, $J = 7.3$ Hz, 1H, Ar-H), 7.15–7.33 (m, 7H, Ar-H), 7.45–7.59 (m, 3H, Ar-H), 7.86 (d, $J = 7.3$ Hz, 2H, Ar-H), 7.95 (d, $J = 8.3$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 61.25, 106.88, 113.56, 122.12, 124.18, 124.61, 125.78, 126.54, 126.80, 128.73, 129.31, 131.11, 131.18, 134.00, 134.66, 138.07, 142.71. Anal. calcd. for $C_{21}H_{17}NO_3S_2$: C, 63.77; H, 4.33; N, 3.54; S, 16.22%. Found: C, 63.94; H, 4.51; N, 3.31; S, 16.03%.

Preparation of 1-Phenylsulfonyl-2-methyl-3-(phenylsulfinyl)indole (2k)

The procedure was similar to that of **2a**. Yield: 0.15 g (90%). Mp: 136–138°C. IR (KBr): 1373 (SO_2), 1183 (SO_2), 1093 (SO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.93$ (s, 3H, $-CH_3$), 7.10 (t, $J = 7.5$ Hz, 1H, Ar-H), 7.26 (t, 1H, $J = 8.4$ Hz, Ar-H), 7.41–7.51 (m, 6H, Ar-H), 7.54–7.61 (m, 3H, Ar-H), 7.84 (d, $J = 7.5$ Hz, 2H, Ar-H), 8.18 (d, 1H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.76, 114.49, 120.02, 121.78, 124.3, 124.45, 124.89, 125.32, 126.52, 129.12, 129.67, 130.29, 134.48, 136.52, 138.63, 141.18, 143.26. MS: m/z, 395 (M^+, 100), 379 (10). Anal. calcd. for $C_{21}H_{17}NO_3S_2$: C, 63.77; H, 4.33; N, 3.54%. Found: C, 63.92; H, 4.54; N, 3.36%.

Preparation of 1-Phenylsulfonyl-2,3-bis((phenylsulfinyl)methyl)indole (2l)

To a solution of H_2O_2 50% (0.54 mL, 7.99 mmol) in acetonitrile (10 mL), 40% aq. HF (0.6 mL, 11.97 mmol) was added and stirred for 30 min at room temperature. To the reaction mixture, a solution of sulfide **1l** (0.5 g, 0.99 mmol) in acetonitrile (10 mL) was added, and stirring was continued for another 2 h. After the sulfide **1l** was consumed (monitored by TLC), the reaction mixture was quenched with ice water (20 mL), extracted with ethyl acetate (2×15 mL), and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (hexane–EA; 3:2) afforded sulfoxide **2l** as a colorless solid. (0.45 g, 85%). Yield: 0.14 g (85%). Mp: 166–168 °C. IR (KBr): 1369 (SO_2), 1180 (SO_2), 1080 (SO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.88 (d, 1H, $J = 14.1$ Hz, –CH), 4.40–4.49 (m, 1H, –CH), 4.69 (d, $J = 14.1$ Hz, 2H, –CH), 6.58 (d, $J = 7.8$ Hz, 1H, Ar-H), 6.90–6.96 (m, 3H, Ar-H), 7.04–7.31 (m, 4H, Ar-H), 7.45–7.61 (m, 6H, Ar-H), 7.72–7.82 (m, 4H, Ar-H), 8.05 (d, $J = 8.4$ Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 51.08, 52.46, 56.49, 57.64, 114.89, 115.19, 118.57, 123.95, 123.99, 125.54, 126.63, 126.67, 128.55, 128.91, 129.18, 129.30, 129.36, 129.43, 129.78, 131.07, 131.26, 131.34, 134.14, 136.08, 137.93, 142.01, 143.00. (^1H and ^{13}C NMR signals are more due to diastereomeric mixture.) Mass (m/z) %: 533 (M^+, 100), 408 (90), 305 (20). Anal. calcd. for $C_{28}H_{23}NO_4S_3$: C, 63.02; H, 4.34; N, 2.62%. Found: C, 63.28; H, 4.52; N, 2.31%.

Preparation of 2,3-Bis((phenylsulfinyl)methyl)benzo[*b*]thiophene (2m)

The procedure was similar to that of **2a**. Yield: 0.15 g (80%). Mp: 160–162 °C. IR (KBr): 1082 (SO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.93, (dd, $J = 13.8$ Hz and 3.6 Hz, 1H, Ar-H), 3.99–4.13 (m, 2H, Ar-H), 4.18 (dd, $J = 14.1$ Hz & 3.6 Hz, 1H, Ar-H), 7.27–7.36 (m, 7H, Ar-H), 7.39–7.47 (m, 6H, Ar-H), 7.29–7.75 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 54.35, 54.74, 56.42, 56.66, 121.75, 122.21, 124.13, 124.48, 124.6, 124.83, 125.01, 125.16, 129.02, 129.17, 131.51, 132.30, 138.64, 138.95, 142.66, 142.84, 143.04. (^1H and ^{13}C NMR signals are more due to diastereomeric mixture.) Mass (m/z) %: 410 (M^+, 40), 284 (50), 272 (40).

Preparation of 1-Phenylsulfonyl-3,4-dibromo-2,5-bis((phenylsulfinyl)methyl)pyrrole (2n)

The procedure was similar to that of **2a.** Yield: 0.15 g (85%). Brown liquid. IR (KBr): 1382 (SO_2), 1175 (SO_2), 1085 (SO) cm^{-1}. ^1H NMR

($CDCl_3$, 300 MHz): δ 4.10–4.58 (m, 4H, $-CH_2$), 7.21–7.34 (m, 3H, Ar-H) 7.47–7.83 (m, 12H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.03, 57.51, 60.41, 124.52, 124.34, 125.74, 126.32, 126.4, 127.18, 127.56, 129.06, 129.39, 130.21, 130.24, 131.74, 142.83. (^1H and ^{13}C NMR signals are more due to diastereomeric mixture.) Anal. calcd. for $C_{24}H_{19}Br_2NO_4S_3$: C, 44.94; H, 2.99; N, 2.18%. Found: C, 44.70; H, 2.78; N, 2.42%.

Preparation of 1,3,5-Trimethyl-2,4,6-tris((phenylsulfinyl)methyl)benzene (2o)

To a solution of 50% H_2O_2 (0.35 mL, 4.93 mmol) in acetonitrile (5 mL), 40% aq. HF (0.37 mL, 7.4 mmol) was added and stirred for 30 min at room temperature. To the reaction mixture, a solution of sulfide (0.2 g, 0.4 mmol) in acetonitrile (5 mL) was added, and stirring was continued for another 2 h. After the sulfide compound **(2o)** was consumed (monitored by TLC), the reaction mixture was quenched with ice water (15 mL), extracted with ethyl acetate (2×10 mL), and dried (Na_2SO_4). Removal of solvent, followed by column chromatographic purification (hexane–EA; 1:1) afforded **(2o)** as a colorless solid. Yield: 0.25 g (80%). Mp: 190 °C. IR (KBr): 1082 (SO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.74–2.16 (m, 9H, $-CH_3$), 3.99–4.13 (m, 3H, $-CH_2$), 4.34–4.45 (m, 3H, $-CH_2$), 7.48–7.52 (m, 15H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): 17.62, 17.81, 59.53, 59.65, 123.96, 124.55, 126.86, 126.99, 129.22, 131.33, 131.39, 131.47, 139.15, 139.32, 143.36, 143.51. (^1H and ^{13}C NMR signals are more due to diastereomeric mixture.) Mass (m/z) %: 534 (M^+, 60%), 408 (20), 282 (10).

1-Phenylsulfonyl(2-((phenylsulfonyl)methyl)-indol-3-yl)ethanone (3)

Colorless solid. Yield: 0.07 g (10%). Mp: 190 °C. IR (KBr): 1385 (SO_2), 1173 (SO_2) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 2.62 (s, 3H, $-CH_3$), 5.70 (s, 2H, $-CH_2$), 7.34–7.37 (m, 2H, Ar-H), 7.39–7.45 (m, 2H, Ar-H), 7.50–7.55 (m, 3H, Ar-H), 7.64–7.69 (m, 1H, Ar-H), 7.75–7.76 (m, 1H, Ar-H), 7.80–7.84 (m, 4H, Ar-H), 7.98–8.02 (m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): 31.80, 52.42, 115.28, 120.95, 124.77, 125.99, 126.43, 126.85, 128.70, 129.12, 129.41, 130.51, 133.95, 134.42, 136.52, 138.04, 138.93, 196.57.

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