Sulfite-Promoted One-Pot Synthesis of Sulfides by Reaction of Aryl Disulfides with Alkyl Halides

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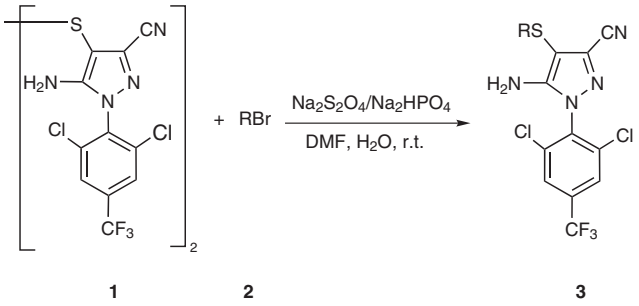
Abstract: A sodium dithionite, sodium thiosulfate and rongalite promoted one-pot synthesis of aryl alkyl sulfides at room temperature has been developed. The reactions of a range of disulfides with alkyl halides proceeded smoothly in the presence of rongalite. Possible reaction pathways are discussed and the effects of these sulfites on disulfides are investigated. The important features of this protocol are metal-free, strong-base-free, and mild reaction conditions, operational simplicity, short reaction times and high yields of products.

Key words: disulfide, sulfide, rongalite, electron transfer, one-pot reaction



1 2 3

Scheme 1

Organic sulfides are useful chemical intermediates in organic synthesis,[1] with the carbon–sulfur bond found in many molecules of biological, pharmaceutical and materials interest.[2] The formation of aryl alkyl sulfides is usually achieved by the reaction of a thiolate or thiol with an organic halide. However, these reactions require harsh conditions and the yields are dependent on the solvent, the presence of a strongly basic catalyst and the acidity of thiol.[3] Recently, Yin and Pidgeon[3c] reported a high-yielding method for the preparation of unsymmetrical sulfides using the very strong base, *n*-butyllithium, whilst Shah et al.[4] have developed a milder synthetic approach to thioethers using cesium fluoride in acetonitrile. Transition-metal-mediated alkylations have also been developed as a mild and efficient preparation of thioethers.[5] For example, a one-pot and base-free conversion of disulfides to sulfides using an in situ generated organocobalt(III) reagent has been reported,[6] as has a general and efficient copper-catalyzed carbon–sulfur bond-formation reaction.[7] Indium(I) iodide mediated cleavage of disulfides and subsequent reaction with alkyl halides at room temperature can also generate the desired products in high yields.[8] Although these metal-mediated synthetic methods have improved the synthesis of thioethers, the development of a one-step synthesis of aryl alkyl sulfides using inexpensive, easily obtainable reagents under neutral conditions is still a goal. Recently, we reported the use of sodium dithionite for the synthesis of pyrazolyl alkyl sulfides **3**,[9] which has insecticidal activity (Scheme 1).

Our interest in exploring and extending the application of this reaction, prompted us to study the sulfite promoted, one-pot synthesis of aryl alkyl sulfides. Wakselman et al.[10] have previously demonstrated that perfluoroalkyl sulfides could be prepared by reactions of perfluoroalkyl halides with disulfides, in the presence of sulfoxylate anion radical precursors. They found that perfluoroalkyl radicals could be easily generated by single-electron reduction of perfluoroalkane halides with inexpensive dithionite or rongalite. However, the sulfite-mediated reduction of aryl disulfides and the synthesis of aryl alkyl sulfides have not yet been investigated. Herein, we wish to report an efficient, one-pot synthesis of aryl alkyl sulfides via reaction of diaryl disulfides with alkyl halides, at room temperature, using sodium dithionite,[11] sodium thiosulfate or rongalite ($HOCH_2SO_2Na$).[12]

Previously we used the $Na_2S_2O_4/Na_2HPO_4$ reaction system for the synthesis of aryl alkyl sulfides, using *N*,*N*-dimethylformamide as a cosolvent with water, at room temperature.[13] Although this synthetic method was very simple, it produced the corresponding alkyl aryl sulfides in only moderate yields and could not be applied to the reaction of alkyl chloride. Our initial aim was to explore whether other, inexpensive sulfites may be more effective for the synthesis of sulfides, and to optimize the reaction conditions through the use of an inorganic salt as a mild base. For this purpose, we systematically evaluated the role of the base and the sulfites in the reaction. We found that potassium carbonate was the most effective base and that when the reaction was conducted under the conditions shown in Scheme 2, disulfide **4b** was converted cleanly. Rongalite was very effective in this reaction, taking only 15 minutes for the conversion of **4b** to **6b** to proceed to completion in high yield (95%). In contrast, when either sodium dithionite or sodium thiosulfate was employed,

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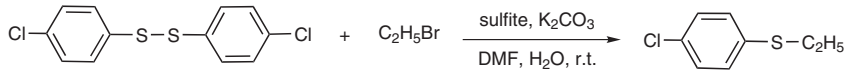


4b 5b 6b

Scheme 2 *Reagents and conditions*: K_2CO_3(2 equiv), sulfite (3 equiv), DMF, H_2O (cat.); sulfite = $Na_2S_2O_4$, $Na_2S_2O_3{\cdot}5H_2O$ or $HOCH_2SO_2Na$ (rongalite).

Table 1 Reaction of **4b** with *n*-Butyl Halides[a]

Entry	X	$Na_2S_2O_4$		$Na_2S_2O_3{\cdot}5H_2O$		$HOCH_2SO_2Na$	
		Time (min)	Yield[b] (%)	Time	Yield[b] (%)	Time (min)	Yield[b] (%)
1	**5f**	50	38	4 h	21	30	81
2	**5g**	30	51	3 h	52	15	92
3	**5h**	20	82	20 min	81	10	96

[a] Reaction conditions: Sulfite (3 equiv), K_2CO_3 (2 equiv), H_2O (cat.), DMF (5mL), r.t.
[b] Isolated yields based on compound **4b**.

the reaction required more time and the product **6b** formed in only moderate yield. It was also found that the presence of catalytic amounts of water could accelerate the reaction and increase the yield.

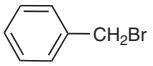
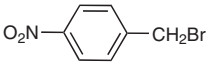
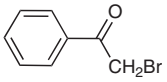
To better understand the effect of each sulfite on this reaction, we investigated the reactions of a range of butyl halides with compound **4b** (Table 1). It can be seen that rongalite was the most effective in this reaction, with all the halides reacting in high yields. Though alkyl chlorides were less active, the reaction of **5f** with compound **4b** still went to completion within 30 minutes, in good yield (81%), in the presence of rongalite. In contrast, when the reaction was conducted in the presence of sodium dithionite or sodium thiosulfate, yields were significantly less, particularly in the case of the chloride **5f**. Iodide **5h** reacted in good yield in all cases (Table 1, entry 3).

In order to explore the potential of rongalite in the synthesis of sulfides, we reacted a broad spectrum of organic halides with diaryl disulfides, to form the corresponding alkyl aryl sulfides. The results are presented in Table 2. We found that alkyl, allylic and benzyl halides as well as bromoacetophenone, all participated in this reaction to form the corresponding products. In general, all reactions were rapid (less than 30 min) and high yielding. Although the synthesis of unsymmetrical sulfides, having branched alkyl chains, was more difficult, the problems were overcome by extending the reaction time (entries 5, 17 and 28). However, aryl halides, vinyl halides, benzyl disulfide and alkyl disulfide, remained inactive in this reaction. It is worth noting that the reactions of **4b** or **4c** with alkyl chlorides smoothly formed the desired products in good yields (entries 15, 18, 26 and 29). However, although the starting disulfide was seen to be completely consumed, the reaction of **4a** with alkyl chloride gave the product only in low yields (entries 3 and 6).

Table 2 Synthesis of Compounds **6a–y** in the Presence of $HOCH_2SO_2Na$

Entry	Disulfide **4**	R′X **5**	Product **6**	Time (min)	Yield[a] (%)
1	**4a**	**5a**; MeI	**6a**	10	97
2	**4a**	**5b**; EtBr	**6b**	15	94
3	**4a**	**5c**; EtCl	**6b**	30	13
4	**4a**	**5d**; *n*-PrBr	**6c**	15	93
5	**4a**	**5e**; *s*-PrBr	**6d**	20	76
6	**4a**	**5f**; *n*-BuCl	**6e**	30	12
7	**4a**	**5g**; *n*-BuBr	**6e**	15	91
8	**4a**	**5h**; *n*-BuI	**6e**	15	96

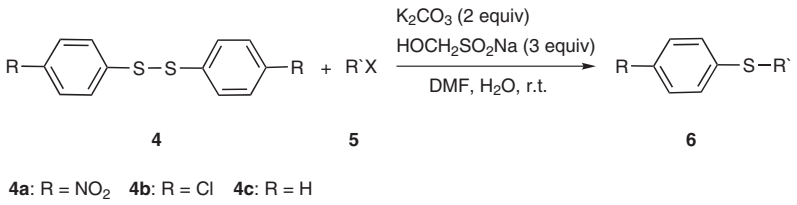
Table 2 Synthesis of Compounds **6a–y** in the Presence of $HOCH_2SO_2Na$ (continued)

Entry	Disulfide **4**	R′X **5**	Product **6**	Time (min)	Yield[a] (%)
9	**4a**	 **5i**	**6f**	15	95
10	**4a**	 **5j**	**6g**	15	96
11	**4a**	 **5k**	**6h**	10	96
12	**4a**	 **5l**	**6i**	15	92
13	**4b**	**5a**	**6j**	15	98
14	**4b**	**5b**	**6k**	15	95
15	**4b**	**5c**	**6k**	30	83
16	**4b**	**5d**	**6l**	15	93
17	**4b**	**5e**	**6m**	20	78
18	**4b**	**5f**	**6n**	30	81
19	**4b**	**5g**	**6n**	15	92
20	**4b**	**5h**	**6n**	10	96
21	**4b**	**5i**	**6o**	15	95
22	**4b**	**5j**	**6p**	15	96
23	**4b**	**5k**	**6q**	10	97
24	**4b**	**5l**	**6r**	15	93
25	**4c**	**5b**	**6s**	15	93
26	**4c**	**5c**	**6s**	30	82
27	**4c**	**5d**	**6t**	15	93
28	**4c**	**5e**	**6u**	25	78
29	**4c**	**5f**	**6v**	30	83
30	**4c**	**5g**	**6v**	15	92
31	**4c**	**5h**	**6v**	10	96
32	**4c**	**5k**	**6y**	15	96

[a] Isolated yields, based on compound **4**.

The effect of sulfites on the disulfides was explored by running the reaction in the absence of any alkyl halide. Though disulfide **4a** was quickly reduced by all three sulfites, with the starting material being completely consumed within ten minutes (Table 3), in the cases of disulfides **4b** or **4c**, some starting material was seen to remain even after three hours reaction time. Upon addition of butyl bromide and additional sulfite, however, the residual disulfide disappeared and the formation of the corresponding sulfide could be followed by TLC.

Theoretical analysis of the reactions of disulfides, involving electron-transfer (ET) processes, have previously been reported.[14–15] Antonello et al.[14] suggested that the S–S bond of diaryl disulfides bearing electron-donating or mildly electron-withdrawing groups, was more susceptible to cleavage. This observation may explain why the reduction of **4a** took place so much more readily than those of **4b** and **4c** (Table 3).

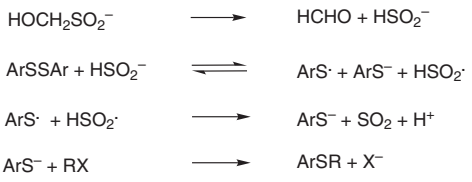


Scheme 3

Table 3 The Effect of Sulfites on Disulfides

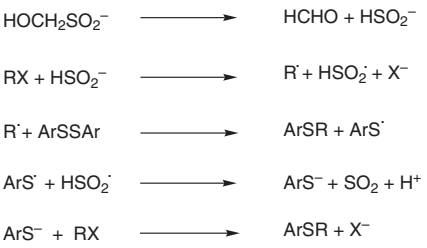
Disulfide	$Na_2S_2O_4$		$Na_2S_2O_3·5H_2O$		$HOCH_2SO_2Na$	
	Time	Reduced disulfide (%)	Time	Reduced disulfide (%)	Time	Reduced disulfide (%)
4a	10 min	100	10 min	100	10 min	100
4b	3 h	46	3 h	68	3 h	35
4c	3 h	41	3 h	63	3 h	32

It has been noted that sodium dithionite[11i–k] and rongalite[12d–i] are capable of producing the perfluoroalkyl free radicals via dehalogenation of alkyl halides. The thus-formed SO_2^- radical anion can be readily detected by electron spin resonance in solutions of decomposing $S_2O_4^{2-}$.[16] According to the above observations, the possibility of ET-induced cleavage,[13] together with the mechanism suggested by Dolbier et al.,[12g] we speculated that the sulfites could form a radical anion and serve as a source of electrons for both the cleavage of the S–S bond or for dehalogenation of alkyl halides. Two possible reaction pathways for the formation of alkyl aryl sulfides are shown in Schemes 4–7. Sodium dithionite and rongalite were taken to illustrate the pathways. The reactions apparently proceed through the intermediacy of a radical and an anion, which are formed readily by the reaction of an electron released by the sulfite with the diaryl disulfide. Thus, the sulfite initially induces the cleavage of the S–S bond, to yield a radical (ArS) and an anion (ArS^-). The anion (ArS^-) could then be alkylated by the alkyl halide (Schemes 4 and 6). Alternatively, the reaction could involve aryl disulfides reacting with alkyl radicals, generated by the reduction of alkyl halides with either rongalite or sodium dithionite (Schemes 5 and 7).

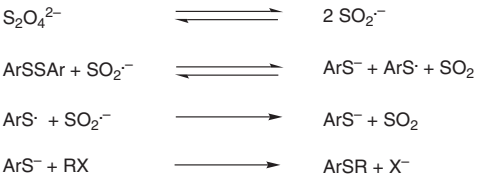


Scheme 4 Possible reaction pathway 1 (with rongalite)

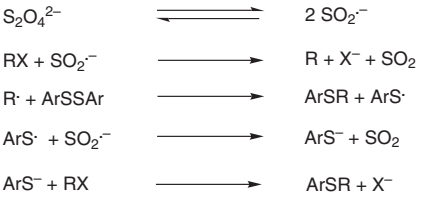
In summary, a one-pot, efficient synthetic method for the preparation of unsymmetrical sulfides by the treatment of diaryl disulfide with alkyl halides in the presence of rongalite has been developed. The present method has the following noteworthy features: (1) the high yield of alkyl aryl sulfides; (2) a simple operation; (3) mild reaction conditions; (4) metal-free and strong-base-free reaction system and (5) inexpensive sulfite reagents. A wide range of aryl alkyl sulfides were synthesized successfully using this reaction system.



Scheme 5 Possible reaction pathway 2 (with rongalite)



Scheme 6 Possible reaction pathway 1 (with sodium dithionite)



Scheme 7 Possible reaction pathway 2 (with sodium dithionite)

All melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a FT-Bruker AT-300 instrument using TMS as an internal standard and $CDCl_3$ as the solvent. Coupling constants (*J*) are given in Hz. Compounds were characterized by elemental analysis using a Carlo-Erba EA1112 instrument. IR spectra were mea-

sured on a Bruker VECTOR55 instrument. Silica gel 60 GF254 was used for analytical and preparative TLC.

General Procedure

To the solution of aryl disulfide **4** (0.32 mmol) in DMF (5 mL; for **4a**, 8 mL), K_2CO_3 (0.09 g, 0.64 mmol) was added. The mixture was stirred for 2 min, then alkyl halide **5** (0.64 mmol; for volatile alkyl halides, 0.7 mmol) was injected into the mixture, followed by $HOCH_2SO_2Na$ (rongalite; 0.113 g, 0.96 mmol) and H_2O (2 drops). After the time indicated in Table 2, H_2O (25 mL) was added and the mixture was extracted with Et_2O (3 × 10 mL). The organic layer was taken, washed with H_2O (2 × 15 mL), dried over $MgSO_4$, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (EtOAc–petroleum) to afford the desired product **6**.

Methylthio-4-nitrobenzene (6a)

Yellow solid; mp 71–72 °C.

IR (KBr): 2912, 1581, 1506, 1332, 838 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, CH_3), 7.28 (dd, *J* = 1.9 Hz, *J* = 9.0 Hz, 2 H, Ar), 8.14 (dd, *J* = 1.9 Hz, *J* = 9.0 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, CD_3Cl): δ = 14.8, 123.9, 125.0, 144.7, 148.8.

Anal. Calcd for $C_7H_7NO_2S$: C, 49.69; H, 4.17. Found: C, 49.51; H, 4.03.

Ethylthio-4-nitrobenzene (6b)

Yellow solid; mp 39–40 °C (Lit.[4] 41–42 °C).

IR (KBr): 3093, 2974, 2923, 1624, 1580, 1507, 1331, 841, 796, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.4 Hz, 3 H, CH_3), 2.56 (q, *J* = 7.4 Hz, 2 H, CH_2), 7.31 (dd, *J* = 1.9 Hz, *J* = 7.1 Hz, 2 H, Ar), 8.12 (dd, *J* = 1.9 Hz, *J* = 7.1 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, CD_3Cl): δ = 13.7, 26.0, 123.9, 126.0, 144.9, 147.9.

Anal. Calcd for $C_8H_9NO_2S$: C, 52.44; H, 4.95. Found: C, 52.32; H, 4.81.

1-Propylthio-4-nitrobenzene (6c)

Yellow liquid.

IR (KBr): 3098, 2964, 2926, 2871, 1583, 1510, 1468, 1335, 843, 791, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.76 (m, 2 H, CH_2), 3.01 (t, *J* = 7.3 Hz, 2 H, CH_2), 7.31 (dd, *J* = 1.8 Hz, *J* = 7.0 Hz, 2 H, Ar), 8.12 (dd, *J* = 1.8 Hz, *J* = 7.0 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, CD_3Cl): δ = 13.4, 21.8, 33.8, 123.8, 125.9, 144.7, 148.0.

Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.63; H, 5.48.

1-(1-Methylethylthio)-4-nitrobenzene (6d)

Yellow solid; mp 44–45 °C (Lit.[4] 46–47 °C).

IR (KBr): 2973, 2928, 2871, 1575, 1505, 1458, 1336, 851, 834, 740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.7 Hz, 6 H, CH_3), 3.60 (m, 1 H, CH), 7.36 (dd, *J* = 2.0 Hz, *J* = 9.0 Hz, 2 H, Ar), 8.12 (dd, *J* = 2.6 Hz, *J* = 9.0 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, CD_3Cl): δ = 23.6, 37.5, 124.8, 128.6, 146.0, 148.0.

Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.60; H, 5.53.

1-Butylthio-4-nitrobenzene (6e)

Yellow liquid.[17]

IR (KBr): 3099, 2959, 2930, 2870, 1579, 1511, 1477, 1337, 851, 741 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.49 (m, 2 H, CH_2), 1.72 (m, 2 H, CH_2), 3.02 (t, *J* = 7.3 Hz, 2 H, CH_2), 7.31 (dd, *J* = 1.8 Hz, *J* = 8.9 Hz, 2 H, Ar), 8.12 (dd, *J* = 1.8 Hz, *J* = 7.1 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, CD_3Cl): δ = 13.5, 22.0, 30.5, 31.6, 123.9, 126.0, 144.9, 148.1.

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20. Found: C, 56.71; H, 6.04.

1-Nitro-4-(2-propenylthio)benzene (6f)

Yellow solid; mp 38–39 °C (Lit.[4] 39–41 °C).

IR (KBr): 3092, 2920, 1628, 1579, 1499, 1331 936, 840 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.68 (d, *J* = 6.5 Hz, 2 H, CH_2), 5.22 (dd, *J* = 1.0 Hz, *J* = 10.5 Hz, 1 H, CH), 5.33 (dd, *J* = 1.0 Hz, *J* = 17.0 Hz, 1 H, CH), 5.85 (m, 1 H, CH), 7.34 (dd, *J* = 2.0 Hz, *J* = 7.0 Hz, 2 H), 8.12 (dd, *J* = 2.0 Hz, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.2, 119.0, 123.8, 126.8, 131.9, 145.2, 146.8.

Anal. Calcd for $C_9H_9NO_2S$: C, 55.37; H, 4.65. Found: C, 55.16; H, 4.51.

1-Nitro-4-(phenylmethylthio)benzene (6g)

Yellow solid; mp 126–127 °C (Lit.[4] 128–129 °C).

IR (KBr): 2922, 1626, 1575, 1506, 1330, 839, 725 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.26 (s, 2 H, CH_2), 7.30 (m, 5 H, Ar), 7.38 (dd, *J* = 1.9 Hz, *J* = 7.5 Hz, 2 H, Ar), 8.12 (dd, *J* = 1.9 Hz, *J* = 7.5 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.0, 123.8, 126.8, 127.8 128.7 128.9, 135.4, 145.2, 147.3.

Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52. Found: C, 63.42; H, 4.38.

1-Nitro-4-(4-nitrophenylmethylthio)benzene (6h)

Yellow solid; mp 89–90 °C.

IR (KBr): 2851, 1597, 1577, 1518, 1334, 854, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.32 (s, 2 H, CH_2), 7.34 (dd, *J* = 2.0 Hz, *J* = 7.8 Hz, 2 H, Ar), 7.55 (dd, *J* = 2.0 Hz, *J* = 7.8 Hz, 2 H, Ar), 8.11 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 2 H, Ar), 8.19 (dd, *J* = 1.9 Hz, *J* = 7.9 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.5, 124.9, 125.0, 128.3, 130.4, 144.2, 146.2, 146.7, 148.4.

Anal. Calcd for $C_{13}H_{10}N_2O_4S$: C, 53.79; H, 3.47. Found: C, 53.46; H, 3.32.

2-[(4-Nitrophenyl)thio]-1-phenyl-1-ethanone (6i)

Yellow solid; mp 115–116 °C.

IR (KBr): 2913, 1626, 1672, 1580, 1503, 1461, 1331, 842, 747, 679 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.46 (s, 2 H, CH_2), 7.42 (d, *J* = 8.9 Hz, 2 H, Ar), 7.50 (m, 2 H, Ar), 7.63 (d, *J* = 7.4 Hz, 1 H, Ar), 8.00 (d, *J* = 7.5 Hz, 2 H, Ar), 8.13 (d, *J* = 8.9 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.1, 124.0, 127.1, 128.6, 128.9, 134.0, 134.9, 145.3, 145.6, 192.7.

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06. Found: C, 61.22; H, 3.89.

1-Chloro-4-methylthiobenzene (6j)
White liquid.

IR (KBr): 2920, 1625, 1476, 1431, 1099, 812 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.18 (dd, *J* = 1.9 Hz, *J* = 8.5 Hz, 2 H, Ar), 7.26 (dd, *J* = 1.9 Hz, *J* = 8.5 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0, 127.8, 128.9, 130.8, 137.0.

Anal. Calcd for C_7H_7ClS: C, 53.00; H, 4.45. Found: C, 52.85; H, 4.31.

1-Chloro-4-ethylthiobenzene (6k)
Colorless liquid.

IR (KBr): 3072, 2970, 2926, 2867, 1628, 1577, 1473, 1443, 1098, 814 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.4 Hz, 3 H, CH_3), 2.92 (q, *J* = 7.4 Hz, 2 H, CH_2), 7.25 (s, 4 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 27.9, 128.9, 130.3, 131.7, 135.1.

Anal. Calcd for C_8H_9ClS: C, 55.65; H, 5.25. Found: C, 55.48; H, 5.09.

1-Chloro-4-propylthiobenzene (6l)
Colorless liquid.

IR (KBr): 3072, 2962, 2926, 2869, 1628, 1577, 1470, 1098, 813 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.62 (m, 2 H, CH_2), 2.85 (t, *J* = 6.5 Hz, 2 H, CH_2), 7.22 (d, *J* = 5.1 Hz, 2 H, Ar), 7.26 (d, *J* = 5.1 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 22.4, 35.8, 128.9, 130.3, 131.6, 135.4.

Anal. Calcd for $C_9H_{11}ClS$: C, 57.90; H, 5.94. Found: C, 57.77; H, 5.77.

1-Chloro-4-(1-methylethylthio)benzene (6m)
Colorless liquid.

IR (KBr): 2958, 2927, 2866, 1490, 1447, 1094, 824 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.7 Hz, 6 H, CH_3), 3.34 (m, 1 H, CH), 7.26 (dd, *J* = 2.0 Hz, *J* = 6.7 Hz, 2 H, Ar), 7.33 (dd, *J* = 2.0 Hz, *J* = 6.7 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.0, 38.5, 128.9, 130.3, 133.2, 134.0.

Anal. Calcd for $C_9H_{11}ClS$: C, 57.90; H, 5.94. Found: C, 57.75; H, 5.81.

1-Chloro-4-butylthiobenzene (6n)
Colorless liquid.

IR (KBr): 2957, 2928, 2869, 1587, 1475, 1387, 1095, 812 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.45 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 2.90 (t, *J* = 7.2 Hz, 2 H, CH_2), 7.25 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 21.9, 31.1, 33.6, 128.9, 130.2, 131.6, 135.6.

Anal. Calcd for $C_{10}H_{13}ClS$: C, 59.84; H, 6.53. Found: C, 59.67; H, 6.31.

1-Chloro-4-(2-propenylthio)benzene (6o)
Colorless liquid.

IR (KBr): 3078, 3012, 2976, 2854, 1636, 1574, 1474, 1419, 1097, 813, 735 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.52 (d, *J* = 6.9 Hz, 2 H, CH_2), 5.08 (dd, *J* = 1.4 Hz, *J* = 7.2 Hz, 1 H, CH), 5.12 (dd, *J* = 1.4 Hz, *J* = 14.1 Hz, 1 H, CH), 5.85 (m, 1 H, CH), 7.26 (s, 2 H, Ar), 7.27 (s, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.4, 117.9, 128.9, 131.3, 132.3, 133.2, 134.3.

Anal. Calcd for C_9H_9ClS: C, 58.53; H, 4.91. Found: C, 58.36; H, 4.75.

1-Chloro-4-(phenylmethylthio)benzene (6p)
White solid; mp 49–50 °C.

IR (KBr): 2917, 1626, 1464, 1097, 810, 703 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.11 (s, 2 H, CH_2), 7.24 (s, 4 H, Ar), 7.31 (m, 5 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.2, 127.2, 128.5, 128.7, 128.9, 131.3, 132.4, 134.6, 137.0.

Anal. Calcd for $C_{13}H_{11}ClS$: C, 66.52; H, 4.72. Found: C, 66.41; H, 4.57.

1-Chloro-4-(4-nitrophenylmethylthio)benzene (6q)
Yellow solid; mp 64–65 °C.

IR (KBr): 3077, 2851, 1600, 1517, 1475, 1389, 1345, 1095, 810, 725 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.11 (s, 2 H, CH_2), 7.20 (dd, *J* = 2.8 Hz, *J* = 6.2 Hz, 2 H, Ar), 7.24 (dd, *J* = 2.8 Hz, *J* = 6.2 Hz, 2 H, Ar), 7.38 (dd, *J* = 2.3 Hz, *J* = 10.9 Hz, 2 H, Ar), 8.13 (dd, *J* = 1.9 Hz, *J* = 7.8 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.0, 124.6, 130.1, 130.4, 133.3, 133.8, 134.4, 145.9, 148.0.

Anal. Calcd for $C_{13}H_{10}ClNO_2S$: C, 55.82; H, 3.60. Found: C, 55.51; H, 3.61.

2-(4-Chlorophenylthio)-1-phenylethanone (6r)
White solid; mp 78–79 °C.

IR (KBr): 2941, 2899, 1683, 1625, 1473, 1090, 878, 742, 684 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.25 (s, 2 H, CH_2), 7.24 (dd, *J* = 2.0 Hz, *J* = 6.5 Hz, 2 H, Ar), 7.31 (dd, *J* = 2.0 Hz, *J* = 6.5 Hz, 2 H, Ar), 7.48 (m, 2 H, Ar), 7.58 (d, *J* = 7.4 Hz, 1 H, Ar), 7.94 (d, *J* = 8.6 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.2, 128.6, 128.7, 129.2 131.9, 133.1, 133.3, 133.6, 135.2, 193.7.

Anal. Calcd for $C_{14}H_{11}ClOS$: C, 64.00; H, 4.22. Found: C, 63.85; H, 4.08.

Ethylthiobenzene (6s)
Colorless liquid.

IR (KBr): 3057, 2971,2926, 1583, 1479, 1440, 738, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.3 Hz, 3 H, CH_3), 2.96 (q, *J* = 7.3 Hz, 2 H, CH_2), 7.16–7.21 (m, 1 H, Ar), 7.29–7.36 (m, 4 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 28.5, 126.6, 129.7, 129.9, 137.5.

Anal. Calcd for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.25; H, 7.11.

1-Propylthiobenzene (6t)
Colorless liquid.

IR (KBr): 3058, 2961, 2927, 1584, 1479, 1438, 737, 690 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.68 (m, 2 H, CH_2), 2.91 (t, *J* = 7.2 Hz, 2 H, CH_2), 7.17–7.20 (m, 1 H, Ar), 7.26–7.37 (m, 4 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 23.4, 36.5, 126.5, 129.6, 129.8, 137.8.

Anal. Calcd for $C_9H_{12}S$: C, 71.00; H, 7.94. Found: C, 70.75; H, 7.76.

1-(1-Methylethylthio)benzene (6u)
Colorless liquid.

IR (KBr): 3056, 2962, 2923, 1582, 1475, 1439, 1382, 742, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (d, *J* = 6.7 Hz, 6 H, CH_3), 3.39 (m, 1 H, CH), 7.20–7.33 (m, 3 H, Ar), 7.40–7.43 (d, *J* = 7.7 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 39.1, 127.5, 129.6, 132.7, 136.4.

Anal. Calcd for $C_9H_{12}S$: C, 71.00; H, 7.94. Found: C, 70.78; H, 7.81.

1-Butylthiobenzene (6v)
Colorless liquid.[7b]

IR (KBr): 3058, 2957, 2928, 2869, 1582, 1478, 1438, 737, 689 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.45 (m, 2 H,CH_2), 1.65 (m, 2 H, CH_2), 2.93 (t, *J* = 7.3 Hz, 2 H, CH_2), 7.26–7.35 (m, 5 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 21.9, 31.2, 33.2, 127.1, 128.9, 129.0, 137.0.

Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49. Found: C, 71.98; H, 8.27.

1-Nitro-4-(phenylthiomethyl)benzene (6y)
Yellow solid; mp 70–71 °C.

IR (KBr): 2926, 2846, 1602, 1576, 1514, 1477, 1435, 858, 742 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.14 (s, 2 H, CH_2), 7.22–7.30 (m, 5 H, Ar), 7.39 (d, *J* = 8.6 Hz, 2 H, Ar), 8.12 (d, *J* = 8.6 Hz, 2 H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.8, 124.5, 128.1, 129.9, 130.4, 131.9, 135.6, 146.4, 147.9.

Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52. Found: C, 63.37; H, 4.23.

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