Novel efficient aromatic arylthiolation by disulfide radical cations generated by oxidation of diaryl disulfides

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The disulfide radical cation was generated by oxidation of diphenyl disulfide using H_2SO_4 in CF_3CO_2H or $SbCl_5$ in CH_2Cl_2, and allowed to react with benzene, toluene, ethylbenzene, chlorobenzene, anisole and alkyl phenyl sulfides to give efficiently *para*-substituted diphenyl sulfides along with a small amount of the *ortho*-isomers. The intermediacy of the radical cation in this aromatic phenylthiolation is consistent with the evidence derived from a Hammett plot with $\rho = -7.0$ (using $SbCl_5$ in CH_2Cl_2), from effects of oxidants, counter-anions and solvents and from electronic absorptions (540 and 650 nm). Using di-4-anisyl, di-4-tolyl and di-4-chlorophenyl disulfides instead of diphenyl disulfide, the aromatic arylthiolation similarly occurs *via* radical cations from their disulfides.

Sulfide radical cations have been proposed to be intermediates in the oxidation process of sulfides[1–3] and to be capable of electrophilic reactions.[4–6] Disulfide radical cations have been detected spectroscopically.[7–10] No one has proved that disulfide radical cations act as reactive species in the reaction of thiolation involving S–S scission because the S–S bond is stronger than that in the unoxidised disulfide by a partial π-character.[11] We are the first to report here that disulfide radical cations generated by oxidation of diaryl sulfides undergo efficiently an aromatic arylthiolation to give preferentially *para*-substituted diaryl sulfides.

The present method for synthesis of diaryl sulfides compared to the methods in the literature[12–19] is valuable since simple reaction conditions and inexpensive starting materials are used. The results are of particular interest as polymers possessing arylthio groups have recently found applications as plastic lenses with high refractive index.[20–22]

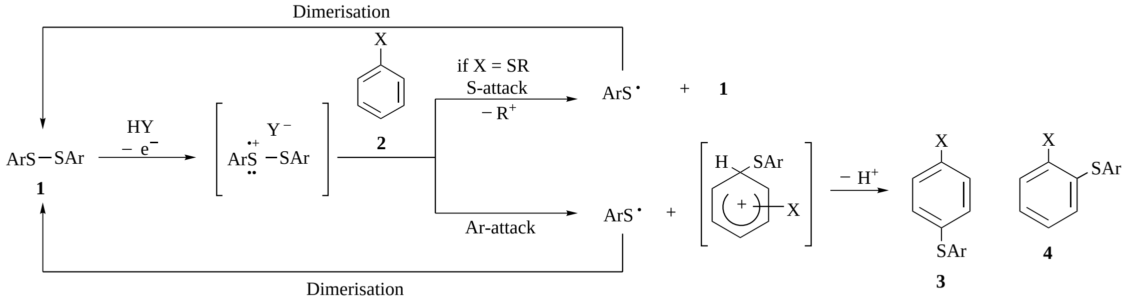
Results and discussion

Reactions of diphenyl disulfide 1a with alkyl phenyl sulfides 2a–e in the presence of an oxidant

Reactions of **1a** with methyl, ethyl, *n*-butyl, *sec*-butyl and *n*-heptyl phenyl sulfides **2a**–**e** in trifluoroacetic acid (TFA) containing H_2SO_4 afforded 4-alkylthiophenyl phenyl sulfides **3a**–**e** in high yields together with low yields of the corresponding *ortho*-isomers **4a**–**e** (Table 1 and Scheme 1). The ratio **3**:**4** in the reactions lasting 0.5 h depends upon the alkyl group R of **2**; $Bu^s > nC_7H_{15} >$ Et and $Bu^n >$ Me (Table 1). This implies that the *ortho*-formation is retarded by steric interference between the attacking reagent and the SR group of **2**.

Effect of oxidants. The total yield of **3** and **4** was much higher in the reaction of **1a** with **2a** using H_2SO_4, $SbCl_5$ or FSO_4H than that in the reaction using HCl, trifluoromethanesulfonic acid (TFSA) or with only TFA was used as an acid (Table 2). HCl hardly operates as an oxidant while H_2SO_4,[1,2] $SbCl_5$[23] or FSO_3H can easily oxidise disulfides to form the radical cation. TFA[24,25] or TFSA[26] seems to be a weak oxidant for the reaction. This suggests that the reaction giving **3** and **4** proceeds *via* a species (such as a radical cation) formed not by protonation but by oxidation of **1a** (Scheme 1). Thus, we can rule out the following mechanism involving the protonated disulfide [reaction(1)].

$$\mathrm{Ph\overset{+}{\underset{H}{S}}SPh} + \mathrm{ArH} \xrightarrow{-H^+} \mathrm{PhSAr} + \mathrm{PhSH} \qquad (1)$$



	Ar
a	Ph
a1	4-ClC$_6$H$_4$
a2	4-MeC$_6$H$_4$
a3	4-MeOC$_6$H$_4$

	X		X
a	SMe	**g**	Me
b	SEt	**h**	Et
c	SBu^n	**i**	H
d	SBu^s	**j**	Cl
e	SnC$_7$H$_{15}$	**k**	Br
f	OMe	**l**	Pr^i

Scheme 1

Table 1 Reactions of diphenyl disulfide **1a** (0.5 mmol) with alkyl phenyl sulfides PhSR (5.0 mmol) such as **2a–e** in TFA (2.5 cm^3) containing H_2SO_4 (1.0 mmol) as an oxidant at 25 °C

PhSR **2**	*t*/h	Recovered % of **1a**	Yield[a] (%) **3**	**4**	**3**:**4**
a; R = Me	0.5	1.8	175	24	7.3
b; R = Et	0.5	42	52	5.1	10.2
b; R = Et	2.0	11	82	13	
c; R = Bu^n	0.5	27	59	6.0	9.8
c; R = Bu^n	2.0	5.0	85	12	
d; R = Bu^s	0.5	59	36	2.7	13.3
d; R = Bu^s	2.0	11	86	9.0	
e; R = nC_7H_{15}	0.5	48	51	4.5	11.6
e; R = nC_7H_{15}	2.0	5.0	84	7.5	

[a] The yields of the products **3** and **4** are based on the **1a** used.

Table 2 Effects of counter-anion and solvent on the reactions of **1a** (0.5 mmol) with thioanisole **2a** (5.0 mmol) in solvent (2.5 cm^3) containing acid (1.0 mmol) at 25 °C for 0.5 h

Acid	Solvent	Counter-anion	Recovered % of **1a**	Yield[a] (%) **3a**	**4a**	**3a**:**4a**
None	TFA	$^-OCOCF_3$	88	1.7	0	
H_2SO_4	TFA	$^-OSO_3H$	1.8	175	24	7.3
FSO_3H	TFA	$^-OSO_2F$	4.6	138	27	5.1
$SbCl_5$	TFA	$^{-\bullet}SbCl_5$	6.4	174	17	10.2
TFSA	TFA	$^-OSO_2CF_3$	71	16	6.5	2.5
$HClO_4$	TFA	$^-ClO_4$	48	50	5.6	8.9
HCl	TFA	^-Cl	84	1.8	0	
H_2SO_4	CH_2Cl_2	$^-OSO_3H$	84	18	1.3	
$SbCl_5$	CH_2Cl_2	$^{-\bullet}SbCl_5$	0	201	17	
$SbCl_5$	CF_3CH_2OH	$^{-\bullet}SbCl_5$	11	190	9.5	
H_2SO_4	CF_3CH_2OH	—	90	0	0	
H_2SO_4	AcOH	—	100	0	0	
H_2SO_4	EtOH	—	100	0	0	
H_2SO_4	H_2O	—	100	0	0	

[a] The yields of the products **3a** and **4a** are based on the **1a** used.

Table 3 Reactions of diphenyl disulfide **1a** (0.5 mmol) with aromatic compounds **2f–l** (5.0 mmol) in TFA containing H_2SO_4 or in CH_2Cl_2 containing $SbCl_5$

X of PhX **2**	Reaction conditions[a]	Recovered % of **1**	Yield[b] (%) **3**	**4**
f; X = OMe	A	2.8	89	4.7
g; X = Me	A	0	9	0
g; X = Me	B	10	52	32
h; X = Et	A	58	6.2	2.0
h; X = Et	B	30	42	11
i; X = H	A	56	0	
i; X = H	B	13	49	
j; X = Cl	A	75	0	0
j; X = Cl	B	13	50	4.9
k; X = Br	B	9	40	0
l; X = Pr^i	B	17	20	0

[a] Condition A; the reaction was performed in TFA (2.5 cm^3) containing H_2SO_4 (1.0 mmol) at 25 °C for 0.5 h. Condition B; the reaction was carried out in CH_2Cl_2 (2.5 cm^3) containing $SbCl_5$ (1.0 mmol) at −30 °C for 15 min under N_2 atmosphere, and continued at −30 °C for 15 min after adding $SbCl_5$ (0.2 mmol). [b] The yields are based on **1** used.

Attack at the Ar and S groups of 2 by the radical cation of 1a. Attack on the Ar group of **2** by the radical cation (*i.e.* an aromatic arylthiolation) may produce **3** and **4**, together with the generation of PhS$^\bullet$ which forms **1a** by dimerisation (Scheme 1). This dimerisation reaction is well known.[27,28] The attack on the Ar group followed by the dimerisation reaction is supported by the fact that the total yield of **3f** and **4f** for the reaction with anisole **2f** is nearly 100% (see Table 3); consequently the yield of product is calculated to be 100% when two molar product is formed from one molar **1**.

The total yield of **3a** and **4a** exceeded 100% for the reaction of **1a** with **2a**, and the sum of both the total yield and the recovered % of **1a** was more than 100% for the reactions with **2b–d** over 2 h (Table 1). These observations show that the radical cation is capable of attack on the sulfur of **2** besides attack at Ar, and gives **1a**, the alkyl cation and PhS$^\bullet$ which generates **1a** by dimerisation (Scheme 1).

Effects of counter-anions and solvents. Experiments in TFA containing various acids as oxidants have been carried out (Table 2). The anions from the acids should be the counter-anions for the disulfide radical cation. Using only TFA as the acid, the counter-anion is $^-OCOCF_3$. The ratio **3a**:**4a** increased with an increase in the soft character (*i.e.* the bulkiness) of the counter-anion (Table 2); $^-OSO_2CF_3$ and $^-OSO_2F$ < $^-OSO_3H$ < ^-O_4Cl < $^{-\bullet}SbCl_5$. Although the results using $^-OSO_2CF_3$ and $^-OSO_2F$ cannot be unambiguously explained at present, the radical cation with the softer counter-anion would be subject to preferential attack at the *para*-position of **2a** rather than the *ortho*-position due to steric effects, leading to the greater **3a**:**4a** ratio.

The total yield of **3a** and **4a** in the presence of H_2SO_4 in CH_2Cl_2 was much lower than that in TFA (Table 2). By contrast, the total yield was markedly high in the presence of $SbCl_5$, and was independent of the solvent such as TFA, CH_2Cl_2 or CF_3CH_2OH (Table 2). The radical cation with a hard $^-OSO_3H$ counter-ion is thought to exist as a solvent-separated ion-pair in TFA, and would be reactive enough towards phenylthiolation. However, the radical cation in CH_2Cl_2 is mostly present as an intimate ion-pair, so that it may be less reactive on account of a strong interaction of the radical cation with the hard counter-anion. On the other hand, the radical cation possessing the much softer counter-anion $^{-\bullet}SbCl_5$ has a high reactivity giving a good total yield regardless of the solvent

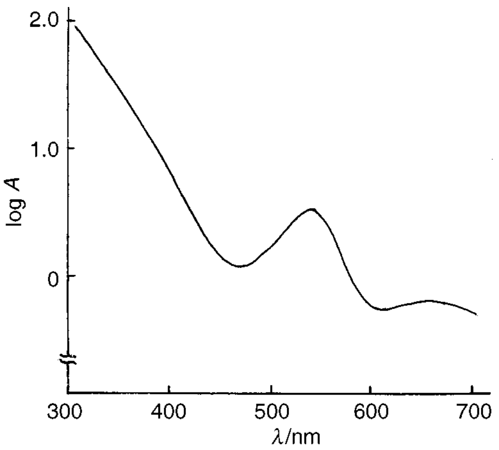


Fig. 1 Electronic spectra after **1a** (4.6 mM) was dissolved at 25 °C for 0.5 h in TFA containing H_2SO_4 (0.376 M)

since the radical cation (even if it exists as the intimate ion-pair) interacts very weakly with the bulky counter-anion.

Electronic absorption of the disulfide radical cation. Using CF_3CH_2OH, AcOH, EtOH or H_2O as a solvent for the reaction of **1a** with **2a**, the addition of H_2SO_4 did not affect the colour of the mixture; H_2SO_4 has no oxidising nature in the above solvent, and almost all of **1a** was recovered by treatment with aqueous Na_2CO_3 after 0.5 h (Table 2). However, addition of H_2SO_4 to the solution of **1a** (1.0 mmol) in TFA (5.0 cm^3) caused the solution to change to a reddish-violet colour immediately at 25 °C, and after 0.5 h, **1a** was completely recovered by neutralisation with aqueous Na_2CO_3. We observed λ_{max} at 540 and 650 nm after **1a** was dissolved at 25 °C for 0.5 h in TFA containing H_2SO_4 (Fig. 1).

The absorptions at 540 and 650 nm represent different electron transitions of the same species. Wertz and Vivo[7] and Yokozawa[8] have reported the EPR spectra of PhSSPh in H_2SO_4, and ascribed the spectrum to the radical cation, hence the colour species with the absorptions may be the radical cation of **1a**. This radical cation would be stable even at room temperature without spontaneous S–S scission owing to the strong S–S bond[11] compared with that in the unoxidised disulfide, but is subject to the proposed S–S cleavage due to attack at Ar and S groups in the presence of **2** as seen in Scheme 1.

The complete recovery of **1a** described above means that the radical cation is non-reactive in the absence of aromatic substrate; in other words, the radical cation can undergo direct aromatic thiolation in the presence of an aromatic compound. If a sulfenium ion[29,30] was generated as the reactive species towards the aromatics[29,30] by S–S scission of the radical cation, complete recovery of **1a** would be impossible even in the absence of an aromatic compound since the highly reactive sulfenium ion would be consumed under the reaction conditions. Thus, this clearly rules out the sulfenium ion mechanism. We consider that the complete recovery of **1a** may result from a fast equilibrium between the radical cation and **1a** or from the formation of **1a** *via* the radical cation by treatment of the reaction mixture with aqueous Na_2CO_3. However, treatment of **1a** (1.0 mmol) with $SbCl_5$ (2.0 mmol) in CH_2Cl_2 (5.0 cm^3) at 25 °C for 0.5 h did not lead to the recovery of **1a** after neutralisation with aqueous Na_2CO_3, and some polymeric material was formed. Since the radical cation with $^{-\bullet}SbCl_5$ as the counter-ion is more reactive than that having $^{-}OSO_3H$, the former cation as well as the latter must be capable of aromatic arylthiolation without spontaneous S–S cleavage.

Reactions of diphenyl disulfide 1a with various aromatic compounds 2f–l in the presence of an oxidant

The reaction of **1a** with anisole **2f** in TFA containing H_2SO_4 gave a high total yield of 4- and 2-anisyl phenyl sulfides **3f** and **4f**, but the total yield of **3** and **4** was extremely low or zero for the reaction using toluene **2g**, ethylbenzene **2h**, benzene **2i** and chlorobenzene **2j** instead of **2f** (Table 3). This indicates that the radical cation is less reactive (owing to the stability as shown above) towards the lower nucleophilic **2g–j** than **2f**. The relatively high consumption of **1a** in spite of lower reactivity shows some side-reaction giving an uncertain product; the high consumption using **2g** compared to **2h–j** is ambiguous at present. On the contrary, the reaction of **1a** with **2g–j** using $SbCl_5$ in CH_2Cl_2 gave higher total yield of **3** and **4** than that using H_2SO_4 in TFA (Table 3). This implies that the radical cation having the very soft counter-anion $^{-\bullet}SbCl_5$ can be considerably reactive even towards the less reactive aromatics **2g–l** compared with **2f**.

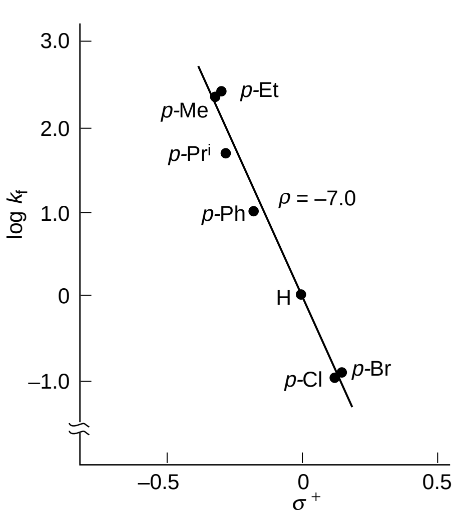


Fig. 2 Hammett plot σ^+ *vs.* log k_f for the formation of 4-substituted aryl phenyl sulfides **3** in the reaction of diphenyl disulfide **1a** with aromatic compounds using $SbCl_5$ in CH_2Cl_2

A Hammett correlation[31] of log k_f *vs.* σ^+ gives a good linear plot with $\rho = -7.0$ where the values of k_f are the *para*-attacking partial rate factors for the phenylthiolation of **2g–j**, bromobenzene **2k**, isopropylbenzene **2l** and biphenyl **2m** using $SbCl_5$ in CH_2Cl_2 at −30 °C (Fig. 2); the coefficient for the correlation is −0.985. The negative ρ value shows that the aromatic phenylthiolation may occur *via* a positive intermediate such as the radical cation of **1a**. This may be reasonable from the high substrate selectivity (*i.e.* the high negative ρ value) and the high positional selectivity giving no *meta*-isomers since the radical cation would be less reactive (*i.e.* more selective) due to electron-delocalisation of the positive charge by partial π-nature[11] of the S–S bond.

As for the Hammett correlation, the k_f values for thioanisole **2a** and anisole **2f** were not adopted; the values were abnormally low as expected from the linear Hammett relationship since the reaction with the high electron-donating **2a** and **2f** probably proceeds in a diffusion-controlled process and the interaction of $SbCl_5$ with **2f** depresses the reactivity as described below. The k_f values for ethylbenzene **2h** and chlorobenzene **2j** deviated slightly from the Hammett relation (Fig. 2), but were reproducible. The reason for the deviation is not clear at present.

Effect of substituent of diaryl disulfides on the arylthiolation

The reaction of bis(4-chlorophenyl) disulfide $\mathbf{1a_1}$ with **2a** did not occur using HCl in TFA. However, using H_2SO_4 instead of HCl led to efficient arylthiolation with lower selectivity (*i.e.* $\mathbf{3a_1}:\mathbf{4a_1} = 1.2$) than that for the reaction using **1a** ($\mathbf{3a}:\mathbf{4a} = 7.3$) in place of $\mathbf{1a_1}$ (Table 4). This suggests that the radical cation of $\mathbf{1a_1}$ is also formed by oxidation with H_2SO_4, and has a higher reactivity (*i.e.* less selectivity) than that of **1a** due to an electron-withdrawing 4-chloro-substituent.

The reaction of $\mathbf{1a_1}$ with anisole **2f** in CH_2Cl_2 containing $SbCl_5$ gave 4- and 2-anisyl 4-chlorophenyl sulfides $\mathbf{3f_1}$ and $\mathbf{4f_1}$, and the reaction using 4-tolyl or 4-anisyl disulfide $\mathbf{1a_2}$ or $\mathbf{1a_3}$

Table 4 Reactions of diaryl disulfide ArSSAr (0.5 mmol) with aromatic compound PhX (5.0 mmol) in TFA containing H_2SO_4 or in CH_2Cl_2 containing $SbCl_5$

Ar of ArSSAr **1**	X of PhX **2**	Reaction conditions[a]	Recovered % of **1**	Yield[b] (%) **3**	**4**	**3**:**4**
a; Ar = Ph	**a**; X = SMe	A	1.8	175	24	7.3
a; Ar = Ph	**f**; X = OMe	A	2.8	89	4.7	
a; Ar = Ph	**f**; X = OMe	C	15	20	0.9	22
a; Ar = Ph	**f**; X = OMe	C′	15	24	1.1	22
a$_1$; Ar = 4-ClC_6H_4	**a**; X = SMe	A	10	44	37	1.2
a$_1$; Ar = 4-ClC_6H_4	**f**; X = OMe	C	55	21	4.5	4.7
a$_1$; Ar = 4-ClC_6H_4	**f**; X = OMe	C′	42	29	5.3	5.5
a$_2$; Ar = 4-MeC_6H_4	**f**; X = OMe	C	16	55	2.4	23
a$_2$; Ar = 4-MeC_6H_4	**f**; X = OMe	C′	0	87	4.3	20
a$_3$; Ar = 4-$MeOC_6H_4$	**f**; X = OMe	C	0	57	0	
a$_3$; Ar = 4-$MeOC_6H_4$	**f**; X = OMe	C′	0	59	0	

[a] The condition A is the condition A described in Table 3. Condition C; the reaction was performed employing $SbCl_5$ (1.0 mmol) in CH_2Cl_2 (2.5 cm^3) at 25 °C for 0.5 h. Condition C′; the reaction time was 2 h under reaction condition C. [b] The yields are based on **1** used.

instead of **1a**$_1$ also yielded 4- and 2-anisyl 4-tolyl sulfides **3f**$_2$ and **4f**$_2$ or di-4-anisyl sulfide **3f**$_3$ (Table 4). The selectivity **3**:**4** for the reaction of **1** with **2f** increased with increased electron-donating power (*i.e.* OMe > Me and H > Cl) of the substituent of **1** (Table 4). The result does not seem to be contradictory because **1** possesses a more electron-donating substituent which can form a more stable radical cation resulting in higher selectivity. However, sulfides with no substituents and with methyl substituents exhibit similar selectivity. We cannot explain this at present.

In the reaction with anisole **2f** using $SbCl_5$, the yield for arylthiolation from **1a**$_3$ was lower than that from **1a**$_2$ (Table 4). The reaction of **1a** with **2f** using H_2SO_4 in TFA gave better arylthiolation than that using $SbCl_5$ in CH_2Cl_2 (Table 4). From these results, arylthiolation from **2f** using $SbCl_5$ is probably depressed by the interaction of $SbCl_5$ with the oxygen atom of **1a**$_3$ or **2f**.

Exclusion of other mechanisms

As shown above, the sulfenium ion mechanism[29,30] can be ruled out for this reaction. A thiyl radical mechanism can also be excluded since the reaction of PhS$^•$ with **2a** does not give **3a** and **4a**.[30] The radical mechanism is, of course, not plausible because of the large negative ρ value.

Experimental

IR spectra were obtained on a Hitachi EPI-G3 spectrometer. ^{1}H NMR spectra were taken with a Nippondenshi PMX-60SI instrument (*J* values are given in Hz). GLC–MS were recorded with a Shimadzu QP-5000 spectrometer having a Shimadzu GC-17A; a column (15 m × 0.25 mm) having DB-1 (0.25 µ film) which is made by J & W Scientific was used. GLC was performed with a Shimadzu GC-8A using a glass column (1 m × 3 mm) packed with 10% SE-30 on 60–80 mesh Chromosorb W (AW-DMCS). Two runs agreed to within 3% error for the yields of the products which are determined by replicate GLC analyses.

Thioanisole **2a**, anisole **2f** and TFA were purified by distillation of reagent grade (Nacalai Tesque). The following compounds were reagent grade (Nacalai Tesque) and used without further purification: diphenyl disulfide **1a**, H_2SO_4, TFSA and CF_3CH_2OH. The compounds **2g–l** and other solvents were purified by standard methods before use.

Ethyl, *n*-butyl, *sec*-butyl and *n*-heptyl phenyl sulfides **2b–e** were synthesized by the method described in the literature.[32–34] 4-Biphenyl phenyl sulfide **3m** was prepared by the literature method,[30] mp 68.0–68.4 °C; ν_{max}(KBr)/cm^{-1} 3040, 1580, 1480, 1440, 1395, 1090, 1030, 1010, 835 (*para*-substituted Ph), 765, 743 and 695; δ_H($CDCl_4$) 7.0–7.8 (14H, m, Aromatic H); *m*/*z* 262 (M$^+$), 185, 184, 153, 115, 77 and 51 (Found: C, 82.3; H, 5.45. $C_{18}H_{14}S$ requires C, 82.4; H, 5.4%).

Reactions of diphenyl disulfide 1a with alkyl phenyl sulfides 2a–e in the presence of an oxidant

The reactions of **1a** with **2a–e** were carried out as shown in Table 1. After the reaction, aq. Na_2CO_3 was added until the solution reached pH > 7. The organic layer was extracted with CH_2Cl_2 and the yields were determined by GLC analysis. The products were isolated by thin layer chromatography using silica gel (Merk 60F254) after column chromatography using silica gel (Fujisiriaru Chem. BW-127ZH). We have already described the characterisation of the structure of *para*-products **3a**, **3c** and **3e** and *ortho*-products **4a**, **4c** and **4e**.[30] The physical and spectroscopic data for **3b** and **3d** are shown below. The mass spectroscopic data (by GLC–MS) for **4b** and **4d** are shown in Table 5; **4b** and **4d** showed characteristic peaks for the *ortho*-structure. The fact that the GLC peak for **4b** or **4d** had a shorter retention time than that of the corresponding *para*-product **3b** or **3d** suggests that **4b** and **4d** are *ortho*-isomers of **3b** and **4b**. The yields of **4b** and **4d** were determined on the assumption that these have the same GLC area-sensitivity as **3b** and **3d** although **4b** and **4d** were not isolated.

4-Ethylthiophenyl phenyl sulfide 3b. Liquid, ν_{max}(neat)/cm^{-1} 3060, 2960, 2920, 1585, 1480, 1445, 1395, 1270, 1120, 1100, 1040, 1025, 825, 750 and 705; δ_H($CDCl_3$) 1.3 (3H, t, *J* 7.1, Me), 2.9 (2H, q, *J* 7.1, CH_2) and 7.2–7.6 (9H, m, phenyl H); *m*/*z* 246 (M$^+$), 217, 184, 154, 109, 77, 69, 65 and 51 (Found: C, 68.25; H, 5.8. $C_{14}H_{14}S_2$ requires C, 68.25; H, 5.75%).

4-*sec*-Butylthiophenyl phenyl sulfide 3d. Liquid, ν_{max}(neat)/cm^{-1} 3040, 2960, 2920, 1580, 1480, 1440, 1380, 1120, 1100, 1025, 825, 750 and 700; δ_H($CDCl_3$) 1.0 (3H, t, *J* 6.7, CH_2Me), 1.25 (3H, d, *J* 6.3, $CHMe$), 1.4–1.8 (2H, m, CH_2), 2.8–3.3 (1H, m, CH) and 7.3–7.6 (9H, m, phenyl H); *m*/*z* 274 (M$^+$), 218, 184, 185, 154, 109, 108, 77, 69, 65, 57 and 51 (Found: C, 69.9; H, 6.65. $C_{16}H_{18}S_2$ requires C, 70.0; H, 6.6%).

Effects of counter-anion and solvent on the reaction of diphenyl disulfide 1a with thioanisole 2a

The effects of counter-anion and solvent were investigated by variation of acid and solvent as shown in Table 2. The procedures used for isolation and characterisation of the products **3a** and **4a** and the determination of their yields are as indicated above.

Reactions of diaryl disulfides 1 with aromatic compounds in the presence of an oxidant

The detailed reaction conditions are indicated in Tables 3 and 4. Isolation of the products was carried out as shown above. The characterisation of **3f**, **3g**, **3i**, **4f** and **4g** has been shown in our

Table 5 Mass spectral data for 2- and 4-substituted aryl phenyl sulfides, RC_6H_4SPh

	R	*m*/*z*
4b	2-SEt	246 (M^+), 218 (M^+ − MeCH), 217, 184, 140 [M^+ − (Ph + Et)], 108, 105, 91, 77, 69, 65 and 51
4d	2-SBu^s	274 (M^+), 218, 184, 152, 140 [M^+ − (Ph + Bu)], 109, 96, 84, 83, 77, 69, 56, 57 and 51
3h	4-Et	214 (M^+), 199, 184, 167, 165, 152, 121, 105, 77, 65 and 51
4h	2-Et	214 (M^+), 199, 197 [M^+ − (Me + 2H)], 185, 184, 165, 135, 136, 105, 103, 77, 78, 65 and 51
3j	4-Cl	222 and 220 (M^+), 184, 152, 139, 125, 108, 92, 79, 77, 75, 69, 65, 51 and 50
4j	2-Cl	222 and 220 (M^+), 185 (M^+ − Cl), 184, 152, 139, 125, 108, 92, 79, 77, 75, 69, 65, 63, 51 and 50
3k	4-Br	266 and 264 (M^+), 185, 184, 152, 108, 92, 77, 69, 65, 51 and 50
3l	4-Pr^i	228 (M^+), 213 (M^+ − Me), 135, 109, 104, 91, 77, 64 and 51

Table 6 Mass spectral data for 2- and 4-substituted aryl aryl sulfides, $R^1C_6H_4SC_6H_4R^2$

	R^1	R^2	*m*/*z*
3a$_1$	4-SMe	4-Cl	268 and 266 (M^+), 251, 219, 216, 184, 108, 96, 82, 75, 69, 63, 51 and 50
4a$_1$	2-SMe	4-Cl	268 and 266 (M^+), 220 and 218 (M^+ − MeSH), 216, 184, 153, 139, 125, 108, 96, 82, 77, 69 and 51
3f$_1$	4-OMe	4-Cl	252 and 250 (M^+), 235 and 237 (M^+ − Me), 215, 200, 172, 171, 139, 108, 107, 96, 95, 92, 85, 75, 70, 69, 64, 63, 51 and 50
4f$_1$	2-OMe	4-Cl	252 and 250 (M^+), 202, 172, 171, 168 (M^+ − ClMeS), 145, 139, 127, 125, 108, 99, 96, 95, 92, 91, 86, 85,80, 77, 75, 73, 70, 69, 65, 64, 63, 58, 52, 51 and 50
3f$_2$	4-OMe	4-Me	230 (M^+), 215 (M^+ − Me), 200, 171, 172, 114, 91, 77, 69, 65, 64, 63, 51 and 50
4f$_2$	2-OMe	4-Me	230 (M^+), 215 (M^+ − Me), 213 (M^+ − MeH_2), 200, 182, 172, 137, 115, 105, 89, 87, 73, 77, 59, 58 and 51

previous report.[30] The *para*-products **3h** and **3j**–**l** were not isolated, but contaminated with the starting material **1**. Their structures were characterised by GLC–MS data seen in Table 5, and their yields were determined as shown above after determining the amount of **1** as an impurity by GLC analysis. *Ortho* products **4k** and **4l** were not formed because of the steric effect of the bulky bromo and isopropyl groups. In fact, GLC analysis showed no peaks corresponding to *ortho*-isomers having a shorter retention time than the *para*-isomers.

The compound **3a**$_1$ was mixed with the *ortho*-product **4a**$_1$ although the isolation was attempted, and their structures were confirmed by GLC–MS data in Table 6 and by elemental analysis of the mixture (Found: C, 58.75; H, 4.25. Calc. for $C_{13}H_{11}ClS_2$: C, 58.5; H, 4.15%). Their yields were determined as described above.

The GLC–MS data of *ortho*-products **4h**, **4j**, **4f**$_1$ and **4f**$_2$ are shown in Tables 5 and 6. The confirmation of their structures and the determination of the yields were carried out as described above. The reaction of di-4-anisyl disulfide **1a**$_3$ with **2f** gave only one product di-4-anisyl sulfide **3f**$_3$: mp 37.6–37.9 °C; ν_{max}(KBr)/cm^{-1} 3000, 2840, 1593, 1496, 1290, 1247, 1185, 1040 and 845 and 820 (*para*-substituted Ph); δ_H($CDCl_3$) 3.8 (6H, s, OMe) and 7.05 (8H, AB q, *J* 9.0, aromatic H); *m*/*z* 246 (M^+), 231 (M^+ − Me), 214, 203, 199, 188, 172, 171, 160, 139, 124, 115, 96, 95, 92, 77, 70, 69, 64, 63, 51 and 50.

Hammett plot

A solution containing **1a** (0.5 mmol) and aromatic substrate [**2i** (80 mmol) and **2g** (10 mmol), **2i** (80 mmol) and **2h** (10 mmol), **2i** (25 mmol) and **2j** (50 mmol), **2i** (10 mmol) and **2k** (50 mmol), **2i** (80 mmol) and **2l** (10 mmol) or **2i** (80 mmol) and **2m** (10 mmol)] in the presence of $SbCl_5$ (1.0 mmol) in CH_2Cl_2 (2.5 cm^3) was allowed to stand at −30 °C for 3 min, resulting in a total yield 45–50% of **3** and **4**. After the reaction mixture was treated as shown above, the relative ratios of **3g**, **3h** and **3j**–**m** to **3i** were determined by GLC. The *para*-attacking partial rate factors (k_f) for **2g**, **2h** and **2j**–**m** were calculated on the basis of the above relative ratios, initial concentration of the aromatics, the number of C–H bonds of benzene and *para*-CH bonds of the substituted aromatics.

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