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One-step arylthiolation of aromatic compounds by disulfide radical cations generated from oxidation of diaryl disulfides with aluminium chloride

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Reactions of di(phenyl and 4-tolyl) disulfides **1a** and **1b** with PhX **3a**–**e** (X = H, Me, Et, Ph and Cl) in the presence of $AlCl_3$ at 25 °C give diaryl sulfides **4**–**6** by aromatic arylthiolation *via* the disulfide radical cations **2**, along with thiophenols **7** formed in the incomplete reactions. Competitive intramolecular reactions of **2a** also yield diphenyl sulfide **4a** or/and thianthrene **8**. However, the reactions of bis(4-chlorophenyl and 4-fluorophenyl) disulfides **1c** and **1d** selectively lead to the aromatic arylthiolation in high yields. The Hammett $\rho = -8.8$ at 25 °C for the phenylthiolation in the reactions of **1a** is more negative than that ($\rho = -7.0$ at -30 °C) using $SbCl_5$ instead of $AlCl_3$, and the value $\rho = -8.0$ for the arylthiolation using **1d** is less negative than that using **1a**. These and the other mechanistic aspects support the arylthiolations *via* **2**.

We have already reported a new type of one-step electrophilic thiolation by Umpolung to cationic species such as disulfide radical cations[1] or sulfenium ions[2] from thiols or thiolate anions which are usually subject to nucleophilic thiolation. In our previous paper, the disulfide radical cations are formed from diaryl disulfides using H_2SO_4 in trifluoroacetic acid at 25 °C or using $SbCl_5$ in CH_2Cl_2 at -30 °C, and are capable of the one-step aromatic arylthiolation.[1] The arylthiolation using H_2SO_4 or $SbCl_5$ as the oxidant requires hard and/or expensive reaction conditions. However, the title arylthiolation conveniently occurs in the presence of an inexpensive oxidant, $AlCl_3$, at room temperature. The disulfide radical cation formed from di(phenyl or 4-tolyl) disulfide brings about an intramolecular reaction competing with the aromatic arylthiolation, but that formed from bis(4-chloro- or 4-fluorophenyl) disulfide selectively leads to the aromatic arylthiolation.

The oxidation to the disulfide radical cation from diphenyl disulfide has been proposed from spectroscopic observations in acid zeolites.[3,4] However, the disulfide radical cation is highly reactive in solution, regardless of whether it is generated by chemical,[5,6] photochemical[7] or electrochemical oxidation,[8] and thus spectral confirmation is very difficult in solution. We here demonstrate mechanistically that the diaryl disulfide radical cations may be reactive intermediates in the title arylthiolation.

Results and discussion

Reactions of diphenyl disulfide 1a with benzene 3a in the presence of $AlCl_3$

Reaction of **1a** with benzene **3a** in the presence of $AlCl_3$ at 25 °C under an atmosphere of N_2 afforded diphenyl sulfide **4a** together with thiophenol **7a** and thianthrene **8** (Table 1). Diphenyl sulfoxide **9** was formed under an atmosphere of air, not N_2 (Table 1). The decrease in yield of **8** with increasing reaction time and increasing amounts of $AlCl_3$ (Table 1) suggests that **8** is unstable under the reaction conditions. In fact, **8** (1.0 mmol) was completely decomposed in **3a** (10 cm^3) in the presence of $AlCl_3$ (4.0 mmol) under N_2 atmosphere for 72 h at 25 °C, and many unidentified products were formed according to GLC analysis. The yield of **7a** decreased with increasing reaction time. In fact, the reaction using **7a** instead of **1a** gave **4a** (59%) (see Experimental section), and thus **7a** must be an intermediate for the formation of **4a**. We propose that **1a** undergoes an oxidation by $AlCl_3$ to give a disulfide radical cation **2a** as shown below, yielding **4a** and $PhS^\bullet$ by aromatic phenylthiolation of **2a** accompanying **7a** (Scheme 1); $PhS^\bullet$ may be dimerised to give the starting material **1a**.[9,10] From the mechanism, the yield of **4a** should be 100% when two molar **4a** is formed from one molar **1a**. Thus, the yields in Tables 1–3 are in agreement with the proposed reaction mechanism.

Table 1 Reaction of diphenyl disulfide **1a** (1.0 mmol) with benzene **3a** (10 cm^3) in the presence of $AlCl_3$ at 25 °C under a N_2 atmosphere

$AlCl_3$/mmol	*t*/h	Yield (%) **4a**	**7a**	**8**	**9**	Recovered (%) **1a**
1.0	72	47	8.1	7.1	0	11
2.5	24	48	12	4.9	0	14
3.0	8.0	60	19	2.2	0	5.6
3.0	24	75	6.7	3.1	0	4.3
4.0	8.0	75	16	1.6	0	1.8
4.0	24	83	3.7	1.7	0	1.0
2.0[a]	24	74	trace	18	trace	0.5
4.0[a]	24	41	trace	0	13	0

[a] In this case, the reaction was carried out under air, and the amount of **3a** was 50 cm^3 instead of 10 cm^3.

The reaction of dimethyl disulfide (1.0 mmol) with **3a** (10 cm^3) in the presence of $AlCl_3$ (4.0 mmol) at 25 °C for 96 h produced thioanisole in 76% yield (see Experimental section). Further, when $AlCl_3$ or AgOAc was dissolved in dimethyl disulfide as the solvent at 25 °C, we could observe an electronic absorption at λ_{max} 375 nm because the sulfide was in excess. These observations exclude the possibility that the intermediate (for the aromatic methylthiolation) having the above absorption is a sulfonium ion $[MeS–S^+(Me)AlCl_2]\ Cl^-$ because $[MeS–S^+(Me)AlCl_2]\ Cl^-$ and $[MeS–S^+(Me)Ag]\ OAc^-$ should have different absorptions. Thus, the intermediate may be the radical cation of dimethyl disulfide since the radical cation generated from different metal oxidants $AlCl_3$ or AgOAc would show the

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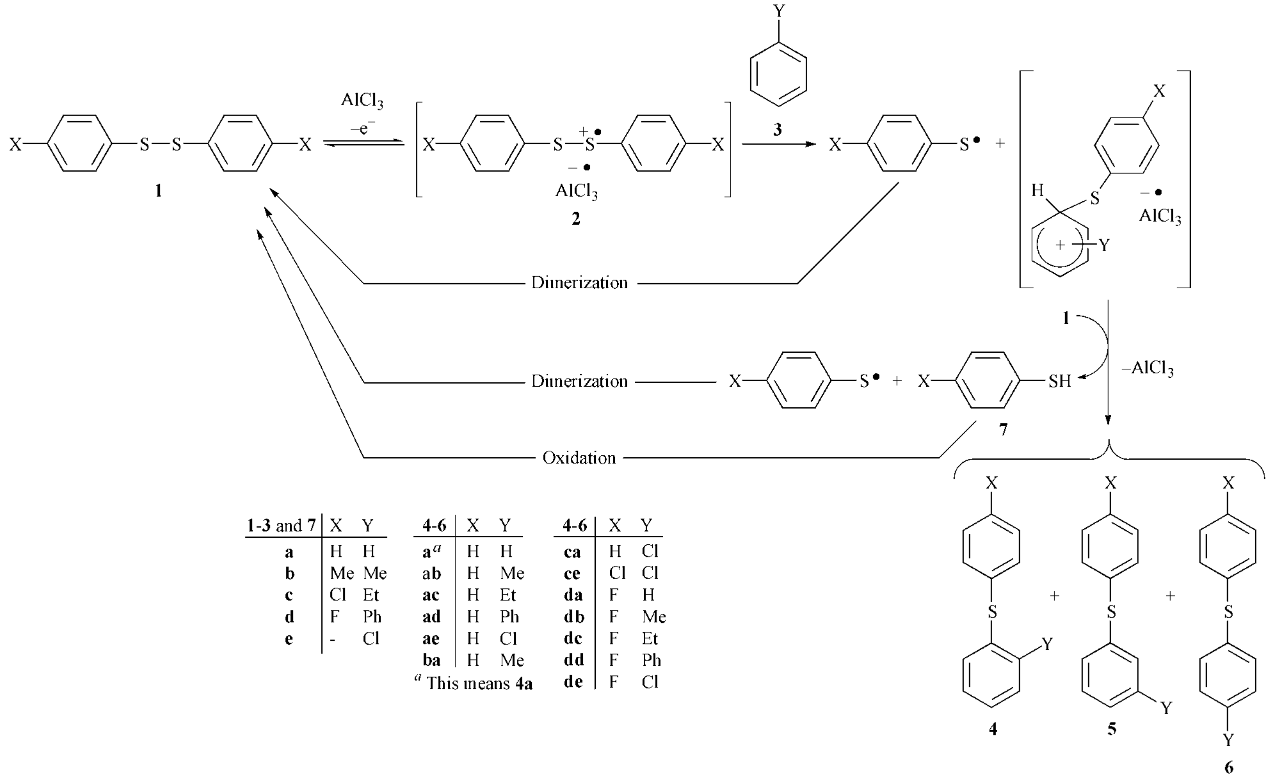


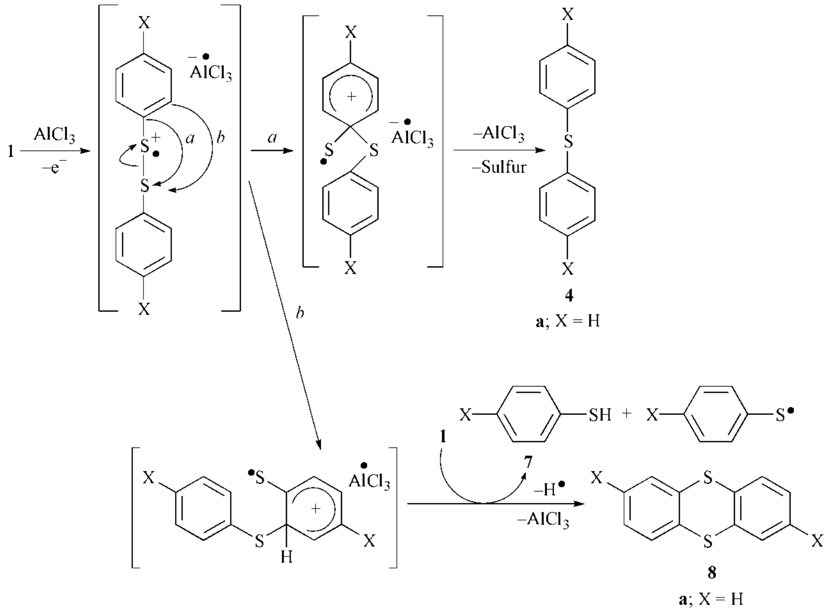
1-3 and **7**	X	Y
a	H	H
b	Me	Me
c	Cl	Et
d	F	Ph
e	-	Cl

4-6	X	Y
a[a]	H	H
ab	H	Me
ac	H	Et
ad	H	Ph
ae	H	Cl
ba	H	Me

[a] This means **4a**

4-6	X	Y
ca	H	Cl
ce	Cl	Cl
da	F	H
db	F	Me
dc	F	Et
dd	F	Ph
de	F	Cl

Scheme 1



Scheme 2

common absorption. It is possible that the diaryl disulfide radical cation **2** is analogously formed. In a previous paper,[1] we reported that diphenyl disulfide radical cation with electronic absorptions at λ_{max} 540 and 650 nm is formed from **1a** in TFA containing H_2SO_4. However, it is undeniable that these absorptions are due to the other species formed from the subsequent intramolecular reactions of **2a** since diphenyl disulfide radical cation has been proposed to have an absorption λ_{max} at 600–1500 nm in acid zeolites.[4]

The reaction of diphenyl disulfide 1a in *n*-hexane. Reaction of **1a** using *n*-hexane in place of benzene **3a** also produced **4a** (54%) and **8** (14%) as reported in the Experimental section. From this result, we propose that the disulfide radical cation **2a** undergoes intramolecular reactions by a heterolytic S–S scission accompanied by a simultaneous *ipso*-attack (step *a*) and *ortho*-attack (step *b*), leading to the formation of **4a** and **8** (Scheme 2). It has been reported that **8** is formed *via* a disulfide dication from the radical cation **2a** in zeolites.[3,4] In our reaction in solvent, it would be impossible for **8** to be formed *via* the dication generated by further oxidation of the unstable **2a**. Therefore, **8** might be formed by the intramolecular reaction competing with the intermolecular arylthiolation, as shown in Scheme 2. There is, however, the possibility that **4a** is formed by the intramolecular reaction of **2a**, not by intermolecular aromatic phenylthiolation. Therefore, the following experiment employing d_6-benzene was carried out in order to examine this possibility.

The reaction of diphenyl disulfide 1a with d_6-benzene. The reaction of **1a** using d_6-benzene in place of **3a** was performed. The GLC-mass analysis for the reaction mixture showed the

Table 2 Reaction of diphenyl disulfide **1a** (1.0 mmol) with aromatic compounds PhY (10 cm^3) such as toluene, ethylbenzene, biphenyl and chlorobenzene **3a–e** in the presence of $AlCl_3$ at 25 °C under a N_2 atmosphere

PhY **3**	$AlCl_3$/ mmol	*t*/h	Yield (%) **4**	**5**	**6**	**4a**	**7**	**8**	Recovered (%) **1a**
b; Y = Me	1.0	0.5	15	1.8	17	0	23	0	33
b; Y = Me	2.5	0.5	24	4.0	27	0	38	0	1.9
b; Y = Me	2.5	8.0	21	5.0	40	0.4	22	0	2.6
b; Y = Me	2.5	24	17	20	37	6.0	2.2	0	5.0
b; Y = Me	4.0	72	15	14	42	8.0	0.9	0	0
c; Y = Et	4.0	2	13	7.5	58	0	16	0	0
c; Y = Et	4.0	24	8.7	21	64	1.6	0	0	0
d; Y = Ph[a]	4.0	2	0	0.3	39	31	11	1.5	0
d; Y = Ph[a]	4.0	24	0	1.9	45	32	1.1	0	0
e; Y = Cl	2.5	24	0.3	1.9	10	21	0	19	1.1
e; Y = Cl	4.0	1.0	0.3	3.5	14	16	0	8.1	16
e; Y = Cl	4.0	24	1.8	4.3	25	37	0	0	12
e; Y = Cl	4.0	72	1.0	5.7	31	14	0	0	0

[a] PhPh **3d** (5.0 mmol) dissolved in *n*-hexane (3.5 cm^3) was used in the reaction.

existence of d_5–d_{10}-PhSPh, not d_0–d_4-PhSPh. If **4a** were formed by intramolecular phenylthiolation to **3a**, the reaction mixture would include d_0–d_4-PhSPh. Therefore, d_5–d_{10}-PhSPh must have been formed only by the intermolecular reaction; d_6–d_{10}-PhSPh can be formed by deuteration of d_5-PhSPh because D^+ is formed from a σ-complex (refer to Scheme 1) given by the reaction of **2a** with d_6-benzene. The reaction with d_0-benzene **3a** produced a small amount of **8** (Table 1), but the reaction with d_6-benzene did not yield **8**. Exactly what is happening here is not clear at the present time.

Reactions of diphenyl disulfide 1a with toluene, ethylbenzene, biphenyl and chlorobenzene 3b–e

The reactions of **1a** with **3b–e** also provided the aromatic phenylthiolation giving phenyl 2-, 3- and 4-substituted phenyl sulfides **4**, **5** and **6** (Table 2). In the reactions with **3b**, **3c** and **3e**, *ortho*-products **4ab**, **4ac** and **4ae** and *para*-products **6ab**, **6ac** and **6ae** tend to isomerise to the *meta*-isomers **5ab**, **5ac** and **5ae** under prolonged reaction conditions or in the presence of large amounts of $AlCl_3$. This reflects the high stability of the *meta*-isomers compared to the *ortho*- and *para*-isomers under these reaction conditions.

The intramolecular products **4a** and **8** are scarcely formed because intermolecular thiolation is favoured by the use of the highly reactive **3b** and **3c**, whereas their yields are high in the unfavourable intermolecular thiolation using the less nucleophilic **3e** or using **3d** diluted with *n*-hexane. These results strongly suggest that the intramolecular reaction (shown in Scheme 2) competes with the intermolecular phenylthiolation shown in Scheme 1.

Thiophenol **7a** is formed in the reactions with **3a–d**, but not produced in the reaction with **3e**. This implies that there is a pre-equilibrium between **1a** and **2a**; according to the Le Chatelier principle, this pre-equilibrium proceeds forward slowly in the reaction with **3e**, which is the less reactive to the phenylthiolation by **2a**, so that **7a** as the intermediate material could be completely consumed by the excess $AlCl_3$ remaining in the reaction system. By contrast, using the highly reactive **3a–d**, **7a** can be observed in the reaction mixture because $AlCl_3$ is rapidly consumed by the arylthiolation of **3a–d**.

Hammett plots. The *para*-attacking partial rate factors k_f were determined for the formation of *para*-products **6ab**, **6ac**, **6ad** and **6ae** in the reactions of **1a** with **3b**, **3c**, **3d** and **3e** in the presence of $AlCl_3$ at 25 °C. A Hammett correlation of log k_f against σ^+ gives a good linear plot with $\rho = -8.8$ (Fig. 1). Similarly, the Hammett correlation for the reaction of bis(4-fluorophenyl) disulfide **1d** gives a linear plot showing $\rho = -8.0$ (Fig. 2). The large negative ρ values in Figs. 1 and 2 indicate that the arylthiolations proceed *via* cationic intermediates such as **2**. The disulfide radical cation **2d** from **1d** may have a less negative ρ value than **2a** from **1a** because the former cation is more reactive than the latter due to the electron-withdrawing group F; the more reactive intermediate shows the less selectivity (*i.e.* the less negative ρ value) for the aromatic substrates by the

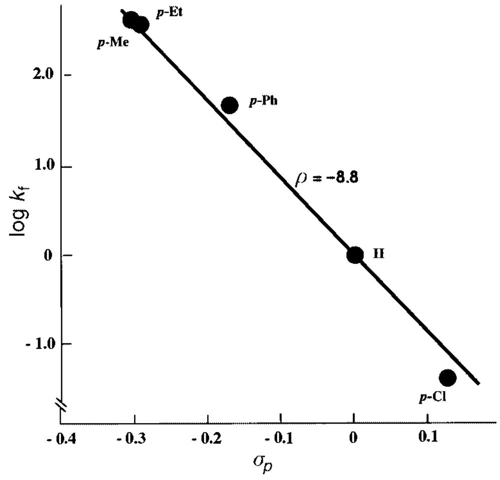


Fig. 1 Hammett plot σ_p *vs.* log k_f for the formation of 4-substituted aryl phenyl sulfides **6** in the reaction of diphenyl disulfide **1a** with aromatic compounds **3** in the presence of $AlCl_3$ at 25 °C.

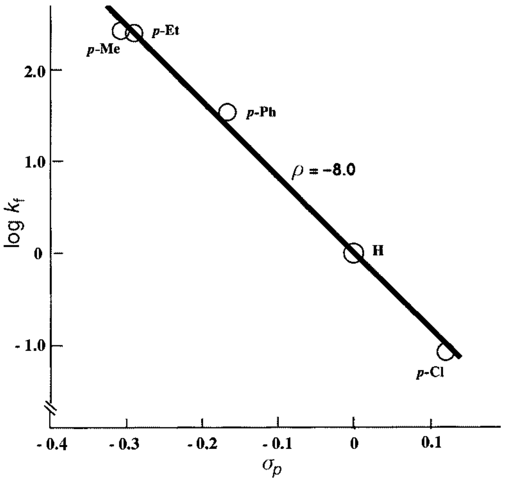


Fig. 2 Hammett plot σ_p *vs.* log k_f for the formation of 4-substituted aryl 4-fluorophenyl sulfides **6** in the reaction of bis(4-fluorophenyl) disulfide **1d** with aromatic compounds **3** in the presence of $AlCl_3$ at 25 °C.

Table 3 Reactions of bis(4-tolyl, 4-chlorophenyl and 4-fluorophenyl) disulfides (4-X-C$_6$H$_4$)$_2$S$_2$ **1b–d** (1.0 mmol) with aromatic compounds PhY **3** (10 cm^3) in the presence of AlCl$_3$ (4.0 mmol) at 25 °C under a N$_2$ atmosphere

X of **1**	Y of **3**	*t*/h	Yield (%)									Recovered (%)
			4	**5**	**6**	**4x**	**5x**	**6x**	**4a**	**7a**	**7**	**1**
b; X = Me	**a**; X = H	0.5	0.3	0	45	5.4	1.9	5.6	2.1	1.8	7.0	8.9
b; X = Me	**a**; X = H	1.0	3.5	3.0	52	6.6	3.2	8.1	5.7	2.9	3.5	1.3
b; X = Me	**a**; X = H	24	3.9	4.2	42	0	0	0	38	0	trace	0
c; X = Cl	**a**; X = H	24	5.0	6.7	67	0	0	0	0	0	11	0
c; X = Cl	**e**; X = Cl	24	4.0	0	69	0	0	0	0	0	6.0	20
d; X = F	**a**; X = H	6.0	0	0	80	0	0	0	0	0	trace	0
d; X = F	**b**; X = Me	3.0	18	9.3	57	0	0	0	0	0	2.2	0
d; X = F	**c**; X = Et	6.0	7.0	9.0	54	0	0	0	0	0	20	0
d; X = F	**d**; X = Ph[a]	3.0	0	6.8	69	0	0	0	0	0	3.7	2.5
d; X = F	**e**; X = Cl	6.0	1.9	11	57	0	0	0	0	0	0	0

[a] PhPh (5.0 mmol) dissolved in *n*-hexane (10 cm^3) was used in this reaction.

reactivity–selectivity principle. Regarding $\rho = -9.1$ for the electrophilic aromatic substitution by acetyl cation using MeCOCl in the presence of AlCl$_3$ in ethylene dichloride at 25 °C,[11] the magnitude of the ρ values in our cases may be reasonable for the electrophilic aromatic arylthiolation by the disulfide radical cation. The possibility that a sulfenium ion ArS$^+$ generated by S–S scission of **2** is the reactive intermediate can be excluded by the large negative ρ value; the sulfenium ion should be highly reactive (*i.e.* less selective to aromatic substrate), so that the ρ value for the sulfenium ion mechanism would be much less negative, as inferred from the values $\rho = -4.5$ or -5.2 reported for an aromatic amination[12,13] by phenylnitrenium ion.

Furthermore, the Hammett ρ value -7.0 for the reaction using SbCl$_5$ is less negative than that (*i.e.* -8.8) for the reaction using AlCl$_3$. According to the reactivity–selectivity principle, the reactive intermediate for the former reaction should be more reactive than that for the latter. This is expected since the disulfide radical cation interacting with the soft counter-anion $SbCl_5^{\bullet -}$ is more reactive than that interacting with the hard counter-anion $AlCl_3^{\bullet -}$. Actually, the reaction using SbCl$_5$ proceeds very rapidly at -30 °C,[1] but the reaction using AlCl$_3$ occurs at a moderate speed at 25 °C.

We should consider another possibility, that the reactive intermediate for the phenylthiolation is a sulfonium ion, [PhS–S$^+$(Ph)AlCl$_2$] Cl$^-$, which has a σ-bond between the S atom and the Al atom.[14] If this were correct, the sulfonium ion [PhS–S$^+$(Ph)SbCl$_4$] Cl$^-$ from SbCl$_5$ and **1a** would be less reactive than the sulfonium ion from AlCl$_3$ because of the steric effect of the very bulky SbCl$_4$ relative to AlCl$_2$. The above result that the reaction using SbCl$_5$ proceeds faster than that using AlCl$_3$ could rule out this possibility. The reaction of **1a** with **3b** or **3c** in the presence of SbCl$_5$[1] or AlCl$_3$ afforded the *ortho*-products **4ab** or **4ac** in considerable yield. From the *ortho*-production, the possibility that the reactive intermediate is the very bulky sulfonium ion with Sb atom seems unlikely. On the other hand, the disulfide radical cation **2** interacting relatively weakly with the soft counter-anion $SbCl_5^{\bullet -}$ would give the *ortho*-products. The exclusion of [MeS–S$^+$(Me)AlCl$_2$] Cl$^-$ as intermediate in the aromatic methylthiolation, as described above, also rules out the sulfonium ion mechanism.

Reactions of bis(4-tolyl, 4-chlorophenyl and 4-fluorophenyl) disulfides 1b–d with aromatic compounds 3 in the presence of AlCl$_3$

The reaction of di(4-tolyl) disulfide **1b** with benzene **3a** in the presence of AlCl$_3$ gave phenyl *o*-, *m*- and *p*-tolyl sulfides **4ba**, **5ba** and **6ba** by the intermolecular arylthiolation, together with 4-methylthiophenol **7b** (Table 3). In this reaction, the intramolecular reaction of the disulfide radical cation **2b** from **1b** cannot be avoided, leading to the formation of *p*-tolyl *o*-, *m*- and *p*-tolyl sulfides **4b**, **5b** and **6b** (Table 3); **4b** and **5b** are probably formed by isomerisation from **6b**. Diphenyl sulfide **4a** or thiophenol **7a** were also formed by demethylation from phenyl tolyl sulfides and ditolyl sulfide or from **7b**, respectively. The demethylation giving **4a** occurs favourably under prolonged reaction conditions (Table 3); in the prolonged reaction, **7a** as well as **7b** was consumed by oxidation.

Interestingly, the reactions of bis(4-chlorophenyl and 4-fluorophenyl) disulfides **1c** and **1d** with aromatic compounds led selectively to intermolecular arylthiolation even if a less reactive aromatic compound, such as chlorobenzene **3e**, was used (Table 3). This selective arylthiolation is very valuable for the synthesis of diaryl disulfides containing Cl or F atoms at the *para*-position. An intramolecular reaction of the disulfide radical cation **2c** or **2d** from **1c** or **1d** does not occur in the presence of an aromatic nucleophile because the electron-withdrawing Cl or F group of **2** deactivates the intramolecular reaction, and thus intermolecular arylthiolation takes place.

Experimental

IR spectra were obtained on a JASCO Corporation A-302 spectrometer. ^{1}H NMR spectra were taken with a Nippondenshi PMX-60SI intrument (*J* values are given in Hz). GLC-MS were recorded with a Shimadzu QP-5000 spectrometer linked to a Shimadzu GC-17A; the column (15 m × 0.25 mm) coated with DB-1 (0.25 μm) is made by J & W Scientific. 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 within 3% error for the yields of the products which were determined by replicate GLC analyses. The isolation or separation (as a mixture) of the products was carried out by thin layer chromatography (using Merck Silica Gel 60PF254).

Benzene **3a**, toluene **3b**, ethylbenzene **3c**, chlorobenzene **3e**, d$_6$-benzene, *n*-hexane and ethyl acetate were purified by standard methods before use. The following compounds were reagent grade (Nacalai Tesque), and used without further purification: diphenyl disulfide **1a**, di(4-tolyl) disulfide **1b**, biphenyl **3d**, diphenyl sulfide **4a**, thiophenol **7a**, 4-methylthiophenol **7b**, 4-chlorothiophenol **7c**, 4-fluorothiophenol **7d**, thianthrene **8** and AlCl$_3$. Bis(4-chlorophenyl and 4-fluorophenyl) disulfides **1c** and **1d** were prepared by oxidation (by bubbling air) of 4-chlorophenyl and 4-fluorophenyl mercaptans in DMSO at room temperature for 70 h, and confirmed by the following data. **1c**: The yellow crystalline product had mp 66.2–68.4 °C; ν_{max} (KBr)/cm^{-1} 3050, 1560, 1467, 1380, 1096, 1010, 815 (*para*-substituted phenyl), 775, 740 and 490; δ_H(CDCl$_3$) 7.37 (8H, AB q, *J* 9.0, phenyl H); *m*/*z* 288 and 286 (M$^+$), 145, 143, 108, 99, 82, 75, 73, 69 and 63 (Found: C, 50.17; H, 2.81. Calc. for C$_{12}$H$_8$S$_2$Cl$_2$: C, 50.18; H, 2.81%). **1d**: Liquid, ν_{max} (Nujol)/cm^{-1} 3040, 1580, 1480, 1390, 1285, 1220, 1158, 1095, 1012, 823 (*para*-substituted phenyl), 618 and 497; δ_H($CDCl_3$) 6.80–7.75 (8H, m, phenyl H); *m*/*z* 254 (M^+), 127, 83, 69 and 57 (Found: C, 56.51; H, 3.37. Calc. for $C_{12}H_8S_2F_2$: C, 56.67; H, 3.17%).

Reactions of diphenyl disulfide 1a with benzene 3a in the presence of $AlCl_3$

The reactions of **1a** with **3a** were carried out in the presence of $AlCl_3$ as shown in Table 1. After the reaction, H_2O (10 cm^3) was added, and the organic layer was extracted with ethyl acetate. The products **4a**, **7a** and **8** were isolated by thin layer chromatography, and showed identical spectra to authentic samples. The yields were determined by GLC analysis (Table 1). The reaction of **1a** (0.5 mmol) with d_6-benzene (5.0 cm^3) was performed in the presence of $AlCl_3$ (2.0 mmol) at 25 °C for 24 h under a N_2 atmosphere. Following similar treatment to that performed on the reaction mixture, the GLC-mass analysis for the organic layer indicated the presence of PhSPh containing not d_0–d_4 but d_5–d_{10}. The products **4a** (54%) and **8** (14%) were also obtained in the reaction of **1a** (1.0 mmol) in *n*-hexane (10 cm^3) in the presence of $AlCl_3$ (2.0 mmol) at 25 °C for 24 h under a N_2 atmosphere; in this case, the reaction mixture was treated as described above.

The reaction with **3a** (10 cm^3) using thiophenol **7a** (1.0 mmol) instead of **1a** was performed employing $AlCl_3$ (4.0 mmol) at 25 °C for 72 h under a N_2 atmosphere, and gave **4a** in 59% yield after treating the reaction mixture as described above.

The reaction with **3a** (10 cm^3) using dimethyl disulfide (1.0 mmol) in place of **1a** was carried out in the presence of $AlCl_3$ (4.0 mmol) at 25 °C for 96 h, and produced thioanisole in 76% yield after similar treatment to that peformed on the reaction mixture.

Reactions of diphenyl disulfide 1a with toluene 3b, ethylbenzene 3c, biphenyl 3d and chlorobenzene 3e in the presence of $AlCl_3$

The reactions of **1a** with **3b**–**e** were performed in the presence of $AlCl_3$, under the conditions described in Table 2. The results are summarised in Table 2. The procedures used for isolation and the determination of their yields are given above. Phenyl 2- and 4-tolyl sulfides **4ab** and **6ab**, 2- and 4-ethylphenyl phenyl sulfides **4ac** and **6ac**, and 2- and 4-chlorophenyl phenyl sulfide **4ae** and **6ac** were confirmed by comparison with their spectral data with those of the compounds synthesized in the previous report.[1]

The following products were also confirmed by the spectral data as shown below.

Phenyl 3-tolyl sulfide 5ab. This compound was obtained as a mixture with **4ab** and **6ab**, and gave the following spectra; *m*/*z* (GLC-MS) 200 (M^+), 185 ($M^+ - Me$), 184, 165, 152, 121, 115, 99, 91, 89, 86, 77, 69, 65, 63 and 51. The order **4ab** < **5ab** < **6ab** for the retention time by GLC supports the *meta*-structure. The yield was determined with the assumption that the GLC response factors of **5ab** and **6ab** are identical.

3-Ethylphenyl phenyl sulfide 5ac. This compound was also obtained as a mixture with **4ac** and **6ac**, and gave the following spectra; *m*/*z* (GLC-MS) 214 (M^+), 199 ($M^+ - Me$), 185 ($M^+ - Et$), 184, 166, 165, 105, 99, 91, 89, 77, 65 and 51. The order **4ac** < **5ac** < **6ac** for the GLC retention times also suggests the *meta*-structure. The yield was determined by the same method as for **5ab**.

3-Phenyldiphenyl sulfide 5ad. This product was obtained as a mixture with **6ad**, and gave the following spectra; *m*/*z* (GLC-MS) 262 (M^+), 185 ($M^+ - Ph$), 184, 152, 151, 115, 77 and 51. The order for the GLC retention times is **5ad** < **6ad**, and *m*/*z* 184 ($M^+ - PhH$) and 152 ($M^+ - PhS$) for **5ad** show almost the same intensity as those for **6ad**. The observations indicate the structure for **5ad** to be the *meta*-isomer; were it the *ortho*-isomer, the intensity for *m*/*z* 184 and 152 should be greatly higher than that for the *para*-product **6ad**. The yield of this compound was determined with the assumption that the GLC response factor of this compound is identical with that of **6ad**.

4-Phenyldiphenyl sulfide 6ad. This compound was obtained as a mixture containing a small amount of **5ad**. The spectra for the mixture are as follows: δ_H($CDCl_3$) 7.0–8.0 (14H, m, phenyl H); *m*/*z* (GLC-MS) 262 (M^+), 185, 184, 152, 151, 115, 77, 63 and 51. The yield of **6ad** was determined as described above.

3-Chlorophenyl phenyl sulfide 5ae. This product was also obtained as a mixture with **4ae** and **6ae**, and showed the following spectra; *m*/*z* (GLC-MS) 222 and 220 (M^+), 186, 184 ($M^+ - HCl$), 152, 139, 108, 92, 79, 77, 75, 69, 65, 63, 51 and 50. The peak *m*/*z* 186 for **4ae** and **6ae** was stronger than the peak *m*/*z* 185 for **5ae**. Under short-duration reaction conditions, the product was almost all **6ae**. These results suggest the structures. The yields for **5ae** were determined by GLC as described above. The GLC retention time order was **4ae** < **6ae** < **5ae**.

Reactions of bis(4-tolyl, 4-chlorophenyl and 4-fluorophenyl) disulfides 1b–d with aromatic compounds 3 in the presence of $AlCl_3$

The reactions of **1b**–**d** with aromatics were conducted under the conditions given in Table 3. The results are summarised in Table 3. The products phenyl *o*-, *m*- and *p*-tolyl sulfides **4ba**, **5ba** and **6ba** in the reaction of **1b** with benzene **3a** are identical with the products **4ab**, **5ab** and **6ab**, respectively, in the reaction of **1a** with **3b**. The products 2-, 3- and 4-chlorophenyl phenyl sulfides **4ca, 5ca** and **6ca** in the reaction of **1c** with **3a** are also identical with **4ae**, **5ae** and **6ae**, respectively. The identities of the following products were confirmed by spectroscopic data.

2-, 3- and 4-Tolyl 4-tolyl sulfides 4b, **5b and 6b**. A mixture of these products and **1b** was obtained: δ_H($CDCl_3$) 2.22–2.53 (6H, br, Me) and 6.93–7.40 (8H, m, phenyl H) (Found: C, 78.30; H, 6.30. Calc. for $C_{14}H_{14}S$: C, 78.46; H, 6.58%). The total amount of **4b**, **5b** and **6b** was determined by the deduction of **1b** from this mixture by GLC analysis. The GLC-MS for these products are as follows. **4b**: *m*/*z* 214 (M^+), 199, 184, 165, 122 ($M^+ -$ 4-MePhH), 121, 105, 91, 78, 77, 65 and 45. **5b**: *m*/*z* 214 (M^+), 199, 184, 165, 121, 105, 91, 77, 65, 44 and 40. **6b**: *m*/*z* 214 (M^+), 199, 184, 165, 105, 91, 77, 65 and 45. The peak for *m*/*z* 122 supports the structure of **4b**. The order (**4b** < **5b** < **6b**) for the retention time by GLC suggests the structures. The yields for the products were determined by GLC as described above.

2-Chlorophenyl 4-chlorophenyl sulfide 4ce. This was obtained as a mixture with bis(4-chlorophenyl) sulfide **6ce**, and the structure was confirmed by the GLC-MS; *m*/*z* 256 and 254 (M^+), 218 ($M^+ - HCl$), 184, 139, 110, 109, 108, 91, 75, 63 and 50. The peak *m*/*z* 218 and the shorter retention time than that of **6ce** strongly support the structure. The yield was determined by GLC analysis as described above.

Bis(4-chlorophenyl) sulfide 6ce. This compound was obtained as a mixture with **4ce**: ν_{max} (KBr)/cm^{-1} 3060, 1570, 1560, 1472, 1390, 1100, 1015, 827 and 817 (*para*-substituted phenyl), 742 (*meta*-substituted phenyl of **5ce**), 557 and 488; δ_H($CDCl_3$) 7.25 (4H, almost singlet, phenyl H); GLC-MS *m*/*z* 256 and 254 (M^+), 219, 184, 110, 109, 108, 91, 75, 69, 63 and 50 (Found: C, 56.50; H, 3.31. Calc. for $C_{12}H_8SCl_2$: C, 56.48; H, 3.16%). The yield was determined as described above.

4-Fluorophenyl phenyl sulfide 6da. Liquid, ν_{max} (Nujol)/cm^{-1} 3060, 1582, 1483, 1472, 1432, 1218, 1085, 1059, 830 (*para*-substituted phenyl), 738 and 688 (mono-substituted phenyl), 625 and 520; δ_H($CDCl_3$) 6.83–7.65 (9H, m, 9H, phenyl H); GLC-MS *m*/*z* 204 (M^+), 183, 170, 102, 77, 65 and 51 (Found: C, 70.57; H, 4.67. Calc. for $C_{12}H_9FS$: C, 70.56; H, 4.41%). The GLC peaks corresponding to the *ortho*- and *meta*-isomers were not observed, and thus the reaction of **1d** with **3a** may selectively produce **6da**. The yield was determined as described above.

4-Fluorophenyl 2-, 3- and 4-tolyl sulfides 4db, 5db and 6db. These compounds were obtained as a mixture; δ_H($CDCl_3$) 2.28, 2.32 and 2.37 (3H, three s, Me) and 6.93–7.80 (8H, m, phenyl H) (Found: C, 71.50; H, 5.01. Calc. for $C_{13}H_{11}FS$: C, 71.53; H, 5.08%). **4db**; GLC-MS *m*/*z* 218 (M^+), 203, 202, 183, 165, 122 ($M^+ - C_6H_5F$), 121, 91, 65 and 45. **5db**; GLC-MS *m*/*z* 218 (M^+), 217, 203, 202, 183, 165, 108, 91, 83, 77, 65, 45 and 40. **6db**; GLC-MS *m*/*z* 218 (M^+), 217, 203, 202, 185, 183, 165, 108, 91, 83, 65 and 45. The peak *m*/*z* 122 indicates the *ortho*-structure **4db**. The relative intensity for *m*/*z* 217 ($M^+ - H$) for **6db** was higher than that for **5db**. The order for the retention time by GLC was **4db** < **5db** < **6db**. The results strongly suggest the structures, and the yields for the compounds were determined by GLC analysis as described above.

4-Fluorophenyl 2-, 3- and 4-ethylphenyl sulfides 4dc, 5dc and 6dc. These products were obtained as a mixture: δ_H($CDCl_3$) 1.20 (3H, t, Me), 2.38–3.09 (2H, m, CH_2) and 6.75–7.75 (8H, m, phenyl H) (Found: C, 72.26; H, 5.62. Calc. for $C_{14}H_{13}FS$: C, 72.38; H, 5.64%). **4dc**; GLC-MS *m*/*z* 232 (M^+), 217, 215, 203, 202, 184, 183, 136, 135, 105, 103, 91, 78, 77, 65 and 51. **5dc**; GLC-MS *m*/*z* 232 (M^+), 217, 203, 202, 184, 183, 107, 105, 83, 77, 63 and 51. **6dc**; GLC-MS *m*/*z* 232 (M^+), 217, 203, 202, 185, 183, 127, 105, 99, 83, 77, 63 and 51. The peak *m*/*z* 215 ($M^+ - CH_4$) shows the *ortho*-structure **4dc**. The relative intensity of *m*/*z* 217 ($M^+ - Me$) for **6dc** was higher than that for **5dc**. The order for the retention times by GLC was **4dc** < **5dc** < **6dc**. The results support the structures, and the yields for the products were determined by GLC analysis as described above.

4-Fluoro-3′- and 4′-phenyldiphenyl sulfides 5dd and 6dd. These were obtained as a mixture; δ_H($CDCl_3$) 6.88–8.08 (13H, m, phenyl H) (Found: C, 77.16; H, 4.66. Calc. for $C_{18}H_{13}FS$: C, 77.11; H, 4.67%). **5dd**; GLC-MS *m*/*z* 280 (M^+), 258, 246, 202, 184, 152, 151, 127, 83, 77, 63, 51 and 40. **6dd**; GLC-MS *m*/*z* 280 (M^+), 258, 248, 246, 202, 184, 152, 151, 127, 115, 83, 77, 75, 63 and 51. The GLC retention time for **5dd** was shorter than that for **6dd**. The relative intensities of *m*/*z* 184 ($M^+ - C_6H_5F$) and 152 ($M^+ - C_6H_5FS$) for **5dd** were almost the same as those for **6dd**; the relative intensities for the *ortho*-isomer should be higher than those for the *meta*- and *para*-isomers. The results fit the structures well, and the yields for the products were determined by GLC analysis as described above.

2-, 3- and 4-Chloro-4′-fluorodiphenyl sulfides 4de, 5de and 6de. A mixture of products was obtained (Found: C, 60.53; H, 3.13. Calc. for $C_{12}H_8ClS$: C, 60.38; H, 3.38%). These products were confirmed by GLC-MS and the GLC retention times **4de** > **6de** > **5de**; in fact, the retention time **4ae** < **6ae** < **5ae** was observed for the chloro-substituted compound, as described above. **4de**; 240 and 238 (M^+), 203, 202, 183, 170, 157, 127, 101, 83, 75, 69, 63, 57, 50 and 40. **5de**; 240 and 238 (M^+), 203, 202, 183, 170, 157, 127, 108, 101, 83, 75, 69, 63, 57, 51, 50 and 45. **6de**; 240 and 238 (M^+), 203, 202, 183, 170, 157, 127, 108, 101, 83, 75, 69, 63, 57, 50 and 45.

Hammett plots

A solution containing **1a** (1.0 mmol) and aromatic substrate [**3a** (91 mmol) and **3b** (19 mmol), **3a** (90 mmol) and **3c** (16 mmol), **3a** (111 mmol) and **3d** (10 mmol), or **3a** (10 mmol) and **3e** (94 mmol)] in the presence of $AlCl_3$ (4.0 mmol) was allowed to stand at 25 °C for 1 h under a N_2 atmosphere. After the reaction mixture had been treated as described above, the relative ratios of **6ab**, **6ac**, **6ad** and **6ae** to **4a** were determined by GLC. The relative ratios were almost the same as those for the reactions of 0.5 h duration. The *para*-attacking partial rate factors (k_f) for **3b**–**e** were calculated on the basis of the above relative ratios, initial concentration of the aromatic compounds, the number of C–H bonds of benzene and *para*-C–H bonds of the substituted aromatics. A linear plot with $\rho = -8.8$ was obtained as seen in Fig. 1. The correlation coefficient was -0.990.

Solutions consisting of **1d** (0.50 mmol) and aromatic substrate [**3a** (51 mmol) and **3b** (5.0 mmol), **3a** (50 mmol) and **3c** (5.0 mmol), **3a** (56 mmol) and **3d** (5.0 mmol), or **3a** (5.8 mmol) and **3e** (46 mmol)] were also treated under the same conditions as above. Using the same procedure as described above, a linear plot with $\rho = -8.0$ (having a correlation coefficient of -0.998) was obtained (Fig. 2).

References

1 H. Takeuchi, T. Hiyama, N. Kamai and H. Oya, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2301.
2 H. Takeuchi, H. Oya, T. Yanase, K. Itou, T. Adachi, H. Sugiura and N. Hayashi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 825.
3 P. S. Lakkaraju, D. Zhou and H. D. Roth, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 1119.
4 V. Marti, L. Fernandez, V. Fornes, H. Garcia and H. D. Roth, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 145.
5 M. Wejchanjudek and B. Perkowskaspiewak, *Polym. Degrad. Stab.*, 1995, **48**, 131.
6 K. Okaizu, N. Iwasaki, K. Yamamoto, H. Nishide and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1456.
7 K. Yamamoto, K. Oyaizu and E. Tsuchida, *Macromol. Chem. Phys.*, 1994, **195**, 3087.
8 K. Yamamoto, E. Tsuchida, H. Nishida, S. Yoshida and Y. S. Park, *J. Electrochem. Soc.*, 1992, **139**, 2401.
9 L. Craine and M. Raban, *Chem. Rev.*, 1989, **89**, 689.
10 F. A. Davis, E. R. Fretz and C. J. Horners, *J. Org. Chem.*, 1973, **38**, 690.
11 J. A. Hirsch, *Concepts in Theoretical Organic Chemistry*, Allyn and Bacon, Inc., Boston, 1974, p. 179.
12 H. Takeuchi and K. Takano, *J. Chem. Soc.*, *Perkin Trans. 1*, 1986, 611.
13 H. Takeuchi, T. Taniguchi and T. Ueda, *J. Chem. Soc.*, *Perkin Trans. 2*, 2000, 295.
14 T. Mukaiyama and K. Suzuki, *Chem. Lett.*, 1993, 1.