Novel Generation of Arylsulfenium Ion Intermediates and Efficient Aromatic Arylthiolation by the Intermediates†

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Reactions of hydrazoic acid and alkyl azides with alkyl aryl sulfide in trifluoroacetic acid containing trifluoromethanesulfonic acid or H_2SO_4 proceeded through an *S*-arylaminosulfonium ion and a protonated *S*-arylsulfenamide, giving efficiently 4-alkylthiophenyl aryl sulfide *via* an arylsulfenium ion interacting with both the counter-anion and the unshared electron pair of the amine. The use of the *S*-arylsulfenamide instead of the azides also afforded the above product by aromatic arylthiolation in a good yield *via* the sulfenium ion along with its *ortho*-isomer, diaryl disulfide and diaryl sulfide. The formation of the sulfenium ion was demonstrated by the effect of the counter-anion, the amine, the aryl substituent of the sulfenamide and the solvent nucleophilicity. We ruled out the possibility that the arylthiolation occurs *via* an arylthiyl radical and an aminium radical from the sulfenamide and by direct reaction of the protonated sulfenamide with alkyl aryl sulfides.

Many researchers[1] have proposed the formation of sulfenium ion intermediates, but there is no clear evidence for their existence; several studies[2] have failed to support their existence; the sulfenium ions have been supposed to have too short a lifetime to exist as free ions, being converted to sulfonium[3] or episulfonium ions[4] by reaction with sulfides or alkenes in the reaction system. However, in this report, we present the first generation of sulfenium ions that are free ions but interact with both the counter-anion and the unshared electron pair of amine. An efficient aromatic arylthiolation by the sulfenium ions should also arouse interest.

Results and Discussion

Reactions of the Hydrazoic Acid **1a** *or the Alkyl Azides* **1f** *and* **h** *with the Alkyl Phenyl Sulfides* **2a–c** *Using Trifluoromethanesulfonic Acid (TFSA) or* H_2SO_4 *in the Presence of Trifluoroacetic Acid (TFA).*—We have already reported direct aromatic amination by the treatment of **1a** with aromatic compounds in the presence of both TFA and TFSA.[5] However, the reactions of **1a** with methyl, butyl and heptyl phenyl sulfides **2a–c** in the presence of both TFSA and TFA at 25 °C gave no arylamines but rather the 4-alkylthiophenyl phenyl sulfides **6a–c** by an aromatic phenylthiolation in high yields, together with the diphenyl disulfide **9a** and the diphenyl sulfide **10a** (Table 1). Compound **6a** was also formed, along with **9a** and **10a**, in the reaction of butyl and heptyl azides **1f** and **h** with **2a**. 2-Methylthiophenyl phenyl sulfide **7a** was produced in a low yield, with **6a**, **9a** and **10a**, in the reaction of **1a** with **2a** at 70 °C (Table 1). Using H_2SO_4 instead of TFSA in the reaction of **1a** or **f** with **2a** gave similar results (Table 1).

(*a*) *Concerted process involving attack of* **2** *on the conjugate acid of azides and elimination of* N_2. The azide **1a** did not decompose in TFA alone, but required in addition TFSA or H_2SO_4. The decomposition of the azides **1f** and **h** occurred in the presence of TFA but not in its absence, and was accelerated in the presence of TFSA or H_2SO_4. Further, the decomposition of these azides was promoted in the presence of **2a**. These results indicate that the denitrogenation proceeds *via* a concerted process involving both nucleophilic attack of **2** on the conjugate acid of **1** and an elimination of N_2 from the conjugate acid to form the aminosulfonium ions **3** (Scheme 1).

Table 1 Reactions[a] of hydrazoic acid **1a** (5.2 mmol) and butyl and heptyl azides **1f** and **1h** (5.2 mmol) with alkyl phenyl sulfides **2a–c** (5.0 cm^3) in the presence of both TFA (5.0 cm^3) and TFSA (1.5 cm^3)

Reagent	R of RSPh **2**	*T*/°C	*t*/h	Yield[b] (%) **6**	**7**	**9a**	**10a**
1a	**a**; Me	25	0.5	99	0	*f*	*f*
1a	**a**; Me	70	0.5	71	3.2	5.0	*f*
1a[c]	**a**; Me	25	24	27	0	0	*f*
1a[d]	**a**; Me	25	0.5	99	0	*f*	0
1a	**b**; Bu	25	0.5	99	0	*f*	*f*
1a	**c**; Hep	25	0.5	99	0	*f*	*f*
1f[e]	**a**; Me	25	0.5	66	0	*f*	2.9
1f	**a**; Me	25	0.5	74	0	7.2	2.4
1h	**a**; Me	25	0.5	64	0	*f*	*f*

[a] The reactions were carried out by adding a mixture of **2** and **1a** dissolved in $CHCl_3$ (3.0 cm^3) to a mixture of TFSA or H_2SO_4 and $CHCl_3$ was not used in the use of **1f** and **h**. [b] The yields are based on the amount of **1** consumed. [c] Only TFA was used as an acid. [d] The reaction was performed by adding a mixture of **2a** (17 mmol) and **1a** (1.5 mmol) dissolved in $CHCl_3$ (1.0 cm^3) was added to a mixture of TFA (5.0 cm^3) and H_2SO_4 (6.0 mmol). [e] A mixture of **1f** (2.5 mmol) and **2a** (17 mmol) was similarly added to a mixture of TFA (5.0 cm^3) and H_2SO_4 (10 mmol). [f] Trace.

(*b*) *Formation of the aminosulfonium ions* **3** *and the protonated sulfenamides* **4**. The formation of the sulfide **6** *via* the aminosulfonium ion **3** is supported by the fact that the reason of *S*-amino-*S*-methyl-*S*-phenylsulfonium mesitylenesulfonate **3a** with **2a** or **c** afforded mainly the sulfides **6a** or **c**, respectively, in the presence of TFA and TFSA (Experimental). The photolysis of 1-aminoquinolinium perchlorate in the presence of both **2a** and TFA gave rise to the sulfide **6a** (53%) (Experimental). A parent nitrenium ion intermediate has been proposed in this photolysis,[6] so that **6a** would be formed *via* **3** given by reaction of the nitrenium ion with **2a** (Scheme 1).

The reaction of **1h** with **2a** for a shorter time produced **6a** in a lower yield and gave a larger proportion of the sulfenamide **5h** after treatment with aq. NaOH (Experimental). This implies that **6** is formed *via* the protonated sulfenamides **4** given by dealkylation of **3** (Scheme 1). In fact, the reaction of **1a** with **2c**

† Preliminary report, H. Takeuchi, T. Yanase, K. Itou, H. Ōya and T. Adachi, *J. Chem. Soc., Chem. Commun.*, 1992, 916.

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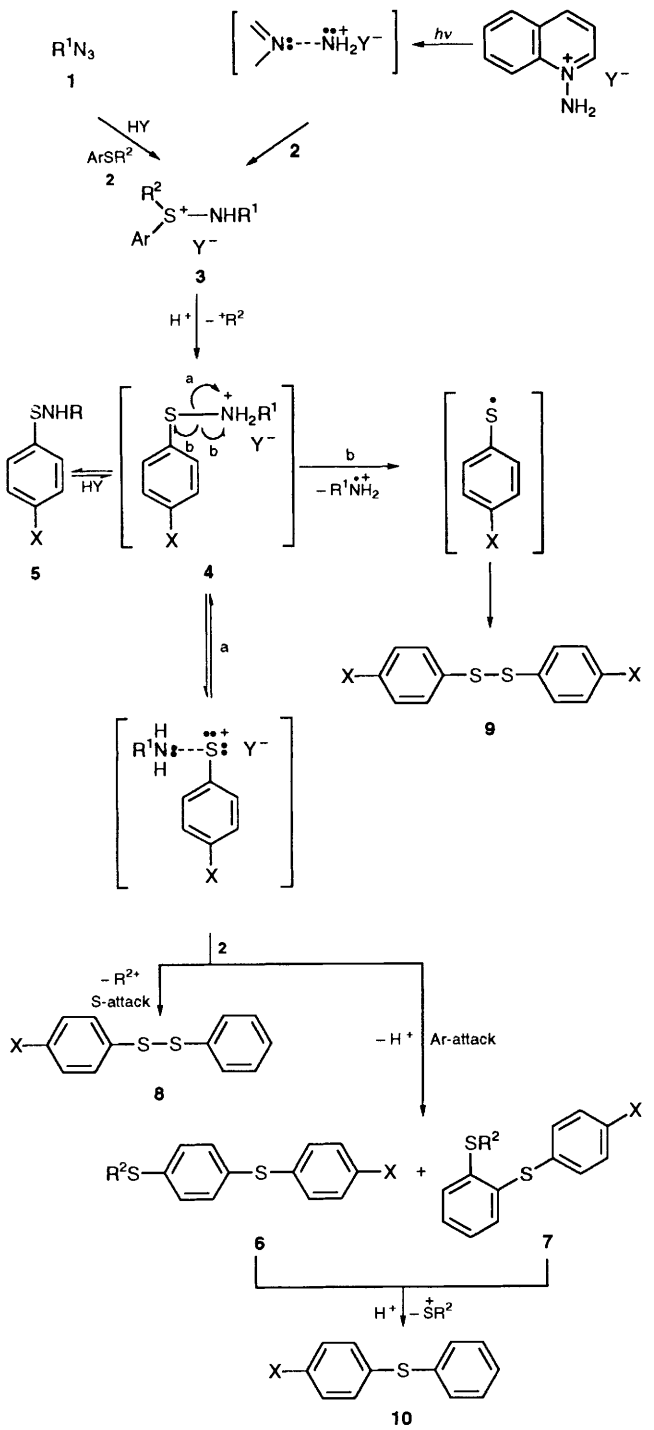


	R¹	R²	X
a	H	Me	H
b	Me	Bu	H
c	Et	Hep	H
d	Pr	Me	H
e	Pr^{i}	Me	H
f	Bu	Me	H
g	Bu^{t}	Me	H
h	Hep	Me	H
c′	Et	Me	Me
c″	Et	Me	NO_2

Scheme 1

gave $C_7H_{15}OCOCF_3$ and $C_7H_{15}OSO_2CF_3$ by dealkylation (Experimental). The formation of **6** from **4** is discussed below in detail.

Reactions of the N-*Alkyl*-S-*arylsulfenamides* **5** *with the Thianisole* **2a** *Using Catalytic Acid in the Presence of TFA.*—*N*-Methyl-, *N*-ethyl-, *N*-propyl-, *N*-isopropyl-, *N*-butyl- and *N*-*tert*-butyl-*S*-phenylsulfenamides **5b–g** were treated with **2a** using H_2SO_4 in the presence of TFA, and **6a** was formed by aromatic phenylthiolation in high yield, along with the sulfides **7a**, **9a** and **10a** (Table 2). A similar reaction of **5c** with **2a** was observed using TFSA or HCl instead of H_2SO_4 and using only TFA as an acid (Table 2), and using CH_2Cl_2, CF_3CH_2OH and EtOH instead of TFA (Table 3). The reaction using *N*-ethyl-*S*-(4-tolyl)sulfenamide **5c′** or *N*-ethyl-*S*-(4-nitrophenyl)sulfenamide **5c″** is also presented in Table 2.

The yields of the products **6–10** were almost independent of the reaction time (0.5 or 1 h) and the reaction method (method a or c) (Experimental). Thus, all the products would appear to be stable under the reaction conditions.

(*a*) *Mechanism for formation of the diaryl disulfide* **9** *and the diaryl sulfide* **10**. The compound **5c** was converted into the disulfide **9a** in CH_2Cl_2 in the presence of TFA, but neither in CH_2Cl_2 alone nor in both CH_2Cl_2 and **2a**, but in the absence of TFA (Experimental). The reaction of **5c′** with **2a** in the presence of TFA gave the products $(4\text{-}MeCH_6H_4S)_2$ **9c′** (38%) and 4-MeC_6H_4SSPh **8c′** (1%) in addition to the sulfides **6c′** and **7c′** (Experimental). This suggests that **9** is formed *via* a protonation of **5** by acid such as TFA, and then the protonated sulfenamide **4** undergoes a homolytic *S–N* scission (shown as path b in Scheme 1) forming an arylthiyl radical, giving **9** by its dimerisation (Scheme 1). This type of dimerisation is well known.[7] The product **8c′** may be formed by an *S*-attack (as a minor route) on **2a** of the sulfenium ion (Scheme 1). The formation of **9** by attack of the sulfenium ion on the *S*-atom of **4** is probably impossible because of the repulsion between their positive charges in the transition state.

The yield of **10a** was somewhat high in the presence of TFSA as a strong acid and in the use of high concentration of H_2SO_4 (Table 2), and **10a** was formed in 5.5% in the reaction of **6a** in the presence of both TFA and TFSA (Experimental). These indicate that **10** is formed by acidic decomposition of **6** and **7** (Scheme 1).

(*b*) *Formation of arylsulfenium ions.* The results shown below suggest that heterolytic S–N scission of **4** (path a giving the sulfides **6** and **7** by aromatic arylthiolation) competes with homolytic S–N scission (path b giving **9**), giving the arylsulfenium ion **2** which interacts with both the unshared electron pair of amine and the counter-anion (Scheme 1). We have proposed a similar interaction of the parent nitrenium ion in earlier work.[6]

(1) *Effect of amines.* Longer chain alkylamines hinder the reactivity of the sulfenium ion interacting with amine by closing the alkyl chain to the *S*-atom of the sulfenium ion. Thus the homolytic path b supervenes by depressing the heterolytic path a due to a fast equilibrium between **4** and the sulfenium ion; in fact, the use of **5d** and **f** (propyl- and butyl-amines) compared to **5b** and **c** (methyl- and ethylamines) reduces the product ratio (**6** + **7**)/**9** (Table 2). Further, a higher proportion of product **6**/**7** was obtained with longer chain amines (Table 2), presumably because the activation energy of *ortho*-attack to give the product **7** is increased by steric crowding.

Isopropyl- and *tert*-butyl-amines are less nucleophilic towards the sulfenium ion than the corresponding straight chain alkylamines because of their bulk, so the sulfenium ion, interacting weakly with these less nucleophilic amines, is more reactive. Thus, using **5e** and **g** (giving isopropyl- and *tert*-butyl-amines) rather than **5d** and **f** (giving propyl- and butyl-amines) gave a higher ratio of (**6** + **7**)/**9** and a lower ratio of **6**/**7** (Table 2).

We obtained butylamine (13%) in the reaction of **5f** with **2a** in TFA containing H_2SO_4 (Experimental). This shows that the

Table 2 Reactions of *N*-alkyl-*S*-arylsulfenamides **5** with thioanisole **2a** in the presence of TFA and a catalytic acid (HY) at 25 °C for 0.5 h

R of RNHPh **5**	HY	Counter-Anion Y^-	Yield[a] (%)				Ratio	
			6	**7**	**9**	**10**	**6**/**7**	(**6** + **7**)/**9**
b; Me[b]	H_2SO_4	$^-OSO_3H$	83	8.3	1.8	0.5	10	51
c; Et[b]	H_2SO_4	$^-OSO_3H$	86	8.8	5.1	0.5	9.7	19
d; Pr[b]	H_2SO_4	$^-OSO_3H$	73	3.4	23	0.9	21	3.3
e; Pr^i[b]	H_2SO_4	$^-OSO_3H$	86	10	0	0.5	8.6	
f; Bu[b]	H_2SO_4	$^-OSO_3H$	67	3.0	29	0.8	22	2.4
g; Bu^t[b]	H_2SO_4	$^-OSO_3H$	79	8.4	12	0.4	9.4	7.3
f; Bu[c]	H_2SO_4	$^-OSO_3H$	91	14	6.0	2.0		
c; Et[d]	H_2SO_4	$^-OSO_3H$	85	9.0	5.8	0.6	9.4	16
c; Et[d]	HCl	^-Cl	54	5.8	39	0.3	9.3	1.5
c; Et[d]	None	$^-O_2CCF_3$	55	6.1	36	0.5	9.0	1.7
c; Et[d]	TFSA	$^-OSO_2CF_3$	53	13	30	3.2	4.1	2.2
c′; Et[e]	H_2SO_4	$^-OSO_3H$	78	10	3.0	0	7.8	29
c″; Et[f]	H_2SO_4	$^-OSO_3H$	75	1.2	0	0	63	

[a] The yields of **6a**, **7a**, **9a** and **10a** are based on the amount of **5** consumed. [b] Method a: the reactions were performed after adding a mixture of **2a** (21 mmol) and **5** (2.5 mmol) to a mixture of TFA (2.5 cm^3) and H_2SO_4 (3.0 mmol). [c] Method b: a mixture of **2a** (17 mmol) and **5f** (2.5 mmol) was added to TFA (5.0 cm^3) and H_2SO_4 (10 mmol). [d] Method c: a mixture of **2a** (17 mmol) and **5** (2.5 mmol) was similarly added to TFA (10 cm^3) and HY (3.75 mmol). [e] *N*-Ethyl-*S*-(4-tolyl)sulfenamine **5c′** as **5** was used in method c, and the products were **6′**, **7c′** and **9c′**. [f] *N*-Ethyl-*S*-(4-nitrophenyl)sulfenamide **5c″** as **5** was used in method c, and the products were **6c″** and **7c″**.

Table 3 Solvent effect on the reaction[a] of *N*-ethyl-*S*-phenylsulfenamide **5c** (2.5 mmol) with thioanisole **2a** (17 mmol) in the presence of both a solvent and H_2SO_4 (3.75 mmol) at 25 °C for 0.5 h

Solvent	Yield[b] (%)			
	6a	**7a**	**9a**	**10a**
TFA	85	9.0	5.8	0.6
CF_3CH_2OH	31	3.2	30	0
CH_2Cl_2	13	0	52	0
C_2H_5OH	0	0	48	0

[a] The reaction was carried out after adding a mixture of **2a** and **5c** to a solution containing a solvent and H_2SO_4. [b] The yields are based on the amount of **5** consumed.

amine is formed by the path a and by hydrogen-abstraction of aminium radical. The low yield of the amine results from instability of the amine under the reaction conditions (Experimental).

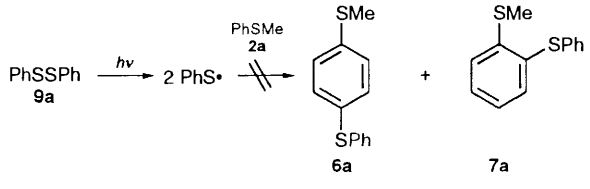
(2) *Effect of counter-anions.* The anion formed from the catalytic acid, TFSA, H_2SO_4 or HCl, should be the counter-anion for the sulfenium ion. Using only TFA as an acid, the counter-anion is $^-OCOCF_3$. The product ratio (**6** + **7**)/**9** increased with the increased 'soft' property ($^-OSO_3H$ > $^-OSO_2CF_3$ > $^-OCO_2CF_3$ > ^-Cl) of the counter-anion (Table 2). This is quite reasonable since the sulfenium ion with the softer counter-anion should be more reactive, favouring formation of **6** and **7**; path b, giving **9**, probably does not depend upon the counter-anion. The ratio **6**/**7** might be insensitive to the counter-anion because although the softer anion promotes higher reactivity of the sulfenium ion it also reduces reactivity by steric crowding.

(3) *Effect of substituent at phenyl ring of arylsulfenium ions.* The reaction of *N*-ethyl-2-(4-tolyl)- or *N*-ethyl-*S*-(4-nitrophenyl)-sulfenamide **5c′** or **c″** in TFA containing H_2SO_4 produced 4- and 2-methylthiophenyl 4-tolyl sulfides **6c′** and **7c′** or 4- and 2-methylthiophenyl 4-nitrophenyl sulfides **6c″** and **7c″** (Table 2). The order of selectivities, **6c″**/**7c″** = 63 > **6a**/**7a** = 9.4 > **6c′**/**7c′** = 7.8 suggests that 4-nitrophenylsulfenium ion has higher positive charge on *S*-atom than phenyl- and 4-tolylsulfenium ions, because of the electron-withdrawing nitro group, and so interacts more strongly with the amine and/or the counter-anion, and is the least reactive (*i.e.* the most selective). In contrast, 4-tolylsulfenium ion with lower positive charge on the *S*-atom is the least selective.

(4) *Effect of solvent nucleophilicity.* The total yield of **6** and **7** increased with a decrease in the solvent nucleophilicity (EtOH > CF_3CH_2OH > TFA) (Table 3). This is in accord with the proposal that **6** and **7** are formed by an ionic mechanism (*via* the sulfenium ion) in which the reactivity of the sulfenium ion is lowered in a highly nucleophilic solvent by solvation and/or their yields are depressed by reaction with the solvent; the sulfenium ion would appear to react with EtOH giving a complex mixture of products because **9a** was formed in only 48% yield although **5** was completely consumed.

When the sulfenium ion is more reactive, path a should be preferred to path b, considering the fast equilibrium between **4** and the sulfenium ion. Path b, giving the radical intermediate, would be insensitive to the solvent nucleophilicity. Therefore, the high reactive sulfenium ion in the low nucleophilic solvent TFA gives a low yield of **9**, whereas the less reactive sulfenium ion in highly nucleophilic EtOH shows a high yield of **9** (Table 3).

(5) *Exclusion of other mechanisms for aromatic arylthiolation.* The photolysis of **9a** in the presence of **2a** did not produce **6a** and **7a**. This excludes from consideration a radical mechanism in which **6** and **7** are formed by reaction of arylthiyl radical with **2** (Scheme 2) since the photolysis is known to form phenylthiyl radical.[8]



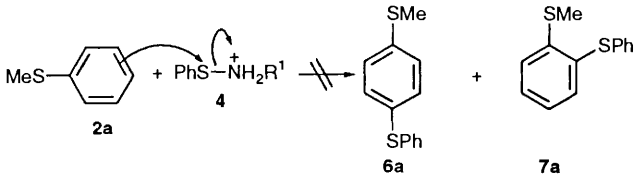
Scheme 2

We can rule out the possibility that a direct reaction of **4** with **2** gives **6** and **7** (Scheme 3): the direct reaction of **4e** or **g** with **2a** should be greatly retarded by substantial overlap between the attacking **2a** and two or three methyl groups of **4e** or **g** in the transition state. However, both **6** and **7** are preferably formed using **5e** or **g** (having two or three methyl groups) rather than **5d** or **f**, respectively (Table 2). The direct reaction might be slightly retarded in going from a less to a more polar solvent because the positive charge dissipates upon passing from the initial to the transition state.[9] The direct reaction is not plausible since the formation of **6** and **7** is completely suppressed in the use of

Table 4 Reactions[a] of *N*-ethyl-*S*-phenylsulfenamide **5c** (2.5 mmol) with aromatic compounds ArH (17 mmol), butyl phenyl sulfide **2b**, 2-methylthioanisole **2i**, anisole **2j**, toluene **2k** and naphthalene **2l**, in the presence of TFA (10 cm^3) and H_2SO_4 (3.75 mmol) at 25 °C for 0.5 h

	Yield[b] (%)			
ArH **2**	**6**	**7**	**9a**	**10a**
2a	85	9.0	5.8	0.6
2b	62	5.0	33	*d*
2i	65	6.1	*d*	*d*
2j	74	0	*d*	*d*
2k	6.6	0.5	7.0	*d*
2l[c]	13		2.4	*d*

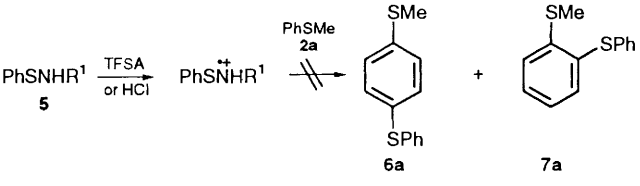
[a] The reactions were performed after adding a mixture of **2** and **5c** to a mixture of TFA and H_2SO_4. [b] The yields are based on the amount of **5c** consumed. [c] CH_2Cl_2 (3.0 cm^3) was added to dissolve **2l**. [d] Trace.



Scheme 3

EtOH as solvent (Table 3). Presumably, the soft property of the counteranion has less effect on the direct reaction as it interacts with the *N*-position of **4**, which is not the reactive position. Thus, the direct reaction would be unlikely, as the ratio (**6** + 7)/**9** depends upon the counter-anion as described above.

The possibility that **6** and **7** are formed by reaction of an aminium radical from **5** with **2** can be eliminated because the reaction of **5** with **2** produces **6** and **7** in a sufficiently high total yield in the presence of HCl or TFSA[10] which has a non-oxidising nature (Scheme 4); *i.e.* when the aminium radical

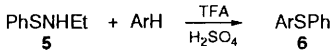


Scheme 4

cannot be formed. In fact, the radical cation of **9a** is formed from **9a** in the presence of H_2SO_4, but not in the presence of HCl, TFSA or TFA; this will be reported in the near future.

Effect of Use of Different Precursors for Formation of the Same Sulfenium Ion.—Both the reaction of **1f** with **2a** and that of **5f** with **2a** were carried out under the same conditions in the presence of both TFA and H_2SO_4 (Tables 1 and 2). These reactions seem to form the same intermediate (*i.e.* the phenylsulfenium ion interacting with both the same amine and counter-anion, butylamine and $^-OSO_3H$), and to give the same products. However, **7a** is not formed in the former reaction using **1f**, but **7a** was obtained in a low yield in the latter using **5f**. The other reactions at 25 °C using **1** did not give **7**, but those using **5** gave **7** in low yields (Tables 1 and 2). The subsequent fates of **1** and **5** play an important role in the difference between the reactions using **1** and **5**, and the details of this are now under investigation.

Electrophilic Character of Phenylsulfenium Ion.—The reactions of sulfenamide **5c** with thioanisole **2a**, butyl phenyl sulfide **2b**, 2-methylthioanisole **2i** and anisole **2j** gave 4-methylthiophenyl, 4-butylthiophenyl, 3-methyl-4-methylthiophenyl and 4-methoxyphenyl phenyl sulfides **6a**, **b**, **i** and **j**, respectively, in good yields, but those with toluene **2k** and naphthalene **2l** produced phenyl 4-tolyl sulfide **6k** and 1-naphthyl phenyl sulfide **6l** in low yields (Table 4 and Scheme 5). The low yield



	Ar
a	4-$MeSC_6H_4$
b	4-$BuSC_6H_4$
i	3-Me-4-$MeSC_6H_3$
j	4-$MeOC_6H_4$
k	4-MeC_6H_4
l	1-Naphthyl

Scheme 5

can be interpreted as follows. Toluene and naphthalene are not as nucleophilic as amines or thioanisole derivatives, and thus the sulfenium ion preferentially reacts with the solvent rather than the aromatics, giving complex mixtures; this is well supported by the fact that the yield of **9** and **10** is lower in spite of the complete consumption of **5**.

Adding anisole **2j** to the reaction system including **1a** and **2a** in TFA and TFSA, the relative reactivity (1.7) for the formation of **6j** to that of **6a** was determined (Experimental). The high relative reactivity of highly electrophilic anisole and the lack of formation of *meta*-isomers of **6a** and **j** are not contradictory to the intermediacy of cationic species such as the sulfenium ion.

Experimental

IR spectra were obtained on a Hitachi EPI-G3 spectrometer. NMR spectra (^1H and ^{13}C) were taken with a Nippondenshi JNM-FX-60Q instrument. Mass spectra were recorded with a Hitachi M-80 spectrometer. GLC was performed with a Shimazu GC-6A chromatograph using a glass column (1 m × 3 mm) packed with 10% silicone SE-30 on 80–100 mesh Chromosorb WAW DMCS. Two runs agreed within ± 3% for the yields of the products which were determined by replicate GLC analyses. Preparative GLC was carried out with a Hitachi model 063-0012 unit using a column (1 m × 3 mm) packed with 10% silicone SE-30 on the above Chromosorb.

Toluene **2k**, dichloromethane, chloroform and ethanol were purified by standard methods before use. TFA was purified by distillation.

The following compounds were reagent grade (Wakō), and used without further purification: thioanisole **2a**, anisole **2j**, TFSA, H_2SO_4, naphthalene **2l**, trifluoroethanol, diphenyl disulfide **7a** and diphenyl sulfide **8a**.

Hydrazoic acid **1a** was obtained as a $CHCl_3$ solution after the reaction of NaN_3 with H_2SO_4 as described in the literature.[11] Butyl azide[12] and heptyl azide[12] **1f** and **h** were prepared by treatment of butyl and heptyl bromide (5.0 mol) with NaN_3 (0.53 mol) in H_2O in the presence of tetrabutylammonium bromide (5.3 mmol) at 70 °C for 2 days.

Alkyl aryl sulfides, butyl phenyl sulfide **2b**, heptyl phenyl sulfide **2c** and 2-methylthioanisole **2i** were synthesised by the following method.[13,14] Sodium salt of phenylmercaptan or 2-methylphenylmercaptan was obtained by treatment of the corresponding mercaptan (0.1 mol) with 17% aq. NaOH (25 cm^3). The solution containing the salt was refluxed for 3 h after addition of alkyl iodide (methyl, butyl or heptyl iodide; 0.1 mol), to give the corresponding product **2**.

S-Amino-*S*-methyl-S-phenylsulfonium mesitylenesulfonate **3a**[15] and 1-aminoquinolinium perchlorate[6] were obtained by the methods mentioned in the literature.

N-Alkyl-*S*-arylsulfenamides **5b–g**, **5c′** and **5c″** are synthesised

Table 5 Physical and spectroscopic data for 4-substituted phenyl aryl sulfides, 4-RC_6H_4SAr, **6**

	R Ar (Formula)	Found (%) (Required)				δ_H [a]		δ_C [a,b]		
		C	H	N	M.p./°C	Arom.	Other	Arom.	Other	m/z [c]
6a [21]	SMe Ph				*f*	7.1–8.1 (m, 9 H)	2.25 (s, 3 H, Me)	126.3, 126.9, 128.7, 129.9, 132.1	15.6 (SMe)	232 (M^+), 217, 184, 108, 77, 51
6b	SBu Ph ($C_{16}H_{18}S_2$)	69.75 (70.0)	6.9 (6.6)		*f*	7.3–7.9 (m, 9 H)	1.0 (t, 3 H, Me), 1.2–2.0 (m, 4 H, $MeCH_2CH_2$), 3.0 (t, 2 H, SCH_2)	126.5, 128.8, 129.0, 130.2, 131.6	13.5 (Me), 21.8 ($MeCH_2$), 30.9 ($MeCH_2CH_2$), 33.0 (SCH_2)	274 (M^+), 218, 184, 109, 77, 51, 41
6c	SHep Ph ($C_{19}H_{24}S_2$)	71.9 (72.1)	7.85 (7.65)		*f*	7.1–8.1 (m, 9 H)	0.6–2.0 [m, 13 H, $Me(CH_2)_5$] 3.45 (t, 2 H, SCH_2)	125.5, 127.9, 128.1, 129.3, 130.6	13.0 (Me), 21.5 ($MeCH_2$), 27.5 [$MeCH_2(CH_2)_2$], 27.9 [$Me(CH_2)_3CH_2$], 28.6 [$Me(CH_2)_4CH_2$], 30.6 (SCH_2CH_2), 32.4 (SCH_2)	
6c′	SMe 4-MeC_6H_4 ($C_{14}H_{14}S_2$)	68.15 (68.25)	5.75 (5.75)		(39–40 °C)	7.2–8.0 (m, 8 H)	2.4 (s, 3 H, Me), 2.45 (s, 3 H, SMe)	126.5, 127.1, 128.4, 129.6, 130.8, 131.2, 133.0, 136.6	15.8 (SMe), 21.0 (Me)	246 (M^+), 231, 199, 185, 165, 140, 123, 108, 91, 65, 45
6c″	SMe 4-$NO_2C_6H_4$ ($C_{13}H_{11}NO_2S_2$)	56.5 (56.3)	3.85 (4.00)	5.00 (5.05)	(75.0 °C)	7.9 (ABq, 4 H) 7.69 (ABq, 4 H)	2.6 (s, 3 H, Me)	123.8, 124.1, 125.8, 126.1, 126.9, 135.0, 137.6, 141.6	15.1 (SMe)	247 (M^+), 231, 215, 184, 155, 139, 108, 91, 69, 45
6i	*d*									264 (M^+), 216, 231, 198, 153, 121, 91, 77
6j [22]	OMe Ph				*f*	6.9–8.2 (m, 5 H) 7.45 (ABq, 4 H)	4.0 (s, 3 H, OMe)	114.6, 125.3, 127.9, 128.5, 135.1		
6k [25]	Me Ph				*f*	7.3–8.1 (m, 9 H)	2.45 (s, 3 H, Me)	125.9, 128.6, 129.4, 129.6, 131.3, 132.1, 136.8, 137.1		200 (M^+), 185, 165, 152, 109, 99, 91, 78, 65, 51, 46
6l [26]	*e*				*f*	7.8–8.9 (m, 12 H)		125.5, 125.7, 126.1, 126.4, 126.6, 126.9, 128.2, 128.7, 128.8, 132.2		

[a] NMR spectra were recorded in $CDCl_3$–CCl_4 with TMS as internal standard. [b] The quaternary carbons of **6a–c**, **j** and **l** did not appear under these conditions. [c] The mass spectra were obtained by EI method. [d] **6i** is 3-methyl-4-methylthiophenyl phenyl sulfide. [e] **6l** is 1-naphthyl phenyl sulfide. [f] Liquid.

Table 6 Mass spectroscopic data for 2-substituted phenyl aryl sulfides, 2-RC_6H_4SAr, **7**

	R	Ar	*m/z* (EI method)	*m/z* (CI method)
7a	SMe	Ph	232 (M^+), 217 (M^+ − Me), 185 (M^+ − SMe),[a] 184, 153, 123, 108, 91, 77, 69, 51, 45	233 (M^+ + 1)
7b	SBu	Ph	274 (M^+), 218, 184, 140 [M^+ − (Ph + Bu)], 109, 91, 77, 69, 65, 57, 51, 41	275 (M^+ + 1)
7c′	SMe	4-MeC_6H_4	246 (M^+), 231, 216 (M^+ − 2Me),[a] 199, 197, 185, 153, 121, 108, 105, 91, 63, 45	247 (M^+ + 1)
7c″	SMe	4-$NO_2C_6H_4$	277 (M^+), 247, 216, 184, 153 (M^+ − $C_6H_6NO_2$), 121 (M^+ − $C_6H_6NO_2S$), 108, 91, 65, 45	
7i		*b*	246 (M^+), 231 (M^+ − Me),[a] 197, 153, 121, 91, 77, 55	
7k	Me	Ph	200 (M^+), 185, 165, 122 (M^+ − PhH), 110, 91, 78, 65, 51, 46	

[a] The relative intensity of these peaks was higher than that of the corresponding *para*-isomers. [b] **7i** is 3-methyl-2-methylthiophenyl phenyl sulfide.

by reaction of the corresponding amine (methyl-, ethyl-, propyl-, isopropyl-, butyl- or *tert*-butyl-amine) with diaryl disulfide [diphenyl, di(4-tolyl) or di(4-nitrophenyl) disulfide] in the presence of $AgNO_3$ as described in the literature.[16] Di(4-tolyl) disulfide **9c′**[17] was obtained by oxidation of 4-tolylmercaptan by dimethyl sulfoxide,[18] and di(4-nitrophenyl) disulfide[19] was prepared by reaction of 4-chloronitrobenzene with sodium sulfide in the presence of sulfur.[20]

Reactions of Hydrazoic Acid **1a** *and Alkyl Azides* **1f** *and* **h** *with Alkyl Phenyl Sulfides* **2a–c** *in the Presence of TFA and TFSA or* H_2SO_4.—The azides were almost completely decomposed under the conditions employed, as shown in Table 1. On completion of 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 products isolated by preparative GLC, with the yields determined by GLC analysis. The reaction of **1a** (3.0 cm^3 of 1.7 mol dm^{-3} $CHCl_3$ solution) with a mixture of **2a** (3.0 cm^3) and anisole **2j** (3.0 cm^3) was carried out in the presence of both TFA (5.0 cm^3) and TFSA (1.5 cm^3) at 25 °C for 0.5 h, and the yield of **6a** (63%) and 4-methoxyphenyl phenyl sulfide **6j** (35%) was determined as shown above. The relative reactivity for the formation of **6j** to that of **6a** was calculated to be 1.7 from the result. The structure of diphenyl disulfide **9a** and diphenyl sulfide **10a** was identified by comparison with the IR and the ^1H and ^{13}C NMR spectra of authentic samples. The physical and spectroscopic data for 4-substituted phenyl phenyl sulfides, **6a** and new compounds **6b**, **c** and **j**, are given in Table 5. The mass spectroscopic data for 2-substituted phenyl phenyl sulfides **7a** and **b** are indicated in Table 6. The fact that the GLC peak for **7a** and **b** had a shorter retention-time than that of the corresponding *para*-products suggests that **7a** and **b** are *ortho*-isomers of **6a** and **b**. The yield of **7a** and **b** was determined on the assumption that these have the same GLC area-sensitivity as **6a** and **b** although **7a** and **b** were not isolated.

Formation of Aminosulfonium Ions **3** *and Protonated Sulfenamides* **4**.—The reaction of *S*-amino-*S*-methyl-*S*-phenylsulfonium mesitylenesulfonate **3a** (2.0 mmol) with **2a** (8.5 mmol) was carried out in the presence of both TFA (2.5 cm^3) and TFSA (0.75 cm^3) at 25 °C for 0.5 h, and gave **6a** (89%), **9a** (2.6%) and **10a** (2.2%). The use of **2c** instead of **2a** produced **6c** (63%) and **9a** (11%). The photolysis of 1-aminoquinolinium perchlorate (210 mg) was performed in the presence of both **2a** (8.0 cm^3) and TFA (7.0 cm^3) at 25 °C for 5 h externally in a quartz tube (25 × 1.8 cm) with a 500 W high pressure Hg lamp (Eikōsha EHB-W-500) after purging with dry N_2 for 15 min, and yielded **6a** (53%). Isolation and characterisation of the products and the determination of the yields were performed by a method similar to that described above.

The reaction of **1h** with **2a** was stopped just after mixing the reagents, and gave **6a** (52%) and *N*-heptyl-*S*-phenyl sulfenamide **5h** after treatment with aq. NaOH. The reaction of **1h** with **2a** for 2 h after mixing the reagents produced **6a** (64%) and **5h**; the amount of **5h** in the former reaction was 2.4 times greater than that in the latter by GLC analysis. The structure of **5h** was identified by GLC–MS (EI method): *m/z* 223 (M^+), 194, 180, 139, 124, 82, 57 and 41; (CI method): *m/z* 224 (M^+ + 1). The reaction of **1a** with **2c** gave the following products besides **6c**, **9a** and **10a**.

Heptyl trifluoroacetate, 14%, liquid; $\delta_H(CDCl_3$–$CCl_4)$ 0.6–2.0 [13 H, m, $Me(CH_2)_5$] and 4.4 (2 H, t, OCH_2); $\delta_C(CDCl_3$–$CCl_4)$ 13.9 (Me), 22.4 ($MeCH_2$), 25.4 ($MeCH_2CH_2$), 28.1 [$Me(CH_2)_2CH_2$], 28.7 [$Me(CH_2)_3CH_2$], 31.5 [OCH_2CH_2] and 67.7 (OCH_2). This compound was also produced by reaction of heptanol with trifluoroacetic anhydride in the usual manner.

Heptyl trifluoromethanesulfoante, 38%, liquid; $\delta_H(CDCl_3$–$CCl_4)$ 0.6–2.2 [13 H, m, $Me(CH_2)_5$] and 4.6 (2 H, t, OCH_2); $\delta_C(CDCl_3$–$CCl_4)$ 13.9 (Me), 22.4 ($MeCH_2$), 25.0 ($MeCH_2$-CH_2), 28.4 [$Me(CH_2)_2CH_2$], 29.1 [$Me(CH_2)_3CH_2$], 31.4 (OCH_2CH_2) and 76.8 (OCH_2). This product was also obtained by reaction of heptyl iodide with CF_3SO_3Ag; this method is similar to that in which $MeSO_3Me$ is synthesised by reaction of $MeSO_3Ag$ with MeOH.[23]

Reactions of N-*Alkyl*-S-*arylsulfenamides* **5** *with Thianisole* **2a** *in the Presence of Both TFA and Catalytic Acid*.—The detailed reaction conditions are indicated in Tables 2 and 3. Almost all of **5** decomposed under the reaction conditions. Isolation and characterisation of the products were performed as indicated above. The yields of the products are shown in Tables 2 and 3. The reaction of *N*-ethyl-*2*-(4-tolyl)sulfenamide **5c′** or *N*-ethyl-*S*-(4-nitrophenyl)sulfenamide **5c″** afforded **6c′** and **7c′** or **6c″** and **7c″**, respectively. The physical and spectroscopic data for new compounds **6c′** and **c″** and the mass spectral data for **7c′** and **c″** are shown in Tables 5 and 6. The confirmation of the *ortho*-structure of **7c′** and **c″** and the determination of their yield were performed as mentioned above.

The yields of **6**, **7**, **9** and **10** were nearly constant in the reactions of **5c** with **2a** by method c for both 1 h and 0.5 h. The yields are also almost insensitive to the reaction method (method a or c in Table 2). These indicate that all the products may be stable under the reaction conditions. However, **6a** (3.0 mmol) was converted into **10a** in 5.6% yield by treatment with both TFA (5.0 cm^3) and TFSA (1.5 cm^3) at 25 °C for 0.5 h. The reaction of **5f** by method b at the high concentration of H_2SO_4 appeared to give a total yield exceeding 100%; the reaction of diphenyl disulfide with **2a** in the presence of H_2SO_4 gave **6a** and **7a** in > 100% yield accompanying a generation of phenylthiyl radical *via* an oxidation of diphenyl disulfide by H_2SO_4. Details of this reaction will be reported in the near future.

The reaction of **5c** (1.1 mmol) in both TFA (2.0 cm^3) and CH_2Cl_2 (0.8 cm^3) at 25 °C for 1 h yielded **9a** in 44% whereas that in CH_2Cl_2 (4.0 cm^3) or in both CH_2Cl_2 (4.0 cm^3) and **2a** (0.8 cm^3) did not give **7a**. The reaction of **5c'** (2.5 mmol) in **2a** (2.0 cm^3) and TFA (10 cm^3) produced 4- and 2-methylthiophenyl 4-tolyl sulfides **6c'** (53%) and **7c'** (7.9%), $(4\text{-}MeC_6H_4S)_2$ **9c'** (38%) and $4\text{-}MeC_6H_4SSPh$ **8c'** (1%). The structure of **9c'** was characterised by comparison of its IR and ^1H and ^{13}C NMR spectra with those of an authentic sample.[17] The structure of **8c'** was identified as follows.

Phenyl 4-tolyl disulfide **8c'**.[24] GLC–MS (EI method): *m/z* 232 (M^+), 199, 168, 123, 108, 91, 65 and 45; (CI method): *m/z* 233 ($M^+ + 1$). Although **8c'** was not isolated, the yield was determined by the assumption that its GLC area-sensitivity is the same as that of **6a**.

The mixture after the reaction of **5f** with **2a** was treated with a powdered Na_2CO_3 until the mixture was neutralised, and the formation of butylamine in 13% yield was determined by GLC analysis. The amine was recovered in 56% yield by the treatment in TFA in the presence of H_2SO_4 (1.5 mol equiv. to the amine) at 25 °C for 0.5 h, and thus the amine may be much unstable under the conditions of the reaction of **5** with **2** in the presence of H_2SO_4.

The photolysis of **9a** (1.0 cm^3) in **2a** (7.0 cm^3) was carried out at 35 °C for 7 h by the photochemical method mentioned above. The products **6a** and **7a** were not found by GLC analysis of the reaction mixture which is treated as described above.

Reactions of N-*Ethyl*-S-*phenylsulfenamide* **5c** *with Butyl Phenyl Sulfide* **2b**, 2-*Methylthioanisole* **2i**, *Anisole* **2j**, *Toluene* **2k** *and Naphthalene* **2l**.—The reaction conditions and the results are shown in Table 4. The procedure of isolation and characterisation of the products **6i**, **7i**, **6k**, **7k** and **6l** and the determination of the yields carried out on the basis of Tables 5 and 6 as shown above.

Especially the 1-naphthyl structure of **6l** was confirmed by the following IR data: ν_{max}(neat)/cm^{-1} 3030, 1580, 1500, 1475, 1440, 1380, 1025, 970, 800 and 770 (1-naphthyl) and 740 and 690 (mono-substituted phenyl).

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