Novel Generation of Phenylsulfenium Ion and Aromatic Phenylthiolation. Reactions of Hydrazoic Acid, Alkyl Azides and Hydroxylamine Derivatives with Alkyl Phenyl Sulfides in the Presence of Both Trifluoromethanesulfonic Acid and Trifluoroacetic Acid

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Reactions of hydrazoic acid and alkyl azides with alkyl phenyl sulfides in the presence of both trifluoromethanesulfonic acid and trifluoroacetic acid gave 4-alkylthiophenyl phenyl sulfides in high yields *via* a phenylsulfenium ion.

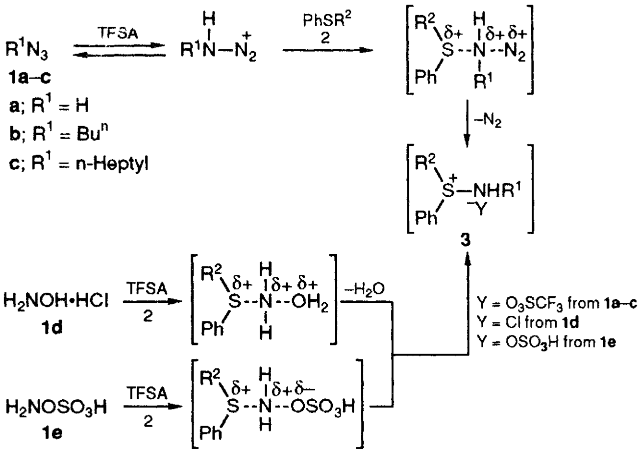
The formation of sulfenium ions has been proposed in many studies,[1] but their existence is controversial because their reactivity would not readily allow their existence as free ions; they would be converted to sulfonium[2] or episulfonium ions[3] by reaction with sulfides or alkenes in the reaction system. We have now found that the phenylsulfenium ion generated in the title reactions mainly leads to aromatic phenylthiolation to give 4-alkylthio phenyl sulfides.

We have already reported direct aromatic amination by hydrazoic acid **1a** in the presence of trifluoromethanesulfonic acid (TFSA) and trifluoroacetic acid (TFA).[4] However, reactions of **1a** with methyl, n-butyl and n-heptyl phenyl sulfides **2a–c** in the presence of TFSA and TFA at 25 °C gave no arylamines but rather the 4-alkylthiophenyl phenyl sulfides **6a–c**, respectively, in high yields along with diphenyl disulfide **7** and sulfide **8** (Table 1). The reaction of the n-butyl and n-heptyl azides **1b** and **c** with **2a** efficiently yielded **6a**, and that of the hydroxylamine derivatives **1d** and **1e** with **2a** produced **7** and **8** in relatively high yield, respectively, together with **6** (Table 1). The *ortho*-isomer **6′** of **6** was formed in the reactions at 75 or 65 °C (Table 1).

Azides **1a–c** decomposed in the presence of TFSA, but did not decompose in the absence of acid. The decomposition was promoted in the presence of **2a**. These results suggest that **1a–c** decompose *via* conjugate acids of **1a–c**, and aminosulfonium ions **3a–c** are formed by a concerted process involving attack of **2** on the conjugate acid and elimination of N_2 (Scheme 1). By the concerted process in Scheme 1, **3d** and **e** may be formed from **1d** and **e**.

The reaction of **1c** with **2a** for a shorter time gave **6a** in a lower yield and a larger proportion of *N*-phenylthioheptylamine **5c** after treatment with aqueous NaOH. This implies that **6** is formed *via* RN^+H_2–SPh **4** from dealkylation of **3** (Scheme 2). In fact, the reaction of **1a** with **2c** gave n-heptylOCOCF$_3$ (14%) and n-heptylOSO$_2$CF$_3$ (38%) by dealkylation.

The reaction of **1a, d** and **e** with **2a** showed an increased yield of **7** and a decreased yield of **8** on addition of CH_2Br_2 (Table 1). The addition decreased the yields of **6** and **6′** from **1d**, but increased their yields from **1a** and **e** (except the yield of **6′** from **1a**) (Table 1). Since the heavy atom bromine promotes singlet–triplet conversion *via* intersystem crossing (ISC), these results suggest that the *ipso*- and S-attack products **8** and **7** are formed *via* a singlet phenylsulfenium ion (S_0) and the corresponding triplet ion (T_1), respectively, which are formed from **4**, and the phenyl-attack products **6** and **6′** are formed from both S_0 and T_1 (Scheme 2). Variation of ratios of **6** or **6′** to **7** or **8** by the heavy-atom effect supports the formation of **6** and **6′** from both S_0 and T_1. The differences in heavy-atom effects between the reactions of **1a** and **e**, and **1d**, perhaps arise

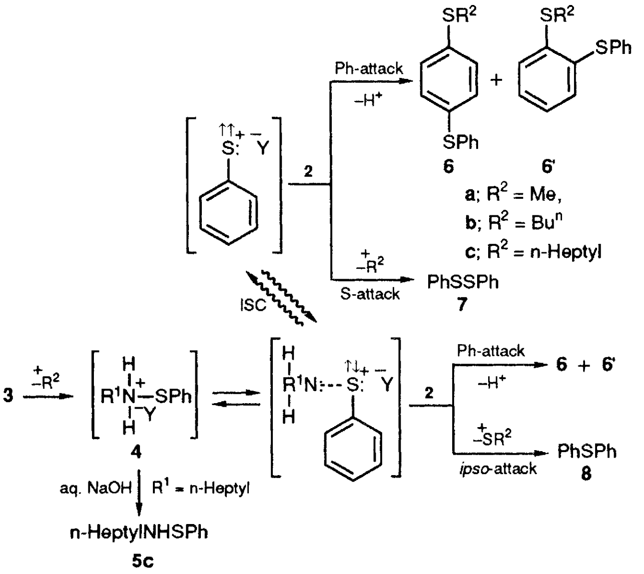


Scheme 1

Table 1 Reaction of hydrazoic acid **1a**[a] (5.2 mmol), alkyl azides **1b** and **1c** (5.2 mmol) or hydroxylamine derivatives **1d** and **e** (5.0 mmol) with alkyl phenyl sulfides **2a–c** (5.0 cm^3) in the presence of both TFSA (1.5 cm^3) and TFA (5.0 cm^3)

Reagent **1**	R of RSPh **2**	Additive	T/°C	t/h	Yield[b] (%) **6**	**6′**	**7**	**8**
1a	**a**; Me	None	25	0.5	99	0	Trace	Trace
1a	**a**; Me	CH_2Br_2[c]	25	0.5	99	0	Trace	Trace
1a	**a**; Me	None	75	0.5	61	8.5	7.0	43
1a	**a**; Me	CH_2Br_2[c]	75	0.5	67	5.7	11	18
1a	**b**; Bu^n	None	25	0.5	100	0	Trace	Trace
1a	**c**; n-Heptyl	None	25	0.5	100	0	Trace	Trace
1b	**a**; Me	None	25	2.0	94	0	1.0	Trace
1c	**a**; Me	None	25	2.0	78	0	Trace	2.6
1d	**a**; Me	None	25	24	6.9	0	19	4.0
1d	**a**; Me	None	60	48	28	10	32	14
1d	**a**; Me	CH_2Br_2[d]	60	48	13	3.0	37	8.0
1e	**a**; Me	None	25	24	20	Trace	Trace	23
1e	**a**; Me	None	60	48	49	25	0.3	60
1e	**a**; Me	CH_2Br_2[e]	60	48	67	28	1.0	44

[a] A solution containing **1a** (1.6 mmol dm^{-3}) in $CHCl_3$ (3.0 cm^3) was used. [b] Yields are based on **1** used. [c] CH_2Br_2 (20% v/v) was added. [d] CH_2Br_2 (8% v/v) was added. [e] CH_2Br_2 (25% v/v) was added.



Scheme 2

because these reactions involve different S_0 and T_1 content as shown below. The heavy-atom effect was observed for the reaction of **1a** with **2a** at 75 °C, not 25 °C (Table 1). This indicates that the S → T conversion needs some activation energy since the T_1 state from **1a** has higher energy than the S_0 state. Valence-orbital expansion of the S atom permits us to infer that T_1 is electrophilic, and brings about the phenyl and S-attack without yielding PhSH by H-atom abstraction.

The reaction of **1a** with **2a** at 75 °C gave a low yield of **6** and high yields of **6′**, **7** and **8** compared with that at 25 °C (Table 1). Since the S → T conversion is promoted by higher temperatures, the variation of the yields of **6** and **7** is reasonable. The variation for **6′** and **8** shows that their formation, which needs a relatively high activation energy, is more favourable at 75 than 25 °C. If a sulfonium ion formed by reaction of the S_0 state with **2** rearranges to give **6** and **6′**, **6′** might be formed in higher yield at lower temperature by some kind of entropy effect.[5] Thus, the rearrangement can be ruled out.

We here propose that the S_0 state interacts with both the counter-ion and the unshared electron pair of NH_3 or RNH_2, and the interaction with the unshared electron pair selectively stabilises S_0 relative to T_1 (Scheme 2). A similar interaction of a parent nitrenium ion has been suggested by us.[6] Considering this proposal, the different reactivities of **1a–c**, **1d** and **1e** can be explained as follows. The S_0 state from **1a–c**, **1d** or **1e** has $^-O_3SCF_3$, Cl^- or $^-OSO_3H$, respectively, as the counter-ion (Y^-), and the extent of localisation of charge of the counter-ion is in the following order: $Cl^- \gg {}^-O_3SCF_3 > {}^-OSO_3H$. As reported for the chemistry of nitrenium ions,[9] we may infer that a stronger ionic interaction of S_0 with the counter-ion having higher localised charge causes more hindrance of the stabilisation of S_0 by the unshared electron pair. Thus, S_0 is stabilised in the following order: S_0 from **1e** > S_0 from **1a** ≫ S_0 from **1d**. Therefore, the reaction of **1d** or **1a** and **e** gives more triplet or singlet products, respectively, as seen in Table 1. The high yield of **8** from **1e** presumably arises from the high reactivity of S_0 having $^-OSO_3H$ as counter-ion of very low charge localisation.

Addition of anisole to the reaction system involving **2a** and **1a** or **c** gave 4-methoxyphenyl phenyl sulfide **9** besides **6a**. The relative yield **9**/**6a** was higher by a factor of 1.25 if **1a** rather than **1c** was used. This is support for S_0 not being free, but interacting with the unshared electron pair. The lack of formation of *meta*-isomers of **6** and **9** suggests the intermediacy of a positive species such as the sulfenium ion.

The total yield of **6–8** exceeded 100% in the reaction giving **8** in high yield. This is under investigation.

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