

## Reaction of Phenylnitrenium Ion with Sulphides. A Novel Synthetic Method for Aminophenyl Sulphide Derivatives

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The reaction of phenyl azide with sulphides in the presence of both trifluoroacetic acid and trifluoromethanesulphonic acid to produce 2- and 4-aminophenyl sulphides (**2**) and (**3**) was investigated in order to obtain information on the following points: the kinetics of decomposition of phenyl azide, the effect of addition of benzene to reaction systems, the replacement of phenyl azide by 1-phenyl-2-methyl-4,6-diphenylpyridinium salt, and the steric and electronic effect of substituents in the sulphides. The products are formed through an azasulphonium ion by reaction of phenylnitrenium ion with sulphide, followed by rearrangement of the alkyl group in the azasulphonium ion. Sulphides with primary alkyl groups larger than propyl result in selective formation of *ortho*-products (**2**), the mechanism of which is discussed in detail.

Phenylnitrenium ion formed in decomposition of phenyl azide in the presence of trifluoroacetic acid (TFA) or trifluoromethanesulphonic acid (TFSA) is capable of aromatic *N*-substitution<sup>1</sup> and addition to olefins.<sup>2</sup> Attack of nitrenium ion on basic positions of DNA induces cancer.<sup>3-6</sup> Reactivity of carcinogens with proteins having sulphur-containing amino acids (such as cysteine<sup>7</sup> and methionylglycine<sup>8</sup>) has been predicted to reflect the extent to which they take part in crucial DNA reactions.

This paper is concerned with use of phenylnitrenium ion for new synthesis of 2- and 4-aminophenyl sulphides (**2**) and (**3**), with emphasis on the ponderal effect<sup>9</sup> which is interesting from the mechanistic and synthetic standpoint in leading to selective formation of *ortho*-products (**2**).†

### Results and Discussion

*Reaction of Phenyl Azide with Sulphides (1a—o) in the Presence of both TFA (50% v/v) and TFSA (7—8% v/v) at Room Temperature.*—The reaction of phenyl azide with sulphides (**1a—n**) yielded alkyl 2- and 4-aminophenyl sulphides (**2a—k**) and (**3a—k**) (after work-up with aqueous NaOH). On the other hand, the reaction with thioanisole (**1o**) gave phenyl 2- and 4-aminophenyl sulphides (**2o**) and (**3o**) and 2- and 4-anilinothioanisoles (**4**) and (**5**) with the ratio [(**2o**) + (**3o**)]/[(**4**) + (**5**)] *ca.* 5 (see Table and Scheme 1).

(a) *Phenylnitrenium ion as intermediate.* We previously reported that decomposition of phenyl azide in benzene–TFA proceeds *via* the conjugate acid of the azide, forming phenylnitrenium ion.<sup>1</sup> In the present reaction of phenyl azide with sulphides, there are two possible pathways for the decomposition of the azide, one *via* the phenylnitrenium ion generated from spontaneous decomposition of the conjugate acid of the azide (step a in Scheme 1) and the other involving *S<sub>N</sub>2*-like attack of sulphide on the conjugate acid of the azide (step a' in Scheme 1). The denitrogenation rate for the reaction with thioanisole at 27 °C is the same as that with *p*-methylthioanisole, and the pseudo-first-order constants ‡ of the azide are the same for both sulphides up to *ca.* 30% decomposition of the azide (1:2 molar ratio of azide to sulphide). If the denitrogenation obeys *S<sub>N</sub>2* kinetics, the rate should be by far

greater with *p*-methylthioanisole than with thioanisole, since the *S<sub>N</sub>2* transition state is much more stabilized for the former anisole than for the latter because of the electron donation of the methyl group of *p*-methylthioanisole. Thus, the result observed rules out the *S<sub>N</sub>2* reaction and supports the pathway in which the conjugate acid of the azide spontaneously loses a nitrogen molecule to give phenylnitrenium ion (Scheme 1).

(b) *Azasulphonium ion (I) as intermediate.* The following findings and inferences (i)–(iv) indicate that the reaction with sulphides proceeds *via* an intermediate azasulphonium ion (I) (Scheme 1): (i) The ponderal effect<sup>9</sup> described below requires the existence of (I).

(ii) An azasulphonium salt was isolated in the reaction of *N*-*t*-butylphenylnitrenium ion with dimethyl sulphide (DMS), and the salt was found to decompose in dimethylformamide (DMF) at 100 °C to give methyl 2- and 4-(*t*-butylamino)phenyl sulphides (**6**) and (**7**).<sup>10</sup>

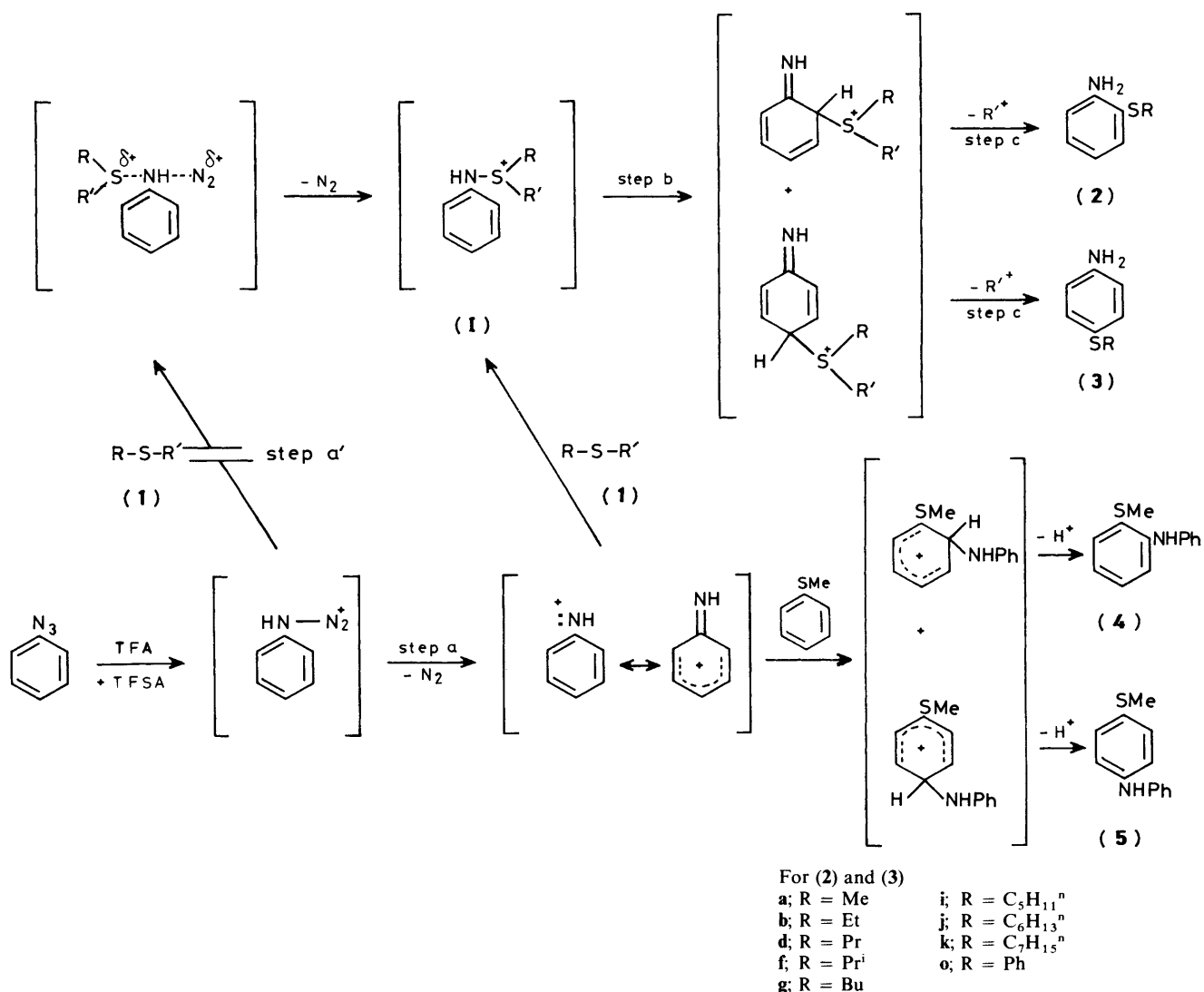
(iii) The phenylnitrenium ion§ generated thermally (152 °C) from 1-anilino-2-methyl-4,6-diphenylpyridinium tetrafluoroborate reacts with DMS in the presence of TFA to give methyl 2- and 4-*N*-(trifluoroacetyl)aminophenyl sulphides (**8**) and (**9**), which are identical with the products formed by trifluoroacetylation of (**2a**) and (**3a**), respectively. The product ratio (**8**):(**9**) is similar to that of (**2a**):(**3a**) for the reaction of azide with DMS. Thus, these two reactions may be considered to proceed *via* a common intermediate (I).

(iv) In the experiment using benzene and DMS as substrates, the yields of diphenylamine (**10**), 2-aminobiphenyl (**11**), and 4-aminobiphenyl (**12**) were substantially reduced on addition of a small amount of the sulphide, and the decrease in yield of

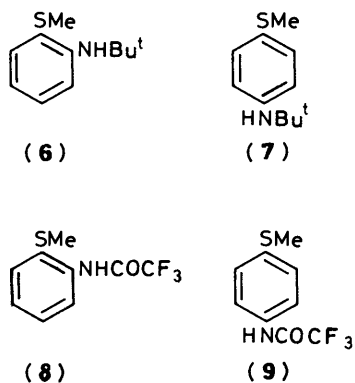
‡ The first-order rate constant  $k_{\text{obs}}$  was  $1.0 \times 10^{-3} \text{ s}^{-1}$  at 27 °C. The first-order kinetics for azide support our assumption of *S<sub>N</sub>1* reaction of the conjugate acid because the concentration of the conjugate acid of azide is proportional to that of the azide;  $[\text{PhNH-N}_2^+]$  is equal to  $K[\text{acid}]_f[\text{PhN}_3]$ , and  $[\text{acid}]_f$  is constant in the initial decomposition ( $K$  is the equilibrium constant for the formation of the conjugate acid from the azide, and  $[\text{acid}]_f$  denotes the concentration of the free acid). In the decomposition beyond *ca.* 30%, the rate is gradually lowered as compared with that expected from the first-order kinetics because of decreased  $[\text{PhNH-N}_2^+]$ ; the increase in the relative concentration of sulphide to azide with increasing decomposition of azide allows sulphide-free acid interaction to proceed in preference to azide-free acid interaction with resulting decreased  $[\text{PhNH-N}_2^+]$ .

§ The formation of phenylnitrenium ion in the thermolysis of the pyridinium salt will be reported in the near future.

† The synthesis of compounds (**2**) and (**3**) has been conducted in multiple steps by employing nitrothiophenols or nitrobenzenesulphonyl chlorides as starting materials.



Scheme 1.



(10), the *N*-attack product of phenylnitrenium ion,<sup>1</sup> was much greater than those of (11) and (12), the *C*-attack products of nitrenium ion<sup>1</sup> (Figure 1). These results indicate that the reactivity of nitrenium ion at the *N*-position compared with the *C*-positions is markedly suppressed by the preferential formation of intermediate (I): the ability of sulphide to trap nitrenium ion [this ability is responsible for the formation of (I)] was *ca.* ten times\* as high as that of benzene. In this experiment,

the yield of *para*-product (3a) decreased more greatly on addition of benzene than did that of *ortho*-product (2a) (Figure 2). This phenomenon implies that the rearrangement from (I) to (3a) is intermolecular, whereas that from (I) to (2a) is intramolecular, which thus confirms the existence of intermediate (I).

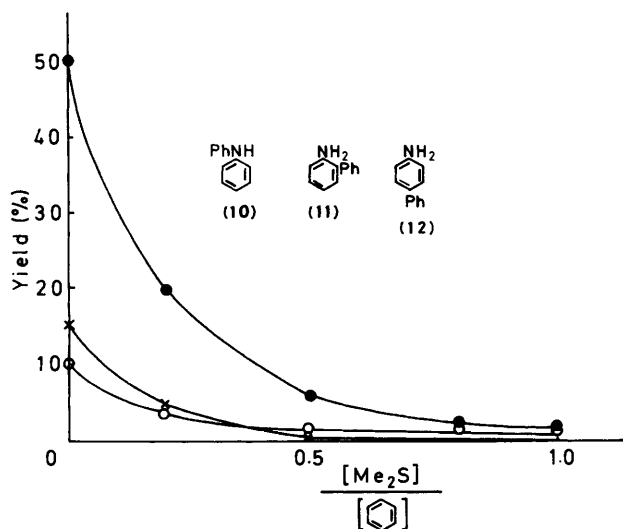
(c) *Electronic effect of substituents in sulphides on elimination.* Alkyl groups are electron-donating and accordingly capable of stabilizing a neighbouring positive charge. This capability is in the order: C<sub>5</sub>H<sub>11</sub><sup>n</sup> > Bu > Pr > Et > Me. When the substituent in the sulphide was changed from C<sub>5</sub>H<sub>11</sub><sup>n</sup> through Bu, Pr, and Et, to Me, the tendency of products to contain that alkyl substituent increased in that order. This observed order implies that in step c alkyl groups are eliminated with an order of ease opposite to that above. The result observed reflects the condition for the early transition state for step c in Scheme 1 that positive charge must exist on the sulphur atom more than on the leaving group (Scheme 2). The phenyl group in the reaction with sulphide (10) may remain in the product because

\* The value was obtained from the relative yield [(2a) + (3a)]/[10] + [(11) + (12)] measured for the reaction using an equimolar mixture of benzene and DMS.

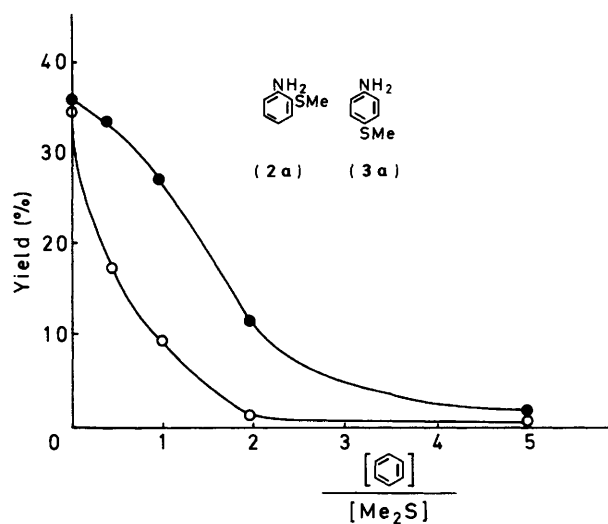
**Table.** Reactions of phenyl azide with sulphides in the presence of both TFA (50% v/v) and TFSA (7–8% v/v) at room temperature<sup>a</sup>

Sulphide (1), R-S-R'	[Azide]/M	[R-S-R']/M	Yield <sup>b</sup> (%)			
			(2) <sup>e</sup>	(3) <sup>e</sup>	(4)	(5)
a; R = R' = Me	0.74	5.2	35	35		
b; R = R' = Et	0.71	5.0	28	1.3		
c; R = Et, R' = Me	0.63	4.4	38 <sup>c</sup> + 5 <sup>d</sup>	11 <sup>c</sup> + 4 <sup>d</sup>		
d; R = Pr, R' = Me	0.53	3.7	49	trace		
e; R = Pr, R' = Et	0.49	3.4	5 <sup>c</sup> + 4 <sup>d</sup>	0		
f; R = Pr <sup>i</sup> , R' = Me	0.53	3.8	55 <sup>c</sup> + trace <sup>d</sup>	0		
g; R = Bu, R' = Me	0.47	3.3	75 <sup>c</sup> + trace <sup>d</sup>	0		
h; R' = Bu, R' = Et	0.30	2.1	26	0		
i; R = C <sub>5</sub> H <sub>11</sub> <sup>n</sup> , R' = Me	0.43	3.0	79	0		
j; R = C <sub>6</sub> H <sub>13</sub> <sup>n</sup> , R' = Me	0.39	2.6	63	0		
k; R = C <sub>7</sub> H <sub>15</sub> <sup>n</sup> , R' = Me	0.34	2.4	17	trace		
l; R = Me, R' = Bu <sup>t</sup>	0.41	2.9	22	34		
m; R = Et, R' = Bu <sup>t</sup>	0.36	2.5	37	25		
n; R = Me, R' = CH <sub>2</sub> Ph	0.70	3.5	21	3		
o; R = Ph, R' = Me	0.65	4.6	25	33	2	10

<sup>a</sup> The reactions using sulphides (1a–c) and (1d–o) were carried out for 3–5 h and 1–1.5 h, respectively. <sup>b</sup> The yields are based on azide consumed. <sup>c</sup> The yields refer to those products containing group R. <sup>d</sup> The values show the yields of products containing group R'. <sup>e</sup> The single values given for reaction of (1a,b), (1d), and (1h–o) are those of products containing group R.



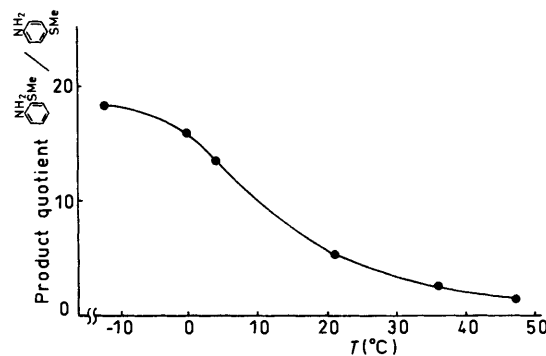
**Figure 1.** Effect of the addition of dimethyl sulphide on the yields of (10)–(12) in the reaction of phenylnitrenium ion with benzene: ●, yield of (10); ○, yield of (11); ×, yield of (12)



**Figure 2.** Effect of the addition of benzene on the yields of (2a) and (3a): ●, yield of (2a); ○, yield of (3a)

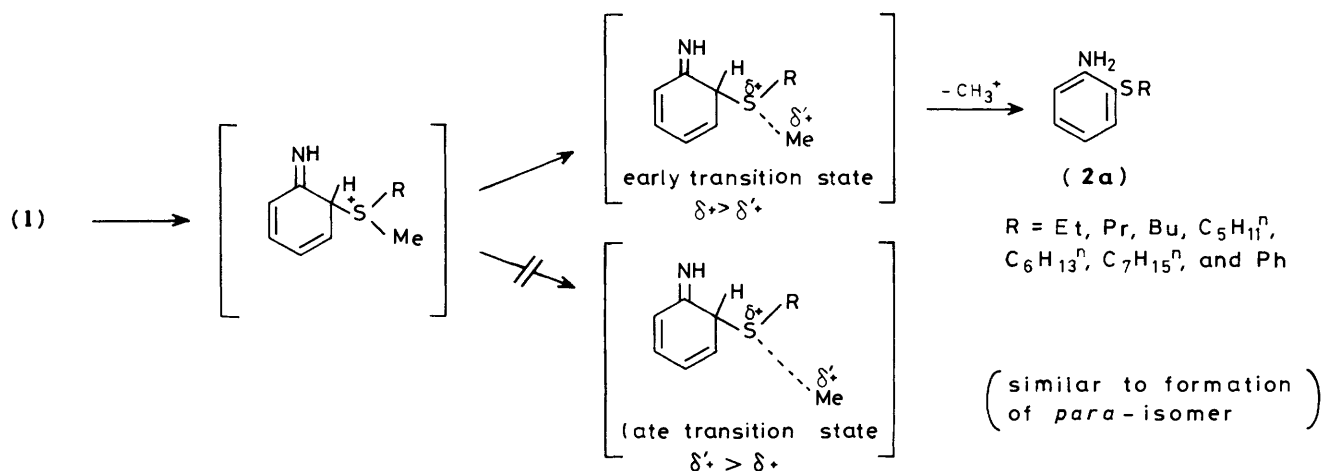
the positive charge is stabilized by the resonance between the sulphur atom and the phenyl group in the early transition state.

(d) *Steric effect of substituents in sulphides on rearrangement from (1).* The reaction with sulphides (1b–k) and (1n) gave *ortho*-products (2b–k) in preference to the corresponding *para*-products (3) whose yields were very low. This result can be interpreted in terms of the ponderal effect<sup>9</sup> (a kind of entropy effect on rearrangement) in that the more bulky the group the easier does *ortho*-migration occur from (1) compared with *para*-migration (step b in Scheme 1). The participation of this effect is also supported by temperature-dependence upon migration: when DMS was used, the product ratio *ortho:para* increased as temperature was lowered (Figure 3). This phenomenon is in line with the characteristic that the ponderal effect operates favourably at lower temperature because of its connection with entropy. The ponderal effect was not observed in the reaction with sulphide (1o), although a phenyl group is attached to the

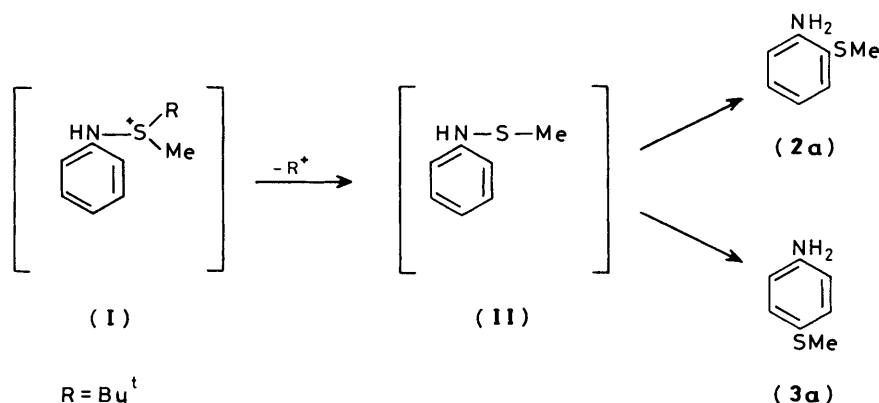


**Figure 3.** Effect of temperature on the reaction of phenyl azide with dimethyl sulphide in the presence of both TFA and TFSA

sulphur. This is because the great stability of the phenyl-azasulphonium ion, due to the resonance between phenyl group and sulphide atom, allows step b to have such a low



Scheme 2.



Scheme 3.

activation energy as to make the *ortho*- and *para*-migrations non-selective.

(e) *Reactions with sulphides having t-butyl and benzyl groups.* The reactions with sulphides (1l) and (1m) possessing a t-butyl group did not give any products with a t-butyl group, but instead gave those with methyl and ethyl groups, with *ortho*-product (2a) or (2b) and *para*-product (3a) or (3b) obtained in nearly equal yields, respectively. According to the above mechanistic considerations, only the *ortho*-product (with a t-butyl group) would be expected to be formed under the influence of the ponderal and electronic effects in steps b and c. This contradiction can be reconciled if we notice that the t-butyl group may be easily eliminated from the intermediate (I) to give intermediate (II)\* because t-butyl cation is so stable as to facilitate the migration of the SR group of (II) to the phenyl position to produce products (2) and (3). The less selective formation of *ortho*- and *para*-products than is expected may be ascribed to the possibility of the rearrangement from (II) (Scheme 3) having a low activation energy.

The reaction with sulphide (1n) having a benzyl group exhibits the ponderal effect in that *ortho*-product (2a) is obtained preferentially over the corresponding *para*-product.

Resonance between the phenyl portion of the benzyl group and the sulphur atom has been reported for this compound.<sup>11</sup> Stabilization due to this resonance makes the elimination of benzyl cation from (I) in step b difficult. On the other hand, the stability of benzyl cation facilitates its elimination in the late transition state of step c (Scheme 2) to produce products (2) and (3) each having a methyl group. Under these circumstances, in the present reaction the ponderal effect led to the preferential production of the *ortho*-product. The formation of the *para*-product in small amount (3%) results from a mechanism similar to that described for the reaction with sulphide having a t-butyl group; that is, the benzyl group is eliminated from (I) to form (II), which results in the less selective formation of compounds (2) and (3).

We detected t-butyl alcohol (*ca.* 5%) formed *via* t-butyl cation. The low yield of t-butyl alcohol, and lack of formation of the corresponding alcohols in the other reactions, arises possibly from preferential polymerization through related cations.

### Experimental

I.r. spectra were obtained on a Hitachi Model EPI-G3 spectrometer. <sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were obtained on a Nippondenshi JNM-FX-60Q instrument with Me<sub>4</sub>Si as internal standard. Mass spectra were recorded on a Hitachi RMU-6E spectrometer. G.l.c. analyses were carried out with a

\* Rearrangement of arenosulphenanilides, which are similar to (II), to 2- and 4-aminophenyl sulphides is known: F. A. Davis, E. R. Fretz, and C. J. Horner, *J. Org. Chem.*, 1973, **38**, 690; F. A. Davis, C. J. Horner, E. R. Fretz, and J. F. Stackhouse, *ibid.*, p. 695.

Shimadzu GC-6A unit using a glass column (1 m × 3 mm) [column A, 10% silicone SE-30 on 60–80 Uniport KS; column B, 10% polyethylene glycol (20 M) on 60–80 Uniport KS]. The analyses of products agreed within <3% on two runs. Preparative g.l.c. was carried out with a Hitachi Model 063-0012 unit using an aluminium column (2 m and/or 1 m × 3 mm) packed with 10% SE-30 on 60–80 Uniport KS.

Trifluoroacetic acid (TFA), trifluoromethanesulphonic acid (TFSA), dimethyl sulphide (DMS) (**1a**), diethyl sulphide (**1b**), ethyl methyl sulphide (**1c**), butyl methyl sulphide (**1g**), thioanisole (**1o**), diphenylamine (**10**), and 2-aminobiphenyl (**11**) were reagent grade (Wako or Aldrich), and used without further purification. The following compounds were prepared by the methods described in the literature: phenyl azide,<sup>12</sup> methyl propyl sulphide (**1d**),<sup>13</sup> ethyl propyl sulphide (**1e**),<sup>13</sup> isopropyl methyl sulphide (**1f**),<sup>13</sup> butyl ethyl sulphide (**1h**),<sup>13</sup> methyl pentyl sulphide (**1i**),<sup>13</sup> hexyl methyl sulphide (**1j**),<sup>13</sup> heptyl methyl sulphide (**1k**),<sup>13</sup> methyl t-butyl sulphide (**1l**),<sup>13</sup> ethyl t-butyl sulphide (**1m**),<sup>13</sup> benzyl methyl sulphide (**1n**),<sup>14</sup> *p*-methylthioanisole,<sup>15</sup> 4-aminobiphenyl (**12**),<sup>16</sup> 2-methyl-4,6-diphenylpyrylium tetrafluoroborate,<sup>17</sup> and trifluoroacetanilide.<sup>18</sup>

**Reactions of Phenyl Azide with Sulphides in the Presence of Both TFA and TFSA.**—A mixture of TFA and TFSA was added to a solution containing the azide and one of the sulphides (**1a–o**) at room temperature, and the mixture was kept under the conditions indicated in the Table. The reaction mixture was diluted with benzene (10 ml), and the solution was basified with aqueous NaOH. The organic layer was washed with water (10 ml). Preparative g.l.c. gave the following materials, identified by i.r., <sup>1</sup>H and <sup>13</sup>C n.m.r., and mass spectra. The yields of the products were determined by g.l.c. using column A.

**2-Aminophenyl methyl sulphide (2a).**<sup>19,20</sup> This compound was a liquid,  $v_{\max}$  (neat) 3 425 and 3 325 (NH<sub>2</sub>), 3 050, 2 960, and 2 900 (CH), 1 610 (NH<sub>2</sub>), 1 475 (aromatic C=C), 1 445 (CH<sub>2</sub>), 1 300 (C–N), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.3 (3 H, s, Me), 3.3–4.5 (2 H, br, NH<sub>2</sub>), and 6.3–7.5 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  17.6 (Me), and 114.4, 118.4, 119.7, 128.7, 133.7, and 147.0 (C-3, -5, -1, -4, -6, and -2 of phenyl group) (Found: C, 60.3; H, 6.5; N, 10.15. Calc. for C<sub>7</sub>H<sub>9</sub>NS: C, 60.4; H, 6.5; N, 10.05%). The <sup>13</sup>C n.m.r. spectra are almost the same as those described in the literature.

**4-Aminophenyl methyl sulphide (3a).**<sup>19</sup> Liquid,  $v_{\max}$  (neat) 3 420 and 3 330 (NH<sub>2</sub>), 3 010, 2 960, and 2 900 (CH), 1 640 (NH<sub>2</sub>), 1 595 and 1 490 (aromatic C=C), 1 420 and 1 435 (CH<sub>2</sub>), 1 280 (C–N), and 820 cm<sup>-1</sup> (*para*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CCl}_3)$  2.4 (3 H, s, Me), 3.0–4.0 (2 H, br, NH<sub>2</sub>), and 6.2–7.4 (4 H, ABq, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  18.7 (Me), and 115.3, 125.7, 131.0, and 144.6 (C-3, -1, -2, and -4 of phenyl group).

**2-Aminophenyl ethyl sulphide (2b).**<sup>21</sup> Liquid,  $v_{\max}$  (neat) 3 440 and 3 330 (NH<sub>2</sub>), 3 050, 2 950, and 2 925 (CH), 1 610 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 450 and 1 420 (CH<sub>2</sub>), 1 305 (C–N), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  1.2 (3 H, t, Me), 2.7 (2 H, q, CH<sub>2</sub>), 3.5–3.7 (2 H, br, NH<sub>2</sub>), and 6.4–7.6 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  14.8 (CH<sub>2</sub>), 28.5 (Me), and 114.4, 117.3, 118.0, 129.3, 135.9, and 148.0 (C-3, -1, -5, -4, -6, and -2 of phenyl group).

**4-Aminophenyl ethyl sulphide (3b).**<sup>22</sup> Liquid,  $v_{\max}$  (neat) 3 430 and 3 330 (NH<sub>2</sub>), 3 010, 2 950, and 2 900 (CH), 1 620 (NH<sub>2</sub>), 1 595 and 1 495 (aromatic C=C), 1 455 and 1 420 (CH<sub>2</sub>), 1 280 (C–N), and 825 cm<sup>-1</sup> (*para*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  1.2 (3 H, s, Me), 2.8 (2 H, q, CH<sub>2</sub>), 2.2–3.2 (2 H, br, NH<sub>2</sub>), and 6.4–7.7 (4 H, ABq, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  14.6 (CH<sub>2</sub>), 30.2 (Me), and 115.1 and 133.8 (C-3 and -2 of phenyl group).

**2-Aminophenyl propyl sulphide (2d).**<sup>23</sup> Liquid,  $v_{\max}$  (neat) 3 450 and 3 300 (NH<sub>2</sub>), 3 050, 2 950, 2 920, and 2 860 (CH<sub>2</sub>), 1 606 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 450 and 1 415 (CH<sub>2</sub>),

1 300 (C–N), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  1.0 (3 H, s, Me), 1.2–1.8 (2 H, quintet, CH<sub>2</sub>CH<sub>2</sub>Me), 2.65 (2 H, t, ArCH<sub>2</sub>), 3.4–4.4 (2 H, br, NH<sub>2</sub>), and 6.2–7.7 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  12.3 (CH<sub>2</sub>CH<sub>2</sub>Me), 21.8 (Me), 35.6 (ArCH<sub>2</sub>), and 113.4, 117.1, 127.8, 128.2, 134.7, and 146.4 (C-3, -5, -1, -4, -6, and -2 of phenyl group) (Found: C, 64.65; H, 7.55; N, 8.6. Calc. for C<sub>9</sub>H<sub>13</sub>NS: C, 64.6; H, 7.85; N, 8.35%).

**4-Aminophenyl propyl sulphide (3d).**<sup>23</sup> Liquid,  $v_{\max}$  (neat) 3 450 and 3 330 (NH<sub>2</sub>), 3 050, 2 950, 2 920, and 2 860 (CH), 1 620 (NH<sub>2</sub>), 1 600 and 1 495 (aromatic C=C), 1 475 (CH<sub>2</sub>), 1 280 (C–N), and 820 cm<sup>-1</sup> (*para*-substituted Ph). No <sup>1</sup>H and <sup>13</sup>C n.m.r. data were obtained because the product was produced in only trace amounts.

**2-Aminophenyl isopropyl sulphide (2f).**<sup>23</sup> Liquid,  $v_{\max}$  (neat) 3 445 and 3 345 (NH<sub>2</sub>), 3 050, 2 950, 2 900, and 2 850 (CH), 1 605 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 445 (CH<sub>2</sub>), 1 380 (CH<sub>2</sub>), 1 305 (C–N), 1 160 (CH), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  1.25 (6 H, d, CHMe<sub>2</sub>), 2.8–3.5 (1 H, m, CHMe<sub>2</sub>), 3.6–4.9 (2 H, br, NH<sub>2</sub>), and 6.4–7.7 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  23.2 (Me), 38.2 (CH), and 114.3, 117.1, 117.9, 129.6, 137.0, and 148.6 (C-3, -1, -5, -4, -6, and -2 of phenyl group) (Found: C, 64.65; H, 7.55; N, 8.65%).

**2-Aminophenyl butyl sulphide (2g).**<sup>23</sup> Liquid,  $v_{\max}$  (neat) 3 445 and 3 345 (NH<sub>2</sub>), 3 050, 2 950, 2 925, and 2 850 (CH), 1 605 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 445 (CH<sub>2</sub>), 1 300 (C–N), and 750s and 675w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  0.9 (3 H, t, Me), 1.2–2.0 (4 H, br, CH<sub>2</sub>CH<sub>2</sub>Me), 2.7 (2 H, t, ArCH<sub>2</sub>), 3.5–4.7 (2 H, br, NH<sub>2</sub>), and 6.3–7.8 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  13.4 (CH<sub>2</sub>Me), 21.6 (Me), 31.6 (CH<sub>2</sub>Et), 34.3 (ArCH<sub>2</sub>), and 114.4, 117.9, 118.1, 129.1, 135.6, and 147.8 (C-3, -1, -5, -4, -6, and -2 of phenyl group) (Found: C, 66.3; H, 8.25; N, 7.3. Calc. for C<sub>10</sub>H<sub>15</sub>NS: C, 66.25; H, 8.35; N, 7.75%).

**2-Aminophenyl pentyl sulphide (2i).** Liquid,  $v_{\max}$  (neat) 3 445 and 3 345 (NH<sub>2</sub>), 3 050, 2 960, 2 905, and 2 850 (CH), 1 610 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 450 (CH<sub>2</sub>), 1 305 (C–N), and 755s and 675w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  0.9 (3 H, t, Me), (6 H, br, [CH<sub>2</sub>]<sub>3</sub>Me), 2.7 (2 H, br, ArCH<sub>2</sub>), 3.6–4.9 (2 H, br, NH<sub>2</sub>), and 6.3–7.8 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  16.3 (CH<sub>2</sub>Me), 22.1 (Me), 29.1 (CH<sub>2</sub>Pr), 30.7 (CH<sub>2</sub>Et), 34.5 (ArCH<sub>2</sub>), and 114.3, 118.0, 129.1, and 135.7 (C-3, -5, -4, and -6 of phenyl group); *m/z* 195 (*M*<sup>+</sup>), 125, 124, 93, and 80 (Found: C, 67.4; H, 8.65; N, 6.8. C<sub>11</sub>H<sub>17</sub>NS requires C, 67.6; H, 8.8; N, 7.2%).

**2-Aminophenyl hexyl sulphide (2j).** Liquid,  $v_{\max}$  (neat) 3 435 and 3 335 (NH<sub>2</sub>), 3 050, 2 940, 2 915, and 2 840 (CH), 1 605 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 445 (CH<sub>2</sub>), 1 305 (C–N), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  0.9 (3 H, t, Me), 1.0–1.9 (8 H, br, [CH<sub>2</sub>]<sub>4</sub>Me), 2.7 (2 H, t, ArCH<sub>2</sub>), 3.4–4.8 (2 H, br, NH<sub>2</sub>), and 6.2–7.9 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  13.9 (CH<sub>2</sub>Me), 22.4 (Me), 28.2 (CH<sub>2</sub>Et), 29.4 (CH<sub>2</sub>Pr), 31.2 (CH<sub>2</sub>Bu), 34.5 (ArCH<sub>2</sub>), and 114.3, 118.0, 129.1, 135.6, and 147.8 (C-3, -5, -4, -6, and -2 of phenyl group); *m/z* 209 (*M*<sup>+</sup>), 125, 124, 80, and 43 (Found: C, 68.7; H, 9.3; N, 6.9. C<sub>12</sub>H<sub>19</sub>NS requires C, 68.8; H, 9.2; N, 6.7%).

**2-Aminophenyl heptyl sulphide (2k).** Liquid,  $v_{\max}$  (neat) 3 445 and 3 335 (NH<sub>2</sub>), 3 050, 2 950, 2 920, and 2 840 (CH), 1 605 (NH<sub>2</sub>), 1 480 (aromatic C=C), 1 450 (CH<sub>2</sub>), 1 305 (C–N), and 750s and 670w cm<sup>-1</sup> (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  0.9 (3 H, t, Me), 1.0–2.0 (10 H, br, [CH<sub>2</sub>]<sub>5</sub>Me), 2.7 (2 H, t, ArCH<sub>2</sub>), 3.4–4.6 (2 H, br, NH<sub>2</sub>), and 6.4–7.7 (4 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  13.9 (CH<sub>2</sub>Me), 22.4 (Me), 28.5 (CH<sub>2</sub>Et), 28.7 (CH<sub>2</sub>Pr), 29.4 (CH<sub>2</sub>Bu), 31.6 (CH<sub>2</sub>Pe), 34.5 (ArCH<sub>2</sub>), and 114.4, 118.1, 129.1, 135.6, and 146.8 (C-3, -5, -4, -6, and -2 of phenyl group); *m/z* 223 (*M*<sup>+</sup>), 164, 125, 124, and 57. Elemental analysis did not give satisfactory values because some impurity was present.

**4-Aminophenyl heptyl sulphide (3k).** Liquid,  $v_{\max}$  (neat) 3 345 (NH<sub>2</sub>), 3 050, 2 950, 2 920, and 2 850 (CH), 1 620 (NH<sub>2</sub>), 1 600

and 1 495 (aromatic C=C), 1 280 (C-N), and 825  $\text{cm}^{-1}$  (*para*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  0.9 (3 H, t, Me), 1.0–1.9 (10 H, br,  $[\text{CH}_2]_5\text{Me}$ ), 2.6 (2 H, t,  $\text{ArCH}_2$ ), 2.9–4.2 (2 H, br,  $\text{NH}_2$ ), and 6.3–7.6 (4 H, ABq, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  13.6 ( $\text{CH}_2\text{Me}$ ), 22.4 (Me), 28.2 ( $\text{CH}_2\text{Et}$ ), 28.7 ( $\text{CH}_2\text{Pr}$ ), 29.1 ( $\text{CH}_2\text{Bu}$ ), 31.2 ( $\text{CH}_2\text{Pe}$ ), 36.2 ( $\text{ArCH}_2$ ), and 115.0 and 133.5 (C-3 and -2 of phenyl group). No elemental analysis was performed because the product contained some impurities (n.m.r.).

**2-Aminophenyl phenyl sulphide (2o).** White crystals, m.p. 42 °C (lit.,<sup>24</sup> 42–43 °C);  $\nu_{\text{max.}}$ (Nujol) 3 450 and 3 350 ( $\text{NH}_2$ ), 3 050 and 3 000 (CH), 1 610 ( $\text{NH}_2$ ), 1 480 (aromatic C=C), 1 310 (C-N), and 740s and 690w  $\text{cm}^{-1}$  (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.8–4.8 (2 H, br,  $\text{NH}_2$ ) and 6.5–7.8 (9 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  114.9, 118.4, 130.7, and 137.3 (C-3, -5, -4, and -6 of phenyl group), and 124.9, 126.1, and 128.6, (C-*p*-, *o*-, and -*m* of SPh group).

**4-Aminophenyl phenyl sulphide (3o).** White crystals, m.p. 95 °C (lit.,<sup>24</sup> 96–97 °C);  $\nu_{\text{max.}}$ (Nujol) 3 445 and 3 345 ( $\text{NH}_2$ ), 3 020 (CH), 1 620 ( $\text{NH}_2$ ), 1 595 and 1 490 (aromatic C=C), 1 295 (C-N), 825 (*para*-substituted Ph), and 740 and 690  $\text{cm}^{-1}$  (mono-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.8–3.8 (2 H, br,  $\text{NH}_2$ ) and 6.2–7.8 (9 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  115.3 and 135.8 (C-3 and -2 of phenyl group), and 124.7, 127.0, and 128.4 (C-*p*-, *o*-, and -*m* of SPh group).

**2-Anilinothioanisole (4).**<sup>25</sup> Liquid  $\nu_{\text{max.}}$ (neat) 3 445 and 3 345 (NH), 3 045 and 2 900 (CH), 1 605 (NH), 1 580 and 1 470 (aromatic C=C), 1 295 (C-N), 760 (*ortho*-substituted Ph), and 745 and 695  $\text{cm}^{-1}$  (mono-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.35 (3 H, s, Me), 1.5–2.5 (1 H, br, NH), and 6.5–7.8 (9 H, m, ArH). The <sup>13</sup>C n.m.r. spectrum was not measured because the product was produced only in trace amounts.

**4-Anilinothioanisole (5).**<sup>25</sup> Liquid,  $\nu_{\text{max.}}$ (neat) 3 450 and 3 350 (NH), 3 050 and 2 900 (CH), 1 620 (NH), 1 580 and 1 470 (aromatic C=C), 1 290 (C-N), 810 (*para*-substituted Ph), and 740 and 690  $\text{cm}^{-1}$  (mono-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.4 (3 H, s, Me), 2.0–2.6 (1 H, br, NH), and 6.8–7.7 (9 H, m, ArH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  15.6 (Me), 128.7 and 132.0 (C-3 and -2 of phenyl group), and 126.2, 127.0, and 129.9 (C-*p*-, *o*-, and -*m* of NHPH group).

**Rate of Decomposition of Phenyl Azide.**—Phenyl azide (4.6 mmol) was dissolved in thioanisole or *p*-methylthioanisole (9.2 mmol). A mixture of TFA (46 mmol) and TFSA (0.45 mmol) was added to the solution at 27 °C. The rate of decomposition of azide was determined at 27 °C by measurement of the volume of nitrogen gas evolved as a function of time. The first-order rate constant  $k_{\text{obs}}$  was  $1.0 \times 10^{-3} \text{ s}^{-1}$  for each sulphide.

**Reactions of Phenyl Azide with Mixtures of Benzene and Dimethyl Sulphide in the Presence of both TFA and TFSA.**—A mixture of TFA (50% v/v) and TFSA (7–8% v/v) was added to a solution of phenyl azide in benzene–DMS (**1a**) at room temperature and the mixture was kept for 5 h. The ratio of benzene to (**1a**) was varied as shown in Figures 1 and 2. The reaction mixture was diluted with benzene and basified with aqueous NaOH. The products were isolated by preparative g.l.c. and identified by comparison with the i.r. and <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of authentic specimens. The yields of the products were determined by g.l.c. using column A. The results are shown in Figures 1 and 2.

**Effect of Temperature on the Reaction of Phenyl Azide with Dimethyl Sulphide.**—The reaction of phenyl azide (4.4 mmol) with DMS (**1a**) (30 mmol) was performed in the presence of both TFA (50% v/v) and TFSA (7–8% v/v) at several temperatures for 5 h. After dilution with benzene (10 ml), the reaction mixture was basified with aqueous NaOH. The products were identified by comparison with the retention times

of g.l.c. peaks of standard materials using columns A and B. The yields of the products were determined by g.l.c. employing column A. The results are shown in Figure 3.

**Preparation of 1-Anilino-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate.**—This borate was prepared by the method of Katritzky *et al.*<sup>26</sup> Phenylhydrazine (20 mmol) was added dropwise to a stirred suspension of 2-methyl-4,6-diphenylpyridinium tetrafluoroborate (10 mmol) in ether (50 ml) at 20 °C. The mixture was stirred for 3 h and was then kept for 12 h. The product was collected by filtration to give a pale yellow powder, m.p. 178–180 °C;  $\nu_{\text{max.}}$ (Nujol) 3 290 (NH), 1 630, 1 600, and 1 570 (aromatic C=C), 1 090 (C-F), and 777 and 690  $\text{cm}^{-1}$  (mono-substituted Ph);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.9 (3 H, s, Me), 6.25–8.4 (17 H, m, ArH), and 8.9 (1 H, br, NH);  $\delta_{\text{C}}(\text{CDCl}_3)$  20.2 (Me), 112.6, 122.3, 128.5, and 143.0 (C-2, -4, -3, and -1 of NHPH group), 125.4, 125.7, 128.1, 129.1, 129.6, 129.8, 130.8, and 130.9 (C-4, -4, -2, -2, -3, -3, -1, and -1 of 4- and 6-Ph groups), and 132.5, 133.3, 156.7, 159.5, and 160.7 (C-3, -5, -2, -6, and -4 of pyridinium ring) (Found: C, 67.6; H, 4.95; N, 6.8.  $\text{C}_{24}\text{H}_{21}\text{BF}_4\text{N}_2$  requires C, 67.95; H, 5.0; N, 6.6%).

**Reaction of 1-Anilino-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate with Dimethyl Sulphide.**—The borate (1.6 mmol) and DMS (2.5 ml) were dissolved in TFA (2.0 ml), and the solution was heated in a sealed tube at 152 °C for 5 h. The following products were isolated by the method described above for the reaction of phenyl azide with DMS.

**2-Methyl-4,6-diphenylpyridine.**<sup>27</sup> White crystals, m.p. 73 °C (lit.,<sup>27</sup> 73 °C) (99%);  $\nu_{\text{max.}}$ (Nujol) 3 020 and 3 060 (aromatic CH), 1 600 and 1 550 (aromatic C=C), and 765 and 700  $\text{cm}^{-1}$  (mono-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.7 (3 H, s, Me) and 7.3–8.4 (13 H, m, ArH).

**Trifluoro-N-(2-methylthiophenyl)acetamide (8).** Black amorphous solid (16%),  $\nu_{\text{max.}}$ (neat) 3 300 (NH), 1 710 (C=O), 1 600 and 1 550 (aromatic C=C), 1 160 (C-O), and 760 and 690  $\text{cm}^{-1}$  (*ortho*-substituted Ph);  $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$  2.4 (3 H, s, Me), 7.0–8.6 (4 H, m, ArH), and 9.0–9.6 (1 H, br, NH);  $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$  18.1 (Me) and 119.3, 124.8, 128.3, and 132.5 (C-3, -5, -4, and -6 of phenyl group). No elemental analysis was attempted.

**Trifluoro-N-(4-methylthiophenyl)acetamide (9).** White crystals, m.p. 135–136 °C (20%);  $\nu_{\text{max.}}$ (Nujol) 3 320 (NH), 1 695 (C=O), 1 590 and 1 530 (aromatic C=C), 1 170 (C-O), and 820  $\text{cm}^{-1}$  (*para*-substituted Ph);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.55 (3 H, s, Me), 7.2–7.8 (4 H, ABq, ArH), and 7.9–8.3 (1 H, br, NH);  $\delta_{\text{C}}(\text{CDCl}_3)$  15.1 (Me), and 121.0, 127.3, 132.2, and 136.6 (C-3, -2, -1, and -4 of phenyl group) (Found: C, 45.7; H, 3.3; N, 6.0.  $\text{C}_9\text{H}_8\text{F}_3\text{NOS}$  requires C, 45.95; H, 3.45; N, 5.95%).

Besides the above products, trifluoroacetanilide (44%) was also formed. The yields of the products were determined by g.l.c. analysis.

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