

## Thermal Reaction of Arylnitrenes with Dimethyl Sulphide, Thioanisole, and Tetrahydrothiophene

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The thermal decomposition of the aryl azides (**1**) into dimethyl sulphide (**2**), thioanisole (**3**), and tetrahydrothiophene (**4**) generally affords the 2-substituted anilines (**5**)—(**7**) in practicable yields by Sommelet–Hauser rearrangement of the intermediate *N*-arylsulphimides (**11a–c**) which result from aryl nitrene attack at the sulphur atom of (**2**)—(**4**). This constitutes a potential synthetic procedure.

Recently, we have shown<sup>1</sup> that singlet phenylnitrene, produced by the thermal decomposition of phenyl azide (**1**; R<sup>1</sup> = H), generally reacts with the sulphur atoms of sulphides to give the *N*-phenylsulphimides (**11**; R<sup>1</sup> = H); the decomposition products that are ultimately formed from these depend on the nature of the substituents on sulphur. In particular, thermal decomposition of compound (**1**; R<sup>1</sup> = H) at 155 °C into dimethyl sulphide (**2**), thioanisole (**3**), and tetrahydrothiophene (**4**) led to the formation of the 2-substituted anilines (**5**)—(**7**) (R<sup>1</sup> = H) in 25–30% yields; a reasonable mechanism would be a Sommelet–Hauser type rearrangement of the intermediate *N*-phenylsulphimides (**11a–c**; R<sup>1</sup> = H) (Schemes 1 and 2).

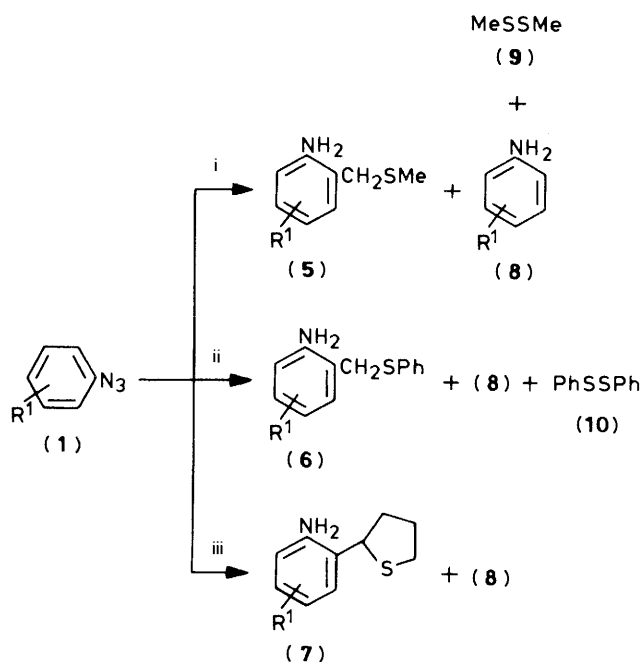
In continuation of this work, we now report the results from a study of the thermal reactions of a series of substituted phenyl azides (**1**) with the sulphides (**2**)—(**4**), which was undertaken in order to explore the generality of the aryl nitrene attack at sulphur and the effect of the substituent in the phenyl ring; moreover it was also of interest to us to explore the potential synthetic value of these reactions as a route to the 2-substituted anilines (**5**)—(**7**), which have been shown by Gassman and his co-workers<sup>2</sup> to be attractive precursors of valuable synthetic intermediates such as *o*-alkylated anilines, *o*-aminobenzaldehydes, and *o*-acetylaminostyrenes.

### Results and Discussion

The thermal decomposition of the aryl azides (**1**) was carried out in the appropriate sulphide (**2**)—(**4**) (0.2M) at 155 °C for *ca.* 10 h, until the azido i.r. band at *ca.* 2120 cm<sup>-1</sup> disappeared, and reaction products were directly separated by column chromatography of the reaction mixtures (Table). As can be seen from the Table, the thermal reactions of the substituted phenyl azides (**1**), bearing an *ortho*-, *meta*-, or *para*-substituent with electronic character varying from electron-donating to electron-withdrawing, with dimethyl sulphide (**2**) led in all cases to the isolation of the 2-methylthiomethylanilines (**5**) in moderate yields. In line with the presumed intermediacy of the *N*-arylsulphimides (**11a**), affording the anilines (**5**) by a Sommelet–Hauser rearrangement, the reactions of *para*- (and *ortho*-) substituted phenyl azides gave only a single product, while *m*-chlorophenyl azide (**1**; R<sup>1</sup> = 3-Cl) yielded a mixture of the isomeric 3- and 5-chloro-2-methylthiomethylanilines (**5**; R<sup>1</sup> = 3-Cl) and (**5**; R<sup>1</sup> = 5-Cl) in the ratio *ca.* 1.9:1, as determined by n.m.r. analysis of the product mixture.

This value is comparable with that observed by Claus (1.8:1) in the rearrangement of *N*-(*m*-chlorophenyl)-*S,S*-dimethylsulphimide (**11a**; R<sup>1</sup> = 3-Cl) in refluxing toluene<sup>3</sup> and with that reported by Gassman (1.5:1) for a similar rearrangement of (**11a**; R<sup>1</sup> = 3-Cl) produced by treatment of the azasulphonium salt (**12**) with sodium methoxide.<sup>2a</sup>

In addition to the previously reported kinetic evidence<sup>1</sup> for the intermediacy of aryl nitrenes in the thermal reaction of the



Scheme 1. Reagents: i, MeSMe (**2**), 155 °C; ii, PhSMe (**3**), 155 °C; iii, tetrahydrothiophene (**4**), 155 °C

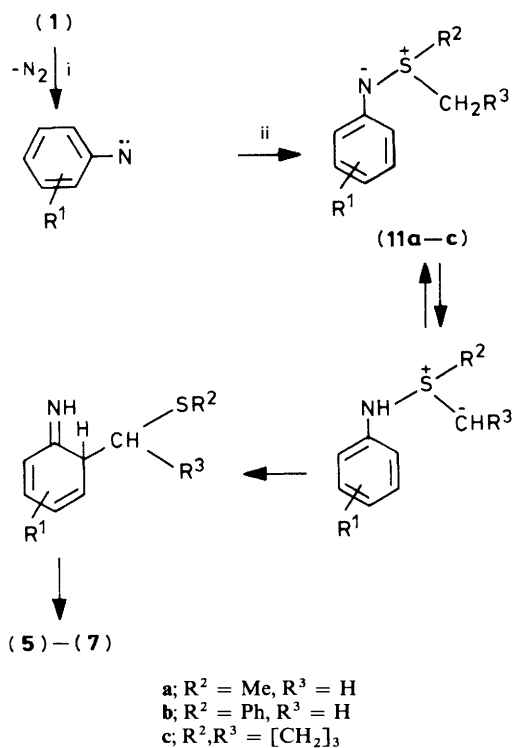
aryl azides (**1**) with sulphides, further support came from our findings that thermal decomposition of 2-azidobiphenyl (**1**; R<sup>1</sup> = 2-Ph) into dimethyl sulphide (**2**) does not lead to any of the Sommelet–Hauser product (**5**; R<sup>1</sup> = 2-Ph); instead carbazole (**13**) and 2-aminobiphenyl (**8**; R = 2-Ph) (92 and 6%, respectively) were formed exclusively (Scheme 3). It is well documented<sup>4</sup> that carbazole, produced by thermolysis of 2-azidobiphenyl (**1**; R<sup>1</sup> = 2-Ph), results from the intermediate singlet 2-nitrenobiphenyl; these results therefore appear to indicate that the sulphur atom of the sulphide (**2**) does not assist the elimination of nitrogen from (**1**; R<sup>1</sup> = 2-Ph), thus allowing formation of the 2-nitrenobiphenyl. Moreover, it may be inferred that intramolecular cyclization leading to (**13**) is much more feasible for singlet 2-nitrenobiphenyl than intermolecular attack at the sulphur atom of (**2**).

As indicated in the Table, the thermal reaction of the substituted phenyl azides (**1**) with thioanisole (**3**) and tetrahydrothiophene (**4**) also afforded the corresponding 2-substituted anilines (**6**) and (**7**) in practicable yields in all cases examined except for that of 4-methoxyphenyl azide (**1**; R<sup>1</sup> = 4-OMe); this led to 4-methoxy-2-phenylthiomethylaniline (**6**; R<sup>1</sup> = 4-OMe) and 4-methoxy-2-tetrahydro-2-thienylaniline (**7**; R<sup>1</sup> = 4-OMe), in poor yields.

**Table** Products from the thermolysis of the substituted phenyl azides (1) in the sulphides (2)–(4) at 155 °C

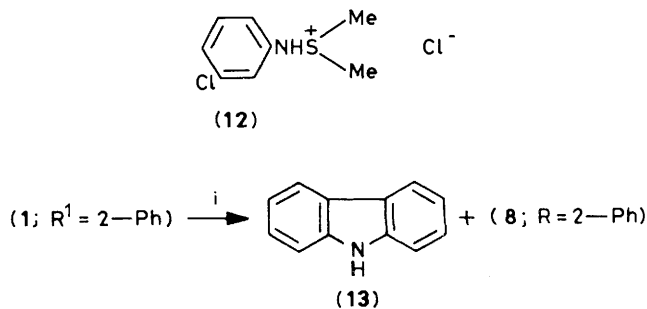
Sulphide	Phenyl azide (1) R <sup>1</sup>	Yield (%)					
		(5)	(6)	(7)	(8)	(9)	(10)
(2)	H <sup>a</sup>	30			12	10	
	4-OMe	18			43	11	
	4-Me	36			29	8	
	4-Cl	48			20	12	
	3-Cl	45 <sup>b</sup>		20	<i>c</i>		
	2-Cl	41 <sup>d</sup>			10	<i>c</i>	
	4-CN	56			14	4	
(3)	4-NO <sub>2</sub>	39			15	<i>c</i>	
	H <sup>a</sup>		25		12		6
	4-OMe		2		27		16
	4-Me		22		33		21
	4-Cl		25		26		19
	4-CN		39		14		8
	4-NO <sub>2</sub>		21		18		22
(4)	H <sup>a</sup>			25	15		
	4-OMe			10	33		
	4-Me			40	23		
	4-Cl			20	40		
	2-Cl			37 <sup>d</sup>	14		

<sup>a</sup> From ref. 1. <sup>b</sup> Mixture of 3-Cl and 5-Cl isomers in the ratio ca. 1.9:1. <sup>c</sup> Yield not determined. <sup>d</sup> R<sup>1</sup> = 6-Cl.

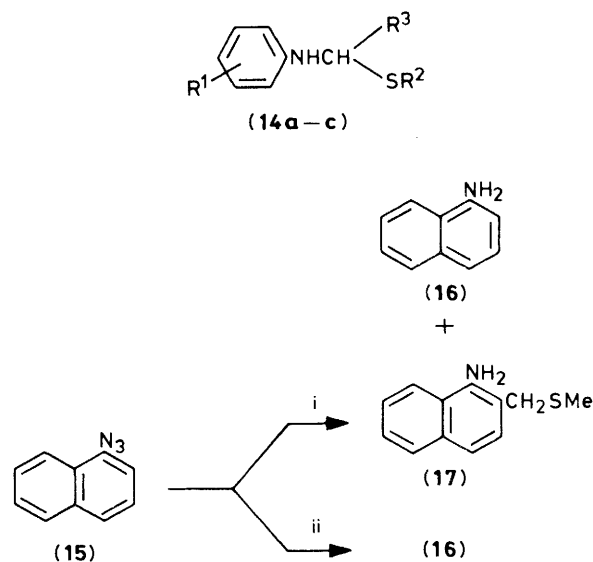


**Scheme 2.** Reagents: i, 155 °C; ii, (2)–(4)

The data reported in the Table show that marked amounts of the arylamines (8) generally accompany the formation of the Sommelet-Hauser rearrangement products (5)–(7); moreover, dimethyl disulphide (9) and diphenyl disulphide (10) are generally produced in significant yields from reaction of the aryl azides (1) with the sulphides (2) and (3), respectively. As we have previously suggested,<sup>1</sup> a possible route to the disulphides (9) and (10) might involve some fragmentation of the unstable



**Scheme 3.** Reagents: i, (2), 155 °C



**Scheme 4.** Reagents: i, (2), 155 °C; ii, (3), (4), 155 °C

aminothioacetals (14a) and (14b), which could be produced by Stevens rearrangement of the sulphimides (11a) and (11b) and/or insertion of aryl nitrene into the C(α)-H bond of the sulphides (2) and (3); however, their formation remains unclear at this stage. The arylamines (8) could be formed by hydrogen abstraction from the sulphide solvent by triplet nitrenes; this is apparently supported by the general trend that the formation of (8) at the expense of the Sommelet-Hauser products (5)–(7) is favoured by electron-releasing substituents, and disfavoured by electron-withdrawing groups. In fact, electron-releasing substituents would be expected to decrease the electrophilic character (and hence the reactivity) of the singlet nitrene,<sup>4,5</sup> thus giving higher yields of triplet products, whereas electron-withdrawing groups should increase the electrophilicity<sup>4,5</sup> and thence favour attack at sulphur.

Further support comes from our observation<sup>6</sup> that the thermal reaction of 1-azidonaphthalene (15) with the sulphides (2)–(4) generally affords 1-naphthylamine (16) in fairly high yields (55–65%), the Sommelet-Hauser product (17) being observed in low yield (10%) only from the reaction of (15) with dimethyl sulphide (2); these results might reflect the apparent propensity of 1-naphthyl nitrene to give triplet derived products<sup>7</sup> (Scheme 4).

However, it should be pointed out that the trends observed in our reactions might be affected to some extent by the relative ease with which the first formed *N*-arylsulphimides (11a–c) undergo the Sommelet-Hauser rearrangement, giving (5)–(7), rather than the other possible decomposition modes such as Stevens rearrangement leading to the aminothioacetals (14a–c)

and then to their possible fragmentation products (the actual nature of which is unknown at the moment) and cleavage of the S-N bond giving back the aryl nitrene and the sulphide.

Data concerning the thermal decomposition of the *N*-arylsulphimides (11) under reaction conditions comparable to those occurring in our reactions are not available at this stage, though a great deal of attention<sup>8</sup> has been devoted to the study of the Sommelet-Hauser rearrangement of the *N*-arylsulphimides (11) under milder conditions and usually in the presence of base. We therefore feel that a full explanation of our present results must be deferred until the actual decomposition modes of the *N*-arylsulphimides (11a-c) under our reaction conditions are clarified; this is currently being investigated.

Finally, we wish to point out that the thermal reaction of the aryl azides (1) with the sulphides (2)-(4) can provide a synthetic approach to the 2-substituted anilines (5)-(7); even though the yields of the anilines (5)-(7) are generally modest, the procedure is quite simple and the starting aryl azides (1) can be readily prepared from the corresponding arylamines as well as from activated and unactivated aryl halides.<sup>9</sup>

## Experimental

Dimethyl sulphide (2), thioanisole (3), and tetrahydrothiophene (4) were commercial products. The aryl azides (1) were prepared by the diazotisation of the corresponding amine followed by treatment with sodium azide. The 2-methylthiomethylanilines (5)<sup>2a,10</sup> and 2-phenylthiomethylanilines (6; R<sup>1</sup> = 4-Me, 4-Cl, and 4-CN)<sup>2c</sup> were identified on the basis of their physical and spectral properties which were in agreement with those reported in the literature; diphenyl disulphide (10), the arylamines (8), and carbazole (13) were identified by spectral comparison with authentic commercial samples. Quantitative determinations of the disulphides (9) and (10) were generally performed by g.l.c. on an aliquot part of the appropriate reaction mixture. Quantitative g.l.c. analyses were carried out by the internal standard method on a Varian 1440 instrument equipped with a flame-ionization detector, using a 5% SP 2250 Supelcoport column. Light petroleum refers to the fraction boiling at 40-60 °C. Ether refers to diethyl ether. Column chromatography was carried out on Merck silica gel (0.040-0.063 particle size).

**Thermal Reactions of the Aryl Azides (1) with the Sulphides (2)-(4). General Procedure.**—The reactions of the aryl azides (1) with the sulphides (2)-(4) were carried out by heating a solution of the azide (10 mmol) in the appropriate sulphide (25 ml) at 155 °C for ca. 10 h [in a sealed tube in the case of sulphides (2) and (4)]. In all cases the reaction products were separated by column chromatography of the reaction mixtures, which were directly employed without elimination of the excess of solvent.

Elution was as follows: light petroleum yielded the sulphides (2)-(4) and the disulphides (9) and (10); ether-light petroleum (10-20%) eluted the 2-substituted anilines (5)-(7) and the carbazole (13); ether-light petroleum (20-30%) gave the arylamines (8); elution with a solvent of higher polarity afforded an intractable tarry material.

The following products were thus obtained: 4-methoxy-2-phenylthiomethylaniline (6; R<sup>1</sup> = 4-OMe), m.p. 69-71 °C,  $v_{\max}$  (CCl<sub>4</sub>) 3 430 and 3 360 cm<sup>-1</sup> (NH<sub>2</sub>);  $\delta$ (CHCl<sub>3</sub>) 3.16 (2 H, br s), 3.6 (3 H, s), 4.0 (2 H, s), and 6.5-7.3 (8 H, m);  $m/z$  245 (M<sup>+</sup>),

136, 109, and 93 (Found: C, 68.95; H, 6.05; N, 5.6; S, 12.95. C<sub>14</sub>H<sub>15</sub>NOS requires C, 68.5; H, 6.15; N, 5.7; S, 13.05%); 4-nitro-2-phenylthiomethylaniline (6; R<sup>1</sup> = 4-NO<sub>2</sub>), m.p. 101-103 °C,  $v_{\max}$  (CHCl<sub>3</sub>) 3 490 and 3 400 cm<sup>-1</sup> (NH<sub>2</sub>);  $\delta$ (CHCl<sub>3</sub>) 3.97 (2 H, s), 4.77 (2 H, br s), and 6.48-7.93 (8 H, m);  $m/z$  260 (M<sup>+</sup>), 151, 110, 105, and 104 (Found: C, 58.8; H, 4.6; N, 10.65; S, 12.4. C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 60.0; H, 4.65; N, 10.75; S, 12.3%); 4-methoxy-2-tetrahydro-2-thienylaniline (7; R<sup>1</sup> = 4-OMe), a pale yellow oil,  $v_{\max}$  (CCl<sub>4</sub>) 3 430 and 3 320 cm<sup>-1</sup> (NH<sub>2</sub>);  $m/z$  209 (M<sup>+</sup>), 123, 108, and 87;  $\delta$ (CCl<sub>4</sub>) 2.1-2.3 (4 H, m), 2.93-3.15 (2 H, m), 3.63 (2 H, br s), 3.68 (3 H, s), 4.43 (1 H, t), and 6.5-6.8 (3 H, m) (Found: C, 62.9; H, 7.25; N, 6.65; S, 15.4. C<sub>11</sub>H<sub>15</sub>NOS requires C, 63.1; H, 7.2; N, 6.7; S, 15.3%); 4-methyl-2-tetrahydro-2-thienylaniline (7; R<sup>1</sup> = 4-Me), a pale yellow oil,  $v_{\max}$  (CCl<sub>4</sub>) 3 440 and 3 320 cm<sup>-1</sup> (NH<sub>2</sub>);  $m/z$  193 (M<sup>+</sup>), 178, 160, 150, and 146;  $\delta$ (CCl<sub>4</sub>) 2.0-2.3 (4 H, m), 2.13 (3 H, s), 2.8-3.1 (2 H, m), 3.73 (2 H, br s), 4.35 (1 H, t), and 6.2-6.9 (3 H, m) (Found: C, 68.6; H, 7.85; N, 7.1; S, 16.5. C<sub>11</sub>H<sub>15</sub>NS requires C, 68.35; H, 7.8; N, 7.25; S, 16.6%); 4-chloro-2-tetrahydro-2-thienylaniline (7; R<sup>1</sup> = 4-Cl), a pale yellow oil,  $v_{\max}$  (CCl<sub>4</sub>) 3 440 and 3 320 cm<sup>-1</sup> (NH<sub>2</sub>);  $m/z$  215 and 213 (M<sup>+</sup>), 182, 180, 178, 172, 170, 168, and 166;  $\delta$ (CCl<sub>4</sub>) 2.1-2.3 (4 H, m), 2.9-3.2 (2 H, m), 3.9 (2 H, br s), 4.4 (1 H, t), and 6.5-7.2 (3 H, m) (Found: C, 56.35; H, 5.6; Cl, 16.55; N, 6.65; S, 15.2. C<sub>10</sub>H<sub>12</sub>ClNS requires C, 56.2; H, 5.65; Cl, 16.6; N, 6.55; S, 15.0%); 6-chloro-2-tetrahydro-2-thienylaniline (7; R<sup>1</sup> = 6-Cl), a pale yellow oil,  $v_{\max}$  (CCl<sub>4</sub>) 3 440 and 3 320 cm<sup>-1</sup> (NH<sub>2</sub>);  $m/z$  215 and 213 (M<sup>+</sup>), 182, 180, 178, 172, 170, 168, and 166;  $\delta$ (CCl<sub>4</sub>) 2.0-2.25 (4 H, m), 2.8-3.05 (2 H, m), 4.35 (1 H, t), 4.5 (2 H, br s), and 6.3-7.1 (3 H, m) (Found: C, 56.0; H, 5.55; Cl, 16.8; N, 6.7; S, 14.9%).

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