N-Phenylsulphimide Formation and Rearrangement in the Thermal Reaction of Phenylnitrene with Sulphides

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Thermal reaction of phenyl azide (1) with thioanisole (2a), dimethyl sulphide (2b), and tetrahydrothiophen (2c) leads to the formation of 2-substituted anilines (3a—c) by Sommelet–Hauser rearrangement of the intermediate N-phenylsulphimides arising from phenylnitrene attack at the sulphur atom of (2a—c). Reaction with ethyl phenyl sulphide (2d) gives benzenesulphenanilide (8) and ethylene by cycloelimination of the resulting N-phenylsulphimide. Reaction with acyclic benzylic sulphides (2e—g) apparently leads only to the insertion products of phenylnitrene into the benzylic C–H bond, presumably through Stevens rearrangement of the intermediate sulphimides, whereas Sommelet–Hauser rearrangement appears to compete favourably with Stevens rearrangement in the sulphimide resulting from reaction of phenylnitrene with the cyclic benzylic sulphide (2h).

Reactions of sulphonyl-, carbonyl-, and acylamino-nitrenes with sulphides have been the object of considerable attention in recent years; results have shown that the sulphur atom of sulphides is generally capable of intercepting such nitrenes, probably in the singlet state, leading either to isolatable sulphimides or to products arising from decomposition of inter-mediate sulphimides, depending on the reaction conditions and the nature of both sulphides and nitrenes.[1]

Despite much effort, attempts to observe arylnitrene attack at sulphur have met so far only with failure.[2] Such failure could be reasonably ascribed to the fact that N-arylsulphim-ides are not capable of surviving the reaction conditions neces-sary to produce arylnitrenes; thus, if a straightforward route leading to well defined decomposition products is not avail-able for the possibly formed N-arylsulphimides,[2c] cleavage of the S–N bond leading back to the arylnitrene and sulphide could occur almost exclusively. We reasoned that N-arylsul-phimides might be diverted from undergoing a simple cleavage of the S–N bond if an alternative intramolecular reaction was available. An attractive scheme to show arylnitrene attack at sulphur was to investigate the reaction of arylnitrenes with suitable sulphides bearing α- and/or β-hydrogen atoms. These would be expected to produce N-arylsulphimides which would afford Sommelet–Hauser-type rearrangement pro-ducts,[1a] or cycloelimination products[1a,3,4] if β-hydrogen atoms are present. In this paper we report our results from a study of the thermal reaction of phenyl azide (1) with a num-ber of sulphides (2a—h) which provide the first examples of sulphimide formation by phenylnitrene attack at the sulphur atom.[5]

Results and Discussion

Thermal decomposition of phenyl azide (1) into thioanisole (2a) (0.2M) at 155 °C for *ca.* 10 h (until the disappearance of the azido i.r. band at 2 120 cm⁻¹) led to the isolation of 2-(phenylthiomethyl)aniline (3a) (30%), aniline (4) (12%), and diphenyl disulphide (5; R = Ph) (6%). Analogous results were obtained from thermolysis of (1) into dimethyl sulphide (2b) and tetrahydrothiophen (2c). These reactions gave 2-(methyl-thiomethyl)aniline (3b) (35%) and 2-o-aminophenyltetra-hydrothiophen (3c) (30%), respectively, together with aniline (4) (12—15%). Formation of dimethyl disulphide (5; R = Me) in 10% yield was also observed from the reaction of (1) with the sulphide (2b) (Scheme 1).

2-Substituted anilines (3a—c) can be reasonably rational-ized by assuming a singlet phenylnitrene attack on the sulphur atoms of (2a—c) leading to intermediate N-phenylsulphimides

PhN₃ + RSCH₂R'

(1)   (2a – c)

↓

(3a–c)   (4)   (5; R = Ph, Me)

a ; R = Ph, R' = H

b ; R = Me, R' = H

c ; R, R' = CH₂CH₂CH₂
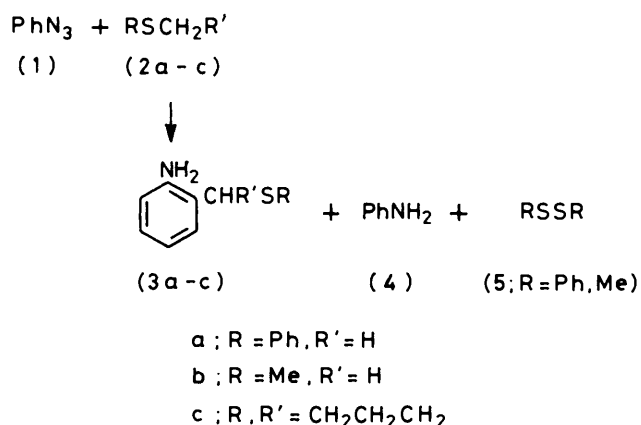
Scheme 1.

(6a—c), from which anilines (3a—c) are expected to be formed by Sommelet–Hauser rearrangement (Scheme 2).

Evidence to support the intermediacy of phenylnitrene was obtained by kinetic studies of the thermal decomposition of phenyl azide (1) in bromobenzene at 152 °C, which showed that the first-order decomposition rate of (1) is not affected by the presence of thioanisole or by its concentration (Table).

On the other hand, singlet phenylnitrene attack is invoked only on the basis that it is generally accepted that the singlet states of nitrenes and carbenes are those which react with sulphides by attack on sulphur.[1a,1b]

As for the disulphides (5; R = Ph, Me), their actual source remains open at present. In our preliminary report of this work[5] we suggested that formation of the disulphide (5; R = Ph) might be due to some decomposition of aniline (3a) occurring under the reaction conditions, since control experi-ments had shown (3a) to exhibit some formation of (5; R = Ph) on prolonged heating at 155 °C. However, aniline (3b) is quite stable under the reaction conditions, and therefore ap-pears not to be responsible for the formation of disulphide (5; R = Me). An alternative route leading to this disulphide (5; R = Me) [and possibly to some (5; R = Ph)] might involve some fragmentation of aminothioacetals RSCH₂NHPh (R = Ph, Me) which in turn might be produced by insertion of phenylnitrene into the C(α)–H bond of (2a,b) or, according to the trend exhibited by N-phenyl-S-benzylsulphimides (11e—h) (see later), by Stevens-type rearrangement of the sulph-imides (6a,b). Compelling evidence for the proposal that N-phenylsulphimides are actually formed by phenylnitrene

PhN + (2a-c)

(6a-c)   ⇌   (7a-c)

(3a-c)
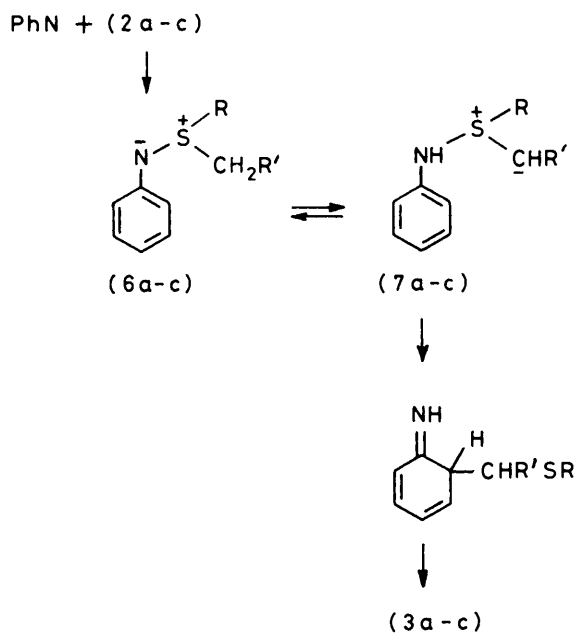
Scheme 2.

Table. Thermal decomposition of phenyl azide (1) in bromobenzene at 152 °C in the presence of thioanisole (2a)

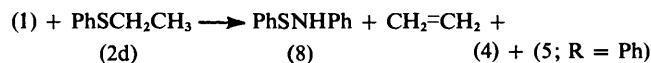| $[PhN_3]/M$	$[PhSMe]/M$	Rate constant/min^{-1}
0.20	0.0	4.08×10^{-3}
0.20	0.4	4.10×10^{-3}
0.20	0.8	4.09×10^{-3}
0.20	1.7	4.10×10^{-3}

attack at sulphur was also obtained from the thermolysis of phenyl azide (1) in phenyl ethyl sulphide (2d) at 155 °C. This reaction furnished benzenesulphenanilide (8) (27%), ethylene (28%), aniline (4) (30%), and diphenyl disulphide (5; R = Ph) (17%) (Scheme 3).
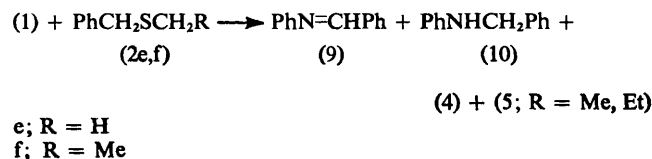
Benzenesulphenanilide (8) and ethylene clearly arise from sulphimide (6; R = Ph, R' = Me) by cycloelimination which is assumed to occur through a five-membered cyclic transition state;[3,4] on the other hand, partial decomposition of compound (8) occurring under the reaction conditions is likely to be responsible for disulphide (5; R = Ph) and aniline (4) (to the major extent), as evidenced by control experiments. Formation of the Sommelet–Hauser rearrangement product (3; R = Ph, R' = Me) was not observed, in agreement with previous reports on rearrangements of N-arylsulphimides bearing an S-alkyl group with a β-hydrogen atom.[3,4]

Decomposition of (1) in benzyl methyl sulphide (2e) gave N-benzylideneaniline (9) (14%), N-benzylaniline (10) (11%), aniline (4) (22%), and dimethyl disulphide (5; R = Me) (60%) as the only identifiable products (Scheme 4). No evidence of either of the two possible Sommelet–Hauser-rearrangement products (3; R = Me, R' = Ph and 3; R = PhCH₂, R' = H) could be obtained.
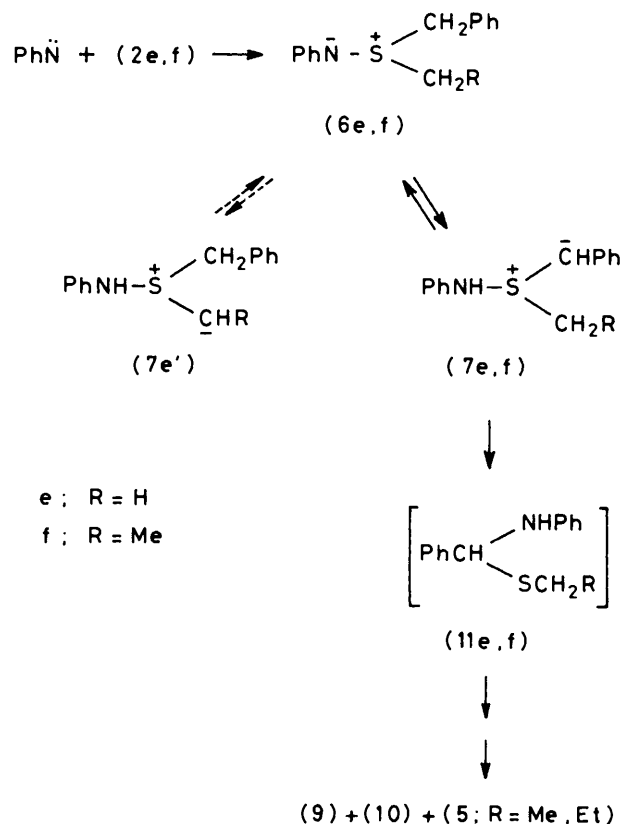
Products (5; R = Me), (9), and (10) are presumably ascribable to some fragmentation of aminothioacetal (11e), the formal insertion product of phenylnitrene into the benzylic C–H bond. In fact, aminothioacetal (11e) might be a reasonable source of (9) and methanethiol, further reaction of (9) with methanethiol being expected to lead to compounds (10) and (5; R = Me).[6] Aminothioacetal (11e) can be assumed to

(1) + PhSCH₂CH₃ ⟶ PhSNHPh + CH₂=CH₂ +
(2d)   (8)   (4) + (5; R = Ph)

Scheme 3.

(1) + PhCH₂SCH₂R ⟶ PhN=CHPh + PhNHCH₂Ph +
(2e,f)   (9)   (10)

(4) + (5; R = Me, Et)

e; R = H
f; R = Me

Scheme 4.

(6e,f)

(7e')   (7e,f)
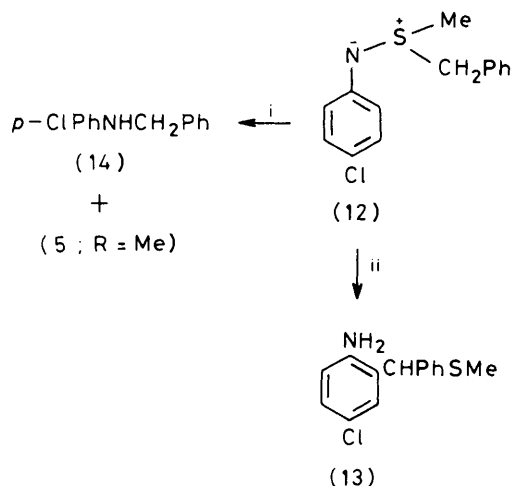
e ; R = H
f ; R = Me

(11e,f)

(9) + (10) + (5; R = Me, Et)

Scheme 5.

be produced through Stevens rearrangement of the sulphonium ylide (7e) arising from the initially formed sulphimide (6e) by proton transfer; on this basis, formation of the acetal (11e) together with suppression of (3; R = Me, R' = Ph) would appear to indicate that Stevens rearrangement is largely preferred over a competing Sommelet–Hauser rearrangement. On the other hand, the absence of the Sommelet–Hauser product (3; R = PhCH₂, R' = H), which might have been formed from the sulphonium ylide (7e'), would suggest that the rearrangement of sulphimide (6e) is governed by the higher acidity of the α-benzylic hydrogens, strongly favouring equilibration of (6e) with the ylide (7e) rather than with the tautomer (7e') (Scheme 5).

Suppression of the aniline (3; R = PhCH₂, R' = H) is in line with earlier findings[3] which have shown that the S-alkyl group bearing the more acidic α-hydrogens is that which governs the rearrangement of unsymmetrical N-aryl-S,S-dialkyl-sulphimides; however, formation of a Stevens-type product

$$\overset{\overset{\displaystyle \overset{+}{S}-Me}{\underset{\displaystyle CH_2Ph}{|}}}{N}$$

p-ClPhNHCH$_2$Ph ◀—ⁱ—

(14)

+

(5 ; R = Me)

Cl

(12)

⬇ ii

NH$_2$

CHPhSMe

Cl

(13)

Scheme 6. *Reagents:* i, PhBr, 155 °C; ii, EtOH–KOH, 80 °C

from (6e) would be somewhat unexpected, since Stevens-type rearrangements are not generally exhibited by N-arylsulph-imides [1a] and in view of previous findings which have shown N-aryl-S-benzylsulphimides to furnish only Sommelet–Hauser products on refluxing in ethanol or toluene in the presence of base.[3,7] We suggest that the Stevens rearrangement exhibited by S-benzylsulphimide (6e) might be ascribable to our different reaction conditions, *i.e.* higher temperature and absence of base. Our suggestion appears to be supported by our observation[8] that N-p-chlorophenyl-S-benzyl-S-methylsulphimide (12) gives no Sommelet–Hauser product (13) on heating in refluxing bromobenzene, the main products being N-benzyl-4-chloroaniline (14) and dimethyl disulphide (5; R = Me) (Scheme 6). Exclusive Sommelet–Hauser re-arrangement has been reported for the sulphimide (12) on refluxing in ethanol in the presence of base.[3]

Analogous products were obtained from the thermal decomposition of phenyl azide (1) in benzyl ethyl sulphide (2f), which afforded compounds (9) (19%), (10) (7%), (4) (29%), and (5; R = Et) (40%) (Scheme 4), thus pointing to analogous behaviour of the intermediate sulphimide (6f). Only trace amounts of ethylene, arising from (6f) by cycloelimination, could be detected. The almost complete suppression of cyclo-elimination observed in such cases appears to be ascribable to the overwhelming effect of the most acidic benzylic hydro-gens.

The general trend exhibited by reactions of phenylnitrene with benzylic sulphides appears to be supported by results obtained from the thermolysis of (1) at 155 °C in *o*-dichloro-benzene containing a four-fold excess of benzyl phenyl sul-phide (2g). This reaction gave compounds (9) (22%), (4) (25%), (5; R = Ph) (26%), and 2,3-diphenyl-2,3-diphenyl-thioethane (15) (8%); also, in such cases, no Sommelet–Hauser product (3; R = R′ = Ph) was observed (Scheme 7).

In analogy with the route suggested for the sulphides (2e,f), reaction products (9) and (5; R = Ph) can be assumed to be formed through Stevens rearrangement of the initially formed N-phenylsulphimide (6; R = R′ = Ph) and subsequent frag-mentation of the resulting aminothioacetal; however, N-benzylaniline (10) was not observed and the reason remains unclear. The dimeric product (15) may be ascribed to hydro-gen abstraction from (2g) by triplet nitrenes leading to α-phenylthiobenzyl and anilino radicals; dimerization of the former radicals would produce (15). The presence of the dimer (15) might indicate that a route involving coupling of α-phenylthiobenzyl and anilino-radicals is likely to play a role

(1) + PhSCH$_2$Ph ⟶ (9) + (4) + (5; R = Ph) +

(2g)   PhS(Ph)CH–CH(Ph)PhS (15)
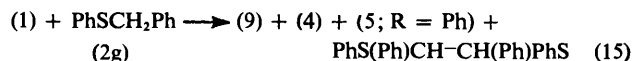
Scheme 7.

(although not an essential one) in the formation of the inter-mediate aminothioacetal. On this basis it should be pointed out that some contribution to the possible formation of amino-thioacetals (11e,f) by an analogous route involving triplet nitrenes cannot be excluded at present, although no products arising from dimerization of α-alkylthiobenzyl radicals could be observed from reactions of phenylnitrene with the sulphides (2e,f).

Finally, thermal decomposition of phenyl azide in refluxing bromobenzene (0.2M) in the presence of equimolar amounts of 6H-dibenzo[b,d]thiopyran (2h) gave (i) 6-(2-aminophenyl)-6H-dibenzo[b,d]thiopyran (16) (13%), (ii) N-(6H-dibenzo-[b,d]thiopyran-6-ylidene)aniline (17) (7%), (iii) 6,6′-bis(6H-dibenzo[b,d]thiopyran) (18) (15%), and (iv) aniline (4) (24%) (Scheme 8). Formation of compound (16) can be readily rationalized by a mechanism analogous to that suggested for the 2-substituted anilines (3a—c), whereas compound (18) may be ascribed to dimerization of 6H-dibenzo[b,d]thio-pyran-6-yl radicals resulting from hydrogen abstraction from (2h) by triplet phenylnitrenes. On the other hand, product (17) most probably arises from further reaction of 6-anilino-6H-dibenzo[b,d]thiopyran (19), the insertion product of phenyl-nitrene into the C(6)–H bond.

The formation of the Sommelet–Hauser product (16) is noteworthy since no analogous products could be detected from reactions of phenylnitrene with acyclic benzylic sul-phides (2e,g). A more favourable stereochemistry for Som-merlet–Hauser rearrangement in the endocyclic sulphonium ylide (7; R,R′ = biphenyl-2,2′-diyl), arising from the inter-mediate sulphimide (6; R,R′ = biphenyl-2,2′-diyl) with res-pect to the corresponding acyclic ylides (7e,f) and (7; R = R′ = Ph), might explain the different behaviour observed.

Compound (19) might, at first sight, be attributed to a competing Stevens rearrangement of the sulphimide (6; R,R′ = biphenyl-2,2′-diyl). However, the presence of notice-able amounts of the dimer (18) as well as the use of reaction conditions which could be expected to favour triplet nitrene reactions, such as a low sulphide concentration and use of bromobenzene as solvent which is known to promote singlet ⟶ triplet nitrene intersystem crossing,[9] would suggest that a route involving triplet nitrenes might be a major contri-bution to the formation of compound (19).

Our results appear to provide the first definite evidence that phenylnitrene is generally capable of reacting with the sulphur atoms of sulphides, leading to N-phenylsulphimides, thus indicating that arylnitrenes are not an exception in the nitrene family. Moreover, these findings seem to indicate that the reactivity of an arylnitrene towards the sulphur atom must be fairly high.

Experimental

Thioanisole (2a), dimethyl sulphide (2b), tetrahydrothiophen (2c), benzyl methyl sulphide (2e), and benzyl phenyl sulphide (2g) were commercial products. Phenyl ethyl sulphide (2d),[10] benzyl ethyl sulphide (2f),[11] and 6H-dibenzo[b,d]thiopyran (2h)[12] were prepared according to the literature.

Reaction products 2-(phenylthiomethyl)aniline (3a),[7] 2-methylthiomethyl)aniline (2b),[4] and 2-o-aminophenyltetra-hydrothiophen(3c)[4] were characterized on the basis of physical and spectral properties; benzenesulphenanilide (8),[13] diphenyl disulphide (5; R = Ph),[14] N-benzylaniline (10),[17] and 2,3-
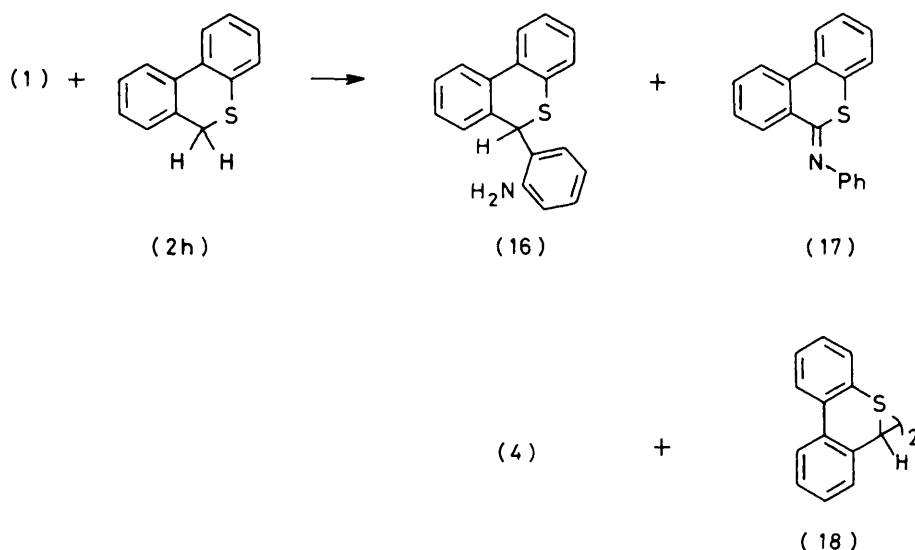
Scheme 8.

diphenyl-2,3-diphenylthioethane (15) [16] were identified by spectral comparison with authentic specimens.

Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size) by gradual elution with light petroleum (b.p. 40—70 °C)–ether (20 : 80).

G.l.c. analyses were performed on a Varian 1 440 instrument equipped with a flame-ionization detector, using a 5% SP 2250 Supelcoport column; quantitative determinations were carried out by the internal standard method.

Kinetic Measurements.—Solutions for kinetic determinations were prepared by dissolving phenyl azide (1) (2 mmol) in 10 ml of a suitable mixture of bromobenzene and thioanisole (2a) (PhBr : PhSMe = 10 : 0, 9.5 : 0.5, 9 : 1, and 8 : 2, respectively). The solution was kept in a thermostatic bath at 152 ± 0.1 °C; portions were removed at regular intervals, suitably diluted with bromobenzene and assayed by measuring the area of the azido-band in the i.r. spectrum at *ca.* 2 120 cm^{-1}. The first portion was removed after 5 min from immersion of the reaction vessel in the thermostatic bath and taken as zero point.

Thermal Reactions of Phenyl Azide (1) *with Sulphides* (2a—h). *General Procedure.*—Reactions of phenyl azide (1) with sulphides (2a—f) were carried out by heating a solution of (1) (0.2M) in the appropriate sulphide at 155 °C for *ca.* 10 h [in a sealed tube in the case of (2b), (2c), and (2e)]. Reactions with sulphides (2g) and (2h) were carried out similarly except that an *o*-dichlorobenzene solution of (1) containing a four-fold excess of (2g), and a bromobenzene solution of (1) containing equimolar amounts of (2h), were used respectively.

Reactions of (1) with sulphides (2d) and (2f) were carried out under a nitrogen stream in a flask equipped with a gas inlet and a condenser which was connected to a solution of bromine (1 ml) in carbon tetrachloride (40 ml) to trap the ethylene evolved. After the reaction, the carbon tetrachloride layer was treated with an aqueous solution of sodium sulphite, dried, and then carefully concentrated. Chlorobenzene (2 mmol) was added as an internal standard to the concentrated mixture which was assayed by n.m.r. and g.l.c. to determine the amount of 1,2-dibromoethane.

In all cases reaction products were separated by column chromatography of the reaction mixtures, which were directly employed without distilling off the excess of solvent.

Reaction of the azide (1) *with thioanisole* (2a). Column chromatography afforded (i) a fraction containing mostly the sulphide (2a) with minor amounts of diphenyl disulphide (5; R = Ph). The latter could be isolated in 6% yield by vacuum distillation of most of (2a) and chromatography of the resulting residue. The next fractions were (ii) 2-(phenylthiomethyl)-aniline (3a) (30%); (iii) aniline (4) (12%); and (iv) tarry material.

Reactions of the azide (1) *with dimethyl sulphide* (2b). Chromatography gave (i) a mixture containing dimethyl disulphide (5; R = Me) with trace amounts of two unidentified products; (ii) 2-(methylthiomethyl)aniline (3b) (35%); (iii) aniline (4) (12%); and (iv) tarry material.

The amount of dimethyl disulphide (5; R = Me) (10%) was determined by quantitative g.l.c. carried out on an aliquot part of the reaction mixture before column chromatography.

Reaction of the azide (1) *with tetrahydrothiophen* (2c). Chromatography gave (i) 2-(*o*-aminophenyl)tetrahydrothiophen (3c) (30%); (ii) aniline (4) (15%); and (iii) tarry material.

Reaction of the azide (1) *with phenyl ethyl sulphide* (2d). Chromatography gave (i) diphenyl disulphide (5; R = Ph) (17%); (ii) benzenesulphenanilide (8) (27%); (iii) aniline (4) (30%); and (iv) tarry material. Ethylene was also detected in 28% yield by the procedure described above in the general procedure.

Reaction of the azide (1) *with benzyl methyl sulphide* (2e). Quantitative g.l.c. analysis of an aliquot part of the reaction mixture gave (i) dimethyl disulphide (5; R = Me) (60%); (ii) aniline (4) (22%); (iii) *N*-benzylideneaniline (9) (14%); and (iv) *N*-benzylaniline (10) (11%).

Column chromatography furnished (i) a fraction which consisted mostly of sulphide (2c) with minor amounts of dimethyl disulphide (5; R = Me); (ii) *N*-benzylaniline (10); (iii) benzaldehyde (not present in the reaction mixture before column chromatography, as evidenced by g.l.c.); (iv) aniline (4); and (v) tarry material.

No *N*-benzylideneaniline (9) was isolated owing to complete hydrolysis occurring during chromatographic separation.

Reaction of the azide (1) *with benzyl ethyl sulphide* (2f). Quantitative g.l.c. analysis of an aliquot part of the reaction mixture gave (i) diethyl disulphide (5; R = Et) (40%); (ii) aniline (4) (29%); (iii) *N*-benzylideneaniline (9) (19%); and (iv) *N*-benzylaniline (10) (7%).

Column chromatography of the remainder led to the separ-

ation of (i) a mixture consisting mainly of sulphide (2f) accompanied by minor amounts of the disulphide (5; R = Et); (ii) *N*-benzylaniline (10); (iii) benzaldehyde; and (iv) aniline. Also, in such cases no *N*-benzylideneaniline could be isolated.

Only trace amounts of ethylene could be detected by g.l.c and n.m.r. according to the procedure described above.

Reaction of the azide (1) *with benzyl phenyl sulphide* (2g). Aniline (4) (25%), diphenyl disulphide (5; R = Ph) (26%) and *N*-benzylideneaniline (9) (22%) were detected by g.l.c. analysis of an aliquot part of the reaction mixture. Column chromatography of the remainder furnished (i) unchanged (2g); (ii) diphenyl disulphide (5; R = Ph) (iii) benzaldehyde; (iv) aniline; (v) 2,3-diphenyl-2,3-diphenylthioethane (15) (8%); and (vi) some tarry material.

Reaction of the azide (1) *with* 6H-*dibenzo*[b,d]*thiopyran* (2h). Column chromatography furnished (i) unchanged (2h); (ii) 6,6′-*bis*(6H-*dibenzo*[b,d]*thiopyran*) (18) (15%), m.p. 175—177 °C; $v_{max.}$ (CHCl$_3$) 740 cm^{-1}; δ(CDCl$_3$) 3.3 (2 H, s), and 5.4—7.3 (16 H, m); *m/z* 394 (*M*$^+$, 5%) and 197 (100) (Found: C, 78.9; H, 4.6; S, 16.3. C$_{26}$H$_{18}$S$_2$ requires C, 79.15; H, 4.60; S, 16.25%); (iii) N-(6H-*dibenzo*[b,d]*thiopyran-6-ylidene*)*aniline* (17) (7%), m.p. 78—81 °C; $v_{max.}$ (CHCl$_3$) 1 590 and 1 570 cm^{-1}; *m/z* 287 (*M*$^+$, 23%) and 184 (100); δ(CDCl$_3$) 5.6—7.3 (m) (Found: C, 79,6; H, 4.6; N, 4.85; S, 11.1. C$_{19}$H$_{13}$NS requires C, 79.4; H, 4.56; N, 4.87; S, 11.16%); (iv) 6-(2-*amino-phenyl*)-6H-*dibenzo*[b,d]*thiopyran* (16) (13%), m.p. 55—57 °C; $v_{max.}$ (CHCl$_3$) 3 450, 3 390, 1 620, and 910 cm^{-1}; δ(CDCl$_3$) 3.85 (2 H, s), 5.25 (1 H, s), and 6.6—7.9 (12 H, m); *m/z* 289 (*M*$^+$, 95%) and 197 (100) (Found: C, 78.7; H, 5.25; N, 4.85; S, 11.15. C$_{19}$H$_{15}$NS requires C, 78.85; H, 5.22; N,4.84; S, 11.08%); and (v) aniline (4) (25%).

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