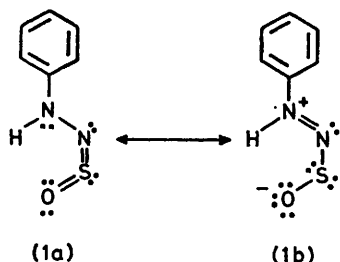


## The Thermolysis of *N*-Phenyl-*N'*-sulphonylhydrazine: an Interesting Source of Phenyl Radicals

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The thermal decomposition of *N*-phenyl-*N'*-sulphonylhydrazine (1) in a number of solvents has been investigated. The isomeric composition of the biphenylic products indicates the intervention of phenyl radicals, which come from the homolysis of (1).

In previous work we have studied the reactivity of compounds containing cumulative double bonds such as



bis(arylimino)sulphur derivatives ( $\text{ArN}=\text{S}=\text{NAr}$ )<sup>1</sup> and the isoelectronic *N*-sulphonylanilines ( $\text{ArN}=\text{S}=\text{O}$ )<sup>2</sup>

We have now investigated the chemical behaviour of *N*-phenyl-*N'*-sulphonylhydrazine ( $\text{PhNH}-\text{N}=\text{S}=\text{O}$ ) (1), the structure of which was recently determined.<sup>3</sup> The

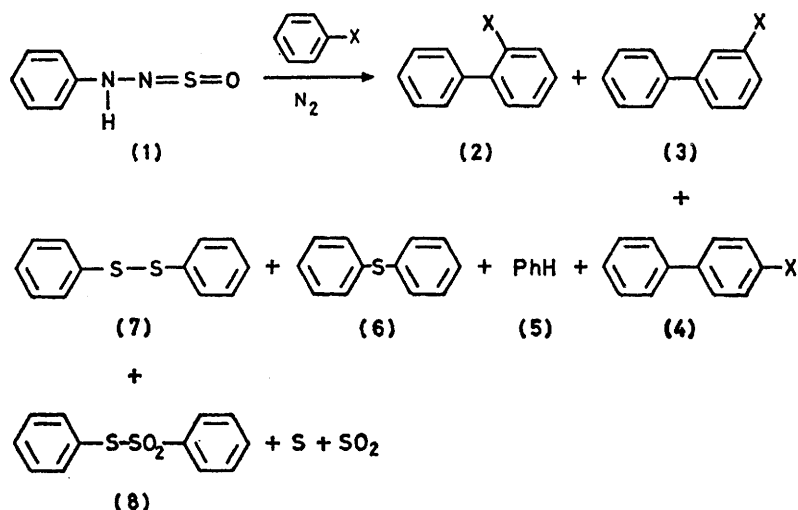
bonds, the acidity of the NH proton, and the basicity of the sulphonyl oxygen (not observed in the *N*-sulphonylanilines). Notes on the reactivity of (1) have appeared in the literature.<sup>4</sup>

### RESULTS AND DISCUSSION

The thermolysis of compound (1), in a number of dry solvents under nitrogen, leads to the formation of the biphenyl products (2), (3), and (4), benzene (5), and in lower yields diphenyl sulphide (6), diphenyl disulphide (7), diphenyl thiosulphone (8), sulphur, and sulphur dioxide (Scheme 1).

The percentage distribution of the biphenyl isomers is shown in Table 1, which is analogous to the distribution obtained with different sources of phenyl radicals (Table 2).

This information leads us to hypothesize the inter-



X = Cl, Br, OMe and NO<sub>2</sub>

SCHEME 1

formal S=N double bond has a *cis* configuration and from the bond lengths and hybridization of the hydrogenated nitrogen, it may be deduced that the mesoionic formula (1b) makes a considerable contribution to the structure.

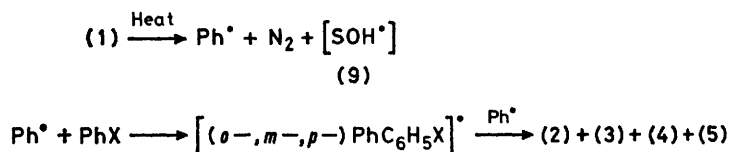
The structure (1b) explains the formation of hydrogen

vention of phenyl radicals [from the decomposition of (1)] which react with the substrates as shown in Scheme 2.

The unstable radical (9) disproportionates to sulphur and other inorganic sulphur species which subsequently yield free sulphur dioxide. The presence of SO<sub>2</sub> was

established by passing the gaseous products of the reaction, according to Stoffer's method,<sup>5</sup> into a neutral solution of potassium permanganate

The phenyl radical reacts mainly with the reaction solvent, following the classic pattern of aromatic homolytic substitution, to yield the biphenylic isomers in the percentages reported and also benzene (5), which was formed in a yield equivalent to that of the biphenylic products. The isolation of small amounts of the sulphur-containing products (6)—(8) can be explained as



SCHEME 2

being due to attack by the phenyl radical on the sulphur atom of undecomposed *N*-phenyl-*N'*-sulphinylhydrazine (1) [as demonstrated by our decomposition<sup>6</sup> of dibenzoyl peroxide in the presence of (1)].

## EXPERIMENTAL

*Preparation and Purification of Materials.*—Chlorobenzene and nitrobenzene were purified as described by Augood *et al.*<sup>7</sup> Bromobenzene was washed with concentrated

TABLE 1

Isomer distribution in the phenylation of *N*-phenyl-*N'*-sulphinylhydrazine (1)

Substrate	Products (%)		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
PhCl	60.8	25.3	13.9
PhBr	49.8	31.5	18.7
PhOMe	63.5	21.5	15.0
PhNO <sub>2</sub>	68.0	12.4	19.6

sulphuric acid, aqueous sodium hydrogencarbonate, and water, then dried with CaCl<sub>2</sub> and fractionally distilled (b.p. 156 °C at 760 mmHg). Anisole was shaken with aqueous sodium hydroxide, washed with water, dried, and distilled (b.p. 154 °C at 760 mmHg). All solvents were degassed by passing a stream of oxygen-free dry nitrogen through them before use. *N*-Phenyl-*N'*-sulphinylhydrazine was synthesized as reported by Klamann *et al.*<sup>4</sup> [m.p. 105 °C (from ethanol)].

Pure reference compounds were prepared as follows: 2-, 3-, and 4-chlorobiphenyl were prepared by means of the Gomberg reaction<sup>8</sup> from *o*-, *m*-, and *p*-chloroaniline and benzene. The 2- and 4-isomers were recrystallized to constant m.p. (34 and 77 °C, respectively), and the 3-chlorobiphenyl, which was a colourless oil, was re-distilled (b.p. 153 °C at 11 mmHg,  $n_D^{20}$  1.619 4). The bromobiphenyl isomers were prepared by the methods described by Augood *et al.*<sup>9</sup> 2-Bromobiphenyl (b.p. 150 °C at 10 mmHg,  $n_D^{20}$  1.627 4) and 3-bromobiphenyl (b.p. 103 °C at 0.2 mmHg,  $n_D^{20}$  1.640 5) were obtained as colourless oils, while 4-bromobiphenyl was crystallized from ethanol (m.p. 90 °C). The isomeric methoxybiphenyls were prepared by the Gomberg reaction, using the corresponding diazotized anisidine and benzene. 2-Methoxybiphenyl was crystal-

lized from light petroleum (m.p. 29 °C) and 4-methoxybiphenyl from ethanol (m.p. 89 °C). 3-Methoxybiphenyl was obtained as an oil (b.p. 140 °C at 5 mmHg,  $n_D^{20}$  1.611 2). The nitrobiphenyl isomers (commercial products from Ega Chemie) were used following crystallization from ethanol [2-nitrobiphenyl (m.p. 37 °C) and 4-nitrobiphenyl (m.p. 113 °C)] and ethanol-water [3-nitrobiphenyl (m.p. 59 °C)]. Diphenyl sulphide (Eastman) and diphenyl disulphide (Fluka) were used without further purification. Diphenyl thiosulphone was prepared by the method of Vinkler and Kliveny<sup>10</sup> (m.p. 39 °C from methanol-water).

*General Procedure for the Reaction.*—*N*-Phenyl-*N'*-sulphinylhydrazine (1.54 g, 0.01 mol) in an excess of the dry solvent was stirred in a thermostat at 135 °C under nitrogen for 72 h. All the reactions were followed by t.l.c. (SiO<sub>2</sub>, light petroleum). The gases from the reactions were trapped at liquid nitrogen temperature and the amount of benzene determined. The reaction mixture was then carefully concentrated under reduced pressure, and analysed quantitatively by g.l.c. (Perkin-Elmer F11-FID unit for analytical use and Carlo-Erba Fractovap ATC/f 410 for preparative use).

The products formed were resolved and identified by the method of Abramovitch and Saha,<sup>11</sup> comparing their retention times with those of authentic specimens, and collecting each compound and comparing its i.r. spectrum with that of an authentic sample.

The chloro-, methoxy-, and nitro-biphenyls were analysed (g.l.c.) on a 2 m × 1/8-in column packed with FFAP (5%)

TABLE 2

Isomer distribution with different sources of phenyl radicals

Radical source	Substrate	Products (%)		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
(PhCO <sub>2</sub> ) <sub>2</sub>	PhCl	50	32	18
AgI(OCOPh) <sub>2</sub>	PhCl	60	24	16
PhN=NNHPh	PhCl	60	24	16
(PhCO <sub>2</sub> ) <sub>2</sub>	PhBr	49.3	33.3	17.4
[PhN <sub>2</sub> <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ]-pyridine	PhBr	55.0	26.3	18.7
(PhCO <sub>2</sub> ) <sub>2</sub> -Cu <sup>II</sup>	PhOMe	64	20	16
Pb(O <sub>2</sub> CPh) <sub>4</sub>	PhOMe	65	20	15
(PhCO <sub>2</sub> ) <sub>2</sub>	PhNO <sub>2</sub>	58	10	32
PhN=NCPh <sub>3</sub>	PhNO <sub>2</sub>	79	7	14

on Chromosorb G AW-DMCS (80—100 mesh); column temperature 90—240 °C at 4 °C min<sup>-1</sup>; 20 minute post hold, carrier gas N<sub>2</sub>, 40 ml min<sup>-1</sup>. Analysis of the bromobiphenyl isomers was carried out on the same column but under different temperature conditions (column temperature 150—240 °C at 4 °C min<sup>-1</sup>).

In all the reactions the analysis of sulphur-containing products was carried out on a 2-m × 1/8-in column packed with Silicone gum rubber E 301 (2.5%) on Chromosorb G AW-DMCS (80—100 mesh); column temperature 90—220 °C at 4 °C min<sup>-1</sup>; carrier gas N<sub>2</sub>, 40 ml min<sup>-1</sup> (Table 3).

TABLE 3

Yields \* of products obtained in the phenylation of chlorobenzene, bromobenzene, anisole, and nitrobenzene

Experiment no.	Substrate	Products (%)							Ratios
		(2)	(3)	(4)	(5)	(6)	(7)	(8)	
1	PhCl	24.9	11.3	6.1	41	0.9	1.2	0.2	58.9 : 26.7 : 14.4
2	PhCl	26.5	10.1	5.7					62.6 : 23.9 : 13.5
									average 60.8 : 25.3 : 13.9
3	PhBr	20.9	12.7	6.9	38	0.8	1.1	0.2	51.6 : 31.3 : 17.1
4	PhBr	19.5	12.9	8.1					48.1 : 31.7 : 20.2
									average 49.8 : 31.5 : 18.7
5	PhOMe	24.2	8.7	5.7	36	0.6	1.3	0.4	62.7 : 22.5 : 14.8
6	PhOMe	24.8	7.9	5.9					64.3 : 20.5 : 15.2
									average 63.5 : 21.5 : 15.0
7	PhNO <sub>2</sub>	16.9	3.3	5.1	25	0.6	0.9	0.4	66.8 : 13.1 : 20.1
8	PhNO <sub>2</sub>	17.5	2.9	4.9					69.2 : 11.7 : 19.1
									average 68.0 : 12.4 : 19.6

\* Based on *N*-phenyl-*N'*-sulphinylhydrazine.

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