

## Homolytic Substitution of Halogenobenzenes by Arylthio- and Arylsulphonyl Radicals

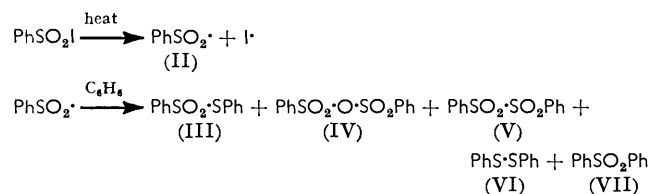
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When arylthio- and arylsulphonyl radicals are generated in chloro-, bromo-, and iodo-benzene at 150–190 °C, the halogen atom is replaced by the arylthio- or arylsulphonyl group. The relative ease of displacement in the reaction with sulphonyl radicals is Cl:Br:I, 1:5.9:18.6; fluorobenzene does not react appreciably under these conditions and only a very low proportion of products formed by direct substitution of hydrogen atoms is present in the reaction mixtures. The reaction is facilitated by electron-releasing substituents on the halogenobenzene. A mechanism for the reaction is proposed.

THERE are many reports of reactions of arylthio-<sup>1</sup> (I) and arylsulphonyl radicals<sup>2</sup> (II) with double or triple bonds to form addition products, but these radicals seem particularly unreactive towards aromatic substrates. When phenylsulphonyl or tosyl radicals are generated in benzene, the only reported products are those of disproportionation and dimerisation;<sup>3</sup> with the more reactive anthracene, however, these radicals do give 9,10-addition products.<sup>4</sup> Arylthio-radicals give, in aromatic solvents, the dimerisation product, diaryl disulphide; the only reported example of aromatic substitution by a thiyl radical is a reaction of the thiophen nucleus, in which alkylthio-radicals were generated by Fenton oxidation,<sup>5</sup> but the highly oxidising medium employed probably plays an important rule in determining the products.

We have reinvestigated the products of the thermal and photochemical generation of phenylsulphonyl and arylthio-radicals in aromatic solvents, in order to determine whether the substitution reaction is energetically forbidden or if under some conditions it is possible to observe products derived from attack on aromatic nuclei. Chromatographic analysis of the products of a reaction in which phenylsulphonyl radicals were generated in benzene by thermal decomposition of benzenesulphonyl iodide led to the separation of the expected dimerisation and disproportionation products (III)–(VI) and a small quantity (*ca.* 1%) of diphenyl sulphone (VII). Analogous results were obtained on photolysis of benzenesulphonyl iodide in benzene.

When phenylsulphonyl radicals were generated in toluene, phenyl *o*-, *m*-, and *p*-tolyl sulphones were separated, but again in only *ca.* 1% yield.



SCHEME 1

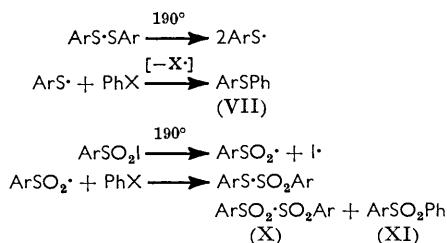
The very small quantity of substitution product obtained in these experiments does not allow any positive

<sup>1</sup> R. M. Kellog, in 'Methods in Free Radical Chemistry,' ed. E. S. Huyser, Marcel Dekker, New York, 1969, vol. 8, p. 1.

<sup>2</sup> W. E. Truce and G. C. Wolf, *Chem. Comm.*, 1969, 150 and references quoted therein.

conclusion to be drawn; the sulphones could be derived from unimportant side-reactions, *e.g.* oxidation of the phenylsulphonyl radical and substitution by the resulting sulphonyl cation.

Surprisingly different results were obtained from reactions in which phenylsulphonyl radicals were generated in chloro-, bromo-, or iodo-benzene at 150–190 °C. In each case the expected dimerisation and disproportionation products were accompanied by a quantity of diphenyl sulphone. It has also been found that when phenylthio-radicals are generated by thermal decomposition of diphenyl disulphide at 190 °C in the same solvents, diphenyl sulphide is obtained. From similar reactions with *para*-tolylthio- and tosyl radicals, the sulphide (VIII) and sulphone (IX) were obtained; this proves that these products are not generated by a reaction such as loss of SO<sub>2</sub> from compound (X) or extrusion of sulphur from the disulphide. No appreciable yields of sulphides or sulphones derived by replacement of hydrogen atoms on the halogenobenzenes were observed.



SCHEME 2 Ar = *p*-tolyl

Chloro- and bromo-benzene are known to be stable at 150–190 °C; a mechanism involving as first step the abstraction of halogen was discounted on the basis of the complete absence of products derived from free aryl radicals. If this mechanism were effective, halogenobiphenyls would have been produced, the reaction of phenyl radicals with aromatic solvents being very fast.

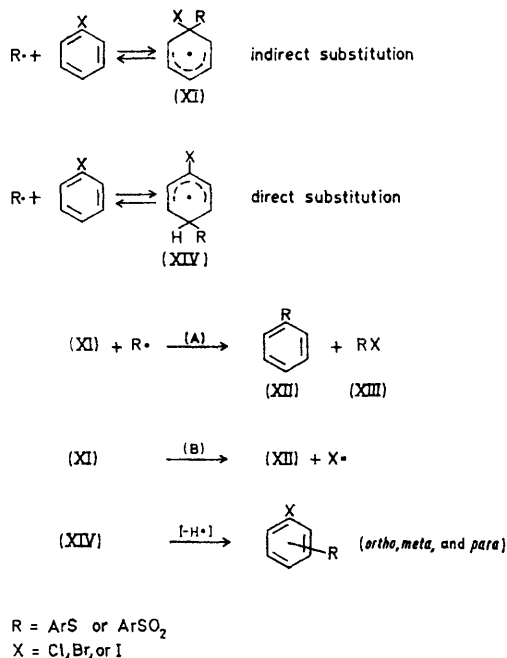
A reasonable possibility is that the reactions leading to the sulphides or sulphones are examples of indirect

<sup>3</sup> I. Degani, S. Gheretti, and A. Tundo, *Ann. Chim. (Italy)*, 1961, **51**, 461; I. Degani, M. Tiecco, and A. Tundo, *ibid.*, p. 550; C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc. (C)*, 1968, 1874.

<sup>4</sup> C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc. (C)*, 1968, 1880.

<sup>5</sup> Ya. A. Gol'dfarb, G. P. Pokhil, and L. I. Belen'kii, *Doklady Chem.*, 1966, **167**, 385.

homolytic aromatic substitution (Scheme 3). Few examples of this kind of reaction have been reported; for instance Shelton and Uzelmeier observed the substitution of the halogen atom in chlorobenzene by cyclohexyl radicals<sup>6</sup> and proposed a mechanism similar to that shown in Scheme 3. This reaction competes with the



SCHEME 3

direct substitution and was explained in terms of the nucleophilicity of the cyclohexyl radical. Williams and his co-workers<sup>7</sup> observed that the decomposition of pentafluorobenzoyl peroxide in bromo- and in chlorobenzene gave phenyl pentafluorobenzoate.

In order to establish the kind of mechanism which is effective in our case, a detailed study of the reactions of sulphonyl and arylthio-radicals with halogenobenzenes was carried out.

The yields of 'substitution products' (XII) are highly temperature-dependent. When phenylsulphonyl radicals were generated in chlorobenzene at room temperature by photolysis of benzenesulphonyl iodide, no diphenyl sulphone at all was obtained. On increasing the temperature of the reaction, the yields of dimerisation and disproportionation products (III)—(VI) decreased steadily, and diphenyl sulphone appeared in the reaction mixture; at 150 °C the yield of substitution product was about 10%. At this temperature the diphenyl disulphone (V) is not stable and decomposes again into sulphonyl radicals.

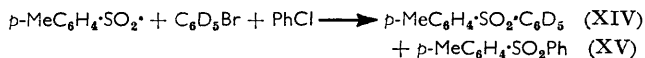
Similar behaviour was observed in the reaction with arylthio-radicals; in this case the yields were higher, the disproportionation reaction not being possible. For instance, when phenylthio-radicals were generated in *p*-

bromoanisole, the yield of *para*-methoxyphenyl phenyl sulphide was about 50%, whereas when phenylsulphonyl radicals were generated in the same solvent the yield of the corresponding sulphone was only 15%.

This temperature-dependence of the yields (based on the amount of radical precursor reacted) indicates that the reaction path leading to substitution products is subject to a high activation energy barrier, and only when the kinetically favoured dimerisation or disproportionation products are not stable is it possible to observe the formation of the sulphide or sulphone.

Accurate analyses of the reaction mixtures were carried out in order to determine the fate of the halogen atom displaced by the incoming group. Unfortunately, sulphonyl or sulphenyl halides (XIII), the expected products derived by halogen abstraction from species (XI) by R• are not stable at the temperature employed, giving again the sulphur radical and a halogen atom. The presence of free halogen in the reaction mixture was detected, and in the aqueous extracts a high concentration of halide ion was present; but for the foregoing reason this is not sufficient to decide whether the loss of halogen from (XI) is spontaneous (path B) or assisted (path A).

In another approach to determining the reaction mechanism the relative reactivity of chloro-, bromo-, and iodo-benzene was studied by the competition method. Tosyl radicals were generated by thermal decomposition of ditolyl disulphone at 190° in equimolecular mixtures of [<sup>2</sup>H<sub>5</sub>]bromobenzene and chlorobenzene or iodobenzene, and the relative amounts of [<sup>2</sup>H<sub>5</sub>]phenyl *p*-tolyl sulphone (XIV) and the unlabelled sulphone (XV) were deter-



mined. The reactivity order obtained was iodobenzene > bromobenzene > chlorobenzene, in the ratio 18.6 : 5.9 : 1.

By the same competitive method, we determined the relative reactivities of bromobenzene and some substituted bromobenzenes with respect to the reactions with phenylsulphonyl and arylthio-radicals; the results are reported in the Table. The reaction is facilitated in both cases by electron-releasing substituents in the bromobenzene. No substitution products were found in the reaction between phenylsulphonyl radicals and bromonitrobenzenes.

We propose for this reaction a mechanism in which electrophilic radicals attack the aromatic nucleus in a reversible reaction;  $\sigma$ -complexes derived from attack both at carbon atoms bearing hydrogen atoms and at carbon atoms bearing halogen are formed (Scheme 3).

The formation mainly of indirect substitution products (XII) is understandable if the aromatisation reaction is kinetically important. The structure of the products is in this case determined by the strength of the C-X bond: for X = I, Cl, or Br the rate of aromatisation is suffi-

<sup>6</sup> J. R. Shelton and C. W. Uzelmeier, *Rec. Trav. chim.*, 1968, **87**, 1211; *Intra-Sci. Chem. Reports*, 1969, **3**, 293.

<sup>7</sup> G. H. Williams, in 'Essays on Free-Radical Chemistry,' *Chem. Soc. Special Publ.* No. 24, 1970, p. 25.

ciently high, but with the stronger C-F and C-H bonds the reverse of the first step is faster than aromatisation.

Reactivities of substituted bromobenzenes towards phenylsulphonyl and phenylthio-radicals (relative to bromobenzene = 1)

$$R \cdot + BrC_6H_4X \xrightarrow{[-Br]} RC_6H_4X$$

X	Relative reactivity <sup>c</sup>	
	R = PhSO <sub>2</sub> <sup>a</sup>	R = PhS <sup>b</sup>
<i>p</i> -OMe	8.78	60
<i>m</i> -OMe	0.68	0.80
<i>p</i> -Me	3.59	1.84
<i>m</i> -Me	2.18	1.20
<i>p</i> -CO <sub>2</sub> Me	0.27	
<i>m</i> -CO <sub>2</sub> Me	0.07	
<i>p</i> -NO <sub>2</sub>		3.00
<i>m</i> -NO <sub>2</sub>		0.63

<sup>a</sup> Mean values obtained by use of radicals from thermolysis of benzenesulphonyl iodide or of diphenyl disulphide at 190 °C.

<sup>b</sup> Thermal decomposition of diphenyl sulphide at 190 °C.

<sup>c</sup> Molar ratios of substitution products obtained from competitive experiments.

## EXPERIMENTAL

G.l.c. analyses were carried out with Varian 1520 and 712 gas chromatographs, equipped with flame-ionisation detectors. N.m.r. spectra were recorded on a JEOL C60 HL 60 MHz instrument. Halogenobenzenes employed as substrates were commercial products of the highest purity grade.

**Reference Compounds.**—*p*- and *m*-Methoxyphenyl phenyl sulphide,<sup>8</sup> phenyl *p*- and *m*-tolyl sulphide,<sup>9</sup> *p*-<sup>10</sup> and *m*-<sup>11</sup> nitrophenyl phenyl sulphide, diphenyl disulphide,<sup>12</sup> di-*p*-tolyl disulphide,<sup>13</sup> and benzenesulphonyl iodide<sup>14</sup> were prepared as reported; sulphones were obtained by oxidation of the corresponding sulphides with 30% hydrogen peroxide in acetic acid.

**Methyl (*p*-phenylthio)benzoate**, prepared from diazotised methyl *p*-aminobenzoate and sodium benzenethiolate, had m.p. 75–76 °C (Found: C, 68.7; H, 5.0; S, 12.8. C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>S requires C, 68.8; H, 4.95; S, 13.1%). The *meta*-isomer, similarly obtained, had b.p. 151 °C at 0.5 mmHg (Found: C, 68.8; H, 5.0; S, 13.0%).

**Generation of Phenylsulphonyl Radicals in Benzene and in Toluene.**—The experimental procedure was essentially the same as that used by Waters and his co-workers; <sup>4</sup> benzenesulphonyl iodide was used as radical precursor instead of toluene-*p*-sulphonyl iodide and no copper powder was used. In addition to the expected products (III)–(V) a small quantity of diphenyl disulphide was detected in both thermal and photochemical reactions. In a thermal reaction from benzenesulphonyl iodide (8 g) in benzene (100 ml) gave compounds (III) (1.3 g), (IV) (2.8 g), (V) (0.30 g), and (VI) (0.2 g). In a photochemical reaction benzenesulphonyl iodide (8 g) in benzene (100 ml) gave compounds (III) (1.20 g), (IV) (1.6 g), (V) (2.5 g), and (VI) (0.1 g).

Preparative g.l.c. of the benzene reaction mixture led to

the separation of diphenyl sulphone (1.25%); when the reaction was repeated with oxygen bubbling through the solution the yield of substitution product increased slightly (to 3.2%).

In the toluene reaction, traces of phenyl *o*-, *m*-, and *p*-tolyl sulphones were detected by g.l.c.

**Substitution of Halogen by Phenylthio- and Phenylsulphonyl Radicals.**—The following reactions serve as examples of the experimental procedure employed.

(A) **Diphenyl disulphide in *p*-bromoanisole.** Diphenyl disulphide (3 g) dissolved in *p*-bromoanisole (20 cm<sup>3</sup>) was placed in a hermetically sealed stainless steel bomb, and the solution was heated at 190 °C for 15 h. Chromatography on silica gel gave traces of diphenyl disulphide, *p*-methoxyphenyl phenyl sulphide (1.18 g), and a small amount of a mixture of two products. This mixture was oxidised with 30% hydrogen peroxide in acetic acid. Chromatography gave 5-bromo-2-methoxyphenyl phenyl sulphone, m.p. 137–138° (Found: C, 47.5; H, 3.5; Br, 24.2; S, 9.9. Calc. for C<sub>13</sub>H<sub>11</sub>BrO<sub>2</sub>S: C, 47.7; H, 3.4; Br, 24.4; S, 9.8%). and 5-bromo-2-hydroxyphenyl phenyl sulphone m.p. 146–147° (Found: C, 46.1; H, 3.0; Br, 25.3; S, 10.4. Calc. for C<sub>12</sub>H<sub>9</sub>BrO<sub>2</sub>S: C, 46.0; H, 2.9; Br, 25.5; S, 10.2%), identified by comparison with authentic specimens prepared by independent synthesis.

(B) **Benzenesulphonyl iodide in *p*-bromoanisole.** Benzenesulphonyl iodide (5 g) was dissolved in *p*-bromoanisole (50 ml). The solution was refluxed for 15 h, washed with aqueous sodium thiosulphate, concentrated, and chromatographed on silica gel. The following products were separated and identified; *S*-phenyl benzenethiosulphonate (III) (0.2 g), diphenyl disulphide (V) (0.8 g), and *p*-methoxyphenyl phenyl sulphone (0.8 g).

(C) **Diphenyl disulphide in *p*-bromoanisole.** Diphenyl disulphide (3.5 g) was dissolved in *p*-bromoanisole (40 ml) and the solution was refluxed for 15 h. Chromatography on silica gel gave *S*-phenyl benzenethiosulphonate (III) (0.1 g), diphenyl disulphide (V) (0.5 g), and *p*-methoxyphenyl phenyl sulphone (1.5 g).

**Competitive Experiments.**—To an equimolecular mixture of bromobenzene and substituted bromobenzene was added the radical precursor (diphenyl disulphide, diphenyl disulphone, or benzenesulphonyl iodide; molar ratio of solvent to radical precursor, 50 : 1), and the solution was heated (190 °C) for 15 h.

The molar ratio between the two substitution products formed was determined by g.l.c., using a flame-ionisation detector, whose response was calibrated with authentic models of the substitution products. Satisfactory analysis was achieved in all cases by using a 5% FFAP on Aeropak 30 (80–100 mesh) column (2 m × 1/8 in int. diam.).

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<sup>14</sup> D. Troger, *Ber.*, 1891, **24**, 485.