521. *Reaction of Arenesulphinic Acids with Azo-compounds and Nitrosonaphthols.*

By WILLIAM BRADLEY and JOHN D. HANNON.

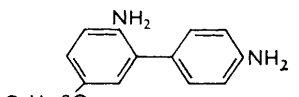
Azobenzene combines with sulphinic acids to form *N*-arylsulphonyl derivatives of hydrazobenzene, which undergo rearrangement and dehydrogenation forming 4-arylsulphonyl derivatives of azobenzene. The same reaction occurs with substitution products of azobenzene, but is not general. With 1-phenylazo-2-naphthol, arylsulphinic acids give 4-amino-3-arylsulphonyloxy-1-naphthyl aryl sulphones, the structures of which are proved. The same products result from arylsulphinic acids and 1-nitroso-2-naphthol. With 2-nitroso-1-naphthol, toluene-*p*-sulphinic acid gives 3-amino-4-tolyl-*p*-sulphonyloxy-1-naphthyl *p*-tolyl sulphone.

AZOBENZENE combines with benzenesulphinic acid in cold alcoholic solution to form the hydrazobenzene derivative (I; R = Ph). When the mixture is heated under reflux this product dissolves and the bright orange 4-phenylsulphonylazobenzene (II; R = Ph) separates. The rearrangement of the arylsulphonyl group is thus accompanied by dehydrogenation and a part of the sulphinic acid is reduced to diphenyl sulphoxide. The structure of the azo-compound was incidentally confirmed by its formation from *p*-aminodiphenyl sulphone and nitrosobenzene.

(I) $Ph\cdot NH\cdot NPh$ with $SO_2\cdot R$ below the second N

$Ph\cdot N=N\cdot C_6H_4\cdot SO_2\cdot R\text{-}p$ (II)

Analogous reactions occurred between azobenzene and toluene-*p*-sulphinic and *p*-chlorobenzenesulphinic acid. However, the reactions are not general for all azo-compounds or all sulphinic acids. Azobenzene itself failed to react with 2,5-dichlorobenzenesulphinic acid, and benzenesulphinic acid did not react with either 4-phenylsulphonylazobenzene or 4-chloroazobenzene. The arylsulphonylazobenzene derivatives (II) gave hydrazobenzene derivatives with alkaline sodium dithionite but these were remarkably stable towards



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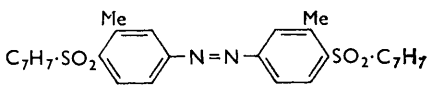


(IV)

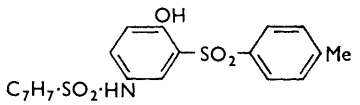
further reduction. In acids the hydrazo-compounds rearrange, yielding 2,4′-diamino-5-*p*-tolylsulphonylbiphenyl (III) as the main product and an amino-*N*-toluene-p-sulphonyldiphenylamine in small amount. The structure of the product (III) follows from many analogies.

Toluene-*p*-sulphinic acid was added in the above way to 4-methylazobenzene but no

reaction occurred with 3,3′-dibromoazobenzene. With 3,3′-dimethylazobenzene again the expected adduct, 3,3′-dimethyl-*N*-toluene-*p*-sulphonylhydrazobenzene, was obtained, but when the reaction mixture was refluxed the product was 3,3′-dimethyl-4,4′-di-(*p*-tolylsulphonyl)azobenzene (IV).

With 4-hydroxyazobenzene toluene-*p*-sulphinic acid gave aniline and 2-hydroxy-5-toluene-*p*-sulphonamidophenyl *p*-tolyl sulphone (V). The structure of this was proved by hydrolysis to a primary amine which on being diazotised and treated with hypophosphorous acid gave *o*-hydroxyphenyl *p*-tolyl sulphone; this in turn was also prepared by reaction of *o*-chloronitrobenzene and toluene-*p*-sulphinic acid in the presence of sodium acetate, to give *o*-nitrophenyl *p*-tolyl sulphone, and subsequent replacement of the nitro-group by hydroxyl.

Toluene-*p*-sulphinic acid and 1-phenylazo-2-naphthol gave aniline, toluene-*p*-sulphonic acid, di-*p*-tolyl disulphoxide, and 4-amino-3-toluene-*p*-sulphonyloxy-1-naphthyl *p*-tolyl sulphone (VI; R = C_7H_7). Hydrolysis with acid or alkali of the sulphone (VI; R = C_7H_7) gave 4-amino-3-hydroxy-1-naphthyl *p*-tolyl sulphone (characterised as a triacetyl derivative), and finally, after heating with sulphuric acid, 3,4-dihydroxy-1-naphthyl *p*-tolyl sulphone (VII; R = C_7H_7).



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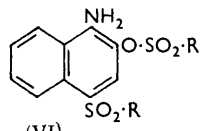

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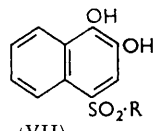
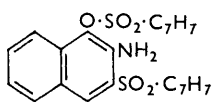


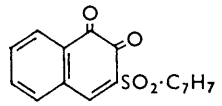
(VII)

A similar series of products was obtained on using benzenesulphinic acid or *p*-chlorobenzenesulphinic acid. With the first of these the end product was 3,4-dihydroxy-1-naphthyl phenyl sulphone (VII; R = Ph) identical with the product of reaction of benzenesulphinic acid with 1,2-naphthaquinone-4-sulphonic acid.

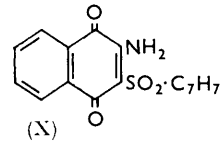
Reaction of toluene-*p*-sulphinic acid with 1-nitroso-2-naphthol likewise gave the sulphone (VI; R = C_7H_7) which was first prepared by Bradley and Robinson.[1] Analogous products were obtained from benzenesulphinic, *p*-chlorobenzenesulphinic, and 2,5-dichlorobenzenesulphinic acid.



(VIII)



(IX)



(X)

With 2-nitroso-1-naphthol, toluene-*p*-sulphinic acid gave 3-amino-4-toluene-*p*-sulphonyloxy-2-naphthyl *p*-tolyl sulphone (VIII). Oxidation of this gave two products: one was an *o*-quinone, which gave a quinoxaline derivative with *o*-phenylenediamine and is considered to be the compound (IX); the second which was the main product was also a quinone but it did not react with the *o*-diamine and it corresponded in composition and properties to the 1,4-quinone (X).

Experimental

The sulphinic acids used were prepared by reduction of the corresponding arenesulphonyl chlorides and each had the required composition.

4-Amino-3-benzenesulphonyloxy-1-naphthyl Phenyl Sulphone.—1-Nitroso-2-naphthol (25 g.) was added to a cold solution of benzenesulphinic acid (75 g.) in ethanol (200 ml.), and the mixture was refluxed for 1 hr., then cooled. The *sulphone* which was precipitated was collected, washed with ethanol, and crystallised from acetic acid, forming pale yellow prismatic needles (39 g.), m. p.

[1] Bradley and Robinson, *J.*, 1934, 1484.

188° (Found: C, 60·2; H, 3·9; N, 3·6; S, 14·4. $C_{22}H_{17}NO_5S_2$ requires C, 60·0; H, 3·9; N, 3·2; S, 14·6%).

4-*Amino*-3-p-*chlorobenzenesulphonyloxy*-1-*naphthyl* p-*chlorophenyl sulphone* was prepared similarly from 1-nitroso-2-naphthol (15 g.) and *p*-chlorobenzenesulphinic acid (40 g.) in ethanol (100 ml.). Purification of it from chlorobenzene gave white crystals (20 g.), m. p. 199° (Found: C, 52·2; H, 2·9; Cl, 14·3; N, 2·9; S, 12·6. $C_{22}H_{15}Cl_2NO_5S_2$ requires C, 52·0; H, 3·0; Cl, 14·0; N, 2·8; S, 12·6%).

4-*Amino*-3-(2,5-*dichlorobenzenesulphonyloxy*)-1-*naphthyl* 2,5-*dichlorophenyl sulphone*, prepared from 1-nitroso-2-naphthol (8·5 g.) and 2,5-dichlorobenzenesulphinic acid (30 g.) in ethanol (150 ml.), was obtained (12 g.) from chlorobenzene as white crystals, m. p. 221° (Found: C, 46·0; H, 2·1; Cl, 24·7; N, 2·3; S, 11·1. $C_{22}H_{13}Cl_4NO_5S_2$ requires C, 45·7; H, 2·2; Cl, 24·6; N, 2·4; S, 11·1%).

The formation of 4-amino-3-toluene-*p*-sulphonyloxy-1-naphthyl *p*-tolyl sulphone from 1-nitroso-2-naphthol and toluene-*p*-sulphinic acid [1] was confirmed. There was no similar reaction when 1-nitroso-2-naphthol (5 g.) and sodium toluene-*p*-sulphinate (15 g.) were refluxed for 20 hr. in ethanol (50 ml.).

4-*Amino*-3-*hydroxy*-1-*naphthyl Phenyl Sulphone*.—Potassium hydroxide (2 g.) in water (20 ml.) was refluxed for 45 min. with a solution of 4-amino-3-benzenesulphonyloxy-1-naphthyl phenyl sulphone (2 g.) in ethanol (100 ml.); a deep yellow solution was formed. Water (50 ml.) was added and the resulting solution was kept for several hours, then filtered. On being saturated with carbon dioxide the filtrate afforded a pink precipitate (1 g.) of the *sulphone* which crystallised from ethanol as light brown needles, m. p. 212—213° (Found: C, 64·3; H, 4·5; N, 4·4. $C_{16}H_{13}NO_3S$ requires C, 64·2; H, 4·3; N, 4·6%).

The same product was obtained when the 3-benzenesulphonyloxy-compound (2 g.) was stirred with 93% sulphuric acid at 40—45° for 2 hr. and the filtered solution was added to ice. The yield of 3-hydroxy-compound, m. p. 212°, was 1 g. after crystallisation from alcohol.

4-Amino-3-hydroxy-1-naphthyl phenyl sulphone is insoluble in water, but it dissolves readily in alcohol forming a yellow solution with a strong bluish fluorescence.

Similar acid hydrolysis of 4-amino-3-toluene-*p*-sulphonyloxy-1-naphthyl *p*-tolyl sulphone (2 g.) gave brown needles (1·1 g.) of 4-*amino*-3-*hydroxy*-1-*naphthyl* p-*tolyl sulphone*, m. p. 189—190° (Found: C, 65·5; H, 5·0. $C_{17}H_{15}NO_3S$ requires C, 65·2; H, 4·8%).

3,4-*Dihydroxy*-1-*naphthyl Phenyl Sulphone*.—A solution of 4-amino-3-benzenesulphonyloxy-1-naphthyl phenyl sulphone (1·0 g.) in 93% sulphuric acid (5 ml.) was kept at 40—45° for 2 hr., then cooled and added to water (200 ml.). The suspension which was formed was refluxed for 20 hr. and then the solid was collected and extracted with cold 5% sodium carbonate solution, and the alkaline extract was filtered and acidified. The solid diol which was precipitated had m. p. 182° (Found: C, 64·2; H, 4·3. Calc. for $C_{16}H_{12}O_4S$: C, 64·0; H, 4·0%) after crystallisation from acetic acid, not depresed by the authentic derivative prepared from 1,2-naphthaquinone and benzenesulphinic acid.[2] The same compound was also formed when potassium 1,2-naphthaquinone-4-sulphonate (2 g.) in water (10 ml.) was shaken for several days with a saturated solution of benzenesulphinic acid (5 g.) in water.

4-*Amino*-3-*hydroxy*-1-*naphthyl Phenyl Sulphone Hydrochloride*.—A solution of the base (1 g.) in ethylene dichloride (200 ml.) was saturated with hydrogen chloride. The almost colourless crystalline *hydrochloride* was precipitated (0·6 g.), having m. p. 181—182° (Found: C, 57·2; H, 4·2; N, 4·0. $C_{16}H_{14}ClNO_3S$ requires C, 57·3; H, 4·1; N, 4·2%). It was immediately hydrolysed by water.

3-*Acetoxy*-4-*diacetamido*-1-*naphthyl Phenyl Sulphone*.—The above hydrochloride (0·5 g.) was heated on a steam-bath for 1·5 hr. with acetic anhydride (4 ml.) and pyridine (1 ml.). The resulting solution was cooled, mixed with alcohol (4 ml.), and added to water (50 ml.) containing concentrated hydrochloric acid (1·5 ml.). The *triacetyl derivative* which separated was obtained from ethanol as pale pink crystals (0·2 g.), m. p. 243—244° (Found: C, 62·5; H, 4·5; N, 3·3. $C_{22}H_{19}NO_6S$ requires C, 62·1; H, 4·5; N, 3·3%).

4-Amino-3-hydroxy-1-naphthyl phenyl sulphone did not react with benzaldehyde in hot alcohol. It crystallised unchanged from a solution of the base (1 g.) in glacial acetic acid (10 ml.) containing 100% sulphuric acid (0·2 g.).

4-*Phenylsulphonylnaphthalene* 1,2-*Diazo-oxide*.—4-Amino-3-benzenesulphonyloxy-1-naphthyl phenyl sulphone (10·5 g.) and fused sodium acetate (2·6 g.) were dissolved in boiling glacial

[2] Hinsburg, *Ber.*, 1895, **28**, 1315.

acetic acid (100 ml.). The resulting solution was cooled to 30° and then sodium nitrite (2·0 g.) was added with stirring. The yellow-brown solution was kept at 30—35° for 30 min., then added to water (1 l.). The light yellow precipitate was collected and dried in a desiccator (7·0 g.); it crystallised from alcohol as bright yellow feathery needles, m. p. 231° (decomp.) (Found: C, 62·0; H, 3·2; N, 9·1; S, 10·6. $C_{16}H_{10}N_2O_3S$ requires C, 61·9; H, 3·2; N, 9·0; S, 10·3%).

The same *diazo-oxide* was formed when the 4-amino-compound (2·0 g.) was warmed to 30° with a solution of sodium nitrite (0·4 g.) in 100% sulphuric acid (10 g.), and the yellow solution was cooled and added to ice.

1-(2-*Hydroxy*-1-*naphthylazo*)-4-*phenylsulphonyl*-2-*naphthol*.—Equimolar amounts of the above diazo-oxide and β-naphthol were warmed together in 40% sodium hydroxide solution. Reaction commenced at 70—80° and at 120° complete dissolution was achieved. After 5 min. at 120° the dark blue solution was cooled and added to water (1 l.), and the suspension which was formed was stirred for 30 min. The solid was collected, washed, dried, and crystallised from glacial acetic acid. The *azo-derivative* was obtained as dark red plates, m. p. 275—276° (Found: C, 68·5; H, 3·9; S, 7·3. $C_{26}H_{18}N_2O_4S$ requires C, 68·7; H, 4·0; S, 7·1%). It gave a brilliant blue solution in concentrated sulphuric acid.

1-(2-*Benzenesulphonyloxy*-4-*phenylsulphonyl*-1-*naphthylazo*)-2-*naphthol*.—4-Amino-3-phenylsulphonyloxy-1-naphthyl phenyl sulphone (5·25 g.) was dissolved in boiling glacial acetic acid (400 ml.). The solution was cooled to 17° and stirred at 18—20° (external cooling) while nitrosylsulphuric acid [from sodium nitrite (0·875 g.) and 100% sulphuric acid (150 g.)] was added during 45 min. The solution so formed was cooled to 5° and one of β-naphthol (30 g.) in glacial acetic acid (100 ml.) at 10° was added. The mixture acquired a dark brown colour which became deep red. After 1 hr. at 20° the solution was added to ice (500 g.) and, the red-brown precipitate was collected, extracted with ethanol (100 ml.) at 40°, and crystallised from acetic acid. This *azo-compound* formed red needles (2·75 g.), m. p. 223—224° (Found: C, 64·8; H, 3·7; N, 4·8; S, 10·7. $C_{32}H_{22}N_2O_6S_2$ requires C, 64·8; H, 3·5; N, 4·7; S, 10·8%), and gave a bluish-violet solution in concentrated sulphuric acid.

On being stirred for 3 hr. at 40—45° in 93% sulphuric acid (10 ml.) a solution of this derivative (1·0 g.) became bright blue. It was then cooled and added to ice (100 g.), and the red precipitate was collected and crystallised from acetic acid. The pure product had m. p. 275—276°, not depressed on admixture with 1-(2-hydroxy-1-naphthylazo)-4-phenylsulphonyl-2-naphthol prepared from 4-phenylsulphonylnaphthalene 1,2-diazo-oxide.

The following compounds were prepared analogously:

4-p-*Tolylsulphonylnaphthalene* 1,2-*diazo-oxide*, m. p. 173—174° (Found: C, 62·9; H, 3·6; N, 8·6. $C_{17}H_{12}N_2O_3S$ requires C, 63·0; H, 3·5; N, 8·6%).

4-p-*Chlorophenylsulphonylnaphthalene* 1,2-*diazo-oxide*, m. p. 175—176° (Found: C, 56·0; H, 2·7; N, 8·3. $C_{16}H_9ClN_2O_3S$ requires C, 55·7; H, 2·6; N, 8·1%).

1-(2-p-*Benzenesulphonyloxy*-4-p-*tolylsulphonyl*-1-*naphthylazo*)-2-*naphthol*, m. p. 190° (Found: C, 65·6; H, 3·9; N, 4·4; S, 10·0. $C_{34}H_{26}N_2O_6S_2$ requires C, 65·5; H, 3·9; N, 4·5; S, 10·3%). This derivative was much more soluble in ethanol than the phenyl analogue and was purified by crystallisation from this solvent. Hydrolysis with 93% sulphuric acid gave 1-(2-*hydroxy*-1-*naphthylazo*)-4-p-*tolylsulphonyl*-2-*naphthol*, m. p. 246—247° (Found: C, 69·4; H, 4·3; N, 6·1; S, 6·8. $C_{27}H_{20}N_2O_4S$ requires C, 69·2; H, 4·3; N, 5·9; S, 6·9%), also prepared by combining 4-*p*-tolylsulphonylnaphthalene 1,2-diazo-oxide with β-naphthol.

1-(2-p-*Chlorobenzenesulphonyloxy*-4-p-*chlorophenylsulphonyl*-1-*naphthylazo*)-2-*naphthol*, m. p. 184° (Found: C, 57·8; H, 3·0; S, 9·7. $C_{32}H_{20}Cl_2N_2O_6S_2$ requires C, 58·0; H, 2·9; S, 10·0%), that resembled the phenyl analogue.

1-[2-(2,5-*Dichlorobenzenesulphonyloxy*)-4-(2,5-*dichlorophenylsulphonyl*)-1-*naphthylazo*]-2-*naphthol*, m. p. 216° (Found: C, 51·9; H, 2·3; S, 8·6. $C_{32}H_{18}Cl_4N_2O_6S_2$ requires C, 52·4; H, 2·5; S, 8·7%). This was the most sparingly soluble compound of the series.

3-*Amino*-4-p-*benzenesulphonyloxy*-2-*naphthyl* p-*Tolyl Sulphone*.—2-Nitroso-1-naphthol (7·5 g.) was added to a cold solution of toluene-*p*-sulphinic acid (20 g.) in ethanol (100 ml.), and the mixture was then refluxed for 1 hr. A pale brown precipitate was formed in the deep red solution, and after the suspension had been cooled the *sulphone* was collected and crystallised from ethanol (yield 10·5 g.; m. p. 216—217°) (Found: C, 61·8; H, 4·5; N, 2·9; S, 13·6. $C_{22}H_{21}NO_5S_2$ requires C, 61·6; H, 4·5; N, 3·0; S, 13·7%). This was much more sparingly soluble in organic solvents than the corresponding product from 1-nitroso-2-naphthol.

The above 3-amino-derivative (2·0 g.) was stirred for 10 min. with concentrated nitric acid (10 ml.). The amine dissolved and a dense yellow precipitate was formed. This was collected after 30 min. and crystallised from aqueous ethanol as needles (1·2 g.), m. p. 205—206° (Found: C, 62·4; H, 3·9; N, 4·3; S, 9·4%). This *substance* (?*2-amino-3-p-tolylsulphonyl-1,4-naphthaquinone*) sublimed when heated and was reduced by zinc and acetic acid to a derivative which rapidly re-formed the original compound. It did not condense with *o*-phenylenediamine.

The nitric acid mother-liquors from which this derivative had been separated were added to water. A yellow precipitate was formed and this was collected, dissolved in glacial acetic acid, and mixed with *o*-phenylenediamine (0·3 g.) in acetic acid (10 ml.). A yellow product separated and this was crystallised from acetic acid and then from toluene. Prismatic needles, m. p. 221° (Found: C, 72·1; H, 4·1; S, 8·9. $C_{23}H_{16}N_2O_2S$ requires C, 71·8; H, 4·1; S, 9·1%), were obtained which consisted of 4-p-*tolylsulphonyl-1,2-benzophenazine*.

Reaction of Azobenzene with Benzenesulphinic Acid.—A solution of benzenesulphinic acid (9·5 g.) in cold ethanol (15 ml.) was shaken with a cold solution of azobenzene (3·9 g.) in ethanol (30 ml.). A dense pale yellow precipitate was formed and this afforded white *N*-phenylsulphonylhydrazobenzene; this had m. p. 107° (Found: C, 67·3; H, 4·9; S, 10·1. Calc. for $C_{18}H_{16}N_2O_2S$: C, 67·1; H, 4·9; S, 10·0%), as described by Hantzsch and Glogauer,[3] after being collected, dissolved in acetone, and reprecipitated by light petroleum (b. p. 40—60°).

In a parallel experiment the reactants were mixed and then refluxed for 10 hr. The yellow solid which was first formed redissolved, an orange solution was formed, and from this bright orange crystals gradually separated. These were collected by filtration of the hot suspension; the filtrate afforded diphenyl disulphoxide (2·0 g.), m. p. 45°, on being cooled. There was no indication of the presence of aniline.

The orange crystals (3·5 g.) were obtained from acetic acid as plates, m. p. 200° (Found: C, 67·0; H, 4·2; N, 8·7. $C_{18}H_{14}N_2O_2S$ requires C, 67·1; H, 4·4; N, 8·7%), identical with 4-*phenylsulphonylazobenzene* prepared as described below.

p-Aminodiphenyl sulphone (3·25 g.) and nitrosobenzene (1·5 g.) were heated together at 80° for 3 hr. in glacial acetic acid (25 ml.). The orange suspension which was formed was then filtered, and the solid was washed with dilute hydrochloric acid, then with water, and crystallised from acetic acid. The m. p. was 200—201° (Found: C, 67·0; H, 4·2; N, 8·6%), not depressed on admixture with 4-phenylsulphonylazobenzene (above). It formed a golden-yellow solution in concentrated sulphuric acid.

When this derivative (0·4 g.) was dissolved in 26% oleum (6 ml.) and the solution was then added to ice (100 g.), an orange precipitate was formed; recrystallisation from ethanol gave orange plates of azobenzene-4-sulphonic acid, m. p. and mixed m. p. 127—128°.

The identical 4-phenylsulphonylazobenzene was also obtained when the yellow solid which was formed when benzenesulphinic acid and azobenzene were mixed in ethanol was collected, then added to ethanol, and refluxed.

There was no reaction between azobenzene and sodium benzenesulphinate in ethanol.

The following derivatives were prepared similarly.

(*a*) *By reaction in the cold.* N-p-*Tolylsulphonylhydrazobenzene*, m. p. 117° (Found: C, 67·6; H, 5·3; N, 7·8. $C_{19}H_{18}N_2O_2S$ requires C, 67·6; H, 5·3; N, 8·2%). N-p-*Chlorophenylsulphonylhydrazobenzene*, m. p. 122—123° (Found: C, 60·7; H, 4·6. $C_{18}H_{15}ClN_2O_2S$ requires C, 60·4; H, 4·2%). 4-*Methyl*-N-p-*tolylsulphonylhydrazobenzene*, m. p. 107° (Found: N, 7·6. $C_{20}H_{20}N_2O_2S$ requires N, 8·0%). 3,3′-*Dimethyl*-N-p-*tolylsulphonylhydrazobenzene*, m. p. 80—82° (Found: C, 69·1; H, 6·0; N, 7·4. $C_{21}H_{23}N_2O_2S$ requires C, 69·0; H, 6·0; N, 7·6%). With other pairs of reactants hydrazo-derivatives were not formed under the conditions described; these included azobenzene with 2,5-dichlorobenzenesulphinic acid, and benzenesulphinic acid with 4-phenylsulphonylazobenzene, 4-chloroazobenzene, or 3,3′-dibromoazobenzene.

(*b*) *By reaction under reflux.* Toluene-*p*-sulphinic acid (10 g.) and azobenzene (5·5 g.) gave 4-p-*tolylsulphonylazobenzene* (5·0 g.), m. p. 224—225° (Found: C, 67·6; H, 4·8; N, 8·4; S, 9·5. $C_{19}H_{16}N_2O_2S$ requires C, 67·8; H, 4·7; N, 8·3; S, 9·5%), and di-*p*-tolyl disulphoxide (2·0 g.), m. p. 76°.

p-Chlorobenzenesulphinic acid (10 g.) and azobenzene (3·4 g.) gave 4-*p*-chlorophenylsulphonylazobenzene (2·8 g.), m. p. 205° (Found: C, 60·4; H, 3·5; N, 7·6. $C_{18}H_{13}ClN_2O_2S$ requires C, 60·7; H, 3·6; N, 7·8%).

[3] Hantzsch and Glogauer, *Ber.*, 1897, **30**, 2555.

Toluene-*p*-sulphinic acid (2·5 g.) and 4-methylazobenzene (1 g.) gave 4-*methyl*-4′-p-*tolylsulphonylazobenzene* (0·37 g.), m. p. 223° (Found: C, 68·5; H. 5·1. $C_{20}H_{18}N_2O_2S$ requires C, 68·4; H, 5·1%).

Toluene-*p*-sulphinic acid (30 g.) and 3,3′-dimethylazobenzene (13 g.), when refluxed for 20 hr. in ethanol (150 ml.), afforded a reddish-orange suspension. This was filtered whilst hot. The solid crystallised from acetic acid as orange plates, m. p. 248—249° (Found: C, 64·7; H, 5·0; N, 5·5. $C_{28}H_{26}N_2O_4S_2$ requires C, 64·8; H, 5·0; N, 5·4%), and was considered to be 3,3′-*dimethyl*-4,4′-*di*-p-*tolylsulphonylazobenzene*. The filtrate afforded an orange product (0·4 g.) on being cooled, and this crystallised from ethanol giving 3,3′-*dimethyl*-4-p-*tolylsulphonylazobenzene*, m. p. 161° (Found: C, 69·4; H, 5·8; N, 7·9. $C_{21}H_{21}N_2O_2$ requires C, 69·2; H, 5·7; N, 7·7%).

Water (50 ml.) was added gradually to a refluxing suspension of the preceding disulphone (1·0 g.) and sodium dithionite (2 g.) in ethanol (200 ml.); after 1 hr. the supension was colourless. The solid *hydrazo-compound* which was formed was collected and crystallised from alcohol. It melted indefinitely about 240° (Found: C, 64·5; H, 5·3. $C_{28}H_{28}N_2O_4S_2$ requires C, 64·6; H, 5·4%).

4-p-*Tolylsulphonylhydrazobenzene*.—4-*p*-Tolylsulphonylazobenzene (10 g.) was refluxed with sodium dithionite (20 g.) in ethanol (700 ml.). Successive amounts of water (20 ml.) were then added at intervals of 5 min. until the solution was colourless. The suspension was then filtered. On being cooled the filtrate afforded a white precipitate which was crystallised from ethanol as needles (9·0 g.) of 4-p-*tolylsulphonylhydrazobenzene*, m. p. 219—220° (Found: C, 67·3; H, 5·4; N, 8·2. $C_{19}H_{18}N_2O_2S$ requires C, 67·4; H, 5·3; N, 8·3%). There was no formation of aniline in the reduction.

Rearrangement: *Formation of* 2,4′-*Diamino*-5-p-*tolylsulphonylbiphenyl and* 4-*Amino*-4′-p-*tolylsulphonyldiphenylamine* (*or* 2-*Amino*-5-p-*tolylsulphonyldiphenylamine*).—4-*p*-Tolylsulphonylhydrazobenzene was dissolved in 93% sulphuric acid at 80° and the yellowish-green solution which was formed was added to water. A reddish-violet suspension was formed and this was filtered; the solid was 4-*p*-tolylsulphonylazobenzene. The filtrate was extracted with ether, and the extract evaporated. A tarry residue was obtained and this was dissolved in an excess of dilute hydrochloric acid, diazotised, and added to an alkaline solution of β-naphthol. A red precipitate was formed and this was collected, washed, and then extracted with alcohol (Soxhlet). A small portion dissolved, leaving a larger residue. The soluble part was recovered and crystallised from aqueous acetic acid. It had m. p. 205—206° (Found: C, 70·2; H, 4·3. $C_{29}H_{23}N_3O_3S$ requires C, 70·5; H, 4·5%). This *monoazo-derivative* dissolved in concentrated sulphuric acid forming a magenta solution. The alcohol-insoluble part had m. p. 303—304° (Found: C, 72·0; H, 4·3. $C_{39}H_{28}N_4O_4S$ requires C, 72·2; H, 4·3%) after crystallisation from acetic acid; this bisazo-derivative, 2,4′-*di*-(2-*hydroxy*-1-*naphthylazo*)-5-p-*tolylsulphonylbiphenyl*, afforded a deep violet solution in concentrated sulphuric acid.

Similar treatment of 4-phenylsulphonylhydrazobenzene gave a *monoazo-derivative*, m. p. 189—190° (Found: C, 69·4; H, 4·2. $C_{28}H_{21}N_3O_3S$ requires C, 70·0; H, 4·3%), and a *bisazo-compound*, m. p. 306° (Found: C, 71·1; H, 4·1. $C_{38}H_{26}N_4O_4S$ requires C, 71·9; H, 4·1%).

Action of Sulphinic Acids on Hydroxyazo-compounds.—(i) 1-*Phenylazo*-2-*naphthol*. (*a*) A solution of toluene-*p*-sulphinic acid (32 g.) and 1-phenylazo-2-naphthol (12 g.) in ethanol (170 ml.) was refluxed for 18 hr. On being cooled the orange solution afforded reddish needles that were collected and extracted with ether. A white residue remained and this on crystallisation from ethanol gave colourless plates (4 g.), m. p. 151° (Found: C, 61·5; H, 4·4; N, 2·8. Calc. for $C_{24}H_{21}NO_5S_2$: C, 61·7; H, 4·6; N, 3·0%), identical with 4-amino-3-*p*-tolylsulphonyloxy-1-naphthyl *p*-tolyl sulphone obtained by the action of toluene-*p*-sulphinic acid on 1-nitroso-2-naphthol. When the ethanol mother-liquors were distilled in steam, aniline was obtained together with a pale yellow non-volatile residue. Extraction of the latter with cold 2% aqueous sodium hydroxide gave a solution which, on being filtered and acidified, afforded toluene-*p*-sulphonic acid (1·7 g.). The alkali-insoluble part gave di-*p*-tolyl disulphoxide (3·5 g.), m. p. 75°, on being crystallised from aqueous ethanol.

(*b*) Under similar conditions benzenesulphinic acid (30 g.) and 1-phenylazo-2-naphthol (12 g.) gave 4-*amino*-3-*phenylsulphonyloxy*-1-*naphthyl phenyl sulphone* (3·5 g.), m. p. 187° (Found: C, 60·3; H, 4·0; N, 3·5. $C_{22}H_{17}NO_5S_2$ requires C, 60·0; H, 3·9; N, 3·5%).

(*c*) *p*-Chlorobenzenesulphinic acid (36 g.) and 1-phenylazo-2-naphthol (12 g.) gave 4-*amino*-3-p-*chlorobenzenesulphonyloxy*-1-*naphthyl* p-*chlorophenyl sulphone* (5·5 g.), m. p. 199° (Found: C, 51·8; H, 3·0; N, 3·0. $C_{22}H_{15}Cl_2NO_5S_2$ requires C, 52·2; H, 2·9; N, 2·8%).

(ii) 4-*Hydroxyazobenzene*. A solution of toluene-*p*-sulphinic acid (20 g.) and 4-hydroxyazobenzene (7 g.) in ethanol (100 ml.) was shaken for 20 hr. at the room temperature, then filtered, made alkaline, and distilled in steam. Aniline passed over and the residual solution on being acidified gave 2-*hydroxy*-5-*toluene*-p-*sulphonamidophenyl* p-*tolyl sulphone* (7·5 g.), m. p. 190° (from ethanol) (Found: C, 57·3; H, 4·7; N, 3·5; S, 15·0. $C_{20}H_{19}NO_5S_2$ requires C, 57·5; H, 4·6; N, 3·4; S, 15·3%).

This derivative (1 g.) was heated at 80—90° for 30 min. with concentrated sulphuric acid (10 g.). The resulting solution was cooled, added to ice (50 g.), then filtered, and the filtrate was kept overnight. White needles separated, m. p. 253—254° (Found: C, 43·5; H, 4·2. $C_{13}H_{15}NO_7S_2$ requires C, 43·2; H, 4·2%), which consisted of 5-*amino*-2-*hydroxyphenyl* p-*tolyl sulphone sulphate*. The *base* was obtained by dissolving the sulphate in water and adding sodium carbonate solution in slight excess; it crystallised from alcohol as fawn plates (0·6 g.), m. p. 182—183° (Found: C, 59·2; H, 5·1; N, 5·4; S, 12·6. $C_{13}H_{13}NO_3S$ requires C, 59·3; H, 4·9; N, 5·3: S, 12·2%), sparingly soluble in water but dissolving in alcohol to a colourless solution with a blue fluorescence.

3-*Tolyl*-p-*sulphonylbenzene* 1,4-*Diazo-oxide*.—The above sulphate (1 g.) was dissolved in hot water (25 ml.) and 50% sulphuric acid (5 ml.). The solution was then cooled, sodium nitrite (0·2 g.) was added, and the yellow solution was stirred for 30 min. A precipitate was formed and this crystallised from ethanol as yellow needles, m. p. 175—177° (Found: C, 57·0; H, 3·8. $C_{13}H_{10}O_3N_2$ requires C, 56·9; H, 3·7%). 3-*Tolyl*-p-*sulphonylbenzene* 1,4-*diazo-oxide* couples readily with β-naphthol in alkaline solution, giving a red colour; resorcinol gives an orange and 1-amino-8-naphthol-3,6-disulphonic acid a violet colour.

o-*Hydroxyphenyl* p-*Tolyl Sulphone*.—5-Amino-2-hydroxyphenyl *p*-tolyl sulphone was diazotised as described and the suspension of the diazo-oxide which was formed was cooled to −5°. 30% Hypophosphorous acid (20 ml.) was then added during 30 min. After 2·5 hr. at −5° and 12 hr. at 0° the solid was collected, washed, and heated with water (100 ml.) to remove unchanged diazo-oxide. The insoluble portion was collected and crystallised from aqueous ethanol as cream leaflets (0·25 g.), m. p. 121° (Found: C, 62·5; H, 4·8. $C_{13}H_{12}O_3S$ requires C, 62·8; H, 4·8%) which consisted of o-*hydroxyphenyl* p-*tolyl sulphone*, also prepared in the following way.

o-*Nitrophenyl* p-*Tolyl Sulphone*.—This was prepared by heating toluene-*p*-sulphinic acid (4·5 g.), *o*-chloronitrobenzene (4·5 g.), and sodium acetate (2·5 g.) in ethanol (12 ml.) at 160° for 3 hr. After being cooled overnight the solution afforded a precipitate; it was collected, washed with a small amount of water and dried (3·5 g.). This *sulphone* formed pale yellow needles, m. p. 156—157° (Found: N, 4·9. $C_{13}H_{11}NO_4S$ requires N, 5·1%).

o-*Aminophenyl* p-*Tolyl Sulphone*.—The finely divided nitro-sulphone was added slowly to a warm solution of stannous chloride (5 g.) in ethanol (40 ml.). After all had dissolved, concentrated hydrochloric acid (8 ml.) was added and most of the ethanol was distilled off. The yellow solution was added slowly and with stirring to 10% aqueous sodium hydroxide (100 ml.). The amino-sulphone which was precipitated was collected and crystallised from ethanol as pale pink plates (1·1 g.), m. p. 139° (Found: N, 5·3. $C_{13}H_{13}NO_2S$ requires N, 5·7%).

A solution of this aminosulphone (1 g.) in concentrated sulphuric acid (5 ml.) was added to ice and the suspension was diazotised with sodium nitrite (0·3 g.). After 45 min. at the room temperature the solution was boiled. Frothing occurred and a brown precipitate was formed. This was collected and extracted with 2% aqueous sodium hydroxide, and the solution was filtered and acidified. The precipitate crystallised from ethanol as plates, m. p. 120°, not depressed on admixture with *o*-hydroxyphenyl *p*-tolyl sulphone prepared as above.

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