

LXV.—*Arylsulphonylnaphthylenediamines and their  
Sulphonic Acids.*

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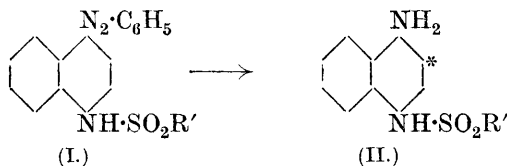
THE reactions described below constitute a simple and general method of preparing the arylsulphonyl derivatives of 1:4-naphthylenediamine and their sulphonic acids. Hitherto the only known

member of this series, benzenesulphonyl-1:4-naphthylenediamine, has been obtained by a roundabout process from  $\alpha$ -naphthylamine through 4-nitro- $\alpha$ -naphthylamine by converting the latter substance into its benzenesulphonyl derivative and by reducing the latter (Morgan and Micklethwait, T., 1905, 87, 1308).

O. N. Witt and Schmitt (*Ber.*, 1894, 27, 2370) showed that toluene-*p*-sulphonyl- $\alpha$ -naphthylamine coupled with benzenediazonium chloride, giving a para-azo-derivative (I) from which by reduction they obtained 1:4-naphthylenediamine.

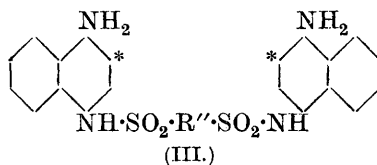
We have found, however, that the reduction can be effected smoothly and completely without the removal by hydrolysis of the arylsulphonyl group. Accordingly, while one reduction product is aniline, which can be recovered quantitatively, the other is toluene-*p*-sulphonyl-1:4-naphthylenediamine (II).

This reaction has been generalised by examining a large number of cases, and in every instance the arylsulphonyl-1:4-naphthylenediamine (II) has been obtained readily and in satisfactory yield (Eng. Pat., application 19392/19. Fr. Pat. 132339). The com-



pounds represented by the general formula II are useful synthetic agents having a high degree of stability when compared with the very oxidisable 1:4-naphthylenediamine. They contain, in the position marked by an asterisk, a reactive hydrogen atom which undergoes replacement in the production of ortho-azo-dyes, thiazole derivatives, and other substitution products which are under investigation.

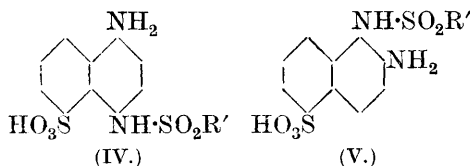
The symbol R' represents a univalent aromatic radicle, such as phenyl, tolyl,  $\alpha$ - or  $\beta$ -naphthyl. This general reaction has also been extended to the production of more complex arylenedisulphonylbis-1:4-naphthylenediamines having the group formula (III).



where R'' is a bivalent radicle such as 1:3-phenylene or a naphthylene group.

The arylsulphonyl- $\alpha$ -naphthylamines and arylenedisulphonylbis- $\alpha$ -naphthylamines produced by condensing  $\alpha$ -naphthylamine respectively with arylsulphonyl and arylenedisulphonyl chlorides all couple readily with diazonium salts such as benzenediazonium chloride to yield the aryl-4-azo-derivatives (I).

By modifying the experimental conditions the  $\alpha$ -naphthylamine-sulphonic acids can be condensed with arylsulphonyl chlorides to furnish arylsulphonyl- $\alpha$ -naphthylaminesulphonic acids. When the sulphonic group is in position 6, 7, or 8, the arylsulphonyl derivatives give 4-azo-compounds reducible to 1:4-naphthylenediamine derivatives, those from  $\alpha$ -naphthylamine-8-sulphonic acid being represented by the formula IV. With the sulphonic group in position 4 or 5, one obtains 2-azo-compounds which on reduction yield derivatives of 1:2-naphthylenediamine, those from  $\alpha$ -naphthylamine-5-sulphonic acid being indicated by formula V.



Of the two groups of substituted diamines, the para-series (IV) give yellow diazo-derivatives coupling to form azo-compounds with phenols and the more reactive aromatic amines, whereas the ortho-series (V) furnishes non-coupling ortho-diazoimides.

## EXPERIMENTAL.

### I. *Arylsulphonyl-1:4-naphthylenediamines* (General Formula II).

Benzenesulphonyl-1:4-naphthylenediamine, the simplest member of this series (Morgan and Micklethwait, *loc. cit.*), more conveniently prepared from benzene-4-azobenzenesulphonyl- $\alpha$ -naphthylamine by reduction with zinc dust and dilute sodium hydroxide solution as detailed below, was obtained in acicular crystals melting at  $188^\circ$  (Found: N = 9.52. Calc., N = 9.39 per cent.).

#### (i) *Toluene-p-sulphonyl-1:4-naphthylenediamine*, $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ .

The starting-point in this preparation was toluene-*p*-sulphonyl- $\alpha$ -naphthylamine, made by triturating 2 parts of  $\alpha$ -naphthylamine with 3 parts of *p*-toluenesulphonyl chloride in the presence of 2 parts of fused sodium acetate, the final product being obtained in theor-

etical yield after the mixture had been washed successively with warm 2*N*-sodium carbonate solution and hot water.

Benzene-4-azotoluene-*p*-sulphonyl- $\alpha$ -naphthylamine, prepared by adding benzenediazonium chloride to a well-stirred alkaline solution of the foregoing sulphonamide, was obtained as a viscous sodium salt soluble in dilute alcohol, from which the free azo-compound was precipitated as a brilliant red powder on the addition of *N*/2-acetic acid. Recrystallised from alcohol, this substance was obtained in fine, felted masses of orange-red crystals melting at 203° (Witt., *loc. cit.*, gives 201°). It was readily and completely reduced by the following methods :—

(1) Equal parts of the azo-compound and zinc dust and 5 parts of 2*N*-sodium hydroxide solution were heated at 100° in a reduction vessel arranged for rapid stirring in a stream of hydrogen. After fifteen minutes the bright colour of the azo-compound had disappeared, the vessel was rapidly cooled in ice, and the contents filtered without delay into excess of *N*/2-acetic acid, when the base was precipitated as a pale mauve, flocculent solid which was washed with chloroform to remove coloured oxidation products : yield 61 per cent. of theory.

(2) Sodium hyposulphite (4 grams) dissolved in 20 c.c. of water was added to 4 grams of benzene-4-azotoluene-*p*-sulphonyl- $\alpha$ -naphthylamine dissolved in 25 c.c. of 5*N*-sodium hydroxide solution diluted with 250 c.c. of water. The solution was warmed at 50–60°, stirred until colourless, and then filtered into dilute acetic acid, the product being crystallised from alcohol.

(3) Ten parts of the azo-compound were dissolved in 40 parts of alcohol diluted with 40 parts of water and containing 1 part of ammonium chloride. To the boiling solution 10 parts of zinc dust were added; the mixture, stirred until the red colour had disappeared, was then filtered into dilute acetic acid.

*Toluene-p-sulphonyl-1:4-naphthylenediamine* crystallised from alcohol in tablets melting at 185–188° (Found : N = 9.07.  $C_{17}H_{16}O_2N_2S$  requires N = 8.97 per cent.). Of the three reduction processes the second gave the purest product, although requiring the longest time for completion.

(ii) *Naphthalene- $\alpha$ -sulphonyl-1:4-naphthylenediamine*,  
 $\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ .

Naphthalene- $\alpha$ -sulphonyl- $\alpha$ -naphthylamine (5.75 grams), prepared from naphthalene- $\alpha$ -sulphonyl chloride and  $\alpha$ -naphthylamine by the general method [I. (i)], was dissolved in 8.5 c.c. of 5*N*-sodium hydroxide diluted with water to 1000 c.c., this naphthalide being very sparingly soluble.

The calculated amount of benzenediazonium chloride was added to the cooled solution with stirring, when a bulky orange precipitate of the azo-compound was obtained : yield 7.5 grams.

The reduction of the azo-compound took place normally, requiring for the above quantity 8 grams of zinc dust and 100 c.c. of 2*N*-sodium hydroxide. The product was a pale mauve powder, m. p. 194° (Found : N = 8.11.  $C_{20}H_{16}O_2N_2S$  requires N = 8.04 per cent.).

(iii) *Naphthalene-β-sulphonyl-1:4-naphthylenediamine*,  
 $\beta\text{-C}_{10}\text{H}_7\text{SO}_2\text{NH}\cdot\text{C}_{10}\text{H}_6\text{NH}_2$ .

Naphthalene-β-sulphonyl-α-naphthylamine was first prepared as in the foregoing cases, when a theoretical yield was obtained. The benzeneazo-compound yielded a sodium salt in a much more granular form than the corresponding compound in I. (ii). The free azo-derivative precipitated from alcoholic solution by dilute acetic acid had a dark brick-red colour and melted at 176°.

By using the method and quantities given under I. (ii) this azo-compound was readily reduced and the base precipitated by *N*/2-acetic acid as a pale mauve solid closely resembling its toluene-sulphonyl homologue. After washing with chloroform the base melted at 199° : yield 90 per cent. (Found : N = 7.82.  $C_{20}H_{16}O_2N_2S$  requires N = 8.04 per cent.).

II. *Arylenedisulphonylbis-1:4-naphthylenediamines*.  
 (General Formula III.)

(i) *Benzene-1:3-disulphonylbis-1:4-naphthylenediamine*,  
 $C_6H_4(SO_2\text{NH}\cdot C_{10}H_6\text{NH}_2)_2$ .

Benzene-1:3-disulphonylbis-α-naphthylamine (m. p. 245°) was prepared by grinding two molecular proportions of α-naphthylamine with one of benzene-1:3-disulphonyl chloride and three of fused sodium acetate. Four grams of the product dissolved in 100 c.c. of dilute sodium hydroxide (5 c.c. of 5*N*-sodium hydroxide and 100 c.c. of water) were treated with a diazonium chloride solution prepared from 1.5 grams of aniline. The dark orange azo-compound was reduced with zinc dust and sodium hydroxide as in former cases, and the product was a pale mauve powder which melted at 190–195° (Found : N = 10.95.  $C_{26}H_{22}O_4N_4S_2$  requires N = 10.81 per cent.).

(ii) *Naphthalene-2:7-disulphonylbis-1:4-naphthylenediamine*,  
 $C_{10}H_6(SO_2\text{NH}\cdot C_{10}H_6\text{NH}_2)_2$ .

Naphthalene-2:7-disulphonyl chloride and the 2:6-isomeride required in the following preparations were obtained from the

recrystallised sodium salts of the corresponding isomeric 2:7- and 2:6-disulphonic acids.

Naphthalene-2:7-disulphonylbis- $\alpha$ -naphthylamine was obtained as a pale lilac product melting above  $250^{\circ}$ , the yield being 80 per cent. of the calculated quantity. The dark reddish-brown benzeneazo-derivative of the foregoing compound was reduced as in former cases, although the time required to complete the reaction was rather longer. The product obtained had the characteristic physical properties of the series and did not darken below  $300^{\circ}$  (Found: N = 9.47.  $C_{30}H_{24}O_4N_4S_2$  requires N = 9.86 per cent.).

(iii) *Naphthalene-2:6-disulphonylbis-1:4-naphthylenediamine.*

This substance prepared by the general method, was a pale—almost colourless—pink powder, darkening at  $150^{\circ}$ , intumescing at  $165^{\circ}$ , and melting at  $180^{\circ}$  (Found: N = 9.36.  $C_{30}H_{24}O_4N_4S_2$  requires N = 9.86 per cent.).

(iv) *Naphthalene-1:6-disulphonylbis-1:4-naphthylenediamine.*

Naphthalene-1:6-disulphonyl chloride (1 gram) was mixed intimately with 0.9 gram of  $\alpha$ -naphthylamine and 0.9 gram of fused sodium acetate, giving a bright orange, almost liquid paste, finally becoming quite hard. This product was ground to powder and warmed cautiously with 10 c.c. of 2*N*-sodium carbonate solution, then collected and finally washed with warm water, when it was obtained as a pale lilac-coloured, granular solid. This dissolved with difficulty in 150 c.c. of *N*/5-sodium hydroxide and to the cooled solution was added benzenediazonium chloride from 0.45 gram of aniline. A yield of 2.5 grams of the bright red azo-compound was obtained on the addition of 10 c.c. of 2*N*-acetic acid. The reduction of this substance was brought about readily by dissolving it (2.5 grams) in 5 c.c. of 5*N*-sodium hydroxide and 100 c.c. of water and treating with 3 grams of zinc dust. The reduction was complete in twenty minutes at  $100^{\circ}$  and the liquid was cooled rapidly and filtered into 50 c.c. of *N*/2-acetic acid, when the base was obtained as an almost white powder darkening slightly when dried, but not melting below  $250^{\circ}$  (Found: N = 9.27.  $C_{30}H_{24}O_4N_4S_2$  requires N = 9.86 per cent.).

(v) *Naphthalene-1:5-disulphonylbis-1:4-naphthylenediamine.*

In this preparation it was found to be essential to start from purified naphthalene-1:5-disulphonyl chloride.

Twelve grams of commercial "Armstrong salt" (sodium naphthalene-1:5-disulphonate) were dried at  $110^{\circ}$ , mixed with 16 grams of phosphorus pentachloride and 10 c.c. of dry toluene, and the

mixture stirred at 100° for thirty minutes. The crude naphthalene-1 : 5-disulphonyl chloride was purified by extraction with benzene and crystallisation from this solvent. The purified sulphonyl chloride melting at 175° was mixed intimately in a warm mortar with two molecular proportions of  $\alpha$ -naphthylamine and anhydrous sodium acetate. The resulting naphthalene-1 : 5-disulphonylbis- $\alpha$ -naphthylamine was coupled in alkaline solution with benzenediazonium chloride (2 mols.) and the azo-derivative was precipitated completely on adding 2*N*-acetic acid. This benzene-azo-compound (Found : N = 11.15. Calc., N = 11.26 per cent.), of which 2.2 grams were obtained from 1 gram of naphthalene-1 : 5-disulphonyl chloride, was reduced with 2 parts of zinc dust and 3 parts of 5*N*-sodium hydroxide in 50 parts of water at 100°. The addition of acetic acid to the filtered solution precipitated the mauve diamine, which did not melt below 250° (Found : N = 9.64.  $C_{30}H_{24}O_4N_4S_2$  requires N = 9.86 per cent.).

### III. *Arylsulphonyl-1 : 4-naphthylenediaminesulphonic Acids.*

When the method described above for the condensation of the sulphonyl chlorides with  $\alpha$ -naphthylamine was applied to similar experiments in which the  $\alpha$ -naphthylaminesulphonic acids were used in place of  $\alpha$ -naphthylamine, it was found that no perceptible reaction took place, but that on addition of a relatively small quantity of pyridine the condensation proceeded to completion.

#### (i) *1-Toluene-p-sulphonyl-1 : 4-naphthylenediamine-8-sulphonic Acid (Formula IV).*

Five grams of  $\alpha$ -naphthylamine-8-sulphonic acid, 4.3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up intimately in a warm mortar; three drops of pure dry pyridine were added and the trituration continued. A reaction occurred, the brown paste formed was boiled with 20 c.c. of *N*/2-sodium carbonate solution forthwith for ten minutes and the liquid then cooled. The condensation product dissolved to a clear solution.

The benzeneazo-compound was made as in former cases, the benzenediazonium chloride from 1.8 grams of aniline being poured into the foregoing solution, to which 5 c.c. of 5*N*-sodium hydroxide solution had been added. The liquid became brilliant scarlet, but no precipitate of azo-compound could be observed even when a portion of the coloured liquid was saturated with sodium chloride. The azo-compound was reduced in solution by boiling with 10 grams of zinc dust and 25 c.c. of 5*N*-sodium hydroxide and with further

quantities of zinc dust (10 grams) and of 5*N*-sodium hydroxide (20 c.c.); the decolorisation of the solution required about one hour, air being excluded by passing hydrogen into the reduction vessel. After cooling, the liquid was filtered into dilute acetic acid, when a fine, yellowish-white precipitate formed. This product, when removed by filtration, washed with a little water and dried, was obtained as a light purple powder, soluble in water (Found: S = 15.43.  $C_{17}H_{15}O_5N_2S_2Na$  requires S = 15.45 per cent.).

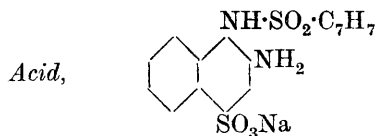
(ii) 1-Toluene-*p*-sulphonyl-1 : 4-naphthylenediamine-6 (7)-sulphonic Acid.

Commercial Cleve's acid was condensed with toluene-*p*-sulphonyl chloride as in the preceding preparation; the resulting toluene-*p*-sulphonyl- $\alpha$ -naphthylamine-6- and 7-sulphonic acids were converted into benzeneazo-derivatives and these colouring matters were reduced as before, yielding a mixture of the sodium salts of the toluene-*p*-sulphonyl-1 : 4-naphthylenediamine-6- and 7-sulphonic acids.

This mixture and the two preceding compounds were diazotised and the diazo-derivatives mixed with  $\beta$ -naphthol and pyridine; in each case coupling occurred, thus showing that these sulphonic acids were all derived from 1 : 4-naphthylenediamine.

IV. Arylsulphonyl-1 : 2-naphthylenediaminesulphonic Acids.

(i) 1-Toluene-*p*-sulphonyl-1 : 2-naphthylenediamine-4-sulphonic



Five grams of naphthionic acid, 4.3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up in a warm mortar, the reaction being promoted by the addition of two drops of pyridine.

The crude product was boiled with 20 c.c. of *N*/2-sodium carbonate solution and the filtered solution cooled and treated successively with 5 c.c. of 5*N*-sodium hydroxide and the diazo-solution from 1.8 grams of aniline. On salting out, a brilliant scarlet precipitate was formed, which tended to coalesce in a viscous mass, but no decomposition was observed. This substance was washed with a little water, warmed to decompose unaltered diazo-compound and then reduced with 10 grams of zinc dust and 50 c.c. of 2*N*-sodium hydroxide. When the reduced solution was filtered into dilute acetic



acid, a yellowish-brown precipitate was deposited of *sodium 1-toluene-p-sulphonyl-1 : 2-naphthylenediamine-4-sulphonate* (yield 1.1 grams) (Found : S = 15.32.  $C_{17}H_{15}O_5N_2S_2Na$  requires S = 15.45 per cent.).

The foregoing reduction was also effected by dissolving the azo-compound in 50 per cent. alcohol and adding an equal weight of zinc dust and one-tenth the weight of ammonium chloride.

(ii) *1-Toluene-p-sulphonyl-1 : 2-naphthylenediamine-5-sulphonic Acid (Formula V).*

Five grams of  $\alpha$ -naphthylamine-5-sulphonic acid, 4.3 grams of toluene-*p*-sulphonyl chloride, and 3 grams of fused sodium acetate were ground up in a warm mortar with 1 c.c. of pyridine. The mixture, at first semi-liquid, rapidly stiffened and was finally washed from the mortar with sodium carbonate solution and then boiled for ten minutes. The whole of the residue passed into solution, 10 c.c. of 5*N*-sodium hydroxide were added, and the benzeneazo-derivative was prepared by adding the diazo-solution from 1.8 grams of aniline. The coupling took place rather slowly, but in about half an hour a brick red precipitate had formed. After one hour, salt was added and the mixture left overnight. The dark red precipitate was then reduced with 10 grams of zinc dust and 50 c.c. of 2*N*-sodium hydroxide, and when the red colour had disappeared (thirty minutes) the solution was cooled and filtered into dilute acetic acid, when sodium 1-toluene-*p*-sulphonyl-1 : 2-naphthylenediamine-5-sulphonate was obtained as a pale yellow precipitate.

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