53. *Preparation of Certain Nuclear-substituted 2-Aminophenolsulphonic Acids.*

By W. F. Beech.

Methods for the preparation of some new 2-aminophenolsulphonic acid derivatives are described. The structures of these substances have been established.

The sulphonic acids of 2-aminophenol and its nuclear-substituted derivatives are of considerable importance on account of their wide use as diazo-components in the preparation of metallisable azo-dyes. During a systematic investigation of the technical properties of such dyes, certain 2-aminophenolsulphonic acid derivatives not previously described were prepared. The structures of these substances were established by orientation experiments.

A new dichloro-2-aminophenol-6-sulphonic acid was obtained from the nitration product of 5-chlorobenzoxazolone-7-sulphonic acid. According to the literature (Meister, Lucius & Brüning, D.R.-P. 197,807), the 6-nitro-derivative is formed, but the evidence given in support of this statement is not very satisfactory. It is known, however, that many benzoxazolone derivatives yield 6-nitrobenzoxazolones by direct nitration and this was found to be the case in the present instance (see below). The nitro-compound, 5-chloro-6-nitrobenzoxazolone-7-sulphonic acid (I; R = Cl, R′ = NO_2) was readily reduced to *5-chloro-6-aminobenzoxazolone-7-sulphonic acid* (I; R = Cl, R′ = NH_2) by iron and hydrochloric acid; the amine yielded 5 : 6-dichlorobenzoxazolone-7-sulphonic acid (I; R = R′ = Cl) (*sodium* salt) by diazotisation and the Sandmeyer reaction. Hydrolysis of this acid with aqueous sodium hydroxide gave 4 : 5-*dichloro*-2-*aminophenol*-6-*sulphonic acid* (II; R = R′ = Cl) which was converted into a sparingly soluble diazo-oxide by the action of nitrous acid. The diazo-oxide was decomposed by ethanol in the presence of cuprous oxide, 3 : 4-dichlorophenol-2-sulphonic acid (III; R = H, R′ = OH) being obtained (*sodium* salt). The potassium salt of the latter gave the known 2 : 3 : 4-trichlorophenol (Groves, Turner, and Sharp, *J.*, 1929, 522) on distillation with phosphorus pentachloride, a result which confirmed the structures assigned to the compounds described above.

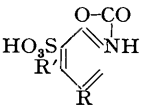
On methylation and subsequent treatment with phosphorus pentachloride in the cold, 3 : 4-dichlorophenol-2-sulphonic acid gave 3 : 4-*dichloroanisole*-2-*sulphonyl chloride* (III; R = Me, R′ = Cl); the latter was converted into a crystalline *ethylanilide* (III; R = Me, R′ = NEtPh) by treatment with ethylaniline.

By sulphonation of 3 : 4-dichlorophenol, a dichlorophenolsulphonic acid differing from the 3 : 4-dichlorophenol-2-sulphonic acid described above was obtained. The *dichloroanisole-sulphonethylanilide* obtained from this substance, although it melted at approximately the same temperature as 3 : 4-dichloroanisole-2-sulphonethylanilide, depressed the m. p. of the latter. On prolonged heating with phosphorus pentachloride, the *potassium* salt of the dichlorophenolsulphonic acid yielded 1 : 2 : 4 : 5-tetrachlorobenzene, from which it follows that the substance was 4 : 5-dichlorophenol-2-sulphonic acid (IV; R = H, R′ = OH, R″ = H). On nitration the latter gave 3 : 4-dichloro-2-nitrophenol-6-sulphonic acid (IV; R = H, R′ = OH, R″ = NO_2) (*sodium* salt) which was reduced to 3 : 4-*dichloro*-2-*aminophenol*-6-*sulphonic acid* (IV; R = H, R′ = OH, R″ = NH_2) by iron and hydrochloric acid. By diazotisation followed by the Sandmeyer reaction, the aminophenolsulphonic acid yielded 2 : 3 : 4-trichlorophenol-6-sulphonic acid (*sodium* salt), the latter being readily converted into the known 2 : 3 : 4-trichlorophenol (*loc. cit.*) by boiling with concentrated hydrochloric or 10N-sulphuric acid.

By reactions similar to those employed for the preparation of 4 : 5-dichloro-2-aminophenol-6-sulphonic acid, 6-nitro-5-methylbenzoxazolone-7-sulphonic acid (I; R = Me, R′ = NO_2) (D.R.-P. 197,807) yielded successively 6-amino- and 6-chloro-5-methylbenzoxazolone-7-sulphonic acid (I; R = Me, R′ = Cl), the latter substance being hydrolysed to 2-*chloro*-5-*amino*-p-*cresol*-3-*sulphonic acid* (II; R = Me, R′ = Cl) by aqueous sodium hydroxide.

The sulphonation of 5-*methoxybenzoxazolone* (V; R = H) with 20% oleum at 100° yielded the 6-sulphonic acid (V; R = SO_3H), as expected. This acid gave 2-*amino*-4-*methoxyphenol*-5-*sulphonic acid* (VI; R = H, R′ = SO_3H) on hydrolysis with sodium hydroxide, the structure of the latter being demonstrated by converting it into 4-*chloro*-2 : 5-*dimethoxybenzenesulphonethylanilide* by diazotisation and Sandmeyer reaction, followed by methylation and subsequent treatment of the 4-chloro-2 : 5-dimethoxybenzenesulphonic acid (*sodium* salt) thus formed with phosphorus pentachloride, the corresponding sulphonyl chloride being obtained. Treatment of the latter with ethylaniline yielded the ethylanilide. An authentic sample of 4-chloro-

2 : 5-dimethoxybenzenesulphonic acid was obtained from 4-chloro-2 : 5-dimethoxyaniline (Gen. Aniline, U.S.P. 1,919,580) by diazotising the latter, treating the diazo-solution with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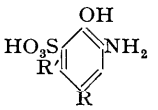
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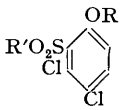
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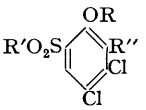
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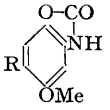
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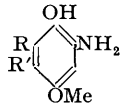
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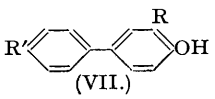
(VII.)

potassium ethyl xanthate (Leuckart, *J. pr. Chem.*, 1890, **41**, 179), and oxidising the product with potassium permanganate. The structure of 4-chloro-2 : 5-dimethoxyaniline does not appear to have been demonstrated with certainty. The substance is obtained from nitro-2 : 5-dimethoxyaniline (*loc. cit.*), which may be prepared either by nitration of 2 : 5-dimethoxyacetanilide and subsequent hydrolysis (Baessler, *Ber.*, 1884, **17**, 2121) or from nitro-4-chloro-2-anisidine by heating with potassium hydroxide and methanol (Badische Anilin- und Soda-Fabrik, D.R.-P. 141,975). It has been found, however, that nitro-2 : 5-dimethoxyaniline gives on reduction a diamine which does not condense with phenanthraquinone; hence, the substance is either 3- or 4-nitro-2 : 5-dimethoxyaniline. Since the chlorine atom of the nitro-4-chloro-2-anisidine is labile, the substance to which it gives rise on heating with potassium hydroxide and methanol is either 4- or 6-nitro-2 : 5-dimethoxyaniline. As the products of the two methods of synthesis are identical (D.R.-P. 141,975) the substance is 4-nitro-2 : 5-dimethoxyaniline.

In the hope of obtaining 2-amino-4-methoxyphenol-6-sulphonic acid (VI; R = SO_3H, R′ = H), 2-amino-4-methoxyphenol was sulphonated with 20% oleum, but the product was found to consist almost entirely of 2-amino-4-methoxyphenol-5-sulphonic acid. Chromatographic analysis of the dye obtained from the crude sulphonation product by diazotisation and coupling with β-naphthol indicated the presence of two coloured substances, one identical with that obtained in a similar manner from 2-amino-4-methoxyphenol-5-sulphonic acid prepared from 5-methoxybenzoxazolone : the second was present in small amount only. A similar analysis with the corresponding dye made from the purified sulphonation product showed the presence of one substance only, the major constituent of the first analysis. That the purified sulphonation product was identical with 2-amino-4-methoxyphenol-5-sulphonic acid prepared from 5-methoxybenzoxazolone was further demonstrated by converting each into 4-chloro-2 : 5-dimethoxybenzenesulphonethylanilide.

By sulphonating 3-nitro-4-hydroxydiphenyl (VII; R = NO_2, R′ = H) with concentrated sulphuric acid at 80° and reducing the product with iron and hydrochloric acid, an amino-hydroxydiphenylsulphonic acid was obtained which may be regarded as a 2-aminophenol derivative bearing a substituent phenyl group. The position of the sulphonic acid group was determined by deaminating the substance and subsequently fusing the *sodium* salt of the product with sodium hydroxide, the product being identified as 4 : 4′-dihydroxydiphenyl. This result establishes the structure of the aminohydroxydiphenylsulphonic acid as *3-amino-4-hydroxydiphenyl-4′-sulphonic acid* (VII; R = NH_2, R′ = SO_3H) and that of the nitro-compound as 3-nitro-4-hydroxydiphenyl-4′-sulphonic acid (VII, R = NO_2, R′ = SO_3H).

Experimental.

(Analyses by Mr. E. S. Morton. M. ps. are uncorrected.)

4 : 5-*Dichlorophenol-2-sulphonic Acid.*—3 : 4-Dichlorophenol (163 g.) was melted (m. p. 68°) and sulphuric acid monohydrate (65 c.c.) added rapidly with shaking. After 10 minutes the temperature rose spontaneously to 105°, crystals of the sulphonic acid separating. The reaction was completed by heating at 95—100° for 2 hours; the product was then dissolved in water (250 c.c.). Potassium chloride (70 g.) was added, and the product removed by filtration. *Potassium* 4 : 5-*dichlorophenol-2-sulphonate* was obtained by dissolving the latter in water and neutralising the resulting solution with potassium carbonate; it was purified by recrystallisation from hot water (Found : S, 11·4; K, 13·5. $C_6H_3O_4Cl_2SK$ requires S, 11·4; K, 13·9%).

Reaction of the potassium salt with phosphorus pentachloride. The dry potassium salt (40 g.) was mixed with phosphorus pentachloride (80 g.) and phosphoryl chloride (5 c.c.). The mixture was boiled gently under reflux for 8 hours and then distilled. The distillate was treated with water (350 c.c.) to

decompose phosphorus pentachloride and phosphoryl chloride, and the solid residue isolated. The latter was washed with N-sodium hydroxide (50 c.c.) and water (50 c.c.) and dried. The product (5 g.) was purified by crystallisation from β-ethoxyethanol and then from benzene until the m. p. became constant (140°) (Found: Cl, 65·2. Calc. for $C_6H_2Cl_4$: Cl, 65·75%). The m. p. was not depressed by admixture with an authentic sample of 1 : 2 : 4 : 5-tetrachlorobenzene.

4 : 5-*Dichloroanisole-2-sulphonamide*.—4 : 5-Dichlorophenol-2-sulphonic acid (potassium salt, 14·1 g.) was dissolved in water (50 c.c.), and the solution treated with 10N-sodium hydroxide (7 c.c.) and methyl sulphate (6 c.c.) at 30°, the reaction being completed by heating to 100°. The solution was then made just acid to Congo-red by addition of hydrochloric acid and evaporated by dryness. The residue was treated with phosphorus pentachloride (15 g.), and the resulting 4 : 5-dichloroanisole-2-sulphonyl chloride converted into 4 : 5-*dichloroanisole-2-sulphonamide* by treatment with excess of ammonia. The sulphonamide was purified by crystallisation from methanol; white needles, m. p. 206° (Found: N, 6·0; Cl, 27·9. $C_7H_7O_3NCl_2S$ requires N, 5·45: Cl, 27·75%).

4 : 5-*Dichloroanisole-2-sulphonethylanilide* was obtained by treating 4 : 5-dichloroanisole-2-sulphonyl chloride with excess of ethylaniline. It crystallised from methanol in white needles, m. p. 118° (Found: N, 3·95; Cl, 19·45. $C_{15}H_{15}O_3NCl_2S$ requires N, 3·9; Cl, 19·7%).

3 : 4-*Dichloro-2-nitrophenol-6-sulphonic Acid*.—3 : 4-Dichlorophenol (163 g.) was sulphonated as described above. The product was dissolved in water (250 c.c.), and the solution treated with nitric acid (72 c.c.. *d* 1·4) at 5°. After 10—15 minutes, a vigorous reaction started, the temperature rising to 55—60°. After being stirred at 55° for 5 minutes, the solution was cooled to 25°, and sodium chloride (70 g.) added. The *sodium* salt of 3 : 4-dichloro-2-nitrophenol-6-sulphonic acid separated as a yellow precipitate; it crystallised from water in yellow needles (Found: N, 4·45. $C_6H_2O_6NCl_2SNa$ requires N, 4·5%). For the next stage, the substance was not recrystallised; the total yield was dissolved in hot water (1 l.), and the solution decanted from a slight insoluble residue.

3 : 4-Dichloro-2-aminophenol-6-sulphonic acid was obtained by adding the hot solution of 3 : 4-dichloro-2-nitrophenol-6-sulphonic acid to a mixture of iron filings (300 g.), water (400 c.c.), and 10N-hydrochloric acid (8 c.c.) at 95—100°, the reaction mixture being subsequently maintained at 95—100° for 1 hour with mechanical stirring. The acid was isolated by rendering the reaction mixture alkaline towards litmus with sodium carbonate, filtering it whilst hot, and acidifying the filtrate with hydrochloric acid. It was purified by boiling the solution of the crude product in dilute sodium carbonate with carbon, filtering, and acidifying. Further purification was effected by crystallisation from hot water, from which the *hemihydrate* separated in the form of white needles (Found: C, 26·8; H, 2·35; N, 5·5; Cl, 26·25; S, 12·05. $C_6H_5O_4NCl_2S,\frac{1}{2}H_2O$ requires C, 26·95; H, 2·25; N, 5·25; Cl, 26·6; S, 12·0%).

2 : 3 : 4-*Trichlorophenol-6-sulphonic Acid*.—3 : 4-Dichloro-2-aminophenol-6-sulphonic acid (26·7 g.), dissolved in a solution of sodium hydroxide (4 g.) in water (150 c.c.), was diazotised at 5—10° by addition of sodium nitrite (7 g.) in water (10 c.c.), followed by 10N-hydrochloric acid (35 c.c.). The diazo-suspension was added to a solution of cuprous chloride (12 g.) in hydrochloric acid (100 c.c., *d* 1·18) at 30°, and the solution heated gradually to 100°. On cooling, the *sodium* salt of 2 : 3 : 4-trichlorophenol-6-sulphonic acid separated; it was purified by crystallisation from methanol (Found: Cl, 36·2; S, 10·7; Na, 7·6. $C_6H_2O_4Cl_3SNa$ requires Cl, 35·55; S, 10·7; Na, 7·7%). On boiling the substance with concentrated hydrochloric or 10N-sulphuric acid for several hours, 2 : 3 : 4-trichlorophenol, m. p. 80°, was obtained (Found: Cl, 53·15. Calc. for $C_6H_3OCl_3$: Cl, 53·95%). The benzoate melted at 142° (Holleman, *Rec. Trav. chim.*, 1920, **39**, 743, gives m. p. 141°).

5-*Chloro-6-aminobenzoxazolone-7-sulphonic Acid*.—5-Chloro-6-nitrobenzoxazolone-7-sulphonic acid (D.R.-P. 197,807) (potassium salt, 332 g.) was added cautiously to a mixture of iron filings (300 g.), water (600 c.c.), and 10N-hydrochloric acid (12 c.c.) at 95°; the reaction mixture was subsequently kept at this temperature for 1 hour and then made alkaline by addition of sodium carbonate. After filtering at the boil, the filtrate was made just acid to Congo-red with hydrochloric acid. For the next stage it was not necessary to isolate 5-*chloro-6-aminobenzoxazolone-7-sulphonic acid*, which is diazotised *in situ*. The substance is easily isolated if required by addition of concentrated hydrochloric acid to the solution (Found: N, 10·8. $C_7H_5O_5N_2ClS$ requires N, 10·6%).

5 : 6-*Dichlorobenzoxazolone-7-sulphonic Acid*.—The solution of 5-chloro-6-aminobenzoxazolone-7-sulphonic acid (total liquor) was diazotised at 0—5° by adding 10N-hydrochloric acid (250 c.c.), followed by sodium nitrite (60 g.) in water (100 c.c.). The diazo-suspension was decomposed by adding it to a solution of cuprous chloride (120 g.) in hydrochloric acid (400 c.c., *d* 1·18) at 30° and subsequently heating to 100°. On concentrating the solution and cooling, 5 : 6-dichlorobenzoxazolone-7-sulphonic acid crystallised out as the *sodium* salt; it was purified by crystallisation from hot water; white needles (Found: N, 4·7; Cl, 22·5; Na, 8·0. $C_7H_2O_5NCl_2SNa$ requires N, 4·6; Cl, 23·2; Na, 7·5%).

4 : 5-*Dichloro-2-aminophenol-6-sulphonic Acid*.—5 : 6-Dichlorobenzoxazolone-7-sulphonic acid (200 g.) was dissolved in hot water (1200 c.c.), and 10N-sodium hydroxide (300 c.c.) added. The solution was kept at 95—100° for 3 hours, neutralised with concentrated hydrochloric acid, concentrated to 750 c.c. and then made strongly acid with hydrochloric acid. The crude 4 : 5-*dichloro-2-aminophenol-6-sulphonic acid* which separated was purified similarly to its 3 : 4-dichloro-analogue (yield, 130 g.). It crystallised from water in white needles (Found: C, 28·0; H, 2·1; N, 5·05; Cl, 27·9; S, 12·25. $C_6H_5O_4NCl_2S$ requires C, 27·9; H, 1·95; N, 5·45; Cl, 27·5; S, 12·4%).

3 : 4-*Dichlorophenol-2-sulphonic Acid*.—4 : 5-Dichloro-2-aminophenol-6-sulphonic acid (43 g.) was dissolved in sodium hydroxide (7 g.) in water (100 c.c.), and a solution of sodium nitrite (12 g.) in water (20 c.c.) added. Diazotisation was effected at 10° by adding 10N-sulphuric acid (85 c.c.) rapidly. The diazo-oxide was filtered off, washed with ethanol (25 c.c.), and suspended in ethanol (500 c.c.). Cuprous oxide (20 g.) was then added, and after the vigorous reaction had subsided, the reaction mixture was boiled under reflux for 3 hours. The ethanol was removed, and the residue extracted with dilute potassium carbonate solution (200 c.c.) at the boil. The solution was filtered, and the filtrate treated with a small quantity of sodium hyposulphite (dithionite), after which the product was isolated by saturating the solution with potassium chloride and cooling to 20°. 3 : 4-Dichlorophenol-2-sulphonic

acid separated as the *potassium* salt, which was purified by crystallisation from hot water; white needles (Found : Cl, 25·4; K, 13·75. $C_6H_3O_4Cl_2SK$ requires Cl, 25·25; K, 13·9%).

3 : 4-*Dichloroanisole-2-sulphonethylanilide* was prepared from 3 : 4-dichlorophenol-2-sulphonic acid by the method described for the isomeric 4 : 5-dichloro-compound; white plates from methanol, m. p. 117° (Found : C, 49·95; H, 4·3; N, 3·75; Cl, 20·15. $C_{15}H_{15}O_3NCl_2S$ requires C, 50·0; H, 4·15; N, 3·9; Cl, 19·7%). The m. p. was depressed on admixture with the isomeric 4 : 5-dichloro-compound.

Reaction of the Potassium Salt of 3 : 4-*Dichlorophenol-2-sulphonic Acid with Phosphorus Pentachloride.*—The reaction and subsequent distillation were performed in the manner described for the 4 : 5-dichloro-analogue. The greater part of the product was soluble in N-sodium hydroxide, from which it was reprecipitated by hydrochloric acid. The substance was purified by steam distillation and subsequent crystallisation from ligroin; white needles, m. p. 80° (Found : Cl, 53·4. Calc. for $C_6H_3OCl_3$: Cl, 53·95%). The benzoate melted at 142° (Holleman, *Rec. Trav. chim.*, 1920, **39**, 743, gives m. p. 141°).

2-*Chloro-5-amino*-p-*cresol-3-sulphonic acid* was prepared from 6-nitro-5-methylbenzoxazolone-7-sulphonic acid (D.R.-P. 197,807) (potassium salt, 312 g.) *via* the corresponding 6-amino- and 6-chloro-acids, the method being the same as for 4 : 5-dichloro-2-aminophenol-6-sulphonic acid. The required acid (110 g.) was purified similarly to 3 : 4-dichloro-2-aminophenol-6-sulphonic acid. It crystallised from water in white needles (Found : C, 35·55; H, 3·8; N, 5·7; S, 13·0; Cl, 15·25. $C_7H_8O_4NClS$ requires C, 35·4; H, 3·4; N, 5·9; S, 13·5; Cl, 14·95%).

2-Nitro-4-methoxyphenol was obtained by boiling technical 3-nitro-*p*-anisidine (168 g.) under reflux with potassium hydroxide (130 g.) in water (1500 c.c.) for 16 hours with stirring. The product was isolated by acidification and cooling. The crude product (155 g., m. p. 80°) was sufficiently pure for the next stage. A small sample, recrystallised from ethanol, melted at 82° (Robinson and Smith, *J.*, 1926, 393, give m. p. 79—80°). Reduction of this in alkaline solution with sodium hyposulphite (dithionite) and addition of sulphuric acid precipitated first 2-amino-4-methoxyphenol as plates which darkened rapidly in air, and then the sulphate, which was dried at 50°.

5-*Methoxybenzoxazolone* was obtained by treating a concentrated, aqueous alkaline solution of 2-amino-4-methoxyphenol with carbonyl chloride at 10—20°, maintaining faint alkalinity until diazotisable material disappeared. On acidifying the solution with 10N-sulphuric acid, the oxazolone separated; it crystallised from hot water in white needles, m. p. 170° (Found : C, 57·95; H, 4·35; N, 8·65 $C_8H_7O_3N$ requires C, 58·2; H, 4·25; N, 8·5%).

5-*Methoxybenzoxazolone-6-sulphonic Acid.*—5-Methoxybenzoxazolone (50 g.) was added to 20% oleum (125 c.c.), the temperature being kept below 50°. The solution was then heated at 95—100° for 2 hours, cooled to 10°, and poured on ice (400 g.). Sodium chloride (120 g.) was added, and the solution stirred for 24 hours. The product was filtered off and washed with brine.

2-*Amino-4-methoxyphenol-5-sulphonic Acid.*—The total yield of the foregoing acid was dissolved in hot water (500 c.c.), and sodium hydroxide (40 g.) added. The solution was kept at 95—100° for 3 hours, made acid to Congo-red with hydrochloric acid and concentrated to 150 c.c. The solution was then made strongly acid with hydrochloric acid and cooled to 10°. Crude 2-*amino-4-methoxyphenol-5-sulphonic acid* (35 g.) separated; it was purified in a similar manner to 3 : 4-dichloro-2-aminophenol-6-sulphonic acid; white needles, turning dark in air (Found : C, 35·65; H, 4·55; N, 6·05. $C_7H_9O_5NS,H_2O$ requires C, 35·45; H, 4·65; N, 5·9%).

Direct Sulphonation of 2-*Amino-4-methoxyphenol.*—The sulphate of 2-amino-4-methoxyphenol (200 g.) was added to 20% oleum (500 c.c.), the temperature being kept below 50°. The solution was heated at 60° for 1 hour and then poured on ice. The product was filtered off and dissolved in dilute sodium carbonate solution (750 c.c.). The solution was decolorised (carbon), filtered, and acidified with hydrochloric acid. The product, consisting mainly of the above 5-sulphonic acid (130 g.), was purified by crystallisation from hot water (Found : N, 5·9; OCH_3, 12·8. $C_7H_9O_5NS,H_2O$ requires N, 5·9; OCH_3, 13·1%).

4-*Chloro-2* : 5-*dimethoxybenzenesulphonic Acid.*—(a) 2-Amino-4-methoxyphenol-5-sulphonic acid (23·7 g.), dissolved in N-sodium hydroxide (100 c.c.), was diazotised at 10° by addition of sodium nitrite (7 g.) followed by 10N-hydrochloric acid (35 c.c.). The diazo-suspension was added to cuprous chloride (11 g.) in hydrochloric acid (70 c.c., *d* 1·18) at 40°, the solution being subsequently raised to the boil. After precipitation of copper salts with hydrogen sulphide and filtering, the filtrate was evaporated to dryness. The residue was dissolved in water (75 c.c.), and the solution made faintly alkaline with sodium carbonate. Methylation was effected by adding sodium hydroxide (5 g.) followed by methyl sulphate (12 c.c.) to the solution at 25° and subsequently heating to 70°. *Sodium* 4-*chloro-2* : 5-*dimethoxybenzenesulphonate* was isolated from the solution by saturating the latter with sodium chloride and cooling to 20°. It crystallised from water in white needles (Found : C, 35·3; H, 3·3; Cl, 12·55; Na, 8·05. $C_8H_8O_5ClSNa$ requires C, 34·95; H, 2·9; Cl, 12·9; Na, 8·4%) and was characterised by conversion into the amide and the ethylanilide.

(b) 4-Chloro-2 : 5-dimethoxyaniline (18·8 g.), dissolved in water (100 c.c.) and 10N-hydrochloric acid (25 c.c.), was diazotised at 0° by addition of a solution of sodium nitrite (6·9 g.) in water (10 c.c.). The diazo-solution was added gradually to a solution of potassium ethyl xanthate (16 g.) in water (100 c.c.) cooled in ice. When addition was complete, the resulting suspension was heated slowly to 90°. The oily substance which separated was removed and dissolved in acetone (200 c.c.). Oxidation was effected by adding a saturated aqueous solution of potassium permanganate at the boil until a slight excess of the latter remained. The solution was then filtered, and the filtrate evaporated to dryness. The product crystallised from water in white needles.

The sulphonic acid (sodium salt, 27·5 g.) was mixed with phosphorus pentachloride (23 g.), the reaction being completed by heating to 95° for 10 minutes. After being stirred with ice, the sulphonyl chloride was filtered off and washed with cold water. Treatment of this with excess of ammonia solution, and crystallisation from methanol afforded the *amide* in white needles, m. p. 207° (Found : C, 38·15; H, 4·2; N, 5·7; $C_8H_{10}O_4NClS$ requires C, 38·15; H, 4·0; N, 5·55%), and the *sulphonethylanilide* was similarly obtained by use of excess of ethylaniline in 50% aqueous alcohol, crystallising from methanol

in large white needles, m. p. 114° (Found : C, 54·5; H, 4·9; N, 4·3. $C_{16}H_{18}O_4NClS$ requires C, 54·0; H, 5·05; N, 3·95%).

The sulphonamide and sulphonethylanilide obtained from 4-chloro-2 : 5-dimethoxybenzenesulphonic acid prepared by method (b) were considered authentic samples, and their m. ps. were not depressed by admixture with similar derivatives obtained from the acid prepared by method (a), this result being obtained irrespective of whether the starting material of (a) was prepared by direct sulphonation of 2-amino-4-methoxyphenol or by hydrolysis of 5-methoxybenzoxazolone-6-sulphonic acid.

3-*Nitro*-4-*hydroxydiphenyl*-4′-*sulphonic Acid.*—3-Nitro-4-hydroxydiphenyl (Raiford and Colbert, *J. Amer. Chem. Soc.*, 1925, **47**, 1454) (86 g.) was added to sulphuric acid (234 c.c. *d* 1·84) at 20°. The temperature was then raised to 80° during 10 minutes, after which the solution was poured on ice. The resulting suspension was diluted with sufficient water to give a clear solution at 50°. The latter was saturated with sodium chloride, cooled to 15°, and the resulting 3-nitro-4-hydroxydiphenyl-4′-sulphonic acid (100 g.) collected.

3-*Amino*-4-*hydroxydiphenyl*-4′-*sulphonic Acid.*—The foregoing acid (100 g.) was added to a mixture of iron filings (100 g.), water (400 c.c.), and 10N-hydrochloric acid (8 c.c.) at 95°. The reaction mixture was kept at 95—100° with stirring for 2 hours, and then made alkaline with sodium hydroxide and filtered whilst hot. The filtrate was acidified with concentrated hydrochloric acid and cooled to 20°, crude 3-*amino*-4-*hydroxydiphenyl*-4′-*sulphonic acid* (80 g.) separating. The substance was purified in a similar manner to 3 : 4-dichloro-2-aminophenol-6-sulphonic acid. It crystallised from water in white needles (Found : C, 50·95; H, 4·7; N, 5·15; S, 11·1. $C_{12}H_{11}O_4NS,H_2O$ requires C, 50·9; H, 4·6; N, 4·95; S, 11·3%).

4-*Hydroxydiphenyl*-4′-*sulphonic Acid.*—4-Amino-4-hydroxydiphenyl-4′-sulphonic acid (5·66 g.), dissolved in sodium hydroxide (2 g.) in water (35 c.c.), was diazotised at 5° by adding 2N-sodium nitrite (10 c.c.) followed by 10N-sulphuric acid (15 c.c.). The diazo-oxide was filtered off, washed with ethanol (10 c.c.), and suspended in ethanol (100 c.c.). After addition of cuprous oxide (5 g.), the suspension was raised to the boil during 15 minutes, and then boiled under reflux for 3 hours. The ethanol was removed, and the residue extracted with boiling dilute sodium carbonate solution (125 c.c.). The solution was filtered, and the filtrate treated with a small quantity of sodium hyposulphite (dithionite). *Sodium* 4-*hydroxydiphenyl*-4′-*sulphonate* separated on cooling; it was purified by crystallisation from hot water (Found : S, 9·5; Na, 7·0; H_2O, 12·3. $C_{12}H_9O_4SNa,2H_2O$ requires S, 10·4; Na, 7·45; H_2O, 11·7%).

4 : 4′-*Dihydroxydiphenyl.*—The foregoing sodium salt was fused with sodium hydroxide as described by Van Meter, Bianculli, and Lowy (*J. Amer. Chem. Soc.*, 1940, **62**, 3146). The product, after purification, melted at 270° (m. p. of 4 : 4′-dihydroxydiphenyl, 272°); it was characterised by conversion into the diacetyl derivative, m. p. and mixed m. p. 161° (Found : C, 70·5; H, 5·15. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%).

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