XXI.—*Nitroarylsulphuric Acids and their Reduction Products.*

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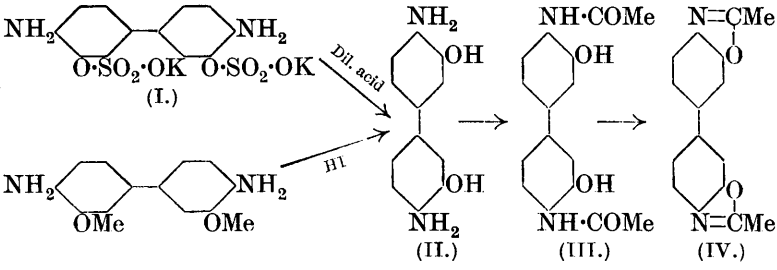
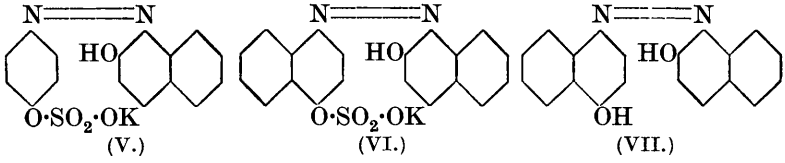
THE method of preparing arylsulphuric acids by the addition of a phenol or naphthol to dimethylaniline chlorosulphonate in carbon disulphide (Burkhardt and Lapworth, J., 1926, 684) has been applied satisfactorily to *o*-, *m*-, and *p*-nitrophenols and to 4-nitro-1-naphthol and 1-nitro-2-naphthol, but only small amounts of the sulphuric ester were formed from 2-nitro-1-naphthol. The potassium salts which were isolated were remarkably stable for derivatives of such acid phenols and were reduced by ferrous hydroxide to amino-compounds, which gave acetyl and benzylidene derivatives without losing the sulphate group. Potassium *o*-nitrophenyl sulphate was reduced in alkaline solution to the azo- and hydrazo-derivatives and converted into *potassium* 4 : 4′-*diaminodiphenylene* 3 : 3′-*disulphate* (I; yield, 50%). The constitution of the last compound was confirmed by hydrolysing it with boiling dilute hydrochloric acid and comparing the dihydroxybenzidine produced with that obtained by demethylating dianisidine with hydriodic

acid (compare German Pat. 70718). The dihydroxybenzidine (II) was characterised by means of the *dianhydrodiacetyl* derivative (IV).



During the diazotisation of aminoaryl sulphates under ordinary conditions the sulphate group was removed whenever it was in the *o*-position to the amino-group. However, whereas 1-amino-2-naphthol in diazotisation gives β-naphthaquinone (Grandmougin and Michel, *Ber.*, 1892, **25**, 972), the sulphuric ester gives the diazo-oxide, indicating that some protective effect is operating even in this case. This splitting off of substituents during diazotisation has many well-known analogies, but displacements are rare in monosubstituted amines.

The aminoaryl sulphates with the amino- and sulphato-groups in the *m*- or *p*-position diazotised normally and the diazo-derivatives coupled with β-naphthol to give azo-compounds containing the sulphato-group, which makes them soluble acid dyes (*e.g.*, V and VI, comparable with Orange II and Fast Red A respectively).



Attempts were made to dye wool and silk with these and subsequently to hydrolyse the dye on the fibre to relatively insoluble products (*e.g.*, VII). The hydrolysis on the fibre was found to be more difficult than in aqueous solution, as Green also observed with the ionamines, and dull shades were produced when such hydrolysis was brought about by heating with 1% sulphuric acid, a much greater strength than is normally used in dyeing operations. Further, the hydroxyazo-dyes, which were insoluble in water, were stripped by soap, as was to be expected with *p*-hydroxyazo-dyes of low molecular weight.

The isomeric 2- and 4-nitro-1-naphthols were separated nearly quantitatively by forming the potassium salts in aqueous alcohol.

EXPERIMENTAL.

Preparation of Nitronaphthols.—1-*Nitro*-2-*naphthol.* Aceto-β-naphthalide was nitrated by Friedländer and Littner's method (*Ber.*, 1915, **48**, 330). The product which crystallised from the benzene extract (yield, 60%) was refluxed for 2 hours with alcohol (2½ vols.) and 50% aqueous potassium hydroxide (1 vol.). The residue after evaporation of the alcohol was twice recrystallised from boiling water, and an aqueous solution acidified to give pure 1-nitro-2-naphthol.

2- *and* 4-*Nitro*-1-*naphthols.* α-Naphthylamine (30 g.) was boiled for 5 minutes with glacial acetic acid (200 c.c.) and acetic anhydride (27 c.c.) (Hodgson and Kilner, J., 1924, **125**, 807), and nitric acid (12·5 c.c.; *d* 1·5) added to the suspension resulting on cooling to 20—25°. After 2 days the solid (30 g.) was filtered off, washed twice with glacial acetic acid, and heated with alcohol (90 c.c.), aqueous caustic potash (60 c.c. of 30%) and water (100 c.c.) were added, and the alcohol was distilled off slowly. When 70 c.c. had distilled, more water (100 c.c.) was added and the distillation continued on a sand-bath until the distillate was free from ammonia (total time, 3½ hours). The potassium 2-nitro-1-naphthoxide separating on cooling was washed twice with 5% potash solution (50 c.c.), the filtrate and washings were warmed slightly and acidified with acetic acid, and the crude 4-nitronaphthol was filtered off and steam-distilled until the 2-nitro-1-naphthol present (0·3 g.) had been removed. The product was purified by boiling with animal charcoal and crystallised (yield, 9·5 g.; m. p. 165—166°). The potassium 2-nitro-1-naphthoxide, acidified in boiling aqueous solution with acetic acid, gave the free nitronaphthol, which was filtered off while hot (yield, 9 g.; m. p. 128—129°). The filtrate deposited a trace of 4-nitro-1-naphthol.

A simple separation was not effected if sodium hydroxide was used instead of potassium hydroxide in the hydrolysis.

Conversion of Nitrophenols and Nitronaphthols into Sulphates (compare Ashworth, Burkhardt, and Lapworth, *loc. cit.*).—Chlorosulphonic acid (1·4 mols.) was added to dimethylaniline (3·7 mols.) in carbon disulphide (500 c.c.), kept below 16°. To the mixture, made mobile by heating to 35°, nitrophenol or nitronaphthol (1 mol.) was added all at once. After an hour's stirring at 35° the product was kept over-night and then poured into a well-stirred solution of caustic potash (4 mols.) in water (2 l. for *o*-nitrophenol, 3 l. for *p*-nitrophenol, 2·5 l. for 1-nitro-2-naphthol, and 5 l. for 4-nitro-1-naphthol), kept below 30°.

In the case of *o*-nitrophenol the base was separated directly by

the addition of a little benzene; ice was then added and when the temperature had fallen to 5° hydrochloric acid was added until all the unchanged nitrophenol had just separated. The solution was filtered, at once made alkaline again with caustic potash, and heated to 50°, and the requisite amount of barium chloride solution was added to convert nearly all the residual potassium sulphate into chloride. On evaporation under reduced pressure the solution gave potassium *o*-nitrophenyl sulphate (80% of the theoretical yield) as a first fraction. If the bulk of the potassium sulphate was not converted into chloride before evaporation, it crystallised with the required product, which was then only obtained pure by a tedious extraction with hot 90% alcohol.

In the case of *p*-nitrophenol the extraction liquor had to be heated to 50° to dissolve the solid matter, and the base was then separated directly while hot by the addition of a little toluene. A short evaporation under reduced pressure completed the removal of the base. Some pure potassium *p*-nitrophenyl sulphate separated on cooling and the remainder was obtained by evaporation under reduced pressure, after the unchanged *p*-nitrophenol had been removed by ether extraction of the solution acidified below 5°. Yield, 80%.

The case of the 1-nitro-2-naphthol was the most difficult in the extraction. The large amount of solid which separated was removed and dissolved in the minimum amount of warm water and this solution and the original filtrate were treated in parallel. The base was separated with benzene, the solution cooled and acidified, and the unchanged nitronaphthol (55%) separated. The solutions, made alkaline with potash, were evaporated under reduced pressure until the required product crystallised (yield, 40%). A further crystallisation from water at 70° was sometimes necessary.

Potassium 4-nitro-1-naphthyl sulphate separated from the alkaline liquor contaminated only with dimethylaniline, which was removed by washing with methylated spirit. The filtrate was treated as usual and a further quantity isolated. One recrystallisation from hot water gave a pure product (yield, 85%).

Potassium o-*nitrophenyl sulphate* was recrystallised from 90% alcohol and then from water (Found: K, 15·3. $C_6H_4O_6NSK$ requires K, 15·2%). The solubility in water at 17° is 16%. It is very sparingly soluble in hot or cold alcohol, but readily in cold 70% alcohol or hot 90%.

Potassium p-*nitrophenyl sulphate* was recrystallised from water (Found: K, 15·1%). The solubility in water at 17° is 6%. It is very sparingly soluble in hot or cold alcohol or aqueous alcohol.

Potassium 1-*nitro*-2-*naphthyl sulphate* is sparingly soluble in cold

water and crystallises from hot water in long, pale yellow needles (Found : K, 11·95. $C_{10}H_6O_6NSK,H_2O$ requires K, 12·0%).

Potassium 4-nitro-1-naphthyl sulphate is sparingly soluble in cold water and crystallises from hot water in fine, pale yellow needles (Found : K, 12·7. $C_{10}H_6O_6NSK$ requires K, 12·7%).

All these compounds are rapidly hydrolysed by very dilute hydrochloric acid at about 70°, and slowly at 100° by 10% barium hydroxide solution or dilute acetic acid containing sodium acetate [contrast to potassium phenyl and naphthyl sulphates (Burkhardt and Lapworth, *loc. cit.*), and sodium acetyl sulphate, which is rapidly hydrolysed by cold water (von Peski, *Rec. trav. chim.*, 1921, **40**, 103)]. The hydrolysis with barium hydroxide or acetic acid is still incomplete after 6 hours. An even slower hydrolysis takes place with aqueous ammonia, which behaves as a weak alkali and shows no sign of replacing the sulphate group, attached to the benzene ring, by an amino-group.

Reduction of Nitrophenyl and Nitronaphthyl Sulphates.—A warm concentrated solution of potassium nitrophenyl or nitronaphthyl sulphate (0·1 mol.) was added in small portions during 1·5 hours to a suspension of precipitated calcium carbonate (1·5 mols.) or barium carbonate (1·2 mols.) in a solution of ferrous sulphate (0·9 mol.) in water (600 c.c.) kept at 70—75° and repeatedly shaken. Barium carbonate was only used for 1-nitro-2-naphthyl sulphate; in this case the reaction, after further addition of ferrous sulphate (0·2 mol.) and barium carbonate (0·25 mol.), was complete only after 4 hours. The liquid was filtered hot, the residue washed with hot water, and the filtrate treated with barium hydroxide (if calcium carbonate was used) to precipitate all the free sulphate ion; passage of carbon dioxide then precipitated all the barium and calcium. The filtered solution was made alkaline with caustic potash and evaporated almost to dryness under reduced pressure, and the product crystallised from 80% alcohol. Yields : potassium *o*- and *p*-aminophenyl sulphates and 1-amino-2-naphthyl sulphate, 90%; 4-amino-1-naphthyl sulphate, 66%.

From solutions of potassium *p*-aminophenyl sulphate and potassium 4-amino-1-naphthyl sulphate the free acids were precipitated by hydrochloric or acetic acid.

Preparation of benzylidene derivative. A mixture of potassium *p*-aminophenyl sulphate (3 g.) and benzaldehyde (6·5 c.c.) was warmed at 70° for 30 minutes, cooled, suspended in a little benzene, and filtered. After being washed with a little benzene, the solid product contained about 85% of the benzylidene derivative, the rest being unchanged material. It was recrystallised from 50% alcohol containing a trace of potash.

Acetylation of amino-groups. Potassium *o*- or *p*-aminophenyl sulphate (3 g.) was dropped into 5 c.c. of acetic anhydride with stirring and water-cooling. The solid product was recrystallised from 80% alcohol (20 c.c.) containing a trace of potash (yield, over 90%).

Acid hydrolysis of the acetyl derivative. A concentrated solution of potassium *p*-acetamidophenyl sulphate was acidified with dilute hydrochloric acid and boiled for 3·5 minutes. On cooling, neutralising, and evaporating it, a 50% yield of crude *p*-acetamidophenol was obtained which was purified (m. p. 166°) by two recrystallisations from aqueous alcohol. A large amount of hydrolysis of the acetyl group had also taken place.

Potassium o-*aminophenyl sulphate* (Found : K, 17·1. $C_6H_6O_4NSK$ requires K, 17·2%) is very soluble in water, but a saturated solution gives no precipitate of the internal salt with acids. Bromine water causes a faint violet coloration. No precipitate is formed on the addition of excess of bromine unless the solution has been acidified, in which case a bright yellow precipitate, soluble in ether, is produced. Ferric chloride gives no coloration.

The p-*aminophenyl sulphate* (Found : K, 15·9. $C_6H_6O_4NSK,H_2O$ requires K, 15·9%) is extremely soluble in water and crystallises from 80% alcohol in poorly defined tablets. Hydrochloric or acetic acid gives a crystalline precipitate of the hydrogen aminophenyl sulphate. Bromine produces a violet coloration in acid solution. This colour is discharged by excess of bromine and a yellow precipitate, readily soluble in ether, is formed which crystallises from aqueous alcohol in nearly colourless plates, m. p. 124°. Ferric chloride gives no coloration.

Hydrogen p-*aminophenyl sulphate* is sparingly soluble in all solvents. Small quantities can be crystallised from warm water, but it is best obtained pure by precipitation from solutions of the pure potassium salt. It is soluble in alkalis, alkali carbonates, ammonia, and excess of potassium acetate, although acetic acid gives a precipitate with solutions of the potassium salt (Found : equiv., with sodium hydroxide, 190. $C_6H_7O_4NS$ requires equiv., 189).

Potassium p-*benzylideneaminophenyl sulphate* (Found : K, 12·1. $C_{13}H_{10}O_4NSK,\frac{1}{2}H_2O$ requires K, 12·1%) is sparingly soluble in cold water, almost insoluble in hot or cold alcohol, but fairly readily soluble in hot aqueous alcohol. On warming with dilute acid to about 50°, benzaldehyde is liberated, and a small amount of hydrogen *p*-aminophenyl sulphate separates on cooling; at the same time the sulphate group is partly removed.

Potassium 1-*amino*-2-*naphthyl sulphate* (Found : K, 13·6. $C_{10}H_8O_4NSK,\frac{1}{2}H_2O$ requires K, 13·7%) crystallises from hot water

in slightly pink plates. The solubility in water at 17° is 1·1%. Acids do not precipitate the internal salt from a saturated solution (compare *o*-aminophenyl sulphate). Bromine water gives a dirty green precipitate which changes to yellow with excess of bromine and becomes soluble in ether, from which it crystallises in yellow needles. This precipitate is also slightly soluble in alkali, giving a dark green solution. Ferric chloride gives first an opalescence and then a blue precipitate which changes to brown.

Potassium 4-amino-1-naphthyl sulphate forms hydrated, apparently efflorescent needles from aqueous alcohol. From concentrated solutions hydrochloric or acetic acid precipitates microscopic needles of *hydrogen 4-amino-1-naphthyl sulphate* (Found : equiv., 241. $C_{10}H_9O_4NS$ requires equiv., 239). This crystallises from much hot water in long needles.

All these potassium aminoaryl sulphates can be boiled in dilute mineral acid solution for a few seconds before hydrolysis is detectable. They are thus rather more difficult to hydrolyse than potassium phenyl sulphate itself. Excess of bromine completely removes the sulphate group.

Diazotisation of Aminophenyl and Aminonaphthyl Sulphates.— Hydrogen *p*-aminophenyl sulphate (4·15 g.), suspended in water (40 c.c.), was cooled to 5°, concentrated hydrochloric acid (3 c.c.) added, and *N*-potassium nitrite (1 mol.) run in. The solid product showed all the properties of the diazo-derivative. The method for the naphthyl sulphate was similar.

Coupling with phenols and naphthols. The whole of the suspension obtained in the diazotisation above was poured slowly into a cold solution of resorcinol (2·75 g.) in water (40 c.c.) containing an excess of potassium carbonate. The reddish-orange solution obtained was treated with acetic acid after 1·5 hours and *potassium dihydroxybenzeneazophenyl sulphate* separated (yield, 88%). This crystallised from hot water in orange plates, sparingly soluble in cold water, readily in hot water, alkalis, or alkaline carbonates, and insoluble in alcohol and other organic solvents (Found : K, 10·5. $C_{12}H_9O_6N_2SK,1\frac{1}{2}H_2O$ requires K, 10·4%). An aqueous solution boiled with dilute hydrochloric acid for 15 minutes gave dihydroxybenzeneazophenol as a powder (yield, over 90%), which crystallised in feathery needles from alcohol.

A diazo-solution, prepared as above and run into a solution (50 c.c.) of β-naphthol (3·2 g.) and potassium hydroxide (2·55 g.), gave, after an hour's stirring, a dark red azo-dye containing the sulphate group (yield, 85%); a further quantity was obtained by salting out with potassium chloride.

Potassium 2-hydroxynaphthaleneazophenyl sulphate, crystallised

from 20% aqueous alcohol, is sparingly soluble in cold water and alcohol and moderately easily soluble in hot water (Found: K, 10·1. $C_{16}H_{11}O_5N_2SK,\frac{1}{2}H_2O$ requires K, 10·0%). It forms red flocculent precipitates in neutral solution with barium and calcium chlorides, bright orange-red needles with mercurous nitrate, and a brown flocculent precipitate with magnesium sulphate. No insoluble salts are formed on adding silver, lead, copper, ferrous, ferric, mercuric and aluminium salts. The sulphate group is rapidly and quantitatively removed on boiling with dilute mineral acid, *p*-hydroxybenzeneazo-β-naphthol (dark purple needles, m. p. 193·5°, from aqueous alcohol; Niementowski, *Chem. Zentr.*, 1902, **73**, 938, gives 194°) being formed.

Potassium 4-2′-hydroxynaphthaleneazo-1-naphthyl sulphate is a red solid, fairly easily soluble in warm water. The free acid is precipitated almost completely on addition of mineral acid to a cold solution of the potassium salt, and if the mixture is then boiled the sulphate group is removed, a dark red precipitate of 4-hydroxynaphthaleneazo-β-naphthol, m. p. 236°, being formed (Niementowski, *loc. cit.*, gives 228—229°).

Dyeings with these Sulphato-azo Dyes (V and VI).—Wool patterns (5 g. each) were dyed in the usual manner in dye-baths (total volume, 400 c.c.) containing 0·10 g. of dye, 0·15 g. of sulphuric acid, and 0·50 g. of sodium sulphate. Half of each pattern was then replaced in half of the exhausted dye-bath, restored to its proper volume (200 c.c.) after the addition of sufficient sulphuric acid (40 c.c. of 5% acid) to form a 1% solution. After an hour's boiling, the shades had changed materially, (V) from a bright orange-scarlet to a dull brownish-orange and (VI) from deep red to a dull greyish-violet.

If solutions were made up similar to the above dye-baths but with the minimum of water and allowed to concentrate on the water-bath, complete hydrolysis and precipitation of the dyes were effected in the course of an hour or so. The hydrolysed dye from (V) was brought into partial solution by the addition of alcohol and water and a dyeing performed in this dye-bath; a dull brownish-orange shade resulted similar to that obtained by dyeing with (V) and subsequent hydrolysis with 1% acid: the latter shade, however, was necessarily slightly duller owing to the relatively drastic treatment involved in the hydrolysis on the fibre.

Action of Nitrous Acid on o-*Aminophenyl and* o-*Aminonaphthyl Sulphates.*—To potassium *o*-aminophenyl sulphate (1·5 g.) in water (20 c.c.) at 0°, concentrated hydrochloric acid (2 c.c.) was added, followed by the requisite amount of *N*-potassium nitrite. The product (which gave a precipitate in acid solution with barium

chloride) was run into β-naphthol (1 g.) in water (15 c.c.) containing caustic potash (1·2 g.), and after 3 hour's stirring excess of acetic acid was added. The precipitate was washed with water, dried, and extracted with ether to remove naphthol. It was insoluble in water and organic solvents and melted at 191°. Niementowski (*loc. cit.*) gives for *o*-hydroxybenzeneazo-β-naphthol, m. p. 193°.

The action of nitrous acid on potassium 1-amino-2-naphthyl sulphate and on the azo-derivative produced by coupling diazotised sulphanilic acid with 1-amino-2-naphthyl sulphate was examined, but more water was used to get as much of the amine into solution as possible. The resulting solutions gave precipitates with barium chloride, but did not couple with any alkaline phenoxide except resorcinol, with which they gave blue and dark green colours respectively. The precipitate obtained from 1-amino-2-naphthol hydrochloride and nitrous acid did not couple with resorcinol.

Naphthalene 1 : 2-diazo-oxide was separated in 96% yield from the aqueous solution, by four extractions with ether, as a yellow solid, m. p. 94—95° after recrystallisation from light petroleum (b. p. 60—80°). Bamberger (*Ber.*, 1894, **27**, 679) gives m. p. 95°.

Potassium 4 : 4′-diaminodiphenylene 3 : 3′-disulphate (I; see p. 151) was tetrazotised with excess of acid and excess of sodium acetate was subsequently added. The tetrazo-compound, which soon separated as orange needles, contained no sulphate group and was apparently identical with the bisdiazo-oxide obtained from 3 : 3′-dihydroxybenzidine (p. 151).

Alkaline Reduction of Potassium o-*Nitrophenyl Sulphate.—Reduction with zinc dust.* Caustic potash (0·27 g.) in water (50 c.c.) was added during 5 hours to a suspension of zinc dust (20 g.; 60% Zn) in a solution of potassium *o*-nitrophenyl sulphate (10 g.) in water (100 c.c.) with mechanical stirring at 60°; then, as reduction was incomplete, a few drops of potassium hydroxide solution were added from time to time, the temperature being raised to 70°, until no more nitro-compound remained (40 hours altogether). The solution was filtered, the residue was washed well with hot water, and the united filtrates were divided into two equal portions A and B.

Portion A was evaporated nearly to dryness under reduced pressure and the solid obtained was dissolved in 85% alcohol at 70°. On cooling, a mixture of the hydrazo-compound (colourless needles) and the azo-compound (yellow crystals) separated (0·8 g.). The filtrate, treated with ether, deposited a mixture containing more of the yellow compound (0·9 g.). Recrystallisations from 80% alcohol separated the two compounds (yield, 36% of the theoretical yield from 5 g. of nitrophenyl sulphate).

Portion B was treated with a few drops of hydrochloric acid in

the cold. The benzidine derivative was rapidly precipitated (0·76 g.; 19% from 5 g. of nitrophenyl sulphate, *i.e.*, 19% of the nitrophenyl sulphate is converted into hydrazo-compound and 17% into azo-compound).

Such modifications as the use of higher concentrations of nitro-compound, more alkali, purer zinc dust, higher temperature, and aqueous alcohol as the solvent gave smaller yields.

Reduction with sodium amalgam. 2% Sodium amalgam (130 g.) was added to a vigorously stirred solution of potassium *o*-nitrophenyl sulphate (2·69 g.) in water (50 c.c.) in the course of 3 hours. After standing over-night, the white solid was separated, washed with a little water and dissolved in warm water, and the solution was treated with hydrochloric acid, cooled rapidly, and filtered. The mother-liquor from the reduction was treated with zinc dust at 50—60° until the red colour had vanished; hydrochloric acid was then added to the filtered solution. Potassium 4 : 4′-diaminodiphenylene 3 : 3′-disulphate separated in both cases (0·69 g. and 0·46 g., respectively; yield, 52%).

Potassium azobenzene 2 : 2′*-disulphate*, $(KO{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}N{:})_2$, crystallises from hot water in orange hexagonal plates insoluble in organic solvents (Found : K, 16·9. $C_{12}H_8O_8N_2S_2K_2,\frac{1}{2}H_2O$ requires K, 17·0%). It is rapidly hydrolysed by hydrochloric acid at 70° (compare nitrophenyl sulphate), giving *oo*′-dihydroxyazobenzene, which crystallises from aqueous alcohol in yellow needles, m. p. 171° (Weselsky and Benedikt, *Ber.*, 1878, **11**, 398; *Annalen*, 1879, **196**, 344, give 171°). The orange-red solution in aqueous sodium hydroxide is rapidly decolorised by warming with zinc dust and then gives a white precipitate of the benzidine derivative when treated with hydrochloric acid.

Potassium hydrazobenzene 2 : 2′-disulphate crystallises from hot water in colourless feathery needles stable in the air. A cold neutral solution also resists oxidation, but the azo-compound is formed when air is passed through a warm alkaline solution and rapidly by warm ferric chloride or nitrous acid. The solubility in water is 3·2% at 19° and 5·4% at 32°. A saturated solution of the hydrazo-compound at 20°, when treated with concentrated hydrochloric acid (0·1 vol.), deposits a 95% yield of 4 : 4′*-diaminodiphenylene dihydrogen* 3 : 3′*-disulphate* in a few minutes. This crystallises in colourless needles from a large bulk of water. It is insoluble in cold water, hot or cold alcohol and ether, but readily soluble in alkalis, ammonia, sodium carbonate and potassium acetate. It is rather more stable to acid hydrolysis than the aminophenyl sulphates [Found : equiv., 210. $C_{12}H_{10}N_2(SO_4H)_2,2\frac{1}{2}H_2O$ requires equiv., 211].

Potassium 4 : 4′-*diaminodiphenylene* 3 : 3′-*disulphate* (I) is prepared by the addition of a concentrated potassium hydroxide solution to a warm aqueous suspension of the free acid. It separates in elongated plates, usually slightly brown in colour (Found : K, 16·5. $C_{12}H_{10}O_8N_2S_2K_2,H_2O$ requires K, 16·6%). The free acid is precipitated from solutions of this salt by mineral acids but not by acetic acid (compare *p*-aminophenyl sulphate).

Characteristic colour reactions similar to those given by benzidine are obtained with bromine and ferric chloride. The cautious addition of very dilute bromine water causes the following series of colour changes : green, blue, olive-green, brown, red; the last colour fades on standing and a test with barium chloride then shows that elimination of the sulphate group has taken place. An intense blue coloration or a dark blue precipitate is obtained with ferric chloride.

Hydrolysis to 3 : 3′-*dihydroxybenzidine.* A suspension of 3·33 g. of the sulphate in 150 c.c. of boiling water was boiled with concentrated hydrochloric acid (20 c.c.) for 2½ hours and the solution was then cooled, filtered, and treated with an excess of sodium acetate solution; the light brown solid precipitated was washed with water and alcohol (yield, almost quantitative).

Demethylation of dianisidine. Powdered dianisdine (10 g.) and hydriodic acid (100 c.c., b. p. 127°) were heated in a bath at 138°; after 24 hours the temperature was raised and the unused hydriodic acid distilled off. A solution of the residue in hot water was filtered, sodium bisulphite added to remove iodine, and the base precipitated with sodium acetate solution. The product was washed and boiled with alcohol to remove dianisidine (yield, 90%).

The dihydroxybenzidine obtained by these two methods is a white powder, slowly darkening on exposure to air, very soluble in alkalis and in hot dilute mineral acids, very sparingly soluble in hot water and organic solvents, and soluble in, but not crystallisable from, hot 80—90% acetic acid. A solution of the hydrochloride in water, when treated with sodium nitrite solution, deposits orange needles which explode violently when heated and show a low reactivity to most phenols. It combines slowly with R-salt and Schäffer's acid in alkaline solution to form purple-blue substantive dyes, rather redder than those from dianisidine. A blue insoluble dye is slowly formed with sodium β-naphthoxide and a fine crimson colour is at once formed with alkaline resorcinol. No combination took place with Naphthol AS.

Acetylation of dihydroxybenzidine. Dihydroxybenzidine was dissolved by boiling with glacial acetic acid (50 c.c.) with subsequent addition of water (12 c.c.). The solution was filtered and acetic

anhydride (50 c.c.) added at about 50°. The almost colourless solid was filtered off after 36 hours and washed with acetic acid (yield, 90%). *Diacetyldihydroxybenzidine* is insoluble in most organic solvents. After crystallising from benzyl alcohol and drying at 150°, it melts at 292° (decomp.) (Found : N, 9·2. $C_{16}H_{16}O_4N_2$ requires N, 9·3%). It is insoluble in acids, but readily soluble in alkalis. An attempt to methylate it to diacetyldianisidine did not give any product insoluble in alkali.

Dehydration. The diacetyl compound (0·75 g.) was heated at 300—320° for ¾ hour and the *dianhydro*-derivative (IV) extracted from the dark mass with boiling alcohol. The extract was filtered and diluted at its boiling point with water, a little animal charcoal added, and the filtered solution allowed to crystallise (yield, 45%). The anhydro-compound is very soluble in benzene, chloroform, acetic acid and hot alcohol and crystallises from the last solvent in ill-defined plates, m. p. 164—165° (Found : N, 10·5. $C_{16}H_{12}O_2N_2$ requires N, 10·6%). It is insoluble in hot alkalis but dissolves in concentrated hydrochloric acid. If this solution is diluted somewhat and heated, dihydroxybenzidine remains in the solution as the hydrochloride. A white precipitate which was noticed in some experiments was dissolved by caustic soda and was probably the diacetyl derivative.

The dihydroxybenzidine obtained from the sulphate was also converted into the diacetyl compound and its dianhydro-derivative and these were shown to be identical with those described above.

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