The Oxidation of Some Aromatic Amines with Persulphate.

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The action of alkaline persulphate on a number of substituted aromatic amines has been investigated. In all cases *o*-aminophenyl sulphates are found, irrespective of the orienting influence of other functional groups.

The action of alkaline persulphate on a number of simple aromatic amines yields the corresponding *o*-aminophenyl sulphate esters (Boyland, Manson, and Sims, *J.*, 1953, 3623), and its action on substituted aromatic amines has now been investigated. In all cases, substituted *o*-aminophenyl sulphates were obtained, and there was no evidence of the introduction of the sulphate group in any other position.

The esters were usually isolated as their sodium or potassium salts and, in most cases, acidification of aqueous solutions of the salts yielded the crystalline free acids. All the esters described were readily hydrolysed by hot acid to the corresponding aminophenols, so that the positions of the sulphate groups could be determined. In some cases, where the identities of the aminophenols were in doubt, the dibenzoyl derivatives were converted into the corresponding 2-phenylbenzoxazoles (and benzoic acid) by the action of heat, reactions characteristic of the derivatives of *o*-aminophenols. The esters, together with the derived aminophenols and 2-phenylbenzoxazoles, are listed in the Table.

Substituted aniline	Substituted *o*-aminophenyl hydrogen sulphate and *o*-aminophenol	Substituted 2-phenyl-benzoxazole	Substituted aniline	Substituted *o*-aminophenyl hydrogen sulphate and *o*-aminophenol	Substituted 2-phenyl-benzoxazole
2-Methyl	3-Methyl [1]	4-Methyl	4-Phenyl	5-Phenyl	(2 : 6-Diphenyl-benzoxazole)
3-Methyl	4-Methyl	—			
4-Methyl	5-Methyl	6-Methyl	4-Bromo	5-Bromo	6-Bromo
2-Carboxy	3-Carboxy	—	3-Chloro	4-Chloro	—
4-Carboxy	5-Carboxy	—	2-Nitro	3-Nitro [1]	—
4-Sulpho	5-Sulpho [2]	—			

[1] The free sulphuric esters did not separate when aqueous solutions of the potassium salts were acidified (cf. 2-aminophenyl hydrogen sulphate, Burkhardt and Wood, *J.*, 1929, 141).
[2] A monopotassium salt was obtained when an aqueous solution of the disalt was acidified.

Examination of the crude sulphates and their acid-hydrolysis products on paper chromatograms showed that only one major product was usually present. In the oxidations of *m*-toluidine and *m*-chloroaniline, however, second products, present in much smaller amounts than the first, were also detected. Both these amines have unsymmetrical free positions *ortho* to the amino-groups, and it seems probable that isomeric *ortho*-aminophenyl sulphates are formed in these cases, although the products isolated were substituted in the 4-position to the methyl and chloro-group respectively. Examination of the oxidation products of anthranilic acid showed the presence of a small amount of a second ester, which we have been unable to identify; the acid hydrolysis products of the crude sulphate do not contain 5-hydroxyanthranilic acid. The acid hydrolysis products of the crude sulphates derived from aniline and dimethylaniline (cf. Boyland *et al.*, *loc. cit.*) showed the presence of *o*-aminophenol and *o*-dimethylaminophenol respectively, but no *para*-substituted amines could be detected.

The aminophenol derived from the sulphanilic acid oxidation had m. p. >300° and, although Doub, Schaefer, Bambas, and Walker (*J. Amer. Chem. Soc.* 1951, **73**, 903) report that 4-amino-2-hydroxybenzenesulphonic acid (the other possible product from our oxidation) has m. p. 275° (decomp.), a preparation of this acid (Thorpe and Williams, *Biochem. J.*, 1941, **35**, 61) did not melt below 300°. Thorpe and Williams (*loc. cit.*; cf. Miller, Mosher, Gray, and Whitmore, *J. Amer. Chem. Soc.*, 1949, **71**, 3559) prepared pyridinium

4-acetamido-2-acetoxybenzenesulphonate, m. p. 170—171°, from the acid with acetic anhydrine and pyridine, whereas our acid, under similar conditions, yielded a pyridinium salt of m. p. 156—158°. It is concluded, therefore, that our acid is 4-amino-3-hydroxybenzenesulphonic acid.

The oxidations were accompanied by the formation of coloured products, evidently arising from attack on the amino-groups; these have not been investigated in detail. Witt and Kopetschni (*Ber.*, 1912, **45**, 1134) found that acidified persulphate (catalysed with silver nitrate) oxidised aromatic amines to nitro-compounds.

Under our experimental conditions, persulphate does not yield sulphuric esters with benzoic acid, nitrobenzene, toluene, benzene, or naphthalene. Aniline, 2-naphthylamine, and dimethylaniline readily form sulphuric esters (Boyland *et al.*, *loc. cit.*), but persulphate is without effect on acetanilide and 2-acetamidonaphthalene. Similarly, pyridine and *cyclo*hexylamine do not yield sulphuric esters with this reagent. The reaction differs from Elbs's persulphate oxidation of phenols, where substitution occurs mainly in the *para*-position, and less readily in the *ortho*-position when the *para*-position is blocked. It is hoped that experiments now in hand will provide some evidence of the mechanism involved in our oxidation.

Experimental

In most cases the m. p.s of the free-acid esters depend on the rate of heating. Occasionally, preparations of these acids darkened at temperatures many degrees below the normal m. p., and did not then melt below 300°.

Persulphate Oxidations.—The amine (5 g.), in water (250 ml.), was brought into solution by the addition of acetone, or, in the case of the amines containing an acidic group, by the addition of 2N-sodium or -potassium hydroxide. 2N-Sodium or -potassium hydroxide (20% excess) was added, followed by the theoretical amount of sodium or potassium persulphate, added in aqueous solution during 8 hr. with continuous stirring. The mixture was kept overnight, evaporated to 200 ml. under reduced pressure, and filtered. The solution was washed with ether and treated as indicated below.

Oxidation of the Toluidines.—The solution obtained as described above was extracted with butanol (6 × 150 ml.), the butanol extract was dried (Na_2SO_4), and a slight excess of 2N-potassium hydroxide was added. The mixture was evaporated under reduced pressure, and the product was washed with ethanol (2 × 20 ml.) and crystallised from 90% aqueous ethanol.

(*a*) *o*-Toluidine gave *potassium* 2-*amino*-m-*tolyl sulphate* (1·9 g.) as flat needles (Found: C, 35·4; H, 3·7; N, 5·6; S, 13·0; K, 15·9. $C_7H_8O_4NSK$ requires C, 34·9; H, 3·3; N, 5·8; S, 13·3; K, 16·2%).

This salt (500 mg.), in water (2 ml.) and concentrated hydrochloric acid (1 ml.), was heated to 100° for 30 min., and the solution was neutralised with 2N-sodium hydroxide. Extraction with ether and evaporation of the solvent yielded 2-amino-*m*-cresol (210 mg.); from light petroleum (b. p. 80—100°) it formed plates, m. p. 149—150° (Found: N, 11·1. Calc. for C_7H_9ON: N, 11·4%). Hodgson and Beard (*J.*, 1925, 498) report m. p. 150°. The *dibenzoate* crystallised from aqueous methanol in needles, m. p. 155—156° (Found: C, 75·6; H, 5·15; N, 4·1. $C_{21}H_{11}O_3N$ requires C, 76·1; H, 5·2; N, 4·2%).

When the dibenzoate (50 mg.) was heated to 210—220° for 3 hr., benzoic acid (10 mg.; m. p. and mixed m. p. 121°) sublimed. The residue was extracted with light petroleum (b. p. 60—80°) (2 ml.), the extract was washed with aqueous sodium hydrogen carbonate, and the solvent was evaporated. The product crystallised from aqueous ethanol to yield 4-*methyl*-2-*phenylbenzoxazole* (25 mg.) as needles, m. p. 92—93° (Found: C, 80·7; H, 5·45; N, 7·15. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%).

(*b*) *m*-Toluidine gave *potassium* 2-*amino*-p-*tolyl sulphate* (Me = 4) (2·55 g.), as light brown elongated plates (Found: N, 5·6; S, 13·1. $C_7H_8O_4NSK$ requires N, 5·8; S, 13·3%).

When a solution of the salt (500 mg.), in water (2 ml.) and ethanol (1 ml.), stood with concentrated hydrochloric acid (0·5 ml.) for some hours, 2-*amino*-p-*tolyl hydrogen sulphate* (260 mg.) separated. The acid was purified by dissolving it in N-sodium hydroxide and acidifying the solution; it formed needles, m. p. 286—288° (decomp.) (Found: C, 41·3; H, 4·5; N, 6·8; S, 16·3%; equiv., 198. $C_7H_9O_4NS$ requires C, 41·4; H, 4·5; N, 6·9; S, 15·8%; equiv., 203).

The ester (500 mg.) was hydrolysed as before, to yield 2-amino-*p*-cresol (226 mg.), separating

from light petroleum (b. p. 80—100°) in needles, m. p. 134—135° (Found: N, 11·5. Calc. for C_7H_9ON: N, 11·4%). Nölting and Kohn (*Ber.*, 1884, **17**, 351) report m. p. 135°. The dibenzoate formed needles (from aqueous ethanol), m. p. and mixed m. p. 191—192° (Found: C, 75·7; H, 5·4; N, 4·5. Calc. for $C_{21}H_{11}O_3N$: C, 76·1; H, 5·2; N, 4·2%), and the diacetate crystallised from light petroleum (b. p. 80—100°) in plates, m. p. and mixed m. p. 143—144° (Found: N, 6·7. Calc. for $C_{11}H_{13}O_3N$: N, 6·8%). Auwers and Czerny (*ibid.*, 1898, **31**, 2692) and Auwers and Eisenlohr (*Annalen*, 1909, **369**, 223) give m. p. 190—191° and 145° respectively for these derivatives.

(*c*) *p*-Toluidine gave *potassium* 6-*amino*-m-*tolyl sulphate* (3·2 g.) as light brown elongated plates (Found: N, 5·8%).

6-*Amino*-m-*tolyl hydrogen sulphate* (210 mg.) separated when the above salt (500 mg.), in water (2 ml.), was acidified with concentrated hydrochloric acid (0·5 ml.). The ester was purified by precipitation with acid from a solution in warm N-sodium hydroxide; it formed plates, m. p. 258—260° (decomp.) (Found: C, 41·2; H, 4·5; N, 6·8; S, 15·75%; equiv., 210).

The *sodium* salt (prepared from the acid) separated from water in light brown irregular plates (Found: N, 5·9; S, 14·7. $C_7H_8O_4NSNa$ requires N, 6·2; S, 14·2%).

The acid (500 mg.) was hydrolysed as before, to yield 6-amino-*m*-cresol (210 mg.), crystallising from light petroleum (b. p. 80—100°) in needles, m. p. 159—160° (decomp.) (Found: C, 68·5; H, 7·3; N, 11·0. Calc. for C_7H_9ON: C, 68·3; H, 7·4; N, 11·4%). Auwers, Borsche, and Weller (*Ber.*, 1921, **54**, 1291) give m. p. 157—159°, and Proskouriakoff and Titherington (*J. Amer. Chem. Soc.*, 1930, **52**, 3978), m. p. 162° (decomp.). The dibenzoate formed needles, m. p. 145—146°: after four recrystallisations from methanol it had m. p. 150° (Found: N, 4·3. Calc. for $C_{21}H_{17}O_3N$: N, 4·2%). Auwers, Borsche, and Weller (*loc. cit.*) report m. p. 152° after four, and m. p. 162—163° after six recrystallisations of this derivative from methanol. The *diacetate* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 153—154° (Found: N, 6·5. $C_{11}H_{13}O_3N$ requires N, 6·8%).

When the dibenzoyl derivative (600 mg.) was heated to 220—230° for 4 hr., benzoic acid (130 mg.; m. p. and mixed m. p. 121°) sublimed. The residue was extracted with light petroleum (b. p. 60—80°), and evaporation of the solvent yielded 6-*methyl*-2-*phenylbenzoxazole* (302 mg.) as needles (from aqueous ethanol), m. p. 98—99° (Found: C, 80·5; H, 5·6; N, 6·5. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%). An ethanolic solution had a violet fluorescence in ultra-violet light.

Oxidation of the Aminobenzoic Acids.—The solution obtained as described above was acidified to pH 2 with 2N-sulphuric acid, and, after filtration, extracted with ether for 24 hr. The pH of the aqueous solution was adjusted to 6 with 2N-potassium hydroxide, and the solution was evaporated under reduced pressure. The residue was extracted with boiling methanol (4 × 50 ml.), and the combined extracts were evaporated to 50 ml. and treated with ether (150 ml.). After a few minutes the coloured precipitate was removed, ether (1 l.) was added to the filtrate during 2 hr., and the product was collected.

(*a*) Anthranilic acid gave a *monopotassium* salt (1·9 g.) of the sulphuric ester, slowly separating from aqueous ethanol in needles, m. p. 210—211° (decomp.) (Found: N, 5·3; S, 12·3; K, 14·8%; equiv., 275. $C_7H_6O_6NSK$ requires N, 5·2; S, 11·8; K, 14·4%; equiv., 271). When sodium persulphate (8·7 g.) was used in the oxidation, a *monosodium* salt was obtained as needles (from methanol–ether) (Found: N, 5·7. $C_7H_6O_6NSNa$ require N, 5·5%).

When the above solution was evaporated at pH > 7, the disalts of the sulphuric ester were obtained. The dipotassium salt formed a gum, but the *disodium* salt was obtained as needles (from methanol–ether) (Found: N, 5·0; S, 11·8. $C_7H_5O_6NSNa_2$ requires N, 5·05; S, 11·6%).

The above monopotassium salt (1 g.), in water (2 ml.) and concentrated hydrochloric acid (0·5 ml.), was kept overnight at 0°; 2-*amino*-3-*carboxyphenyl hydrogen sulphate* separated; from water it formed needles, m. p. 285—288° (decomp.) (Found: N, 6·0; S, 13·9%; equiv., 115. $C_7H_7O_6NS$ requires N, 6·0; S, 13·7%; equiv., 116). Solutions of the salts had a faint blue fluorescence in daylight, and a bright blue fluorescence in ultra-violet light.

The ester (1 g.) was hydrolysed with hydrochloric acid, and 2N-sodium hydroxide was added dropwise to the solution until crystals separated. 3-Hydroxyanthranilic acid (620 mg.), purified by precipitation with acid from a solution in aqueous sodium hydroxide containing a trace of sodium hydrogen sulphite, was obtained in needles, decomp. 230—250° (Found: C, 54·5; H, 4·9; N, 9·0. Calc. for $C_7H_7O_3N$: C, 54·9; H, 4·6; N, 9·15%). Methyl 3-hydroxyanthranilate, prepared from the acid with hydrogen chloride in methanol (Musajo, Spada, and Coppini, *J. Biol. Chem.*, 1952, **196**, 185), crystallised from light petroleum (b. p. 60—80°) in plates, m. p. and mixed m. p. 94° (Found: N, 8·2. Calc. for $C_8H_9O_3N$: N, 8·4%).

(*b*) *p*-Aminobenzoic acid gave a *monopotassium* salt (2·1 g.) of the sulphuric ester, separating from ether–methanol in needles (Found: N, 5·0; S, 11·8; K, 14·0%; equiv., 273). The salt (1 g.), in water (2 ml.), was kept overnight at 0° with concentrated hydrochloric acid (0·5 ml.). *2-Amino-5-carboxyphenyl hydrogen sulphate* (310 mg.) separated; from ether–ethanol it formed pale pink prismatic needles, m. p. 208—210° (decomp.) (Found: N, 6·3; S, 13·4%; equiv., 119).

The ester (500 mg.) was hydrolysed with hydrochloric acid, the pH of the solution was adjusted to 5 with 2N-sodium hydroxide, and the solution was extracted with ether. Evaporation of the ether afforded 4-amino-3-hydroxybenzoic acid (210 mg.), separating from aqueous ethanol or from ethanol–benzene in light brown needles, m. p. 210—211°, raised to 216—217° by three recrystallisations from aqueous ethanol (Found: N, 8·8%; equiv. 156. Calc. for $C_7H_7O_3N$: N, 9·15%; equiv., 153). Bray, Lake, Neale, Thorpe, and Wood (*Biochem. J.*, 1948, **42**, 434) give m. p. 226°, and Einhorn and Pfyl (*Annalen*, 1900, **311**, 43) m. p. 216°. The methyl ester, prepared from the acid with hydrogen chloride in methanol (cf. Musajo *et al.*, *loc. cit.*), crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 119—120° (Found: N, 8·25. Calc. for $C_8H_9O_3N$: N, 8·4%). Einhorn *et al.* (*loc. cit.*) report m. p. 121° for methyl 4-amino-3-hydroxybenzoate.

Oxidation of Sulphanilic Acid.—The aqueous solution was acidified to pH 4 with 2N-sulphuric acid, and filtered, and the filtrate was washed with butanol (10 × 200 ml.). The pH of the solution was adjusted to 7 with 2N-potassium hydroxide, and the solution was evaporated under reduced pressure. The residue was extracted with boiling methanol (4 × 100 ml.), and the extracts were evaporated to 50 ml. and allowed to crystallise; a reddish-brown solid and a brown gum separated. Two crystallisations of the solid from 90% ethanol afforded the *dipotassium* salt of *2-amino-5-sulphophenyl hydrogen sulphate* (2·8 g.) as colourless elongated plates (Found: N, 3·8; K, 22·3. $C_6H_5O_7NS_2K_2$ requires N, 4·1; K, 22·6%).

When the above salt (750 mg.), in water (2 ml.) and concentrated hydrochloric acid (0·5 ml.), was kept for some hours, the *monopotassium* salt (480 mg.) separated; from water it formed needles, m. p. 293—294° (decomp.) (Found: N, 4·7; S, 21·0; K, 13·0%; equiv., 303. $C_6H_6O_7NSK$ requires N, 4·6; S, 20·9; K, 12·7%; equiv., 307).

When this salt (200 mg.) was heated to 100° for 30 min. with concentrated hydrochloric acid (1 ml.), 4-amino-3-hydroxybenzenesulphonic acid (92 mg.) separated; it crystallised from water in needles, m. p. >300° (Found: C, 38·0; H, 4·0; N, 7·2. Calc. for $C_6H_7O_4NS$: C, 38·1; H, 3·7; N, 7·4%).

The acid (500 mg.) slowly dissolved in a mixture of pyridine (2 ml.) and acetic anhydride (1 ml.). After 24 hr., the excess of the reagents was evaporated and the oil, in ethanol (2 ml.), was treated with dry ether at 0°. The solid was recrystallised four times from ether–ethanol, to yield *pyridinium 4-acetamido-3-acetoxybenzenesulphonate* (400 mg.) as prismatic needles, m. p. 156—158° (Found: N, 8·0, 7·9. $C_{15}H_{16}O_6N_2S$ requires N, 7·95%). A mixture with pyridinium 4-acetamido-2-acetoxybenzenesulphonate (m. p. 167—170°) had m. p. 138—143°.

4-Amino-2-hydroxybenzenesulphonic acid, prepared from *m*-aminophenol by the method of Thorpe and Williams (*loc. cit.*), crystallised from water in needles, m. p. >300° (Found: N, 7·55%). Doub *et al.* (*loc. cit.*) report m. p. 275°.

Oxidation of p-*Diphenylylamine.*—The aqueous solution obtained as described above was evaporated to 100 ml. under reduced pressure and filtered, and the filtrate was kept overnight at 0°. *Potassium 4-amino-3-diphenylyl sulphate* (225 mg.) separated; from aqueous ethanol it formed light brown plates (Found: N, 4·7; S, 10·9. $C_{12}H_{10}O_4NSK$ requires N, 4·6; S, 10·6%). With sodium persulphate the *sodium* salt was obtained, separating from aqueous ethanol in plates (Found: N, 4·9. $C_{12}H_{10}O_4NSNa$ requires N, 4·9%).

The filtrate was acidified with 2N-sulphuric acid and kept at 0° overnight, *4-amino-3-diphenylyl hydrogen sulphate* (610 mg.) separating; on repeated recrystallisation from aqueous ethanol it formed elongated plates, m. p. 292—293° (decomp.) (Found: C, 54·6; H, 4·4; N, 5·4; S, 11·8%; equiv., 259. $C_{12}H_{11}O_4NS$ requires C, 54·3; H, 4·2; N, 5·3; S, 12·1%; equiv., 265). The above acid (mixed m. p.) was also obtained when a suspension of the potassium salt in water was acidified. Solutions of the ester had a blue fluorescence in ultra-violet light.

The ester (500 mg.), in water (10 ml.), was heated to 100° with concentrated hydrochloric acid (3 ml.) for 30 min. Water (250 ml.) was added and the mixture was heated under reflux for 15 min. and filtered. 4-Amino-3-hydroxydiphenyl sulphate (280 mg.) separated from the filtrate in plates. The filtrate was neutralised with 2N-sodium hydroxide, when *4-amino-3-hydroxydiphenyl* (120 mg.) separated; from aqueous ethanol it formed plates, m. p. 182—184°

(Found : C, 77·6; H, 6·2; N, 7·5. $C_{12}H_{11}ON$ requires C, 77·8; H, 6·0; N, 7·6%). Ethanolic solutions had a light blue fluorescence in ultra-violet light.

The *dibenzoate* separated from aqueous ethanol or from light petroleum (b. p. 80—100°) in needles, m. p. 148—149° (Found : C, 79·2; H, 5·1; N, 3·4. $C_{26}H_{19}O_3N$ requires C, 79·4; H, 4·9; N, 3·6%). The *diacetate* crystallised from aqueous ethanol as needles, m. p. 123—124° (Found : N, 4·9. $C_{16}H_{15}O_3N$ requires N, 5·2%).

The dibenzoate (100 ml.) was heated to 200—210° for 6 hr.; benzoic acid (20 mg.; m. p. and mixed m. p. 121°) sublimed. The residual gum was extracted with light petroleum (b. p. 60—80°) (5 ml.), the solvent was evaporated, and the residue crystallised from aqueous ethanol, to give 2 : 6-*diphenylbenzoxazole* (55 mg.) as needles, m. p. 107° (Found : N, 5·0. $C_{19}H_{13}ON$ requires N, 5·2%), An ethanolic solution of the benzoxazole had a violet fluorescence in ultra-violet light.

Oxidation of p-*Bromoaniline*.—The aqueous solution was acidified with 2N-sulphuric acid, the precipitate was separated, the pH of the filtrate was adjusted to 7 with 2N-potassium hydroxide, and the solution was evaporated to dryness under reduced pressure. The residue was extracted with methanol (3 × 100 ml.), and the extract was evaporated to small bulk and allowed to crystallise. *Potassium 2-amino-5-bromophenyl sulphate* (1·9 g.) separated from 90% ethanol in flat needles (Found : N, 4·6; S, 10·5. $C_6H_5O_4NBrSK$ requires N, 4·6; S, 10·5%).

When the above salt (1 g.), in water (5 ml.), was kept overnight with concentrated hydrochloric acid (0·5 ml.), *2-amino-5-bromophenyl hydrogen sulphate* was obtained; from water it formed greyish plates, m. p. 239—240° (decomp.) (Found : N, 5·3; S, 12·0%; equiv., 270. C_6H_6ONBrS requires N, 5·2; S, 12·0%; equiv., 268).

The *sodium* salt (prepared from the acid) crystallised from water in brownish irregular plates (Found : N, 4·55. $C_6H_5O_4NBrSNa$ requires N, 4·8%).

The ester (500 mg.) in water (2 ml.) was hydrolysed with hydrochloric acid (2 ml.) as before, and 2N-sodium hydroxide was added to the cooled solution until the product separated. 5-Bromo-*o*-aminophenol (190 mg.) crystallised from water in plates, m. p. 149·5—150·5° (Found : N, 7·5. Calc. for C_6H_6ONBr : N, 7·45%). Hodgson and Kershaw (*J.*, 1928, 2703) report m. p. 150°. The *dibenzoyl* derivative separated from aqueous methanol in needles, m. p. 133—134° (Found : C, 60·5; H, 3·7; N, 3·5. $C_{20}H_{14}O_3NBr$ requires C, 60·6; H, 3·6; N, 3·5%).

When the dibenzoyl derivative was heated to 220—225° for 3 hr., benzoic acid (m. p. and mixed m. p. 121°) sublimed, and the product was isolated with light petroleum (b. p. 60—80°). Evaporation of the solvent afforded *6-bromo-2-phenylbenzoxazole*; from aqueous ethanol it formed pale pink plates, m. p. 104—105° (Found : N, 5·2; Br, 29·15. $C_{13}H_8ONBr$ requires N, 5·1; Br, 29·1%).

Oxidation of m-*Chloroaniline*.—The aqueous solution was treated as in the last experiment, and the product was isolated as before. *Potassium 2-amino-4-chlorophenyl sulphate* separated from aqueous ethanol in brownish plates (Found : N, 5·2; S, 12·2. $C_6H_5O_4NClSK$ requires N, 5·35; S, 12·25%).

Acidification of an aqueous solution of the potassium salt with hydrochloric acid yielded *2-amino-4-chlorophenyl hydrogen sulphate*, slowly separating from water in prismatic needles, m. p. 268—271° (decomp.) (Found : N, 6·1; S, 14·1. $C_6H_6O_4NClS$ requires N, 6·3; S, 14·3%)

The acid ester was hydrolysed in the usual manner with hydrochloric acid, and the product was isolated with ether, to yield 4-chloro-*o*-aminophenol in plates (from water), m. p. 137° (Found : N, 9·7. Calc. for C_6H_6ONCl: N, 9·8%). Upson (*J. Amer. Chem. Soc.*, 1904, **32**, 40) reports m. p. 138°, and Mottier (*Arch. Sci. phys. nat.*, 1934, **16**, 301) m. p. 137·5—138·5°. The *dibenzoate* crystallised from aqueous ethanol in needles, m. p. 157—158° (Found : C, 68·25; H, 4·3; N, 3·9. $C_{20}H_{14}O_3NCl$ requires C, 68·3; H, 4·1; N, 4·0%).

Oxidation of o-*Nitroaniline*.—The aqueous solution was acidified with 10N-sulphuric acid, washed with ether (2 × 250 ml.), and extracted with butanol (8 × 150 ml.). The extract was dried (Na_2SO_4) and a slight excess of 2N-potassium hydroxide was added. The mixture was evaporated under reduced pressure and the dark residue was extracted with methanol (3 × 50 ml.). The methanolic extract was evaporated to small bulk and allowed to crystallise. The solid, in a minimum of methanol, was treated with an equal volume of ether. The coloured precipitate was filtered off and the residue was treated with excess of ether to yield *potassium 2-amino-3-nitrophenyl sulphate* (1·2 g.) as a yellow powder. After three recrystallisations from ether–methanol it formed yellow needles (Found : C, 26·4; H, 2·2; N, 10·0; S, 11·3. $C_6H_5O_6N_2SK$ requires C, 26·5; H, 1·85; N, 10·3; S, 11·3%).

The potassium salt was hydrolysed with hot hydrochloric acid, and the product was isolated with ether. 3-Nitro-*o*-aminophenol was obtained; from water it formed red needles, m. p.

210—212° (decomp.) (Found: N, 18·0. Calc. for $C_6H_6O_3N_2$: N, 18·2%). King (*J.*, 1927, 1058) gives m. p. 216—217° and Fourneau, Tréfouël, and Tréfouël (*Bull. Soc. chim.*, 1927, **41**, 448) give m. p. 212°.

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