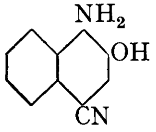
320. *Kationoid Reactivity of Aromatic Compounds. Part II. The Action of Potassium Cyanide on* 1-*Nitroso*-2-*naphthol and* 1-*Benzeneazo*-2-*naphthol.*

By W. BRADLEY and ROBERT ROBINSON.

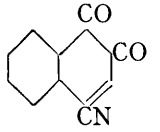
IN Part I (J., 1932, 1254) we discussed the general plan and theoretical basis of this investigation, and the present section extends analogies in reactivity existing between quinones and nitrosophenols, and *o*-hydroxyazo-compounds.

From the fact that sodium hydrogen sulphite converts many quinones into sulphonic acids of the related quinols, combined with the occurrence of a similar reaction with 1-nitroso-2-naphthol, we concluded that the behaviour of the latter substance towards other anionoid agents should be of interest.

As the typical anionoid reagent we selected potassium cyanide and found that 1-nitroso-2-naphthol (as β-naphthaquinoneoxime) reacts with this salt in aqueous solution at 80—90° with formation of 1-*amino*-2-*hydroxy*-4-*cyanonaphthalene* (I), a substance which shows some unexpected properties. For example, we have not yet been able to diazotise the base. Nevertheless, the constitution follows from its transformations; it yields a *trimethyl* derivative, $C_{10}H_5(CN)(OMe)(NMe_2)$ (II), which can be hydrolysed to an *amide*, $C_{10}H_5(CO{\cdot}NH_2)(OMe)(NMe_2)$ (III). Further, on oxidation with chromic acid, 4-*cyano*-β-*naphthaquinone* (IV) is produced; this may be reduced to a quinol and then methylated and hydrolysed to 3 : 4-*dimethoxy*-1-*naphthoic acid*, $C_{10}H_5(OMe)_2{\cdot}CO_2H$ (V). The acetylation of (I) furnishes a *triacetyl* derivative, $C_{10}H_5(CN)(OAc)(NAc_2)$ (VI), which loses two acetyl groups on gentle hydrolysis by means of alkalis. The *methyl ether* of the product (VII) could be independently synthesised by the method schematically illustrated below, and by hydrolysis, followed by oxidation with chromic acid, it yielded 2-*methoxy*-1 : 4-*naphthaquinone*. This quinone was also obtained by the oxidation of the *acetamidomethoxyaminonaphthalene* figured below.



(I.)



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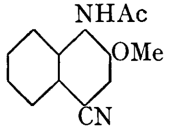
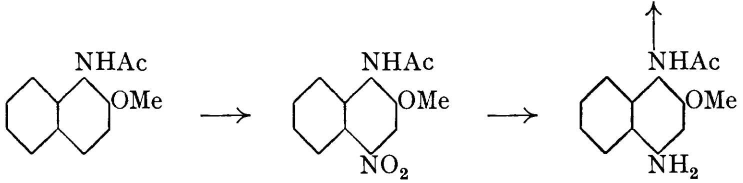


(VII.)



If, as many chemists believe, benzeneazo-2-naphthol possesses the hydrazone structure, its reactions should simulate those of nitroso-2-naphthol (β-naphthaquinoneoxime). Actually the formation of the aminohydroxycyanonaphthalene (I) from benzeneazo-2-naphthol and sulphobenzeneazo-2-naphthol by the action of potassium cyanide is a very smooth process.

In this, as in all similar cases, we regard the reaction as essentially the addition of cyanidion to the katio-enoid system of the azo-compound in its quinonehydrazone modification; the subsequent stages are probably very complex. The by-products in the fission of benzeneazo-2-naphthol include aniline and a complex phenolic substance of undetermined constitution. The analytical results for this product agree best with the formula $C_{33}H_{22}O_4N_6$, but this is improbable, as it involves loss of a carbon atom from $2C_{16}H_{12}ON_2$ and 2HCN required to give N_6. A more probable formula is $C_{17}H_{13}O_2N_3$, which represents a cyano-derivative of benzeneazonaphthol + H_2O. The action of potassium cyanide on other azo-compounds may be summarised, but the work is not ripe for communication in detail. Reaction occurs in the following cases: 1-benzeneazo-2-naphthol-6 : 8-disulphonic acid; 1-benzeneazo-2-naphthol-6-sulphonic acid; *p*-sulphobenzeneazo-2-naphthol-3-carboxylic acid; *p*-sulphobenzeneazo-2-naphthol-3-carboxyanilide; 4-benzeneazo-1-naphthol (with formation, apparently, of an isomeride of I). There was no reaction in the following instances when the azo-compound was boiled during 20—30 hours in aqueous alcoholic suspension with potassium cyanide: 1-benzeneazo-2-naphthylamine; *p*-aminoazobenzene; benzeneazo-*p*-cresol; benzeneazo-*p*-hydroxydiphenyl. In other instances the reaction proceeds slowly on account of the sparing solubility of the azo-compound in aqueous potassium cyanide solution and examples are: *o*-carboxybenzeneazo-2-naphthol and 1-benzeneazo-2-naphthol-3-carboxylic acid.

The interaction of 1-nitroso-2-naphthol and *p*-toluenesulphinic acid furnishes a sulphone sulphonate, $C_{10}H_5(SO_2{\cdot}C_7H_7)(O{\cdot}SO_2{\cdot}C_7H_7)(NH_2)(4:2:1)$ (VIII), the constitution resting on the analytical results and the ready hydrolysis of the substance with formation of a compound capable of triacetylation to $C_{10}H_5(SO_2{\cdot}C_7H_7)(OAc)(NAc_2)$ (IX). The position of the *p*-tolylsulphone group is indicated by analogy, and the hydrolysable sulphonyl residue is unlikely to be attached to nitrogen.

EXPERIMENTAL.

1-*Amino*-2-*hydroxy*-4-*cyanonaphthalene* (I).—(A) *From* 1-*nitroso*-2-*naphthol*. The crude 1-nitroso-2-naphthol obtained from β-naphthol (100 g.) (Lagodzinski and Hardine, *Ber.*, 1894, **27**, 3076) was collected, washed, and suspended in water (1000 c.c.); a solution of potassium cyanide (300 g.) in water (800 c.c.) was added, and the mixture maintained at 80—90° during 1—1½ hours. The nitrosonaphthol passed into a clear brownish-yellow solution, from which ammonia was evolved, and the cooled filtered liquid was acidified with concentrated hydrochloric acid (300 c.c.). The light brown, crystalline precipitate was collected and washed (yield, 88 g.; m. p. 180—185°). Purification of this product could be effected by extraction with hot water, but much of the material was converted into a black insoluble mass. The pale yellow, aqueous extract afforded, on cooling, a white crystalline precipitate of almost pure 1-amino-2-hydroxy-4-cyanonaphthalene, m. p. 195—200°. A more satisfactory procedure was to extract the dry crude product with ether in a Soxhlet apparatus; a portion dissolved easily and the ethereal solution, treated with dry hydrogen chloride, furnished a grey crystalline precipitate of the hydrochloride of the base; this was collected and washed with ether (yield, 50 g.). The free base resulted by trituration of the hydrochloride with water. No homogeneous material could be obtained by recrystallisation of the portion of the product that was sparingly soluble in ether, but on acetylation a variable amount of the triacetyl derivative of 1-amino-2-hydroxy-4-cyanonaphthalene was obtained.

1-*Amino*-2-*hydroxy*-4-*cyanonaphthalene* crystallised from water and then from benzene or alcohol in colourless slender prisms, m. p. 200—201° (decomp.) (Found: C, 72·0; H, 4·4; N, 15·2. $C_{11}H_8ON_2$ requires C, 71·7; H, 4·4; N, 15·2%). Exposed to air, the base slowly developed a bluish-green colour. It was sparingly soluble in water to a colourless solution, from which a green insoluble substance separated after heating for some time. It was easily soluble in alcohol and ether to solutions which exhibited a strong bluish fluorescence. It dissolved in dilute aqueous sodium hydroxide to a yellow solution, and this developed a greenish fluorescence on addition of alcohol. The base was insoluble in hydrochloric acid of any concentration, and the hydrochloride prepared from a solution of the base in ether was instantly hydrolysed in contact with water. The alcoholic solution became green on addition of a trace of aqueous ferric chloride, but the colour changed to yellow with excess of the reagent. The base reduced hot Fehling's solution.

Diazotisation was not effected when a concentrated aqueous solution of sodium nitrite was added gradually to one of the base in concentrated sulphuric acid at − 10° to − 5°. The product separated as an orange-yellow solid on dilution with water and this could not be coupled with resorcinol in alkaline solution. The base was recovered unchanged after being stirred with an acidified solution of copper sulphate and sodium nitrite (compare the method for the diazotisation of 1-amino-2-naphthol-4-sulphonic acid, D.R.-P., 171024, Frdl. **8**, 640). Attempts to hydrolyse the nitrile to 4-amino-3-hydroxy-1-naphthoic acid were unsuccessful. (a) Aminohydroxynaphthonitrile hydrochloride (1 g.) was boiled with water (3·3 g.) and concentrated sulphuric acid (6·6 g.) during 7 hours. The product was a dark violet phenolic mass. According to Friedländer and Weisberg (*Ber.*, 1895, **28**, 1839), 4-amino-1-naphthoic acid is easily decomposed into α-naphthylamine and carbon dioxide by heating with acids. (b) The hydrochloride (1 g.) was boiled with potassium hydroxide (5 g.) in water (20 c.c.) in a current of nitrogen during 16 hours. The clear solution was cooled, diluted, and acidified, and the crystalline yellow precipitate collected; this was easily soluble in aqueous potassium bicarbonate, but it was not found possible to purify the product. We recognise that the properties of the aminohydroxycyanonaphthalene are abnormal, but we cannot devise any explanation of the facts other than that put forward in the text.

(B) *From* 1-*benzeneazo*-2-*naphthol*. A solution of potassium cyanide (100 g.) in water (250 c.c.) was added to one of 1-benzeneazo-2-naphthol (50 g.) in alcohol (500 c.c.). The deep orange solution of the azo-compound became dark red, but the colour slowly changed on boiling and finally became intense yellow after 90 hours. The alcohol was removed as completely as possible under reduced pressure and the residue was extracted with ether; the ethereal solution, dried and evaporated, afforded aniline (8·4 g.). The aqueous layer was filtered from insoluble material (R, 8 g.) and acidified. The yellow precipitate (yield, 25·5 g.; m. p. 174—176°) crystallised from benzene in thin colourless prisms, m. p. 200—201°, identical with the base obtained as in (A). The yellow insoluble residue (R) was washed with aqueous sodium hydroxide (it is the sodium salt of a quasi-acidic substance) and then with hydrochloric acid (10%), becoming orange. The substance crystallised from acetic acid in brownish-yellow needles, m. p. 235° (decomp.) (Found: C, 69·9, 69·9; H, 3·9, 4·0; N, 14·8, 14·8. $C_{16}H_{11}O_2N_3$ requires C, 69·3; H, 3·8; N, 14·5. $C_{17}H_{11}O_2N_3$ requires C, 70·6; H, 4·0; N, 15·2. $C_{17}H_{13}O_2N_3$ requires C, 70·1; H, 4·5; N, 14·4. $C_{33}H_{22}O_4N_6$ requires C, 69·9; H, 3·9; N, 14·8%). The substance is very sparingly soluble in hot dilute sodium hydroxide to a yellow solution; it is insoluble in dilute acids. The solution in concentrated sulphuric acid is red. The deep yellow solution in acetic acid is decolorised on the addition of stannous chloride.

A *methyl* ether was obtained by refluxing the sodium salt with acetone and methyl sulphate in the presence of potassium carbonate. It crystallised from alcohol in red matted needles, m. p. 206° after sintering at 196° (decomp. at 215°) (Found: N, 13·9, 14·1, 14·1. $C_{18}H_{13}O_2N_3$ requires N, 14·2%). This derivative is reduced with difficulty and gives no diazotisable amine as a result. On the other hand the reduced solution may be oxidised to a quinone (?), a yellow substance which appears to form a flocculent orange 2 : 4-dinitrophenylhydrazone.

(C) *From* 1-p-*sulphobenzeneazo*-2-*naphthol*. A solution of potassium cyanide (30 g.) and the recrystallised sodium salt of 1-*p*-sulphobenzeneazo-2-naphthol (10 g.) in water (120 c.c.) was boiled during 2 hours, then cooled, filtered, and saturated with carbon dioxide. The yellow crystalline precipitate (2·6 g., m. p. 194—196°) was identical with the base obtained by methods (A) and (B). The yield was increased (3·3 g., m. p. 192—196°) when the reaction was carried out at 85—90° during 60 hours. The *triacetyl* derivative formed colourless prisms, m. p. 164° (Found: N, 9·0. $C_{17}H_{14}O_4N_2$ requires N, 9·0%).

1-*Diacetamido*-2-*acetoxy*-4-*naphthonitrile* (VI).—Aminohydroxycyanonaphthalene (3 g.) was added to acetic anhydride (20 c.c.) and pyridine (1 c.c.) and heated on the steam-bath during an hour. After a short time some crystals separated but these redissolved. The cooled solution was diluted with alcohol (20 c.c.) and poured into water containing hydrochloric acid (4 c.c.). The crystalline precipitate, washed and recrystallised from alcohol (charcoal), formed colourless parallelepipeds, m. p. 163—164° (Found: C, 65·9; H, 4·6; N, 9·5; *M*, in camphor, 330, 338. $C_{17}H_{14}O_4N_2$ requires C, 65·8; H, 4·6; N, 9·0%; *M*, 310).

1-*Dimethylamino*-2-*methoxy*-4-*cyanonaphthalene* (II).—Aminohydroxycyanonaphthalene hydrochloride (15 g.), suspended in water (200 c.c.), was methylated in the cold by shaking with methyl sulphate (30 c.c.) and 10% aqueous sodium hydroxide (330 g.). The product crystallised and it was collected, ground with aqueous sodium hydroxide, washed, and recrystallised from alcohol, forming colourless plates, m. p. 93—93·5° (Found: C, 74·1; H, 6·3; N, 12·3; *M*, in camphor, 233, 242. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%; *M*, 226), easily soluble in dilute hydrochloric acid and reprecipitated on the addition of alkali.

4-*Dimethylamino*-3-*methoxy*-1-*naphthoamide* (III).—(a) A solution of dimethylaminomethoxycyanonaphthalene (1 g.) in concentrated sulphuric acid (10 c.c.) was kept at room temperature during 14 days, then poured into water and made alkaline. The precipitate (0·9 g., m. p. 160°) crystallised from alcohol in colourless needles, m. p. 183°.

(b) The nitrile (4·5 g.) was boiled for 24 hours with a solution of sodium hydroxide (15 g.) in water (30 c.c.). The oil crystallised and the solution was then diluted, and the solid collected and washed (2·8 g., m. p. 130—135°). Recrystallised from water, in which it was very sparingly soluble, the product was obtained in colourless needles, m. p. 183°, alone or when mixed with the product from experiment (a) (Found : C, 68·9; H, 6·5; N, 11·5. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6; N, 11·5%). The *amide* was easily soluble in dilute hydrochloric acid and was reprecipitated on the addition of alkali to the solution. Boiling concentrated hydrochloric acid effected hydrolysis to a product which was readily soluble in dilute hydrochloric acid and in aqueous potassium bicarbonate and was doubtless the related naphthoic acid.

4-*Cyano*-1 : 2-*naphthaquinone* (IV).—1-Amino-2-hydroxy-4-cyanonaphthalene (77 g., m. p. 200—201°) was added during 1 hour to a mixture made from concentrated sulphuric acid (195 g.), chromium trioxide (42 g.), and ice (700 g.). After stirring for 2 hours the ochre-yellow product was collected, washed, and recrystallised from glacial acetic acid (charcoal) (yield, 62 g.; m. p. 174—175°). Oxidation by means of nitric acid (compare Heller, *Ber.*, 1912, **45**, 674) afforded a much less pure product.

4-*Cyano*-1 : 2-*naphthaquinone* crystallises from benzene in orange prisms, m. p. 175—176° (Found : C, 72·3; H, 2·9; N, 7·8. $C_{11}H_5O_2N$ requires C, 72·1; H, 2·7; N, 7·7%), sparingly soluble in alcohol and glacial acetic acid; it is insoluble in cold dilute aqueous sodium hydroxide, but is slowly changed by this reagent into a dark green substance, which then dissolves to a pale yellow solution.

4-*Cyano*-1 : 2-*benzphenazine* separated immediately when hot solutions of 4-cyano-1 : 2-naphthaquinone (0·9 g.) and *o*-phenylenediamine (0·6 g.) in glacial acetic acid were mixed. The substance crystallised from acetic acid in yellow needles, m. p. 247° (Found : N, 16·5. $C_{17}H_9N_3$ requires N, 16·5%). This derivative is very sparingly soluble in alcohol to a yellow solution which becomes intensely yellow on the addition of concentrated hydrochloric acid, and then deep red on the introduction of zinc dust. The solution in concentrated sulphuric acid is deep red. Boiling 40% aqueous sodium hydroxide solution effected hydrolysis to an acid, m. p. 298—301°, which separated from glacial acetic acid in deep yellow prisms, m. p. 305° (Found : N, 10·4. $C_{17}H_{10}O_2N_2$ requires N, 10·2%). The substance is evidently 1 : 2-*benzphenazine*-4-*naphthoic acid*; Ullmann and Heisler (*Ber.*, 1909, **42**, 4263) describe the isomeric 1 : 2-benzphenazine-3-naphthoic acid as yellow needles, m. p. 275—278°.

4-*Cyano*-1 : 2-*dihydroxynaphthalene*.—The crude quinone from aminohydroxycyanonaphthalene (63 g.) was suspended in boiling alcohol (200 c.c.) and reduced by passage of sulphur dioxide. The colourless solution, diluted with water, afforded 4-*cyano*-1 : 2-*dihydroxynaphthalene* (yield, 51 g.; m. p. 196—201°), which crystallised from alcohol in colourless slender rods, m. p. 210—211° (Found : C, 71·2; H, 4·0; N, 7·7. $C_{11}H_7O_2N$ requires C, 71·3; H, 3·8; N, 7·6%). The alcoholic solution exhibits faint bluish fluorescence and the colourless solution becomes green on the addition of ferric chloride. Exposure to air results in the formation of a bluish-green substance.

4-*Cyano*-1 : 2-*dimethoxynaphthalene*.—Methylation of cyanodihydroxynaphthalene in an inert atmosphere by means of methyl sulphate and aqueous sodium hydroxide gave a product which consisted mainly of material sparingly soluble in alcohol and of m. p. >300°.

Freshly fused potassium carbonate (40 g.) was added in 4 portions during 4 hours to a boiling solution of dihydroxycyanonaphthalene (27 g.) and methyl iodide (30 c.c.) in pure acetone (150 c.c.), and the heating continued during 2 hours. The product was isolated, by evaporating the solvent, dissolving the residue in ether and water, washing the ethereal solution with dilute aqueous sodium hydroxide and then with water, and drying and evaporating it, as a colourless crystalline mass (26 g.), m. p. 109°. Crystallisation from alcohol furnished faintly yellow, slender prisms, m. p. 110° (Found : N, 6·8. $C_{13}H_{11}O_2N$ requires N, 6·6%).

3 : 4-*Dimethoxy*-1-*naphthoic Acid* (V).—A suspension of 4-cyano-1 : 2-dimethoxynaphthalene (10 g.) in water (75 c.c.) containing potassium hydroxide (25 g.) was boiled during 8 hours. A potassium salt separated on cooling and this was collected and dissolved in water, and the filtered solution acidified. The precipitate was washed, dissolved in aqueous potassium bicarbonate, and recovered from the filtered solution by acidification (yield, 4·3 g.).

3 : 4-*Dimethoxy*-1-*naphthoic* acid crystallised from aqueous alcohol in plates, m. p. 161—161·5° (Found : C, 67·1; H, 5·3; equiv., 235. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%; equiv., 232).

1-*Acetamido*-2-*hydroxy*-4-*cyanonaphthalene*.—1-Diacetamido-2-acetoxy-4-cyanonaphthalene (37 g.) was added to a hot solution of potassium hydroxide (17 g.) in water (250 c.c.), and the deep yellow liquid filtered after 5 minutes from unchanged material, which was then further heated on the steam-bath with potassium hydroxide (5 g.) in water (100 c.c.) until completely dissolved. The united alkaline solutions were acidified and crystallisation of the product from alcohol gave 22·2 g. of material, m. p. 224°, and 8·9 g., m. p. 204—205°.

1-*Acetamido*-2-*hydroxy*-4-*cyanonaphthalene* forms colourless prisms, m. p. 224° (Found : N, 12·4. $C_{13}H_{10}O_2N_2$ requires N, 12·4%). The potassium salt is easily soluble and the sodium salt more sparingly soluble in water. Oxidation by means of alkaline permanganate afforded phthalic acid.

1-*Acetamido*-2-*methoxy*-4-*cyanonaphthalene* (VII).—(A) A solution of the above naphthol (4·5 g.) and methyl iodide (5 g.), along with freshly ignited potassium carbonate (4·5 g.), in acetone (40 c.c.) was refluxed for 2 hours. The initial solution of the potassium salt changed to a colourless suspension of the methyl ether. Water was added, and the product collected (yield, 4·3 g.) and crystallised from alcohol, forming colourless needles, m. p. 275° (Found : C, 70·1; H, 5·1; N, 11·8. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0; N, 11·7%). The following sections lead to an independent synthesis of this substance.

1-*Amino*-2-*methoxynaphthalene*.—Concentrated hydrochloric acid (700 c.c.) was added to a boiling suspension of 1-nitro-2-methoxynaphthalene (90 g.) in alcohol (700 c.c.) and zinc dust (200 g.) was then gradually introduced during 15 minutes. The colourless filtered solution, mixed with concentrated hydrochloric acid (700 c.c.), afforded after 2 hours a precipitate of the amine hydrochloride (83 g.), from which the free base was liberated.

1-Amino-2-methoxynaphthalene crystallises from methyl alcohol in colourless prisms, m. p. 55° (Schroeter, *Annalen*, 1912, **426**, 137, gives m. p. 54°; Davis, *Chem. News*, 1896, **74**, 302, m. p. 84°) (Found : N, 8·0. Calc. for $C_{11}H_{11}ON$: N, 8·1%). The acetyl derivative crystallised when acetic anhydride (27 g.) was added to a solution of the base (41 g.) in benzene (120 c.c.); m. p. 178—179° (yield, 47·5 g.) (Davis, *loc. cit.*, gives m. p. 175°) (Found : N, 6·7. Calc. for $C_{13}H_{13}O_2N$: N, 6·5%). The preparation of 1-amino-2-ethoxynaphthalene by an almost identical method was described by Paul (*Z. angew. Chem.*, 1896, **10**, 621), but this paper contains no record of the analysis of the methoxy- or ethoxy-naphthylamine and no melting points are cited.

4-*Nitro*-1-*acetamido*-2-*methoxynaphthalene*.—Nitric acid (11 c.c., *d* 1·42) was added during 1 hour to a stirred suspension of the above acetyl derivative (32 g.) in acetic acid (64 c.c.) below 5°. After 3 hours water was added and the granular precipitate was collected, washed, and crystallised from alcohol, in which it was very sparingly soluble (yield, 7·6 g.; m. p. 249—251°).

4-*Nitro*-1-*acetamido*-2-*methoxynaphthalene* crystallises from alcohol in pale yellow prisms, m. p. 251° (Found : C, 60·2; H, 4·7; N, 11·0. $C_{13}H_{12}O_4N_2$ requires C, 60·0; H, 4·6; N, 10·8%).

1-*Acetamido*-4-*amino*-2-*methoxynaphthalene*.—Attempts to reduce the nitro-compound by means of zinc and hydrochloric acid or by means of sodium sulphide were fruitless.

Sodium hydrosulphite (30 g.) was stirred into a boiling suspension of 1-acetamido-2-methoxy-4-nitronaphthalene (12 g.) in water (65 g.). The yellow colour was rapidly discharged and after 10 minutes ice and aqueous ammonia (80 c.c., *d* 0·88) were added. The granular product was collected after 2 hours, washed with water (yield, 3·1 g.; m. p. 185—190°), and crystallised from alcohol, forming colourless flat prisms, m. p. 196° (Found : C, 67·5; H, 6·3; N, 12·2. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1; N, 12·2%). A violet-red insoluble azo-compound resulted when the diazotised base was coupled with β-naphthol. Oxidation with alkaline potassium permanganate afforded phthalic acid, m. p. 213° alone or when mixed with an authentic specimen.

1-*Acetamido*-2-*methoxy*-4-*cyanonaphthalene* (VII).—(B) Concentrated hydrochloric acid (1·5 c.c.) was added to a stirred suspension of the preceding base (1·15 g.) in water (10 c.c.) and the temperature was maintained at 0° by addition of ice while aqueous sodium nitrite (2·5 c.c. of 2*N*) was added through a capillary during 5 minutes. The resulting clear solution was kept for 10 minutes and then added portionwise to an alkaline potassium nickel cyanide solution [nickel nitrate (7·3 g.) in water (10 c.c.) was mixed with a solution of potassium cyanide (8·3 g.) and sodium hydroxide (2·0 g.) in water (25 c.c.) and 10% aqueous sodium hydroxide added to the filtered solution (compare McRae, *J. Amer. Chem. Soc.*, 1930, **52**, 4550)]. The almost colourless solid was collected, washed with water, and crystallised from alcohol, forming colourless needles, m. p. 275° alone or when mixed with the material prepared by the method (A) above (yield, 0·8 g.) (Found : N, 11·9. $C_{14}H_{12}O_2N_2$ requires N, 11·7%).

2-*Methoxy*-1 : 4-*naphthaquinone*.—(A) 1-Acetamido-4-amino-2-methoxynaphthalene (0·5 g.) was suspended in benzene (50 c.c.) cooled to 0° and shaken while a solution of chromium trioxide (0·6 g.) in 10% sulphuric acid (25 c.c.) was added during 10 minutes. Shaking was continued during 2 hours and the benzene layer was then separated, washed with water, dried, and evaporated. The residual solid crystallised from alcohol in pale yellow needles, m. p. 184—185°, unchanged by admixture with the material prepared by method (B) below. A dilute solution in aqueous alcohol gives a flocculent orange precipitate on the addition of 2 : 4-dinitrophenylhydrazine hydrochloride dissolved in water.

(B) 1-Acetamido-2-methoxy-4-cyanonaphthalene (5 g.) was mixed with alcohol (10 c.c.) and then boiled during 10 hours with potassium hydroxide (20 g.) and water (50 c.c.). After dilution with water (150 c.c.) the solution was filtered and acidified with dilute sulphuric acid, and chromium trioxide (10 g.) added; a dark flocculent deposit was removed by filtration. After a few hours a crystalline substance separated from the filtrate and this was collected, washed with water, and crystallised from alcohol, forming pale yellow needles, m. p. 184—185° (Found : C, 70·2, 70·1; H, 4·2, 4·3; MeO, 16·7. $C_{11}H_8O_3$ requires C, 70·2; H, 4·2; 1MeO, 16·5%). This *quinone* is insoluble in cold aqueous sodium carbonate and on heating it gradually dissolves to an orange solution; in aqueous sodium hydroxide it rapidly dissolves in the cold to a deep orange solution. These observations do not indicate the presence of a hydroxyl group but rather the ready introduction of one, possibly by hydrolysis. The orange-red solution in aqueous sodium hydroxide was acidified and extracted with ether; sodium carbonate then sufficed to extract the product from the separated ethereal solution, regenerating the orange-coloured sodium salt. Addition of a drop of aqueous sodium hydroxide to an alcoholic solution does not immediately give an orange-red solution; the colour appears in a few seconds. The substance sublimed readily and without decomposition when heated in a dry tube. According to Sachs, Berthold, and Zaar (*Z. Farb. Ind.*, 1907, **6**, 62, 81) the product of methylation of 2-hydroxy-1 : 4-naphthaquinone, regarded as 2-methoxynaphthaquinone, has m. p. 146—147°. This disagreement is being investigated.

1-*Amino*-2-p-*toluenesulphonyloxy*-4-*naphthyl*-p-*tolylsulphone* (VIII).—1-Nitroso-2-naphthol (10 g., 1 mol.) was added to a cold solution of *p*-toluenesulphinic acid (27 g., 3 mols.) in alcohol (50 c.c.) and the mixture was then refluxed for 1 hour. On cooling, the whole solidified to a crystalline mass and after keeping for 12 hours the solid was collected and crystallised from alcohol (70 c.c.) (yield, 13·4 g., m. p. 148—151°). When less than 2·5 mols. of *p*-toluenesulphinic acid were used, the product was oily; but further increase in the proportion of the reagent influenced neither the yield nor the purity of the product. Recrystallised from alcohol (charcoal) it was obtained in colourless flat prisms, m. p. 151—152° (Found : C, 61·7; H, 4·6; N, 3·0; S, 13·8. $C_{24}H_{21}O_5NS_2$ requires C, 61·6; H, 4·5; N, 3·0; S, 13·7%). The substance was sparingly soluble in ether or benzene, but easily soluble in chloroform and the solution afforded no precipitate with dry hydrogen chloride. It was insoluble in cold dilute sodium hydroxide solution and in concentrated or dilute hydrochloric acid. The substance was not oxidised by hot Fehling's solution. It dissolved in concentrated sulphuric acid to a blue solution and this on warming became green and then yellowish-green.

1-*Diacetamido*-2-*acetoxy*-4-*naphthyl*-p-*tolylsulphone* (IX).—A solution of the condensation product (34 g.), described in the last section, in alcohol (100 c.c.) was mixed with one of potassium hydroxide (34 g.) in water (340 c.c.) and refluxed during 45 minutes. The deep yellow liquid was diluted with water (400 c.c.), cooled, filtered after several hours, and saturated with carbon dioxide. A pink solid separated (17 g., m. p. 180—183°). It became violet when heated with benzene or toluene and dissolved sparingly to a deep violet solution. It was very sparingly soluble in ether and the solution gave with dry hydrogen chloride a grey precipitate of a hydrochloride. The hydrochloride (3·5 g.) was heated with acetic anhydride (20 c.c.) and pyridine (5 c.c.) on a boiling water-bath during 1·5 hours. The resulting solution was cooled, mixed with alcohol (25 c.c.), and added to water (300 c.c.) containing concentrated hydrochloric acid (10 c.c.). The crystalline product separated from alcohol in pink parallelepipeds, m. p. 191—192° (Found : C, 63·0; H, 4·8; N, 2·9; S, 7·3. $C_{23}H_{21}O_6NS$ requires C, 62·8; H, 4·8; N, 3·2; S, 7·3%).

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