

120. The Nitration of 1 : 8-Dihydroxynaphthalene.

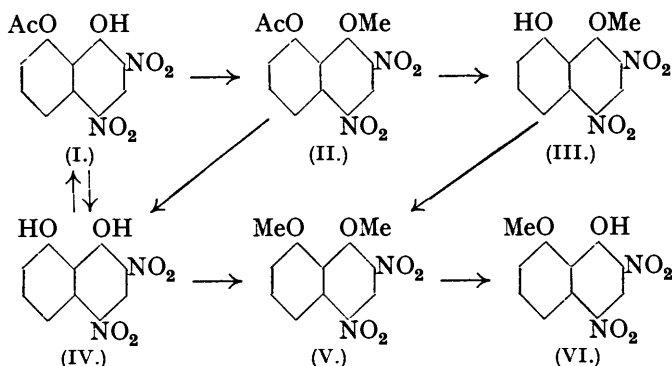
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ONLY a few disubstituted 1 : 8-dihydroxynaphthalene derivatives of well-established constitution are known, and none suitable for ascertaining the orientation of the nitro-groups in a dinitro-1 : 8-naphthadioxin (Carnero and Calvet, *Anal. Fís. Quím.*, 1934, **32**, 1166). This was our primary reason for studying the nitration of 1 : 8-dihydroxynaphthalene.

1 : 8-Dihydroxynaphthalene is almost completely destroyed in the ordinary methods of nitration. Attempts to prepare 1 : 8-dimethoxynaphthalene gave, in agreement with Staudinger, Schlenker, and Goldstein (*Helv. Chim. Acta*, 1921, **4**, 334; contrast Heller and Kretschmann, *Ber.*, 1921, **54**, 1106), 1-hydroxy-8-methoxynaphthalene. 1 : 8-Dihydroxynaphthalene was, however, readily diacetylated and also methylenated, and the nitration of these two derivatives is now described.

(1) The action of nitric acid (*d* 1.4) upon 1 : 8-diacetoxynaphthalene at the ordinary temperature produces 2 : 4-dinitro-1-hydroxy-8-acetoxynaphthalene (I). Nitration without removal of an acetyl group has not been accomplished. 2 : 4-Dinitro-1-hydroxy-8-acetoxynaphthalene cannot be acetylated or benzoylated, but is easily methylated by diazomethane. 2 : 4-Dinitro-8-acetoxy-1-methoxynaphthalene (II), treated with cold dilute aqueous sodium hydroxide, is hydrolysed to 2 : 4-dinitro-8-hydroxy-1-methoxynaphthalene (III).

By the action of boiling methyl-alcoholic potassium hydroxide, both 2 : 4-dinitro-1-hydroxy-8-acetoxynaphthalene and 2 : 4-dinitro-8-acetoxy-1-methoxynaphthalene yield 2 : 4-dinitro-1 : 8-dihydroxynaphthalene (IV). This can be easily methylated to 2 : 4-dinitro-1 : 8-dimethoxynaphthalene (V) by means of diazomethane, but when acetylated it furnishes 2 : 4-dinitro-1-hydroxy-8-acetoxynaphthalene.



2 : 4-Dinitro-1 : 8-dimethoxynaphthalene is easily hydrolysed to 2 : 4-dinitro-1-hydroxy-8-methoxynaphthalene (VI) by the action of boiling alcoholic potassium hydroxide. Both

2 : 4-dinitro-1 : 8-dihydroxynaphthalene and 2 : 4-dinitro-1-hydroxy-8-methoxynaphthalene can be reduced to the corresponding diamino-derivatives, only isolable as *dihydrochlorides*.

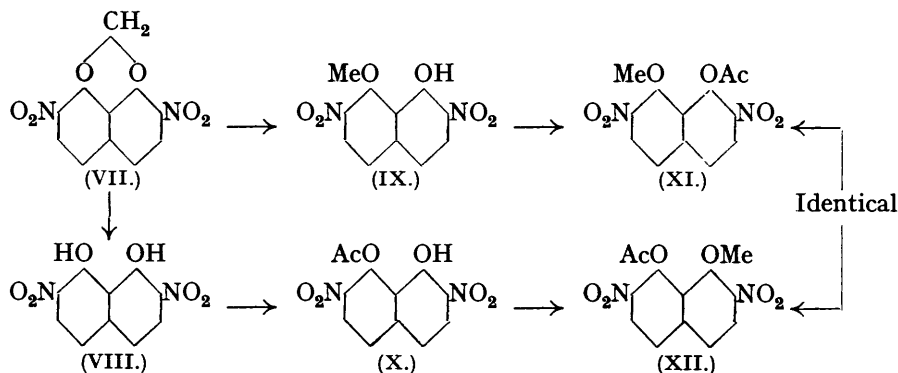
When 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene dihydrochloride is boiled with dilute nitric acid, 3-methoxyphthalic acid is produced, identical with the acid prepared from 3-nitrophthalic acid; its formation establishes the constitutions of 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene, 2 : 4-dinitro-1 : 8-dihydroxynaphthalene, and their derivatives. From 2 : 4-diamino-1 : 8-dihydroxynaphthalene, a *tetrabenzoyl* derivative has been prepared.

(2) The nitration of 1 : 8-methylenedioxy-naphthalene by a mixture of equal volumes of fuming nitric acid (*d* 1.5) and glacial acetic acid produces 2(?) : 7(?)*-dinitro-1 : 8-methylenedioxy-naphthalene* (VII) and 4 : 5-dinitro-1 : 8-methylenedioxy-naphthalene, which are easily separated by fractional crystallisation.

2(?) : 7(?)*-Dinitro-1 : 8-methylenedioxy-naphthalene* is hydrolysed by boiling aqueous potassium hydroxide and by alcoholic potassium hydroxide to 2(?) : 7(?)*-dinitro-1 : 8-dihydroxynaphthalene* (VIII) and 2(?) : 7(?)*-dinitro-1-hydroxy-8-methoxynaphthalene* (IX), respectively. These yield the same dinitrodimethoxynaphthalene by the action of diazomethane.

When acetylated with acetic anhydride and sodium acetate, 2(?) : 7(?)*-dinitro-1 : 8-dihydroxynaphthalene* gives a *monoacetyl* derivative (X) at the ordinary temperature and the diacetyl compound at the boiling point.

If it is assumed that for some structural reason (*e.g.*, an unsymmetrical distribution of the two nitro-groups) there exists a difference in the acidity of the two hydroxyl groups in this dinitrodihydroxynaphthalene, the monomethyl derivative (IX) which results from the action of alcoholic potassium hydroxide on its methylene ether must have its methoxy-group attached in the same position as the acetoxy-group in the acetyl derivative (X), and the product (XI) obtained by acetylation of the methyl derivative ought to be an isomeride of the substance (XII) produced by methylation of the monoacetyl derivative. The two products, (XI) and (XII) are, however, identical. This is the only experimental evidence we can put forward to support the symmetrical constitutions proposed for the dinitro-1 : 8-dihydroxynaphthalene (VIII) and its methylene ether (VII).



2(?) : 7(?)*-Dinitro-1 : 8-dihydroxynaphthalene* is easily reduced to the diamino-dihydroxynaphthalene, from which a *tetrabenzoyl* derivative has been prepared.

4 : 5-Dinitro-1 : 8-methylenedioxy-naphthalene is readily hydrolysed by boiling aqueous potassium hydroxide to 4 : 5-dinitro-1 : 8-dihydroxynaphthalene, which on reduction gives 4 : 5-diamino-1 : 8-dihydroxynaphthalene, of which the *tetrabenzoyl* derivative was isolated. The constitutions of these substances are established through the identity of this *tetrabenzoyl* derivative with that obtained by reduction and benzoylation of the bisazo-dye resulting from the coupling of diazotised aniline with 1 : 8-dihydroxynaphthalene (Heller and Kretschmann, *Ber.*, 1921, 54, 1102).

EXPERIMENTAL.

Nitration of 1:8-Diacetoxynaphthalene.—The finely powdered diacetyl derivative (6 g.) (Erdmann, *Annalen*, 1888, 247, 345, 359; cf. Carnero and Calvet, *loc. cit.*, p. 1157) is slowly added to 30 c.c. of concentrated nitric acid, kept at 25–30°. The crystalline product is washed with water, dried on the steam-bath (yield, 5.4 g.), and recrystallised from boiling acetic acid (charcoal). 2:4-Dinitro-1-hydroxy-8-acetoxynaphthalene (I) forms yellow hexagonal prisms, m. p. 200° (decomp.) (Found: C, 49.5; H, 2.7; N, 9.6. $C_{12}H_8O_7N_2$ requires C, 49.3; H, 2.7; N, 9.6%), sparingly soluble in alcohol, easily soluble in boiling acetic acid, and soluble in dilute aqueous alkali, from which at higher alkali concentrations the sodium or potassium salt separates in dark red prisms.

2:4-Dinitro-8-acetoxy-1-methoxynaphthalene (II).—The 1-hydroxy-compound (I) (2 g.) is added to a slight excess of diazomethane (4 c.c. of nitrosomethylurethane, 11 c.c. of 20% methylalcoholic potassium hydroxide, and 350 c.c. of dry ether). The solid remaining after evaporation of the ether is washed with a dilute solution of sodium hydroxide, crystallised from methyl alcohol (charcoal) (yield, 1.25 g.), and recrystallised from methyl or ethyl alcohol, giving pale yellow plates, m. p. 115–117° (Found: C, 51.2; H, 3.0; N, 9.2. $C_{13}H_{10}O_7N_2$ requires C, 51.0; H, 3.25; N, 9.15%), of 2:4-dinitro-8-acetoxy-1-methoxynaphthalene, insoluble in water or dilute alkali solution.

2:4-Dinitro-1:8-dihydroxynaphthalene (IV).—A solution of 4 g. of potassium hydroxide in 100 c.c. of methyl alcohol is boiled with 2 g. of 2:4-dinitro-8-acetoxy-1-hydroxynaphthalene for 1 hour, the alcohol driven off in steam, the dark red potassium salt dissolved in boiling water, and excess of hydrochloric acid added. The 2:4-dinitro-1:8-dihydroxynaphthalene obtained crystallises from methyl alcohol or boiling water in brilliant red prisms (1.45 g.), m. p. 180–182° (decomp.) (Found: C, 47.9; H, 2.6; N, 11.2. $C_{10}H_6O_6N_2$ requires C, 48.0; H, 2.4; N, 11.2%), sparingly soluble in cold water, rather more soluble in boiling water, giving an orange solution, and slightly soluble in methyl or ethyl alcohol. The dried and finely powdered substance has a distinct sternutatory power. It dyes wool and silk orange. It is very soluble in dilute alkali solutions, but the sparingly soluble potassium salt separates on addition of concentrated potassium hydroxide solution; after two crystallisations from boiling water, this forms brilliant scarlet prisms (Found: N, 9.8. $C_{10}H_6O_6N_2K$ requires N, 9.7%). The silver salt, prepared from it and the theoretical quantity of silver nitrate in boiling water, crystallises in small violet prisms of metallic sheen (Found: N, 7.7. $C_{10}H_6O_6N_2Ag$ requires N, 7.85%).

2:4-Dinitro-1:8-dimethoxynaphthalene (V).—The dihydroxy-compound (3 g.) is treated with ethereal diazomethane and the solid left after spontaneous evaporation of the ether is washed with dilute aqueous sodium hydroxide and twice crystallised from methyl alcohol (charcoal), 2:4-dinitro-1:8-dimethoxynaphthalene separating in long, deep yellow prisms or needles (1.7 g.), m. p. 137–139° (Found: C, 51.9; H, 3.7; N, 10.0. $C_{12}H_{10}O_6N_2$ requires C, 51.8; H, 3.6; N, 10.1%), insoluble in water or aqueous alkali, readily soluble in methyl or ethyl alcohol.

2:4-Dinitro-8-hydroxy-1-methoxynaphthalene (III).—2:4-Dinitro-8-acetoxy-1-methoxynaphthalene (1 g.) is dissolved in a cold solution of 0.5 g. of potassium hydroxide in 50 c.c. of methyl alcohol and after 5–10 minutes an excess of hydrochloric acid is added; 2:4-dinitro-8-hydroxy-1-methoxynaphthalene separates in yellow needles, accompanied by a small quantity of scarlet prisms of the monopotassium salt of 2:4-dinitro-1:8-dihydroxynaphthalene. These are easily removed by recrystallisation from ethyl alcohol, 2:4-dinitro-8-hydroxy-1-methoxynaphthalene separating in silky yellow needles (0.5 g.), m. p. 170–171° (Found: C, 49.7; H, 2.7; N, 10.7. $C_{11}H_8O_6N_2$ requires C, 50.0; H, 3.0; N, 10.6%). It dissolves with a cherry-red colour in dilute alkali solution. When boiled with alcoholic potassium hydroxide, it is hydrolysed to 2:4-dinitro-1:8-dihydroxynaphthalene.

2:4-Dinitro-1-hydroxy-8-methoxynaphthalene (VI).—2:4-Dinitro-1:8-dimethoxynaphthalene (2 g.) is boiled with 180 c.c. of 2*N*-sodium hydroxide for 1½ hours, enough boiling water added to dissolve the separated sodium salt, and the filtered solution strongly acidified with hydrochloric acid; the 2:4-dinitro-1-hydroxy-8-methoxynaphthalene obtained (1.6 g.) is recrystallised from boiling alcohol, in which it is only sparingly soluble, and separates in small yellow plates, m. p. 179–180° (decomp.), mixed m. p. with 2:4-dinitro-8-hydroxy-1-methoxynaphthalene 145–155° (Found: C, 49.9; H, 3.1; N, 10.7. $C_{11}H_8O_6N_2$ requires C, 50.0; H, 3.0; N, 10.6%). It dissolves with some difficulty in dilute alkali solutions, producing a red colour. The sodium salt is very sparingly soluble in water.

2:4-Diamino-1-hydroxy-8-methoxynaphthalene.—2:4-Dinitro-1-hydroxy-8-methoxynaphth-

alene (1.2 g.) is heated with 6 g. of granulated tin and 18 c.c. of concentrated hydrochloric acid on a water-bath for 20 minutes, and a solution of the double salt produced in 15 c.c. of hot water is freed from tin by hydrogen sulphide, cooled in ice, and saturated with hydrogen chloride; 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene dihydrochloride crystallises in thin colourless needles (0.7 g.). It can be purified by solution in a few c.c. of cold water and saturation with hydrogen chloride. In the air, the hydrochloride gradually becomes pink or red; the oxidation is more rapid in solution. For analysis the compound was dried on a porous plate (Found : N, 9.9. $C_{11}H_{12}O_2N_2 \cdot 2HCl$ requires N, 10.1%).

Oxidation of 2 : 4-Diamino-1-hydroxy-8-methoxynaphthalene.—The hydrochloride of the base (1 g.) is boiled under reflux with 3 c.c. of concentrated nitric acid and 9 c.c. of water for 1 hour and an ethereal extract of the product is allowed to evaporate first in the air and then over potassium hydroxide and concentrated sulphuric acid in a vacuum desiccator. The well-formed rhombohedra produced after 2 days are picked out and recrystallised from a few c.c. of boiling water in a vacuum desiccator. 3-Methoxyphthalic acid, obtained in colourless prisms, m. p. 170—171° (gas evolution) (Found : C, 55.3; H, 3.95. Calc. for $C_9H_8O_5$: C, 55.05; H, 4.1%), gives the fluorescein test and is identical (m. p. and mixed m. p.) with the acid prepared from 3-hydroxyphthalic acid (Girardet, *Helv. Chim. Acta*, 1931, **14**, 511), the anhydride of which was methylated with diazomethane (Corbellini and Rossi, *Gazzetta*, 1931, **61**, 281) and the 3-methoxyphthalic anhydride (crystals, m. p. 159—160°, from toluene) hydrolysed with boiling water.

Derivatives of 2 : 4-Diamino-1 : 8-dihydroxynaphthalene.—The dihydrochloride, obtained from the dinitro-compound by the reduction method described above, crystallises in small colourless needles which gradually redden in the air (Found : N, 10.6. $C_{10}H_{10}O_2N_2 \cdot 2HCl$ requires N, 10.65%). The free base is extraordinarily prone to auto-oxidation.

The tetrabenzoyl derivative is prepared by shaking a solution of the hydrochloride (0.5 g.), potassium hydroxide (6 g.), and sodium hydrosulphite (2 g.) in water (45 c.c.) with benzoyl chloride (4 g.) for $\frac{1}{2}$ hour. The microcrystalline solid is collected after 12 hours, washed with water, dried on a porous plate and then on a steam-bath, extracted with cold benzene, and crystallised twice from acetic acid (charcoal), small, almost colourless needles (0.5 g.), m. p. 257—258° (decomp.), being obtained (Found : C, 75.4; H, 4.2; N, 4.6. $C_{38}H_{26}O_6N_4$ requires C, 75.25; H, 4.3; N, 4.6%), moderately easily soluble in acetic acid.

Nitration of 1 : 8-Methylenedioxy-naphthalene.—A solution of 3 g. of the methylene ether (Carnero and Calvet, *loc. cit.*, p. 1164) in 3 c.c. of glacial acetic acid is dropped into a mixture of 9 c.c. of fuming nitric acid (*d* 1.5) and 9 c.c. of glacial acetic acid, appreciable heating being prevented by cooling. After 2 hours, the product which has crystallised is collected and dissolved in 65 c.c. of boiling acetic acid; on cooling, 2(?) : 7(?)-dinitro-1 : 8-methylenedioxy-naphthalene (VII) crystallises in long, pale yellow prisms (1.9 g.), m. p. 198—200° (Found : C, 50.6; H, 2.2; N, 10.6. $C_{11}H_8O_6N_2$ requires C, 50.4; H, 2.3; N, 10.7%), insoluble in water or alkali, but readily soluble in boiling alcohol or acetic acid.

The original acetic acid mother-liquor is concentrated ($\frac{1}{2}$ vol.); on slow cooling, a mixture of silky needles and short prisms (of the preceding compound) separates. The needles are picked out and crystallised twice from alcohol, 4 : 5-dinitro-1 : 8-methylenedioxy-naphthalene being obtained in well-formed prisms (0.35 g.), m. p. 177—179° (Found : C, 50.2; H, 2.2; N, 10.8%), insoluble in water or in alkali, moderately easily soluble in alcohol, and easily soluble in acetic acid.

2(?) : 7(?)-Dinitro-1 : 8-dihydroxynaphthalene (VIII).—The methylene ether (3 g.) is boiled with 200 c.c. of 2*N*-sodium hydroxide for 1 hour, and an excess of concentrated hydrochloric acid added; on cooling, 2(?) : 7(?)-dinitro-1 : 8-dihydroxynaphthalene separates. Rapidly recrystallised from boiling water, it forms yellowish-green prisms (1.5 g.), m. p. 171—173° (decomp.). The substance usually contains one molecule of water of crystallisation, but was anhydrous when isolated for the first time (Found for anhydrous material : C, 47.9; H, 2.4. $C_{10}H_6O_6N_2$ requires C, 48.0; H, 2.4%). Found for hydrated material : C, 45.1; H, 2.8; N, 10.4. $C_{10}H_6O_6N_2 \cdot H_2O$ requires C, 44.8; H, 3.0; N, 10.45%). It can be recrystallised from chloroform without losing its water of crystallisation (Found : C, 44.9; H, 2.8; N, 10.25; loss after 5 hours at 110° over phosphoric oxide in a vacuum, 7.6. $C_{10}H_6O_6N_2 \cdot H_2O$ requires H_2O , 6.7%). It readily forms an orange-red solution in boiling water, but is only sparingly soluble in chloroform; the former solution darkens after some time and the compound is destroyed. The powdered substance is somewhat sternutatory.

The monoacetyl derivative is obtained when the dinitrodihydroxynaphthalene (1 g.) reacts with sufficient acetic anhydride to dissolve it; the product is removed after 1 hour and rapidly

recrystallised from warm acetic acid (if boiled or heated with acetic acid for too long, the substance is decomposed), forming yellowish-green polyhedra (0.5 g.), m. p. 125—170° (decomp.). The crystals are dried in a vacuum desiccator (Found : N, 9.2. $C_{12}H_8O_7N_2$ requires N, 9.55%).

The *diacetyl* derivative separates when the dinitrodihydroxynaphthalene is boiled for 5 seconds with a small quantity of acetic anhydride and a trace of sodium acetate; recrystallised from acetic acid, it forms short, well-shaped, pale yellow prisms, m. p. ca. 228° (decomp.) (Found : N, 8.5. $C_{14}H_{10}O_8N_2$ requires N, 8.4%), insoluble in water and in aqueous alkali, but sparingly soluble in boiling alcohol.

2(?) : 7(?) -Dinitro-1 : 8-dimethoxynaphthalene is obtained when the dihydroxy-compound is treated with ethereal diazomethane (see preparation of II and V); twice crystallised from acetic acid, it forms long yellow prisms, m. p. 268—270° (decomp.; after darkening at 250°) (Found : C, 51.8; H, 3.5; N, 10.2. $C_{12}H_{10}O_6N_2$ requires C, 51.8; H, 3.6; N, 10.1%), insoluble in aqueous alkali, sparingly soluble in boiling alcohol, and easily soluble in boiling acetic acid.

2(?) : 7(?) -Dinitro-1-hydroxy-8-methoxynaphthalene (IX).—2(?) : 7(?) -Dinitro-1 : 8-methylenedioxy-naphthalene (2 g.) is boiled with 4 g. of potassium hydroxide in 100 c.c. of methyl alcohol for 45 minutes and the red potassium salt is removed, dissolved in boiling water, and acidified with hydrochloric acid, 2(?) : 7(?) -dinitro-1-hydroxy-8-methoxynaphthalene separating in silky yellow needles; recrystallised from acetic acid, it forms greenish-yellow prisms, m. p. 218—220°. Prolonged boiling with acetic acid must be avoided (Found : C, 50.0; H, 3.1; N, 10.6. $C_{11}H_8O_6N_2$ requires C, 50.0; H, 3.0; N, 10.6%). It is practically insoluble in water, soluble in alkali solution, sparingly soluble in boiling methyl or ethyl alcohol, and moderately easily soluble in acetic acid. When methylated with diazomethane in the usual way, it yields 2(?) : 7(?) -dinitro-1 : 8-dimethoxynaphthalene.

2(?) : 7(?) -Dinitro-1-acetoxy-8-methoxynaphthalene (XI and XII) is obtained by the action of warm acetic anhydride and a drop of concentrated sulphuric acid or some anhydrous sodium acetate; recrystallised from warm glacial acetic acid, it forms pale yellow prisms, m. p. 183—185° (Found : C, 50.9; H, 3.2; N, 9.2. $C_{13}H_{10}O_7N_2$ requires C, 51.0; H, 3.3; N, 9.15%). The same compound is formed when 2(?) : 7(?) -dinitro-1-hydroxy-8-acetoxynaphthalene is methylated with diazomethane; m. p. and mixed m. p. 183—185° (Found : C, 50.8; H, 3.2; N, 9.2%).

Reduction of 2(?) : 7(?) -Dinitro-1 : 8-dihydroxynaphthalene.—The reduction is effected as in the preparation of 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene. The hydrochloride (very small needles) is benzoylated, and the crude product recrystallised from boiling nitrobenzene, the *tetrabenzoyl* derivative separating in long, colourless, hair-like needles, m. p. ca. 300° (decomp.). Before analysis, it was well washed with boiling alcohol (Found : N, 4.1. $C_{38}H_{26}O_6N_2$ requires N, 4.6%). It is very sparingly soluble in boiling acetic acid, but dissolves readily in boiling nitrobenzene.

4 : 5 - Dinitro-1 : 8 - dihydroxynaphthalene.—4 : 5 - Dinitro-1 : 8 - methylenedioxy-naphthalene (1 g.) is boiled with 70 c.c. of 2*N*-sodium hydroxide for 1 hour and the separated sodium salt is dissolved in boiling water and acidified with hydrochloric acid; recrystallised from methyl alcohol, 4 : 5-dinitro-1 : 8-dihydroxynaphthalene forms short brown prisms, m. p. (rapidly heated) ca. 225° (decomp.) (Found : C, 48.2; H, 2.4; N, 11.2. $C_{10}H_6O_6N_2$ requires C, 48.0; H, 2.4; N, 11.2%), sparingly soluble in water and methyl alcohol but readily in alkali solution.

The *diacetyl* derivative (boiling with acetic anhydride and sodium acetate for a few seconds), after addition of methyl alcohol, crystallises in well-formed brownish-yellow prisms, m. p. 158—160° (Found : N, 8.6. $C_{14}H_{10}O_8N_2$ requires N, 8.4%).

4 : 5-Dinitro-1 : 8-dimethoxynaphthalene, obtained from the dihydroxy-compound and diazomethane, crystallises from methyl alcohol in fine reddish-brown needles, m. p. 147—150° (decomp., after darkening at 140°) (Found : N, 10.1. $C_{12}H_{10}O_6N_2$ requires N, 10.1%).

Reduction of 4 : 5-Dinitro-1 : 8-dihydroxynaphthalene.—The *tetrabenzoyl* derivative of 4 : 5-diamino-1 : 8-dihydroxynaphthalene is obtained from 4 : 5-dinitro-1 : 8-dihydroxynaphthalene by the method used in the preparation of the isomeride. Recrystallised from acetic acid, it forms small colourless prisms, m. p. 255—256° (decomp.; after darkening at 245°) (Found : N, 4.35. $C_{38}H_{26}O_6N_2$ requires N, 4.6%).