70. *The Nitration of* 1 : 5-*Dihydroxy- and* 1 : 5-*Diacetoxy-naphthalene,* 1-*Acetoxy*-5-*methoxynaphthalene,* 5-*Methoxy*-1-*naphthol, and* 1 : 5-*Dimethoxynaphthalene.*

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Nitration of the compounds named in the title has been studied. Oxidation to a methoxynaphthaquinone or to a nitromethoxyphthalic acid, or conversion into and comparison with a bromo-compound, has enabled the products to be orientated. Thus, the 2 : 6-*dinitro-* and 2 : 4 : 6 : 8-*tetranitro*-derivatives are obtained from 1 : 5-dihydroxynaphthalene; the 2 : 4-*dinitro-* and 2 : 4 : 6-*trinitro*-5-*acetoxy*-1-*naphthols* from 1 : 5-diacetoxynaphthalene; the 2 : 4-*dinitro*-derivative from 5-methoxy-1-naphthol; 8-*nitro-* and 6 : 8-*dinitro*-derivatives and 2 : 8-*dinitro*-5-*methoxy*-1-*naphthol* from 1-acetoxy-5-methoxynaphthalene; and 4-*nitro-*, 4 : 8-*dinitro-*, 2 : 4 : 8-*trinitro-*, and 2 : 4 : 6 : 8-*tetranitro*-derivatives from 1 : 5-dimethoxynaphthalene.

Bentley, Robinson, and Weizmann (*J.*, 1907, **91**, 104) prepared mono- and di-nitro-derivatives of 1 : 5-dimethoxynaphthalene, but did not determine their constitutions. We have now orientated the former by reduction and conversion of the amino-compound into a bromo-1 : 5-dimethoxynaphthalene, different from 2-bromo-1 : 5-dimethoxynaphthalene (Carter, Race, and Rowe, *J.*, 1942, 236), but identical with the product obtained by Fischer and Bauer (*J. pr. Chem.*, 1916, **94**, 15) by direct monobromination of 1 : 5-dimethoxynaphthalene. Since 1 : 5-dimethoxynaphthalene is converted by dibromination into 4 : 8-dibromo-1 : 5-dimethoxynaphthalene (Carter, Race, and Rowe, *loc. cit.*,) the monobromo-compound must be 4-*bromo*-1 : 5-*dimethoxynaphthalene*. Further, reduction of nitro-1 : 5-dimethoxynaphthalene and oxidation of the amino-1 : 5-dimethoxynaphthalene with chromic acid resulted in elimination of the methoxyl group in the *p*-position to the amino-group with formation of 5-*methoxy*-1 : 4-*naphthaquinone*, a product which cannot be prepared directly from 5-hydroxy-1 : 4-naphthaquinone (juglone) by methylation. Thus, the mononitro-derivative of 1 : 5-dimethoxynaphthalene is 4-*nitro*-1 : 5-*dimethoxynaphthalene* (I), which was also obtained by mononitration of 1-acetoxy-5-methoxynaphthalene, followed by hydrolysis and methylation. Reduction of the mononitro-1-acetoxy-5-methoxynaphthalene (VII) and oxidation of the product with chromic acid did not give a quinone, indicating that the amino- and the acetoxy-group are in different rings in the naphthalene nucleus, and this was confirmed by further nitration to 6 : 8-*dinitro*-1-*acetoxy*-5-*methoxynaphthalene* (XI). Hence mononitration of 1-acetoxy-5-methoxynaphthalene, followed by hydrolysis of the product, gave 8-*nitro*-5-*methoxy*-1-*naphthol* (VIII).

Nitration of 1 : 5-diacetoxynaphthalene gave a dinitro-acetoxynaphthol, which, when hydrolysed and methylated, afforded a dinitro-1 : 5-dimethoxynaphthalene, m.p. 153° (VI), also obtained from 5-methoxy-1-naphthol by nitration with diacetyl orthonitric acid followed by methylation, as well as by further nitration of (VII) with diacetyl orthonitric acid followed by hydrolysis and methylation. One nitro-group is therefore in the *p*-position to a methoxyl group, and, since oxidation of the dinitroacetoxynaphthol with dilute nitric acid gave 4 : 6-*dinitro*-3-*hydroxyphthalic acid*, both nitro-groups must be in the same ring in the naphthalene nucleus. Thus, nitration of 1 : 5-diacetoxynaphthalene gave 2 : 4-*dinitro*-5-*acetoxy*-1-*naphthol* (XIV), as shown by the fact that this was converted by methylation into 6 : 8-*dinitro*-1-*acetoxy*-

5-*methoxynaphthalene* (XI), identical with the product afforded by nitration of (VII) with diacetyl orthonitric acid. Hydrolysis of (XI) with dilute sodium hydroxide solution gave 2 : 4-*dinitro*-1 : 5-*dihydroxynaphthalene* (XII) with elimination of both the acetyl and the methoxyl group, whilst boiling (XI) with water hydrolysed the methoxyl group with formation of 2 : 4-*dinitro*-5-*acetoxy*-1-*naphthol*, whereas boiling (XI) with methyl-alcoholic ammonia solution removed the acetyl group with formation of 6 : 8-*dinitro*-5-*methoxy*-1-*naphthol* (XIII), m. p. 202—204°, which was not identical with 2 : 4-*dintro*-5-*methoxy*-1-*naphthol* (V), m. p. 173° (decomp.), prepared by nitration of 5-methoxy-1-naphthol. Thus, in the nitration of 5-methoxy-1-naphthol, both nitro-groups enter the ring of the naphthalene nucleus which contains the hydroxyl group, whereas in the nitration of 1-acetoxy-5-methoxynaphthalene, both nitro-groups enter the ring containing the methoxyl group, as would be anticipated from electronic considerations. The dinitromethoxy-1-naphthols and some other methoxy-derivatives in this series resisted demethylation and gave consistently low results in methoxyl determinations.

The great lability of substituents in the α-position in 2 : 4-dinitro-compounds, indicated by the hydrolysis of the methoxyl group in 6 : 8-dinitro-1-acetoxy-5-methoxynaphthalene by boiling with water, was further illustrated by the ease with which a methoxyl group in 2 : 4-dinitro-1 : 5-dimethoxynaphthalene was replaced by an amino-group by reaction with ammonia in boiling alcoholic solution, forming 2 : 4-*dinitro*-5-*methoxy*-1-*naphthylamine*. Moreover, an attempted monoreduction of 2 : 4-dinitro-1 : 5-dimethoxynaphthalene with aqueous sodium sulphide gave 2 : 4-dinitro-5-methoxy-1-naphthol.

1 : 5-Dimethoxynaphthalene on nitration gives a dinitrodimethoxynaphthalene, m. p. 275°, converted by oxidation with dilute nitric acid into 6-nitro-3-methoxyphthalic acid, so the nitro-groups are in different rings in the naphthalene nucleus. In view of the *p*-directing influence of the methoxyl groups it is to be expected that the second nitro-group would enter the nucleus in position 8 to form a symmetrical compound (cf. dibromination of 1 : 5-dimethoxynaphthalene; Carter, Race, and Rowe, *loc. cit.*). This was supported by the isolation of this dinitro-compound as the sole product of dinitration of 1 : 5-dimethoxynaphthalene, by formation of 6-nitro-3-methoxyphthalic acid on oxidation, and by the general stability of the compound, particularly its failure to react with ammonia when heated in a sealed tube at 200°. Thus, dinitration of 1 : 5-dimethoxynaphthalene gave 4 : 8-*dinitro*-1 : 5-*dimethoxynaphthalene* (II).

1-Acetoxy-5-methoxynaphthalene is converted by nitric acid at 0° into a dinitro-5-methoxy-1-naphthol, m. p. 183° (gas evolution) (IX), different from (V) and (XIII), and (IX) was also obtained from 8-nitro-1-acetoxy-5-methoxynaphthalene (VII) by the action of nitric acid at 5°. Methylation of (IX) gave a dinitro-1 : 5-dimethoxynaphthalene (X), m. p. 135°. Since compound (X), which is the third dinitrodimethoxynaphthalene containing a nitro-group in position 4, is not identical with (II) or (VI), it must be 2 : 8-*dinitro*-1 : 5-*dimethoxynaphthalene*, and (IX) is 2 : 8-*dinitro*-5-*methoxynaphthol*.

Nitration of 1 : 5-dihydroxynaphthalene with copper nitrate in acetic anhydride gave a dinitrodihydroxynaphthalene (XX), not identical with (XII), and converted by methylation into a dinitro-1 : 5-dimethoxynaphthalene, m. p. 222° (XXI). Since this compound is not identical with any of the dinitro-1 : 5-dimethoxynaphthalenes (II), (VI), or (X) already described, it must be 2 : 6-*dinitro*-1 : 5-*dimethoxynaphthalene*, and its formation is analogous to the dibromination of 1 : 5-dihydroxynaphthalene (Carter, Race, and Rowe, *loc. cit.*).

Further nitration of 2 : 4-dinitro-1 : 5-dimethoxynaphthalene (VI) and of 4 : 8-dinitro-1 : 5-dimethoxynaphthalene (II) gave the same trinitro-derivative, which is therefore 2 : 4 : 8-*trinitro*-1 : 5-*dimethoxynaphthalene* (III).

1 : 5-Diacetoxynaphthalene with nitric acid at 50° gave a trinitro-5-acetoxy-1-naphthol, converted by hydrolysis and methylation into trinitro-1 : 5-dimethoxynaphthalene, m. p. 238° (XVII), which was not identical with (III) and so is 2 : 4 : 6-*trinitro*-1 : 5-*dimethoxynaphthalene*.

Finally, nitration of 2 : 4 : 8-trinitro-1 : 5-dimethoxynaphthalene gave a tetranitro-derivative, which was also obtained by nitrating 1 : 5-dihydroxynaphthalene with diacetyl orthonitric acid, followed by methylation of the product, and this compound is 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*dimethoxynaphthalene* (IV).

Experimental.

(Where identity is specified, this was established by mixed m. p.)

4-*Nitro*-1 : 5-*dimethoxynaphthalene* (I) (Bentley, Robinson, and Weizmann, *J.*, 1907, **91**, 107).—Nitric acid (*d* 1·42, 4 c.c.) in acetic acid (4 c.c.) was added slowly to a stirred suspension of 1 : 5-dimethoxynaphthalene (10 g.) in acetic acid (400 c.c.) at room temperature. After 30 mins., the mixture was

warmed to 80° until complete dissolution was obtained, and then allowed to cool. 4-*Nitro*-1 : 5-*dimethoxynaphthalene* crystallised from acetic acid in yellow rhombic plates, m. p. 167° (11 g.; 89%) (Found: C, 62·1; H, 4·6; N, 6·1. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7; N, 6·0%).

4 : 8-*Dinitro*-1 : 5-*dimethoxynaphthalene* (II).—Twice as much nitric acid was used as in the preparation of (I) and the suspension was boiled. 4 : 8-*Dinitro*-1 : 5-*dimethoxynaphthalene* separated from acetic acid in pale yellow prismatic needles, m. p. 275°, which darkened on prolonged exposure to light (12·5 g.; 84%) (Found: C, 52·1; H, 3·55; N, 10·2. $C_{12}H_{10}O_6N_2$ requires C, 51·8; H, 3·9; N, 10·1%).

2 : 4 : 8-*Trinitro*-1 : 5-*dimethoxynaphthalene* (III).—Nitric acid (*d* 1·5, 15 c.c.) was added to a solution of compound (II) (2 g.) in boiling acetic acid (150 c.c.). After being refluxed for 1 hr., the solution was cooled and poured into water. The precipitate of 2 : 4 : 8-*trinitro*-1 : 5-*dimethoxynaphthalene* crystallised from dilute acetic acid in long yellow needles, m. p. 180° (1 g.; 43%) (Found: C, 44·7; H, 3·0; N, 12·8. $C_{12}H_9O_8N_3$ requires C, 44·6; H, 2·8; N, 13·0%).

2 : 4 : 6 : 8-*Tetranitro*-1 : 5-*dimethoxynaphthalene* (IV).—Compound (III) (1·5 g.) was added in small amounts to nitric acid (*d* 1·5, 15 c.c.) at 0°, with stirring. After standiug for 1 hr., the solution was poured on ice and the precipitate crystallised, first from acetic acid, and then from toluene in light orange rhombic plates, m. p. 255° (gas evolution) (0·4 g.; 23%) (Found: C, 38·9; H, 2·1; N, 14·9. $C_{12}H_8O_{10}N_4$ requires C, 39·1; H, 2·2; N, 15·2%).

2 : 4-*Dinitro*-5-*methoxy*-1-*naphthol* (V) (cf. Hodgson and Smith, *J.*, 1935, 671).—To a stirred suspension of 5-methoxy-1-naphthol (10 g.) in acetic anhydride (40 c.c.) at 0°, an ice-cold solution of diacetyl orthonitric acid (12 c.c.) in acetic anhydride (10 c.c.) was added dropwise during 1 hr. Stirring was continued for 90 mins., after which the mixture was poured on ice, the black precipitate being collected, washed with water, and dried. The product was repeatedly extracted with 2% sodium carbonate solution, and the extracts combined and acidified. The yellow precipitate was crystallised several times from carbon tetrachloride (charcoal), from which it separated in orange needles, m. p. 173° (decomp.) (0·7 g.; 6%) (Found: C, 49·95; H, 3·5; N, 10·6. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6%). Acetylation of compound (V) with acetic anhydride containing a trace of concentrated sulphuric acid afforded 2 : 4-*dinitro*-1-*acetoxy*-5-*methoxynaphthalene*, fine yellow needles, m. p. 154° (gas evolution) (Found: C, 50·5; H, 3·15; N, 10·0. $C_{13}H_{10}O_7N_2$ requires C, 51·0; H, 3·3; N, 9·15%). Attempts to mononitrate 5-methoxy-1-naphthol were unsuccessful.

2 : 4-*Dinitro*-1 : 5-*dimethoxynaphthalene* (VI).—A suspension of compound (V) (1·4 g.) in ether (50 c.c.) at −10° was methylated with diazomethane, prepared by the action of potassium hydroxide solution (10 c.c., 50%) on nitrosomethylurea (3 g.) in ether (30 c.c.). After 3 hrs., the *product* was collected and crystallised from dilute acetic acid in yellow needles, m. p. 153° (Found: C, 51·5; H, 3·5; N, 10·1 $C_{12}H_{10}O_6N_2$ requires C, 51·8; H, 3·6; N, 10·1%). Nitric acid (*d* 1·5, 5 c.c.) was added to compound (VI) (2 g.) in hot acetic acid (30 c.c.), and the solution refluxed gently for 30 mins. The crystals which separated on cooling (0·4 g.; 17%), after recrystallisation from dilute acetic acid, formed yellow needles, m. p. 180°, identical with compound (III). A solution of compound (VI) (1 g.) in hot acetic acid (10 c.c.) was refluxed gently with nitric acid (*d* 1·5, 5 c.c.) for 30 mins. Crystals were deposited on cooling, and these, when recrystallised from toluene, furnished light orange rhombic plates, m. p. 255° (gas evolution), identical with compound (IV).

8-*Nitro*-1-*acetoxy*-5-*methoxynaphthalene* (VII).—Nitric acid (*d* 1·42, 1·5 c.c.) in acetic acid (3·5 c.c.) was added slowly to a stirred solution of 1-acetoxy-5-methoxynaphthalene (5 g.) in acetic acid (20 c.c.) at room temperature during 1 hr. The mixture was poured on ice, and the product crystallised from dilute acetic acid in golden-yellow needles or plates, m. p. 136° (2·3 g.; 38%) (Found: C, 59·9; H, 4·4; N, 5·5; OMe, 11·0. $C_{13}H_{11}O_5N$ requires C, 59·8; H, 4·2; N, 5·4; OMe, 11·9%).

8-*Nitro*-5-*methoxy*-1-*naphthol* (VIII).—Compound (VII) (2 g.) was hydrolysed by boiling gently with sodium hydroxide solution (20 c.c., 5%) for 5 mins.; the deep red solution was diluted with water, cooled, and acidified, the precipitate which formed being collected and crystallised from dilute alcohol, forming brown needles or plates, m. p. 165° (1·65 g.; 95%) (Found: C, 60·2; H, 4·2; N, 6·1; OMe, 12·5. $C_{11}H_9O_4N$ requires C, 60·3; H, 4·1; N, 6·4; OMe, 14·2%). Compound (VIII) (1 g.) was dissolved in sodium hydroxide solution (220 c.c., 0·125%) and warmed to 30°. Excess of methyl sulphate was added and, after being shaken for 30 mins., the precipitate was collected and crystallised from acetic acid, forming yellow rhombic plates, m.p. 167°, identical with compound (I).

2 : 8-*Dinitro*-5-*methoxy*-1-*naphthol* (IX).—1-Acetoxy-5-methoxynaphthalene (20 g.) was added gradually, with stirring, to nitric acid (*d* 1·42, 100 c.c.) at 0°. The yellow crystals were filtered off, washed with water, and recrystallised from alcohol; yellow needles, m. p. 183° (gas evolution) (8·3 g.; 40%) (Found: C, 49·7; H, 2·9; N, 10·0. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6%). Concentration of the alcoholic filtrate afforded 6 : 8-dinitro-5-methoxy-1-acetoxynaphthalene (XI) (2·2 g.), m. p. 134°. 2 : 8-*Dinitro*-5-*methoxy*-1-*naphthol* was soluble in alkali, but all attempts to acetylate it were unsuccessful.

2 : 8-*Dinitro*-1 : 5-*dimethoxynaphthalene* (X).—Compound (IX) (1 g.) was suspended in ether (30 c.c.) at −10° and methylated with diazomethane. 2 : 8-*Dinitro*-1 : 5-*dimethoxynaphthalene* crystallised from dilute acetic acid in fine pale yellow needles, m. p. 135° (Found: C, 51·3; H, 3·4; N, 9·7. $C_{12}H_{10}O_6N$ requires C, 51·8; H, 3·9; N, 10·1%).

6 : 8-*Dinitro*-1-*acetoxy*-5-*methoxynaphthalene* (XI).—1-Acetoxy-5-methoxynaphthalene (10 g.) was added gradually with stirring to nitric acid (*d* 1·42, 50 c.c.) at 40°. The mixture was poured on ice, and the precipitate crystallised from alcohol in pale yellow needles or plates, m. p. 134° (1·3 g.; 9%) (Found: C, 51·0; H, 3·25; N, 9·0; OMe, 9·85. $C_{13}H_{10}O_7N_2$ requires C, 51·0; H, 3·3; N, 9·15; OMe, 10·1%).

Both compounds (IX) and (XI) were obtained by nitration of 8-nitro-1-acetoxy-5-methoxynaphthalene, a factor of importance in determining the orientation of the second nitro-group. Diacetyl orthonitric acid (2 c.c.) was added slowly to 8-nitro-1-acetoxy-5-methoxynaphthalene (1 g.) in acetic anhydride (4 c.c.), the temperature rising to 90°. The solution was poured on ice, and the product crystallised from dilute acetic acid in pale yellow needles, m. p. 134° (0·5 g.; 43%), identical with compound (XI). 8-Nitro-1-acetoxy-5-methoxynaphthalene (3·7 g.) was added in small amounts to

nitric acid (*d* 1·42, 18 c.c.) at 5°. The crystals were collected, washed with water, and recrystallised from alcohol in yellow needles, m. p. 183° (gas evolution) (0·5 g.; 13%), identical with compound (IX).

2 : 4-*Dinitro*-1 : 5-*dihydroxynaphthalene* (XII).—Compound (XI) (1·75 g.) was suspended in sodium hydroxide solution (50 c.c., 2%) and refluxed for 10 mins. The dark red solution was cooled and acidified, and the precipitate which formed crystallised from dilute acetic acid in golden-brown needles, m. p. 247° (decomp.) (1 g.; 66%), and contained no methoxyl group (Found : C, 48·4; H, 2·5; N, 10·8. $C_{10}H_6O_6N_2$ requires C, 48·0; H, 2·4; N, 11·2%). Methylation of compound (XII) with diazomethane afforded yellow plates, m. p. 153°, identical with compound (VI), whilst the product of methylation with excess of methyl sulphate in alkaline solution was orange needles, m. p. 173° (decomp.), identical with 2 : 4-dinitro-5-methoxy-1-naphthol (V).

The methoxyl group in compound (XI) (1 g.) was also hydrolysed by vigorously refluxing a suspension in water (800 c.c.) for 5 hrs. The orange solution was filtered and allowed to cool; the small yellow prisms (0·5 g.; 62%) which were deposited recrystallised from alcohol in yellow needles, m. p. 189°, identical with 2 : 4-dinitro-5-acetoxy-1-naphthol (XIV).

6 : 8-*Dinitro*-5-*methoxy*-1-*naphthol* (XIII).—A solution of 6 : 8-dinitro-1-acetoxy-5-methoxynaphthalene (1 g.) in methyl alcohol (40 c.c.) was refluxed with ammonia (*d* 0·880, 0·3 c.c.) for 1 hr. The solution was concentrated to 15 c.c., diluted with water (30 c.c.), and allowed to cool. Crystals (0·6 g.; 66%) were deposited and after several recrystallisations from aqueous methyl alcohol, 6 : 8-*dinitro*-5-*methoxy*-1-*naphthol* formed orange-brown needles, m. p. 202—204° (Found : C, 50·3; H, 3·4; N, 11·6. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6%).

2 : 4-*Dinitro*-5-*acetoxy*-1-*naphthol* (XIV).—1 : 5-Diacetoxynaphthalene (5 g.) was added in small portions to nitric acid (*d* 1·42, 25 c.c.) at 20°. A crystalline solid separated which, after standing for 30 mins., was collected, washed with water, and crystallised from dilute acetic acid, forming glistening yellow needles, m. p. 189° (3·2 g.; 54%) (Found : C, 48·8; H, 2·8; N, 9·7. $C_{12}H_8O_7N_2$ requires C, 49·3; H, 2·7; N, 9·6%). It could not be acetylated, and 1 : 5-diacetoxynaphthalene could not be mononitrated. Hydrolysis of compound (XIV) with dilute sodium hydroxide solution afforded orange-brown needles, m. p. 247° (decomp.), identical with compound (XII), whilst methylation with diazomethane yielded 6 : 8-dinitro-1-acetoxy-5-methoxynaphthalene (XI), pale yellow needles, m. p. 134°.

2 : 4 : 6-*Trinitro*-5-*acetoxy*-1-*naphthol* (XV).—1 : 5-Diacetoxynaphthalene (30 g.) was added gradually to well-stirred nitric acid (*d* 1·42, 150 c.c.) at 50°. Considerable oxidation occurred and the temperature was lowered to 40° towards the end of the addition, after which the suspension was cooled rapidly to 0°. The product was filtered off and washed with water; it crystallised from acetic acid in yellow needles, m. p. 223° (decomp.) (2·1 g.; 5·1%) (Found : C, 42·6; H, 2·1; N, 12·8. $C_{12}H_7O_9N_3$ requires C, 42·7; H, 2·1; N, 12·5%).

2 : 4 : 6-*Trinitro*-1 : 5-*dihydroxynaphthalene* (XVI).—A suspension of compound (XV) (2·1 g.) in sodium hydroxide solution (20 c.c., 2%) was boiled. The clear deep-red solution was diluted with water and acidified; the precipitate crystallised from dilute acetic acid in yellow needles, m. p. 260° (decomp.) (1·4 g.; 59%) (Found : C, 41·1; H, 1·9; N, 14·2. $C_{10}H_5O_8N_3$ requires C, 40·7; H, 1·7; N, 14·2%).

2 : 4 : 6-*Trinitro*-1 : 5-*dimethoxynaphthalene* (XVII).—Compound (XVI) (1 g.) was suspended in ether (50 c.c.) and methylated with diazomethane. The *product* crystallised from acetic acid in fine yellow needles, m. p. 238° (0·65 g.; 60%) (Found : C, 44·8; H, 3·1; N, 12·7. $C_{12}H_9O_8N_3$ requires C, 44·6; H, 2·8; N, 13·0%).

2 : 4 : 6-*Trinitro*-5-*acetoxy*-1-*methoxynaphthalene* (XVIII).—An ethereal suspension of compound (XV) (1·2 g.) was treated with diazomethane and the product crystallised from acetic acid in pale yellow needles, m. p. 184° (Found : C, 44·7; H, 2·8; N, 12·2; OMe, 9·2. $C_{13}H_9O_9N_3$ requires C, 44·4; H, 2·6; N, 12·0; OMe, 8·8%). It behaved in a similar manner to 6 : 8-dinitro-1-acetoxy-5-methoxynaphthalene, being hydrolysed by dilute sodium hydroxide solution to 2 : 4 : 6-trinitro-1 : 5-dihydroxynaphthalene (XVI), whilst boiling water demethylated it with formation of 2 : 4 : 6-trinitro-5-acetoxy-1-naphthol (XV).

2 : 4 : 6 : 8-*Tetranitro*-1 : 5-*dihydroxynaphthalene* (XIX).—Compound (XIV) (6 g.) was added gradually to nitric acid (*d* 1·5, 12 c.c.) at 0°. After standing for 30 mins., the suspension was filtered off, washed with water, and dried. Fractional crystallisation from acetone afforded a little unchanged compound (XIV) (0·45 g.), together with 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*dihydroxynaphthalene*, small yellow needles, which decomposed violently between 250° and 265° according to the rate of heating (1·1 g.; 16%) (Found : C, 35·15; H, 1·4; N, 15·5. $C_{10}H_4O_{10}N_4$ requires C, 35·3; H, 1·2; N, 16·5%).

Direct nitration of 1 : 5-dihydroxynaphthalene also afforded the tetranitro-derivative. An ice-cold solution of diacetyl orthonitric acid (7 c.c.) in acetic anhydride (10 c.c.) was run slowly into a stirred suspension of 1 : 5-dihydroxynaphthalene (5 g.) in acetic anhydride (30 c.c.) at 0° during 1½ hrs. The dark brown mixture was poured on ice, and the black precipitate collected, washed, and dried. After extraction with acetic acid and concentration of the extract (charcoal) to small bulk, brown needles were deposited on cooling, and these, when recrystallised from acetone, formed yellow needles decomposing violently at 250—265° (0·6 g.; 6%). The compound was sparingly soluble in most organic solvents, and coloured red by alkalis without dissolution. Methylation with diazomethane gave 2 : 4 : 6 : 8-tetranitro-1 : 5-dimethoxynaphthalene (IV).

2 : 6-*Dinitro*-1 : 5-*dihydroxynaphthalene* (XX) (cf. Mencke, *Rec. Trav. chim.*, 1925, **44**, 269).—A suspension of 1 : 5-dihydroxynaphthalene (20 g.) in acetic acid (100 c.c.) was added slowly to a well-stirred suspension of copper nitrate (20 g.) in acetic anhydride (50 c.c.) at 10°, and the temperature was then allowed to rise slowly to 25°. After gentle effervescence had occurred, the mixture was stirred for 15 mins. below 40° and poured into water. The precipitate was collected, washed, dried, and repeatedly extracted with dilute sodium carbonate solution. The violet-red extracts were combined and acidified, the precipitate which formed crystallising from acetic acid (charcoal) in glistening orange leaflets, m. p. 246° (decomp.) (0·5 g.; 1·6%) (Found : C, 49·1; H, 2·6; N, 11·4. $C_{10}H_6O_6N_2$ requires C, 48·0; H, 2·4; N, 11·2%).

2 : 6-*Dinitro*-1 : 5-*dimethoxynaphthalene* (XXI).—Compound (XX) was methylated with diazomethane and crystallised from acetic acid in fine straw-coloured needles, m. p. 222° (Found : C, 51·8; H, 3·6; N, 8·9. $C_{12}H_{10}O_6N_2$ requires C, 51·8; H, 3·9; N, 10·1%).

4-*Amino*-1 : 5-*dimethoxynaphthalene* (XXII).—Compound (I) (10 g.), granulated tin (15 g.), and hydrochloric acid (100 c.c.) were refluxed for 3 hrs. The hydrochloride, which separated on cooling, recrystallised from dilute hydrochloric acid in minute grey plates, decomposing without melting at 264° (approx.) (10 g.; 97%). The hydrochloride was dissolved in dilute hydrochloric acid (600 c.c.) and basified with sodium hydroxide solution. The *base* crystallised from alcohol in glistening leaflets, m. p. 160° (4·1 g.; 47%) (Found : C, 70·8; H, 6·8; N, 7·0. $C_{12}H_{13}O_2N$ requires C, 70·9; H, 6·4; N, 6·9%), readily oxidisable and becoming violet in air. When this was warmed with acetic anhydride the *monoacetyl* derivative was obtained, crystallising from alcohol in colourless needles or plates, m. p. 186° (Found : C, 68·4; H, 6·1; N, 5·6. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·1; N, 5·7%). The base was diazotised in dilute hydrochloric acid at −10° and coupled with β-naphthol in alkaline solution; 1 : 5-*dimethoxynaphthaleneazo-β-naphthol* crystallised from toluene in bronze-green needles, m. p. 214° (Found : C, 73·6; H, 5·3; N, 8·2. $C_{22}H_{18}O_3N_2$ requires C, 73·7; H, 5·1; N, 8·0%).

4-*Bromo*-1 : 5-*dimethoxynaphthalene*.—The hydrochloride (6 g.) of compound (XXII) was boiled with water (100 c.c.) and hydrochloric acid (4·5 c.c.), the solution being cooled rapidly to 0°. Sodium nitrite solution was added slowly beneath the surface, with stirring. After 15 mins. the diazo-solution was filtered, added in portions to cuprous bromide solution at 0°, with shaking between additions, and the mixture warmed on the water-bath for 30 mins. until evolution of nitrogen ceased. The product was filtered off, washed, dried, and extracted with alcohol (charcoal), the extract being concentrated to small bulk and diluted with water. 4-Bromo-1 : 5-dimethoxynaphthalene recrystallised from dilute alcohol in colourless leaflets, m. p. 106·5° (0·2 g.; 3%) (Found : Br, 29·7. Calc. for $C_{12}H_{11}O_2Br$: Br, 29·9%) (cf. Fischer and Bauer, *loc. cit.*, who recorded m. p. 115°), identical with the product of monobromination of 1 : 5-dimethoxynaphthalene.

8-*Nitro*-4-*amino*-1 : 5-*dimethoxynaphthalene* (XXIII).—Sodium sulphide (24 g.) in water (150 c.c.) was added to a suspension of compound (II) (8 g.) in alcohol (500 c.c.), refluxed vigorously for 1 hr., and the dark red-brown solution then filtered and concentrated to 400 c.c. The nitro-amine, which was deposited on cooling, recrystallised from alcohol in glistening orange leaflets, m. p. 200° (6·07 g.; 94%) (Found : C, 56·7; H, 4·8; N, 10·8. $C_{12}H_{12}O_4N_2$ requires C, 58·0; H, 4·8; N, 11·3%). The *acetyl* derivative, obtained when the base was warmed with acetic anhydride and poured into water, crystallised from alcohol in flat yellow needles, m. p. 209° (Found : C, 56·4; H, 4·6; N, 9·7. $C_{14}H_{14}O_5N_2$ requires C, 57·9; H, 4·8; N, 9·7%). The base was diazotised in hydrochloric acid at 0° and coupled with β-naphthol in alkaline solution. 8-*Nitro*-1 : 5-*dimethoxynaphthaleneazo-β-naphthol* crystallised from nitrobenzene in minute reddish-brown prisms with a green reflex, m. p. 280° (Found : C, 64·6; H, 4·2; N, 10·1. $C_{22}H_{17}O_5N_3$ requires C, 65·5; H, 4·2; N, 10·3%).

4 : 8-*Diamino*-1 : 5-*dimethoxynaphthalene* (XXIV).—Compound (II) (25 g.), granulated tin (50 g.), and hydrochloric acid (300 c.c.) were refluxed for 3 hrs. The solid which was deposited on cooling was recrystallised from dilute hydrochloric acid, forming fine colourless needles, charring at 280° (approx.) without melting (20 g.; 70%) (Found : C, 49·4; H, 5·7; N, 9·8; Cl, 23·4. $C_{12}H_{16}O_2N_2Cl_2$ requires C, 49·5; H, 5·5; N, 9·6; Cl, 24·4%). The *hydrochloride* was dissolved in dilute hydrochloric acid (1000 c.c.) and basified with sodium hydroxide solution. The *base* (13 g.; 66%) crystallised with difficulty from alcohol in minute violet crystals with a metallic lustre, m. p. 180° (Found: C, 65·8; H, 6·5; N, 12·8. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·4; N, 12·8%), sparingly soluble in most organic solvents with a faint bluish-violet fluorescence, and rapidly oxidised in air. The *diacetyl* derivative, obtained by refluxing the base with acetic anhydride and pouring on ice, crystallised from acetic anhydride (charcoal) in colourless rhombic plates, m. p. 304° (Found : C, 63·6; H, 5·9; N, 10·3. $C_{16}H_{18}O_2N_2$ requires C, 63·6; H, 6·0; N, 9·3%).

8-*Amino*-1-*acetoxy*-5-*methoxynaphthalene* (XXV).—Compound (VII) (10 g.) was refluxed with sodium hyposulphite (dithionite) (30 g.), alcohol (200 c.c.), and water (70 c.c.) for 2 hrs., and the solution filtered and diluted with water (500 c.c.). The solid which was deposited on keeping crystallised from alcohol in pale brown needles, m. p. 154° (2·2 g.; 24%) (Found: C, 67·4; H, 5·8; N, 6·4. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%).

5-*Methoxy*-1 : 4-*naphthaquinone* (XXVI).—4-Amino-1 : 5-dimethoxynaphthalene hydrochloride (10 g.) was dissolved in boiling water (1000 c.c.) containing concentrated sulphuric acid (30 c.c.), and oxidised with potassium dichromate solution (800 c.c., 1·25%), the mixture being warmed to 60—70° until the quinone began to separate. 5-*Methoxy*-1 : 4-*naphthaquinone* was collected; it crystallised from alcohol in orange-brown prismatic needles, m. p. 189° (3·8 g.; 48%) (Found : C, 70·0; H, 4·35; OMe, 17·2. $C_{11}H_8O_3$ requires C, 70·2; H, 4·3; OMe, 16·5%). The *oxime*, obtained by refluxing the quinone with hydroxylamine hydrochloride in alcoholic solution, crystallised in fine yellow needles, m. p. 233° (decomp.) (Found : C, 64·3; H, 4·5; N, 6·6, $C_{11}H_9O_3N$ requires C, 65·0; H, 4·4; N, 6·9%). 5-*Methoxy*-1 : 4-*naphthaquinone* 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene in small dark red needles, m. p. 286° (decomp.) (Found : C, 55·6; H, 3·2; N, 14·85. $C_{17}H_{12}O_6N_4$ requires C, 55·4; H, 3·3; N, 15·2%). The quinone was reduced by phenylhydrazine in boiling alcoholic solution to 5-*methoxy*-1 : 4-*dihydroxynaphthalene*, which crystallised from benzene in colourless needles, m. p. 190° (Found : C, 69·6; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%).

Oxidation of 8-*Amino*-1-*acetoxy*-5-*methoxynaphthalene*.—The base (3·25 g.) was suspended in acetic acid (40 c.c.), and a solution of chromium trioxide (6·5 g.) in water (13 c.c.) added rapidly with stirring. A vigorous reaction occurred, the temperature rising to 80°. The crystals deposited on cooling recrystallised from acetic acid in minute red needles, m. p. >350°. The product was not a quinone and was not identified (Found : C, 61·8; H, 4·6; N, 6·5%).

Oxidation of 4-*Nitro*-1 : 5-*dimethoxynaphthalene to* 6-*Nitro*-3-*methoxyphthalic Anhydride* (XXVII).—A suspension of the nitro-compound (10 g.) in dilute nitric acid (*d* 1·14, 750 c.c.) was refluxed vigorously for 5 hrs. The resultant solid, which was filtered off, was 4 : 8-dinitro-1 : 5-dimethoxynaphthalene and crystallised from acetic acid in yellow needles, m. p. 275°. The filtrate was evaporated to dryness and the residue separated from ether–ligroin as a sticky yellow solid. Recrystallisation from nitrobenzene afforded 6-*nitro*-3-*methoxyphthalic anhydride* in cream-coloured plates, m. p. 164—165° (Found : C, 48·5; H, 2·3; N, 6·55. $C_9H_5O_6N$ requires C, 48·4; H, 2·2; N, 6·3%). The anhydride gave the

fluorescein reaction when fused with resorcinol, but did not react with sodium bicarbonate solution, and the acid (XXVIII) was obtained by acidifying an alkaline solution of the anhydride.

Oxidation of 4 : 8-*Dinitro*-1 : 5-*dimethoxynaphthalene to* 6-*Nitro*-3-*methoxyphthalic Acid* (XXVIII).—4 : 8-Dinitro-1 : 5-dimethoxynaphthalene (10 g.) was refluxed with nitric acid (*d* 1·14, 750 c.c.) for 2 hrs., the solution filtered, and the filtrate evaporated to dryness on the water-bath. The residue was extracted with ether, and the extract diluted with ligroin. After several crystallisations from ether–ligroin 6-*nitro*-3-*methoxyphthalic acid* was obtained in small colourless prisms, m. p. 179—180° (gas evolution), which became opaque and coloured on drying (1 g.; 12%) (Found : C, 44·8; H, 3·0; N, 5·7. $C_9H_7O_7N$ requires C, 44·7; H, 2·9; N, 5·8%). The acid dissolved in water with a yellow colour, liberated carbon dioxide from sodium bicarbonate solution, and gave a positive fluorescein reaction when fused with resorcinol.

Oxidation of 2 : 4-*Dinitro*-5-*acetoxy*-1-*naphthol to* 4 : 6-*Dinitro*-3-*hydroxyphthalic Acid* (*Ammonium Salt*) (XXIX).—A suspension of the naphthol (10 g.) in dilute nitric acid (*d* 1·15, 140 c.c.) was refluxed for 1½ hrs., filtered, diluted with water (50 c.c.), and cooled. The solution was extracted with ether, and the ether removed in a stream of air. The residue was very soluble in water, alcohol, and ether, insoluble in ligroin, and gave the fluorescein reaction when fused with resorcinol. 4 : 6-Dinitro-3-hydroxyphthalic acid was isolated as the ammonium salt, which crystallised under reduced pressure from a little water containing a drop of ammonia in brownish-yellow plates, or, when cooled rapidly, in yellow needles (1·2 g.; 17%) (Found : C, 31·2; H, 3·2; N, 18·5. Calc for $C_8H_{10}O_9N_4$: C, 31·4; H, 3·3; N, 18·3%) (cf. Bernthsen and Semper, *Ber.*, 1885, **18**, 204).

Action of Ammonia and Methylamine on Nitro-1 : 5-*dimethoxynaphthalenes.*—4-Nitro-1 : 5-dimethoxynaphthalene and 4 : 8-dinitro-1 : 5-dimethoxynaphthalene did not react with ammonia in a sealed tube at 200°.

2 : 4-Dinitro-1 : 5-dimethoxynaphthalene (0·5 g.) in alcohol (30 c.c.) was refluxed for 2 hrs. with ammonia (*d* 0·880, 2 c.c.). 2 : 4-*Dinitro*-5-*methoxy*-1-*naphthylamine* crystallised from alcohol in fine orange-yellow needles, m. p. 225° (Found : C, 50·5; H, 3·7; N, 15·5. $C_{11}H_9O_5N_3$ requires C, 50·2; H, 3·4; N, 16·0%). The *acetyl* derivative, obtained by warming the base with acetic anhydride containing a drop of concentrated sulphuric acid, crystallised from dilute acetic acid in yellow, feathery needles, m. p. 262° (Found : C, 51·3; H, 3·7; N, 14·3. $C_{13}H_{11}O_6N_3$ requires C, 51·2; H, 3·6; N, 13·8%). Similarly, 2 : 4 : 8-trinitro-1 : 5-dimethoxynaphthalene, when refluxed in alcoholic solution with excess of methylamine, yielded 2 : 4 : 8-*trinitro*-1-*methylamino*-5-*methoxynaphthalene*, crystallising from dilute acetic acid in orange needles, m. p. 204° (Found : C, 44·7; H, 3·2; N, 17·4. $C_{12}H_{10}O_7N_4$ requires C, 44·7; H, 3·1; N, 17·4%).

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