393. *Studies in the Naphthalene Series. Part I. Preparation of Polyhydroxy-derivatives of Naphthalene.*

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1 : 2 : 6- and 1 : 2 : 7-Trihydroxy- and 1 : 2 : 5 : 6- and 1 : 2 : 7 : 8-tetrahydroxynaphthalene could not be prepared from the corresponding amino- or bromo-compounds. The two *trihydroxynaphthalenes* were obtained from 2 : 6- and 2 : 7-dihydroxynaphthalene by the sequence of changes: nitroso-compound, amino-compound, hydroxy-quinone, trihydroxynaphthalene; and various derivatives were prepared.

IN attempts to prepare tri- and tetra-hydroxynaphthalenes containing respectively one and two catechol nuclei, 2 : 6-dimethoxynaphthalene (Chakravarti, *J. Indian Chem. Soc.*, 1933, **10**, 694) was converted into the *mono-* and the *di-nitro*-compound and these were reduced to the corresponding amino-compounds: similar reactions were carried out with 2 : 7-dimethoxynaphthalene. None of the four amino-compounds, however, could be converted into the corresponding hydroxy-compound through the diazonium salt.

Halogen atoms in the 1 : 5-positions in naphthalene are reactive and readily form Grignard reagents (Salkind, *Ber.*, 1934, **67**, 1031). It was found, however, that although 1-bromo-2-methoxynaphthalene could be converted into 2-methoxy-1-naphthol in very poor yield through the Grignard compound, the conversion of 1 : 5-*dibromo*-2 : 6-*dimethoxynaphthalene* into 1 : 5-dihydroxy-2 : 6-dimethoxynaphthalene could not be brought about. Attempts to replace the bromine atoms directly by hydroxyl by means of aqueous or alcoholic potash, or by fusion with caustic potash, did not yield encouraging results.

Finally, 2 : 7-dihydroxynaphthalene was converted into its monomethyl ether; this was nitrosated, the nitroso-compound reduced to the corresponding amino-compound, and the hydrochloride of the base oxidised to 7-*methoxy*-1 : 2-*naphthaquinone*, which was readily reduced to 1 : 2-*dihydroxy*-7-*methoxynaphthalene* by sulphurous acid. 1 : 2 : 7-*Trihydroxynaphthalene* was even more readily obtained from 2 : 7-dihydroxynaphthalene by a similar series of reactions. Both compounds on methylation with methyl iodide and anhydrous potassium carbonate in dry acetone, gave the same trimethoxynaphthalene, characterised by its *picrate*, m. p. 115°.

The above method also produced 1 : 2 : 6-*trihydroxynaphthalene* from 2 : 6-dihydroxynaphthalene, but it could not be applied to 1 : 2 : 7-trihydroxynaphthalene, because this compound, on attempted nitrosation or nitration, was oxidised to the hydroxy-quinone. With the object, therefore, of preparing 1 : 2 : 7 : 8-tetrahydroxynaphthalene, 8-*nitro*-7-*hydroxy*-1 : 2-*naphthaquinone*, obtained by the nitration of 7-hydroxy-1 : 2-naphtha-

quinone, was reduced (1) to 8-amino-1 : 2 : 7-trihydroxynaphthalene by means of stannous chloride and hydrochloric acid, and (2) to 8-*nitro*-1 : 2 : 7-*trihydroxynaphthalene* by means of sulphurous acid; the latter compound was methylated, and the 8-*nitro*-1 : 2 : 7-*trimethoxynaphthalene* reduced to 8-amino-1 : 2 : 7-trimethoxynaphthalene. Neither amino-compound, however, could be oxidised to a naphthaquinone, and their amino-group could not be replaced by hydroxyl. The latter amino-compound was diazotisable and 8-*iodo*-1 : 2 : 7-*trimethoxynaphthalene* was readily prepared from it in the usual way.

Experimental.

1-*Nitro- and* 1 : 5-*Dinitro*-2 : 6-*dimethoxynaphthalene*.—(1) 2 : 6-Dimethoxynaphthalene (8 g.) in glacial acetic acid was treated with a mixture of nitric acid (9 g.; *d* 1·42) and glacial acetic acid (9 g.) at room temperature and after ½ hour the product was poured into ice-cold water. 1-*Nitro*-2 : 6-*dimethoxynaphthalene* crystallised from benzene in orange needles, m.p. 189° (Found: C, 61·6; H, 4·9; N, 6·1. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7; N, 6·0%).

(2) 2 : 6-Dimethoxynaphthalene (10 g.) in glacial acetic acid (150 c.c.) was similarly treated with a mixture of nitric acid (80 g.; *d* 1·42) and glacial acetic acid (80 g.), a mixture of sulphuric acid (20 g.) and glacial acetic acid (20 g.) being added before the ½ hour's standing. 1 : 5-*Dinitro*-2 : 6-*dimethoxynaphthalene* crystallised from pyridine in golden-yellow needles, m. p. 265° (Found: N, 10·1. $C_{12}H_{10}O_6N_2$ requires N, 10%); yield, almost quantitative.

1-*Amino- and* 1 : 5-*Diamino*-2 : 6-*dimethoxynaphthalene*.—(1) The mononitro-compound (5 g.) was warmed on the water-bath with stannous chloride (16 g.) in anhydrous alcohol (40 c.c.) saturated with dry hydrogen chloride. After ½ hour, on cooling, the *hydrochloride* of 1-amino-2 : 6-dimethoxynaphthalene separated; it crystallised from water in silky needles, m. p. 270° (decomp.) (Found: N, 5·9. $C_{12}H_{13}O_2N$,HCl requires N, 5·8%).

(2) The dinitro-compound (5 g.) was similarly treated (stannous chloride, 32 g.; anhydrous alcohol, 80 c.c.) for 1 hour with vigorous shaking. The hydrochloride of the base was collected after ½ hour, washed with dilute hydrochloric acid, and recrystallised from water, forming silky needles, m. p. 265° (decomp.). When its aqueous solution was basified, the *diamine* was precipitated; it crystallised from benzene in brown plates, m. p. 192° (Found: C, 66·1; H, 6·6; N, 12·9. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·4; N, 12·8%).

2 : 7-*Dihydroxynaphthalene*.—The sodium salt of naphthalene-2 : 7-disulphonic acid (80 g.) was mixed with caustic potash (240 g.) in a nickel crucible and heated carefully with vigorous stirring at 290° for ½ hour and at 290—300° for 10 minutes. The melt was allowed to cool, lixiviated with water (1·2 l.), and acidified with concentrated hydrochloric acid (0·5 l.); 2 : 7-dihydroxynaphthalene (25 g.) separated in white plates, m. p. 194° after recrystallisation from dilute alcohol.

2 : 7-Dimethoxynaphthalene, prepared under conditions similar to those used for the 2 : 6-isomer (Chakravarti, *loc. cit.*), crystallised from alcohol in white needles, m. p. 138°.

1-Nitro-2 : 7-dimethoxynaphthalene, m. p. 141° (crystallised from alcohol), and 1 : 8-dinitro-2 : 7-dimethoxynaphthalene, m. p. 286° (crystallised from pyridine), were prepared by Fischer's method (*J. pr. Chem.*, 1916, **94**, 35).

1-*Amino*-2 : 7-*dimethoxynaphthalene*.—The nitro-compound was reduced in the same way as 1-nitro-2 : 6-dimethoxynaphthalene; on cooling, a stannichloride separated. This was dissolved in water and decomposed with hydrogen sulphide, and the filtered solution basified; the 1-*amino*-2 : 7-*dimethoxynaphthalene* obtained crystallised from aqueous alcohol in long silky needles, m. p. 83° (Found: N, 6·9. $C_{12}H_{13}O_2N$ requires N, 6·9%).

1 : 8-*Diamino*-2 : 7-*dimethoxynaphthalene*, prepared in the same way as 1 : 5-diamino-2 : 6-dimethoxynaphthalene, crystallised from aqueous alcohol in brownish needles, m. p. 115° (Found: N, 13·0. $C_{12}H_{14}O_2N_2$ requires N, 12·8%).

2-*Methoxy*-1-*naphthyl Benzoate*.—1-Bromo-2-methoxynaphthalene (Underwood, *J. Amer. Chem. Soc.*, 1930, **52**, 4090) (50 g.) was dissolved in dry ether (150 c.c.), magnesium turnings (6 g.) added, followed by bromine (0·5 c.c.) to start the reaction, and the whole was heated under reflux for 18 hours with vigorous shaking. Dry oxygen was slowly passed for 3 hours through the cold Grignard solution, which warmed perceptibly. The product was decomposed with dilute hydrochloric acid and extracted thrice with ether, and the extract shaken with 1% sodium hydroxide solution, which was then acidified and extracted with ether (five times). These extracts on evaporation left a residue, which was benzoylated in the usual manner. A benzene extract of the product was washed several times with 10% sodium hydroxide solution and with water, dried (sodium sulphate), and concentrated to a small volume, and sufficient

light petroleum added to produce a turbidity. On scratching and keeping for several hours, a substance (? dinaphthyl derivative), m. p. above 300°, separated; the mother-liquor, on further concentration and keeping, deposited 2-*methoxy*-1-*naphthyl benzoate* in cubic crystals, m. p. 110° after recrystallisation from benzene–light petroleum (Found: C, 77·5; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).

1 : 5-*Dibromo*-2 : 6-*dimethoxynaphthalene*.—2 : 6-Dimethoxynaphthalene (5 g.) in glacial acetic acid (150 c.c.) was brominated (bromine, 8·6 g., in glacial acetic acid, 16 c.c.) and after 1 hour the mixture was poured into water. The precipitated *dibromo*-compound was very sparingly soluble in all the usual organic solvents, but crystallised from nitrobenzene in colourless leaflets, m. p. 257° (Found: C, 41·3; H, 2·7. $C_{12}H_{10}O_2Br_2$ requires C, 41·6; H, 2·9%).

1 : 5-*Dibromo*-2 : 6-*dihydroxynaphthalene* separated when bromine (4 g.) in glacial acetic acid (8 c.c.) was gradually added to 2 : 6-dihydroxynaphthalene (2 g.) in glacial acetic acid (60 c.c.); recrystallised from alcohol, it formed needles, m. p. 223° (Found: C, 37·4; H, 1·6; Br, 49·8. $C_{10}H_6O_2Br_2$ requires C, 37·7; H, 1·9; Br, 50·2%). Methylation with methyl sulphate and alkali in methyl-alcoholic solution gave the preceding dimethoxy-compound, m. p. 257°.

7-*Methoxy*-1 : 2-*naphthaquinone*.—To a suspension of the hydrochloride [long needles, m. p. 257° (decomp.)] of 1-amino-7-methoxy-2-naphthol (10 g.) in 5% sulphuric acid (100 c.c.) below 0°, a cold solution of potassium dichromate (5 g.) in water (35 c.c.) was gradually added. The *quinone* was collected, washed with cold water, air-dried, and crystallised from benzene, separating in orange-yellow needles, m. p. 183° (Found: C, 70·0; H, 4·3. $C_{11}H_8O_3$ requires C, 70·2; H, 4·2%).

1 : 2-*Dihydroxy*-7-*methoxynaphthalene*.—A solution of the quinone (2 g.) in alcohol (50 c.c.) was warmed while sulphur dioxide was passed in. Part of the alcohol was then removed, and the residue diluted with water and extracted with ether. The extract was dried (sodium sulphate), and solvent removed. The residue solidified when scratched with a little benzene–light petroleum and on recrystallisation from ligroin the *dihydroxy*-compound separated in colourless leaflets, which turned brown in air; m. p. 127° (Found: C, 69·4; H, 5·5. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). The *picrate* formed needles, m. p. 156°, from alcohol (Found: N, 10·3. $C_{11}H_{10}O_3,C_6H_3O_7N_3$ requires N, 10·0%). The *diacetoxy*-compound, obtained by heating with acetic anhydride and sodium acetate for 2 hours on the steam-bath, crystallised from dilute alcohol in long needles, m. p. 122° (Found: C, 65·7; H, 5·2. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%).

7-Hydroxy-1 : 2-naphthaquinone was prepared by Dimroth and Kerkovius's method (*Annalen*, 1913, **399**, 42; see also *Ber.*, 1889, **22**, 522; 1897, **30**, 1123). It can be obtained in 95% yields and in an excellent state of purity if the amine hydrochloride is freshly prepared and recrystallised from hydrochloric acid containing a small quantity of stannous chloride, which serves as an anti-oxidant (compare Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 493).

6-Hydroxy-1 : 2-naphthaquinone, prepared by the series of reactions outlined on p. 1859, starting from 2 : 6-dihydroxynaphthalene, crystallised from acetone in orange-yellow needles, m. p. 165°.

1 : 2 : 7-*Trihydroxynaphthalene*.—Sulphur dioxide was passed through a suspension in warm water of 7-hydroxy-1 : 2-naphthaquinone (10 g.), which gradually dissolved. An ethereal extract of the filtered solution was dried and evaporated, and the residue of 1 : 2 : 7-*trihydroxynaphthalene* crystallised from ligroin or xylene; it formed microscopic cubic crystals, m. p. 197° (Found: C, 68·3; H, 4·6. $C_{10}H_8O_3$ requires C, 68·1; H, 4·5%).

1 : 2 : 6-*Trihydroxynaphthalene*, similarly prepared from 6-hydroxy-1 : 2-naphthaquinone, crystallised from ligroin in small needles, m. p. 188° (Found: C, 68·3; H, 4·7%).

1 : 2 : 7-*Trimethoxynaphthalene*.—1 : 2-Dihydroxy-7-methoxy- or 1 : 2 : 7-trihydroxy-naphthalene was refluxed in dry acetone with an excess of methyl iodide and potassium carbonate for 8 hours. Most of the acetone was then removed, and the residue diluted with water and extracted with ether. The extract was washed with aqueous sodium hydroxide, dried (sodium sulphate), and evaporated, leaving an oily residue of 1 : 2 : 7-trimethoxynaphthalene, the *picrate* of which crystallised from dilute alcohol in red needles, m. p. 115° (Found: C, 51·3; H, 3·9. $C_{13}H_{14}O_3,C_6H_3O_7N_3$ requires C, 51·0; H, 3·8%).

1 : 2 : 6-*Trimethoxynaphthalene*, prepared by the same method, crystallised from methyl alcohol–light petroleum in small cubes, m. p. 55° (Found: C, 71·8; H, 6·3. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·4%). The *picrate* formed red needles, m. p. 98°, from aqueous alcohol (Found: C, 51·2; H, 3·7%).

1 : 2 : 7- and 1 : 2 : 6-*Triacetoxynaphthalene*, obtained by heating the trihydroxy-compounds with acetic anhydride and sodium acetate on the water-bath for ½ hour, crystallised from

toluene in colourless cubes, m. p. 181—182° (Found: C, 63·6; H, 4·8%) and 262° (Found: C, 63·7; H, 4·8. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%), respectively.

8-*Nitro*-7-*hydroxy*-1 : 2-*naphthaquinone*.—Nitric acid (10 c.c.; *d* 1·42) was added all at once with vigorous stirring to a suspension of 7-hydroxy-1 : 2-naphthaquinone (20 g.) in glacial acetic acid (160 c.c.) and the mixture was stirred for an hour, the temperature throughout being kept below 35°. The product was poured into water, and the precipitate of 8-*nitro*-7-*hydroxy*-1 : 2-*naphthaquinone* crystallised from glacial acetic acid, forming clusters of red needles, m. p. 210° (decomp.) (Found: C, 54·8; H, 2·3; N, 6·6. $C_{10}H_5O_5N$ requires C, 54·8; H, 2·3; N, 6·4%).

5-*Nitro*-6-*hydroxy*-1 : 2-*naphthaquinone*, similarly obtained from 6-hydroxy-1 : 2-naphthaquinone, crystallised from alcohol and glacial acetic acid in needles, m. p. 205° (Found: N, 6·5%).

8-*Nitro*-1 : 2 : 7-*trihydroxynaphthalene*.—Sulphur dioxide was passed through a suspension of 8-nitro-7-hydroxy-1 : 2-naphthaquinone (5 g.) in water (100 c.c.) at 60°; the nitro-compound dissolved and then 8-*nitro*-1 : 2 : 7-*trihydroxynaphthalene* was almost immediately precipitated. It crystallised from dilute alcohol in red needles, m. p. 220° (Found: N, 6·1. $C_{10}H_7O_5N$ requires N, 6·3%).

8-*Nitro*-1 : 2 : 7-*trimethoxynaphthalene*, prepared from the preceding compound by the method described for 1 : 2 : 7-trimethoxynaphthalene, crystallised from alcohol in golden-yellow needles, m. p. 98° (Found: N, 5·5. $C_{13}H_{13}O_5N$ requires N, 5·3%).

5-*Nitro*-1 : 2 : 6-*trimethoxynaphthalene*, obtained from 5-nitro-6-hydroxy-1 : 2-naphthaquinone by a similar series of reactions, crystallised from alcohol in golden-yellow needles, m. p. 93° (Found: N, 5·5%).

8-*Amino*-1 : 2 : 7-*trihydroxynaphthalene*.—8-Nitro-7-hydroxy-1 : 2-naphthaquinone (1 g.) was warmed on the water-bath with stannous chloride (6 g.) and hydrochloric acid (5 c.c.) until it dissolved. The solution was then saturated with dry hydrogen chloride and left overnight; the *amine hydrochloride* separated in long clusters of needles, m. p. 270—275° (decomp.) (Found: N, 6·2. $C_{10}H_9O_3N$,HCl requires N, 6·2%).

8-*Amino*-1 : 2 : 7-*trimethoxynaphthalene*.—8-Nitro-1 : 2 : 7-trimethoxynaphthalene (4 g.) was warmed on the water-bath with a slight excess of stannous chloride and fuming hydrochloric acid; reduction was complete in 10 minutes and, on cooling, long colourless needles of the *amine hydrochloride* separated, m. p. 255° (decomp.) after recrystallisation from concentrated hydrochloric acid (Found: N, 5·4. $C_{13}H_{15}O_3N$,HCl requires N, 5·2%).

8-*Iodo*-1 : 2 : 7-*trimethoxynaphthalene*.—8-Amino-1 : 2 : 7-trimethoxynaphthalene (0·63 g.) was stirred in 10% sulphuric acid (5 c.c.) cooled in a freezing mixture, and sodium nitrite (0·2 g. in 1 c.c. of water) gradually added. When the reaction was over, potassium iodide (0·6 g. in 1 c.c. of water) was gradually added with stirring and after some time the mixture was heated on the steam-bath for 1 hour. The *product* was extracted with ether, dried (sodium sulphate), and recovered as an oily residue, which separated from light petroleum (b. p. 80—90°) in rhombic crystals, m. p. 72° (Found: C, 45·2; H, 3·6. $C_{13}H_{13}O_3I$ requires C, 45·4; H, 3·8%).

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