223. *Quinoxalines and Related Compounds. Part VI.*[1] *Substitution of 2,3-Dihydroxyquinoxaline and its 1,4-Dimethyl Derivative.*

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Electrophilic substitution of 2,3-dihydroxyquinoxaline and its 1,4-dimethyl derivative occurs at positions 6 and 7. Nitration and bromination of *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine give 4,5-disubstituted derivatives, and hydrolysis of these products affords 4,5-dinitro- and 4,5-dibromo-*o*-phenylenediamine, respectively.

2,3-Dihydroxyquinoxaline was converted into 2,3-dihydroxy-6-nitroquinoxaline when treated in sulphuric acid solution with one equivalent of potassium nitrate; with two equivalents of potassium nitrate, the 6,7-dinitro-compound was obtained. Reaction of quinoxaline itself with hot aqueous nitric acid furnished 2,3-dihydroxy-6-nitroquinoxaline,[2] presumably owing to oxidation and subsequent nitration, and further nitration of the 6-nitro-compound in sulphuric acid gave 2,3-dihydroxy-6,7-dinitroquinoxaline. 2,3-Dihydroxy-6-nitro- and 2,3-dihydroxy-6,7-dinitro-quinoxaline were converted into the

[1] Part V, *J.*, 1961, 1246.
[2] Asai, *Yakugaku Zasshi*, 1959, **79**, 260; *Chem. Abs.*, 1959, **53**, 13,160.

corresponding 2,3-dichloro-derivatives; the other dihydroxyquinoxalines prepared in this investigation were similarly characterised. Mono- and di-nitration of 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline similarly gave the 6-nitro- and the 6,7-dinitro-derivative. For proof of structure, these compounds were also prepared from the corresponding dihydroxy-compounds by treatment with methyl sulphate and potassium hydroxide. A monomethyl compound previously isolated by reaction of 2,3-dihydroxy-6-nitroquinoxaline with methyl sulphate and sodium hydroxide,[3] has now been obtained by treatment of 1,2-dihydro-1-methyl-2-oxoquinoxaline in acetic acid with an excess of fuming nitric acid; it is not identical with the unambiguously synthesised 1,2-dihydro-3-hydroxy-1-methyl-6-nitro-2-oxoquinoxaline [1] and must therefore be the isomeric 7-nitro-derivative. It is noteworthy that 2-hydroxyquinoxaline is also nitrated in acetic acid at position 7 and with an excess of fuming nitric acid is converted into 2,3-dihydroxy-6-nitroquinoxaline.[1]

6,7-Dibromo-2,3-dihydroxyquinoxaline was prepared both by condensation of 4,5-dibromo-*o*-phenylenediamine with ethyl oxalate and by treatment of 2,3-dihydroxyquinoxaline in sulphuric acid with two equivalents of bromine and silver sulphate. Bromination of 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline under similar conditions gave the 6,7-dibromo-derivative; with one equivalent of bromine and silver sulphate, a mixture of 6-bromo- and 6,7-dibromo-compounds was obtained. Mixtures of the mono- and the di-bromo-derivative were isolated on bromination of the 1,4-dimethyl compound in water or acetic acid. The dibromo-compound was also obtained by treatment of 6,7-dibromo-2,3-dihydroxyquinoxaline with methyl sulphate and potassium hydroxide. 6-Bromo-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline had been prepared previously by methylation of 6-bromo-2,3-dihydroxyquinoxaline; [4] it has now been obtained by reaction of diazomethane and 6-bromo-1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline. The latter compound resulted on condensation of 2-amino-4-bromo-*N*-methylaniline and ethyl oxalate.

6-Chloro-2,3-dihydroxyquinoxaline was isolated on chlorination of 2,3-dihydroxyquinoxaline in sulphuric acid. Further chlorination gave 6,7-dichloro-2,3-dihydroxyquinoxaline, which was also prepared from 4,5-dichloro-*o*-phenylenediamine and ethyl oxalate. Treatment of 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline in acetic acid at room temperature with an excess of chlorine gave the 6-chloro-derivative; at 95° the 6,7-dichloro-compound was formed. This compound was also obtained by treatment of 6,7-dichloro-2,3-dihydroxyquinoxaline with methyl sulphate and potassium hydroxide; with diazomethane it gave the isomeric *ON*-dimethyl derivative.

Nitration of *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine in glacial acetic acid gave the 4,5-dinitro-derivative, which on hydrolysis with aqueous sulphuric acid furnished 4,5-dinitro-*o*-phenylenediamine. The structure of the diamine was confirmed both by reduction and subsequent acetylation to the known 1,2,4,5-tetra-acetamidobenzene [5] and by ring closure with acetic acid to 2-methyl-5,6-dinitrobenzimidazole; this compound had been prepared previously by nitration of 2-methyl-5-nitrobenzimidazole.[6] Bromination of the *NN'*-toluene-*p*-sulphonyl compound in acetic acid and hydrolysis of the product furnished similarly 4,5-dibromo-*o*-phenylenediamine.

Experimental

Light petroleum was a fraction of b. p. 60—80°. The identity of samples was confirmed by comparison of their infrared absorption.

2,3-*Dihydroxy*-6-*nitroquinoxaline*.—Powdered potassium nitrate (3·0 g., 0·03 mole) was added rapidly at 0° to a stirred solution of 2,3-dihydroxyquinoxaline (4·86 g., 0·03 mole) in concentrated sulphuric acid (32 ml.). The mixture was stirred at 0° for 30 min. and at room

[3] Landquist, *J.*, 1953, 2816.
[4] Curd, Davey, and Stacey, *J.*, 1949, 1271.
[5] Arient, Marhan, and Täublova, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1602.
[6] Kym and Ratner, *Ber.*, 1912, **45**, 3238.

temperature for 4 hr., then slowly poured into ice–water (*ca.* 300 ml.). The precipitate of 2,3-dihydroxy-6-nitroquinoxaline (6·14 g.) was filtered off, washed with water, and dried. A portion was converted into 2,3-dichloro-6-nitroquinoxaline,[3] m. p. and mixed m. p. 152—153°.

2,3-*Dihydroxy*-6,7-*dinitroquinoxaline*.—(*a*) The dinitro-compound was prepared from potassium nitrate (6·0 g., 0·06 mole), 2,3-dihydroxyquinoxaline (4·86 g., 0·03 mole), and concentrated sulphuric acid (32 ml.), similarly to 2,3-dihydroxy-6-nitroquinoxaline above. The product (6·11 g.) had m. p. >360°. A portion was converted into 2,3-dichloro-6,7-dinitroquinoxaline, m. p. 211—214°.

(*b*) 2,3-Dihydroxy-6-nitroquinoxaline (2·88 g., 0·014 mole) in concentrated sulphuric acid (30 ml.) was caused to react with potassium nitrate (2·0 g., 0·02 mole) similarly to 2,3-dihydroxyquinoxaline above. The product weighed 2·52 g. A portion was converted into 2,3-dichloro-6,7-dinitroquinoxaline, m. p. 212—215°.

(*c*) A mixture of 4,5-dinitro-*o*-phenylenediamine (1·0 g.) and ethyl oxalate (10 ml.) was heated under reflux for 1 hr. and then cooled. The precipitate of 2,3-*dihydroxy*-6,7-*dinitroquinoxaline* (0·76 g.) was filtered off and washed with 96% ethanol. The analytical specimen (from a large volume of glacial acetic acid) had m. p. >360° (Found: N, 22·3. $C_8H_4N_4O_6$ requires N, 22·2%).

2,3-*Dichloro*-6,7-*dinitroquinoxaline*.—2,3-Dihydroxy-6,7-dinitroquinoxaline (3·0 g.), freshly distilled phosphoryl chloride (9 ml.), and dimethylaniline (2 ml.) were heated under reflux for 90 min., then cooled and slowly poured into stirred ice–water. The precipitate was filtered off, washed with water, and dried in a vacuum-desiccator ($KOH–P_2O_5$). Extraction with benzene (100 ml.) and concentration of the filtered extract at reduced pressure to *ca.* 15 ml. gave 2,3-*dichloro*-6,7-*dinitroquinoxaline* (1·83 g.), m. p. 210—212°. The m. p. was raised to 216—218° by crystallisation (charcoal) from 96% ethanol (100 parts) (Found: C, 33·4; H, 0·75; N, 19·7; Cl, 24·4. $C_8H_2Cl_2N_4O_4$ requires C, 33·25; H, 0·7; N, 19·4; Cl, 24·5%).

1,2,3,4-*Tetrahydro*-1,4-*dimethyl*-6-*nitro*-2,3-*dioxoquinoxaline*.—(*a*) 1,2,3,4-Tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (5·7 g., 0·03 mole) in concentrated sulphuric acid (60 ml.) was caused to react with powdered potassium nitrate (3·0 g., 0·03 mole) similarly to 2,3-dihydroxyquinoxaline above. Crystallisation of the product from glacial acetic acid gave the 6-*nitro-compound* (6·02 g.), m. p. (mainly) 259—263°. A sample, crystallised from 96% ethanol (200 parts) and glacial acetic acid (10 parts), had m. p. 263—264° (Found: C, 51·1; H, 3·9; N, 17·6. $C_{10}H_9N_3O_4$ requires C, 51·05; H, 3·9; N, 17·9%).

(*b*) A mixture of 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (1·9 g.) and 2N-nitric acid (50 ml.) was heated under reflux for 17 hr. and then cooled. The precipitate of the 6-nitro-compound (2·30 g.), m. p. (mainly) 260—263°, was filtered off.

(*c*) A solution of 2,3-dihydroxy-6-nitroquinoxaline (2·07 g., 0·01 mole) in N-potassium hydroxide (100 ml.) was shaken with methyl sulphate (9·4 ml., 0·1 mole) for 15 min. The mixture was heated at 95° for 30 min., further N-potassium hydroxide being added to keep the pH at 7, and then filtered. Crystallisation of the precipitate from 96% ethanol and then from glacial acetic acid gave 1,2,3,4-tetrahydro-1,4-dimethyl-6-nitro-2,3-dioxoquinoxaline (1·23 g.), m. p. and mixed m. p. 259—262°.

1,2,3,4-*Tetrahydro*-1,4-*dimethyl*-6,7-*dinitro*-2,3-*dioxoquinoxaline*.—(*a*) 1,2,3,4-Tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (0·95 g., 0·005 mole) in concentrated sulphuric acid (20 ml.) was caused to react with potassium nitrate (2·0 g., 0·02 mole) similarly to 2,3-dihydroxyquinoxaline above. Crystallisation of the product (1·28 g.) from glacial acetic acid gave the 6,7-*dinitro-compound*, m. p. 276—280°. A specimen, crystallised from 96% ethanol (400 parts) and glacial acetic acid (16 parts), had m. p. 279—280° (Found: C, 43·2; H, 3·2; N, 19·9. $C_{10}H_8N_4O_6$ requires C, 42·85; H, 2·9; N, 20·0%).

(*b*) A solution of 2,3-dihydroxy-6,7-dinitroquinoxaline (2·52 g., 0·01 mole) in N-potassium hydroxide (100 ml.) was caused to react with methyl sulphate (9·4 ml., 0·1 mole) similarly to 2,3-dihydroxy-6-nitroquinoxaline above. Repeated crystallisation of the product from 96% ethanol gave 1,2,3,4-tetrahydro-1,4-dimethyl-6,7-dinitro-2,3-dioxoquinoxaline, m. p. and mixed m. p. 279—281°.

Nitration of 1,2-*Dihydro*-1-*methyl*-2-*oxoquinoxaline*.—Fuming nitric acid (8·8 ml., 0·2 mole) in glacial acetic acid (10 ml.) was added to a water-cooled solution of the quinoxaline (3·2 g., 0·02 mole) in glacial acetic acid (15 ml.) so that the temperature remained below 50°. The mixture was heated at 95° for 2 hr. and then filtered. Crystallisation of the precipitate from

glacial acetic acid gave 1,2-dihydro-3-hydroxy-1-methyl-7-nitro-2-oxoquinoxaline (0·59 g.), m. p. >360°. A specimen, crystallised from glacial acetic acid (200 parts) (Found: C, 49·1; H, 3·2; N, 18·8. Calc. for $C_9H_7N_3O_4$: C, 48·9; H, 3·2; N, 19·0%), had infrared absorption identical with that of a specimen prepared by Landquist's method.[3]

6,7-*Dibromo*-2,3-*dihydroxyquinoxaline*.—(*a*) A mixture of 4,5-dibromo-*o*-phenylenediamine (1·2 g.) and ethyl oxalate (10 ml.) was heated under reflux for 1 hr. and then cooled. The precipitate (1·4 g.) was filtered off, washed with 96% ethanol, and dissolved in N-sodium hydroxide (50 ml.). Treatment of the alkaline extract with charcoal and acidification with acetic acid gave 6,7-*dibromo*-2,3-*dihydroxyquinoxaline*, m. p. >360° (from acetic acid) (Found: C, 30·3; H, 1·2; N, 8·5; Br, 49·85. $C_8H_4Br_2N_2O_2$ requires C, 30·0; H, 1·3; N, 8·75; Br, 50·0%).

(*b*) Bromine (6·4 g., 0·04 mole) was added to a stirred solution of 2,3-dihydroxyquinoxaline (3·24 g., 0·02 mole) and silver sulphate (6·24 g., 0·02 mole) in concentrated sulphuric acid (30 ml.). After 24 hr., the precipitate of silver bromide was filtered off and the filtrate poured into ice–water. The product (5·6 g.) was filtered off and washed with water. A portion was converted into 6,7-dibromo-2,3-dichloroquinoxaline, m. p. 182—183°.

6,7-*Dibromo*-2,3-*dichloroquinoxaline*.—6,7-Dibromo-2,3-dihydroxyquinoxaline (2·0 g.) was caused to react with freshly distilled phosphoryl chloride (6 ml.) and dimethylaniline (1 ml.) similarly to 2,3-dihydroxy-6,7-dinitroquinoxaline above, except that the mixture was heated under reflux for 4½ hr. The crude product was extracted with light petroleum (100 ml.), and insoluble matter was removed. The extract gave 6,7-*dibromo*-2,3-*dichloroquinoxaline* (0·87 g.), m. p. (mainly) 177—180°. The m. p. was raised to 182—183° by two further crystallisations (charcoal) from 96% ethanol (130 parts) (Found: C, 26·9; H, 0·8; N, 7·8. $C_8H_2Br_2Cl_2N_2$ requires C, 26·9; H, 0·6; N, 7·85%).

Bromination of 1,2,3,4-*Tetrahydro*-1,4-*dimethyl*-2,3-*dioxoquinoxaline*.—(*a*) Bromine (1·6 g., 0·01 mole) was caused to react with a solution of the quinoxaline (0·95 g., 0·005 mole) and silver sulphate (1·56 g., 0·005 mole) in concentrated sulphuric acid (20 ml.) similarly to 2,3-dihydroxyquinoxaline above, except that the mixture was shaken for 3 hr. Crystallisation of the product (1·65 g.) from glacial acetic acid gave the 6,7-*dibromo-compound* (1·21 g.). When crystallised from glacial acetic acid (25 parts) it had m. p. 311—312° (Found: C, 34·5; H, 2·3; N, 8·0; Br, 45·7. $C_{10}H_8Br_2N_2O_2$ requires C, 34·5; H, 2·3; N, 8·05; Br, 45·9%).

(*b*) Bromine (1·6 g., 0·01 mole) was caused to react with a solution of the quinoxaline (1·9 g., 0·01 mole) and silver sulphate (1·56 g., 0·005 mole) in concentrated sulphuric acid (20 ml.) similarly to 2,3-dihydroxyquinoxaline above, except that the mixture was shaken for 3 hr. Dilution of the acid filtrate to 200 ml. gave a precipitate (0·79 g.), which after crystallisation from 96% ethanol and then from glacial acetic acid furnished the 6,7-dibromo-compound (0·57 g.), m. p. 311—312°. Further dilution of the initial aqueous sulphuric acid filtrate and cooling to 0° gave a precipitate (1·11 g.), m. p. (mainly) 203—207°. Successive crystallisation from water and 96% ethanol gave 6-bromo-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (0·70 g.) which, when crystallised from 96% ethanol (65 parts), had m. p. 214—216°, not depressed on admixture with an authentic specimen [4] (Found: C, 44·6; H, 3·5; N, 10·3; Br, 29·65. Calc. for $C_{10}H_9BrN_2O_2$: C, 44·6; H, 3·4; N, 10·4; Br, 29·7%). Curd, Davey, and Stacey [4] give m. p. 205—206°.

6-*Bromo*-1,2-*dihydro*-3-*hydroxy*-1-*methyl*-2-*oxoquinoxaline*.—A solution of 2-amino-4-bromo-*N*-methylaniline (4·62 g., 0·02 mole) in methanol (40 ml.) was hydrogenated over Raney nickel (B.D.H.; stabilised; 2 g.) at room temperature and pressure until 0·06 mole of hydrogen had been absorbed. Solvent and catalyst were removed and the residual diamine was heated under reflux with ethyl oxalate (20 ml.) for 2 hr. After cooling to 0°, the precipitate (2·9 g.) was filtered off and washed with 96% ethanol. Crystallisation (charcoal) from 96% ethanol gave 6-*bromo*-1,2-*dihydro*-3-*hydroxy*-1-*methyl*-2-*oxoquinoxaline* (2·0 g.), m. p. (mainly) 330—333°. Crystallised from 96% ethanol (250 parts) and then from glacial acetic acid (30 parts) it had m. p. 339—340° (Found: C, 42·7; H, 2·8; N, 11·0; Br, 30·8. $C_9H_7BrN_2O_2$ requires C, 42·4; H, 2·8; N, 11·0; Br, 31·3%).

Methylation of 6-*Bromo*-1,2-*dihydro*-3-*hydroxy*-1-*methyl*-2-*oxoquinoxaline*.—Ethereal diazomethane (from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide, 21·5 g.) was added to a stirred and ice-cooled suspension of the hydroxyquinoxaline (2·4 g.) in dry methanol (10 ml.). The mixture was stirred at 0° for 2 hr., then left overnight at 0°. The precipitate (1·78 g.) was filtered off and extracted with benzene (25 ml.). Crystallisation of the residue from 96%

ethanol (charcoal) and then from benzene gave 6-bromo-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline (0·33 g.), m. p. and mixed m. p. 214—215°.

Methylation of 6,7-*Dibromo*-2,3-*dihydroxyquinoxaline*.—A solution of the hydroxyquinoxaline (0·5 g.) in dimethylformamide (20 ml.) and 5% aqueous potassium hydroxide (20 ml.) was shaken with methyl sulphate (1·26 ml.). The mixture was treated with three further similar portions of 5% aqueous potassium hydroxide and methyl sulphate, then diluted with water (100 ml.) and heated to 95°. Crystallisation of the precipitate (0·18 g.) from 96% ethanol gave colourless needles of 6,7-dibromo-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline, m. p. and mixed m. p. 311—312°.

Chlorination of 2,3-*Dihydroxyquinoxaline*.—Chlorine in carbon tetrachloride (10% w/v; 50 ml.) was added to a solution of 2,3-dihydroxyquinoxaline (3·24 g., 0·02 mole) and silver sulphate (6·24 g., 0·02 mole) in concentrated sulphuric acid (25 ml.). The mixture was shaken at room temperature for 90 min., then filtered to remove silver chloride. The filtrate was separated into two layers, and the sulphuric acid layer poured into ice–water. The precipitate (2·75 g.) was collected, washed with water, and dried. A portion (1·5 g.) was heated under reflux for 2½ hr. with freshly distilled phosphoryl chloride (6 ml.) and dimethylaniline (1 ml.). The product (1·75 g.) was isolated in the usual manner and gave, on crystallisation from light petroleum and then acetone, 2,3,6-trichloroquinoxaline, m. p. 141—142°, not depressed on admixture with an authentic specimen.[3]

6,7-*Dichloro*-2,3-*dihydroxyquinoxaline*.—(*a*) Chlorine in carbon tetrachloride (10% w/v; 10 ml.) was added to 6-chloro-2,3-dihydroxyquinoxaline (1·97 g., 0·01 mole) and silver sulphate (1·56 g., 0·005 mole) in concentrated sulphuric acid (25 ml.). The mixture was shaken at room temperature for 2 hr. and then filtered from silver chloride. The filtrate was separated into two layers, and the sulphuric acid layer poured into ice–water. The precipitate (1·95 g.) was filtered off, washed with water, and dried. A portion (1·5 g.) was heated under reflux for 3½ hr. with freshly distilled phosphoryl chloride (6 ml.) and dimethylaniline (1 ml.). The product (1·82 g.) was isolated in the usual manner; repeated crystallisation from light petroleum and then from ethanol gave 2,3,6,7-tetrachloroquinoxaline, m. p. and mixed m. p. 169—172° (cf. below).

(*b*) A mixture of 4,5-dichloro-*o*-phenylenediamine (1·5 g.) and ethyl oxalate (12·5 ml.) was heated under reflux for 1 hr. and then cooled. The precipitate of 6,7-*dichloro*-2,3-*dihydroxyquinoxaline* (1·95 g.) was filtered off and washed with 96% ethanol. Crystallised from much glacial acetic acid it had m. p. >360° (Found: C, 41·8; H, 1·7; N, 12·55; Cl, 30·9. $C_8H_4Cl_2N_2O_2$ requires C, 41·6; H, 1·75; N, 12·1; Cl, 30·7%).

2,3,6,7-*Tetrachloroquinoxaline*.—6,7-Dichloro-2,3-dihydroxyquinoxaline (1·0 g.) reacted with freshly distilled phosphoryl chloride (6 ml.) and dimethylaniline (1 ml.) similarly to 2,3-dihydroxy-6,7-dinitroquinoxaline above, except that the mixture was heated under reflux for 3 hr. The crude product (1·26 g.) was extracted with light petroleum. Concentration of the extract to *ca.* 10 ml. gave 2,3,6,7-tetrachloroquinoxaline (0·27 g.), m. p. 173—174°. The m. p. was unchanged by crystallisation from ethanol (100 parts) (Found: C, 36·05; H, 1·3; N, 10·4; Cl, 53·0. Calc. for $C_8H_2Cl_4N_2$: C, 35·9; H, 0·7; N, 10·5; Cl, 52·9%). Landquist [3] gives m. p. 170—170·5°. The petroleum-insoluble fraction (0·88 g.) gradually dissolved when heated under reflux with 2N-sodium hydroxide; acidification gave 6,7-dichloro-2,3-dihydroxyquinoxaline (0·62 g.), which had the same infrared absorption as the starting material.

Chlorination of 1,2,3,4-*Tetrahydro*-1,4-*dimethyl*-2,3-*dioxoquinoxaline*.—(*a*) A solution (18 ml.) of chlorine in glacial acetic acid (8·7 g. of chlorine in 104 ml. of glacial acetic acid) was added to a solution of the quinoxaline (1·9 g.) in glacial acetic acid (25 ml.). The mixture was set aside at room temperature for 4 days, then poured into water. The precipitate (1·4 g.), m. p. 184—187°, was filtered off. Crystallisation from 96% ethanol gave 6-chloro-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline, m. p. 191—192°, not depressed on admixture with an authentic specimen.[7]

(*b*) Sulphuryl chloride (3·0 g., 0·022 mole) was added to a solution of the quinoxaline (1·9 g., 0·01 mole) in glacial acetic acid (25 ml.) and acetic anhydride (1 ml.). The mixture was left overnight at room temperature, then heated for 1 hr. at 95°. Water (150 ml.) was added and the precipitate filtered off. Crystallisation from 96% ethanol and then glacial acetic acid gave the 6,7-*dichloro-derivative* (0·50 g.), m. p. 298—300° (from acetic acid) (Found: C, 46·7; H, 3·3; N, 10·8; Cl, 26·65. $C_{10}H_8Cl_2N_2O_2$ requires C, 46·3; H, 3·1; N, 10·8; Cl, 27·4%).

[7] Crowther, Curd, Davey, and Stacey, *J.*, 1949, 1260.

Refrigeration of the initial aqueous acetic acid filtrate gave the impure 6-chloro-derivative (0·28 g.), m. p. (mainly) 181—189°. Treatment of the monochloro-compound (1·4 g.) with an excess of chlorine in acetic acid at 95° also gave the dichloro-derivative (0·86 g.), m. p. 298—300°.

Methylation of 6,7-*Dichloro*-2,3-*dihydroxyquinoxaline*.—(a) *With diazomethane*. The dihydroxyquinoxaline (0·73 g.) was caused to react with diazomethane (from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide, 10·8 g.) similarly to 6-bromo-1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline above. Crystallisation of the product from 96% ethanol and then from glacial acetic acid to constant m. p. gave 6,7-*dichloro*-1,2-*dihydro*-3-*methoxy*-1-*methyl*-2-*oxoquinoxaline* (0·13 g.), m. p. 228—230° (Found: C, 46·4; H, 3·15; N, 11·2; Cl, 27·3%). The product showed strong carbonyl absorption at *ca.* 1675 cm.$^{-1}$ and further strong absorption at 1600 cm.$^{-1}$, which is characteristic of monocarbonyl compounds in this series.[8] Strong absorptions due to the methoxy-group were observed at 1300 and 1250 cm.$^{-1}$.

(b) *With methyl sulphate*. When methyl sulphate (1·26 ml.) was shaken with the hydroxyquinoxaline (0·35 g.) in 5% aqueous potassium hydroxide (20 ml.), a precipitate was soon formed. The mixture was treated with two further similar portions of methyl sulphate and 5% aqueous potassium hydroxide, then heated to 95° and filtered. Crystallisation of the precipitate (0·29 g.) from 96% ethanol gave 6,7-dichloro-1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline, m. p. and mixed m. p. 301—305°.

4,5-*Dinitro*-NN′-*ditoluene*-p-*sulphonyl*-o-*phenylenediamine*.—About one-third of a solution of fuming nitric acid (12·9 ml., 0·3 mole) in glacial acetic acid (15 ml.) was added to a stirred suspension of *NN′*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine (62·4 g., 0·15 mole) in acetic acid (450 ml.) at 60°. After the initial reaction, addition was completed so that the temperature was kept below 70°. The mixture was heated at 70° for a further 30 min., then cooled and filtered. Crystallisation of the precipitate from glacial acetic acid (1·4 l.) gave the *dinitro-compound* as yellow needles (51·0 g.), m. p. 248—250° (decomp.), raised to 253—254° (decomp.) by further crystallisation from 96% ethanol (125 parts) and glacial acetic acid (25 parts) (Found: C, 47·5; H, 3·1; N, 10·9; S, 12·5. $C_{20}H_{18}N_4O_8S_2$ requires C, 47·4; H, 3·6; N, 11·05; S, 12·7%).

4,5-*Dinitro*-o-*phenylenediamine*.—The preceding dinitro-compound (34·0 g.) was heated in concentrated sulphuric acid (34 ml.) and water (3·4 ml.) on the steam-bath for 4 hr., then poured into ice–water. The mixture was diluted to *ca.* 3 l. and gently warmed until the yellow salt had disappeared. The precipitate of 4,5-*dinitro*-o-*phenylenediamine* (7·2 g.), m. p. (mainly) 215—217°, was collected; a further crop (2·1 g.), m. p. 209—214°, was obtained from the mother-liquor by neutralisation with solid sodium carbonate. A specimen, crystallised from 50% ethanol (40 parts) and water (130 parts), had m. p. 216—218° (Found: C, 36·1; H, 3·1; N, 28·4. $C_6H_6N_4O_4$ requires C, 36·4; H, 3·0; N, 28·3%). The diamine separated from hot aqueous ethanol or water as dark red needles and from cold ethanolic solution as dark green, flattened needles.

Benzene-1,2,4,5-*tetra-amine Tetrahydrochloride*.—4,5-Dinitro-*o*-phenylenediamine (2·0 g.) was added in portions to a water-cooled solution of stannous chloride dihydrate (18·0 g.) in concentrated hydrochloric acid (18 ml.). The mixture was heated to 100° for 30 min., then cooled to 0° and saturated with hydrogen chloride. The precipitate was collected, redissolved in boiling 0·5N-hydrochloric acid (20 ml.), and treated with hydrogen sulphide until no further precipitation of tin sulphide occurred. The hot mixture was filtered, freed from the excess of hydrogen sulphide, and evaporated in a vacuum. The residual tetra-amine tetrahydrochloride weighed 2·0 g.

The hydrochloride (1·0 g.) in water (10 ml.) was treated with an excess of sodium acetate and acetic anhydride. Crystallisation (charcoal) of the precipitate (0·75 g.) from water (200 parts) gave 1,2,4,5-tetra-acetamidobenzene as colourless needles, m. p. >315° (decomp.) (Found: C, 54·9; H, 5·4; N, 18·3. Calc. for $C_{14}H_{18}N_4O_4$: C, 54·9; H, 5·9; N, 18·3%). Arient, Marhan, and Täublova [5] give m. p. 330° (decomp.), and Nietzki and Muller [9] give m. p. 287°. A sample of the tetra-amide prepared by the recorded method [9,10] had an m. p. and infrared absorption identical with those of the specimen obtained as above.

2-*Methyl*-5,6-*dinitrobenzimidazole*.—4,5-Dinitro-*o*-phenylenediamine (1·0 g.) and glacial

[8] Cheeseman, Katritzky, and Øksne, *J.*, 1961, 3983.
[9] Nietzki and Muller, *Ber.*, 1889, **22**, 440.
[10] Nietzki and Hagenbach, *Ber.*, 1887, **20**, 334; Nietzki, *ibid.*, p. 2114.

acetic acid (1 ml.) were heated in 2N-hydrochloric acid (10 ml.) at 180° for 2 hr. The mixture was cooled, the pH adjusted to 4, and the precipitate (1·0 g.) collected. Crystallisation (charcoal) from 50% ethanol (10 ml.) gave 2-methyl-5,6-dinitrobenzimidazole (0·77 g.), m. p. (mainly) 231—235°, raised to 234—239° by two further crystallisations from 50% ethanol (Found: C, 43·5; H, 2·85; N, 25·0. Calc. for $C_8H_6N_4O_4$: C, 43·2; H, 2·7; N, 25·2%). Kym and Ratner [6] give m. p. 223°.

4,5-*Dibromo*-NN′-*ditoluene*-p-*sulphonyl*-o-*phenylenediamine*.—Bromine (19·2 g., 0·12 mole) was added dropwise to a water-cooled and stirred suspension of *NN*′-ditoluene-*p*-sulphonyl-*o*-phenylenediamine (25·0 g., 0·06 mole) and anhydrous sodium acetate (10·0 g.) in glacial acetic acid (100 ml.). The mixture was stirred and heated at 100° for 2 hr., then cooled and diluted with water (300 ml.). The precipitate gave colourless crystals of the dibromo-compound (25·8 g.), that after three crystallisations from glacial acetic acid had m. p. 221—224° (Found: C, 42·7, 42·9; H, 3·2, 3·1; N, 4·9, 4·9; Br, 28·8, 27·0. Calc. for $C_{20}H_{18}Br_2N_2O_4S_2$: C, 41·8; H, 3·2; N, 4·9; Br, 27·8%). Further crystallisation did not improve the purity.

4,5-*Dibromo*-o-*phenylenediamine*.—The preceding dibromo-compound (8·5 g.) was heated in concentrated sulphuric acid (17 ml.) and water (0·85 ml.) for 2 hr., then poured into ice–water and neutralised with 50% sodium hydroxide solution. The precipitate (3·57 g.) had m. p. 143—144° (decomp.). Crystallisation from 50% ethanol (25 parts) gave 4,5-dibromo-*o*-phenylenediamine, m. p. 148—149° (decomp.). The m. p. was raised to 150—151° (lit.,[11] 155°) by further crystallisation from 50% ethanol, and was not depressed on admixture with a sample prepared by reduction of 1,2-dibromo-4,5-dinitrobenzene.[11] The two samples showed identical infrared absorption.

4,5-*Dichloro*-o-*phenylenediamine*.—1,2-Dichloro-4,5-dinitrobenzene [12] (9·48 g.) and stannous chloride dihydrate (108 g.) were ground together in a mortar, then added gradually with stirring to concentrated hydrochloric acid (330 ml.). The whole was heated and stirred at 100° for 1 hr. After cooling to 0°, the crystalline complex was filtered off and decomposed with 50% sodium hydroxide solution. The precipitate gave, on crystallisation from 15% ethanol, 4,5-dichloro-*o*-phenylenediamine (4·61 g.), m. p. 163—164° (decomp.) (lit.,[13] 161°).

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[11] Tomlinson, *J.*, 1959, 417.
[12] Turner and Le Fèvre, *J.*, 1927, 1113; Acheson and Taylor, *J.*, 1956, 4727.
[13] Acheson, Taylor, and Tomlinson, *J.*, 1958, 3750.