634. *Hydroxy-quinoxalines and -phenazines, and Experiments on the Preparation of Hydroxyquinoxaline Di-*N*-oxides.*

By F. E. King, N. G. Clark, and P. M. H. Davis.

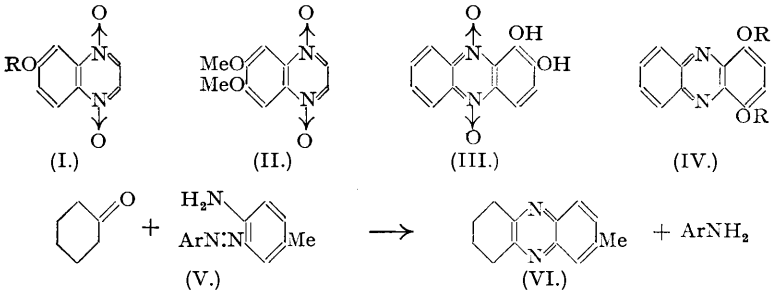
By demethylation of their methyl ethers with aluminium chloride, the six possible *Bz*-hydroxy- and -dihydroxy-quinoxalines have been prepared, and from the 6-hydroxy-, 6-methoxy-, and 6 : 7-dimethoxy-compounds *di-N-oxides* have been obtained. Condensation of the dimethoxy-*o*-diamines synthesised in the course of this work with *cyclo*hexane-1 : 2-dione has given 1 : 2-, 1 : 3-, and 1 : 4-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazines*, of which the 1 : 4-isomer has been converted by dehydrogenation and hydrolysis into 1 : 4-*dihydroxyphenazine*, not identical with the phenazine obtained by the reduction of iodinin.

Iodinin, the purple-coloured metabolite of *Chromobacterium iodinum*, has been shown by Clemo and McIlwain (*J.*, 1938, 479) to be a dihydroxyphenazine di-*N*-oxide—from recent studies, either the 1 : 5- or the 1 : 8-dihydroxy-compound (Clemo and Daglish, *Nature*, 1948, **162**, 776). The pigment possesses antibiotic activity, a property shared to some extent by phenazine di-*N*-oxide, though not by phenazine (McIlwain, *J.*, 1943, 322; see also *Biochem. J.*, 1943, **37**, 265). Similarly the di-*N*-oxides of quinoxaline and of 2-methyl- and 2-methyl-3-*n*-

amyl-quinoxaline inhibit certain pathogenic bacteria (McIlwain, *loc. cit.*), and it was therefore of interest to synthesise hydroxyquinoxaline *N*-oxides in order to evaluate their bacteriostatic properties.

No hydroxyquinoxaline dioxides are mentioned in the literature, and only two *Bz*-hydroxyquinoxalines have been described. These are 6-hydroxy- and 6 : 7-dihydroxy-quinoxaline, synthesised from the requisite hydroxy-*o*-diamines and glyoxal (Hinsberg and Autenrieth, *Ber.*, 1892, **25**, 494; Ehrlich and Bogert, *J. Org. Chem.*, 1947, **12**, 522). By use of the appropriate methoxy-*o*-diamines, 5-*methoxy*-, 6-methoxy- (Körner, *Ber.*, 1884, **17**, Ref. 573), 5 : 6-*dimethoxy*-, 5 : 7-*dimethoxy*-, 5 : 8-dimethoxy-, and 6 : 7-dimethoxy-quinoxalines (Ehrlich and Bogert, *loc. cit.*) have been prepared, and by demethylation with aluminium chloride in boiling benzene, all six possible *Bz*-mono- and *Bz*-di-hydroxyquinoxalines have now been obtained. The hydroxy compounds give unsatisfactory analytical results and cannot readily be identified owing to their indefinite melting points; they are best characterised as *acetyl* derivatives. Certain of the diacetoxyquinoxalines have similar melting points, but the parent hydroxy-compounds can be distinguished by their acid, alkali, and ferric chloride colour reactions which are tabulated in the experimental section.

By the action of hydrogen peroxide in acetic acid solution *di*-N-*oxides* of 6-methoxy- (I; R = Me), 6 : 7-dimethoxy- (II) and 6-hydroxy-quinoxaline (I; R = H) were obtained, but 6 : 7-dihydroxyquinoxaline could not be converted into an oxide owing to its sparing solubility in organic solvents. The three other dihydroxyquinoxalines were extensively decomposed on attempted oxidation with hydrogen peroxide, even under comparatively mild conditions.



The structure of iodinin was, at the inception of these experiments on quinoxalines (see P. M. H. Davis, B.A. [Part II] Thesis, Oxford, June 1948), regarded as (III), the oxidation of the derived dihydroxyphenazine apparently indicating the attachment of both hydroxyls to the same benzene ring. Of the four alternatives, the 1 : 2-isomer was preferred on the evidence afforded by absorption spectra, etc. (Clemo and McIlwain, *loc. cit.*), and the opportunity was therefore taken to attempt a direct proof of the chosen structure by utilising the intermediate dimethoxy-*o*-phenylenediamines for the synthesis, through the tetrahydro-derivatives, of the relevant dihydroxyphenazines (Clemo and McIlwain, *J.*, 1934, 1991).

The condensation of 3 : 4-diaminoveratrole with *cyclo*hexane-1 : 2-dione gave 1 : 2-dimethoxy-5 : 6 : 7 : 8-tetrahydrophenazine, since reported by Clemo and Daglish (*Nature*, 1947, **160**, 752), which was characterised by a *picrate*. At this phase of the investigation a communication came to our notice (Hegedüs, *Festschrift für E. Barrell*, Basel, 1946, 388; *Chem. Abstr.*, 1947, **41**, 6262) describing the synthesis of 1 : 2-dihydroxyphenazine and its diacetyl compound which are shown not to be identical with the corresponding derivatives of iodinin. Experiments on the 1 : 2-dihydroxyphenazine were therefore discontinued in favour of the unknown other isomers.

Reduction of 2 : 3-dinitroquinol dimethyl ether and condensation of the product with *cyclo*hexane-1 : 2-dione gave 1 : 4-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine*, easily dehydrogenated at 200° over palladised charcoal to give a good yield of 1 : 4-dimethoxyphenazine (IV; R = Me) (Slack and Slack, *Nature*, 1947, **160**, 437). Demethylation was smoothly effected with aluminium chloride in refluxing benzene to give 1 : 4-*dihydroxyphenazine* (IV; R = H), which from its red colour and melting point of 230° (*diacetate*, m. p. 194°) was obviously not the dihydroxyphenazine (yellow prisms, m. p. 273—274°; diacetate, m. p. 234°) obtained from iodinin.

Attempts were then made to synthesise the 1 : 3-isomer from 4 : 5-diaminoresorcinol dimethyl

ether, but the 1 : 3-*dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine* was extremely resistant to dehydrogenation (see Experimental section). 2 : 3-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine* was also prepared, and when oxidised with hydrogen peroxide gave a *di*-N-*oxide*, but difficulties in the aromatisation of the tetrahydrophenazine prevented the synthesis of the 2 : 3-dihydroxyphenazine.

An alternative route to tetrahydrophenazines was devised by extending Crippa's synthesis (*Gazzetta*, 1929, **59**, 330) of quinoxalines from *o*-aminoazobenzenes and ketomethylene compounds to 2-(toluene-*p*-azo)-*p*-toluidine (V; Ar = *p*-C_6H_4Me) and *cyclo*hexanone, 2-*methyl*-5 : 6 : 7 : 8-*tetrahydrophenazine* (VI) being obtained. The condensation of (V; Ar = *p*-C_6H_4Me) with phloroglucinol, which might have afforded a direct synthesis of a 1 : 3-dihydroxyphenazine, could not, however, be accomplished.

Experimental.

6 : 7-*Diacetoxyquinoxaline*.—A solution of 6 : 7-dimethoxyquinoxaline (1 g.) (Ehrlich and Bogert, *loc. cit.*) in dry benzene (20 c.c.) was heated under reflux for 15 hours with finely powdered, anhydrous aluminium chloride (3 g.). After cooling, the supernatant liquid was decanted and the tarry residue treated with crushed ice to yield 6 : 7-dihydroxyquinoxaline which, when collected, washed and dried, was obtained as a fine orange powder (0·7 g., 82%), m. p. *ca.* 260° (decomp.). A portion (0·5 g.) was heated under reflux for 1 hour with pyridine (10 c.c.) and acetic anhydride (1 c.c.), and the dark product distilled under reduced pressure; 6 : 7-*diacetoxyquinoxaline* was obtained as a light-yellow oil solidifying to buff-coloured needles (0·6 g., 79%), m. p. 112° (Found: C, 58·3; H, 4·2; N, 10·8. $C_{12}H_{10}O_4N_2$ requires C, 58·5; H, 4·1; N, 11·4%).

6-*Acetoxyquinoxaline*.—6-Methoxyquinoxaline (3 g.) (Körner, *loc. cit.*) was demethylated as above and the aluminium complex decomposed with warm dilute hydrochloric acid. After neutralisation of the solution with solid sodium hydrogen carbonate and extraction with ether, 6-hydroxyquinoxaline was obtained by sublimation at low pressure as a white crystalline powder (1 g., 37%), m. p. 242° (decomp.). Hinsberg and Autenrieth (*loc. cit.*) give m. p. 245° (decomp.). The *acetate* distilled under reduced pressure as a pale yellow liquid setting to colourless needles, m. p. 80—81° (Found: C, 63·6; H, 4·2; N, 14·9. $C_{10}H_8O_2N_2$ requires C, 63·8; H, 4·3; N, 14·9%).

5 : 8-*Dimethoxyquinoxaline*.—Quinol dimethyl ether (20 g.) in glacial acetic acid (50 c.c.) was treated with concentrated nitric acid (25 c.c.; *d* 1·42), and after the vigorous reaction had subsided a further 25 c.c. of nitric acid were added. The mixture was then heated for 5 minutes at 70—80°, and the yellow crystalline solid (26 g., 80%), m. p. 156—160°, obtained on cooling and dilution with water (500 c.c.) was collected and thoroughly washed with water. The product, a mixture of 2 : 3- and 2 : 5-dinitroquinol dimethyl ether, could not be separated by fractional crystallisation from ethyl acetate (cf. Nietzki and Rechberg, *Ber.*, 1890, **23**, 1216) or by any other convenient method. The mixed dinitro-compounds (10 g.) dissolved in methanol (60 c.c.) were accordingly reduced with Raney nickel and hydrogen at 2—3 atmospheres. The filtered liquid was rapidly added to an aqueous solution of glyoxal sodium bisulphite (7 g. in 50 c.c.) and after the addition of concentrated hydrochloric acid (3 drops) was heated under reflux for 2 hours. Evaporation of the methanol and cooling gave a grey crystalline solid, darkening in air, which was presumably 2 : 5-diaminoquinol dimethyl ether and was discarded. The filtrate was evaporated to dryness, and the residue extracted with hot ethanol (50 c.c.) which was then evaporated. The solid remaining was dissolved in dilute sulphuric acid (20 c.c. of concentrated acid in 40 c.c. of water), cooled to 5°, and treated with aqueous sodium nitrite (5 g. in 15 c.c.) to remove the remaining diamine. The excess of nitrous acid was destroyed by the addition of urea (5 g.), and the solution poured into boiling sulphuric acid (10 c.c. of concentrated acid in 20 c.c. of water). The cooled mixture was filtered from tarry material and treated with charcoal, the resulting red solution basified, and 5 : 8-*dimethoxyquinoxaline* (1 g., 12%) isolated with ether. Distillation under reduced pressure yielded a deep-yellow oil setting to yellow needles, m. p. 146° (Found: C, 63·3; H, 5·2; N, 14·7. $C_{10}H_{10}O_2N_2$ requires C, 63·1; H, 5·3; N, 14·7%).

5 : 8-*Diacetoxyquinoxaline*.—5 : 8-Dimethoxyquinoxaline (0·5 g.) was heated under reflux for 16 hours with anhydrous aluminium chloride (1·5 g.) in dry benzene (20 c.c.), the benzene decanted, and the solid product dissolved in warm dilute hydrochloric acid. Solid sodium hydrogen carbonate was added until the solution became cloudy, the liquid cleared with a few drops of acid, and excess of saturated copper sulphate solution added. The precipitated copper complex was collected, washed, and decomposed by passing hydrogen sulphide into an aqueous suspension of it. After removal of copper sulphide the product was isolated from the filtrate with ether. A considerable quantity of the dihydroxyquinoxaline adsorbed on the copper sulphide was removed from the dried precipitate by sublimation at low pressure. The product then obtained was a crystalline orange power (0·25 g., 60%), darkening rapidly at 200° and melting indistinctly at *ca.* 230°. The *diacetate* distilled at reduced pressure as a white crystalline solid, m. p. 209° (Found: C, 58·5; H, 4·0; N, 11·3. $C_{12}H_{10}O_4N_2$ requires C, 58·5; H, 4·1; N, 11·4%).

5-*Methoxyquinoxaline*.—2 : 3-Dinitroanisole (2·5 g.) (Holleman, *Rec. Trav. chim.*, 1903, **22**, 271) in ethanol (20 c.c.) was reduced over Raney nickel, and the diamine solution heated under reflux for 2 hours with aqueous glyoxal sodium bisulphite (5 g. in 30 c.c.) and concentrated hydrochloric acid (3 drops). After evaporation of the ethanol, the solution was basified and the base (1·2 g., 59%) isolated with ether. Distillation under reduced pressure yielded the *quinoxaline* as a pale yellow solid, m. p. 72—73° (Found: C, 68·2; H, 5·0; N, 17·0. $C_9H_8ON_2$ requires C, 67·5; H, 5·0; N, 17·5%).

5-*Acetoxyquinoxaline*.—5-Methoxyquinoxaline (0·4 g.) was demethylated by aluminium chloride (1 g.) in refluxing benzene (15 c.c.) (16 hours), and the hydroxyquinoxaline isolated through the copper complex; sublimation at low pressure yielded a yellow crystalline powder (0·11 g., 30%), m. p. 100—101°.

The *acetate* was obtained after distillation as a white, glossy solid, m. p. 103—104° (Found : C, 63·9; H, 4·4; N, 15·3. $C_{10}H_8O_2N_2$ requires C, 63·8; H, 4·3; N, 14·9%).

5 : 6-*Dimethoxyquinoxaline*.—3 : 4-Dinitroveratrole (5 g.) (Pollecoff and Robinson, *J.*, 1918, **113**, 650) was catalytically reduced in methanol (30 c.c.) to the diamine and condensed with aqueous glyoxal sodium bisulphite (6·5 g. in 50 c.c.), to yield 5 : 6-*dimethoxyquinoxaline* as a pale yellow oil setting to a yellow crystalline solid (1·5 g., 36%), m. p. 69—70° (Found : C, 62·9; H, 5·3; N, 14·3. $C_{10}H_{10}O_2N_2$ requires C, 63·1; H, 5·3; N, 14·7%).

5 : 6-*Diacetoxyquinoxaline*.—5 : 6-Dihydroxyquinoxaline was obtained by demethylation of the dimethoxyquinoxaline (1 g.) with aluminium chloride (2 g.) in boiling benzene (25 c.c.) and isolation through the copper complex, and sublimation at low pressure yielded a yellow crystalline powder (0·2 g., 26%), m. p. *ca.* 190° (decomp.). The *diacetate* formed white needles, m. p. 112° (Found : C, 58·9; H, 4·4; N, 11·6. $C_{12}H_{10}O_4N_2$ requires C, 58·5; H, 4·1; N, 11·4%).

5 : 7-*Dimethoxyquinoxaline*.—4 : 5-Dinitroresorcinol dimethyl ether (3·7 g.) (Blanksma, *Rec. Trav. chim.*, 1908, **27**, 254) in methanol (30 c.c.) was catalytically reduced and the resulting diamine solution heated for 2 hours under reflux with glyoxal sodium bisulphite (6 g.) in water (50 c.c.) containing concentrated hydrochloric acid (1 c.c.); the *quinoxaline* was initially isolated, by evaporation to small bulk, as highly hydrated light-brown crystals, but on distillation under reduced pressure it was obtained as colourless needles (2·1 g., 68%), m. p. 110° (Found : C, 63·5; H, 5·4; N, 14·5%).

5 : 7-*Diacetoxyquinoxaline*.—5 : 7-Dimethoxyquinoxaline (0·5 g.) was demethylated by heating it in benzene (20 c.c.) with aluminium chloride (1·5 g.) under reflux for 15 hours, and the dihydroxyquinoxaline isolated by means of its sparingly soluble copper complex. It was then obtained by sublimation at low pressure as a bright yellow crystalline powder (0·25 g., 59%), m. p. *ca.* 250° (decomp.). The *diacetate* distilled as a pale yellow oil setting to a mass of colourless needles, m. p. 113° (Found C, 58·4; H, 4·4; N, 11·4%).

Colour reactions of the hydroxyquinoxalines.

	Monohydroxy-.		Dihydroxy-.			
Reagent.	5-.	6-.	5 : 6-.	5 : 7-.	5 : 8-.	6 : 7-.
2N-HCl	yellow	yellow	orange	orange	orange-red	yellow
2N-NaOH	yellow	yellow	purple-red	orange	purple-red	yellow
Aq. $FeCl_3$	dull greyish-green	slight darkening	no change	deep yellowish-green	brown	no change
Alcoholic $FeCl_3$	black	slight darkening	no change	deep yellowish-green	brown	dull green to turquoise

1 : 4-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine*.—A solution of the mixed 2 : 3- and 2 : 5-dinitroquinol dimethyl ethers (5 g.) in acetic acid (30 c.c.) was hydrogenated over Raney nickel and then filtered, and the colourless diamine solution heated under reflux for 2 hours with *cyclo*hexane-1 : 2-dione (2 g.) (Butz, Davis, and Gaddis, *J. Org. Chem.*, 1947, **12**, 128) and anhydrous sodium acetate (5 g.) in acetic acid (10 c.c.). Cooling and basification of the reaction mixture with sodium hydroxide solution yielded a brown tarry solid; this was digested with boiling water (50 c.c.) which was filtered hot. The 1 : 4-*dimethoxytetrahydrophenazine* separated on cooling, and was obtained as yellow needles (1·25 g., 24%), m. p. 152°, after recrystallisation from hot water (Found : C, 68·9; H, 6·6; N, 11·8. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6; N, 11·5%).

1 : 4-*Dimethoxyphenazine* (IV; R = Me).—An intimate mixture of 1 : 4-dimethoxy-5 : 6 : 7 : 8-tetrahydrophenazine (2 g.) and palladised charcoal (1 g.) was heated for 1 hour at 200—230°, the cooled mixture broken up, and the crude product obtained by distillation *in vacuo* as a red oil, which solidified when kept. Recrystallised from benzene–light petroleum (b. p. 60—80°), it was obtained as blood-red fine needles (1 g., 50%), m. p. 185° (Slack and Slack, *loc. cit.*, give 185°) (Found : C, 70·5; H, 5·0; N, 11·4. Calc. for $C_{14}H_{12}O_2N_2$: C, 70·0; H, 5·0; N, 11·6%).

1 : 4-*Dihydroxyphenazine* (IV; R = H).—A solution of 1 : 4-dimethoxyphenazine (0·5 g.) in dry benzene (25 c.c.) was heated under reflux for 16 hours with anhydrous aluminium chloride (1 g.), the reactants were cooled, and the benzene was decanted. The tarry aluminium complex decomposed slowly on addition of crushed ice (10 g.), to yield a rose-red solid (0·4 g., 91%) which was collected, washed, and dried. By sublimation at low pressure the *dihydroxyphenazine* was obtained as deep-red needles, m. p. 230° (Found : C, 67·8; H, 4·2; N, 13·2. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8; N, 13·2%). The *diacetate* crystallised from ethanol in tarnished-gold needles, m. p. 193·5—194° (Found : C, 64·6; H, 4·1; N, 10·0. $C_{16}H_{12}O_4N_2$ requires C, 64·9; H, 4·1; N, 9·5%).

1 : 2-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine*.—3 : 4-Dinitroveratrole (0·8 g.) was hydrogenated over Raney nickel, and the resulting diamine solution condensed under nitrogen with *cyclo*hexane-1 : 2-dione (0·4 g.) in presence of fused sodium acetate (0·6 g.) in refluxing acetic acid (10 c.c.). The tetrahydrophenazine was isolated from the cooled, basified reaction mixture with ether, and on crystallisation from light petroleum (b. p. 40—60°) formed pale brown needles (0·5 g., 60%), m. p. 82—83° (Clemo and Daglish, *loc. cit.*, give m. p. 82—83°). The *picrate* separated from ethanol in yellowish-brown prisms, m. p. (after preliminary darkening) 128° (decomp.) (Found : C, 50·9; H, 4·2; N, 14·2. $C_{14}H_{16}O_2N_2,C_6H_3O_7N_3$ requires C, 50·8; H, 4·0; N, 14·8%).

1 : 3-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine*.—4 : 5-Dinitroresorcinol dimethyl ether (2·5 g.) in acetic acid (20 c.c.) was reduced over Raney nickel, and the filtered solution of the diamine heated under reflux in the presence of fused sodium acetate (3 g.) with an acetic acid solution of *cyclo*hexane-1 : 2-dione (1·25 g. in 10 c.c.). The *tetrahydrophenazine* separated as a yellow-buff solid (2·2 g., 94%) when the cooled mixture was poured into aqueous sodium hydroxide (250 c.c. of 10%). When crystallised from aqueous ethanol it formed yellow needles, m. p. 119° (Found : C, 68·2; H, 6·6; N, 11·7. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6; N, 11·5%).

2 : 3-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine*.—A solution of 4 : 5-diaminoveratrole obtained by catalytic reduction of the dinitro-compound (5 g.) in acetic acid (20 c.c.) was condensed with *cyclo*hexane-1 : 2-dione (2·5 g.) in the usual manner. On basification of the reaction mixture, a light-brown precipitate of the 2 : 3-*dimethoxytetrahydrophenazine* (4·7 g., 88%) resulted, which when crystallised from aqueous ethanol afforded lemon-yellow needles, m. p. 119—120° (Found: C, 69·2; H, 6·8; N, 11·7%).

2-*Methyl*-5 : 6 : 7 : 8-*tetrahydrophenazine* (VI).—A solution of 2-(toluene-*p*-azo)-*p*-toluidine (V) (2 g.) (Noelting and Witt, *Ber.*, 1884, **17**, 78) in *cyclo*hexanone (20 c.c.) was heated under reflux for 2 hours with concentrated hydrochloric acid (1 drop), and the majority of the solvent evaporated at ordinary pressure. The residue was dissolved in ether and extracted with dilute hydrochloric acid, and the oil liberated on making alkaline the aqueous solution was isolated by means of ether. Distillation under reduced pressure yielded *p*-toluidine as a low-boiling first fraction, and then a yellow oil which solidified when kept; on redistillation, the *tetrahydrophenazine* (VI) was obtained as a yellow solid (0·85 g., 45%), m. p. 81° (Found: C, 78·5; H, 7·2; N, 13·7. $C_{13}H_{14}N_2$ requires C, 78·7; H, 7·1; N, 14·1%).

Dehydrogenations.—Although 1 : 4-dimethoxy-5 : 6 : 7 : 8-tetrahydrophenazine can be very readily dehydrogenated by heating it with palladised charcoal, and the corresponding 1 : 2-compound yields to the same treatment with moderate ease, attempts to dehydrogenate the 1 : 3- and 2 : 3-dimethoxy-tetrahydrophenazines were unsuccessful. The compounds were recovered unchanged after the action of palladised charcoal at 200° either alone or dissolved in diphenyl or *p*-cymene, whilst higher temperatures resulted in general decomposition. Sulphur under similar conditions was also ineffective, merely causing discoloration, whilst the materials were unaffected by Raney nickel in refluxing *cyclo*hexene. Chloranil (cf. Barclay and Campbell, *J.*, 1945, 530) was ineffective in refluxing acetone, and partial decomposition occurred in benzene. Rapid destruction of the 1 : 2-dimethoxytetra-hydrophenazine occurred on heating it under reflux with chloranil in xylene.

6 : 7-*Dimethoxyquinoxaline Di*-N-*oxide* (II).—A solution of 6 : 7-dimethoxyquinoxaline (1 g.) in acetic acid (25 c.c.) was heated for 20 hours at 60° with hydrogen peroxide (5 c.c.; 100 vol.); the cooled reaction mixture was neutralised with sodium hydroxide solution in the presence of ice. The resulting precipitate of the *di*-N-*oxide* (II) (0·7 g., 60%) was collected, and on crystallisation from water was obtained as pale yellow needles, which began to darken at 220° and decomposed without melting at *ca.* 250° (Found: C, 54·7; H, 4·4; N, 14·2. $C_{10}H_{10}O_4N_2$ requires C, 54·1; H, 4·5; N, 14·2%).

6-*Methoxyquinoxaline Di*-N-*oxide* (I; R = Me).—6-Methoxyquinoxaline (1 g.) was oxidised with hydrogen peroxide in acetic acid solution as described above, the reaction mixture neutralised with aqueous sodium hydroxide and the *di*-N-*oxide* (0·5 g., 42%) isolated with chloroform. It crystallised from water as pale yellow needles, which decomposed with effervescence at 207—210° (Found: N, 14·0. $C_9H_8O_3N_2$ requires N, 14·6%).

6-*Hydroxyquinoxaline Di*-N-*oxide* (I; R = H).—A solution of 6-hydroxyquinoxaline (0·5 g.) in glacial acetic acid (10 c.c.) was treated with hydrogen peroxide (3 c.c., 100 vol.) at 60° for 20 hours. On cooling of the solution, clusters of orange needles separated; a further small quantity was obtained by neutralising the filtrate and extracting it with chloroform. Recrystallisation from water gave the *dioxide* (0·2 g., 33%) as long, yellow, hair-like needles, m. p. 245° (effervescence) (Found: C, 51·6; H, 3·5; N, 15·0. $C_8H_6O_3N_2,\frac{1}{2}H_2O$ requires C, 51·3; H, 3·7; N, 15·0%).

2 : 3-*Dimethoxy*-5 : 6 : 7 : 8-*tetrahydrophenazine Di*-N-*oxide*.—2 : 3-Dimethoxy-5 : 6 : 7 : 8-tetra-hydrophenazine (1 g.) was oxidised in acetic acid as described above, and the *dioxide* obtained as a yellow solid on neutralising the reaction mixture (0·75 g., 66%). It separated from water as very fine, pale yellow needles, which decomposed with effervescence at 215—220° (Found: N, 10·3. $C_{14}H_{16}O_4N_2$ requires N, 10·15%).

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.
UNIVERSITY OF NOTTINGHAM.

[*Received, July 25th*, 1949.]