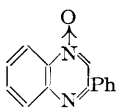
568. *Quinoxaline* N-*Oxides. Part II.* Oxides of* Py-*Substituted Quinoxalines.*

By J. K. Landquist and G. J. Stacey.

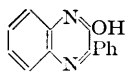
N-Oxides of quinoxalines bearing alkyl, aralkyl, or aryl groups in the 2- and 3-positions are prepared. Steric hindrance to *N*-oxidation is caused by *iso*propyl or aryl groups, and by substituents in the 5-position. Hydrogenation of 2-styrylquinoxalines over Raney nickel gives 2-aralkylquinoxalines, or 2-aralkyl-1 : 2 : 3 : 4-tetrahydroquinoxalines if the 3-position is unoccupied. The reaction of ethylmagnesium bromide with 2 : 3-dihydroxyquinoxaline and with 1 : 2 : 3 : 4-tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline is described.

In Part I* the oxidation of quinoxaline derivatives with organic peracids, particularly with 1·2M-peracetic acid in acetic acid, is described. Under similar conditions 2-ethyl- and 2 : 3-di(lower alkyl)-quinoxalines are readily oxidised to the corresponding 1 : 4-dioxides, but 2-methyl-3-*iso*propylquinoxaline gives a considerable proportion of mono-*N*-oxide, and 2 : 3-di*iso*propylquinoxaline is unchanged by hot peracetic or performic acid. Examination of models shows that the *iso*propyl group is likely to cause steric hindrance.

Maffei (*Gazzetta*, 1946, **76**, 239; see also Linsker and Evans, *J. Amer. Chem. Soc.*, 1946, **68**, 403) claimed that oxidation of 2 : 3-diphenylquinoxaline with hydrogen peroxide in acetic acid gives 2 : 3-diphenylquinoxaline 1 : 4-dioxide, but the main product under the conditions he described proved to be 2 : 3-diphenylquinoxaline 1-oxide. With more concentrated peracetic acid, mixtures yielding 50—60% of monoxide and 25—45% of dioxide are obtained. 2 : 3-Di-*p*-methoxyphenylquinoxaline on oxidation gives 65% of mono-*N*-oxide and 10—15% of di-*N*-oxide. 2-Phenylquinoxaline with peracetic or performic acid gives a monoxide, which we regard as 2-phenylquinoxaline 4-oxide (I), and



(I)



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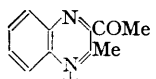
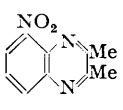


(III)

only traces of 2-phenylquinoxaline 1 : 4-dioxide; (I) is not oxidised further to the dioxide, but on prolonged treatment with peracetic acid gives 2-hydroxy-3-phenylquinoxaline (II) and other (unidentified) substances. This is surprising since 2-phenyl-3-methylquinoxaline readily yields a di-*N*-oxide. Other groups in the 2-position which prevent the attachment of oxygen to the adjacent nitrogen atom are Cl (Part I), OH, OEt, and CO_2H (Newbold and Spring, *J.*, 1948, 519). 2-Acetyl-3-methylquinoxaline affords only a mono-*N*-oxide (III).

Oxidation of 2 : 3-dimethylquinoxalines substituted in the carbocyclic nucleus resembles that of the related 2 : 3-unsubstituted compounds, the steric hindrance from groups in the 5-position being more pronounced. 2 : 3-Dihydroxy-compounds are not formed as by-



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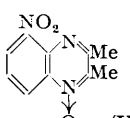

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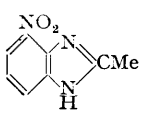


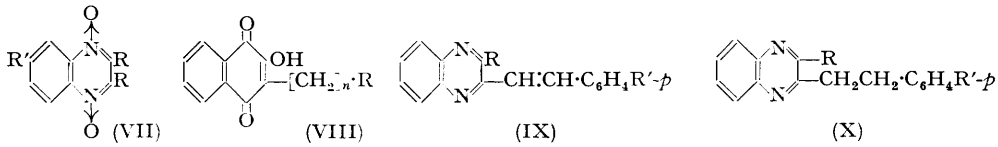
(VI)

products, and moderate yields of 2 : 3-dimethyl-6-nitro- and 6-cyano-2 : 3-dimethylquinoxaline 1 : 4-dioxide are obtainable. Peracetic acid oxidation of 2 : 3-dimethyl-5-nitroquinoxaline (IV) gives the monoxide (V) and 2-methyl-4-nitrobenziminazole (VI). Only the mono-*N*-oxide has been obtained from 6 : 7-dichloro-2 : 3-dimethylquinoxaline.

The methyl groups in 2 : 3-dimethylquinoxaline 1 : 4-dioxide do not show the enhanced reactivity of quinaldine methiodide, there being no reaction with reagents such as *p*-di-

* Part I, preceding paper.

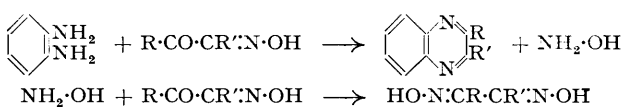
methylaminobenzaldehyde. Methyl iodide reacts slowly with 2 : 3-dimethylquinoxaline 1-oxide in boiling acetonitrile, giving a dark quaternary salt, but no methiodide was obtained from 2 : 3-diphenylquinoxaline 1-oxide. Vivian (*J. Amer. Chem. Soc.*, 1949, **71**, 1139) showed that the chlorine atom in 2-chlorophenazine di-*N*-oxide is labile, but attempts to demonstrate similar reactivity in 6-chloro-2 : 3-dimethylquinoxaline 1 : 4-dioxide by condensation with piperidine or 3-piperidinopropylamine gave no definite result. 6-Aminoquinoxaline 1 : 4-dioxide and 6-amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide which are obtained by acid hydrolysis of the 6-acetamido-compounds gave no characterisable derivatives with a number of usual reagents for aromatic amines, and, although they could be diazotised, the replacement of the diazonium group by halogen was unsatisfactory. A few derivatives (VII; R = Me, R′ = *p*-Me·C_6H_4·SO_2·NH, *p*-NHAc·C_6H_4·SO_2·NH, and 2-amino-1 : 6-dimethylpyrimidinium-4-amino) have been obtained.



(VII) (VIII) (IX) (X)

In view of the antimalarial activity of certain 2-hydroxy-1 : 4-naphthaquinones (VIII) bearing large alkyl or aralkyl groups in the 3-position (Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3151 *et seq.*), the preparation of some analogously constituted quinoxaline 1 : 4-dioxides was attempted. Hydrogenation of the mono- and di-styryl derivatives obtained from 2 : 3-dimethylquinoxaline and *p*-chlorobenzaldehyde (IX; R = Me or CH:CH·C_6H_4Cl, R′ = Cl) over Raney nickel gave the corresponding 2-*p*-chlorophenylethyl derivatives (X; R = Me or CH_2·CH_2·C_6H_4Cl, R′ = Cl) from which di-*N*-oxides were made. Similarly, (IX; R = Me, R′ = OMe) and (IX; R = OH, R′ = Cl) were reduced to (X; R = Me, R′ = OMe) and (X; R = OH, R′ = Cl), but hydrogenation of 2-styrylquinoxalines unsubstituted in the 3-position gave 1 : 2 : 3 : 4-tetrahydro-2-2′-phenylethylquinoxalines. 2-2′-Ethoxyethyl-3-methylquinoxaline and 2-methyl-3-2′-phenoxyethylquinoxaline gave di-*N*-oxides, but attempts to convert these into the corresponding 2-bromoethyl derivatives were unsuccessful.

Condensation of hydroxyimino-ketones with *o*-phenylenediamine proceeds according to the following scheme (Henderson, *J.*, 1929, 466), the product in some cases being a molecular compound of the quinoxaline with the dioxime (separable into its components by treatment with alkali). In spite of the loss occasioned by this side reaction no improve-



ment in overall yield was obtained by first hydrolysing the hydroxyimino-ketone to the 1 : 2-diketone and condensing the latter with *o*-phenylenediamine. Oxidation of acyloins with cupric acetate in acetic acid (Bloch, Lehr, Erlenmeyer, and Vogler, *Helv. Chim. Acta*, 1945, **28**, 1410) is a most satisfactory preparative method for symmetrical 1 : 2-diketones.

(XI) (XII)

Some alternative methods of preparing 2 : 3-dialkylquinoxalines were examined. Reaction of ethylmagnesium bromide with 2 : 3-dihydroxyquinoxaline gave a little 2 : 3-diethylquinoxaline, together with 2-ethyl-3-hydroxyquinoxaline and a compound, m. p. 158—160°, tentatively regarded as 1 : 3-diethyl-1 : 2-dihydro-2-hydroxyquinoxaline (XI). Molecular-weight determinations on this compound gave anomalous results, and attempts to acetylate it or to oxidise it to 1 : 3-diethylquinoxal-2-one were unsuccessful. It was also obtained in small yield from ethylmagnesium bromide and 2 : 3-dichloroquinoxaline, no 2 : 3-diethylquinoxaline being isolated in this case [Ogg and Bergstrom (*J. Amer. Chem.*

Soc., 1931, **53**, 1846) prepared 2 : 3-di-*n*-propylquinoxaline from propylmagnesium bromide and 2 : 3-dichloroquinoxaline]. 1 : 2 : 3 : 4-Tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline and ethylmagnesium bromide gave a rather intractable product which analysed as a hydrate of 2 : 3-diethyl-1 : 2 : 3 : 4-tetrahydro-2 : 3-dihydroxy-1 : 4-dimethylquinoxaline (XII) and gave hexane-3 : 4-dione on acid hydrolysis.

Experimental

3-Hydroxyimino-1-phenoxypentan-4-one.—Ethyl α-2-phenoxyethylacetoacetate (Robinson and Watt, *J.*, 1934, 1536) (83 g.), water (385 c.c.), and potassium hydroxide (21 g.) were stirred overnight in a closed flask, and the aqueous layer was separated from undissolved ester (17 g.), washed with ether, and added to sodium nitrite (23 g.) in water (80 c.c.). The solution was cooled, stirred, and treated dropwise with 20% sulphuric acid at $<10°$ until acid to Congo-red. After 5 min. the mixture was made alkaline with sodium hydroxide solution and extracted with ether (500 c.c.), and the ether was washed repeatedly with dilute sodium hydroxide solution until the latter was no longer yellow. The combined alkaline solutions were acidified and extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave *3-hydroxyimino-1-phenoxypentan-4-one* (46 g.), m. p. *ca.* 60°, which formed colourless needles, m. p. 66—67°, from light petroleum (Found : N, 6·85. $C_{11}H_{13}O_3N$ requires N, 6·75%). When distilled with 20% sulphuric acid it gave a solid (pale yellow plates, m. p. 51—52°, from light petroleum) which was not the required diketone.

The following hydroxyimino-ketones were made by the same method : hydroxyiminoacetone, 1-hydroxyiminobutan-2-one, m. p. 53—54° (Sharp and Spring, *J.*, 1948, 1862, found m. p. 55°), 3-hydroxyiminopentan-2-one, 3-hydroxyiminoheptan-4-one, 1-ethoxy-3-hydroxyiminopentan-4-one (Tota and Elderfield, *J. Org. Chem.*, 1942, **7**, 313), and 3-hydroxyiminooctan-2-one. 1-Hydroxyimino-1-phenylpropan-2-one was obtained from hydroxyiminoacetone and benzenediazonium chloride (Borsche, *Ber.*, 1907, **40**, 737).

Quinoxalines.—The following exemplify the general methods of preparation used.

(*a*) *o*-Phenylenediamine (67·5 g.), dissolved in hot water (750 c.c.), was treated with diacetyl (55 c.c.) and heated on the steam-bath 1 hr. 2 : 3-Dimethylquinoxaline dihydrate was filtered off when cold, and dried by azeotropic distillation with benzene, and the anhydrous compound was crystallised from light petroleum (b. p. 100—120°) (yield, 73·5 g.; m. p. 104°).

(*b*) 4-Chloro-*o*-phenylenediamine (71 g.) was heated in 10% (v/v) aqueous acetic acid (600 c.c.) on the steam-bath with diacetyl (44 c.c.) for 1 hr., then was made alkaline to Clayton Yellow paper with aqueous sodium hydroxide, and *6-chloro-2 : 3-dimethylquinoxaline* was isolated by steam-distillation.

In some instances the diamine hydrochloride and sodium acetate were used; less volatile quinoxalines were isolated by filtration and then distilled or recrystallised.

(*c*) 3-Hydroxyiminopentan-2-one (41 g.) was added to *o*-phenylenediamine (40 g.) dissolved in acetic acid (32·4 c.c.), water (112 c.c.), and concentrated hydrochloric acid (16·7 c.c.), and the mixture was boiled for 3 min., cooled, and filtered. 2-Ethyl-3-methylquinoxaline was extracted from this solid and from the aqueous filtrate with light petroleum (b. p. 60—80°), and the extract was washed with 2% sulphuric acid, 5% sodium hydroxide solution, and water, dried (Na_2SO_4), and distilled (yield, 20 g.). The residual solid (31·7 g.) was 2 : 3-dihydroxyiminopentane, colourless needles (from benzene), m. p. 171° (Found : C, 46·3; H, 7·7; N, 21·0. Calc. for $C_5H_{10}O_2N_2$: C, 46·2; H, 7·7; N, 21·5%). In other preparations the hydrochloric acid was omitted and the reaction time was increased to 1—1·5 hr.

(*d*) *o*-Phenylenediamine (130 g.), 1-ethoxy-3-hydroxyiminopentan-4-one (151 g.) and 40% sodium hydrogen sulphite solution (525 c.c.) were stirred at 60° for 3 hr., and the solid product was collected when cold, washed with water, extracted with cold 5% sodium hydroxide solution, and crystallised from acetone or benzene, giving 2-2′-ethoxyethyl-3-methylquinoxaline (72 g.). Acidification of the alkaline extract gave *5-ethoxy-2 : 3-dihydroxyiminopentane* (30 g.), colourless platelets (from benzene), m. p. 126° (Found : C, 48·5; H, 7·85; N, 15·4. $C_7H_{14}O_3N_2$ requires C, 48·3; H, 8·05; N, 16·1%).

The following dioximes were isolated from reactions of types (*c*) and (*d*) :

Methylglyoxime, isolated as its *molecular compound* with 2 : 6 : 7-trimethylquinoxaline, m. p. 148° (from aqueous ethanol) (Found : C, 60·8; H, 6·5; N, 20·6. $C_{11}H_{12}N_2,C_3H_6O_2N_2$ requires C, 61·3; H, 6·55; N, 20·4%).

Ethylglyoxime, microscopic white needles (from light petroleum), m. p. 126—128° (Found : N, 24·0. Calc. for $C_4H_8O_2N_2$: N, 24·15%).

2 : 3-Dihydroxyimino-octane, white plates (from benzene), m. p. 170° (Found : C, 55·9; H, 9·3; N, 15·9. Calc. for $C_8H_{16}O_2N_2$: C, 55·8; H, 9·3; N, 16·3%) (isolated, but not identified by McIlwain, *J.*, 1943, 322).

Phenylglyoxal dioxime, obtained as its *molecular compound* with 2-phenylquinoxaline, fine white needles (from ethanol), m. p. 131° (Found : C, 71·6; H, 4·9; N, 14·9. $C_{14}H_{10}N_2,C_8H_8O_2N_2$ requires C, 71·35; H, 4·85; N, 15·1%). This substance was formed from hydroxyiminoacetophenone and *o*-phenylenediamine in ethanol, but not in aqueous acetic acid.

In addition to the new quinoxalines listed in Table 1 the following were prepared by the method indicated : 2 : 3-dimethylquinoxaline (*a*) (Gabriel and Sonn, *Ber.*, 1907, **40**, 4852), 2-ethyl-3-methylquinoxaline (*a*, *c*) (Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54), 2-methyl-3-*n*-propylquinoxaline (*a*) (*idem*, *loc. cit.*), 2-methyl-3-*iso*propylquinoxaline (*a*), m. p. 40—42° (Pauly and Lieck, *Ber.*, 1900, **33**, 500, found m. p. 37°), 2-methyl-3-phenylquinoxaline (*c*) (von Auwers, *Ber.*, 1917, **50**, 1177), 2-benzyl-3-methylquinoxaline (Moureu, *Ann. Chim.*, 1930, **14**, 352), 2 : 3-diethylquinoxaline (*a*) (Urion, *ibid.*, 1934, **1**, 55), 2 : 3-di-*n*-propylquinoxaline (*a*) (Ogg and Bergstrom, *loc. cit.*), 2-phenylquinoxaline (*a*, *c*) (Hinsberg, *Annalen*, 1896, **292**, 246),

TABLE 1. *Alkylquinoxaline derivatives.*

Substituents	Method of prepn.	Formula	M. p.	Found, % C	Found, % H	Found, % N	Required, % C	Required, % H	Required, % N
2-Ethyl	*c*	$C_{10}H_{10}N_2$	(i)	75·2	6·2	17·4	75·9	6·3	17·7
2-Ethyl-3-*n*-propyl	*a*	$C_{13}H_{16}N_2$	45°	—	—	14·1	—	—	14·0
2 : 3-Di*iso*propyl	*a*	$C_{14}H_{18}N_2$	74	78·4	8·2	—	78·5	8·4	—
2-2′-Ethoxyethyl-3-methyl	*d*	$C_{13}H_{16}ON_2$	64	71·9	7·55	13·1	72·2	7·4	13·0
2-Methyl-3-2′-phenoxyethyl	*d*	$C_{17}H_{16}ON_2$	156—156·5	77·65	6·1	10·2	77·27	6·05	10·6
2 : 3 : 5-Trimethyl	*a*	$C_{11}H_{12}N_2$	72—73 (ii)	—	—	16·5	—	—	16·3
2 : 6 : 7-Trimethyl	*c*	$C_{11}H_{12}N_2$	116	76·7	6·9	16·1	76·75	6·95	16·3
2 : 3 : 6 : 7-Tetramethyl	*b*	$C_{12}H_{14}N_2$	189—190	—	—	14·8	—	—	14·5
2 : 3-Dimethyl-5 : 6-benzo	*a*	$C_{14}H_{12}N_2$	101	—	—	13·6	—	—	13·5
5-Methoxy-2 : 3-dimethyl	*a*	$C_{11}H_{12}ON_2$	118	—	—	14·3	—	—	14·9
5-Ethoxy-2 : 3-dimethyl	*b*	$C_{12}H_{14}ON_2$	90—92	—	—	13·8	—	—	13·9
6-Ethoxy-2 : 3-dimethyl	*b*	$C_{12}H_{14}ON_2$	107—109	—	—	13·8	—	—	13·9
5 : 6-Dimethoxy-2 : 3-dimethyl	*a*	$C_{12}H_{14}O_2N_2$	105—107	—	—	13·3	—	—	12·85
6 : 7-Dimethoxy-2 : 3-dimethyl	*b*	$C_{12}H_{14}O_2N_2$	173—174	—	—	12·7	—	—	12·85
5-Chloro-2 : 3-dimethyl	*b*	$C_{10}H_9N_2Cl$	78—80 (iii)	—	—	14·6	—	—	14·55
6-Chloro-2 : 3-dimethyl	*b*	$C_{10}H_9N_2Cl$	91—92	—	—	14·7	—	—	14·55
6-Bromo-2 : 3-dimethyl	*b*	$C_{10}H_9N_2Br$	84—85	—	—	12·3	—	—	11·8
6-Iodo-2 : 3-dimethyl	*b*	$C_{10}H_9N_2I$	75—75·5	—	—	10·3	—	—	9·85
6-Chloro-2 : 3 : 7-trimethyl	*b*	$C_{11}H_{11}N_2Cl$	154	64·4	5·5	14·2	63·9	5·3	13·6
6-Bromo-2 : 3 : 7-trimethyl	*b*	$C_{11}H_{11}N_2Br$	145	—	—	11·4	—	—	11·15
5 : 8-Dichloro-2 : 3-dimethyl	*b*	$C_{10}H_8N_2Cl_2$	146—148	—	—	12·2	—	—	12·3
6 : 7-Dichloro-2 : 3-dimethyl	*b*	$C_{10}H_8N_2Cl_2$	191—192	52·9	3·4	12·5	52·8	3·5	12·3
2 : 3-Dimethyl-5-nitro	*b*	$C_{10}H_9O_2N_3$	131—131·5	—	—	20·3	—	—	20·7
2 : 3-Dimethyl-6-nitro	*b*	$C_{10}H_9O_2N_3$	133—134	—	—	21·2	—	—	20·7
2 : 3-Dimethyl-6-trifluoromethyl	*b*	$C_{11}H_9N_2F_3$	93	—	—	12·5	—	—	12·4
6-Cyano-2 : 3-dimethyl	*a*	$C_{11}H_9N_3$	199—200	—	—	22·6	—	—	22·95

(i) B. p. 97—100°/3 mm. (ii) B. p. 134—137°/10 mm. (iii) B. p. 158°/10 mm.

2 : 3-diphenylquinoxaline (Hinsberg and König, *Ber.*, 1894, **27**, 2181), 2 : 3-di-*p*-methoxyphenylquinoxaline (Bost and Towell, *J. Amer. Chem. Soc.*, 1948, **70**, 903), 6-methoxy-2 : 3-dimethylquinoxaline (*a*) (*idem*, *loc. cit.*), 6-amino-2 : 3-dimethylquinoxaline (*b*) (Gilman and Broadbent, *ibid.*, p. 2619), 2 : 3 : 6-trimethylquinoxaline (*a*) (von Pechmann, *Ber.*, 1888, **21**, 1411), and 2-acetyl-3-methylquinoxaline (*a*) (Sachs and Barschall, *Ber.*, 1901, **34**, 3054).

6-*Acetamido*-2 : 3-*dimethylquinoxaline* (first prepared in these laboratories by Dr. A. F. Crowther). 6-Amino-2 : 3-dimethylquinoxaline (15 g.), acetic anhydride (11·5 c.c.), and benzene (150 c.c.) were boiled under reflux for 1 hr. On cooling, the *product* (13·6 g.) crystallised; it had m. p. 192—193° (Found : C, 67·1; H, 6·05; N, 19·7. $C_{12}H_{13}ON_3$ requires C, 67·0; H, 6·05; N, 19·5%).

6-p-*Acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline*. 6-Amino-2 : 3-dimethylquinoxaline (3·45 g.) was treated at room temperature with *p*-acetamidobenzenesulphonyl chloride (4·7 g.) in pyridine (20 c.c.). After 5 hr. the pyridine was distilled off under reduced pressure and the residue was washed well with dilute hydrochloric acid and extracted with 8% sodium hydroxide solution (100 c.c.). The extract was clarified by carbon and treated with 50% acetic acid to precipitate crude 6-p-*acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* (3·65 g.; m. p. 310—312°) which was best purified by re-treatment with alkali and acid,

forming colourless, microscopic prisms, m. p. 315—316° (decomp.) (Found: C, 54·8; H, 5·05; N, 13·85. $C_{18}H_{18}O_3N_4S,1{\cdot}5H_2O$ requires C, 54·5; H, 5·3; N, 14·2%).

Reaction of 6-*aminoquinoxaline with diethylmalonyl chloride.* 6-Aminoquinoxaline (17·6 g.) in pyridine (120 c.c.), treated with diethylmalonyl chloride (12 g.) at room temperature, gave NN′-*di*-6-*quinoxalinyldiethylmalonamide* (1·5 g.), which formed cream prisms, m. p. 213—214°, from *n*-propanol (Found: C, 66·35; H, 5·1; N, 20·95. $C_{23}H_{22}O_2N_6$ requires C, 66·65; H, 5·35; N, 20·3%), and 6-*diethylmalonimidoquinoxaline* (7·8 g.), which crystallised as minute colourless prisms, m. p. 73—74°, from aqueous ethanol [Found: C, 66·95; H, 5·3; N, 15·6; 15·55%; *M* (Rast), 240, 245, 235. $C_{15}H_{15}O_2N_3$ requires C, 66·9; H, 5·6; N, 15·6%; *M*, 269]. The latter compound did not react with 6-aminoquinoxaline, but, heating it in an excess of aniline at 170° for 30 min. gave N-*phenyl*-N′-6-*quinoxalyldiethylmalonamide*, m. p. 206—207° (from methanol) (Found: C, 69·6; H, 6·05; N, 15·65. $C_{21}H_{22}O_2N_4$ requires C, 69·6; H, 6·1; N, 15·45%).

6-*Diethylmalonimido*-2 : 3-*dimethylquinoxaline*, prepared in a similar manner from 6-amino-2 : 3-dimethylquinoxaline, crystallised from aqueous ethanol as colourless needles, m. p. 96—97° (Found: C, 68·3; H, 6·35; N, 14·2. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·45; N, 14·15%).

Reaction of 2 : 3-*dihydroxyquinoxaline with ethylmagnesium bromide.* Dry, powdered 2 : 3-dihydroxyquinoxaline (35 g.) was added to ethylmagnesium bromide prepared from magnesium (24 g.) and ethyl bromide (109 g.) in ether (500 c.c.), and the mixture was stirred and refluxed for 36 hr., and then treated with water (250 c.c.) and saturated ammonium chloride solution (250 c.c.). The ethereal layer was separated and the aqueous layer and undissolved solid were extracted with ether (800 c.c.). The insoluble material (4·8 g.) was collected, washed with dilute hydrochloric acid, and dried. It melted above 300°, but on methylation it gave 3-ethyl-1 : 2-dihydro-1-methyl-2-oxoquinoxaline (see below). The ethereal solutions were extracted twice with 2N-sodium hydroxide (250 c.c.) and then with water (250 c.c.), and the aqueous extracts were acidified, to precipitate 2-*ethyl*-3-*hydroxyquinoxaline* (1·9 g.; m. p. 190°) which crystallised from light petroleum (b. p. 80—100°) in colourless needles, m. p. 194—196° (Found: C, 69·05; H, 5·55; N, 15·8. $C_{10}H_{10}ON_2$ requires C, 68·95; H, 5·75; N, 16·1%). Evaporation of the dried (Na_2SO_4) ethereal layer gave a red syrup which crystallised slowly, and on recrystallisation from light petroleum (b. p. 80—100°) gave a *substance* (*ca.* 8 g.), m. p. 158—160° [Found: C, 70·4; H, 8·25; N, 13·45%; *M* (ebullioscopic), 266—283 (in benzene), 125 (in methanol), 137—153 (in ethanol). $C_{12}H_{16}ON_2$ requires C, 70·5; H, 7·8; N, 13·7%; *M*, 204]. Evaporation of the mother-liquor and chromatographic purification (benzene–light petroleum; alumina) gave 2 : 3-diethylquinoxaline (0·7 g.), m. p. and mixed m. p. 48—49° (Found: N, 15·5. Calc. for $C_{12}H_{14}N_2$: N, 15·05%), a red oil (6·0 g.), and 2-ethyl-3-hydroxyquinoxaline (1·0 g.).

3-*Ethyl*-1 : 2-*dihydro*-1-*methyl*-2-*oxoquinoxaline.* 2-Ethyl-3-hydroxyquinoxaline, dissolved in sodium hydroxide solution, was shaken with methyl sulphate at room temperature. The *product* separated in long yellow needles, m. p. 106°, from its colourless aqueous solution (Found: C, 70·3; H, 6·45; N, 15·2. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4; N, 14·9%).

Reaction of 1 : 2 : 3 : 4-*tetrahydro*-1 : 4-*dimethyl*-2 : 3-*dioxoquinoxaline with ethylmagnesium bromide.* 1 : 2 : 3 : 4-Tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline (39 g.), suspended in ether (250 c.c.), was added gradually to the Grignard reagent from magnesium (12·5 g.) and ethyl bromide (55 g.) in ether (200 c.c.). When the vigorous reaction had subsided the mixture was stirred and refluxed for 6 hr., cooled, and decomposed with ammonium chloride solution. Evaporation of the ethereal layer gave a syrup which partly crystallised after several weeks. The solid was collected, washed with benzene, and crystallised from ethyl acetate. 2 : 3-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-2 : 3-*dihydroxy*-1 : 4-*dimethylquinoxaline trihydrate* formed colourless needles, m. p. 54—55° (Found: C, 55·25; H, 8·6; N, 9·5; loss over P_2O_5 in a vacuum-desiccator, 15·7. $C_{14}H_{22}O_2N_2,3H_2O$ requires C, 55·25; H, 9·2; N, 9·2; H_2O, 17·75%). When distilled with 10% (v/v) sulphuric acid it gave hexane-3 : 4-dione, characterised by conversion into 2 : 3-diethylquinoxaline.

Condensation of 2 : 3-*dimethylquinoxaline with* p-*chlorobenzaldehyde.* 2 : 3-Dimethylquinoxaline (7·9 g.), *p*-chlorobenzaldehyde (7·0 g.), and acetic anhydride (25 c.c.) were heated under reflux in an oil-bath at 160° for 3 hr. When cold, the solid (3·4 g.) was filtered off, dried, and crystallised from 2-ethoxyethanol and then from benzene, to give 2 : 3-di-*p*-chlorostyrylquinoxaline, m. p. 216° (Bennett and Willis, *J.*, 1928, 1960). The mother-liquors from the reaction were steam-distilled to remove unchanged *p*-chlorobenzaldehyde, and the non-volatile residue was extracted with ether. Evaporation of the dried (K_2CO_3) extract and crystallisation from methanol gave 3-p-*chlorostyryl*-2-*methylquinoxaline* (4·8 g.), yellow needles, m. p. 109—110° (Found: C, 72·3; H, 4·6; N, 9·7. $C_{17}H_{13}N_2Cl$ requires C, 72·7; H, 4·65; N, 10·0%).

The following compounds were made similarly :

2-*Styrylquinoxaline*, orange-yellow rods [from light petroleum (b. p. 80—100°)], m. p. 105° (Found : C, 82·3; H, 5·3; N, 12·0. $C_{16}H_{12}N_2$ requires C, 82·7; H, 5·2; N, 12·1%).

2-p-*Chlorostyrylquinoxaline*, pale yellow needles [from light petroleum (b. p. 80—100°)], m. p. 143° (Found : C, 71·7; H, 4·4; N, 10·3. $C_{16}H_{11}N_2Cl$ requires C, 72·0; H, 4·1; N, 10·5%).

3-p-*Chlorostyryl*-2-*hydroxyquinoxaline*, yellow needles (from acetic acid), m. p. 273—273·5° (Found : C, 68·1; H, 3·6; N, 10·5. $C_{16}H_{11}ON_2Cl$ requires C, 68·0; H, 3·9; N, 9·9%).

2-*p*-Methoxystyryl-3-methyl- and 2 : 3-di-*p*-methoxystyryl-quinoxaline were made similarly, following the method of McKee, McKee, and Bost (*J. Amer. Chem. Soc.*, 1947, **69**, 468).

2-(2-p-*Chlorophenylethyl*)-3-*methylquinoxaline*. 2-*p*-Chlorostytyl-3-methylquinoxaline (2 g.) in ethanol (120 c.c.) was hydrogenated over Raney nickel at room temperature and pressure. When 1 equivalent of hydrogen had been absorbed, evaporation of the filtered solution gave a sticky yellow solid from which 2-(2-p-*chlorophenylethyl*)-3-*methylquinoxaline* was obtained by repeated crystallisation from light petroleum (b. p. 40—60°) as almost colourless rods, m. p. 106—106·5° (Found : C, 72·0; H, 5·2; N, 9·5. $C_{17}H_{15}N_2Cl$ requires C, 72·2; H, 5·3; N, 9·9%).

The following compounds were prepared similarly :

2-(2-p-*Methoxyphenylethyl*)-3-*methylquinoxaline*, cream prisms (from methanol), m. p. 79·5° (Found : C, 77·2; H, 6·7; N, 9·6. $C_{18}H_{18}ON_2$ requires C, 77·7; H, 6·5, N, 10·1%).

2 : 3-*Di*-(2-p-*chlorophenylethyl*)*quinoxaline*, cream plates (from ethanol), m. p. 150—150·5° (Found : C, 70·5; H, 4·9; N, 6·8. $C_{24}H_{20}N_2Cl_2$ requires C, 70·75; H, 4·9; N, 6·9%).

1 : 2 : 3 : 4-*Tetrahydro*-2-2′-*phenylethylquinoxaline*, colourless rods [from light petroleum (b. p. 60—80°)], m. p. 68·5—69·5° (Found : C, 80·9; H, 7·4; N, 11·9. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6; N, 11·8%).

2-(2-p-*Chlorophenylethyl*)-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, colourless plates [from light petroleum (b. p. 80—100°)], m. p. 103° (Found : C, 70·6, 70·1; H, 6·4, 5·8; N, 10·4. $C_{16}H_{17}N_2Cl$ requires C, 70·4; H, 6·3; N, 10·3%).

3-(2-p-*Chlorophenylethyl*)-2-*hydroxyquinoxaline*, pale buff needles (from methanol), m. p. 212—214° (Found : C, 67·5; H, 4·6; N, 10·1. $C_{16}H_{13}ON_2Cl$ requires C, 67·5; H, 4·6; N, 9·8%).

Formation of N-*Oxides*.—Quinoxaline 1 : 4-dioxides prepared by oxidation with 1·2M-peracetic acid at 50° (see Part I) are listed in Table 2. Quinoxaline mono-*N*-oxides and di-*N*-oxides not prepared by the standard method are described below.

TABLE 2. *Quinoxaline* 1 : 4-*dioxides prepared by means of peracetic acid.*

Substituents	Formula	M. p.	Found, % C	H	N	Required, % C	H	N
2-Ethyl	$C_{10}H_{10}O_2N_2$	150—152°	63·4	4·8	14·6	63·15	5·25	14·7
2 : 3-Dimethyl	$C_{10}H_{10}O_2N_2$	189—190	63·5	5·3	14·7	63·15	5·25	14·7
2-Ethyl-3-methyl	$C_{11}H_{12}O_2N_2$	139—141	65·4	5·7	13·9	64·7	5·9	13·1
2-Methyl-3-*n*-propyl	$C_{12}H_{14}O_2N_2$	108—110	66·3	6·1	12·7	66·05	6·4	12·85
2-Methyl-3-*iso*propyl	$C_{12}H_{14}O_2N_2$	193—194	66·5	6·8	12·85	66·05	6·4	12·85
2-Methyl-3-phenyl	$C_{15}H_{12}O_2N_2$	193—194	71·5	4·7	11·2	71·4	4·75	11·1
2-Benzyl-3-methyl	$C_{16}H_{14}O_2N_2$	155	71·7	4·8	10·0	72·2	5·25	10·5
2-Methyl-3-(2-*p*-chlorophenylethyl)	$C_{17}H_{15}O_2N_2Cl$	168—169	65·0	5·1	8·8	64·85	4·8	8·9
2-2′-Ethoxyethyl-3-methyl	$C_{13}H_{16}O_3N_2$	117	62·55	6·6	11·25	62·9	6·45	11·3
2-Methyl-3-2′-phenoxyethyl	$C_{17}H_{16}O_3N_2$	146	68·75	5·5	9·6	68·9	5·4	9·45
2 : 3-Diethyl	$C_{12}H_{14}O_2N_2$	108—110	66·4	6·4	12·9	66·05	6·4	12·85
2-Ethyl-3-*n*-propyl	$C_{13}H_{16}O_2N_2,H_2O$	85—87	62·15	7·05	11·7	62·4	7·2	11·2
2 : 3-Di-*n*-propyl	$C_{14}H_{16}O_2N_2$	74—76	68·4	7·1	11·6	68·3	7·3	11·4
2 : 3-Di-(2-*p*-chlorophenylethyl)	$C_{24}H_{20}O_2N_2Cl_2$	150—151	65·5	4·8	—	65·5	4·55	—
2 : 3 : 6-Trimethyl	$C_{11}H_{12}O_2N_2$	154—155	—	—	13·6	—	—	13·7
2 : 6 : 7-Trimethyl	$C_{11}H_{12}O_2N_2$	185—187	64·65	5·9	13·7	64·6	5·9	13·7
5-Methoxy-2 : 3-dimethyl	$C_{11}H_{12}O_3N_2$	206—208	59·7	5·6	12·9	60·0	5·45	12·7
6-Methoxy-2 : 3-dimethyl	$C_{11}H_{12}O_3N_2$	197—198	59·5	5·4	13·1	60·0	5·45	12·7
6-Ethoxy-2 : 3-dimethyl	$C_{12}H_{14}O_3N_2$	160—162	61·75	6·1	12·25	61·5	6·0	11·95
6-Chloro-2 : 3-dimethyl	$C_{10}H_9O_2N_2Cl$	175—176	53·2	4·0	12·5	53·45	4·0	12·5
6-Bromo-2 : 3-dimethyl	$C_{10}H_9O_2N_2Br$	186—188	45·0	3·3	10·3	44·6	3·3	10·4
2 : 3-Dimethyl-6-trifluoromethyl	$C_{11}H_9O_2N_2F_3$	155—156	51·5	3·45	10·7	51·15	3·5	10·9
2 : 3-Dimethyl-6-nitro	$C_{10}H_9O_4N_3$	192—194	51·3	3·9	17·8	51·0	3·8	17·9
6-Cyano-2 : 3-dimethyl	$C_{11}H_9O_2N_3$	216—218	61·1	4·4	19·5	61·3	4·2	19·5
6-Acetamido-2 : 3-dimethyl	$C_{12}H_{13}O_3N_3$	259—260	58·3	5·25	16·7	58·3	5·25	17·0
6-Diethylmalonimido-2 : 3-dimethyl	$C_{17}H_{19}O_4N_3$	198—201	61·95	5·9	13·05	62·0	5·8	12·75
2 : 3 : 6 : 7-Tetramethyl	$C_{12}H_{14}O_2N_2$	247—249	65·8	6·3	12·7	66·05	6·4	12·85
6 : 7-Dimethoxy-2 : 3-dimethyl	$C_{12}H_{14}O_4N_2$	275—277	57·8	6·0	11·1	57·6	5·6	11·2
6-Chloro-2 : 3 : 7-trimethyl	$C_{11}H_{11}O_2N_2Cl$	250—252	54·85	4·65	11·75	55·35	4·6	11·7
6-Bromo-2 : 3 : 7-trimethyl	$C_{11}H_{11}O_2N_2Br$, $0{\cdot}5C_2H_5{\cdot}OH$	242—244	47·45	4·1	9·0	47·05	4·6	9·15

2 : 3-*Dimethylquinoxaline* 1-*oxide*. 2 : 3-Dimethylquinoxaline (7·9 g.) and 1·2M-peracetic acid (42 c.c., 1 equiv.) were heated at 50° overnight, poured on ice (150 g.), and neutralised with aqueous sodium hydroxide. The precipitated *monoxide* (5·2 g.; m. p. 55°) was collected, washed with water, and crystallised repeatedly from light petroleum (b. p. 100—120°), to give colourless needles, m. p. 92—93° (depressed to 82° by 2 : 3-dimethylquinoxaline) (Found : N, 16·6. $C_{10}H_{10}ON_2$ requires N, 16·1%). By extraction of the aqueous mother-liquors with chloroform a mixture of the mono- and di-*N*-oxides (3·2 g.) was recovered.

2 : 3 : 5-*Trimethylquinoxaline* 1-*oxide*. 2 : 3 : 5-Trimethylquinoxaline (5 g.) and 1·2M-peracetic acid (100 c.c.) were heated at 50° overnight, evaporated at 10—15 mm. to 15—20 c.c., poured on ice (50 g.), and neutralised with aqueous sodium hydroxide. The *product* (4 g.) was collected, washed with water, and crystallised from light petroleum (b. p. 80—100°) or *cyclo*hexane in colourless needles, m. p. 98—99° (Found : N, 14·7. $C_{11}H_{12}ON_2$ requires N, 14·9%).

The following were prepared similarly :

2 : 3-*Dimethyl*-5 : 6-*benzoquinoxaline* 1-*oxide*, colourless needles [from light petroleum (b. p. 100—120°)], m. p. 165—167° (Found : N, 12·8. $C_{14}H_{12}ON_2$ requires N, 12·5%).

5-*Chloro*-2 : 3-*dimethylquinoxaline* 1-*oxide*, colourless needles (from *cyclo*hexane), m. p. 114—116° (Found : C, 57·6; H, 4·5; N, 13·3. $C_{10}H_9ON_2Cl$ requires C, 57·55; H, 4·3; N, 13·4%).

6 : 7-*Dichloro*-2 : 3-*dimethylquinoxaline* 1-*oxide*, yellow laminæ (from ethanol), m. p. 238° (Found : C, 48·7, 49·0; H, 3·2, 3·3; N, 11·2; Cl, 28·6. $C_{10}H_8ON_2Cl_2$ requires C, 49·3; H, 3·3; N, 11·5; Cl, 29·2%).

2-*Acetyl*-3-*methylquinoxaline* 4-*oxide*, pale yellow needles (from *cyclo*hexane), m. p. 92—94° (Found : C, 65·3; H, 4·7; N, 14·2. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 4·95; N, 13·9%).

5-*Methoxy*-2 : 3-*dimethylquinoxaline* 1-*oxide*. 5-Methoxy-2 : 3-dimethylquinoxaline (6 g.) and 1·2M-peracetic acid (120 c.c.) were heated at 50° overnight, evaporated at 10—15 mm., and neutralised with ice (200 g.) and sodium hydroxide solution. The product was extracted with chloroform and the dried (Na_2SO_4) extract evaporated. The waxy residue (6·9 g.) was extracted with boiling *cyclo*hexane (200 and 100 c.c.), leaving an insoluble residue of di-*N*-oxide (2 g.) (Table 3). The *mono*-N-*oxide* crystallised from *cyclo*hexane in cream needles, m. p. 155—156° (Found : N, 13·9. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

The following were obtained similarly as by-products in the preparation of the di-*N*-oxides :

2-*Methyl*-3-iso*propylquinoxaline* 1(?)-*oxide*, colourless rhombs (from *cyclo*hexane), m. p. 72—73° (Found : C, 71·45; H, 6·75; N, 13·8. $C_{12}H_{14}ON_2$ requires C, 71·25; H, 7·0; N, 13·85%).

2 : 6 : 7-*Trimethylquinoxaline mono*-N-*oxide*, yellow microcrystalline solid [from light petroleum (b. p. 100—120°)], m. p. 133—135° (Found : N, 15·05. $C_{11}H_{12}ON_2$ requires N, 14·9%).

6-*Cyano*-2 : 3-*dimethylquinoxaline mono*-N-*oxide*, yellow nodules (from *cyclo*hexane), m. p. 169—171° (Found : N, 21·0. $C_{11}H_9ON_3$ requires N, 21·1%).

2 : 3-*Dimethyl*-5-*nitroquinoxaline* 1-*oxide*. 2 : 3-Dimethyl-5-nitroquinoxaline (3·5 g.) in dry dioxan (35 c.c.) was added to a 0·5M-solution of monoperphthalic acid in ether (60 c.c.). After 60 hr. at room temperature the solution was evaporated under reduced pressure and the residue neutralised with aqueous sodium carbonate and extracted with chloroform. Evaporation of the extract and chromatographic purification (benzene–ethyl acetate; alumina) gave unchanged 2 : 3-dimethyl-5-nitroquinoxaline (0·55 g.) and 2 : 3-*dimethyl*-5-*nitroquinoxaline* 1-*oxide* (1·05 g.), yellow prisms (from ethanol or benzene), m. p. 157—158° (Found : C, 54·7; H, 4·3; N, 19·4. $C_{10}H_9O_3N_3$ requires C, 54·8; H, 4·1; N, 19·2%). Oxidation of 2 : 3-dimethyl-5-nitroquinoxaline with peracetic acid gave the same *N*-oxide, together with 2-methyl-4-nitrobenziminazole, m. p. 215—216° (Found : C, 54·6; H, 4·1; N, 23·3. Calc. for $C_8H_7O_2N_3$: C, 54·25; H, 3·95; N, 23·7%).

2 : 3-*Diphenylquinoxaline* 1-*oxide and* 1 : 4-*dioxide*. (*a*) 2 : 3-Diphenylquinoxaline (2·82 g.), glacial acetic acid (40 c.c.), and 30% hydrogen proxide (10 c.c.) were heated at 50° overnight, cooled, and filtered from almost pure 2 : 3-*diphenylquinoxaline* 1-*oxide* (0·65 g.; m. p. 196°). Dilution of the filtrate with water (50 c.c.) precipitated some impure monoxide (1·1 g.; m. p. 188°) and neutralisation of the mother-liquors with 40% sodium hydroxide solution and ice precipitated 2 : 3-diphenylquinoxaline 1 : 4-dioxide (0·9 g.) which crystallised from ethanol in large yellow prisms, m. p. 216° (Found : C, 76·4; H, 4·4. Calc. for $C_{20}H_{14}O_2N_2$: C, 76·3; H, 4·45%). 2 : 3-Diphenylquinoxaline 1-oxide crystallised from ethanol or acetic acid in long pale yellow prisms, m. p. 197°, becoming red-orange on exposure to light (Found : C, 80·4; H, 4·7. $C_{20}H_{14}ON_2$ requires C, 80·5; H, 4·7%).

(*b*) 2 : 3-Diphenylquinoxaline (32 g.) and 1·2M-peracetic acid (400 c.c.) were heated at 50°

overnight, cooled, and diluted with water (400 c.c.) to precipitate the mono-*N*-oxide (20·4 g.; m. p. 192—193°). Further dilution with water (800 c.c.) precipitated di-*N*-oxide (9·9 g.; m. p. 209—211°), and neutralisation with 40% aqueous sodium hydroxide gave a further 6 g.

The following were prepared similarly :

2 : 3-*Di*-p-*methoxyphenylquinoxaline* 1-*oxide*, pale yellow needles (from ethanol), m. p. 156° (Found : N, 7·9. $C_{22}H_{18}O_3N_2$ requires N, 7·8%).

2 : 3-*Di*-p-*methoxyphenylquinoxaline* 1 : 4-*dioxide*, yellow prisms (from ethanol), m. p. 183—184° (Found : N, 7·5. $C_{22}H_{18}O_4N_2$ requires N, 7·5%).

2-*Phenylquinoxaline* 4-*oxide and* 1 : 4-*dioxide*. 2-Phenylquinoxaline (13 g.), anhydrous formic acid (150 c.c.), and 30% hydrogen peroxide (50 c.c.) were heated overnight at 50° (after checking the initial exothermic reaction by cooling), evaporated at 10—15 mm. to 50—60 c.c., and poured into ice water (200 c.c.). The monoxide, which separated as an oil, crystallised rapidly and was collected (13 g.; m. p. 135—137°) and washed with water. Neutralisation of the mother-liquor with aqueous sodium hydroxide precipitated the dioxide (0·8 g.), a small amount more being recovered from the aqueous solution by extraction with chloroform. 2-*Phenylquinoxaline* 4-*oxide* crystallised from ethanol in orange-yellow needles, m. p. 137—138° (Found : N, 13·2. $C_{14}H_{10}ON_2$ requires N, 12·6%). 2-*Phenylquinoxaline* 1 : 4-*dioxide* formed lemon-yellow needles (from ethanol), m. p. 202—203° (Found : C, 69·4; H, 4·7; N, 11·4. $C_{14}H_{10}O_2N_2$ requires C, 70·5; H, 4·2; N, 11·8%). Oxidation of 2-phenylquinoxaline 4-oxide with 1·2M-peracetic acid (60°, 96 hr.) gave a mixture containing 2-hydroxy-3-phenylquinoxaline, m. p. 242—243° (Found : C, 75·7; H, 5·2; N, 12·6. Calc. for $C_{14}H_{10}ON_2$: C, 75·7; H, 4·5; N, 12·6%), and with 8M-peracetic acid (45—50°; 5 hr.) some 2-phenylbenziminazole, m. p. 281—283°, was obtained, but in no case did the further oxidation give di-*N*-oxide.

6-*Aminoquinoxaline* 1 : 4-*dioxide*. 6-Acetamidoquinoxaline 1 : 4-dioxide (Part I) was boiled under reflux with 10% hydrochloric acid for 20 min. The solution was then made slightly alkaline with aqueous sodium hydroxide and the *product* was collected. It formed orange needles, m. p. 245° (decomp.), from water (Found : C, 54·8; H, 4·25; N, 23·95. $C_8H_7O_2N_3$ requires C, 54·25; H, 4·0; N, 23·7%). The *hydrochloride* crystallised from dilute hydrochloric acid as small brownish-red prisms, m. p. 208° (decomp.) (Found : C, 45·1; H, 4·0; N, 19·9. $C_8H_7O_2N_3$,HCl requires C, 45·0; H, 3·8; N, 19·65%).

6-*Amino*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*, obtained similarly by hydrolysis of the acetyl derivative, formed yellow-orange needles (from water), decomp. 268° (Found : C, 58·65; H, 5·65; N, 20·35. $C_{10}H_{11}O_2N_3$ requires C, 58·5; H, 5·4; N, 20·5%). The *hydrochloride*, brown prisms from dilute hydrochloric acid, decomposed at 240° (Found : C, 49·4; H, 5·0; N, 16·95. $C_{10}H_{11}O_2N_3$,HCl requires C, 49·7; H, 5·0; N, 17·4%).

2 : 3-*Dimethyl*-6-p-*toluenesulphonamidoquinoxaline* 1 : 4-*dioxide*, obtained from 6-amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide and excess of toluene-*p*-sulphonyl chloride in pyridine at 0—10°, formed pale yellow prisms (from dimethylformamide), decomp. *ca.* 276° (Found : C, 56·95; H, 4·9; N, 11·5. $C_{17}H_{17}O_4N_3S$ requires C, 56·8; H, 4·8; N, 11·7%).

6-p-*Acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*. 6-Aminoquinoxaline 1 : 4-dioxide and *p*-acetamidobenzenesulphonyl chloride (10% excess) were added alternately in small quantities to pyridine, stirred at 10°. The mixture was heated on the steam-bath for 45 min., cooled, filtered, and evaporated. After trituration with dilute hydrochloric acid the residue was dissolved in dilute sodium hydroxide solution (charcoal) and acidified with acetic acid. The precipitated *product* formed small yellow rods, decomp. *ca.* 290°, from ethylene glycol (Found : C, 53·0; H, 4·8; N, 13·7. $C_{18}H_{18}O_5N_4S$ requires C, 53·7; H, 4·5; N, 13·95%). This compound, also obtained in small yield by peracetic acid oxidation of 6-*p*-acetamidobenzenesulphonamido-2 : 3-dimethylquinoxaline, was hydrolysed by hot 10% hydrochloric acid to 6-p-*aminobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*, yellow prisms, decomp. 265° (Found : C, 52·6; H, 3·85; N, 14·9; S, 8·9. $C_{16}H_{16}O_4N_4S$ requires C, 53·3; H, 4·5; N, 15·55; S, 8·9%).

2-*Amino*-1 : 6-*dimethyl*-4-(2′ : 3′-*dimethyl*-6′-*quinoxalinyl*)*aminopyrimidinium iodide* 1′ : 4′-*dioxide*. 6-Amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide (4·1 g.), 2-amino-4-chloro-1 : 6-dimethylpyrimidinium iodide (Ainley *et al.*, *J.*, 1953, 59) (5·7 g.), water (115 c.c.) and 2N-hydrochloric acid (10 c.c.) were refluxed for 30 min., then cooled, and the *product* (6·75 g.) was collected. It crystallised from water in yellow prisms, decomp. *ca.* 240° (Found : C, 39·4; H, 4·85; N, 16·8; I, 25·35. $C_{16}H_{19}O_2N_6I,2H_2O$ requires C, 39·2; H, 4·75; N, 17·15; I, 25·9%).

Reaction of 2 : 3-*dimethylquinoxaline oxide with methyl iodide*. 2 : 3-Dimethylquinoxaline 1-oxide (2·1 g.), methyl iodide (4 g.), and methyl cyanide (20 c.c.) were refluxed overnight and then evaporated to dryness under reduced pressure. The residue was extracted three times

with boiling *cyclo*hexane to remove unchanged 2 : 3-dimethylquinoxaline 1-oxide (*ca.* 1 g.) and was crystallised twice from methanol, giving 1 : 2 : 3-*trimethylquinoxalinium tri-iodide* 4-*oxide* (*ca.* 100 mg.) as dark brown prisms, m. p. 144—145° (Found : C, 23·5; H, 2·2; N, 4·1; I, 66·5. $C_{11}H_{13}ON_2I_3$ requires C, 23·15; H, 2·3; N, 4·9; I, 66·8%).

Some of the work described in this paper is incorporated in B.P. 668,412.

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