567. *Quinoxaline Derivatives. Part VI.* Molecular Rearrangements of 3,4-Dihydro-4-methyl-3-oxoquinoxaline-2-carboxy-N-methylanilide 1-Oxide, and of Nitromalonbis-N-methylanilide.*

By J. W. Clark-Lewis and G. F. Katekar.

The *N*-oxide (I) named in the title undergoes chlorination and cyclisation to 6-chloro-1,2,3,4,2′,3′-hexahydro-4,1′-dimethyl-3,2′-dioxoquinoxaline-2-spiro-3′-indole when boiled with ethanolic hydrogen chloride, and similarly affords the 1-acetyl derivative of the spiroindole when boiled with acetyl chloride.

Usherwood and Whiteley's [1] " 3,4-dihydro-4-methyl-3-oxoquinoxaline 1-oxide " is recognised as *N*-methylisatin β-oxime. Formation of this oxime from nitromalonbis-*N*-methylanilide involves a molecular rearrangement similar to that occurring in hydrolysis of 1-nitroparaffins to hydroxylamine and aliphatic acids.

Usherwood and Whiteley [1] found that 3,4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxy-*N*-methylanilide 1-oxide (I) undergoes a number of interesting transformations, *e.g.*, when added to sulphuric acid it gives an amine * (II; R = H), although it yields a different product when the order of mixing is reversed. They found that ethanolic hydrogen chloride converted the *N*-oxide (I) into a compound $C_{17}H_{16}O_2N_3Cl$, whereas acetyl chloride gave a compound $C_{19}H_{18}O_3N_3Cl$; no structures were proposed for these products. Both products have now been shown to contain two fewer hydrogen atoms and

* Part V, *J.*, 1957, 439.

[1] Usherwood and Whiteley, *J.*, 1923, **123**, 1069.

to be the quinoxalinespiroindoles (III; R = H and Ac). The first indications of these structures came from ultraviolet-light absorption spectra compatible with a tetrahydroquinoxaline ring system, from an N–H stretching band (in III; R = H), and from carbonyl bands at 5·94 and 5·79 μ, the latter being typical of 5-membered lactams and close to the values 5·80—5·83 μ reported [2] for some 1-methyloxindoles.

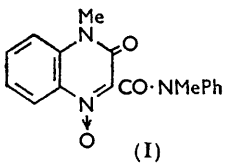
The resistance of the compounds to reducing agents [1] is understandable from the structures (III), and hydrolysis leads to steam-volatile 4-chloro-2-methylaminoaniline, which presumably is the base mistaken for *N*-methylaniline by Usherwood and Whiteley. The spiroindole (III; R = H) was inert to acetic anhydride but with acetyl chloride gave the 1-acetyl derivative (III; R = Ac). Hydrolysis of this derivative gave 4-chloro-2-methylaminoaniline and *N*-methylisatin, the latter arising from an acidic intermediate, presumably by decarboxylation and aerial oxidation of 1-methyldioxindole-3-carboxylic acid. The main product of this hydrolysis with ethanolic hydrochloric acid was, however, 6-chloro-3,4-dihydro-4-methyl-2-*o*-methylaminophenyl-3-oxoquinoxaline (II; R = Cl); this was synthesised from 4-chloro-2-methylaminoaniline and acetylisatin by the method described [3] for the parent amine (II; R = H), and for comparison the 7-chloro-isomer was likewise prepared from 5-chloro-2-methylaminoaniline. The chloro-amine (II; R = Cl) retains the bond formed in generating the indole ring, and isolation of this hydrolysis product and also *N*-methylisatin provides powerful support for the quinoxalinespiroindole structures (III; R = H and Ac). The substitution of chlorine in the 6-position of these quinoxalinespiroindoles is analogous to the conversion of 3-ethoxy-2-methylquinoxaline 1-oxide into 6-chloro-3-hydroxy-2-methylquinoxaline.[4]

The mechanism of the formation of the quinoxalinespiroindole (III; R = H) from the *N*-oxide (I) under the influence of ethanolic hydrogen chloride is particularly interesting because the yield of product exceeds 50%, so that the *N*-oxide group apparently does not participate in both the cyclisation and the chlorination stage. Electrophilic chlorination thus seems to be excluded as formation of such a chlorinating species would consume the *N*-oxide function, and subsequent cyclisation would then be difficult to understand. Protonation of the *N*-oxide to the conjugate acid (IV) presumably is the first step, and the powerful inductive effect of the hydroxylammonium ion would then promote intramolecular electrophilic substitution at the *ortho*-position of the methylanilide by the quinoxaline 2-C-atom to give the *N*-hydroxy-compound (V). *N*-Phenylhydroxylamines when treated with hydrochloric acid yield predominantly *p*-chloro-anilines by a reaction considered to be nucleophilic [5] substitution by chloride ions, and with the intermediate (V) this leads to the isolated 6-chloro-1,2,3,4,2′,3′-hexahydro-4,1′-dimethyl-3,2′-dioxoquinoxaline-2-spiro-3′-indole (III; R = H).

Probably the compound (V) is also an intermediate in the conversion of the *N*-oxide (I) into the amine (II; R = H). This conversion occurs in concentrated sulphuric acid, and the fact that added aromatic amines are not incorporated into the product (II; R = H) supports the assumption that reaction is intramolecular. Dilution of the sulphuric acid by these bases promotes formation of a neutral by-product which is the main product when sulphuric acid is added to the *N*-oxide instead of *vice versa*. Usherwood and Whiteley [1] formulated this neutral substance as the quinoxalinoquinoxaline (VI; R = Me or Et), which in current formulation may be written as (VII; R = Me or Et), the nature of the group R depending on the solvent used in crystallisation. The methyl and the ethyl group can be exchanged by heating with ethanol or with methanol respectively, but no exchange occurred with butan-1-ol. Detailed investigation of the structure (VII) has not been undertaken.

[2] Wenkert, Bose, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5514.
[3] Clark-Lewis, *J.*, 1957, 439.
[4] Dawson, Newbold, and Spring, *J.*, 1949, 2579.
[5] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 621; Heller, Hughes, and Ingold, *Nature*, 1951, **168**, 909.

Landquist [6] has drawn attention to the discrepancy in m. p. of 3,4-dihydro-4-methyl-3-oxoquinoxaline 1-oxide (VIII) prepared by him and that reported by Usherwood and Whiteley [1] for the product obtained from nitromalonbis-*N*-methylanilide. Direct comparison has now confirmed that the two compounds are different, and Usherwood and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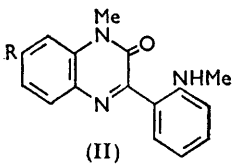
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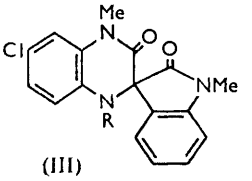
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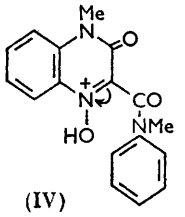
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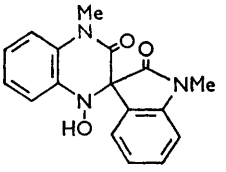
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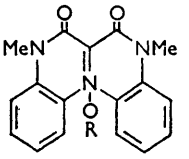
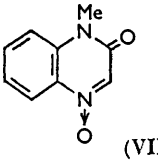
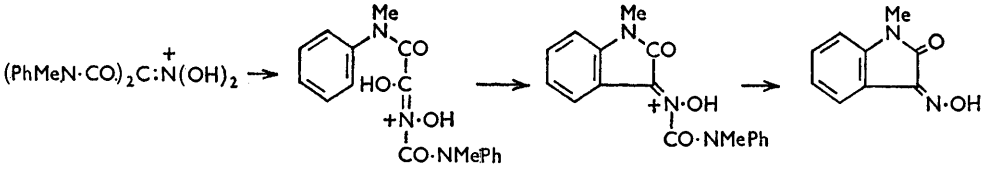

(VI)


(VII)


(VIII)

Whiteley's compound has been identified as *N*-methylisatin β-oxime by its infrared spectrum and by a mixed m. p. with the oxime prepared from *N*-methylisatin. This interesting conversion of nitromalonbis-*N*-methylanilide into *N*-methylisatin β-oxime occurs in



sulphuric acid, and appears to involve rearrangement similar to the Beckmann transformation, *e.g.*, of the protonated *aci*-nitro-compound followed by cyclisation and hydrolysis as shown. Several mechanisms [7] have been proposed for the similar rearrangement occurring in the hydrolysis of 1-nitroalkanes [8] to carboxylic acids and hydroxylamine.

Experimental

6-Chloro-1,2,3,4,2′,3′-hexahydro-4,1′-dimethyl-3,2′-dioxoquinoxaline-2-spiro-3′-indole (III; R = H).—(*a*) 3,4-Dihydro-4-methyl-3-oxoquinoxaline-2-carboxy-*N*-methylanilide 1-oxide [1,3] (2 g.) was boiled under reflux for 2 hr. with 5% ethanolic hydrogen chloride (50 c.c.), and the solution was then evaporated under reduced pressure. Recrystallisation of the residue from ethanol gave an *ethanol solvate* (1·3 g., 61%) of the spiran as prisms, m. p. 240° raised by recrystallisation to m. p. 241—242° (Found: C, 61·5; H, 5·6; N, 11·1; Cl, 8·9. $C_{17}H_{14}O_2N_3Cl,C_2H_5\cdot OH$ requires C, 61·0; H, 5·1; N, 11·2; Cl, 9·5. Found, on material dried to constant weight at 150° over P_2O_5: C, 62·2; H, 4·3; N, 12·8; Cl, 10·3. $C_{17}H_{14}O_2N_3Cl$ requires C, 62·3; H, 4·3; N, 12·8; Cl, 10·8%), $\lambda_{max.}$ in 95% ethanol 232 (ε 35,600) and 306 mμ

[6] Landquist, *J.*, 1953, 2830.
[7] Yale, *Chem. Rev.*, 1943, **33**, 226.
[8] Hass and Riley, *ibid.*, 1943, **32**, 395.

(ε 4800), $\lambda_{min.}$ at 212 (14,600) and 280 mμ (ε 2700). When methanolic hydrogen chloride was used similarly the *N*-oxide (2 g.) gave the *methanol solvate* in prisms (1·2 g., 59%), m. p. 241—242° alone or when mixed with the ethanol solvate (Found: C, 60·2; H, 5·0; N, 11·4; Cl, 9·4. $C_{17}H_{14}O_2N_3Cl,CH_3{\cdot}OH$ requires C, 60·1; H, 5·0; N, 11·7; Cl, 9·9%).

(*b*) The finely powdered 1-acetyl derivative (see below) (0·5 g.) was added slowly to 92% sulphuric acid at 50°. It dissolved with effervescence and release of acetic acid (odour). The red solution was poured into water and crystallisation of the precipitate from ethanol gave prisms (0·4 g., 80%), m. p. 240° not depressed by admixture with the ethanol solvate described under (*a*).

1-*Acetyl*-6-*chloro*-1,2,3,4,2′,3′-*hexahydro*-4,1′-*dimethyl*-3,2′-*dioxoquinoxaline*-2-*spiro*-3′-*indole* (III; R = Ac).—(*a*) 3,4-Dihydro-4-methyl-3-oxoquinoxaline-2-carboxy-*N*-methylanilide 1-oxide (2 g.) was heated with acetyl chloride (20 c.c.) for 1½ hr. on a steam-bath before removal of acetyl chloride under reduced pressure. The residue of 1-*acetyl derivative* (1·2 g., 39%) crystallised from ethanol in prisms, m. p. 226—227° (Found: C, 61·8; H, 4·5; N, 11·2; Cl, 10·1. $C_{19}H_{16}O_3N_3Cl$ requires C, 61·7; H, 4·4; N, 11·4; Cl, 9·6%), $\lambda_{max.}$ in 95% ethanol 238 (ε 33,900) and 292 mμ (ε 6500), $\lambda_{min.}$ 224 (ε 21,000) and 278 mμ (ε 5900).

(*b*) The spiran (III; R = H) (1·2 g.) was boiled for 1 hr. with acetyl chloride (10 c.c.) and acetic anhydride (50 c.c.). Evaporation under reduced pressure left a residue of the 1-acetyl derivative (1 g., 83%), m. p. 225°, which crystallised from ethanol in prisms, m. p. and mixed m. p. 226°.

4-*Chloro*-2-*methylaminoaniline Hydrochloride*.—2,4-Dichloro-1-nitrobenzene (38·4 g.), pyridine (80 g.), and aqueous 25—30% methylamine (37 g.) were heated in a closed container at 100° for 28 hr. and the product was collected by filtration of the cold solution. The filtrate was evaporated under reduced pressure and the combined solid products were dissolved in the minimum quantity of 12N-hydrochloric acid. The filtered (glass wool) solution was diluted with water (*ca.* 5 l.), and the precipitate was collected; 5-chloro-*N*-methyl-2-nitroaniline [9] (24 g., 64%) crystallised from benzene–light petroleum (b. p. 60—90°) in needles, m. p. 104—105°. The nitro-amine (9·3 g.) in ethanol (100 c.c.) was hydrogenated over Raney nickel (W7) and the suspension was then filtered into 12N-hydrochloric acid (10 c.c.). The amine hydrochloride (3·6 g.) crystallised in colourless leaflets, m. p. 225—229° (decomp.), and a further crop (1·4 g.) was obtained by concentrating the mother-liquors. Crystallisation of the product (5 g., 52%) from ethanol–ether (Na-dried) gave 4-*chloro*-2-*methylaminoaniline hydrochloride* in leaflets, m. p. 229° (decomp.) (Found: C, 43·6; H, 5·1; Cl, 36·8. $C_7H_{10}N_2Cl_2$ requires C, 43·5; H, 5·2; Cl, 36·7%). The hydrochloride was rapidly oxidised in water or ethanol (became red); the free base decomposed on attempted distillation under reduced pressure.

Acid-hydrolysis of 6-*Chloro*-1,2,3,4,2′,3′-*hexahydro*-4,1′-*dimethyl*-3,2′-*dioxoquinoxaline*-2-*spiro*-3′-*indole* (III; R = H).—The spiro-indole (1·5 g.) was boiled for 4 hr. with concentrated hydrochloric acid (30 c.c.) and ethanol (30 c.c.). The dark red solution was concentrated under reduced pressure, and steam-distilled after basification with aqueous sodium hydroxide. The distillate was collected in an excess of hydrochloric acid, which was then evaporated under reduced pressure. Crystallisation of the red residue from methanol–ether (Na-dried) gave 4-chloro-2-methylaminoaniline hydrochloride (0·135 g., 15%) in leaflets, m. p. and mixed m. p. 221—223° (decomp.) (Found: C, 43·4; H, 5·3; Cl, 37·0%).

Acid-hydrolysis of 1-*Acetyl*-6-*chloro*-1,2,3,4,2′,3′-*hexahydro*-4,1′-*dimethyl*-3,2′-*dioxoquinoxaline*-2-*spiro*-3′-*indole* (III; R = Ac).—The acetyl compound (6 g.) was boiled for 4 hr. with ethanol (120 c.c.) and concentrated hydrochloric acid (120 c.c.), then treated as above, affording 4-chloro-2-methylaminoaniline hydrochloride (0·6 g., 19%), leaflets, m. p. and mixed m. p. 225—228° (decomp.). 6-*Chloro*-3,4-*dihydro*-4-*methyl*-2-o-*methylaminophenyl*-3-*oxoquinoxaline* (1·59 g., 33%) crystallised from the alkaline solution remaining after steam-distillation, and recrystallised from ethanol in orange needles, m. p. 188—189° not depressed by admixture with a specimen, m. p. 190—191°, synthesised as described below (Found: C, 64·0; H, 4·8; N, 13·8; Cl, 11·7. $C_{16}H_{14}ON_3Cl$ requires C, 64·1; H, 4·7; N, 14·0; Cl, 11·8%), $\lambda_{max.}$ in 95% ethanol 309 (ε 8800), 352 (ε 10,500), 368 (ε 9100), 428 (ε 6300), and 443 mμ (ε 6600); $\lambda_{min.}$ 274 (ε 5200), 329 (ε 7000), 363 (ε 8400), 389 (ε 3100), and 430 mμ (ε 2400). The alkaline filtrate from the methylaminoquinoxaline was extracted with chloroform until pale yellow and was then acidified with hydrochloric acid (red colour developed) before re-extraction with chloroform. Evaporation

[9] Blanksma, *Rec. Trav. chim.*, 1902, **21**, 273.

of the latter, orange extract left a red crystalline residue of *N*-methylisatin (0·3 g., 13%), m. p. 131° raised by recrystallisation from ethanol–water (1 : 10) to m. p. and mixed m. p. 132° (β-oxime, m. p. and mixed m. p. 190—191°).

2-o-*Aminophenyl*-6-*chloro*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline*.—4-Chloro-2-methylaminoaniline, from the hydrochloride (1·9 g.) and aqueous sodium acetate (1·4 g.), was heated on a steam-bath for 4 hr. with 1-acetylisatin [10] (1·9 g.) in ethanol (100 c.c.). 2-o-*Acetamidophenyl*-6-*chloro*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (0·8 g.) crystallised from the cold solution, and a further quantity (0·3 g.; total, 1·1 g., 34%) was obtained from the mother-liquors; it crystallised from ethanol in yellow needles, m. p. 264—265° (Found: C, 62·4; H, 4·3; N, 12·7; Cl, 10·2. $C_{17}H_{14}O_2N_3Cl$ requires C, 62·3; H, 4·3; N, 12·8; Cl, 10·8%). The acetyl compound (1·7 g.) was boiled with ethanol (100 c.c.) and hydrochloric acid (100 c.c.) for 4 hr. and the solution was concentrated under reduced pressure before basification with aqueous ammonia. The precipitated 2-o-*aminophenyl*-6-*chloro*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (1·1 g., 75%) crystallised from methanol in pale yellow needles, m. p. 147—148° (Found: C, 63·1; H, 4·3. $C_{15}H_{12}ON_3Cl$ requires C, 63·1; H, 4·3%).

6-*Chloro*-3,4-*dihydro*-4-*methyl*-2-o-*methylaminophenyl*-3-*oxoquinoxaline* (II; R = Cl).—The foregoing aminophenylquinoxaline (0·7 g.), toluene-*p*-sulphonyl chloride (0·56 g.), and pyridine (2·5 c.c.) were heated at 100° for 2 hr. and then poured into water. The precipitated *toluene*-p-*sulphonyl derivative* (0·9 g., 80%), m. p. 243°, crystallised from ethanol in needles, m. p. 245—246° (Found: C, 60·5; H, 4·1. $C_{22}H_{18}O_3N_3ClS$ requires C, 60·1; H, 4·1%). The sulphonanilide (0·75 g.) with methyl iodide (0·8 c.c.) and anhydrous potassium carbonate (1 g.) in acetone (10 c.c.) for 2 hr. gave the N-*methyltoluene*-p-*sulphonanilide* (0·66 g., 86%), needles (from methanol), m. p. 202—203° (Found: C, 61·4; H, 4·6. $C_{23}H_{20}O_3N_3ClS$ requires C, 60·9; H, 4·4%). This anilide (0·45 g.) was heated at 100° for 1½ hr. with 2 c.c. of a mixture of sulphuric acid (10 c.c.) and glacial acetic acid (4·5 c.c.), and the solution was diluted with water and basified with aqueous sodium hydroxide. The precipitated 6-chloro-3,4-dihydro-4-methyl-2-*o*-methylaminophenyl-3-oxoquinoxaline (0·25 g., 86%) crystallised from ethanol in orange needles, m. p. 190—191° (Found: C, 64·2; H, 4·9. Calc. for $C_{16}H_{14}ON_3Cl$: C, 64·1; H, 4·7%). It gave a colourless *N*-nitroso-derivative.

7-*Chloro*-3,4-*dihydro*-4-*methyl*-2-o-*methylaminophenyl*-3-*oxoquinoxaline*.—5-Chloro-2-methylaminoaniline was prepared by hydrogenation of the 4-chloro-*N*-methyl-2-nitroaniline, m. p. 105°, obtained from 2,5-dichloro-1-nitrobenzene and methylamine, and was converted into the quinoxaline as described for the 6-chloro-isomer: the diamine hydrochloride (5·6 g.) and acetylisatin (5·6 g.) in boiling ethanol (250 c.c.) gave 2-o-*acetamidophenyl*-7-*chloro*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (3·85 g., 41%), m. p. 243—244° (Found: C 62·4; H, 4·2; N, 12·5; Cl, 11·2. $C_{17}H_{14}O_2N_3Cl$ requires C, 62·3; H, 4·3; N, 12·8; Cl, 10·8%). Hydrolysis of the acetyl compound (1 g.) yielded 2-o-*aminophenyl*-7-*chloro*-3,4-*dihydro*-4-*methyl*-3-*oxoquinoxaline* (0·8 g., 70%) in golden needles, m. p. 195—196° (Found: C, 63·3; H, 4·2; N, 14·3; Cl, 12·4. $C_{15}H_{12}ON_3Cl$ requires C, 63·1; H, 4·2; N, 14·7; Cl, 12·4%). The base (0·55 g.) gave the *toluene*-p-*sulphonyl derivative* (0·72 g., 90%), yellow needles (from ethanol), m. p. 230° (Found: C, 59·8; H, 4·1. $C_{22}H_{18}O_3N_3ClS$ requires C, 60·1; H, 4·1%), and with methyl iodide gave the N-*methyltoluene*-p-*sulphonanilide* (74%), prisms, m. p. 215—216° (Found: C, 60·7; H, 4·5. $C_{23}H_{20}O_3N_3ClS$ requires C, 60·8; H, 4·4%). Hydrolysis of this derivative (0·3 g.) then yielded 7-*chloro*-3,4-*dihydro*-4-*methyl*-2-o-*methylaminophenyl*-3-*oxoquinoxaline* (0·15 g., 80%), orange needles, m. p. 165° (Found: C, 64·4; H, 4·7; N, 13·4. $C_{16}H_{14}ON_3Cl$ requires C, 64·1; H, 4·7; N, 14·0%).

3,4-*Dihydro*-4-*methyl*-3-*oxoquinoxaline*-2-*carboxy*-N-*methylanilide* 1-*Oxide and its Behaviour with Sulphuric Acid in the Presence of Bases*.—(*a*) The *N*-oxide [1,3] (I) (3 g.) gave 1,2-dihydro-1-methyl-3-*o*-methylaminophenyl-2-oxoquinoxaline [3] (1·8 g., 69%), m. p. 131—133°, when stirred with 92% sulphuric acid (10 c.c.). This, in 95% ethanol, had $\lambda_{max.}$ 296 (ε 8400), 350 (ε 8700), 366 (ε 7600), and 440 mμ (ε 5400), $\lambda_{min.}$ 272 (ε 4800), 326 (ε 5800), 362 (ε 6700), and 389 mμ (ε 3600), and an inflexion at 420 mμ (ε 4900).

(*b*) The *N*-oxide (0·5 g.) was finely powdered and slowly added to a mixture of 92% sulphuric acid (5 c.c.) and ethylaniline (3 c.c.) which was stirred and warmed to effect dissolution before being poured into water. The precipitate (A) was collected and basification of the filtrate and removal of ethylaniline in steam gave the methylaminophenylquinoxaline (0·18 g., 42%);

[10] Suida, *Ber.*, 1878, **11**, 585.

crystallisation of half the product from ethanol gave prisms of 1,2-dihydro-1-methyl-3-*o*-methylaminophenyl-2-oxoquinoxaline, m. p. and mixed m. p. 133°, and the other half after chromatography on alumina (single band) with benzene gave needles, m. p. 135°, from ethanol. The precipitate (A) crystallised from ethanol in pale yellow needles, consisting of 2-ethoxy-3,4,3′,4′-tetrahydro-4,4′-dimethyl-3,3′-dioxo-2*H*-quinoxalino(1′,2′:1,2)quinoxaline (0·2 g., 36%), m. p. 239° alone and when mixed with the compound described below.

(*c*) These reagents with *N*-oxide (0·5 g.) similarly gave the *o*-methylaminophenylquinoxaline (0·2 g., 47%), m. p. and mixed m. p. 135°, which was homogeneous when chromatographed, together with the quinoxalinoquinoxaline (0·17 g., 31%), m. p. 242°.

(*d*) With sulphuric acid and *NN*-dimethylaniline the *N*-oxide gave results similar to those described under (*b*) and (*c*).

2-*Ethoxy*-3,4,3′,4′-*tetrahydro*-4,4′-*dimethyl*-3,3′-*dioxo*-2H-*quinoxalino*(1′,2′:1,2)*quinoxaline* (VII; R = Et).—92% Sulphuric acid (0·5 c.c.) was added to the *N*-oxide (0·3 g.), which dissolved with slight effervescence to form a bright red solution.[1] The solutions from seven such experiments were poured into water (200 c.c.), and the yellow precipitate was treated with chloroform–ethanol. Crystallisation gave the *quinoxalinoquinoxaline* in pale yellow prisms (1·4 g., 60%), m. p. 243° (Found: C, 67·7; H, 5·7; N, 12·5; OEt, 11·6. $C_{19}H_{19}O_3N_3$ requires C, 67·6; H, 5·7; N, 12·5; OEt, 13·4%). A small quantity of the amine (II; R = H) was obtained as a by-product.

3,4,3′,4′-*Tetrahydro*-2-*methoxy*-4,4′-*dimethyl*-3,3′-*dioxo*-2H-*quinoxalino*(1′,2′:1,2)*quinoxaline* (VII; R = Me) was obtained by the method used for the ethoxy-analogue except that the precipitate was treated with chloroform–methanol. Crystallisation gave pale yellow prisms (1·38 g., 60%), m. p. 276—278° (Found: C, 66·6; H, 5·3; N, 13·0. $C_{18}H_{17}O_3N_3$ requires C, 66·9; H, 5·3; N, 13·0). When boiled with ethanol (25 c.c.) for 2 hr. the methoxy-compound (0·5 g.) gave the ethoxy-analogue (0·45 g., 90%), m. p. and mixed m. p. 243—244°. Neither compound exchanged its alkyl group with butan-1-ol under similar conditions.

Nitromalonbis-N-*methylanilide*.—Nitric acid (*d* 1·44; 2 c.c.) was added to a solution of hydroxyiminomalonbis-*N*-methylanilide (5 g.) in chloroform (30 c.c.), and the mixture was heated to the b. p. and then allowed to evaporate spontaneously to a syrupy liquid. Ethanol (30 c.c.) was added and the precipitated nitro-compound (2·4 g., 46%) was collected; it crystallised from aqueous methanol (charcoal) in colourless elongated prisms, m. p. 155—156° (Found: C, 62·7; H, 5·1; N, 12·8. Calc. for $C_{17}H_{17}O_4N_3$: C, 62·4; H, 5·2; N, 12·8%).

N-*Methylisatin* β-*Oxime from Nitromalonbis*-N-*methylanilide*.—Finely powdered nitromalonbis-*N*-methylanilide (4 g.) was added slowly to 92% sulphuric acid (30 c.c.), and the deep red solution was warmed gently until evolution of carbon dioxide (lime-water) ceased. The cooled mixture was added to water (300 c.c.), and the product (1·4 g., 65%), which separated slowly, was collected; the oxime crystallised from water in bright yellow needles, m. p. 192°, which changed their crystal form when dried at 120° over phosphoric oxide (Found: C, 61·1; H, 4·7; N, 15·8. Calc. for $C_9H_8O_2N_2$: C, 61·4; H, 4·6; N, 15·9%). It was insoluble in aqueous sodium carbonate but soluble in aqueous sodium hydroxide, and showed an O–H band at 3560 cm.$^{-1}$ and a carbonyl band at 1725 cm.$^{-1}$. The oxime prepared in this way was reported [1] to be 3,4-dihydro-4-methyl-3-oxoquinoxaline 1-oxide (VIII), but a mixture of the authentic *N*-oxide [6] (m. p. 208—209°) with the oxime melted at 150—156°. The product from nitromalonbis-*N*-methylanilide was indistinguishable from the oxime [11] prepared from *N*-methylisatin.[12]

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[11] Borsche and Sander, *Ber.*, 1914, **47**, 2823.
[12] Borsche and Jacobs, *ibid.*, p. 361.