Some Quinoline-5 : 8-quinones.

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The preparation of some quinoline-5 : 8-quinones is described.*

The study of quinones derived from the highly antibacterial 8-hydroxyquinoline was undertaken in order to determine the effect of this structural alteration on the biological activity of the latter compound. Quinoline-5 : 8-quinone was prepared by Fischer and Renouf (*Ber.*, 1884, **17**, 1644) by oxidation of 5-amino-8-hydroxyquinoline with chromic acid. This method with appropriate modifications was employed in the present investigation. The required quinoline *Bz*-aminophenols were obtained by converting 8(5)-hydroxyquinolines into the 5(8)-nitroso-, -nitro-, or -arylazo-derivatives, which were then reduced to the corresponding amines. A choice of reducing agents was available for this purpose. Thus 8-hydroxy-5-nitrosoquinoline had been reduced with stannous chloride (von Kostanecki, *Ber.*, 1891, **24**, 153), ammonium sulphide (Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1917, **39**, 2219), phenylhydrazine (Cohn, *J. pr. Chem.*, 1911, **83**, 504), or hydrogen and Raney nickel (Albert and Magrath, *Biochem. J.*, 1947, **41**, 534). An electrolytic method had been applied to 8-hydroxy-5-nitroquinoline (Gattermann, *Ber.*, 1894, **27**, 1939), and stannous chloride had been used for its 7-iodo-derivative (Matsumura, *J. Amer. Chem. Soc.*, 1927, **49**, 815). In our hands, these methods proved only of limited value, but reductions of the hydroxy-nitroso- and -nitro-quinolines with sodium dithionite (hydrosulphite) in hot, aqueous, faintly alkaline solution was simple and rapid, giving the pure amines in yields exceeding 60%.

2- and 7-Methylquinoline-5 : 8-quinone were prepared from 8-hydroxy-2- and -7-methyl-5-nitrosoquinoline, respectively. 5-Hydroxy-6-methylquinoline, required for conversion into 6-methylquinoline-5 : 8-quinone (Christiansen and Doliver, *J. Amer. Chem. Soc.*, 1941, **63**, 1470), could not be prepared by Noelting and Trautmann's procedure (*Ber.*, 1890, **23**, 3654), diazotisation of 5-amino-6-methylquinoline giving only tars. By heating 5-amino-6-methyl-8-phenylazoquinoline with 10% aqueous-alcoholic hydrochloric acid, however, hydrolysis of the 5-amino-group was achieved (cf. Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1920, **42**, 2280) with formation of 5-hydroxy-6-methyl-8-phenylazoquinoline in 60% yield. Catalytic reduction furnished the corresponding aminophenol, which passed smoothly into 6-methylquinoline-5 : 8-quinone on oxidation. 2 : 6-Dimethylquinoline-5 : 8-quinone was similarly obtained.

The preparation of 7-iodoquinoline-5 : 8-quinone was undertaken as this compound is a potential oxidation product of the amœbicide 8-hydroxy-5 : 7-di-iodoquinoline. 8-Hydroxy-5-nitroquinoline, required as an intermediate, has been obtained by oxidising 8-hydroxy-5-nitrosoquinoline (i) with alkaline potassium ferricyanide followed by sublimation of the product (Vis, *J. pr. Chem.*, 1892, **45**, 540) and (ii) with 61% nitric acid (*d* 1·38) (von Kostanecki, *loc. cit.*). Method (i) was unsuitable for preparative work. Method (ii) gave largely 8-hydroxy-5 : 7-dinitroquinoline. By using 38% nitric acid (*d* 1·24), under controlled conditions, however, it proved possible to obtain the 5-nitro-compound in yields exceeding 85%. 8-Hydroxy-5-nitrosoquinaldine was similarly converted in 60% yield into the corresponding 5-nitro-analogue, *ca.* 20% of 8-hydroxy-5 : 7-dinitroquinaldine also being formed. Bromination and iodination in aqueous alkaline solution of these two mononitro-compounds gave the 7-halogeno-derivatives which, on reduction with sodium dithionite and oxidation, furnished 7-bromo- and 7-iodo-quinoline and quinaldine-5 : 8-quinone as comparatively unstable solids which decomposed within 3—4 weeks.

Attempts to prepare 6-iodo-quinoline- and -quinaldine-5 : 8-quinone were not successful. Preparation of 6-iodoquinoline from *p*-iodoaniline by the Skraup reaction gave quinoline

* Certain compounds described herein are recorded in a paper by Long and Schofield (*J.*, 1953, 3161) published after this paper had been submitted.

as main product together with $<5\%$ of 6-iodoquinoline, converted into 6-iodo-5-nitroquinoline (cf. the nitration of 6-chloroquinoline; Fourneau, Trefouel, Trefouel, and Wancolle, *Bull. Soc. chim.*, 1930, **47**, 738), but the overall yield at this stage was too low for the synthesis to be pursued. Nitration of 6-iodoquinaldine gave 6-iodo-5-nitroquinaldine, the constitution of which followed from its ready condensation with aniline. The corresponding 5-amino-6-iodo-derivative, however, failed to react with benzenediazonium chloride and the preparation was consequently abandoned.

Quinoline-5 : 8-quinone is weakly basic. Its hydrochloride is decomposed by water; the quinone does not appear to form quaternary derivatives or an *N*-oxide. An indirect approach to the latter compound was consequently examined. 8-Hydroxyquinoline was smoothly converted into the *N*-oxide by treatment with perphthalic acid. This compound, in contrast to 8-hydroxyquinoline which so readily passes into the 5 : 7-dinitro-derivative, gave only 8-hydroxy-5(?)-nitroquinoline *N*-oxide on treatment with concentrated nitric acid in acetic acid. Reduction furnished 5(?)-amino-8-hydroxyquinoline *N*-oxide which did not, however, appear to yield the required 5 : 8-quinone on oxidation. Thiols readily added to the quinone but the products could not be obtained pure.

Experimental

Quinoline-5 : 8-quinone.—A solution of 5-amino-8-hydroxyquinoline sulphate (1 g.) in 10% sulphuric acid (10 ml.) was treated with sodium dichromate in a little water. When reaction was complete the mixture was extracted 4 times with chloroform (15-min. intervals), and the combined extracts were washed with water and evaporated to small bulk. Addition of light petroleum led to separation of quinoline-5 : 8-quinone (350 mg.) in light yellow needles, m. p. 129° (decomp.) (Found : C, 67·9; H, 3·1; N, 8·6. Calc. for $C_9H_5O_2N$: C, 67·7; H, 3·1; N, 8·8%). Fischer and Renouf (*loc. cit.*) give m. p. 110—120° (decomp.).

Quinaldine-5 : 8-quinone.—8-Hydroxy-5-nitrosoquinaldine (5·8 g.) in water (100 ml.) and sodium hydroxide (6·3 g.) was treated at 70° with sodium dithionite (*ca.* 13 g.) until the brown colour had disappeared. Acetic acid was added until the solution was neutral, and the 5-amino-8-hydroxyquinaldine collected after cooling. Oxidation as above furnished *quinaldine-5 : 8-quinone* (2 g.), yellow-green prisms, m. p. 145° (decomp.) (Found : C, 69·6; H, 4·2; N, 7·9. $C_{10}H_7O_2N$ requires C, 69·4; H, 4·1; N, 8·1%), after crystallising from ethanol–light petroleum (b. p. 80—100°).

5-Amino-8-hydroxy-7-methylquinoline.—The corresponding nitroso-compound (2 g.) was reduced in 10% sodium dithionite solution with sodium dithionite (4·2 g.), the *amine* separating on cooling. It recrystallised from benzene as yellow prisms, m. p. 155° (decomp.) (Found : C, 69·0; H, 5·8; N, 16·1. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·8; N, 16·2%).

7-Methylquinoline-5 : 8-quinone, obtained (55%) by oxidation of the foregoing amine, separated from ethanol–light petroleum (b. p. 80—100°) in light yellow needles, m. p. 181—182° (decomp.) (Found : C, 69·3; H, 4·1; N, 8·1. $C_{10}H_7O_2N$ requires C, 69·4; H, 4·1; N, 8·1%).

5-Amino-6-methyl-8-phenylazoquinoline Hydrochloride.—A solution of benzenediazonium chloride [from aniline hydrochloride (7 g.) and sodium nitrite (4 g.)] was added during 20 min. at 0—3° to 5-amino-6-methylquinoline (8·5 g.) in acetic acid (50 ml.) and water (200 ml.) containing sodium acetate (25 g.). The solution rapidly became dark red, after which the dye began to separate. Next morning, the *product* (9 g.) was collected and purified from ethanol–light petroleum, from which it separated in red-brown plates, m. p. 216° (Found : N, 18·9. $C_{16}H_{14}N_4$,HCl requires N, 18·8%).

5-Hydroxy-6-methyl-8-phenylazoquinoline hydrochloride, m. p. 212° (Found : N, 12·1; Cl, 9·9. $C_{16}H_{13}ON_3$,HCl,C_2H_5·OH requires N, 12·2; Cl, 9·9%), after crystallisation from ethanol, separated (7 g.) when the corresponding 5-amino-compound (12 g.) was hydrolysed by boiling it with concentrated hydrochloric acid (60 ml.), water (50 ml.), and ethanol (150 ml.) for 2½ hr., and the mixture cooled. The *base* crystallised from ethanol in fine red needles, m. p. 177° (Found : C, 73·4; H, 4·9. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 4·9%), after liberation with aqueous ammonia.

8-Amino-5-hydroxy-6-methylquinoline.—5-Hydroxy-6-methyl-8-phenylazoquinoline (1·5 g.) was reduced with hydrogen in ethanol in the presence of palladium–charcoal until the solution was colourless. The catalyst was removed, and the filtrate evaporated to crystallisation.

8-*Amino*-5-*hydroxy*-6-*methylquinoline* (500 mg.) separated from ethanol in pale brown plates, m. p. 216° (Found : C, 68·6; H, 5·8; N, 16·1. $C_{10}H_{10}ON_2$ requires C, 69·0; H, 5·6; N, 16·1%).

6-Methylquinoline-5 : 8-quinone, yellow needles, m. p. 188° (decomp.) (Found : C, 69·8; H, 4·3; N, 7·9. Calc. for $C_{10}H_7O_2N$: C, 69·4; H, 4·1; N, 8·1%), after purification from chloroform–light petroleum (b. p. 60—80°), was obtained by oxidation of the foregoing compound. Christiansen and Doliver (*loc. cit.*) record m. p. 167—168°.

2 : 6-*Dimethyl*-5-*nitroquinoline*.—2 : 6-Dimethylquinoline (3·0 g.) in cold concentrated sulphuric acid (8·5 ml.) was treated with concentrated nitric acid (1·5 ml.) in concentrated sulphuric acid (2·0 ml.). After 2 hr. on the steam-bath the mixture was poured into cold dilute ammonia, and the precipitated solids were collected and purified from light petroleum. 2 : 6-*Dimethyl*-5-*nitroquinoline* (3·8 g.) formed pale yellow prisms, m. p. 106° (Found : C, 65·5; H, 4·9; N, 13·6. $C_{11}H_{10}O_2N_2$ requires C, 65·4; H, 4·9; N, 13·9%).

5-*Amino*-2 : 6-*dimethylquinoline*, prepared by reducing the foregoing compound (2·5 g.) in 80% ethanol (25 ml.) and concentrated hydrochloric acid (1 ml.) with reduced iron (6 g.) for 1½ hr., separated (2·0 g.) from benzene–light petroleum (b. p. 80—100°) in green needles, m. p. 190° (Found : C, 77·0; H, 6·8; N, 15·8. $C_{11}H_{12}N_2$ requires C, 76·8; H, 6·9; N, 16·3%).

2 : 6-*Dimethylquinoline*-5 : 8-*quinone* separated (60%) from chloroform–light petroleum (b. p. 60—80°) in yellow plates, m. p. 150° (Found : C, 70·2; H, 4·6; N, 7·5. $C_{11}H_9O_2N$ requires C, 70·6; H, 4·8; N, 8·0%). It was obtained from the foregoing compound *via* 5-*amino*-2 : 6-*dimethyl*-8-*phenylazoquinoline hydrochloride* (80%), red plates with a green reflex, m. p. 210° (Found : N, 17·8. $C_{17}H_{16}N_4$,HCl requires N, 17·7%), and 5-*hydroxy*-2 : 6-*dimethyl*-8-*phenylazoquinoline* (63%), dark red fluffy needles, m. p. 168° (Found : C, 73·7; H, 5·6; N, 15·3. $C_{17}H_{15}ON_3$ requires C, 73·6; H, 5·4; N, 15·2%), after crystallisation from ethanol. 8-Amino-5-hydroxy-2 : 6-dimethylquinoline proved very sensitive to aerial oxidation and was used directly without purification.

8-*Hydroxy*-5-*nitroquinoline*.—Finely powdered 8-hydroxy-5-nitroquinoline (3 g.) was added with vigorous stirring to a mixture of concentrated nitric acid (9 ml.) and water (6 ml.) at 17°. Oxides of nitrogen were evolved, and the nitrosoquinoline was rapidly converted into insoluble 8-hydroxy-5-nitroquinoline nitrate. After 1¼ hr. with occasional stirring the mixture was diluted with water, cooled to 0°, and made alkaline with cold potassium hydroxide solution. The red potassium salt was decomposed with acetic acid, and the product collected, washed with water, and recrystallised from ethanol. 8-Hydroxy-5-nitroquinoline (2·9 g., 87%) separated in yellow needles, m. p. 180°. von Kostanecki (*loc. cit.*) gives m. p. 173° and Vis (*loc. cit.*) gives m. p. 178°.

8-*Hydroxy*-5-*nitroquinaldine*.—Finely powdered 8-hydroxy-5-nitrosoquinaldine (2 g.) was oxidised by addition to concentrated nitric acid (6 ml.) and water (4 ml.) at room temperature with stirring. As soon as the material had dissolved, the solution was diluted with water to prevent further dinitration and the precipitated nitrates were collected and decomposed as above. The mixture of bases was extracted with benzene, the soluble fraction yielding 8-*hydroxy*-5-*nitroquinaldine*, silky yellow needles (1·3 g., 60%), m. p. 136° (Found : C, 58·6; H, 4·1; N, 13·8. $C_{10}H_8O_3N_2$ requires C, 58·8; H, 3·9; N, 13·7%) after crystallisation from benzene–light petroleum (b. p. 80—100°). In contact with solvent or on warming, the material changed to dark red prismatic needles.

Extraction of the benzene-insoluble fraction with pyridine gave 8-*hydroxy*-5 : 7-*dinitroquinaldine* in small yellow needles, m. p. >300° (Found : N, 16·9. $C_{10}H_7O_5N_3$ requires N, 16·9%).

7-*Halogeno*-8-*hydroxy*-5-*nitroquinolines*.—The compounds listed below were prepared by the following method : The finely powdered nitro-compound (1 g.) was dissolved in water (300 ml.) containing potassium hydroxide (900 mg.) by stirring at room temperature, after which bromine or iodine (1 mol.) dissolved in a solution of the appropriate potassium salt was added. Stirring was continued at room temperature for 2 hr., and the product was then precipitated by acidification, collected, washed with ethanol, and recrystallised from 2-ethoxyethanol. Yields were 60—70%.

7-*Bromo*-8-*hydroxy*-5-*nitroquinoline*, felted red needles, m. p. 200° (Found : C, 39·9; H, 1·8; N, 10·3; Br, 29·6. $C_9H_5O_3N_2Br$ requires C, 40·1; H, 1·9; N, 10·4; Br, 29·7%). 7-*Bromo*-8-*hydroxy*-5-*nitroquinaldine*, red plates, m. p. 265° (decomp.) (Found : C, 42·5; H, 2·3; N, 9·7; Br, 28·4. $C_{10}H_7O_3N_2Br$ requires C, 42·4; H, 2·5; N, 9·9; Br, 28·3%). 8-*Hydroxy*-7-*iodo*-5-*nitroquinaldine*, bright red plates, m. p. 244° (Found : N, 8·4; I, 38·2. $C_{10}H_7O_3N_2I$ requires N, 8·5; I, 38·5%).

5-*Amino*-7-*halogeno*-8-*hydroxyquinolines*.—Typical reduction : Finely powdered 7-bromo-

8-hydroxy-5-nitroquinoline (1·5 g.) was added to a solution of potassium hydroxide (2·5 g.) in water (20 ml.) with vigorous stirring so as to produce as fine a suspension of the potassium salt as possible. The mixture was heated nearly to boiling, and sodium dithionite (5 g.) added. Reduction was completed by boiling for 1 min., and the solution was cooled and neutralised with acetic acid. *5-Amino-7-bromo-8-hydroxyquinoline* (900 mg., 68%) separated. It crystallised from ethyl acetate–light petroleum as light brown needles, m. p. 184° (decomp.) (Found : N, 11·4; Br, 32·7. $C_9H_7ON_2Br$ requires N, 11·7; Br, 33·4%).

5-Amino-7-bromo-8-hydroxyquinaldine formed golden-brown needles, m. p. 176° (decomp.) (Found : N, 10·7; Br, 31·5. $C_{10}H_9ON_2Br$ requires N, 11·1; Br, 31·6%). *5-Amino-8-hydroxy-7-iodoquinaldine* separated from ether–light petroleum in yellow needles, m. p. 162° (decomp.) (Found : C, 40·2; H, 3·1; N, 9·4; I, 42·2. $C_{10}H_9ON_2I$ requires C, 40·0; H, 3·0; N, 9·3. I, 42·3%).

7-Halogenoquinoline-5 : 8-quinones.—The amines were oxidised with sodium dichromate (see p. 571). The quinones were sparingly soluble in water and separated at once from the oxidation mixture. *7-Bromoquinoline-5 : 8-quinone* formed pale yellow needles, m. p. 182° (Found : N, 5·5; Br, 33·0. $C_9H_4O_2NBr$ requires N, 5·9; Br, 33·6%), after crystallisation from chloroform–light petroleum (b. p. 60—80°). *7-Iodoquinoline-5 : 8-quinone* separated from chloroform–light petroleum in unstable yellow-brown needles, m. p. 160° (decomp.) (Found : N, 4·6; I, 41·1. $C_{10}H_6O_2NI$ requires N, 4·7; I, 42·5%).

7-Bromoquinaldine-5 : 8-quinone crystallised from chloroform–light petroleum in orange-yellow needles, m. p. 178° (decomp.) (Found : N, 5·5; Br, 31·8. $C_{10}H_7O_2NBr$ requires N, 5·5; Br, 31·6%).

7-Iodoquinaldine-5 : 8-quinone formed yellow-brown needles, m. p. 160° (decomp.) (Found : N, 4·6. $C_{10}H_6O_2NI$ requires N, 4·7%).

6-Iodoquinoline.—*p*-Iodoaniline (42 g.), dry glycerol (70 g.), and arsenic pentoxide (33 g.) were heated together at 120° with mechanical stirring, and concentrated sulphuric acid (20 ml.) added dropwise at such a rate that the temperature did not rise unduly. The mixture was heated under reflux for 4 hr., diluted with water (600 ml.), filtered (charcoal), and basified with ammonia solution The crude product was extracted with benzene, which was then in turn extracted with 6N-hydrochloric acid. The bases were liberated with sodium hydroxide, isolated with chloroform, and distilled at 1 mm. After a forerun of quinoline, identified as the picrate, m. p. 203°, 6-iodoquinoline passed over at 120° and was recrystallised from light petroleum, forming pale yellow prisms, m. p. 88°. Ullmann (*Annalen*, 1904, **332**, 80) gives m. p. 91°.

6-Iodo-5-nitroquinoline.—The foregoing base (1·5 g.) in concentrated sulphuric acid (4·5 ml.) was treated with concentrated nitric acid (0·8 ml.) in concentrated sulphuric acid (1·0 ml.), and the mixture heated at 100° for 1 hr. *6-Iodo-5-nitroquinoline* was precipitated when the mixture was poured into aqueous ammonia, and after recrystallisation from light petroleum (b. p. 80—100°) containing a drop of benzene formed pale yellow needles (1·5 g.), m. p. 163° (Found : N, 9·1. $C_9H_5O_2N_2I$ requires N, 9·3%).

6-Iodoquinaldine.—*p*-Iodoaniline (25 g.) was mixed with concentrated hydrochloric acid (20 ml.) and paraldehyde (20 ml.) under an efficient reflux condenser. After being kept overnight the mixture was refluxed for 2 hr., water added, and the solution decanted from the resinous residue, which was extracted twice with 2N-hydrochloric acid. The combined acid extracts (charcoal) were basified to give 6-iodoquinaldine (5·9 g.), prisms, m. p. 112° (Found : N, 5·1. Calc. for $C_{10}H_8NI$: N, 5·2%), after crystallisation from light petroleum (b. p. 60—80°). Borscher, Weissmann, and Fritzsche (*Ber.*, 1924, **57**, 1772) give m. p. 107—108°.

6-Iodo-5-nitroquinaldine separated from ethanol in pale yellow needles (90%), m. p. 146° (Found : N, 9·1; I, 41·3. $C_{10}H_7O_2N_2I$ requires N, 8·9; I, 40·5%).

6-Anilino-5-nitroquinaldine.—6-Iodo-5-nitroquinaldine (5·0 g.) was heated with aniline (25 g.) at 180° for 2 hr. Sodium acetate solution was added, and excess of aniline removed in steam. The residue was extracted with benzene, and the dried extract percolated through a column of alumina (10 cm. × 7 sq. cm.) and evaporated. Crystallisation of the residue from ethanol yielded *6-anilino-5-nitroquinaldine*, felted orange needles, m. p. 147—148° (Found : N, 14·9. $C_{16}H_{13}O_2N_3$ requires N, 15·1%).

5-Amino-6-iodoquinaldine.—The nitro-compound (2·5 g.), reduced iron (7·0 g.), and ethanol (20 ml.) containing 5 drops of concentrated hydrochloric acid were heated under reflux for 2 hr. The solids were removed by filtration and extracted twice with ethanol, and the combined extracts basified with aqueous ammonia and evaporated. *5-Amino-6-iodoquinaldine* (2 g.) separated from benzene–light petroleum (b. p. 80—100°) in golden plates, m. p. 206° (decomp.) (Found : N, 10·0; I, 44·8. $C_{10}H_9N_2I$ requires N, 9·9; I, 44·7%).

8-Hydroxyquinoline N-*Oxide*.—8-Hydroxyquinoline (2 g.) in chloroform was mixed with ethereal perphthalic acid (2 mols.). The following day the mixture was taken to dryness, and the residue ground with aqueous ammonia and purified from benzene–light petroleum. *8-Hydroxyquinoline* N-*oxide* formed golden-yellow needles, m. p. 138° (Found : C, 67·5; H, 4·2; N, 8·6. $C_9H_7O_2N$ requires C, 67·1; H, 4·4; N, 8·7%).

8-Hydroxy-5(?)-iodoquinoline N-*Oxide*.—Iodine (5·1 g.) in aqueous potassium iodide solution was added dropwise to a solution of the foregoing base (3·2 g.) in 0·2% sodium hydroxide solution (400 ml.). The *oxide* was collected after 24 hr., dried, and extracted with benzene, forming yellow needles, m. p. 169° (Found : N, 4·9; I, 44·3. $C_9H_6O_2NI$ requires N, 4·9; I, 43·7%).

8-Hydroxy-5(?)-nitroquinoline N-*Oxide*.—A solution of 8-hydroxyquinoline *N*-oxide (1·6 g.) in acetic acid (10 ml.) was treated at $\not>20°$ with concentrated nitric acid (1 ml.). After 1 hr. the nitrate was collected and decomposed by reprecipitation from 5N-potassium hydroxide with acetic acid. The *nitro*-derivative (70%) separated from ethanol in small yellow needles, m. p. 191—193° (Found : C, 52·4; H, 3·1; N, 13·4. $C_9H_6O_4N_2$ requires C, 52·4; H, 2·9; N, 13·5%).

8-Hydroxy-5(?)-nitrosoquinoline N-*Oxide*.—8-Hydroxyquinoline *N*-oxide (1·6 g.) was dissolved in concentrated hydrochloric acid (5·0 ml.) and cooled to 0°, the hydrochloride crystallising. Sodium nitrite (900 mg.) in a little water was added; the hydrochloride rapidly dissolved and an orange product separated. This was collected after 45 min., dissolved in the minimum of 5N-potassium hydroxide, and reprecipitated with dilute acetic acid. *8-Hydroxy-5(?)-nitrosoquinoline* N-*oxide* was purified by extraction with alcohol and formed a light brown powder, m. p. 217—218° (decomp.) (Found : C, 56·8; H, 3·7; N, 14·5. $C_9H_6O_3N_2$ requires C, 56·8; H, 3·2; N, 14·8%).

5(?)-Amino-8-hydroxyquinoline N-*Oxide*.—The foregoing compound (2·0 g.) was dissolved in hot water containing potassium hydroxide (3·4 g.) and sodium dithionite (5·5 g.) was added. The *amine* separated on cooling and was purified from benzene to give orange-red needles, m. p. 180—182° (decomp.) (Found : C, 61·3; H, 4·5; N, 16·0. $C_9H_8O_2N_2$ requires C, 61·4; H, 4·5; N, 15·9%).

6(7)-Anilinoquinoline-5 : 8-quinone.—Quinoline-5 : 8-quinone (750 mg.) and redistilled aniline (1·2 g.) were heated under reflux in ethanol (10 ml.) for 1 hr., and the deep red solution was poured into dilute acetic acid. The precipitated solids were purified from benzene–light petroleum (b. p. 80—100°), to give the quinone in scarlet needles, m. p. 213° (decomp.) (Found : C, 72·0; H, 4·2; N, 11·3. Calc. for $C_{15}H_{10}O_2N_2$: C, 72·0; H, 4·0; N, 11·2%). Fischer and Renouf (*loc. cit.*) give m. p. *ca.* 190°.

6-Anilino-7-bromoquinoline-5 : 8-quinone.—7-Bromoquinoline-5 : 8-quinone (100 mg.), aniline hydrochloride (53 mg.), and sodium acetate (50 mg.) were heated under reflux in alcohol (5 ml.) for 2 hr. The solution was poured into water, and the product collected and recrystallised from benzene–light petroleum (b. p. 80—100°). *6-Anilino-7-bromoquinoline-5 : 8-quinone* (100 mg.) separated in dark red prisms, m. p. 189° (decomp.) (Found : C, 55·2; H, 2·7; N, 8·2; Br, 24·0. $C_{15}H_9O_2N_2Br$ requires C, 54·7; H, 2·7; N, 8·5; Br, 24·3%).

8-Hydroxy-7-morpholinomethyl-5-nitroquinoline.—8-Hydroxy-5-nitroquinoline (2 g.) in ethanol (20 ml.) under reflux was treated with formaldehyde (2 ml. of 36%) and morpholine (2 ml.). The *product* separated almost immediately. It was collected after 30 min. and purified from 2-ethoxyethanol, from which it separated in small yellow needles (2·3 g.), m. p. 231° (decomp.) (Found : C, 58·2; H, 5·4; N, 14·7. $C_{14}H_{15}O_4N_3$ requires C, 58·2; H, 5·2; N, 14·5%). Catalytic reduction in 2-ethoxyethanol, followed by oxidation, gave the *quinone*, yellow prisms which rapidly discoloured, m. p. 112° (decomp.) (Found : C, 63·6; H, 5·7; N, 11·6. $C_{14}H_{14}O_3N_2$ requires C, 65·1; H, 5·4; N, 10·8%).

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