430. *The Nitration of 4-Hydroxy- and 4-Chloro-3-methylquinoline.*

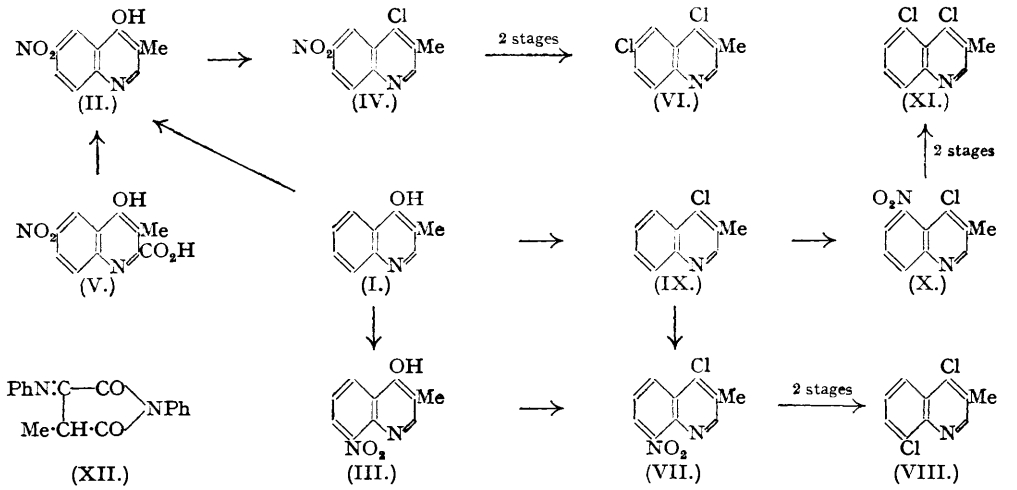
By A. Adams and D. H. Hey.

The nitration of 4-hydroxy-3-methylquinoline gives mainly 6-nitro-4-hydroxy-3-methylquinoline and a smaller proportion of 8-nitro-4-hydroxy-3-methylquinoline. From the product of the nitration of 4-chloro-3-methylquinoline, 4-chloro-5-nitro-3-methylquinoline and 4-chloro-8-nitro-3-methylquinoline are isolated. The identity of these nitration products is proved by their conversion into dichloro-3-methylquinoline of known constitution.

The synthesis of some arylamino(dialkylaminoalkylamino)-quinaldines and -lepidines has recently been described (Adams and Hey, *J.*, 1949, 3185). In view of the antimalarial properties claimed for Sontochin [7-chloro-4-(1′-methyl-4′-diethylaminobutylamino)-3-methylquinoline] it was considered that attention should be directed to arylamino(dialkylaminoalkylamino)-derivatives of 3-methylquinoline. The present communication describes the preparation of some of the intermediate 4-chloro-*Bz*-nitro-3-methylquinolines required for the synthesis of 4-arylamino(dialkylaminoalkylamino)-3-methylquinolines. Although many substituted 4-chloro-3-methylquinolines have been described (Steck, Hallock, and Holland, *J. Amer. Chem. Soc.*, 1946, **68**, 129, 132, 380, and 1241; Breslow, Bloom, Shivers, Adams, Weiss, Yost, and Hauser, *ibid.*, p. 1232; Steck, Hallock, Holland, and Fletcher, *ibid.*, 1948, **70**, 1012; Steck and Hallock, *ibid.*, 1949, **71**, 890) there appears to be no record of the preparation of any 4-chloro-nitro-3-methylquinolines. Since previous experience in the quinaldine and lepidine series had shown that direct syntheses from nitroanilines were unlikely to be promising, attention was directed to the nitration of 4-chloro- and 4-hydroxy-3-methylquinoline, which compounds were readily accessible from ethyl ethoxalylpropionate and aniline by the method described by Steck, Hallock, and Holland (*ibid.*, 1946, **68**, 129).

Nitration of 4-hydroxy-3-methylquinoline (I), by using a mixture of concentrated nitric acid and sulphuric acid at 0—5°, proceeded smoothly and gave a mixture of nitro-4-hydroxy-3-methylquinolines in 83% yield, from which two pure isomerides were obtained. The greater portion (isolated as 76% of the mixture), m. p. >360°, which was almost insoluble in alcohol, proved to be 6-nitro-4-hydroxy-3-methylquinoline (II). The lesser portion (isolated as 21% of the mixture), m. p. 239—241°, which was readily soluble in alcohol, was 8-nitro-4-hydroxy-3-methylquinoline (III). The structure of (II) was proved by its conversion, on treatment with phosphorus oxychloride, into 4-chloro-6-nitro-3-methylquinoline (IV), identical with a specimen

prepared in small yield from ethyl ethoxalylpropionate and *p*-nitroaniline. When these compounds were boiled in benzene solution for 48 hours and the product ring-closed in boiling



phenyl ether, ethyl 6-nitro-4-hydroxy-3-methylquinoline-2-carboxylate was formed. Alkaline hydrolysis of this ester gave 6-nitro-4-hydroxy-3-methylquinoline-2-carboxylic acid (V) which, by being boiled with quinoline and copper bronze (cf. Kermack and Weatherhead, *J.*, 1940, 1168), was decarboxylated to give (II). Treatment of (II) with phosphorus oxychloride gave 4-chloro-6-nitro-3-methylquinoline (IV); further confirmation of the structures was obtained by reduction of (IV) to the amino-quinoline which, on diazotisation and treatment with cuprous chloride, gave 4 : 6-dichloro-3-methylquinoline (VI), the melting point of which was identical with that recorded by Breslow *et al.* (*loc. cit.*).

The structure of (III) was proved by its conversion on treatment with phosphorus oxychloride into 4-chloro-8-nitro-3-methylquinoline (VII), which was reduced to the 8-amino-compound and converted by a Sandmeyer reaction into 4 : 8-dichloro-3-methylquinoline (VIII), identical with an authentic specimen, prepared from *o*-chloroaniline and ethyl ethoxalylpropionate as described by Steck, Hallock, and Holland (*J. Amer. Chem. Soc.*, 1946, **68**, 132).

Similar nitration of 4-chloro-3-methylquinoline (IX) proceeded smoothly and gave a mixture of 4-chloro-nitro-3-methylquinolines in 70% yield. Separation of the isomerides proved to be difficult, probably owing to the formation of a eutectic mixture which could not be separated by crystallisation from alcohol, benzene, light petroleum (b. p. 60—80°), or N-hydrochloric acid, or by fractional precipitation from an acid solution by addition of alkali. Partial separation of the mixture was finally achieved by distillation with steam. After two recrystallisations from ethyl alcohol, the solid portion of the distillate gave 4-chloro-5-nitro-3-methylquinoline (X), whilst purification of the distillation residue gave the 8-nitro-compound (VII), identical with that previously described. The structure of (X) was proved by its reduction to 4-chloro-5-amino-3-methylquinoline and subsequent conversion by the Sandmeyer reaction into 4 : 5-dichloro-3-methylquinoline (XI), identical with an authentic specimen. The latter was prepared from ethyl ethoxalylpropionate and *m*-chloroaniline, as described by Steck, Hallock and Holland (*ibid.*, p. 380). No 4-chloro-6-nitro-3-methylquinoline was isolated from the nitration mixture.

Treatment of (II) with alkali and methyl sulphate gave 6-nitro-1 : 3-dimethyl-4-quinolone. On the other hand, when (IV) was boiled with a solution of sodium methoxide in methyl alcohol 6-nitro-4-methoxy-3-methylquinoline was obtained. By heating (IV) with *p*-chloroaniline, 6-nitro-4-*p*-chloroanilino-3-methylquinoline was formed, which was reduced with stannous chloride and concentrated hydrochloric acid to 6-amino-4-*p*-chloroanilino-3-methylquinoline.

The formation of ethyl 6-nitro-4-hydroxy-3-methylquinoline-2-carboxylate in low (22%) yield from ethyl ethoxalylpropionate and *p*-nitroaniline has been reported above; the overall yield of 6-nitro-4-hydroxy-3-methylquinoline was only 5%. The reaction between ethyl ethoxalylpropionate and *m*-nitroaniline gave a mixture of esters in 11% yield from which was isolated ethyl 5(or 7)-nitro-4-hydroxy-3-methylquinoline-2-carboxylate. No quinolinecarboxylic ester could be isolated from the product from ethyl ethoxalylpropionate and *o*-nitroaniline.

It is well-known that the reaction between aniline and ethyl acetoacetate gives either ethyl β-anilinocrotonate or acetoacetanilide according to whether low- or high-temperature conditions are employed. The crotonate may be cyclised above 250° to 4-hydroxyquinaldine (Conrad and Limpach, *Ber.*, 1887, **20**, 944, 947), whereas ring-closure of the anilide in concentrated sulphuric acid gives 2-hydroxylepidine (Knorr, *Annalen*, 1886, **236**, 75). Ewins and King (*J.*, 1913, **103**, 105) subsequently reported that acetoacetanilide could more readily be prepared by boiling the reactants under reflux for ninety seconds. It was considered of interest to investigate the reaction between aniline and ethyl ethoxalylpropionate at high temperatures for a very short period, in the hope that such conditions might provide a new route to 2-hydroxy-3-methylquinolines, but after an equimolecular mixture of aniline and ethyl ethoxalylpropionate had been boiled under reflux for only two minutes, the sole product isolated proved to be 2 : 5-diketo-4-phenylimino-1-phenyl-3-methylpyrrolidine (XII) (Wislicenus and Spiro, *Ber.*, 1889, **22**, 3351).

Experimental.

4-Hydroxy- and 4-Chloro-3-methylquinoline.—4-Hydroxy-3-methylquinoline, m. p. 231°, and 4-chloro-3-methylquinoline, m. p. 59—60°, were prepared as reported by Steck, Hallock, and Holland (*J. Amer. Chem. Soc.*, 1946, **68**, 131). The ethyl ethoxalylpropionate, b. p. 117—118°/11 mm., was prepared by the method described by Cox and McElvain (*Org. Synth.*, 1943, Coll. Vol. II, p. 272).

Nitration of 4-Hydroxy-3-methylquinoline.—The solution obtained by stirring a mixture of nitric acid (*d* 1·42; 4·9 c.c.) and concentrated sulphuric acid (5·0 c.c.) into a solution of 4-hydroxy-3-methylquinoline (10·6 g.) in concentrated sulphuric acid (50 c.c.) at 0—5°, was kept for two hours at room temperature and then poured on crushed ice (2000 g.). Next morning, the yellow precipitate was collected; no further product was obtained on making the filtrate alkaline with aqueous ammonia. The washed and dried product (11·3 g., 83%) was boiled vigorously with ethyl alcohol (500 c.c.) for fifteen minutes, and the mixture cooled and filtered. Recrystallisation of a small portion of the residue (8·5 g., 76% of the mixture) from a large quantity of alcohol gave *6-nitro-4-hydroxy-3-methylquinoline*, in pale yellow needles, m. p. >360° (Found: C, 58·5; H, 4·1. $C_{10}H_8O_3N_2$ requires C, 58·8; H, 3·9%). Evaporation to dryness of the original alcoholic filtrate gave *8-nitro-4-hydroxy-3-methylquinoline* (2·4 g., 21% of the mixture), which crystallised from alcohol in yellow needles, m. p. 239—241° (Found: C, 59·1; H, 3·9. $C_{10}H_8O_3N_2$ requires C, 58·8; H, 3·9%).

6-Nitro-1 : 3-dimethyl-4-quinolone.—A mixture of 6-nitro-4-hydroxy-3-methylquinoline (1·0 g.), potassium hydroxide (0·4 g.), water (10 c.c.), and methyl sulphate (0·7 g.) was shaken for 30 minutes. Next morning the precipitate was collected, washed with water, dried, and recrystallised from alcohol; *6-nitro-1 : 3-dimethyl-4-quinolone* (0·6 g.) separated in pale-yellow needles, m. p. 263—265° (Found: C, 60·7; H, 4·6. $C_{11}H_{10}O_3N_2$ requires C, 60·5; H, 4·6%).

4-Chloro-6-nitro-3-methylquinoline.—6-Nitro-4-hydroxy-3-methylquinoline (8·5 g.) was boiled under reflux with phosphorus oxychloride (50 c.c.) for two hours. The cooled solution was poured on crushed ice (1000 g.), and made alkaline with aqueous sodium hydroxide. The white precipitate was collected, washed with water, and dried. Recrystallisation from alcohol gave *4-chloro-6-nitro-3-methylquinoline* (6·0 g.) in colourless needles, m.p. and mixed m. p. 171·5° (with an authentic specimen prepared from *p*-nitroaniline as described below) (Found: C, 53·7; H, 3·2. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·2%).

6-Nitro-4-methoxy-3-methylquinoline.—4-Chloro-6-nitro-3-methylquinoline (1·0 g.) was boiled under reflux for three hours with a solution of sodium (0·11 g.) in methyl alcohol (40 c.c.). The cooled solution was stirred into water (400 c.c.), and the needles which separated were filtered off, washed with water, dried, and crystallised from light petroleum (b. p. 60—80°). *6-Nitro-4-methoxy-3-methylquinoline* (0·7 g.) separated in colourless rhombohedra, m. p. 146—147° (Found: C, 60·0; H, 4·6. $C_{11}H_{10}O_3N_2$ requires C, 60·5; H, 4·6%).

4-Chloro-8-nitro-3-methylquinoline.—*4-Chloro-8-nitro-3-methylquinoline*, prepared (in 92% yield) in the same way as the 4-chloro-6-nitro-compound (see above) and crystallised from alcohol in colourless needles, m. p. 125° (Found: C, 53·6; H, 3·6. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·2%).

Nitration of 4-Chloro-3-methylquinoline.—4-Chloro-3-methylquinoline (8·75 g.) was dissolved slowly, with mechanical stirring, in a mixture of fuming nitric acid (*d* 1·5; 30 c.c.), concentrated sulphuric acid (30 c.c.) at 0—5°. The solution was heated on the water-bath for five minutes and, after two hours at room temperature, was poured into ice-water (1 l.). No precipitate was formed. The following methods were used in attempts to isolate the products.

(*a*) The solution was made alkaline with aqueous sodium hydroxide, and the precipitated solid was collected, washed with water, and dried (7·75 g., 70%; m. p. 94—97°). Crystallisation from alcohol gave needles, m. p. 100—103°; recrystallisation from the same solvent did not raise the melting point of the bulk of the material, but a few crystals, m. p. 125° and m. p. 141·5°, were obtained from mother-liquors. The melting point of the main fraction was not raised by recrystallisation from light petroleum (b. p. 60—80°), methyl alcohol, benzene, or N-hydrochloric acid

(*b*) The aqueous solution was titrated with 8N-sodium hydroxide, and the precipitates collected after addition of 70, 130, 180, and 200 c.c. These fractions melted at 97—100°, 97—100°, 90—98°, and 85—95° respectively, and each was raised to *ca.* 100—103° by repeated recrystallisation from alcohol.

(*c*) The solution was made alkaline with aqueous sodium hydroxide, and the precipitated 4-chloro-nitro-3-methylquinolines were collected, washed with water, and dried (7·8 g., 70%; m. p. 94—97°). The solid was steam-distilled for 36 hours. The solid distillate was collected, washed, and dried (2·5 g.; m. p. 110—130°), and two recrystallisations from alcohol gave *4-chloro-5-nitro-3-methylquinoline* (1·1 g.;

15% of the mixture) in almost colourless needles, m. p. 141·5° (Found : C, 54·2; H, 3·3. $C_{10}H_7O_3N_2Cl$ requires C, 53·9; H, 3·2%). A further fraction, m. p. 100—103° (0·7 g.), was obtained from the mother-liquors. The solid residue from the steam-distillation was collected, washed, dried (2·2 g.; m. p. 105—115°), and recrystallised twice from alcohol. 4-Chloro-8-nitro-3-methylquinoline (0·75 g.; 11% of the mixture) separated in almost colourless needles, m. p. and mixed m. p., with a specimen prepared from 8-nitro-4-hydroxy-3-methylquinoline, 125°. A further fraction, m. p. 100—103° (0·8 g.), was obtained from the mother-liquors.

Proof of the Constitution of 4-*Chloro-6-nitro-3-methylquinoline.*—*Ethyl* 6-*nitro-4-hydroxy-3-methylquinoline-2-carboxylate* (cf. Steck, Hallock, and Holland, *J. Amer. Chem. Soc.*, 1946, **68**, 131). A solution of *p*-nitroaniline (10·0 g.) and ethyl ethoxalylpropionate (10·1 g.) in benzene (120 c.c.) was boiled under reflux for 24 hours and, after cooling, filtered from excess of *p*-nitroaniline (7·8 g.; m. p. 148°). The filtrate was washed with 0·5N-hydrochloric acid (3 × 60 c.c.), water (100 c.c.), 0·5N-aqueous sodium hydroxide (3 × 60 c.c.), and water (3 × 100 c.c.). The solution was then dried (Na_2SO_4), and the solvent removed by distillation. The residual oil was added slowly to boiling phenyl ether (100 c.c.), and boiling was continued for 10 minutes. After cooling, the precipitated *ethyl* 6-*nitro*-4-*hydroxy*-3-*methylquinoline*-2-*carboxylate* (3·0 g.) was collected, washed with light petroleum (b. p. 60—80°), and recrystallised from alcohol. It separated in straw-coloured needles, m. p. 274—276° (Found : C, 56·6; H, 4·3. $C_{13}H_{12}O_5N_2$ requires C, 56·5; H, 4·4%).

6-*Nitro*-4-*hydroxy*-3-*methylquinoline*-2-*carboxylic acid* (cf. Steck, Hallock, and Holland, *loc. cit.*). Ethyl 6-nitro-4-hydroxy-3-methylquinoline-2-carboxylate (2·8 g.) was boiled with 5% aqueous sodium hydroxide (50 c.c.) for three hours. The cooled, red solution was acidified with concentrated hydrochloric acid, and the precipitate collected and washed with water. Recrystallisation from alcohol gave 6-*nitro*-4-*hydroxy*-3-*methylquinoline*-2-*carboxylic acid* (2·3 g.) in yellow prisms, m. p. >360° (Found : C, 53·4; H, 2·9. $C_{11}H_8O_5N_2$ requires C, 53·2; H, 3·2%).

4-*Chloro*-6-*nitro*-3-*methylquinoline* (cf. Kermack and Weatherhead, *J.*, 1940, 1168). A mixture of 6-nitro-4-hydroxy-3-methylquinoline-2-carboxylic acid (1·1 g.), copper bronze (0·5 g.), and quinoline (10 c.c.) was boiled under reflux for 6 hours. The cooled solution was filtered, and the solid residue extracted with ethyl alcohol (50 c.c.). Evaporation of the extract to dryness gave 6-nitro-4-hydroxy-3-methylquinoline (0·1 g.; m. p. >360°) as a yellow-brown powder. The quinoline filtrate was added to water (200 c.c.) and steam-distilled until no quinoline remained. Evaporation of the residual aqueous solution to dryness gave a further yield of 6-nitro-4-hydroxy-3-methylquinoline (0·1 g.; m. p. >360°) as a yellow-brown powder.

The total product (0·2 g.) was converted into the 4-chloro-compound as already described; authentic 4-chloro-6-nitro-3-methylquinoline (0·05 g.) was obtained in fawn needles, m. p. 171·5°.

4-*Chloro*-6-*amino*-3-*methylquinoline*. 4-Chloro-6-nitro-3-methylquinoline (1·6 g.) and Raney-nickel sludge (2 c.c.) were suspended in ethyl alcohol (100 c.c.) and shaken with hydrogen at atmospheric pressure until absorption of hydrogen ceased (approximately 500 c.c.). The catalyst was filtered off and washed with alcohol, and the filtrate and washings were evaporated to dryness. Crystallisation of the residue from alcohol gave 4-*chloro*-6-*amino*-3-*methylquinoline* (0·5 g.) in grey plates, m. p. 228° (Found : C, 62·4; H, 5·0. $C_{10}H_9N_2Cl$ requires C, 62·3; H, 4·7%). The amine dissolves in alcohol to give a yellow solution with a violet fluorescence.

4 : 6-*Dichloro*-3-*methylquinoline*. Copper sulphate (2·8 g.) and sodium chloride (0·95 g.) were dissolved in water (10 c.c.) at 55—60°, and a solution of sodium metabisulphite (1·4 g.) in water (2·5 c.c.) was added. The mixture was cooled to 10—15°, and the precipitated cuprous chloride was collected, washed with water, and dissolved in a mixture of water (2·0 c.c.) and concentrated hydrochloric acid (2·0 c.c.). 4-Chloro-6-amino-3-methylquinoline (0·06 g.) was dissolved in water (0·15 c.c.)–concentrated hydrochloric acid (0·15 c.c.) and the solution cooled to 0—5°. A solution of sodium nitrite (0·05 g.) in water (0·15 c.c.) was added, and after a few minutes the combined solution was added to the cuprous chloride solution (0·3 c.c.) at 60°. After 10 minutes at room temperature and 15 minutes on the boiling water-bath the mixture was added to water (50 c.c.), made just alkaline with aqueous sodium hydroxide, and steam-distilled. The white solid distillate was collected, and crystallisation from aqueous alcohol gave 4 : 6-dichloro-3-methylquinoline (0·014 g.) in colourless needles, m. p. 118—119°. This m. p. is identical with that quoted by Breslow *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1233).

Proof of the Constitution of 4-*Chloro-5-nitro-3-methylquinoline.*—4 : 5-*Dichloro-3-methylquinoline.* This compound was prepared from 4-chloro-5-nitro-3-methylquinoline (0·32 g.) as already described for the preparation of the 4 : 6-dichloro-compound. It (0·04 g.) separated from aqueous alcohol in colourless, feathery needles, m. p. 70—71°. The melting point was not depressed on admixture with an authentic specimen, prepared as described by Steck, Hallock, and Holland (*J. Amer. Chem. Soc.* 1946, **68**, 382) from ethyl ethoxalylpropionate and *m*-chloroaniline.

Proof of the Constitution of 4-*Chloro-8-nitro-3-methylquinoline.*—4-*Chloro-8-amino-3-methylquinoline.* 4-Chloro-8-nitro-3-methylquinoline (1·3 g.) was reduced as described above for the preparation of the 6-amino-compound, and gave 4-*chloro*-8-*amino*-3-*methylquinoline* (0·7 g.) in colourless needles, m. p. 111° (from aqueous alcohol) (Found : C, 62·4; H, 4·6. $C_{10}H_9N_2Cl$ requires C, 62·3; H, 4·7%).

4 : 8-*Dichloro*-3-*methylquinoline*. 4-Chloro-8-amino-3-methylquinoline (0·20 g.) underwent the Sandmeyer reaction as described above for the 4 : 6-dichloro-compound. 4 : 8-Dichloro-3-methylquinoline (0·04 g.) separated from aqueous alcohol in slightly pink, feathery needles, m. p. 98°. The melting point was not depressed on admixture with an authentic specimen, prepared from *o*-chloroaniline and ethyl ethoxalylpropionate as described by Breslow *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1233).

Ethyl 5(or 7)-*Nitro*-4-*hydroxy*-3-*methylquinoline*-2-*carboxylate.*—The interaction of ethyl ethoxalylpropionate (20·2 g.) and *m*-nitroaniline (15·0 g.), as described above for the preparation of the 6-nitro-ester,

gave a mixture of ethyl 5- and 7-nitro-4-hydroxy-3-methylquinoline-2-carboxylates (3·0 g.; m. p. 220—230°), which was recrystallised repeatedly from alcohol. *Ethyl* 5(or 7)-*nitro*-4-*hydroxy*-3-*methylquinoline*-2-*carboxylate* separated in straw-coloured needles, m. p. 268—269° (Found: C, 56·3; H, 4·4. $C_{13}H_{12}O_5N_2$ requires C, 56·5; H, 4·4%).

6-*Nitro*-4-p-*chloroanilino*-3-*methylquinoline*.—An intimate mixture of 4-chloro-6-nitro-3-methylquinoline (3·5 g.) and *p*-chloroaniline (2·1 g.) was heated in a wax-bath. Reaction occurred at 120° and the temperature rose quickly to 150°, where it was maintained for five minutes When cold, the solid product was powdered, dissolved in hot glacial acetic acid (150 c.c.), and poured into water (600 c.c.). The precipitated 6-*nitro*-4-p-*chloroanilino*-3-*methylquinoline* (4·0 g.) was collected, washed with water, and dried. Crystallisation from toluene gave bright-yellow needles, m. p. 173—174° (Found: C, 61·4; H, 3·8. $C_{16}H_{12}O_2N_3Cl$ requires C, 61·3; H, 3·8%).

6-*Amino*-4-p-*chloroanilino*-3-*methylquinoline*. A solution of stannous chloride (20·0 g.) in concentrated hydrochloric acid (20 c.c.) was added to a solution of 6-nitro-4-*p*-chloroanilino-3-methylquinoline (4·0 g.) in glacial acetic acid (40 c.c.). The mixture was heated for one hour on a boiling water-bath and then left at room temperature for 48 hours. The solution was made strongly alkaline with 50% aqueous sodium hydroxide, and boiled until the precipitated yellow stannichloride had decomposed. The grey residue was collected, boiled with 25% aqueous sodium hydroxide (100 c.c.) for five minutes, filtered off, washed with dilute aqueous sodium hydroxide and much water, and dried. Crystallisation from toluene gave 6-*amino*-4-p-*chloroanilino*-3-*methylquinoline* (1·8 g.) in fawn prisms, m. p. 229—230° (Found: C, 68·1; H, 4·8. $C_{16}H_{14}N_3Cl$ requires C, 67·7; H, 4·9%). The amine dissolves in alcohol and in toluene to give yellow solutions with a violet fluorescence. The *picrate* separated from alcohol in golden plates, m. p. 238—239° (Found: C, 51·6; H, 3·4. $C_{16}H_{14}N_3Cl,C_6H_3O_7N_3$ requires C, 51·5; H, 3·3%).

Reaction between Aniline and Ethyl Ethoxalylpropionate at High Temperatures.—Aniline (2·32 g., 0·025 mole) and ethyl ethoxalylpropionate (5·05 g., 0·025 mole) were boiled together under reflux for two minutes. After cooling overnight, the solid product was filtered off, washed with methyl alcohol, and dried. Recrystallisation from ethyl alcohol gave 2 : 5-diketo-4-phenylimino-1-phenyl-3-methylpyrrolidine (3·70 g.) in glistening yellow plates, m. p. 158° (Found: C, 73·2; H, 5·2; N, 10·2. Calc. for $C_{17}H_{14}O_2N_2$: C, 73·4; H, 5·0; N, 10·1%). Wislicenus and Spiro (*loc. cit.*) reported m. p. 158—160°.

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[*Received, March 23rd*, 1950.]