86. *Cinnolines. Part XVI. 4-Hydroxy-3-methylcinnolines.*

By J. R. Keneford and J. C. E. Simpson.

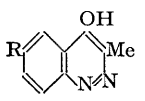
A description is given of the synthesis of a series of Bz-substituted 4-hydroxy-3-methylcinnolines from propiophenone by way of fully authenticated intermediates.

The recent publications of Leonard and Boyd (*J. Org. Chem.*, 1946, **11**, 405, 419) on the preparation of 4-hydroxycinnolines by methods similar to those described in earlier papers of this series (*J.*, 1945, 520, 646) contain an account of the synthesis of 4-hydroxy-3-methylcinnoline

(I; R = H) and its 6-bromo- and 6-nitro-derivative (I; R = Br and NO_2). Experiments which we began several years ago followed closely similar lines, but, in addition, provided unambiguous evidence for the structures of the products.

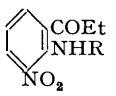
The nitration of propiophenone to *o*- and *m*-nitropropiophenone has been described by Elson, Gibson, and Johnson (*J.*, **1930**, 1128), by Leonard and Boyd (*loc. cit.*), and by Zenitz and Hartung (*ibid.*, **1946**, **11**, 444). In our hands, the reaction also yielded a small amount of a weakly acidic *substance* of probable formula $C_9H_8O_4N_2$, which does not appear to be any obvious simple derivative of propiophenone. Reduction of the nitro-ketones to *o*- and *m*-amino-propiophenone proceeded smoothly when tin and stannous chloride, respectively, in hydrochloric acid were used, each method being, apparently, an improvement on previous results (Elson, Gibson, and Johnson, *loc. cit.*; Leonard and Boyd, *loc. cit.*). Some 5-chloro-2-aminopropiophenone was formed by nuclear chlorination during the reduction of *o*-nitropropiophenone, as shown by the fact that diazotisation and cyclisation of (distilled) material produced small amounts of the corresponding chlorohydroxycinnoline in addition to 4-hydroxy-3-methylcinnoline; when, however, *o*-aminopropiophenone regenerated from the *acetyl* derivative was so treated, only 4-hydroxy-3-methylcinnoline was obtained.

Nitration of *o*-acetamidopropiophenone, in our experience, follows the same course as that of *o*-acetamidoacetophenone (*J.*, 1947, 237), and yields both 5-nitro- (II; R = Ac) and (in smaller amount) 3-*nitro*-2-*acetamidopropiophenone* (III; R = Ac). Leonard and Boyd (*loc. cit.*), on the other hand, obtained only a poor yield of a single product, which they correctly assumed to be (II; R = Ac). 5-*Nitro*-2-*aminopropiophenone* (II; R = H), obtained from (II; R = Ac), gave *m*-nitropropiophenone on deamination; and, as the reduction product of 3-*nitro*-2-*amino-propiophenone* (III; R = H) readily condensed with phenanthraquinone to the phenazine (IV), the orientations of both nitroaminopropiophenones are established.



(I.)

(II.)



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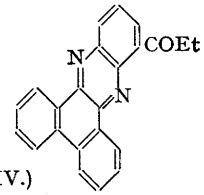

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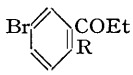

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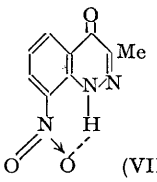

(VII.)

m-Chloro- and *m*-bromo-propiophenone, obtained from *m*-aminopropiophenone, gave on nitration 5-*chloro*- and 5-*bromo*-2-*nitropropiophenone* (V and VI; R = NO_2). Reduction of these compounds yielded 5-*chloro*- and 5-bromo-2-aminopropiophenone (V and VI; R = NH_2); the latter amine is without doubt identical with the substance which Leonard and Boyd (*loc. cit.*) obtained *via* the bromination of *o*-acetamidopropiophenone, and for which they assumed the same structure. The orientations of our products were established by conversion into 5-*chloro*- and 5-*bromo*-2-*benzamidopropiophenone* (V and VI; R = NHBz), identical with the products obtained from (II; R = H) by successive benzoylation and reduction followed by the appropriate Sandmeyer reaction.

Diazotisation of the foregoing *o*-amino-ketones, followed by cyclisation, yielded 4-hydroxy- (I; R = H), 6-*chloro*-4-*hydroxy*- (I; R = Cl), 6-bromo-4-hydroxy- (I; R = Br), 6-nitro-4-hydroxy- (I; R = NO_2), and 8-*nitro*-4-*hydroxy*-3-*methylcinnoline* (VII). 4-Hydroxy- and 6-nitro-4-hydroxy-3-methylcinnoline were readily converted into the corresponding 4-*acetoxy*-derivatives (cf. Schofield and Simpson, *J.*, 1945, 512). The 8-nitro-compound, however, was not attacked by boiling acetic anhydride; in this respect it resembles 8-nitro-4-hydroxycinnoline itself (*J.*, 1947, 237), and is accordingly formulated as (VII). The hydrogen bonding is not, however, sufficiently strong to withstand the action of a mixture of phosphorus pentachloride and oxychloride, which converted (VII) smoothly into the 4-chloro-derivative, from which 8-*nitro*-4-*phenoxy*-3-*methylcinnoline* was prepared. Analogous *derivatives* were also prepared from (I; R = H) and from (I; R = NO_2), the former of which was also converted into 4-*anilino*-3-*methylcinnoline*.

Experimental.

(M. ps. are uncorrected.)

Nitration of Propiophenone.—A mixture of the ketone (60 c.c.) and acetic acid (8 c.c.) was added during ½—¾ hour to nitric acid (300 c.c., *d* 1·5) at −10° to 0°. After a further ½ hour at −5°, the mixture was poured on ice (1200 g.) and the crude solid filtered off (filtrate *A*) and recrystallised from alcohol, giving *m*-nitropropiophenone, m. p. 101—102°. Filtrate *A* was made alkaline with solid sodium carbonate and extracted with ether. The extract was washed with aqueous sodium hydroxide (solution *B*), dried, and evaporated, and the residue combined with the solvent-free material contained in the alcoholic filtrates from the *m*-nitro-ketone. In this way 425 g. of propiophenone gave 298 g. of pure *m*-nitro-ketone and 181 g. of crude *o*-nitropropiophenone (total nitro-ketones, 84%; if the treatment of filtrate *A* is omitted, the yield is 70—75%). Acidification of solution *B* gave a solid which separated from benzene in almost colourless prismatic needles (12 g.), m. p. 158—159° (Found: C, 51·4; H, 3·85; N, 13·2. $C_9H_8O_4N_2$ requires C, 51·9; H, 3·9; N, 13·45%). This *substance* is readily soluble in dilute aqueous sodium hydroxide, but insoluble in aqueous sodium carbonate; it is stable to air in the dark, but it darkens when kept in daylight in an evacuated desiccator, the m. p. falling to *ca.* 150° after a few days.

Preparation of o- *and* m-*Aminopropiophenone.*—The crude *o*-nitro-ketone (520 g.) was reduced with tin and hydrochloric acid exactly as described for *o*-aminoacetophenone (*J.*, 1945, 646), using 25 g. batches; the *o*-aminopropiophenone (332 g., 76%) had b. p. 142—146°/15—17 mm. and crystallised on cooling, but contained some 5-chloro-2-aminopropiophenone, which was readily removed by crystallisation of the acetyl derivative. o-*Acetamidopropiophenone* [crude, 93 g., m. p. 64—70°, from the amine (77·3 g.) and acetic anhydride (150 c.c.) heated for 1 hour at 90—95°] crystallised from ether–ligroin (b. p. 60—80°) in gross colourless prisms, m. p. 73—74° (82 g.) (Found: C, 68·95; H, 6·6. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·85%); Leonard and Boyd (*loc. cit.*) give m. p. 70—71° for unanalysed material.

A solution of *m*-nitropropiophenone (21·6 g.) in warm glacial acetic acid (60 c.c.) was added to a stirred solution of stannous chloride dihydrate (100 g.) in hydrochloric acid (7·5 N, 240 c.c.); after 1 hour at 90—95° the amine (17·3 g., 96%) was isolated as a pale yellow oil (which slowly crystallised) by addition of excess of aqueous sodium hydroxide and extraction with ether. Using iron and acetic acid, Elson, Gibson, and Johnson (*J.*, 1930, 1128) found that the reaction was erratic, but we observed a smooth reaction under the conditions described (*J.*, 1945, 646) for *o*-aminoacetophenone, although the yield was somewhat lower than that given by the stannous chloride method. Acetylation of material obtained by either method gave, quantitatively, m-*acetamidopropiophenone* as stout polyhedra, m. p. 92—93°, from benzene–ligroin (b. p. 40—60°) (Found: C, 69·55; H, 6·55. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·85%); nitration of this under conditions which were successful (*loc. cit.*) with *m*-acetamidoacetophenone gave only resinous material. m-*Acetamidopropiophenone semicarbazone*, colourless needles from aqueous alcohol, had m. p. 196—197° after shrinking at 188° (Found: N, 23·0. $C_{12}H_{16}O_2N_4$ requires N, 22·6%).

m-*Chloropropiophenone and its Derivatives.*—The following compounds were prepared by methods corresponding precisely to those described below for the bromo-compounds. *m*-Chloropropiophenone [29·8 g. (77%) from 34·6 g. of amine] had b. p. 124°/14 mm., m.p. 48—49°; Zenitz and Hartung (*loc. cit.*) give m. p. 45—46°, and yield 73%. 5-*Chloro*-2-*nitropropiophenone* [crude, 12·1 g. (95%), m. p. 64—71°, from 10 g. of chloro-ketone], formed long, colourless, prismatic needles, m. p. 78—78·5°, from alcohol (Found: C, 50·8; H, 3·9. $C_9H_8O_3NCl$ requires C, 50·55; H, 3·8%). 5-*Chloro*-2-*aminopropiophenone* (crude, 98%), pale yellow irregular blades from ligroin (b. p. 60—80°), had m. p. 80—80·5° (Found: N, 7·85. $C_9H_{10}ONCl$ reauires N, 7·6%). 5-*Chloro*-2-*benzamidopropiophenone*, prepared both from the above amine and also from 5-amino-2-benzamidopropiophenone (*q.v.*), separated from alcohol in minute glittering needles, m. p. 125—126° (Found: N, 5·15; Cl, 12·1. $C_{16}H_{14}O_2NCl$ requires N, 4·9; Cl, 12·3%).

m-*Bromopropiophenone.*—A solution of *m*-aminopropiophenone (17 g.) in hydrobromic acid (40 c.c., *d* 1·5) and water (80 c.c.) was diazotised with 20% aqueous sodium nitrite and added during 10 minutes to a solution of cuprous bromide (from 37·5 g. of copper sulphate crystals) in hydrobromic acid (65 c.c., *d* 1·5) and water (35 c.c.). After 1 hour at room temperature, the mixture was kept at 50—60° for 20 minutes. The bromo-ketone, collected with ether, distilled as a heavy sweet-smelling oil at 138—140°/17 mm. (17 g.; 70%) which rapidly crystallised [m. p. 41—42° from ligroin (b. p. 40—60°)] (Found: C, 50·9; H, 4·4. Calc. for C_9H_9OBr: C, 50·7; H, 4·2%). Elson, Gibson, and Johnson (*loc. cit.*) give m. p. 36° (52% yield); Zenitz and Hartung (*loc. cit.*) give m. p. 37·5—40° (44% yield).

5-*Bromo*-2-*nitropropiophenone.*—The bromo-ketone (2 g.) was added during 10 minutes to nitric acid (12 c.c., *d* 1·5) at −5 to −3°. After a further 20 minutes at −3° the solution was poured into ice–water; 5-*bromo*-2-*nitropropiophenone* crystallised from aqueous alcohol in long colourless needles (1·35 g.), m. p. 74·5—76° (Found: C, 42·0; H, 3·2. $C_9H_8O_3NBr$ requires C, 41·9; H, 3·1%).

5-*Bromo*-2-*aminopropiophenone.*—The foregoing compound (1 g.) was reduced with acetic acid (6 c.c.), water (6 c.c.), and iron filings (1·5 g.) by the method previously described (*J.*, 1945, 646). The amine, isolated by means of ether, formed slender yellow needles (0·7 g.), m. p. 79—80°, from aqueous alcohol (Found: C, 47·4; H, 4·6. Calc. for $C_9H_{10}ONBr$: C, 47·4; H, 4·4%). Leonard and Boyd (*loc. cit.*) give m. p. 79—80°.

Nitration of o-*Acetamidopropiophenone.*—The acetyl derivative (53·4 g.) was added during 30 minutes to a stirred mixture (325 c.c.) of nitric acid (*d* 1·48) and concentrated sulphuric acid [5 : 1 v/v] at −13° to −5°. After a further 15 minutes, the solution was poured on ice (2 kg.); the crude 5-nitro-2-acetamidopropiophenone so obtained (53·5 g., 80%, m. p. 137—138°) crystallised from alcohol in long, soft colourless needles, m. p. 145—145·5° (Found: C, 56·2; H, 4·8; N, 11·5. Calc. for $C_{11}H_{12}O_4N_2$: C, 55·9; H, 5·1; N, 11·9%); Leonard and Boyd (*loc. cit.*) give m. p. 144—145° (40% yield). The aqueous acid mother liquor was basified with solid sodium carbonate, the solid (*A*) filtered off, and the filtrate extracted with ether; the extract was washed dried, and concentrated, and the residue combined with (*A*) and crystallised from alcohol, yielding crude 3-*nitro*-2-*acetamidopropiophenone* (12·5 g., 19%), m. p. 100—103°;

the pure compound formed almost colourless prismatic needles, m. p. 109—110°, from alcohol (Found : C, 56·1; H, 5·1; N, 12·1. $C_{11}H_{12}O_4N_2$ requires C, 55·9; H, 5·1; N, 11·9%).

5-*Nitro*-2-*aminopropiophenone*.—A mixture of the acetamido-compound (53·5 g.) and hydrochloric acid (5N, 320 c.c.) was refluxed for ½ hour, cooled, made alkaline with ammonia, and the crude amine (43·3 g., m. p. 120—122°) recrystallised from alcohol; 5-*nitro*-2-*aminopropiophenone* formed spherical aggregates of yellow needles, m. p. 129—130° (Found : N, 14·8. $C_9H_{10}O_3N_2$ requires N, 14·4%). A hot solution of the amine (2 g.) in concentrated hydrochloric acid (25 c.c.) was cooled rapidly and treated with a solution of sodium nitrite (0·8 g.) in water (2 c.c.). Hypophosphorous acid (30%, 35 c.c.) was added at 0° during 10 minutes to the filtered solution with stirring, and the whole was left at 0° for 24 hours. The solid was then collected (0·55 g., m. p. 96—100°) and sublimed at 70—80°/0·5 mm., yielding *m*-nitropropiophenone, m. p. and mixed m. p. 100—102°.

5-*Bromo*-2-*benzamidopropiophenone*.—(*a*) Benzoylation (pyridine and benzoyl chloride) of 5-nitro-2-aminopropiophenone (1·5 g.) gave 5-*nitro*-2-*benzamidopropiophenone* (2·05 g.) as fine colourless needles, m. p. 185·5—186°, from benzene (Found : C, 64·7; H, 4·8. $C_{16}H_{14}O_4N_2$ requires C, 64·4; H, 4·7%), which (1·9 g.) was reduced at 90—95° with iron powder (4 g.), acetic acid (25 c.c.), and water (24 c.c.) (cf. *J.*, 1945, 646) to 5-*amino*-2-*benzamidopropiophenone*, greenish-yellow hair-like needles, m. p. 178·5—179·5°, from benzene (Found : C, 71·5; H, 6·1. $C_{16}H_{16}O_2N_2$ requires C, 71·6; H, 6·0%). This amine (1 g.) was warmed with a mixture of hydrobromic acid (5 c.c., *d* 1·5) and water (20 c.c.), and the cold suspension diazotised with 5% aqueous sodium nitrite (7·5 c.c.) and added to a solution of cuprous bromide (from 2·4 g. of copper sulphate) in hydrobromic acid (7·5 c.c., *d* 1·5). After being kept at 60° for ¼ hour, the product, isolated with ether, was crystallised repeatedly from alcohol and finally from ligroin (b. p. 60—80°), giving the bromobenzamido-compound (poor yield), m. p. 115—116° alone and in admixture with the sample described below.

(*b*) Benzoylation of 5-bromo-2-aminopropiophenone (prepared from *m*-bromopropiophenone) and crystallisation of the product from ligroin (b. p. 60—80°) yielded 5-*bromo*-2-*benzamidopropiophenone* as long, lemon-yellow needles, m. p. 117—118° (Found : C, 58·15; H, 4·45. $C_{16}H_{14}O_2NBr$ requires C, 57·85; H, 4·25%).

3-*Nitro*-2-*aminopropiophenone*.—Prepared similarly to the above isomer, this *amine* (8·9 g. from 12·5 g. crystallised from alcohol in fine, deep orange needles, m. p. 90—91° (Found : N, 14·0. $C_9H_{10}O_3N_2$ requires N, 14·4%). Reduction of this compound (0·5 g.) with iron powder (0·8 g.), acetic acid (4 c.c.), and water (4 c.c.) (cf. *J.*, 1945, 646) gave the diamine (0·45 g.) as a slowly crystallising oil; this was converte dwith phenanthraquinone (0·5 g.) in alcohol (75 c.c.) into the *phenazine*, which separated from acetic acid in long, almost colourless needles, m. p. 181—182° (Found : C, 82·3; H, 4·9. $C_{23}H_{16}ON_2$ requires C, 82·1; H, 4·8%).

4-*Hydroxy*-3-*methylcinnoline*.—Pure *o*-acetamidopropiophenone (60 g.) and hydrochloric acid (5N, 300 c.c.) were refluxed for ½ hour; the resultant amine (45·5 g.) in concentrated hydrochloric acid (1·2 l.) was treated with cold sodium nitrite (23 g.) in water (30 c.c.) and filtered; concentrated hydrochloric acid (4 l.) was added, and the whole kept at 60° for 4 hours and then evaporated to a small volume (reduced pressure). Addition of excess of saturated aqueous sodium acetate precipitated almost pure 4-hydroxy-3-methylcinnoline (40·7 g.; 83%), which separated from 50% aqueous alcohol in slender silvery needles, m. p. 241—242° (Found : C, 67·3; H, 5·1; N, 17·3. Calc. for $C_9H_8ON_2$: C, 67·45; H, 5·05; N, 17·5%). Leonard and Boyd (*loc. cit.*) give m. p. 248—249° (corr.); yield, 18%. The use of *o*-aminopropiophenone (5 g.), purified by distillation but not by acetylation, in an otherwise similar experiment furnished, as the least soluble fraction, 6-chloro-4-hydroxy-3-methylcinnoline (yield of almost pure material, 0·23 g.), having m. p. 325—326° alone and in admixture with authentic material (*q.v.*), and giving a positive Beilstein test; the filtrates gave 4-hydroxy-3-methylcinnoline (2·65 g.). 4-*Acetoxy*-3-*methylcinnoline*, prepared from the hydroxy-compound and acetic anhydride (6 parts) by refluxing for ½ hour, formed colourless prismatic needles, m. p. 117—117·5°, from alcohol (yield, almost quantitative) (Found : C, 65·4; H, 4·95; N, 14·2. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 5·0; N, 13·85%).

6-*Nitro*-4-*hydroxy*-3-*methylcinnoline*.—A hot solution of 5-nitro-2-aminopropiophenone (34·5 g.) in concentrated hydrochloric acid (750 c.c.) was quickly cooled, diazotised with 50% aqueous sodium nitrite (30 c.c.), kept at 90° for 3 hours, and the solid collected and washed (30 g.). After dissolution in aqueous sodium hydroxide, precipitation with acetic acid, and crystallisation (acetic acid), 6-nitro-4-hydroxy-3-methylcinnoline formed brown irregular blades, which darkened at 340° but did not melt at 360° (Found : C, 53·1; H, 3·5; N, 20·3. Calc. for $C_9H_7O_3N_3$: C, 52·65; H, 3·45; N, 20·5%). Leonard and Boyd (*loc. cit.*) give m. p. >350° (yield, 65%). 6-*Nitro*-4-*acetoxy*-3-*methylcinnoline*, from the hydroxy-compound and acetic anhydride (10 parts) under reflux for 1 hour, crystallised from benzene in colourless, fern-like blades, m. p. 194—194·5° (Found : C, 53·55; H, 3·6; N, 16·65. $C_{11}H_9O_4N_3$ requires C, 53·4; H, 3·7; N, 17·0%).

8-*Nitro*-4-*hydroxy*-3-*methylcinnoline*.—A solution of 3-nitro-2-aminopropiophenone (11·05 g.) in acetic acid (120 c.c.) and sulphuric acid (85%, v/v; 40 c.c.) was treated with powdered sodium nitrite (4·3 g.) during ½ hour with stirring; after a further 3 hours at 0° and 9 hours at 65—70°, the mixture was poured into water (1 l.) and the solid collected, washed, and dried (11·2 g., m. p. 225—228°). Crystallisation from acetic acid gave 8-*nitro*-4-*hydroxy*-3-*methylcinnoline* as lustrous, yellow, irregular plates, m. p. 238—239° (Found : C, 52·3; H, 3·7; N, 20·2. $C_9H_7O_3N_3$ requires C, 52·65; H, 3·45; N, 20·5%). Recovery was quantitative after the compound had been refluxed for 1 hour with acetic anhydride (12 parts).

6-*Chloro*-4-*hydroxy*-3-*methylcinnoline*.—Prepared as for the bromo-analogue (*q.v.*), this compound [2·45 g., from the amine (2·45 g.), hydrochloric acid (5N, 24 c.c.), and aqueous sodium nitrite (11%, 10 c.c.)] crystallised from acetic acid in colourless micro-needles, m. p. 328—329° (Found : C, 55·3; H, 4·2; N, 14·2. $C_9H_7ON_2Cl$ requires C, 55·5; H, 3·65; N, 14·4%).

6-*Bromo*-4-*hydroxy*-3-*methylcinnoline*.—The suspension of hydrochloride formed from 5-bromo-2-aminopropiophenone (0·5 g.) and 2N-hydrochloric acid (6 c.c.) was treated with aqueous sodium nitrite (10%, 2 c.c.) and heated on the steam-bath for 40 minutes. The cinnoline, easily soluble in cold aqueous

sodium hydroxide, and sparingly in hot alcohol and acetic acid, crystallised from acetic acid in small, soft, colourless needles, m. p. 331—332° (0·3 g.) (Found: C, 44·45; H, 2·95; N, 12·15. Calc. for $C_9H_7ON_2Br$: C, 45·15; H, 2·9; N, 11·7%). Leonard and Boyd (*loc. cit.*) give m. p. 326—327°.

Preparation of 4-*Phenoxy*-3-*methylcinnolines*.—The requisite 4-chloro-compounds were prepared by heating a mixture of the hydroxy-compound (5 parts), phosphorus pentachloride (9—13 parts), and phosphorus oxychloride (12—18 parts) for 1 hour on the steam-bath. 4-Chloro-3-methylcinnoline and its 8-nitro-derivative were isolated by ether or chloroform extraction from an alkaline medium as described for other 4-chlorocinnolines (*J.*, 1947, 917) and had m. p. 99—100° (colourless tetrahedra, stable in air for some days but melting over a wide range after 3 months) and 180—181° (yellow prisms) respectively; 4-chloro-6-nitro-3-methylcinnoline (yellow needles, m. p. 146—147°) was usually isolated by precipitation with ligroin from the reaction mixture. A solution in ether (*ca.* 50 c.c.) of the chloro-compound from 4-hydroxy-3-methylcinnoline (10·2 g.) was added to one of potassium hydroxide (3·6 g.) in phenol (36 g.), the ether removed, and the residue heated at 95° for 1 hour. Dilution with water, basification, extraction with ether, and crystallisation from ligroin (b. p. 60—80°) gave 4-*phenoxy*-3-*methylcinnoline* (12·6 g.; 84% based on hydroxy-compound) as colourless prismatic needles, m. p. 78—79°, very soluble in alcohol (Found: C, 76·3; H, 5·2; N, 12·0. $C_{15}H_{12}ON_2$ requires C, 76·25; H, 5·1; N, 11·85%). The chloro-compound from 6-nitro-4-hydroxy-3-methylcinnoline (25 g.) was added to a mixture of phenol (80 g.) and powdered ammonium carbonate (60 g.) (cf. following paper); after the initial reaction had subsided, the mixture was kept at 90—95° for 1 hour, and the product was isolated as above. Digestion with a little warm 20% aqueous acetic acid (to remove a trace of 6-nitro-4-amino-3-methylcinnoline; see following paper) and crystallisation from alcohol gave 6-*nitro*-4-*phenoxy*-3-*methylcinnoline* (13·6 g.; 40% based on hydroxy-compound) as long, yellow, striated blades, m. p. 129—130° (Found: C, 64·15; H, 3·8; N, 14·95. $C_{15}H_{11}O_3N_3$ requires C, 64·0; H, 3·95; N, 14·95%). 8-*Nitro*-4-*phenoxy*-3-*methylcinnoline* (6·15 g.), prepared similarly from the chloro-compound (8·05 g.), phenol (35 g.), and powdered ammonium carbonate (25 g.), crystallised from benzene–ligroin (b. p. 60—80°) in pale yellow prismatic needles, m. p. 137·5—138° (Found: C, 64·5; H, 4·05; N, 15·15. $C_{15}H_{11}O_3N_3$ requires C, 64·0; H, 3·95; N, 14·95%).

4-*Anilino*-3-*methylcinnoline*.—Hydrochloric acid (2N; 2 drops) was added to a warm solution of 4-chloro-3-methylcinnoline (0·5 g.) and aniline (0·25 g.) in 50% aqueous acetone (6 c.c.). The solution was refluxed for 25 minutes, cooled, and basified (ammonia), and the precipitated 4-*anilino*-3-*methylcinnoline* (0·63 g., m. p. 215—216°) recrystallised from alcohol, from which it formed bright yellow prismatic needles, m. p. 217—218° (Found: C, 77·0; H, 5·6. $C_{15}H_{13}N_3$ requires C, 76·6; H, 5·6%).

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