801. *Reactions of Methazonic Acid. Part IV.* Further Experiments with 3-Amino-4-arylquinolines.*

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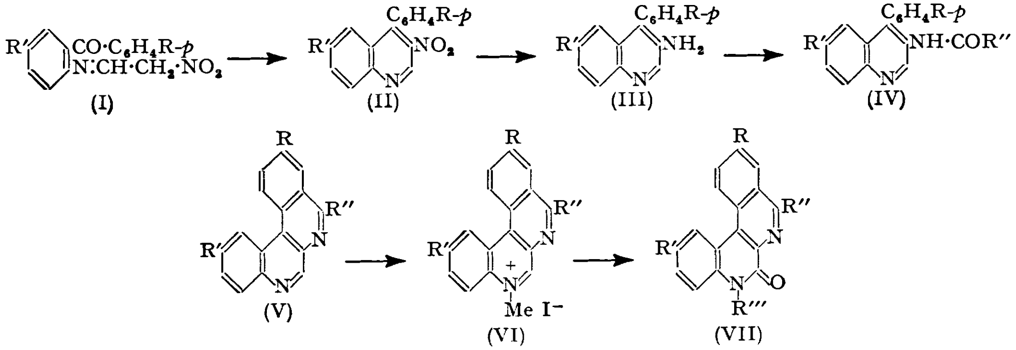
Some new 3-amino- and 3-acylamino-4-arylquinolines are described. The diazotised amines gave low yields of 4-aryl-3-pyridylquinolines with pyridine.

3-Acylamino-4-arylquinolines with stannic chloride and phosphorus oxychloride in nitrobenzene gave high yields of substituted *iso*quinolino(3′ : 4′-3 : 4)quinolines. The site of quaternisation of some of these compounds has been established. The quaternary salts showed no activity against *T. equiperdum.*

Some ultra-violet extinction curves are recorded.

Earlier in this series Schofield and Theobald (*J.*, 1950, 395) described the preparation of some 4-aryl-3-nitroquinolines, and subsequently (*J.*, 1951, 2992) the formation from two of these of 3-amino-4-phenyl- and 3-amino-4-*p*-methoxyphenyl-quinoline. 3-Benzamido-4-phenylquinoline was used to prepare 1′-phenyl*iso*quinolino(3′ : 4′-3 : 4)quinoline (V; R = R′ = H, R″ = Ph).† We have now extended this work.



2-Amino-5-chlorobenzophenone, 2-amino-4′-methylbenzophenone, and 2-aminophenyl 1-naphthyl ketone reacted readily with methazonic acid, giving good yields of nitroethylideneamino-compounds (I). The derivative (I; R = H, R′ = Cl) was converted into 6-chloro-3-nitro-4-phenylquinoline during recrystallisation. Under the conditions usually found satisfactory for cyclising such compounds (Schofield and Theobald, *loc. cit.*) (I; R = Me, R′ = H) was merely hydrolysed, but the reaction proceeded readily in anhydrous acetone. The differing effects of chloro- and methyl substituents in these cases are understandable in terms of the factors discussed by Schofield and Theobald (*loc. cit.*). A nitroquinoline could not be obtained from the nitroethylidene derivative of *o*-aminophenyl 1-naphthyl ketone in any circumstances. From anhydrous acetone, after treatment with alumina, the compound was recovered unchanged, and it seems likely that a steric factor is operative.

3-Nitro-4-*p*-tolylquinoline and 6-chloro-3-nitro-4-phenylquinoline were readily reduced to the corresponding amines (III; R = Me, R′ = H; and R = H, R′ = Cl), either catalytically or with stannous chloride. By standard procedures a number of acyl derivatives (IV) were prepared from these amines, and also from 3-amino-4-phenylquinoline.

Schofield and Theobald (*loc. cit.*) described the reaction of diazotised 3-aminolepidine with pyridine, two pyridyl-lepidines (as dipicrates) being isolated in low yield. The low yields were to be expected in view of the complicated nature of the diazotisation of 3-amino-

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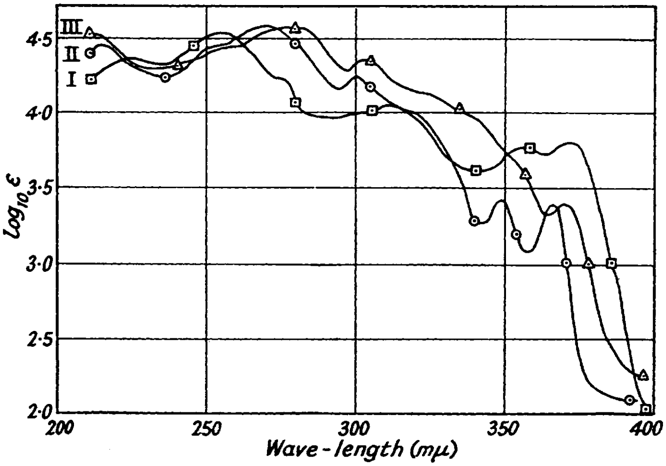
* Part III, *J.*, 1953, 1915.

† In an earlier paper (*J.*, 1951, 2992) such compounds were termed dibenzonaphthyridines, but the nomenclature now used seems preferable, particularly for the quaternary salts.

lepidine (Ockenden and Schofield, *J.*, 1953, 1915), but the absence of such complications renders the results obtained in similar experiments with 3-amino-4-arylquinolines disappointing. 3-Amino-4-phenylquinoline furnished unsatisfactory yields of the picrates of two 4-phenyl-3-pyridylquinolines, and from 3-amino-4-*p*-tolylquinoline only one picrate was isolated. Chromatographic purification afforded two pyridyl compounds after reaction of pyridine with diazotised 3-amino-6-chloro-4-phenylquinoline.

Formerly 1′-phenyl*iso*quinolino(3′ : 4′-3 : 4)quinoline (V; R = R′ = H, R″ = Ph) was prepared from 3-benzamido-4-phenylquinoline by the action of phosphoric oxide at 270—280°. This reagent failed with 3-acetamido-4-phenylquinoline and 3-acetamido- and 3-benzamido-4-*p*-methoxyphenylquinoline. Phosphorus oxychloride was also ineffective, but converted the last-named compound into an unidentified product, possibly $C_{16}H_{13}O_2N$. For similar cyclisations in the phenanthridine series the combined action of stannic chloride and phosphorus oxychloride in nitrobenzene has proved highly effective (Ockenden and Schofield, *J.*, 1953, 717), and we have now established its utility in the present instance. A number of 3-acetamido-4-aryl-, 4-aryl-3-benzamido-, and 4-aryl-3-*p*-nitrobenzamidoquinolines were thus converted into (V; R″ = Me, Ph, or $C_6H_4{\cdot}NO_2$-*p*) in high yields. Especially noteworthy is the case of 3-benzamido-4-*p*-methoxyphenylquinoline which, despite the presence of the methoxyl group *meta* to the point of cyclisation, yielded 53% of 7′-methoxy-1′-phenyl*iso*quinolino(3′ : 4′-3 : 4)quinoline (V; R = OMe, R′ = H, R″ = Ph).



I, 1-*Methyl*iso*quinolino*(3′ : 4′-3 : 4)-2-*quinolone*.
II, 1′-*Methyl*iso*quinolino*(3′ : 4′-3 : 4)*quinoline*.
III, 1′-*Phenyl*iso*quinolino*(3′ : 4′-3 : 4)*quinoline*.

An attempt to obtain *iso*quinolino(3′ : 4′-3 : 4)quinoline itself, by similar cyclisation of 3-formamido-4-phenylquinoline, failed. 1′-Methyl*iso*quinolino(3′ : 4′-3 : 4)quinoline appeared to offer a route to the parent member of the series, and for this purpose it was converted into [V; R = R′ = H, R″ = $CH(CH_2{\cdot}OH)_2$] by the action of formaldehyde (Ritchie, *Proc. Roy. Soc. N.S.W.*, 1945, **78**, 134). The dihydroxy*iso*propyl compound was oxidised by chromic acid to a mixture of an acid and some non-acidic material. Decarboxylation of the acid in hot benzophenone (Schofield and Simpson, *J.*, 1945, 512) gave a compound $C_{16}H_{10}ON_2$, which we regard as (VII; R = R′ = R″ = R‴ = H). Evidently the chromic acid produced (VII; R = R′ = R‴ = H, R″ = CO_2H), and the non-acidic material accompanying the acid may have been the impure decarboxylated derivative.

Several of the *iso*quinolinoquinolines were converted into their methosulphates. The nitro-compounds required use of hot nitrobenzene as solvent, whilst boiling benzene sufficed for the other examples. In no case was the reaction complete, small amounts of starting material invariably being isolated. When benzene was the solvent this recovered material could be used again, but nitrobenzene caused considerable decomposition. The methosulphates were converted into the methiodides. Schofield and Theobald (*loc. cit.*) isolated the methiodide (V; R = R′ = H, R″ = Ph) as the black monohydrate. In the present work we obtained the orange hemihydrate, and hydration was almost universal in these compounds. Particularly remarkable is the methiodide (VI; R = H, R′ = Cl, R″ = $C_6H_4\cdot NO_2$-*p*) which retained five molecules of water. The sites of quaternisation in the compounds (VI; R = Me, R′ = H, R″ = Ph; and R = H, R′ = Cl, R″ = Ph) were established by the method also used in our earlier work, namely, by oxidation with ferricyanide to (VII; R = R‴ = Me, R′ = H, R″ = Ph; and R = H, R′ = Cl, R″ = Ph, R‴ = Me). The methiodides [including the impure amine obtained by reducing (VI; R = R′ = H, R″ = $C_6H_4\cdot NO_2$-*p*)] showed no useful activity against *T. equiperdum*, but their insolubility made tests difficult.

The ultra-violet light-extinction curves of (V; R = R′ = H, R″ = Me; and R = R′ = H, R″ = Ph) and (VII; R = R′ = R″ = R‴ = H) are recorded. That of the phenyl compound shows the expected differences from that of the methyl derivative, produced by conjugation of the nucleus with the substituent, and the curve for the lactam is consistent with the proposed structure. There is an interesting similarity between the curves for (V; R = R′ = H, R″ = Me) and 4-azabenzo[*c*]phenanthrene (Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1950). In both of these compounds the nitrogen atoms cause considerable intensification of absorption in the twin peaks found in the 350—370 mμ region with 5-methylbenzo[*c*]phenanthrene itself (Friedel and Orchin, *op. cit.*).

EXPERIMENTAL

2-*Amino*-4′-*methylbenzophenone*.—Kippenburg's method (*Ber.*, 1897, **30**, 1133) was modified as follows: *o*-*p*′-Toluoylbenzoic acid (21 g.), thionyl chloride (8 c.c.), and chloroform (40 c.c.) were heated 1 hr. on the water-bath. Solvent and excess of thionyl chloride were removed, and chloroform (4 c.c.) was added and distilled off at reduced pressure. This process was repeated. The acid chloride was stirred in benzene (60 c.c.) and treated with dry ammonia for 3 hr. The benzene was removed in steam, the dried product was dissolved in the minimum of alcohol, and the alcoholic solution was added to boiling water (4 l.). The filtered solution gave pure *o*-*p*′-toluoylbenzamide (10·5 g.; 173—175°). A solution of the amide (20 g.), sodium hydroxide (10 g.), and water (100 c.c.) was added slowly to sodium hypobromite solution [from bromine (4·5 c.c.), sodium hydroxide (10 g.), and water (50 c.c.)] at 0°. The mixture was heated at 95° for 9 hr., and the product was crystallised twice from alcohol, giving the amine (12·9 g.), m. p. 92—95°.

2-2′-*Nitroethylideneaminoaryl Ketones*.—The amino-ketone and methazonic acid (1 equiv.) were dissolved in water, concentrated hydrochloric acid, and acetone. After 12 hr. the product was collected. The experiments are tabulated below.

Ketone	Wt. (g.)	Water (c.c.)	Conc. HCl (c.c.)	Acetone (c.c.)	Crude product: m. p.	Crude product: yield (%)
2-Amino-5-chlorobenzophenone ...	12·0	50	50	200	186—188°	92 [1]
2-Amino-4′-methylbenzophenone...	20·0	200	200	400	174—178	88 [2]
2-Aminophenyl 1-naphthyl ketone	1·0	10	10	15	167—173	76 [3]

[1] Attempted recrystallisation caused cyclisation. [2] 4′-*Methyl*-2-2′-*nitroethylideneaminobenzophenone* formed yellow prisms, m. p. 179—181° (Found: C, 68·0; H, 5·2. $C_{16}H_{14}O_3N_2$ requires C, 68·1; H, 5·0%), from acetone. [3] 1-*Naphthyl* 2-*nitroethylideneaminophenyl ketone* gave pale yellow leaflets, m. p. 173—175° (Found: C, 71·7; H, 5·0. $C_{19}H_{14}O_3N_2$ requires C, 71·7; H, 4·5%), from aqueous acetone. In other experiments a form, m. p. 145—148°, was encountered, but crystallisation gave the compound, m. p. 173—175°.

3-*Nitroquinolines*.—The chloro-nitroethylideneamino-compound (13·8 g.) in acetone was kept overnight with activated alumina (138 g.). Filtration, evaporation, and recrystallisation of the residue from aqueous alcohol gave yellow-green needles (11·8 g.) of 6-*chloro*-3-*nitro*-4-*phenylquinoline*, m. p. 162—163° (Found: C, 63·8; H, 3·4. $C_{15}H_9O_2N_2Cl$ requires C, 63·3; H, 3·2%).

Similarly, except that anhydrous acetone was used, the tolyl-nitroethylideneamino-compound (13 g.) gave 3-*nitro*-4-p-*tolylquinoline* (10 g.), which formed pale yellow prisms, m. p. 98—100° (Found: C, 72·6; H, 4·5. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·6%), from ethanol.

3-*Aminoquinolines*.—The chloro-nitro-compound (5 g.), methanol (700 c.c.), and palladium–

charcoal (1 g.) were shaken with hydrogen. Reduction was complete in 1 hr. Filtration, evaporation, and crystallisation from ether–light petroleum (b. p. 40—60°) gave needles of 3-*amino*-6-*chloro*-4-*phenylquinoline* (80%), m. p. 161—162° (Found : C, 70·7; H, 4·3. $C_{15}H_{11}N_2Cl$ requires C, 70·7; H, 4·3%).

Alternatively, the chloro-nitro-compound (5 g.), stannous chloride (12 g.), and concentrated hydrochloric acid (100 c.c.) were heated for 1 hr. at 95°. After basification and ether-extraction the product (m. p. 160—161°) was isolated in 78% yield.

Similarly, 3-nitro-4-*p*-tolylquinoline (5 g.), methanol (400 c.c.), and palladium–charcoal (1 g.), or the nitro-compound (5 g.), stannous chloride (13 g.), and concentrated hydrochloric acid (150 c.c.), gave 80% and 75% respectively of 3-*amino*-4-p-*tolylquinoline*, which formed pale yellow needles, m. p. 160—162° (Found : C, 81·7; H, 5·3. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0%), from benzene–light petroleum (b. p. 60—80°).

3-*Acylamino*-4-*arylquinolines*.—3-Amino-4-phenylquinoline (0·7 g.) and formic acid (15 c.c. of 98%) were refluxed for 1 hr. The product (0·72 g.) was isolated by dilution and basification. 3-*Formamido*-4-*phenylquinoline* formed fawn plates, m. p. 135—137° (Found : C, 77·7; H, 5·1. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·9%), from benzene–light petroleum (b. p. 60—80°). The same amine (0·5 g.), acetic anhydride (10 c.c.), and one drop of 2N-sulphuric acid, when refluxed for 12 hr., gave, in the usual way, 3-*diacetylamino*-4-*phenylquinoline* (0·41 g.), buff-coloured plates, m. p. 139—141° (from aqueous alcohol) (Found : C, 74·8; H, 5·1. $C_{19}H_{16}O_2N_2$ requires C, 75·0; H, 5·3%).

The acyl compounds described below were isolated in the usual way after the appropriate amine and aroyl chloride (1 equiv.) had been kept in pyridine for 24 hr. 3-p-*Nitrobenzamido*-4-*phenylquinoline* (50%) formed small colourless needles, or pale yellow prisms, m. p. 179—181° (Found : C, 70·9; H, 4·3. $C_{22}H_{15}O_3N_3$ requires C, 71·5; H, 4·1%), from aqueous alcohol. From the same solvent 3-*benzamido*- (65%) and 3-p-*nitrobenzamido*-4-p-*tolylquinoline* (67%) formed needles, m. p. 166—168° (Found : C, 81·5; H, 5·5. $C_{23}H_{18}ON_2$ requires C, 81·6; H, 5·4%), and small yellow plates, m. p. 155—156° (Found : C, 69·7; H, 4·7. $C_{23}H_{17}O_3N_3,\frac{1}{2}H_2O$ requires C, 70·4; H, 4·6%), respectively. 3-*Benzamido*-6-*chloro*- (53%) separated as needles, m. p. 208—210° (Found : C, 73·3; H, 4·4. $C_{22}H_{15}ON_2Cl$ requires C, 73·6; H, 4·2%), from aqueous alcohol, and 6-*chloro*-3-p-*nitrobenzamido*-4-*phenylquinoline* (51%) gave very pale yellow plates, m. p. 205—207° (Found : C, 66·2; H, 3·5. $C_{22}H_{14}O_3N_3Cl$ requires C, 65·4; H, 3·5%), from alcohol.

Pyridylquinolines.—(i) The diazonium solution from 3-amino-4-phenylquinoline (0·5 g.), concentrated hydrochloric acid (2 c.c.), water (3 c.c.), and aqueous sodium nitrite (0·18 g. in 3 c.c.) was added gradually to pyridine (25 c.c.) at 50°. After 24 hr. at room temperature the solution was treated with aqueous sodium hydroxide and steam-distilled. The oily residue was extracted with ether, and the oil (0·54 g.) obtained from the dry (Na_2CO_3) extract was treated in ethanol (15 c.c.) with picric acid (1·1 g.) in the same solvent (15 c.c.). The resulting red gum when dissolved in acetone (20 c.c.) gave a solid (0·42 g.) which on recrystallisation from methanol provided orange needles of a *dipicrate*, m. p. 177—181° [Found : C, 51·1; H, 3·1; N, 15·1. $C_{20}H_{14}N_2,(C_6H_3O_7N_3)_2$ requires C, 51·8; H, 2·7; N, 15·1%]. A more soluble component (0·15 g.) from the acetone gave from methanol lemon-coloured plates of an impure monopicrate, m. p. 169—172° (Found : C, 59·1; H, 3·5; N, 13·1. Calc. for $C_{20}H_{14}N_2,C_6H_3O_7N_3$: C, 61·1; H, 3·4; N, 13·7%).

(ii) In the same way the reaction mixture from 3-amino-4-*p*-tolylquinoline (0·5 g.) gave after steam-distillation and ether-extraction an oil (0·55 g.) which was treated in ethanol (20 c.c.) with picric acid (1 g.) in acetone (20 c.c.). A solid (0·55 g.) separated, which on recrystallisation from benzene gave small yellow prisms of a solvated *monopicrate*, m. p. 230—232° (Found : C, 64·6; H, 4·1. $C_{21}H_{16}N_2,C_6H_3O_7N_3,\frac{1}{2}C_6H_6$ requires C, 63·8; H, 3·9%). No other homogeneous product could be isolated.

(iii) 3-Amino-6-chloro-4-phenylquinoline (0·5 g.) in concentrated hydrochloric acid (3 c.c.) and water (3 c.c.) was diazotised with sodium nitrite (0·15 g.) in water (2 c.c.). A suspension resulted and hydrochloric acid (40 c.c.) and acetic acid (10 c.c.) were added to cause dissolution. The solution was added to pyridine (150 c.c.) at 50°, and the mixture was worked up as usual. The resulting oil (0·55 g.) in benzene was passed over an alumina column and gave first a *substance* which formed soft, pink needles, m. p. 170—171° (Found : C, 75·8; H, 4·2. $C_{20}H_{13}N_2Cl$ requires C, 75·8; H, 4·1%), from ether–light petroleum (b. p. 40—60°), and then a *substance* which separated from the same solvent as small prisms, m. p. 184—186° (Found : C, 75·8; H, 4·2%).

iso*Quinolino*(3′ : 4′-3 : 4)*quinolines*.—The acylaminoquinoline (0·2 g.), nitrobenzene (2 c.c.), phosphorus oxychloride (1 c.c.), and stannic chloride (1 equiv.) were refluxed for 4 hr. After steam-distillation the residual suspension was basified, and the product was recrystallised. The yields were not dimimished in larger (*ca.* 1 g.)-scale experiments. The products are tabulated below.

*iso*Quinolino(3′ : 4′-3 : 4)quinoline	Solvent	Yield (%)	Colour	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
(1) 1′-Methyl-	Ether	65	—	134—135°	$C_{17}H_{12}N_2,\frac{3}{2}H_2O$	75·8	5·6	75·3	5·6
(2) 1′-Phenyl- * †	Aq. EtOH	85	Cream	157—158	—	—	—	—	—
(3) 1′-*p*-Nitrophenyl-	Acetone	78	Yellow	250—251	$C_{22}H_{13}O_2N_3$	74·5	3·9	75·2	3·6
(4) 7′-Methyl-1′-phenyl-	EtOH	90	—	199—201	$C_{23}H_{16}N_2$	86·4	5·1	86·2	5·0
(5) 7′-Methyl-1′-*p*-nitrophenyl-	,,	84	Yellow	237—238	$C_{23}H_{15}O_2N_3,\frac{3}{2}H_2O$	70·2	4·4	70·4	4·6
(6) 6-Chloro-1′-phenyl- †	,,	80	Fawn	190—192	$C_{22}H_{13}N_2Cl$	78·8	4·0	77·5	3·8
(7) 6-Chloro-1′-*p*-nitrophenyl-	Pyridine	90	Pale yellow	315—316	$C_{22}H_{12}O_2N_3Cl$	67·6	3·1	68·5	3·1
(8) 7′-Methoxy-1′-phenyl-	Aq. EtOH	53	—	166—167	$C_{23}H_{16}ON_2$	81·7	5·1	82·2	4·8

* See Schofield and Theobald (*loc. cit.*). † Plates; the other compounds formed needles.

1′-(2-*Hydroxy*-1-*hydroxymethylethyl*)iso*quinolino*(3′ : 4′-3 : 4)*quinoline*.—The 1′-methyl compound (2·3 g.), alcohol (50 c.c.), and aqueous formaldehyde (25 c.c. of 40%) were refluxed for 24 hr. Most of the solvent was removed, alcohol and formaldehyde (20 c.c. of each) were added, and refluxing was continued for 24 hr. more. The solution was evaporated, and evaporated several times with small quantities of benzene. The residue, when crystallised from benzene, gave material (1·55 g.) pure enough for the next step. The *product* formed plates, m. p. 193—195° (Found: C, 74·8; H, 5·2. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5%).

A boiling solution of the dihydroxy-compound (0·2 g.) in 2N-sulphuric acid (2·5 c.c.) was treated during ½ hr. with potassium dichromate (0·4 g.) in water (2 c.c.) and concentrated sulphuric acid (0·3 c.c.). After 2½ hr. the mixture was diluted and the precipitated acid [0·1 g.; m. p. 320—330° (decomp.)] was used directly in the next stage. A similar oxidation of the dihydroxy-compound (1·2 g.) gave a very impure product (0·51 g.). Treatment with 2N-sodium hydroxide left a neutral residue (0·2 g.; m. p. 240—270°) which was not further examined, whilst neutralisation of the filtrate with acetic acid gave the above acid [0·3 g.; m. p. 320—325° (decomp.)].

The carboxylic acid (0·1 g.) and benzophenone (0·5 g.) were heated at 210°. Gas evolution was complete in ½ hr., and after 10 min. more the mixture was treated with ether and extracted with 2N-hydrochloric acid. Basification of the acid solution and crystallisation of the precipitate from acetone gave the *lactam* (0·03 g.) as white needles, m. p. 337—338° (Found: C, 77·9; H, 4·1. $C_{16}H_{10}ON_2$ requires C, 78·0; H, 4·1%).

Methiodides. (*a*) The *iso*quinolino(3′ : 4′-3 : 4)quinoline (0·2 g.), benzene (10 c.c.), and methyl sulphate (1 equiv.) were refluxed for 3 hr. The solvent was removed and the product was dissolved in hot water and filtered from unchanged starting material (*ca.* 0·03 g., suitable for further use). Addition of potassium iodide solution precipitated the practically pure methiodide which was recrystallised.

(*b*) The nitro-compound (0·2 g.), nitrobenzene (20 c.c.), and methyl sulphate (1 equiv.) were kept at 150° for 2 hr. After steam-distillation the hot aqueous solution was filtered, and treated with potassium iodide. The substantially pure methiodide separated and was recrystallised.

The results are tabulated below. Yields were unchanged on a larger (*ca.* 0·8 g.) scale.

Methiodide of base no.[a]	Solvent	Yield (pure cpd.) (%)	M. p.[b]	Form	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
(2) [c]	EtOH	80	238—240°	Orange needles	$C_{23}H_{17}N_2I,\frac{1}{2}H_2O$	59·9	3·9	60·4	4·0
(3)	H_2O–AcOH	69	272—274	Orange needles	$C_{23}H_{16}O_2N_3I,\frac{1}{2}H_2O$	55·0	3·3	55·0	3·4
(4)	EtOH	80	234—235	Brown plates	$C_{24}H_{19}N_2I,2H_2O$	57·8	4·4	57·8	4·7
(5)	H_2O–AcOH	66	278—281	Orange needles	$C_{24}H_{18}O_2N_3I$	56·6	3·7	56·8	3·6
(6)	EtOH	86	238—240	Yellow needles	$C_{23}H_{16}N_2ClI,\frac{3}{2}H_2O$	54·4	3·4	54·2	3·2
(7)	H_2O–AcOH	42	304—306	Red-brown plates	$C_{23}H_{15}O_2N_3ClI,5H_2O$	44·7	2·6	44·7	2·4

[a] No. refers to previous Table. [b] All with decomp. [c] Cf. Schofield and Theobald, *loc. cit.*

1 : 7′-Dimethyl-1′-phenyl*iso*quinolino(3′ : 4′-3 : 4)quinolinium iodide (0·1 g.), potassium ferricyanide (0·3 g.), water (25 c.c.), and 2N-sodium hydroxide (10 c.c.) were stirred at 95° for 1 hr. Extraction of the solution with benzene, and crystallisation of the product from benzene–light petroleum (b. p. 60—80°), gave small prisms of the *quinolone* (VII; R = R‴ = Me, R′ = H,

R″ = Ph), m. p. 190—191° (Found : C, 82·5; H, 5·2. $C_{24}H_{18}ON_2$ requires C, 82·3; H, 5·2%). In the same way, the *quinolone* (VII; R = H, R′ = Cl, R″ = Ph, R‴ = Me) was obtained as pale yellow needles, m. p. 204—205° (Found : C, 76·0; H, 4·5. $C_{23}H_{15}ON_2Cl,\frac{1}{2}C_6H_6$ requires C, 76·2; H, 4·5%).

1-Methyl-1′-*p*-nitrophenyl*iso*quinolino(3′ : 4′-3 : 4)quinolinium iodide (0·2 g.), water (50 c.c.), and acetic acid (20 c.c.) were stirred at 95° and treated with iron powder (0·4 g.) during ¼ hr. After 1 hr. more the mixture was filtered and concentrated. Repeated crystallisation from water gave small red needles of the impure amine (Found : C, 57·0; H, 4·4%).

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