Convenient Routes to Pyrrolo[3,2-*b*]-, Pyrrolo[3,2-*c*]-, and Pyrrolo[2,3-*c*]-quinolines, and a Study of the Pyrolysis of 2-Quinolylhydrazones

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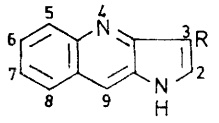
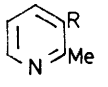
A useful one-step synthesis of pyrrolo[3,2-*b*]quinoline (1) from 3-amino-2-methylquinoline and the preparations of derivatives of pyrrolo[3,2-*c*]- (12) and pyrrolo[2,3-*c*]-quinoline (21) are described. Pyrolysis of deoxybenzoin 2-quinolylhydrazone (26) is shown to give 2-aminoquinoline (31), 2,3-diphenylimidazo[1,2-*a*]quinoline (32), and tetraphenylpyrrole (36); butan-2-one 2-quinolylhydrazone (27) gives the aminoquinoline (31), 2,2'-azoquinoline (35), and what is probably an aminodiquinolylamine (33). The mechanisms of these pyrolyses are discussed.

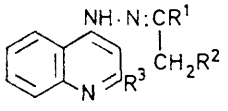
THE small number of recorded synthetic routes to derivatives of the fully aromatic pyrrolo[3,2-*b*]quinoline



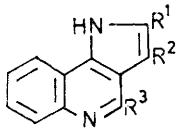
(1) R = H
(2) R = CHO
(3) R = NO_2



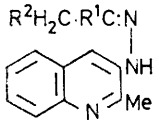
(4) R = N:CH·OEt
(5) R = N:CH·NMe_2



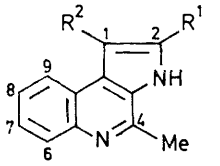
(6) R^1 R^2 = $[CH_2]_4$, R^3 = H
(7) R^1 = R^2 = Me, R^3 = H
(8) R^1 = R^2 = Ph, R^3 = H
(9) R^1 R^2 = $[CH_2]_3$, R^3 = H
(10) R^1 = R^2 = R^3 = Me, HCl
(11) R^1 R^2 = $[CH_2]_4$, R^3 = Me, HCl



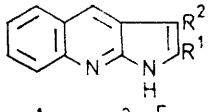
(12) R^1 = R^2 = R^3 = H
(13) R^1 R^2 = $[CH_2]_4$, R^3 = H
(14) R^1 = R^2 = Me, R^3 = H
(15) R^1 = R^2 = Ph, R^3 = H
(16) R^1 R^2 = $[CH_2]_3$, R^3 = H
(17) R^1 = R^2 = R^3 = Me
(18) R^1 R^2 = $[CH_2]_4$, R^3 = Me



(19) R^1 = R^2 = Me
(20) R^1 R^2 = $[CH_2]_4$



(21) R^1 = R^2 = H
(22) R^1 = R^2 = Me
(23) R^1 R^2 = $[CH_2]_4$



(24) R^1 = Me, R^2 = $[CH_2]_2 \cdot NH_2$
(25) R^1 = R^2 = Ph

nucleus [1] (1) and the pyrrolo[3,2-*c*]quinoline ring system (12),[2] together with the recent interest in the potential medicinal use of derivatives of (12) [3] and the related pyrrolo[2,3-*c*]quinoline (21),[4] prompts us to record useful routes to these three heterocycles.

The parent pyrrolo[2,3-*b*]quinoline (1) may be obtained in one step (63%) from 3-amino-2-methylquinoline by treatment with triethyl orthoformate in the presence of an acid catalyst. This behaviour contrasts with that of 3-amino-2-methylpyridine which yielded only the formimidate (4) in an analogous reaction,[5] but is in agreement with the different reactivity of the two amino-methyl-heterocycles with the Vilsmeier reagent: the quinoline gave the cyclisation product (2),[1] whereas the pyridine afforded only the formamidine (5).[6] In the present work, the 3-formylpyrroloquinoline (2) was obtained by the reaction of the Vilsmeier reagent with the pyrroloquinoline (1), and the nitration product from (1) was therefore thought to be the 3-isomer (3).

We have found that substituted pyrrolo[3,2-*c*]-quinolines (13)—(16) are readily formed in high yield when the corresponding 4-quinolylhydrazones (6)—(9) are refluxed in an inert solvent. Cyclisation of 4-quinolylhydrazones is difficult under acidic conditions and only one (6) has been converted into a pyrrolo[3,2-*c*]-quinoline (13) (in unspecified yield).[7] Interestingly, the hydrochlorides of the 2-methyl-3-quinolylhydrazones (10) and (11) gave high yields of pyrroloquinolines (17) and (18) when heated in a solvent, presumably because the hydrogen chloride is expelled from the hot mixture and the free hydrazone then cyclises readily.

Isolation of cyclohexanone 2-methyl-3-quinolylhydrazone has been reported [8] to be difficult, owing to formation of an oxygen-containing derivative, and the pyrrolo[2,3-*c*]quinoline (23) (m.p. 226°) was therefore obtained by heating 3-hydrazino-2-methylquinoline and a large excess of cyclohexanone in the presence of acetic acid without isolation of the hydrazone. Even after

[1] B. A. J. Clark, J. Parrick, P. J. West, and A. H. Kelly, *J. Chem. Soc.*, 1970, 498.
[2] S. Beveridge and J. L. Huppatz, *Austral. J. Chem.*, 1972, **25**, 1341.
[3] G. C. Wright, E. J. Watson, F. F. Ebetino, G. Lougheed, B. F. Stevenson, and A. Winterstein, *J. Medicin. Chem.*, 1971, **14**, 1060.
[4] T. Tanaka, T. Iwaka, M. Miyazki, M. Wagatsuma, and I. Iijima, *Chem. and Pharm. Bull. (Japan)*, 1972, **20**, 109.
[5] R. R. Lorentz, B. F. Tullar, C. F. Koelsch, and S. Archer, *J. Org. Chem.*, 1965, **30**, 2531.
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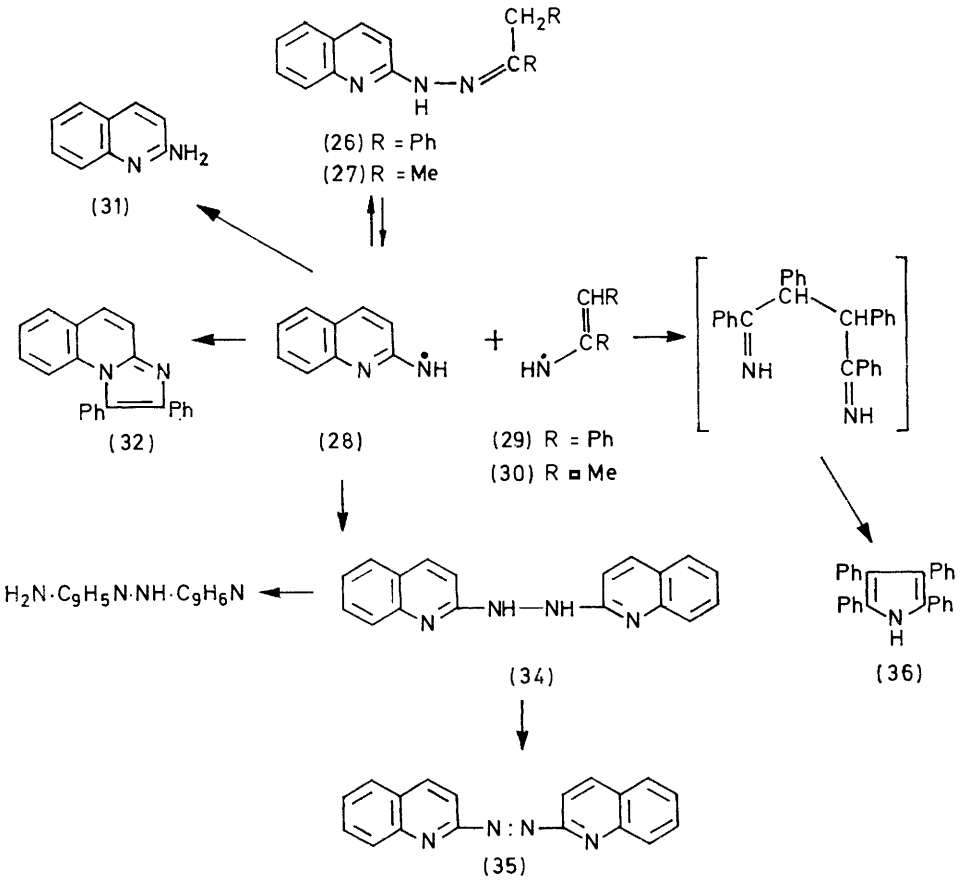
[8] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 1924, 827.

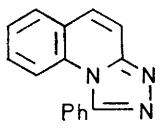
making allowance for the known relative ease of cyclisation of cyclohexanone arylhydrazones and the presence of the 2-methyl substituent, the mild conditions used for this acid-catalysed reaction are in marked contrast to those required for the cyclisation of the corresponding 4-quinolylhydrazone [7] and of other 3-quinolylhydrazones [9] which required the presence of zinc chloride at high temperatures. In the present work 2-methyl-3-quinolylhydrazones of butanone (19) and cyclohexanone (20) (identified by elemental analysis and i.r. and n.m.r. data) were isolated, and both were cyclised readily on heating in the absence of acid. The pyrrolo[2,3-*c*]-quinoline structures (22) and (23) were assigned on the basis of spectroscopic evidence, but (23) was found to have m.p. 288—289°. These differences between our results and those reported are unexplained.

Recently, Grandberg and Yaryshev [10] have reported the formation of 3-(β-aminoethyl)-2-methyl-1*H*-pyrrolo-[2,3-*b*]quinoline (24) on boiling 2-hydrazinoquinoline with methyl γ-chloropropyl ketone. If it is assumed that the process involves hydrazone formation and subsequent pyrrole ring synthesis, this is an unexpected result since cyclisation of a 2-quinolylhydrazone at the 3-position would be expected to involve a higher energy transition state than that for reaction at the 1-position. Attempts to cyclise 2-quinolylhydrazones have been unsuccessful, *viz.* in the presence of acid no reaction was observed for several 2-quinolylhydrazones [11] (not now an unexpected result), while in the absence of catalyst Potts and Schneller [12] found the 2-quinolylhydrazones stable up to 200 °C but decomposition occurred at 280 °C to yield 2-aminoquinoline and uncharacterised tar. Because of the Russian report and the knowledge that later investigations (in which modified, but still neutral, conditions were used) have given different results from those reported by Potts and Schneller for the pyrolysis of 2-pyridyl- [13] and pyrazin-2-yl-hydrazones,[14] we decided to investigate the pyrolysis of deoxybenzoin and butan-2-one 2-quinolylhydrazones; the former since it was likely to give readily isolable products and the latter because it was a simple aliphatic analogue.



[9] T. R. Govindachari, S. Rajappa, and V. Sudarsanam, *Tetrahedron*, 1961, **16**, 1.
[10] T. Grandberg and N. G. Yaryshev, *Otkrytiya, Izobret, Prom. Obraztsy, Tovarnye Znaki*, 1969, **46**, 23.
[11] R. G. Fargher and R. Furness, *J. Chem. Soc.*, 1915, 688.
[12] K. T. Potts and S. W. Schneller, *J. Heterocyclic Chem.*, 1968, **5**, 485.
[13] A. H. Kelly and J. Parrick, *Canad. J. Chem.*, 1966, **44**, 2455.
[14] B. A. J. Clark, R. J. Dorgan, and J. Parrick, *Chem. and Ind.*, 1975, 215.

2-Aminoquinoline (31) and two other solid products were isolated when deoxybenzoin 2-quinolylhydrazone (26) was heated in dry diethylene glycol. One solid had elemental analysis and a molecular ion corresponding to $C_{28}H_{21}N$, an i.r. absorption at 3 420 cm^{-1}, and an exchangeable proton signal (1 H, s) in its n.m.r. spectrum, and was shown to be 2,3,4,5-tetraphenylpyrrole (36). The final product had a molecular formula, $C_{23}H_{16}N_2$, which does not agree with the triazoloquinoline structure (37) expected by analogy with the product obtained [15] on pyrolysis of the quinoxalin-2-ylhydrazone (38). The



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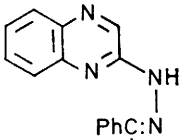

(38)

molecular formula does agree with the pyrroloquinoline (25) or imidazoquinoline (32) formulation. The ^1H n.m.r. spectrum suggested the presence of the quinolyl nucleus and two phenyl groups, but did not show a signal for an NH group. The 2,3-diphenylimidazo-[1,2-*a*]quinoline (32) structure was confirmed by independent synthesis from 2-aminoquinoline and 2-chloro-2-phenylacetophenone.

Pyrolysis of butan-2-one 2-quinolylhydrazone (27) in boiling diethylene glycol again gave 2-aminoquinoline (31) and also a red solid and a third component. The red solid had m.p. 228°, close to that reported (230°) for 2,2′-azoquinoline (35). The elemental analysis and spectral data agreed with this possibility and the structure was confirmed by synthesis of 2,2′-hydrazoquinoline (34) from 2-chloroquinoline and 2-hydrazinoquinoline and its subsequent oxidation to the azoquinoline. The third component, isolated as its hydrochloride, was not fully identified, but its mass spectrum contained a molecular ion, *m/e* 286 ($C_{18}H_{14}N_4$) and showed fragmentation by loss of NH_2. It seems likely that the compound is an aminodiquinolylamine (33). The same products were obtained when diphenyl ether (dried over sodium) was used as solvent.

Apart from the formation of the 2-aminoquinoline in each case, there are marked differences between the products isolated from the two quinolylhydrazones. It is tempting to speculate that two competing processes occur in the pyrolysis of the deoxybenzoin hydrazone: (i) an intramolecular cyclisation on to nitrogen to give the imidazoquinoline (this process might be concerted and analogous to the proposed mechanism of cyclisation of heteroarylhydrazones at carbon [16]); and (ii) homolysis of the N·N bond to give the stabilised quinolylamino- (28) and vinylamino- (29) radicals, the latter giving rise to the pyrrole (36) and the hydrazoquinoline (34), which then undergoes oxidation to the azoquinoline (35).

A similar homolysis of the butanone hydrazone would yield a more reactive vinylamino-radical (30), which might not survive long enough to give the tetramethylpyrrole. However, it is not clear why the expected dimethylimidazoquinoline is not formed if the cyclisation occurs by an intramolecular process. It therefore seems possible that the imidazoquinoline is also formed by a radical process. The azoquinoline and the aminodiquinolylamine may be formed by dimerisation of the aminoquinoline and subsequent oxidation or rearrangement.

2,2′-Hydrazonaphthalene is known to undergo the thermal benzidine rearrangement particularly readily [17] and it seems that the aminodiquinolylamine is formed by the closely related semidine rearrangement of the hydrazoquinoline. An alternative route *via* formation of a nitrene and its attack on the aminoquinoline seems less likely, though Potts, Kutz, and Nachod [18] have recently reported the formation of an aminodiquinolylamine upon pyrolysis of 8-hydroxyaminoquinoline and have given evidence in support of a nitrene intermediate.

EXPERIMENTAL

The i.r. and n.m.r. spectra were recorded as described previously,[19] except that here solutions in $(CD_3)_2SO$ were used for the latter, unless otherwise stated.

1H-*Pyrrolo*[3,2-b]*quinoline* (1).—A mixture of 3-amino-2-methylquinoline [20] (2.1 g) and triethyl orthoformate (10 g) was treated with saturated ethanolic hydrogen chloride (0.2 cm^3) and heated to 130 °C. This temperature was maintained until no more ethanol distilled off through a short fractionating column. A slight excess of hydrochloric acid (5M) was added to the residue and the solution was decolourised with charcoal and basified. The precipitate was crystallised from ethanol–water to give 1H-*pyrrolo*[3,2-b]*quinoline* (1.4 g), m.p. 239—240° (Found: C, 78.5; H, 4.9; N, 16.6%; *M*, 168. $C_{11}H_8N_2$ requires C, 78.6; H, 4.8; N, 16.6%; *M*, 168), $\nu_{max.}$ 3 150 cm^{-1} (NH), δ 6.7 (2 H, d, 2- and 3-H), 7.5—8.0 (4 H, m, 5-, 6-, 7-, and 8-H), 8.3 (1 H, s, 9-H), and 11.5 (1 H, s, exchangeable with D_2O, NH). Treatment of the pyrroloquinoline with acetic anhydride yielded 1-*acetylpyrrolo*[3,2-b]*quinoline*, m.p. 301—302° (from ethanol) (Found: C, 74.3; H, 4.8; N, 13.4. $C_{13}H_{10}N_2O$ requires C, 74.3; H, 4.8; N, 13.3%), $\nu_{max.}$ 1 690 cm^{-1} (CO), δ 2.5 (3 H, s, Me), 6.7 (1 H, d, 3-H, *J* 3 Hz), 6.9 (1 H, d, 2-H, *J* 3 Hz), 7.2—8.2 (4 H, m, 5-, 6-, 7-, and 8-H), and 8.4 (1 H, s, 9-H).

1H-*Pyrrolo*[3,2-b]*quinoline*-3-*carbaldehyde* (2).—Phosphoryl chloride (5 cm^3) was added slowly to dimethylformamide (16 g) while the temperature was maintained at 10—20 °C. Pyrrolo[3,2-*b*]quinoline (8.4 g) in dimethylformamide (4 g) was then slowly added with stirring while

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[16] T. D. Duffy and D. G. Wibberley, *J.C.S. Perkin I*, 1974, 1921.
[17] H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, p. 171.
[18] K. T. Potts, A. A. Kutz, and F. C. Nachod, *Tetrahedron*, 1975, **31**, 2163.
[19] P.-Y. How and J. Parrick, *J.C.S. Perkin I*, 1976, 1363.
[20] W. Lawson, W. H. Perkin, jun., and R. Robinson, *J. Chem. Soc.*, 1924, 636.

the temperature was kept between 20 and 30 °C, and, after the addition was complete, the mixture was kept at 35 °C for 45 min. It was then poured on to crushed ice and the solution was basified with sodium hydroxide solution. The mixture was boiled for 1 min and the crystals which formed on cooling were collected and recrystallised from ethanol to give the aldehyde (6 g), m.p. 282—283° (lit.,[1] 283°).

3-*Nitro*-1H-*pyrrolo*[3,2-b]*quinoline* (3).—The pyrroloquinoline was added slowly to ice-cold fuming nitric acid (10 cm^3) over 20 min. The mixture was maintained at 0 °C for ½ h and then poured on to ice and neutralised with sodium hydrogen carbonate. The precipitate yielded yellow 3-*nitro*-1H-*pyrrolo*[3,2-b]*quinoline* (1.3 g), m.p. 194—195° (from ethanol) (Found: C, 61.5; H, 3.4; N, 19.2. $C_{11}H_7N_3O_2$ requires C, 62.0; H, 3.3; N, 19.7%), $\nu_{max.}$ 3 450 cm^{-1} (NH), δ($CDCl_3$) 8.3 (1 H, s, 2-H), 7.6—8.4 (4 H, m, 5-, 6-, 7-, and 8-H), 9.0 (1 H, s, 9-H), and 11.5br (1 H, s, 1-H, exchanged on addition of D_2O).

4-*Hydrazinoquinoline and* 4-*Hydrazino*-2-*methylquinoline Hydrochloride*.—The first was obtained when 4-chloroquinoline 1-oxide was refluxed (5 h) with a large excess of hydrazine hydrate in ethanol (a similar deoxygenation process has been reported for 2-chloroquinoline 1-oxide [21]). 4-Chloro-2-methylquinoline and hydrazine hydrate (1 mol. equiv.) yielded 4-*hydrazino*-2-*methylquinoline hydrochloride*, m.p. 334—335° (from propan-1-ol) (Found: C, 57.6; H, 5.9. $C_{10}H_{12}ClN_3$ requires C, 57.4; H, 5.8%).

4-*Quinolylhydrazones* (6)—(9) *and* 2-*Methyl*-4-*quinolylhydrazone Hydrochlorides* (10) *and* (11).—Equimolar quantities of the ketone and 4-hydrazinoquinoline or 4-hydrazino-2-methylquinaldine hydrochloride in methanol were heated on a water-bath for 1 h and the products were crystallised from chloroform–light petroleum (b.p. 60—80 °C) to give the 4-quinolylhydrazones (70—80%) of cyclohexanone, m.p. 145—146° (lit.,[7] 144—145°); *butan*-2-*one*, m.p. 136—137° (Found: N, 20.0. $C_{13}H_{15}N_3$ requires N, 19.7%); *benzyl phenyl ketone*, m.p. 47—48° (Found: N, 12.0. $C_{23}H_{19}N_3$ requires N, 12.5%); *cyclopentanone*, m.p. 91—92° (Found: N, 18.5. $C_{14}H_{15}N_3$ requires N, 18.7%); and the 2-methyl-4-quinolylhydrazone hydrochlorides of *butan*-2-*one*, m.p. 141—142° (Found: C, 63.8; H, 6.9; N, 15.5. $C_{14}H_{18}N_3Cl$ requires C, 63.7; H, 6.8; N, 15.8%); and *cyclohexanone*, m.p. 179—180° (Found: C, 66.1; H, 6.9; N, 14.3. $C_{16}H_{20}ClN_3$ requires C, 66.3; H, 7.1; N, 14.5%).

1H-*Pyrrolo*[3,2-c]*quinolines* (13)—(18).—A solution (*ca.* 15%) of the 4-quinolylhydrazone or 2-methyl-4-quinolylhydrazone hydrochloride in diethylene glycol was refluxed (2—7 h), cooled, and poured into ice–water. Crystallisation of the precipitate from chloroform–petroleum gave the pyrrolo[3,2-*c*]quinolines: 7,9,10,11-tetrahydro-8*H*-indolo-[3,2-*c*]quinoline (80%), m.p. 291—292° (lit., 292—293°); 2,3-*dimethylpyrrolo*[3,2-c]*quinoline* (82%), m.p. 318—319° (Found: C, 79.8; H, 6.3; N, 13.9. $C_{13}H_{12}N_2$ requires C, 79.6; H, 6.1; N, 14.3%), δ 2.3 (6 H, s, 2 × Me), 7.5 (2 H, m, 7- and 8-H), 8.0 (1 H, m, 9-H), 8.3 (1 H, m, 6-H), 8.9 (1 H, s, 4-H), and 11.9 (1 H, s, NH, disappeared on addition of D_2O); 2,3-*diphenylpyrrolo*[3,2-c]*quinoline* (70%), m.p. 240—241° (Found: C, 86.3; H, 5.2; N, 8.5. $C_{23}H_{16}N_2$ requires C, 86.2; H, 5.0; N, 8.8%), δ 7.5 (12 H, m, 2 × Ph + 7- and 8-H), 8.0 (1 H, m, 9-H), 8.3 (1 H, m, 6-H), 8.9 (1 H, s, 4-H), and 12.6 (1 H, s, NH, disappeared on addition of D_2O); 7,8,9,10-*tetrahydrocyclopenta*[4,5]*pyrrolo*-[3,2-c]*quinoline* (75%), m.p. 284—285° (Found: C, 80.9; H, 5.9; N, 13.2. $C_{14}H_{12}N_2$ requires C, 80.8; H, 5.8; N, 13.5%), δ 3.3 (6 H, m, 3 × CH_2), 7.4 (2 H, m, 2- and 3-H), 7.9 (1 H, m, 1-H), 8.2 (1 H, m, 4-H), 9.0 (1 H, s, 6-H), and 12.1 (1 H, s, NH, exchangeable with D_2O); 2,3,4-*trimethylpyrrolo*[3,2-c]*quinoline* (82%), m.p. 270—271° [from ethanol–petroleum (b.p. 60—80°)] (Found: C, 80.5; H, 6.5; N, 12.9. $C_{14}H_{14}N_2$ requires C, 80.0; H, 6.7; N, 12.8%), δ 2.3 (9 H, s, 3 × Me), 7.4 (2 H, m, 7- and 8-H), 8.1 (1 H, m, 9-H), 8.2 (1 H, m, 6-H), and 11.8 (1 H, s, NH, disappeared an addition of D_2O); 7,9,10,11-*tetrahydro*-6-*methyl*-8H-*indolo*[3,2-c]*quinoline* (80%), m.p. 284—285° (from ethanol–water) (Found: C, 81.1; H, 7.0; N, 11.9. $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.9%), δ 1.7 (3 H, s, Me), 3.2 (8 H, m, 4 × CH_2), 7.4 (2 H, m, 2- and 3-H), 7.8 (1 H, m, 1-H), 8.5 (1 H, m, 4-H), and 11.9 (1 H, s, NH, exchangeable with D_2O).

2-*Methyl*-3-*quinolylhydrazones* (19) *and* (20).—These were obtained from 3-hydrazino-2-methylquinoline [8] and the appropriate ketone as described for the 4-quinolylhydrazones and gave the hydrazones from *butanone*, m.p. 100—101° (Found: C, 74.4; H, 7.6; N, 18.2. $C_{14}H_{17}N_3$ requires C, 74.0; H, 7.5; N, 18.5%); and *cyclohexanone*, m.p. 133—134° (Found: C, 76.1; H, 7.7; N, 16.2. $C_{16}H_{19}N_3$ requires C, 75.9; H, 7.5; N, 16.6%), $\nu_{max.}$ 3 610 (NH) and 1 625 cm^{-1} (C:N).

3H-*Pyrrolo*[2,3-c]*quinolines* (22) *and* (23).—Cyclisation of the 2-methyl-3-quinolylhydrazones in refluxing diethylene glycol yielded, after crystallisation from aqueous ethanol, 1,2,4-*trimethylpyrrolo*[2,3-c]*quinoline* (70%), m.p. 278—279° (Found: C, 80.2; H, 6.8; N, 13.0. $C_{14}H_{14}N_2$ requires C, 80.0; H, 6.7; N, 13.4%), $\nu_{max.}$ 3 410 cm^{-1} (NH), δ 2.2 (9 H, s, 3 × Me), 7.3 (2 H, m, 7- and 8-H), 8.1 (1 H, m, 9-H), 8.2 (1 H, m, 6-H), and 11.5 (1 H, s, NH, disappeared an addition of D_2O); and 8,9,10,11-*tetrahydro*-6-*methyl*-7H-*indolo*[2,3-c]*quinoline* (75%), m.p. 288—289° (lit.,[8] 226°) (Found: C, 81.5; H, 6.9; N, 11.5. $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.9%), $\nu_{max.}$ 3 445 cm^{-1} (NH), δ 1.8 (3 H, s, Me), 3.3 (8 H, s, 4 × CH_2), 7.3 (2 H, s, 2- and 3-H), 7.7 (1 H, m, 1-H), 8.4 (1 H, m, 4-H), and 11.7 (1 H, s, NH, disappeared an addition of D_2O).

2-*Quinolylhydrazones* (26) *and* (27).—2-Hydrazinoquinoline [22] and the appropriate ketone gave the 2-*quinolylhydrazones* of *deoxybenzoin*, m.p. 112—114° (Found: N, 12.2. $C_{23}H_{19}N_3$ requires N, 12.5%); and *butanone*, m.p. 89—90° (Found: N, 20.1. $C_{13}H_{15}N_3$ requires N, 19.7%).

Pyrolysis of Deoxybenzoin 2-*Quinolylhydrazone*.—The 2-quinolylhydrazone (5 g) and diethylene glycol (40 cm^3) were refluxed for 7 h, and the cooled mixture was poured into ice–water. A viscous oil and a suspension of solid in water were formed, and these were separated by decantation.

The aqueous suspension was made just acid by addition of dilute hydrochloric acid and the mixture was extracted with ether. This extract yielded a solid which crystallised from chloroform–petroleum (b.p. 60—80 °C) to give 2,3,4,5-tetraphenylpyrrole (1.6 g), m.p. 211—212° (lit.,[23] 214°) (Found: C, 90.4; H, 5.6; N, 3.8%; *M*, 371. Calc. for $C_{28}H_{21}N$: C, 90.6; H, 5.7; N, 3.8%; *M*, 371), $\nu_{max.}$ 3 420 cm^{-1} (NH), δ($CDCl_3$) 7.2 (10 H, s, 2 × Ph), 7.3 (10 H, s, 2 × Ph), and 8.4br (1 H, s, NH, exchangeable with D_2O). Basification of the aqueous solution gave 2-aminoquinoline (1.6 g), m.p. 128—129° (lit.,[24] 127.6—128.3°).

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The oil was dissolved in hot methanol (charcoal); addition of water gave a precipitate which crystallised from aqueous methanol as 2,3-*diphenylimidazo*[1,2-a]*quinoline* (1.3 g), m.p. 164—165° (Found: C, 85.7; H, 5.2; N, 9.1%; *M*, 320. $C_{23}H_{16}N_2$ requires C, 86.3; H, 5.0; N, 8.8%; *M*, 320), δ($CDCl_3$) 7.25 (6 H, m, ArH) and 7.6 (10 H, s, ArH), identical (m.p., mixed m.p., and i.r. and n.m.r. spectra) with that obtained by heating 2-chloro-2-phenylacetophenone (0.05 mol) and 2-aminoquinoline (0.15 mol) to 130 °C for 3 h, dissolving the cooled melt in benzene, washing with water, evaporation, and crystallising the residue from aqueous methanol.

Pyrolysis of Butan-2-one 2-Quinolylhydrazone.—The 2-quinolylhydrazone (5 g) was pyrolysed in a similar way to that described above and also gave an oil and solid suspended in water, which were separated.

Addition of dilute hydrochloric acid to the oil gave a solid which was filtered off and crystallised from ethanol to give a yellow hydrochloride (0.8 g), m.p. 270—271° (Found: C, 66.9; H, 4.7; N, 17.4. Calc. for $C_{18}H_{14}N_4$,HCl: C, 67.0; H, 4.7; N, 17.4%. Found: *M*, 286. Calc. for $C_{18}H_{14}N_4$: *M*, 286), $\nu_{max.}$ 3 450 (NH) and 2 720 cm^{-1} (NH_3^+). Addition of aqueous ammonia to the acidic filtrate gave a precipitate of 2-aminoquinoline (0.5 g), m.p. 128—129°.

Extraction of the aqueous suspension with ether yielded red 2,2′-azoquinoline (1.4 g), m.p. 227—228° (lit.,[25] 230°) (Found: C, 75.8; H, 4.5; N, 19.6%; *M*, 286. Calc. for $C_{18}H_{12}N_4$: C, 76.1; H, 4.2; N, 19.7%; *M*, 286), identical with the 2,2′-azoquinoline obtained by the reaction of 2-chloroquinoline with 2-hydrazinoquinoline followed by aerial oxidation of the resulting hydrazo-compound in boiling water.[25]

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