Reissert Compound Chemistry. Part 5.[1] Formation of Pyrrolo[1,2-*a*]-quinolines and Pyrrolo[2,1-*a*]isoquinolines

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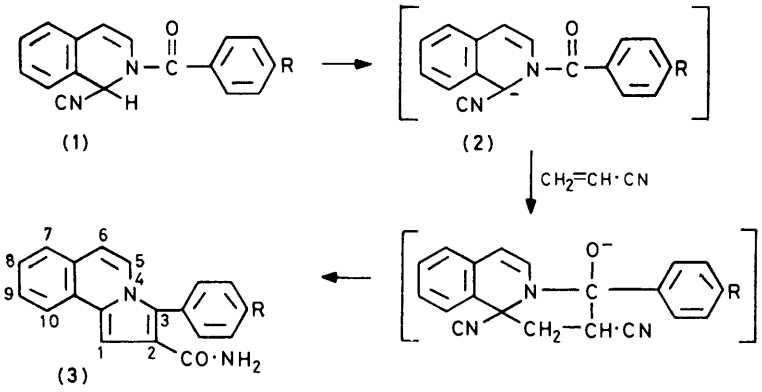
Treatment of a quinoline Reissert compound carrying a blocking group at the 4-position with base in the presence of acrylonitrile can lead in modest yield to the pyrrolo[1,2-*a*]quinoline system (8) and to an open chain ketone (11) derived *via* an intermediate tetrahydropyrrolo[1,2-*a*]quinoline. This behaviour contrasts with the more ready formation of the pyrrolo[2,1-*a*]isoquinoline system (3) by a similar process.

PYRROLO[2,1-*a*]ISOQUINOLINES [2] [*e.g.* (3)] can be synthesised [3] by condensation at 0 °C of acrylonitrile with an anion of the type (2) generated from an isoquinoline Reissert compound (1) by phenyl-lithium in ether–dioxan. Extension of this process to a quinoline Reissert compound would provide useful access to the analogous, but less well known,[4] pyrrolo[1,2-*a*]quinoline series. Boekelheide and Godfrey reported,[3] however, that use of these conditions with *N*-benzoyl-1,2-dihydroquinoline-2-carbonitrile (4; $R^1 = R^2 = H$, R = Ph) sert compound (4; $R^1 = H$, $R^2 = Me$, R = Ph) is known to give not a 4,4- but a 2,4-disubstituted product.[5b]

The anion from (4; $R^1 = H$, $R^2 = Me$, R = Ph) was generated by sodium hydride in dimethylformamide.[6] Addition of acrylonitrile at 0 °C resulted only in 2-benzoyl-4-methylquinoline (7; R = Ph). Such a 1,2-rearrangement *via* a Reissert compound anion is normally observed in the absence of a competing electrophile.[5b,7] In the case of alkylation we have observed that use of



gave a product corresponding only to simple cyanoethylation, although they did not establish whether the condensation had occurred at the 2-position or at the allylic 4-position of the quinoline ring. The latter site seems the more likely since, for example, we have observed that alkylation of the anion from 6-methylquinoline Reissert compound (4; $R^1 = Me$, $R^2 = H$, R = Ph) with methyl iodide gives the 4,6-dimethyl product (6; $R^1 = R^2 = Me$, $R^3 = H$).[5] The presence of allylic coupling of the 4-methyl group with the C-3 proton in the ^1H n.m.r. spectrum of (6; $R^1 = R^2 = Me$, $R^3 = H$) excludes the other possible structures (5; $R^1 = R^2 = Me$, $R^3 = H$) and (6; $R^1 = R^3 = Me$, $R^2 = H$).

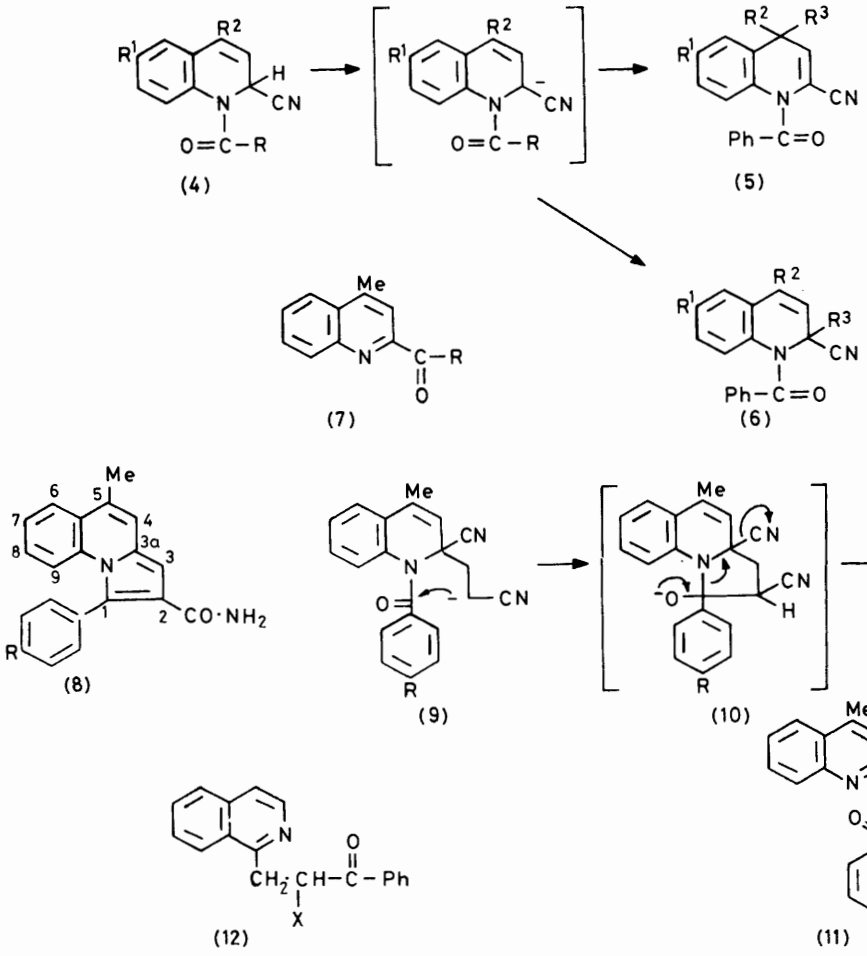
We have therefore re-examined the condensation of acrylonitrile with a quinoline Reissert compound, but with a blocking group at its 4-position. It was considered unlikely that a structure of type (5) would result since alkylation of the anion of 4-methylquinoline Reis-

low temperatures (0 °C or less) can suppress the rearrangement,[7] and we therefore repeated the procedure at −30 °C. Work-up provided a solid which crystallised from ethyl acetate as deep orange needles, m.p. 136—137 °C, and was identified as 5-methyl-1-phenylpyrrolo[1,2-*a*]quinoline-2-carboxamide (8; R = H). A two-proton ^1H n.m.r. signal at δ 6.55, removed by D_2O and i.r. bands at 3 435, 3 285, and 1 625 cm^{-1} confirmed that the nitrile had undergone hydrolysis to the amide. The remaining ^1H n.m.r. signals were in the aromatic region except that for the 5-methyl group at δ 2.47. The u.v. spectrum of (8; R = H) was similar to that of the pyrrolo[2,1-*a*]isoquinoline analogue (3; R = H), showing $\lambda_{max.}$ 260 (log ε 4.19), 291 (4.40), 370 (3.73), and 429 nm (3.91) [(3; R = H) shows $\lambda_{max.}$ 250 (4.46), 256sh, 298 (4.61), 381 (3.40), and 437 nm (3.45)]. The yield of the pyrrolo[1,2-*a*]quinoline (8; R = H) was 25%; some polymerisation, presumably of the acrylonitrile, had occurred.

On repeating the cyclisation but with the analogous

[1] Part 4, B. C. Uff, J. R. Kershaw, and S. R. Chhabra, *J.C.S. Perkin I*, 1974, 1146.
[2] W. L. Mosby, 'Heterocyclic Systems with Bridgehead Nitrogen Atoms,' Part 1, Interscience, New York, 1961, p. 344.
[3] V. Boekelheide and J. C. Godfrey, *J. Amer. Chem. Soc.*, 1953, **75**, 3679.
[4] Ref. 2, p. 335.
[5] See also (*a*) F. D. Popp and J. M. Wefer, unpublished work, cited in F. D. Popp, *Adv. Heterocyclic Chem.*, 1968, **9**, 12; (*b*) V. Boekelheide and J. Weinstock, *J. Amer. Chem. Soc.*, 1952, **74**, 660.
[6] B. C. Uff and J. R. Kershaw, *J. Chem. Soc.* (*C*), 1969, 666.
[7] B. C. Uff, J. R. Kershaw, and S. R. Chhabra, *J.C.S. Perkin I*, 1972, 479.

p-methoxyphenyl Reissert compound of 4-methylquinoline (4; R^1 = H, R^2 = Me, R = 4-MeO·C_6H_4) at −30 °C 1-(*p*-methoxyphenyl)-5-methylpyrrolo[1,2-*a*]quinoline-2-carboxamide (8; R = OMe) was obtained, as ochre needles, in only 2% yield. Accompanying it, also in low yield, was a second product of the same molecular weight. This showed a nitrile i.r. absorption at 2 250 cm^{-1} and a carbonyl band at 1 660 cm^{-1}, and we assign it

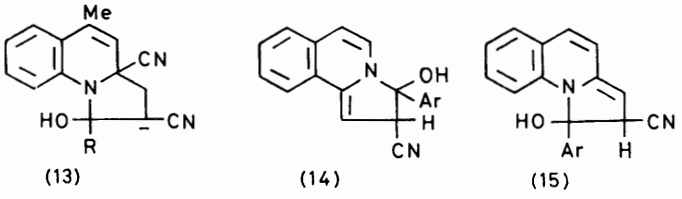


structure (11; R = OMe), in accord with other spectroscopic data.

Compound (11; R = OMe) could arise by cyclisation *via* (9; R = OMe) to the intermediate tetrahydropyrrolo[1,2-*a*]quinoline (10; R = OMe), followed by fragmentation in the manner shown. When the reaction was conducted at room temperature the ' ring-opened ' compound (11; R = OMe) was not isolated, the only material obtained being (7; R = 4-MeO·C_6H_4), product of a 1,2-rearrangement. Formation of a ketone analogous to (11) has been observed in the isoquinoline series. Addition of ethyl acrylate to the anion (2) gives compound (12; X = CO_2Et); addition of 2-vinylpyridine gives the ketone (12; X = 2-pyridyl).[3]

To progress from the intermediate (10) to the ring-opened product (11) does not require intervention of a proton source, in contrast to the pathway to the pyrrolo[1,2-*a*]quinoline (8). In the aprotic sodium hydride–dimethylformamide system this latter pathway may be achieved by an equilibration of (10) with (13). However employment of a base–solvent system such as sodamide in liquid ammonia, from which protons could be abstracted, might encourage pyrrolo[1,2-*a*]quinoline formation at the expense of the fragmentation sequence.

Under these conditions the pyrrolo[1,2-*a*]quinoline (8; R = OMe) was obtained in the improved yield of 20%, and (8; R = H) was formed in only 10% yield. Again polymerisation was evident, and in the hope of



reducing this we examined the less nucleophilic[8] base potassium t-butoxide.

As its use in t-butyl alcohol alone proved unsatisfactory on solubility grounds, dimethyl sulphoxide was employed

[8] D. E. Pearson and C. A. Buehler, *Chem. Rev.*, 1974, **74**, 45; J. Wemple, *Tetrahedron Letters*, 1975, 3255.

as solvent, bearing in mind that 1 mol. equiv. of t-butyl alcohol would be produced *in situ* on initial carbanion formation. Application to the isoquinoline series at room temperature gave yields of up to 90% of pyrrolo-[2,1-*a*]isoquinolines (3; R = H, OMe, or Me). However, use of the quinoline Reissert compound (4; R^1 = H, R^2 = Me, R = Ph) under the same conditions resulted in only 1,2-rearrangement to (7; R = Ph) and no cyclisation. In dimethylformamide at −40 °C use of t-butoxide was more satisfactory, giving 5-methyl-1-phenylpyrrolo[1,2-*a*]quinoline-2-carboxamide (8; R = H) in 20% yield.

Even under these conditions the pathway to the ring-opened structure (11) evidently had similar energy requirements to the route to (8), since use of t-butoxide–dimethylformamide at −40 °C with (4; R^1 = H, R^2 = Me, R = 4-MeC_6H_4) and (4; R^1 = H, R^2 = Me, R = 4-MeO·C_6H_4) gave (11; R = Me) and (11; R = OMe) in yields of 46 and 40%, respectively.

Thus the apparent reluctance of the reactions to provide the fully aromatic pyrrolo[1,2-*a*]quinolines in more than modest yield contrasts with the pyrrolo[2,1-*a*]isoquinoline formation; this difference seems not to be due only to reaction conditions. Models show that if loss of cyanide precedes dehydration in the aromatisation of the five-membered ring, the isoquinoline-derived intermediate (14) benefits considerably more from resonance stabilisation than does the quinoline-derived analogue (15), owing to a much greater twisting out of plane of the conjugated system in the latter case; this may be a critical factor.

EXPERIMENTAL

N.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32 instrument. Light petroleum was dried over sodium wire, and dimethylformamide over molecular sieves (Union Carbide, type 4A); dimethyl suphoxide was distilled from calcium hydride and stored over molecular sieves. Tetrahydrofuran and t-butyl alcohol were distilled from lithium aluminium hydride and calcium hydride, respectively, prior to use.

N-Benzoyl-4,6-dimethyl-1,2-dihydroquinoline-2-carbonitrile (6; R^1 = R^2 = Me, R^3 = H).—A suspension of sodium hydride (1.5 g, 0.062 5 mol) [from a 60% suspension in oil, washed with dry light petroleum (b.p. 40—60 °C)] in dry dimethylformamide (125 ml) was stirred at 0 °C under nitrogen. *N*-Benzoyl-6-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = Me, R^2 = H, R = Ph) (15 g, 0.054 7 mol), m.p. 147—149 °C (lit.,[9] 144 °C) (from ethyl acetate), in dry dimethylformamide (75 ml) was added and a deep red colour developed with evolution of hydrogen. After about 15 min methyl iodide (8.514 g, 0.06 mol) was added during 0.5 h. The mixture was stirred for a further 0.5 h at 0 °C and overnight at room temperature, after which its colour was pale yellow. Ethanol was added to destroy the excess of sodium hydride and most of the solvent was evaporated off under reduced pressure. The residue was suspended in water and extracted with chloroform. The extracts were combined, washed with dilute hydrochloric acid, dried (K_2CO_3), and evaporated. Column chromatography of the resulting red oil on neutral alumina with toluene–ethyl acetate (4 : 1) gave a pale yellow solid (5 g, 40%). Recrystallisation from ethyl acetate afforded *N*-benzoyl-4,6-dimethyl-1,2-dihydroquinoline-2-carbonitrile (6; R^1 = R^2 = Me, R^3 = H) as colourless rhombs, m.p. 132—134 °C (lit.,[9] 130—131 °C), $\nu_{max.}$ 2 240 (CN), 1 660 (N–C=O), and 1 600 cm^{-1} (C=C), δ 7.5—6.4 (8 H, m, aromatic), 6.1 (1 H, d, 2-H $J_{2,3}$ 7 Hz), 5.85 (1 H, q, 3-H, $J_{2,3}$ 7 Hz, $J_{3\text{-H},4\text{-Me}}$ 1.3 Hz), 2.28br (3 H, s, 6-Me), and 2.18 (3 H, d, 4-Me, $J_{4\text{-Me},3\text{-H}}$ 1.3 Hz).

Preparation of 4-Methylquinoline Reissert Compounds.—4-Methylquinoline, b.p. 87—89 °C at 1.2 mmHg, n_D^{20} 1.619, was prepared in bulk from aniline hydrochloride and methyl vinyl ketone by the method of Campbell and Schaffner.[10] By the general procedure of Popp and Blount,[11] the following Reissert compounds were prepared: *N*-benzoyl-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = Ph), m.p. 174—175 °C (lit.,[9] 173—175 °C); *N*-(*p*-methoxybenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeO·C_6H_4), m.p. 157—158 °C (lit.,[12] 156—157 °C); *N*-(*p*-methylbenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeC_6H_4), m.p. 166—167 °C (lit.,[12] 166—167 °C).

Reaction of 4-Methylquinoline Reissert Compounds with Acrylonitrile.—(a) *With sodium hydride in dimethylformamide.* A suspension of sodium hydride (1.0 g, 0.04 mol) in dry dimethylformamide (50 ml) was stirred at 0 °C under nitrogen. *N*-Benzoyl-4-methyl-1,2-dihydroquinoline-2-carbonitrile (6.3 g, 0.023 mol) in dry dimethylformamide (30 ml) was aded dropwise during 5—10 min. The mixture was stirred for a further 15 min to allow complete formation of the Reissert anion (hydrogen was evolved). Acrylonitrile (2.2 g, 0.04 mol) in dry dimethylformamide (20 ml) was added dropwise during 5 min. The mixture was stirred for a further 3 h at 0 °C and then allowed to warm to room temperature. Most of the dimethylformamide was distilled off under reduced pressure. Water (100 ml) was added and the pH adjusted to 7 with dilute hydrochloric acid. Extraction with chloroform and evaporation of the extract after washing with dilute hydrochloric acid and water and drying (K_2CO_3), gave a dark red oil. Column chromatography on neutral alumina [toluene–ethyl acetate (4 : 1) as eluant] and recrystallisation from ethyl acetate gave 2-benzoyl-4-methylquinoline (14%) (7; R = Ph) as colourless rhombs, m.p. 112—113 °C (lit.,[13] 109 °C), $\nu_{max.}$ 1 660 cm^{-1} (C=O), δ 8.4—7.5 (10 H, m, aromatic) and 2.79br (3 H, s, 4-Me), *m/e* 247 ($M^{+\cdot}$ and 105 ($C_6H_5CO^+$).

Use of *N*-(*p*-methoxybenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeO·C_6H_4) at room temperature similarly gave 2-(p-*methoxybenzoyl*)-4-*methylquinoline* (7; R = *p*-MeO·C_6H_4) (50%) as yellow needles, m.p. 121—122 °C (from methanol) (Found: C, 78.1; H, 5.5; N, 5.1. $C_{18}H_{15}NO_2$ requires C, 78.0; H, 5.5; N, 5.1%), $\nu_{max.}$ 1 655 cm^{-1} (C=O), δ 8.5—7.0 (9 H, m, aromatic), 3.95 (3 H, s, *p*-OMe), and 2.73br (3 H, s, 4-Me), *m/e* 277 ($M^{+\cdot}$) and 135 (*p*-MeO·$C_6H_4^+$).

The previous experiments were repeated at −30 °C.

[9] F. D. Popp, W. Blount, and P. Melvin, *J. Org. Chem.*, 1961, **26**, 4930.
[10] K. N. Campbell and I. J. Schaffner, *J. Amer. Chem. Soc.*, 1945, **67**, 86.
[11] F. D. Popp and W. Blount, *Chem. and Ind.*, 1961, 550.
[12] B. C. Uff and H. N. Burdess, unpublished work.
[13] R. F. Knott, J. Circe, and J. G. Breckenridge, *Canad. J. Chem.*, 1953, **31**, 615.

Condensation of *N*-benzoyl-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = Ph) with acrylonitrile gave *5-methyl-1-phenylpyrrolo*[1,2-a]*quinoline-2-carboxamide* (8; R = H) (25%) as deep orange needles, m.p. 136—137 °C (from ethyl acetate) (Found C, 79.9; H, 5.3; N, 9.1. $C_{20}H_{16}N_2O$ requires C, 80.0; H, 5.4; N, 9.3%), $\nu_{max.}$ 3 435 and 3 285 (NH_2) and 1 625 cm^{-1} (N–C=O), δ 8.5—6.75 (11 H, m, aromatic), 6.55br (2 H, exchangeable, NH_2), and 2.47br (3 H, s, 5-Me), $\lambda_{max.}$ 260 (log ε 4.19), 291 (4.40), 370 (3.73), and 429 nm (3.91), *m/e* 300.

Use of *N*-(*p*-methoxybenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeO·C_6H_4) under the same conditions gave a dark red oil on evaporation of the chloroform. T.l.c. showed two major components. These were separated by elution from neutral alumina with toluene–ethyl acetate (4 : 1). Evaporation of the first fraction, R_F [ethyl acetate–toluene [1 : 1)] 0.55 on alumina, gave 1-(p-*methoxyphenyl*)-5-*methylpyrrolo*[1,2-a]*quinoline-2-carboxamide* (8; R = MeO) (2%) as ochre needles (from ethyl acetate), m.p. 135—136 °C (Found C, 75.8; H, 5.5; N, 8.4. $C_{21}H_{18}N_2O_2$ requires C, 76.3; H, 5.5; N, 8.5%), $\nu_{max.}$ 3 360 and 3 255 (NH_2) and 1 615 cm^{-1} (N–C=O), δ 8.6—6.5 (10 H, m, aromatic), 6.41br (2 H, s, exchangeable, NH_2), 3.97 (3 H, s, *p*-OCH_3), and 2.41br (3 H, s, 5-Me), $\lambda_{max.}$ 263 (log ε 4.13), 298 (4.28), 380 (3.87), and 432 nm (4.06), *m/e* 330. Evaporation of the second fraction, R_F [ethyl acetate–toluene (1 : 1)] 0.15 on alumina, gave 2-[β-*cyano*-β-(p-*methoxybenzoyl*)*ethyl*]-4-*methylquinoline* (11; R = OMe) (5%), as pale yellow rhombs, m.p. 133—134 °C (from ethyl acetate) (Found C, 76.0; H, 5.5; N, 8.2. $C_{21}H_{18}N_2O_2$ requires C, 76.3; H, 5.5; N, 8.5%), $\nu_{max.}$ 2 250 (CN) and 1 660 cm^{-1} (C=O), δ 8.2—6.8 (9 H, m, aromatic), 5.45 (1 H, t, β-H, $J_{\beta\text{-H},\alpha\text{-H}}$ 7 Hz), 3.86 (1 H, q, α-H, $J_{\alpha\text{-H}_2\text{-}gem}$ 16, $J_{\alpha\text{-H},\beta\text{-H}}$ 7 Hz), 3.85 (3 H, s, *p*-OCH_3), 3.51 (1 H, q, α-H, $J_{\alpha\text{-H}_2\text{-}gem}$ 16, $J_{\alpha\text{-H},\beta\text{-H}}$ 7 Hz), and 2.62br (3 H, s, 4-Me), *m/e* 330.

(b) *Use of sodamide in liquid ammonia.* *N*-(*p*-Methoxybenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeO·C_6H_4) (5 g, 0.016 4 mol) in dry tetrahydrofuran (75 ml) was added dropwise to a solution of sodium (1.0 g) in liquid ammonia containing a catalytic amount of iron(III) chloride. A dark red colour developed. After stirring for a further 15 min, a solution of acrylonitrile (3.75 g, 0.07 mol) in dry tetrahydrofuran (25 ml) was added during 5 min. Stirring was continued for a further 2 h, after which ammonium chloride (3 g) was added and the mixture was left overnight. Evaporation left a red-brown solid. This was suspended in water and extracted with chloroform. The combined organic extracts were washed with 50% hydrochloric acid and water, dried (K_2CO_3), and evaporated to a red oil. Column chromatography on neutral alumina and crystallisation from ethyl acetate gave 1-(*p*-methoxyphenyl)-5-methylpyrrolo[1,2-*a*]-quinoline-2-carboxamide (8; R = OMe) (20%), identical (i.r. and n.m.r. spectra) with the sample described above.

Use of *N*-benzoyl-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = Ph) similarly gave 1-phenyl-5-methylpyrrolo[1,2-*a*]quinoline-2-carboxamide (8; R = H) (10%) as orange needles, m.p. 136—137 °C (from ethyl acetate), identical (i.r. and n.m.r. spectra) with the sample described above.

(c) *Use of potassium t-butoxide.* White powdered potassium t-butoxide was prepared by adding potassium (1.06 g, 0.027 3 mol) to dry t-butyl alcohol (30 ml) and heating under reflux under nitrogen until all the metal was dissolved. The t-butyl alcohol was distilled off and the white solid was heated to an oil-bath temperature of 150 °C at 0.1 mmHg for 2 h. Dry dimethyl sulphoxide (75 ml) was added after cooling and the mixture was stirred to produce a suspension under nitrogen at room temperature. *N*-Benzoyl-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = Ph) (5 g, 0.018 2 mol) in dry dimethyl sulphoxide (25 ml) was added dropwise over 5 min, resulting in a dark red colour. After stirring for a further 5 min, acrylonitrile (1.466 g, 0.027 mol) was added. The mixture was stirred for a further 1 h and most of the dimethyl sulphoxide was evaporated off under reduced pressure. The residue was suspended in water and extracted with chloroform after adjusting to neutral pH. Evaporation of the extract after washing with water and drying (K_2CO_3) gave 2-benzoyl-4-methylquinoline (7; R = Ph) (0.6 g, 13%) as colourless rhombs, m.p. 112—114 °C (from ethyl acetate). This compound had i.r. and n.m.r. spectra identical with those of the sample described above, and the mixed m.p. was undepressed.

The latter reaction was repeated with potassium t-butoxide in dimethylformamide at −40 °C under nitrogen. Evaporation, and column chromatography of the resulting red oil on neutral alumina gave 1-phenyl-5-methylpyrrolo-[1,2-*a*]-quinoline-2-carboxamide (8; R = H) (20%) as orange needles, m.p. 136—137 °C (from ethyl acetate), identical (i.r. and n.m.r. spectra) with the sample described previously.

On repeating the above reaction with *N*-(*p*-methoxybenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeO·C_6H_4), the only product isolated was 2-[β-cyano-β-(*p*-methoxybenzoyl)ethyl]-4-methylquinoline (11; R = OMe) (46%), m.p. 133—134 °C, identical (i.r. and n.m.r. spectra) with the previously prepared compound.

Use of the above procedure with *N*-(*p*-methylbenzoyl)-4-methyl-1,2-dihydroquinoline-2-carbonitrile (4; R^1 = H, R^2 = Me, R = *p*-MeC_6H_4) and acrylonitrile gave 2-(β-*cyano*-β-p-*methylbenzoylethyl*)-4-*methylquinoline* (11; R = Me) (40%) as pale yellow rhombs, m.p. 124—126 °C (from ethyl acetate) (Found C, 80.0; H, 5.7; N, 8.9. $C_{21}H_{18}N_2O$ requires C, 80.2; H, 5.8; N, 8.9%), $\nu_{max.}$ 2 245 (CN) and 1 695 cm^{-1} (C=O), δ 8.1—7.1 (9 H, m, aromatic), 5.48 (1 H, t, β-H, $J_{\beta\text{-H},\alpha\text{-H}}$ 7 Hz), 3.85 (1 H, q, α-H, $J_{\alpha\text{-H}_2\text{-}gem}$ 15, $J_{\alpha\text{-H},\beta\text{-H}}$ 7 Hz), 3.50 (1 H, q, α-H, $J_{\alpha\text{-H}_2\text{-}gem}$ 15, $J_{\alpha\text{-H},\beta\text{-H}}$ 7 Hz), 2.65br (3 H, s, 4-Me), and 2.42br (3 H, s, *p*-Me).

Reaction of Isoquinoline Reissert Compounds with Acrylonitrile using Potassium t-Butoxide. White powdered potassium t-butoxide (0.02 mol) was prepared as described above. Dry dimethyl sulphoxide (75 ml) was added after cooling and the mixture was stirred to produce a suspension under nitrogen at room temperature. *N*-Benzoyl-1,2-dihydroisoquinoline-1-carbonitrile (1; R = H) (5 g, 0.018 3 mol) dissolved in dry dimethyl sulphoxide (25 ml) was added dropwise over 5 min. After stirring for a further 5 min, acrylonitrile (2.9 g, 0.054 7 mol) was added. The mixture was stirred for a further 20 min and most of the dimethyl sulphoxide was evaporated off under reduced pressure. The residue was suspended in water and extracted with chloroform after adjusting to neutral pH. Evaporation of the extract after washing with water and drying (K_2CO_3) gave 3-phenylpyrrolo[2,1-*a*]isoquinoline-2-carboxamide (3; R = H). Crystallisation from benzene–light petroleum (b.p. 60—80 °C) (9 : 1) gave red rhombs (2.8 g, 64%), m.p.

168—169 °C (lit.,[3] 168—169 °C), $\lambda_{max.}$ 250 (log ε 4.46), 256sh, 298 (4.61), 381 (3.40), and 437 nm (3.45).

N-(*p*-Methoxybenzoyl)-1,2-dihydroisoquinoline-1-carbonitrile (1; R = OMe) and acrylonitrile by this method gave 3-(*p*-methoxyphenyl)pyrrolo[2,1-*a*]isoquinoline-2-carboxamide (3; R = OMe) as greenish yellow rhombs, m.p. 174—175 °C (90%) from benzene–light petroleum (b.p. 60—80 °C) (9 : 1) (Found: C, 75.8; H, 4.9; N, 8.8. $C_{20}H_{16}N_2O_2$ requires C, 75.9; H, 5.1; N, 8.9%), $\nu_{max.}$ 3 300 and 3 400 (NH_2) and 1 640 cm^{-1} (N–C=O), δ 8.0—6.5 (11 H, m, aromatic) and 3.91 (3 H, s, *p*-OMe), *m/e* 316, $\lambda_{max.}$ 258 (log ε 4.10), 296 (4.51), 370 (3.87), and 427 nm (3.90).

N-(*p*-Methylbenzoyl)-1,2-dihydroisoquinoline-1-carbonitrile (1; R = Me) with acrylonitrile under similar conditions afforded the analogous 3-(p-*methylphenyl*)*pyrrolo*[2,1-a]-*isoquinoline*-2-*carboxamide* (3; R = Me) as brownish orange needles (58%), m.p. 209—210 °C (from benzene) (Found: C, 80.2; H, 5.4; N, 9.4. $C_{20}H_{16}N_2O$ requires C, 80.0; H, 5.4; N, 9.3%), $\nu_{max.}$ 3 400 and 3 300 (NH_2) and 1 640 cm^{-1} (N–C=O), δ 8.0—6.5 (11 H, m, aromatic), 7.94br (2 H, s, NH_2), and 2.46br (3 H, s, *p*-Me), *m/e* 300, $\lambda_{max.}$ 256 (log ε 4.12), 294 (4.51), 369 (3.80), and 428 nm (3.83).

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