Acyliminium Ion Cyclisations to Pyrrolo- and Pyrido-[1,2-*f*]phenanthridine and Benzo[*de*]pyrrolo[2,1-*a*]isoquinoline Ring Systems

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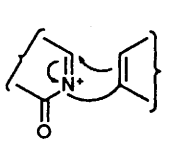
Pyrrolo- and pyrido-[1,2-*f*]phenanthridines and benzo[*de*]pyrrolo[2,1-*a*]isoquinolines are obtained by acid-catalysed cyclodehydration of appropriate hydroxy lactams and keto amides derived from *N*-substituted succinimide and glutarimide derivatives.

In previous syntheses of pyrido[1,2-*f*]phenanthridine derivatives, the additional pyridine ring was elaborated onto a preformed phenanthridine.[1] Also, pyrrolo- and pyrido-[1,2-*f*]phenanthridine derivatives are among the products obtained from phenanthridine, 6-methylphenanthridine, and its 5-oxide with acetylenic esters.[2] We wished to test an alternative approach involving the versatile method of acyliminium ion cyclisation (see structure **1**)[3] for the construction of fused heterocyclic systems containing a bridgehead nitrogen. More specifically, this approach follows that of our earlier synthesis of isoindolo[2,1-*f*]phenanthridines **2**,[4] and other examples in which the C=C bond undergoing cyclisation in structure **1** is part of an aromatic ring.[5] Although reactions of this kind have been reported with intermediates derived from succinimides and glutarimides,[3,6–8] they have not previously been applied to the synthesis of those fused heterocyclic systems which are described herein.



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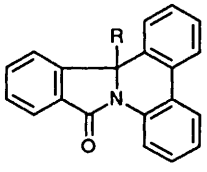
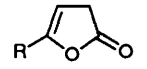


2

$PhCO[CH_2]_nCO_2H$

3a; $n = 3$
b; $n = 2$



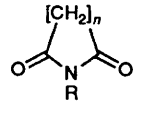
4a; R = Me
b; R = Ph

$PhCO[CH_2]_nCONHR$

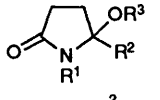
5a; $n = 3$, R = *o*-PhC_6H_4
b; $n = 2$, R = *o*-PhC_6H_4
c; $n = 2$, R = $PhCH_2$
d; $n = 2$, R = α-$C_{10}H_7CH_2$

o-$PhC_6H_4NHCO[CH_2]_nOH$

6a; $n = 4$
b; $n = 3$



7a; $n = 3$, R = *o*-PhC_6H_4
b; $n = 2$, R = *o*-PhC_6H_4
c; $n = 2$, R = $PhCH_2$
d; $n = 2$, R = α-$C_{10}H_7CH_2$



8a; R^1 = *o*-PhC_6H_4, R^2 = Me, R^3 = H
b; R^1 = *o*-PhC_6H_4, $R^2 = R^3$ = H
c; $R^1 = PhCH_2$, R^2 = H, R^3 = Et
d; R^1 = α-$C_{10}H_7CH_2$, $R^2 = R^3$ = H
e; R^1 = α-$C_{10}H_7CH_2CH_2$, $R^2 = R^3$ = H

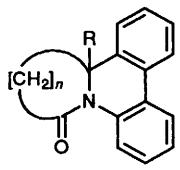
Results and Discussion

The requisite precursors for cyclisation *via* acyliminium ion intermediates were keto amides **5** or hydroxy lactam derivatives **8**, in which the hydroxy group is α to the nitrogen. These were variously obtained starting from keto acids **3**, enol lactones **4**, or appropriate *N*-substituted imides **7**, as described in the Experimental section. The result of heating of the keto amide **5b** in polyphosphoric acid (PPA) was a double cyclisation in 62% yield to give the pyrrolo[1,2-*f*]phenanthridine **9b**, analogous to the formation of compound **2** (R = Ph).[4] In the same way, the homologous keto amide **5a** was cyclised to the pyrido[1,2-*f*]-phenanthridine **9a**, which was also obtained in a single step (27% yield) from keto acid **3a** and *o*-aminobiphenyl in hot PPA.

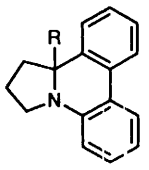
The hydroxy lactam **8a** was obtained either by Grignard addition to the succinimide **7b** or by heating α-angelicalactone **4a** with *o*-aminobiphenyl. Heating of lactam **8a** in PPA afforded the pyrrolo[1,2-*f*]phenanthridine **9c** (75%). Reduction of the same imide **7b** with sodium borohydride in the presence of acid, the method developed by Speckamp and co-workers,[9] gave a mixture of the desired hydroxy lactam **8b** (48%) and by-product amido alcohol **6b** (40%). The latter is the result of ring-opening and over-reduction of imide **7b**, which is a common side-reaction occurring with *N*-aryl imides.[9–11] Reduction of *N*(*o*-biphenylyl)glutarimide **7a** under similar conditions afforded only the corresponding open-chain product **6a**, a result which is consistent with the greater ease of ring-opening of the 6-membered in comparison with the 5-membered cyclic imide. Cyclodehydration of the hydroxy lactam **8b** in PPA gave the tetracyclic lactam **9d**. Lithium aluminium hydride reduced lactams **9a** and **9b** to the tertiary amines **10a** and **10b**, respectively; as compound **10a** was a somewhat air-sensitive oil, it was characterised as the picrate.

Sodium borohydride reduction of the *N*-benzylic substituted succinimides **7c** and **7d** was uncomplicated by ring-opening. The hydroxy lactam **8d** was obtained from imide **7d** by using alkaline conditions for work-up, and the ethoxy lactam **8c** from imide **7c** using acidic conditions for work-up. No cyclisation to pyrrolo[2,1-*a*]isoindole derivatives **12** was observed on acid treatment of lactam **8c** or of the related keto amide **5c** under conditions of varying severity, despite the presence of a phenyl group to stabilise the iminium ion intermediate (**11**; R = Ph) derived from keto amide **5c**. These and other examples[5,11] reflect the general difficulty of 5-*endo-trigonal* cyclisation of an *N*-benzyliminium ion (**11**). The only products detected, but incompletely characterised, were compound **13** and a dimeric product from lactam **8c** on heating in trifluoroacetic acid (TFA). The structure of the dimer is probably **14** on analogy with others already known.[9,12]

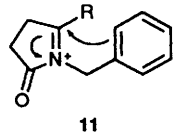
On the other hand, an alternative 6-*endo-trigonal* cyclisation (to the naphthalene 8-position) is available in an intermediate iminium ion containing an *N*-α-naphthylmethyl group. Thus, the keto amide **5d** and the related hydroxy lactam **8d** underwent cyclodehydration in refluxing TFA to give the benzo[*de*]pyrrolo[2,1-*a*]isoquinoline derivatives **15a** and **15b**, respectively. These structures are analogous to those of



9a; $n = 3$, R = Ph
b; $n = 2$, R = Ph
c; $n = 2$, R = Me
d; $n = 2$, R = H



10a; R = H
b; R = Pn



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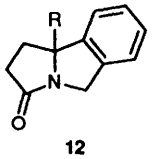

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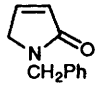

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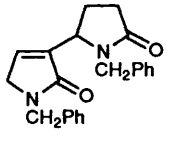

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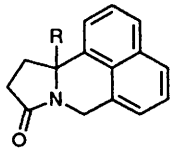
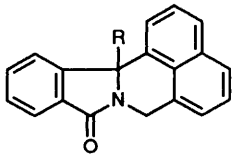
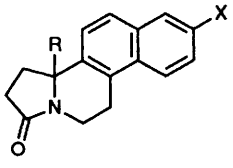


15a; R = Ph
b; R = H



16a; R = Ph
b; R = H



17a; X = H
b; X = OMe

products (**16a**, **b**) obtained in the same way from precursors derived from *N*-(α-naphthylmethyl)phthalimide.[5] In contrast, the hydroxy lactam **8e**, the homologue of **8d**, is reported to undergo cyclisation to the naphthalene 2-position to give compound **17a**.[6]

Three groups of resonances for the aryl hydrogen atoms were clearly resolved in the 300 MHz ^{1}H NMR spectrum of compound **15b**. By comparison with the spectrum of 1,8-dimethylnaphthalene,[13] these could be assigned to 1-H and 6-H (δ 7.25–7.33, two doublets), 2-H and 5-H (δ 7.42–7.51, two *pseudo*-triplets), and 3-H and 4-H (δ 7.72–7.77, two overlapping doublets), respectively. Appropriate selective NMR decoupling experiments confirmed the correctness of these assignments and hence of the 1,8-naphthalene substitution pattern in structure **15b**. Irradiation at the frequency of the resonance assigned to 1-H caused collapse of the 2-H resonance to a doublet; similarly irradiation of the 6-H resonance caused collapse of the 5-H resonance to a doublet, but no other changes in the NMR spectrum. Characteristically, the most abundant ion-peaks in the mass spectra of compounds **15a** and **15b** and of the other fused heterocyclic compounds **9a–d** were always due to loss of the atom or group at the ring junction adjacent to nitrogen. For this reason, the elemental composition of tetracycles **9d** and **15b** was confirmed by high-resolution measurement of *m/z* for the ion $[M - H]^+$.

Experimental

IR spectra were recorded for Nujol mulls and calibrated with polystyrene (Pye-Unicam 1025 and SP3-200 and Perkin-Elmer 257 and 1420 spectrophotometers). ^{1}H NMR spectra were recorded at 60 (Varian EM360-A), 90 (JEOL-JNM-FX90Q), or 300 (Bruker MSL300) and ^{13}C NMR spectra at 22.5 MHz (JEOL-JNM-FX90Q) for solutions in [^{2}H]chloroform (unless otherwise stated) with tetramethylsilane as internal standard. *J*-Values are given in Hz. Mass spectra were obtained by electron impact at 70 eV (Kratos MS30). Preparative TLC (PLC) was performed on silica-coated plates by using centrifugal assistance to achieve radial separation (Chromatron), whereby all new compounds were obtained chromatographically pure. Light petroleum refers to the fraction boiling in the range 40–60 °C. Diethyl ether and tetrahydrofuran (THF) for Grignard reactions were dried before use.

Keto Amides **5a–d**.—*o*-Aminobiphenyl (1.4 g) and 5-oxo-5-phenylpentanoic acid **3a** (1.6 g) were heated together at 150 °C for 2.5 h. The mixture was cooled, dissolved in chloroform, and washed successively with dil. hydrochloric acid and aq. sodium hydrogen carbonate. After evaporation of the chloroform, the crude product was redissolved in ethanol and boiled with addition of charcoal; the solution was filtered and the filtrate was evaporated to dryness; the residue afforded the *keto amide* **5a** (0.2 g), m.p. 74–78 °C (from toluene–light petroleum) (Found: M^+, 343.1570. $C_{23}H_{21}NO_2$ requires M, 343.1572); ν_{max}/cm^{-1} 3220br (NH) and 1680 and 1640 (C=O); ^{1}H and ^{13}C NMR spectra were complicated by the effects of restricted rotation of the *N*-*o*-biphenylyl group; *m/z* 343 (M^+, <1%), 192 (7), 169 (4), 120 (12), 105 (100) and 77 (31).

o-Aminobiphenyl (1.8 g) and 5-phenylfuran-2(3*H*)-one **4b** (1.7 g) were heated togethet at 100 °C for 1 h. The melt was cooled and the resulting solid was crushed, and washed successively with dil. hydrochloric acid and water, then recrystallised to give the *keto amide* **5b** (2.5 g, 71%), m.p. 132–133 °C (from MeOH) (Found: C, 79.9; H, 5.8; N, 4.6. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.3%); ν_{max}/cm^{-1} 3260 (NH) and 1690 and 1665 (C=O); δ_H[($^2H_3C)_2SO$] 2.58 and 3.26 (each 2 H, t, CH_2), 7.2–8.1 (14 H, m, ArH) and 9.30 (1 H, s, NH); *m/z* 329 (M^+, 8%), 170 (14), 169 (100), 161 (53), 105 (28) and 77 (21).

A solution of *N*-benzylsuccinimide **7c** (0.20 g) in dry THF (5 cm^3) was added to the Grignard reagent prepared from bromobenzene (0.33 g) and magnesium (0.05 g) in dry diethyl ether (4 cm^3). The mixture was stirred at room temperature for 24 h. Aq. ammonium chloride was added; the organic layer was separated and evaporated to dryness; the residue was chromatographed and eluted with ethyl acetate–chloroform (1:4 v/v) to give the *keto amide* **5c** (0.23 g, 81%), m.p. 108.5–110 °C (from EtOH) (Found: M^+, 267.1256. $C_{17}H_{15}NO_2$ requires *M*, 267.1259); ν_{max}/cm^{-1} 3300 (NH) and 1690 and 1635 (C=O); δ_H 2.67 and 3.38 (each 2 H, t, *J* 7, CH_2CO), 4.42 (2 H, d, *J* 5.5, CH_2N), 6.33 (1 H, br, NH), 7.2–7.7 (6 H, m, ArH) and 7.9–8.1 (2 H, m, ArH); *m/z* 267 (M^+, 5%), 189 (19), 161 (15), 132 (10), 106 (100), 105 (39), 91 (35) and 77 (60).

A solution of *N*-(α-naphthylmethyl)succinimide **7d** (0.20 g) in dry THF (4 cm^3) was added to the Grignard reagent prepared from bromobenzene (0.26 g) and magnesium (0.04 g) in dry diethyl ether (5 cm^3). The mixture was stirred at room temperature for 23 h, then acidified with dil. hydrochloric acid. The organic layer was separated and evaporated to dryness. The residue was chromatographed and eluted with ethyl acetate–chloroform (1:3 v/v) to give the *keto amide* **5d** (0.23 g, 91%), m.p. 129–131 °C (from EtOH) (Found: M^+, 317.1452. $C_{21}H_{19}NO_2$ requires *M*, 317.1452); ν_{max}/cm^{-1} 3295 (NH) and 1680 and 1640 (C=O); δ_H 2.60 and 3.33 (each 2 H, t, *J* 6.5, CH_2CO), 4.88 (2 H, d, *J* 5.5, CH_2N), 6.19 (1 H, br t, NH) and 7.25–8.06 (12 H, m, ArH);

m/z 317 (M^+, 12%), 239 (6), 156 (100), 149 (16), 141 (28), 105 (19) and 77 (22).

Imides **7a–d**.—The general method was to treat equimolar quantities of glutaric or succinic anhydride with the appropriate amine in refluxing THF or toluene, then to dehydrate the resulting amido acid by heating it in refluxing acetic anhydride or by heating it alone until a condensate of water was seen on a cold surface above the heated sample. Imides **7a–c** obtained by this procedure had m.p., after recrystallisation, in agreement with lit. values.[14,15]

Sodium hydride (0.58 g) was added to a solution of succinimide (2.0 g) in anhydrous *N,N*-dimethylformamide (DMF) (20 cm^3) at 0 °C and the mixture was stirred for 2.5 h while it was allowed to warm to room temperature. A solution of 1-(chloromethyl)naphthalene (3.3 g) in DMF (10 cm^3) was added and the mixture was stirred for 14 h, diluted with chloroform, and extracted with water; the chloroform extract was then dried ($MgSO_4$) and evaporated to dryness; the residue afforded the imide **7d** (3.36 g, 70%), m.p. 103–104 °C (from EtOH); ν_{max}/cm^{-1} 1770 and 1695 (C=O); δ_H 2.48 (4 H, s, ring CH_2), 4.95 (2 H, s, CH_2N) and 7.15–8.37 (7 H, m, ArH); *m/z* 239 (M^+, 100%), 210 (29), 183 (19), 182 (15), 167 (15), 154 (22) and 141 (18).

Hydroxy and Ethoxy Lactams **8a–d**.—*o*-Aminobiphenyl (1.2 g) and angelicalactone **4a** (0.7 g) were heated together at 100 °C for 1.5 h. The mixture was cooled, and triturated with diethyl ether; the resulting solid was filtered off and recrystallised from toluene to give 1-(o-*biphenylyl*)-5-*hydroxy*-5-*methylpyrrolidin*-2-*one* **8a** (0.5 g, 28%), m.p. 113–115 °C (Found: C, 76.3; H, 6.4; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.3%); ν_{max}/cm^{-1} 3400br (OH) and 1680br (C=O); δ_H 0.77 and 1.27 (together 3 H, 2 s, Me of two rotamers), 1.5–2.8 (4 H, m, 2 × CH_2), 3.9 (1 H, br, OH, exchangeable), and 7.30 and 7.38 (9 H, 2 s, ArH); δ_C 26.0 (q, Me), 29.4 and 34.8 (2 t, CH_2), 91.5 (s, C-5), 127.3–131.1 (7 lines, ArCH), 132.9, 139.7 and 142.5 (3 s, ArC), 177.1 (s, CO) and several less intense lines attributable to the minor rotamer; *m/z* 267 (M^+, 25%), 249 (22), 234 (14), 169 (100) and 99 (13).

The other compounds (**8b–d**) were prepared by the following general procedure. The appropriate imide was dissolved or suspended in ethanol, cooled, and stirred with addition of an excess of sodium borohydride and of 10 drops of either hydrochloric or toluene-*p*-sulfonic acid (PTSA) (2 mol dm^{-3} in ethanol). Further acid was added at the rate of 1 drop every 5 min during the reaction time and at the temperature stated. 'Basic work-up' involved pouring the reaction mixture into an excess of aq. sodium hydrogen carbonate and extraction with dichloromethane; the extract was washed successively with dil. hydrochloric acid and aq. sodium hydrogen carbonate, dried ($MgSO_4$), and filtered, and the filtrate was evaporated under reduced pressure. Alternatively, 'acidic work-up' involved the addition of more ethanolic acid until the pH of the solution was <2, then allowing the mixture to warm to room temperature and to stand for 48 h, after which it was poured into an excess of saturated aq. sodium hydrogen carbonate and the organic product(s) was(were) extracted into dichloromethane or chloroform, as above for 'basic work-up'. The residue left after evaporation of solvent was purified by PLC, and the following products were obtained.

From the imide **7a** (0.20 g) and sodium borohydride (0.15 g) in ethanol (75 cm^3) with addition of PTSA (2 mol dm^{-3} in ethanol) and acidic work-up after reaction for 5.5 h at −20 °C; elution with chloroform–ethyl acetate (1:1 v/v) gave only N-(o-*biphenylyl*)-5-*hydroxypentanamide* **6a** (0.19 g, 96%) as a viscous oil (Found: M^+, 269.1412. $C_{17}H_{19}NO_2$ requires *M*, 269.1416); ν_{max}/cm^{-1} 3260–3420br (OH) and 1665 (C=O); δ_H 1.30–1.70 (4 H, m, 2 × CH_2), 2.19 (2 H, t, *J* 6.3, CH_2CO), 3.02 (1 H, s, OH), 3.49 (2 H, t, *J* 6.3, CH_2OH), 7.01–7.56 (9 H, m, ArH) and 8.09 (1 H, s, NH); *m/z* 269 (M^+, 11%), 169 (100) and 168 (64).

From the imide **7b** (0.50 g) and sodium borohydride (0.52 g) in ethanol (75 cm^3) with addition of hydrochloric acid (2 mol dm^{-3} in ethanol) and basic work-up after reaction for 7 h at −30 °C; chloroform–ethyl acetate (1:1 v/v) eluted first 1-(o-*biphenylyl*)-5-*hydroxypyrrolidin*-2-*one* **8b** (0.24 g, 48%), m.p. 148–149 °C (from toluene–light petroleum) (Found: C, 75.9; H, 5.9; N, 5.55%; M^+, 253.1089. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%; *M*, 253.1103); ν_{max}/cm^{-1} 3220 (OH) and 1675 (C=O); δ_H 1.55–2.75 (4 H, m, 2 × CH_2), 3.89 (1 H, d, *J* 6, OH), 4.70 (1 H, br s, 5-H) and 7.35 (9 H, br s, ArH); *m/z* 253 (M^+, 100%), 252 (43), 236 (29), 206 (18), 180 (58), 170 (25), 169 (61), 168 (32), 167 (27), 154 (35) and 152 (22).

Further elution afforded N-(o-*biphenylyl*)-4-*hydroxybutanamide* **6b** (0.20 g, 40%), m.p. 82.5–84 °C (from toluene–light petroleum) (Found: C, 75.3; H, 6.7; N, 5.5. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); ν_{max}/cm^{-1} 3350br (OH), 3230br (NH) and 1680 (C=O); δ_H 1.85 (2 H, quintet, *J* 6, CH_2CH_2OH), 2.30 (2 H, t, *J* 6, CH_2CO), 3.60 (2 H, t, *J* 6, CH_2OH), 7.10–7.60 (9 H, m, ArH) and 8.17 (1 H, br s, OH); *m/z* 255 (M^+, 16%), 169 (100), 168 (32) and 167 (25).

From the imide **7c** (0.20 g) and sodium borohydride (0.20 g) in ethanol (70 cm^3) with addition of PTSA (2 mol dm^{-3} in ethanol) and acidic work-up after reaction for 5 h at 0 °C; chloroform–ethyl acetate (1:1 v/v) eluted 1-*benzyl*-5-*ethoxypyrrolidin*-2-*one* **8c** (0.20 g, 85%) as an oil (Found: M^+, 219.1255. $C_{13}H_{17}NO_2$ requires *M*, 219.1259); ν_{max}/cm^{-1} 1700 (C=O); δ_H 1.17 (3 H, t, *J* 7, Me), 1.85–2.80 (4 H, m, 2 × CH_2), 3.39 (2 H, q, *J* 7, CH_2Me), 4.03 and 4.91 (each 1 H, d, *J* 15, CH_2N), 4.70 (1 H, m, 5-H) and 7.24 (5 H, s, ArH); *m/z* 219 (M^+, 9%), 174 (20), 146 (22), 104 (18) and 91 (100).

From the imide **7d** (0.30 g) and sodium borohydride (0.34 g) in ethanol (75 cm^3) with addition PTSA (2 mol dm^{-3} in ethanol) and basic work-up after reaction for 4.5 h at 0 °C; diethyl ether eluted 5-*hydroxy*-1-(α-*naphthylmethyl*)*pyrrolidin*-2-*one* **8d** (0.26 g, 86%), m.p. 140–143 °C (from toluene–light petroleum) (Found: M^+, 241.1105. $C_{15}H_{15}NO_2$ requires *M*, 241.1103); ν_{max}/cm^{-1} 3275br (OH) and 1675 (C=O); δ_H 1.60–2.80 (4 H, m, 2 × CH_2), 4.52 and 5.29 (each 1 H, d, *J* 15.5, CH_2N), 4.93 (1 H, br t, *J* 7.5, 5-H), 6.25 (1 H, d, *J* 7.5, OH) and 7.40–8.45 (7 H, m, ArH); *m/z* 241 (M^+, 9%) 223 (28), 154 (10), 142 (19), 141 (100) and 115 (18).

Pyrido- and Pyrrolo-[1,2-f]-*phenanthridines* **9** *and* **10**.—The keto amide **5a** (72 mg) was dissolved in PPA (10 g) and the solution was heated at 150 °C for 1 h, then at 170 °C for 15 min. The mixture was cooled, stirred with ice–water, and extracted with chloroform. The extract was washed with aq. sodium hydrogen carbonate, dried ($MgSO_4$), then filtered, and the filtrate was evaporated to dryness. PLC of the residue with chloroform as developer afforded 11,12,13,13a-*tetrahydro*-13a-*phenylpyrido*[1,2-f]*phenanthridin*-10-*one* **9a** (24 mg, 35%), m.p. 192–194 °C (from toluene–light petroleum) (Found: M^+, 325.1451. $C_{23}H_{19}NO$ requires *M*, 325.1466); ν_{max}/cm^{-1} 1660 (C=O); δ_H 1.85–3.02 (6 H, m, 3 × CH_2) and 6.95–7.89 (13 H, m, ArH); *m/z* 325 (M^+, 8%), 256 (15), 248 (M − Ph, 22), 93 (40) and 91 (100). The same product (**9a**) (0.15 g, 27%) was also obtained by heating *o*-aminobiphenyl (0.30 g) and 5-oxo-5-phenylpentanoic acid **3a** (0.37 g) in PPA (10 g) at 150 °C for 2.5 h, followed by work-up as above.

The keto amide **5b** (3.0 g) was dissolved in PPA (45 g) and heated to 200 °C for 45 min. The mixture was cooled and poured onto stirred, crushed ice; then, after storage for 1 h, the orange precipitate was collected, washed with water, and recrystallised several times from aq. acetic acid with addition of charcoal to afford 12,12a-*dihydro*-12a-*phenylpyrrolo*[1,2-f]-

phenanthridin-10(11H)-*one* **9b** (1.75 g, 62%), m.p. 220–222 °C (Found: C, 84.8; H, 5.4; N, 4.5. $C_{22}H_{17}NO$ requires C, 84.9; H, 5.5; N, 4.5%); ν_{max}/cm^{-1} 1695 (C=O), 1600 and 1490; δ_H 2.2–2.8 (4 H, m, 2 × CH_2) and 6.7–8.3 (13 H, m, ArH); δ_C 24.4 and 29.4 (2 t, CH_2) 61.8 (s, C-12b), 115.6–136.9 (12 lines, aromatic carbons) and 168.1 (s, CO); *m/z* 311 (M^+, 13%), 235 (17), 234 (M − Ph, 100), 233 (10) and 206 (10).

This lactam **9b** (0.5 g) was heated with lithium aluminium hydride (0.2 g) in dry THF (10 cm^3) under reflux for 17 h. The mixture was cooled, aq. ammonium chloride (10%) was added, the mixture was filtered, the filtrate was evaporated to dryness, and the residue was recrystallised to give 10,11,12,12a-*tetrahydro*-12a-*phenylpyrrolo*[1,2-f]*phenanthridine* **10b** (0.16 g, 34%), needles, m.p. 170–172 °C (from $CHCl_3$–MeOH) (Found: C, 88.9; H, 6.4; N, 4.7. $C_{22}H_{19}N$ requires C, 89.0; H, 6.4; N, 4.7%); δ_H 2.02, 2.72 and 3.70 (each 2 H, m, CH_2) and 6.8–7.8 (13 H, m, ArH); *m/z* 297 (M^+, 10%), 221 (18), 220 (M − Ph, 100) and 217 (14). Solutions of **10b** developed a blue colour on storage.

The hydroxy lactam **8a** (0.90 g) was heated with PPA (15 g) at 150 °C for 45 min, then at 170 °C for 15 min. The mixture was cooled, poured onto crushed ice, and extracted with diethyl ether. The extract was separated, washed, dried, and evaporated under reduced pressure. The residue afforded 12,12a-*dihydro*-12a-*methylpyrrolo*[1,2-f]*phenanthridin*-10(11H)-*one* **9c** (0.63 g, 75%), m.p. 164–165 °C (from toluene–light petroleum, then from CCl_4) (Found: C, 82.0; H, 6.1; N, 5.5. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.1; N, 5.6%); ν_{max}/cm^{-1} 1690 (C=O); δ_H 1.32 (3 H, s, Me), 2.3–2.8 (4 H, m, 2 × CH_2), 7.0–7.4 and 7.6–7.9 (7 H, m, ArH) and 8.28 (1 H, dd, *J* 7 and 2, 8-H); *m/z* 249 (M^+, 11%), 235 (18), 234 (M − CH_3, 100), 206 (13) and 178 (14).

The hydroxy lactam **8b** (0.50 g) was heated with PPA (30 g) at 150 °C for 1 h, then at 170 °C for 15 min. After the usual work-up procedure and PLC with chloroform–ethyl acetate (1:1 v/v) as developer, the *pyrrolo*[1,2-f]*phenanthridin*-10-*one* **9d** (0.39 g, 84%) was obtained as a solid which darkened on exposure to air, more rapidly in solution (Found: M^+ − 1, 234.0921. $C_{16}H_{12}NO$ requires *m/z*, 234.0919); ν_{max}/cm^{-1} 1780 (C=O); δ_H 2.18–2.94 (4 H, m, 2 × CH_2), 5.05 (1 H, m, 12a-H) and 7.09–7.47, 7.68–7.88 and 8.28–8.41 (5 H, 2 H and 1 H, respectively, m, ArH); *m/z* 235 (M^+, 73%), 234 (100), 180 (38) and 179 (28).

Reduction of compound **9d** with lithium aluminium hydride (0.24 g) in dry THF (45 cm^3) heated under reflux for 46 h, followed by work-up with aq. sodium hydroxide and extraction of organic material into chloroform, gave 10,11,12,12a-tetrahydropyrrolo[1,2-f]phenanthridine **10a** as a greenish oil, which with saturated ethanolic picric acid gave a red precipitate of the *picrate*, m.p. 184–189 °C (decomp.) (from water) (Found: C, 58.3; H, 3.9; N, 12.3. $C_{22}H_{18}N_4O_7$ requires C, 58.7; H, 4.0; N, 12.4%); ^1H and ^{13}C NMR spectra in $(^2H_3C)_2CO$ confirmed the presence of three CH_2 groups, but the 12a-H and C-12a resonances were obscured by absorptions due to the solvent.

Benzo[de]*pyrrolo*[2,1-a]*isoquinolines* **15**.—The keto amide **5d** (57 mg) was dissolved in TFA (4 cm^3) and the solution was heated under reflux for 5.8 h; the mixture was then cooled and worked up as described above. PLC with chloroform–ethyl acetate (3:1 v/v) afforded 11,11a-*dihydro*-11a-*phenylbenzo*[de]-*pyrrolo*[2,1-a]*isoquinolin*-9(7H,10H)-*one* **15a** (35 mg, 62%), m.p. 177–179 °C (from EtOH) (Found: M^+, 299.1312. $C_{21}H_{17}NO$ requires *M*, 299.1310); ν_{max}/cm^{-1} 1675 (C=O); δ_H 2.40–3.10 (4 H, m, 2 × CH_2), 4.16 and 5.37 (each 1 H, d, *J* 16.5, CH_2N) and 6.72–7.92 (11 H, m, ArH); *m/z* 299 (M^+, 25%), 223 (15) and 222 (M − Ph, 100).

The hydroxy lactam **8d** (112 mg) was dissolved in TFA (4 ml) and the solution was heated under reflux for 5 h. The mixture was cooled, poured into an excess of saturated aq. sodium hydrogen carbonate, and extracted with chloroform. The extract was washed, dried, filtered, and evaporated to dryness, and the residue was purified by PLC (ethyl acetate). The product **15b** (67 mg, 65%) darkened on exposure to air (Found: M − 1, 222.0917. $C_{15}H_{12}NO$ requires *m/z*, 222.0919); δ_H 2.00–3.02 (4 H, m, 2 × CH_2), 4.38 and 5.38 (each 1 H, d, *J* 17.2, CH_2N), 5.04 (1 H, t, *J* 7.0, 11a-H) and 7.16–7.85 (6 H, m, ArH); *m/z* 223 (M^+, 66%), 222 (100), 167 (29) and 166 (20).

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