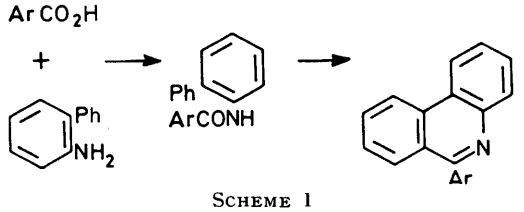
Preparation of Some Isoindolo[2,1-*f*]phenanthridine Derivatives

By **Munir Ahmed** and **John M. Vernon,*** Department of Chemistry, University of York, Heslington, York YO1 5DD

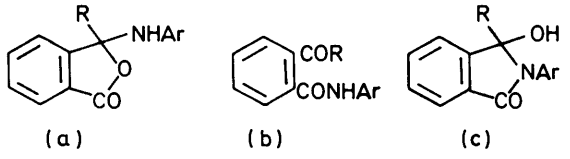
3-*o*-Biphenylylaminophthalide derivatives on treatment with hot phosphoric trichloride or polyphosphoric acid are converted by rearrangement and cyclodehydration into isoindolo[2,1-*f*]phenanthridin-10(14b*H*)-ones. Some other synthetic approaches to this new ring system are explored. The ψ-chloride obtained from 2-(6-phenanthridyl) benzoic acid (26) is also an isoindolo[2,1-*f*]phenanthridine derivative; some of its reactions give ring-opened products related to the acid (26).

PHENANTHRIDINES are most commonly synthesised from *o*-substituted biphenyls,[1-3] and cyclodehydration of *o*-benzamidobiphenyl derivatives in strongly acidic conditions has been widely used to prepare 6-arylphenanthridines (Scheme 1). If one starts from an *o*-acylbenzoic acid, the situation is complicated by ring–chain tautomerism of the intermediate *N*-*o*-biphenylylamide, *e.g.* (1a—c),[4] and a different cyclisation occurs to give isoindolo[2,1-*f*]phenanthridin-10-one derivatives. We describe the characterisation of several compounds containing this new fused heterocyclic system.

When the oxo-amide (2b) or its cyclic tautomer (2a) was heated in phosphoric trichloride, dehydration occurred to give the fused phenanthridine derivative (7) rather than 2-(6-phenanthridyl)benzophenone (25) as expected according to Scheme 1. The same product (7) was also obtained in one step, but in lower yield, from *o*-benzoylbenzoic acid and *o*-aminobiphenyl in hot polyphosphoric acid.[5] Similarly, treatment of the phthalaldehydic acid derivative (1a) with polyphosphoric acid or of compound (4) with phosphoric trichloride afforded the cyclised products (6) and (5), respectively. Two of these new products, (7) and (5), are isomeric with compound



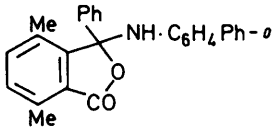
SCHEME 1



(1) R = H, Ar = *o*-PhC_6H_4
(2) R = Ph, Ar = *o*-PhC_6H_4
(3) R = Ar = Ph

(25) and a dimethyl derivative, respectively, which we had previously obtained [6] as the end-products of photochemical autoxidation of some polysubstituted isoindoles.

A variety of evidence from spectra and reactions fully supports the identification of the above products as the isoindolo[2,1-*f*]phenanthridin-10(14b*H*)-one



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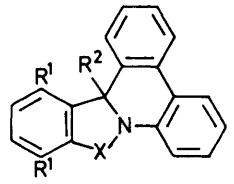
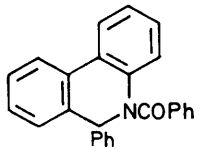


(5) R^1 = Me, R^2 = Ph, X = CO
(6) R^1 = R^2 = H, X = CO
(7) R^1 = H, R^2 = Ph, X = CO
(8) R^1 = H, R^2 = Cl, X = CO
(9) R^1 = H, R^2 = OMe, X = CO
(10) R^1 = R^2 = H, X = CH_2
(11) R^1 = H, R^2 = Ph, X = CH_2
(12) R^1 = H, R^2 = Ph, X = CPh(OH)



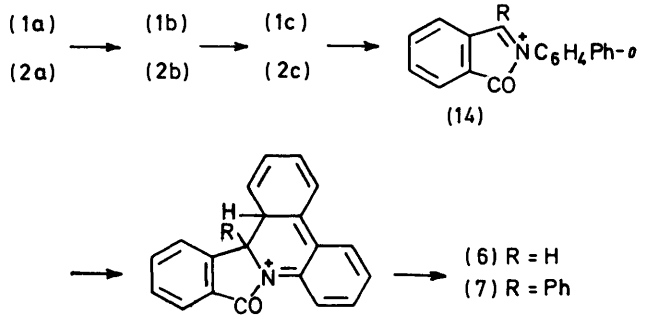
(13)

derivatives (5)—(7). All three compounds showed i.r. absorption for a lactam carbonyl group (*ca.* 1 700 cm^{-1}) but not the weaker absorption for a ring vibration (effectively that of the C=N bond, *ca.* 1 610 cm^{-1}), which is usually shown by phenanthridine derivatives [*cf.* the i.r. spectra of compounds (28) and (29) in the Experimental section and of others in ref. 6]. For both compounds (6) and (7) the most intense peak in the mass spectrum was at *m/e* 282, which is attributable to formation of the 10-oxoisoindolo[2,1-*f*]phenanthridinylium ion (30). Compound (5) showed the same mass spectral fragmentation, losing the 14b-bridgehead phenyl group from its molecular ion. The u.v. spectrum of compound (7) [$\lambda_{max.}$ (MeOH) 263 and 300sh nm (ε 273 and 68 m^2 mol^{-1})] resembles that of the known [7] 5-benzoyl-5,6-dihydro-6-phenylphenanthridine (13) [$\lambda_{max.}$ (MeOH) 262 nm (ε 253 m^2 mol^{-1})], which was prepared for comparison.

[1] L. P. Walls in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1952, vol. 4, ch. 4.
[2] R. S. Theobald and K. Schofield, *Chem. Rev.*, 1950, **46**, 171.
[3] B. R. T. Keene and P. Tissington, *Adv. Heterocyclic Chem.*, 1971, **13**, 315, and references therein.
[4] M. Ahmed and J. M. Vernon, *J.C.S. Perkin I*, 1975, 2048.
[5] *Cf.* the synthesis of 6-phenylphenanthridine in one step from benzoic acid and *o*-aminobiphenyl: B. Staskun, *J. Org. Chem.*, 1964, **29**, 2856.
[6] M. Ahmed, L. J. Kricka, and J. M. Vernon, *J.C.S. Perkin I*, 1975, 71.
[7] J. J. Eisch and R. M. Thompson, *J. Org. Chem.*, 1962, **27**, 4171.

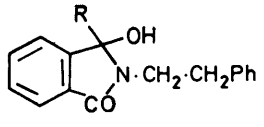
The lactam (7) reacted with aluminium lithium hydride and with phenyl-lithium to give the oxygen-free base (11) and the carbinolamine (12), respectively. Their characterisation by analysis and spectra is given in the Experimental section.

Formation of the isoindolo[2,1-*f*]phenanthridinine derivatives (6) and (7) is best explained as outlined in Scheme 2. Thus, we have already shown [4] that the oxo-amide (2b) forms the cyclic tautomer (2c) in solutions in inert solvents and that the *ψ*-anilide (3a) of *o*-benzoylbenzoic acid is converted to the corresponding open chain oxo-amide (3b) by being heated in phosphoric trichloride and then quenched with water. [Cyclisation to a phenanthridine derivative requires an *N*-*o*-biphenylyl substituent, which is lacking in (3a—c).] The intense

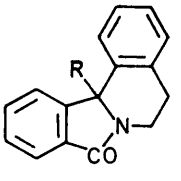


SCHEME 2

red colours observed during the reactions leading to compounds (6) and (7) may be due to intermediate iminium ions (14) (Scheme 2) [*cf.* the red chloride (30) described below]. Analogous cyclisations of *N*-(2-phenylethyl)-*ψ*-amides (15) and (16) in concentrated sulphuric acid have been reported [8] to give the isoindolo-[1,2-*a*]isoquinoline derivatives (17) and (18), respectively.

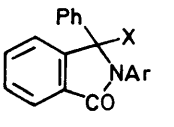


(15) R = H
(16) R = Ph

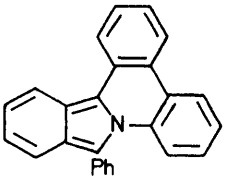


(17) R = H
(18) R = Ph

Since compounds (5)—(7), (11), and (12) appear to be the first isoindolo[2,1-*f*]phenanthridine derivatives to be described, some alternative approaches to the synthesis of this new ring system were briefly explored. One such attempt involved u.v. irradiation of bromine and the phthalimidine derivative (19) with the expectation of forming the bromide (20), which might cyclise to structure (7) by either a free radical or a polar mechanism. The reaction apparently stopped at the bromide (20), and this was converted into the lactam ether (21) by methanol used for recrystallisation. Spectroscopic evidence for the assignment of structure (21) is presented in the Experimental section. The same compound was obtained independently by recrystallisation of the open-chain oxo-amide (2b) from methanol–chloroform containing hydrochloric acid [*cf.* the formation of the related lactam ether (22) from (3b) [4]].



(19) Ar = *o*-PhC_6H_4, X = H
(20) Ar = *o*-PhC_6H_4, X = Br
(21) Ar = *o*-PhC_6H_4, X = OMe
(22) Ar = Ph, X = OEt



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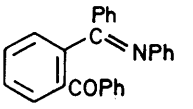
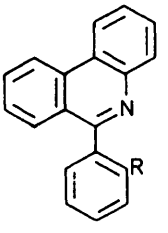


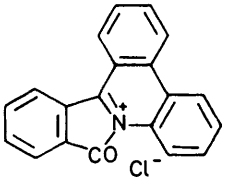
(24)

The same phthalimidine derivative (19) was heated in phosphoric trichloride in an attempt to induce cyclodehydration to structure (23). Unexpectedly 2-(6-phenanthridyl)benzophenone (25) was obtained in very low yield from this reaction, but its formation is presumably the result of autoxidation of the desired heterocycle (23). The relationship between 1,2,3-triphenylisoindole and the first product (24) of its autoxidation [6] is exactly the same as that between structures (23) and (25).

Instead of trying to build a phenanthridine ring system onto an isoindole or phthalimidine starting material, the opposite approach was examined, starting with some 5- or 6-substituted phenanthridines. *N*-Benzylphenanthridinium bromide did not cyclise to structure (10) in hot nitrobenzene, and a related attempt to obtain (11) by using 6-phenyl-phenanthridine and benzyl bromide was no more successful. On the other hand, 2-(6-phenanthridyl)benzoic acid (26) provided another convenient route



(25) R = COPh
(26) R = CO_2H
(27) R = COCl
(28) R = CO_2Me
(29) R = $CPh_2(OH)$



(30)

to the isoindolo[2,1-*f*]phenanthridine ring system and to compound (7) in particular.

When 2-(6-phenanthridyl)benzoic acid (26) was heated in thionyl chloride, a red compound was obtained, which reacted with water to regenerate the acid (26) and an

[8] M. Winn and H. E. Zaugg, *J. Org. Chem.*, 1968, **33**, 3779.

equimolar amount of chloride ion. This compound is formulated as 10-oxoisoindolo[2,1-*f*]phenanthridinylium chloride (30) to account for the u.v.-visible absorption spectrum [$\lambda_{max.}$ (H_2SO_4) 341, 366, and 490 nm (ε 668, 596, and 223 m^2 mol^{-1}, respectively)] and the i.r. absorption for the carbonyl group ($\nu_{max.}$ 1 805 cm^{-1}).† ‡

The red chloride (30) was almost insoluble in non-polar solvents, and reactive to nucleophiles. Attempted recrystallisation from acetonitrile or dioxan caused the red colour to be discharged, but the recovered solid still contained 1 equiv. of ionisable chlorine. The i.r. absorption at 1 698 cm^{-1} suggests that this colourless compound is the lactam ψ-chloride (8) rather than the normal acid chloride (27).‡ Unlike the acid (26) from which it was derived, the ψ-chloride (8) dissolved in concentrated sulphuric acid with regeneration of the red colour of the ionic chloride (30). A solution of the ψ-chloride (8) in acetonitrile also developed a very similar red colour (broad absorption, $\lambda_{max.}$ *ca.* 480 nm) and carbonyl absorption ($\nu_{max.}$ 1 810 and 1 825sh cm^{-1}) due to (30) on addition of anhydrous aluminium chloride.

The red chloride (30) reacted with methanol to give the known ester (28). Since this compound shows an important mass spectral fragmentation involving direct loss of CO_2Me (as well as the stepwise loss of OMe followed by CO, supported by appropriate metastable peaks), an alternative formulation as the cyclic ψ-ester (9) is excluded. However, there is no evidence to implicate the occurrence of the normal acid chloride (27) in tautomeric equilibrium with either (30) or (8), since the products (26) and (28) can arise by nucleophilic attack of water or methanol, respectively, on the carbonyl group of (30) or (8). When the red chloride (30) was treated with an excess of phenyl-lithium, two phenyl groups were incorporated with formation of the carbinol (29), which was also synthesised directly from 2-(6-phenanthridyl)benzophenone (25) with phenyl-lithium. This carbinol (29) dissolved in concentrated sulphuric acid with an orange–red colour ($\lambda_{max.}$ 418 and 440sh nm), whereas the isomeric carbinolamine (12) gave a yellow solution.

A different phenylation of the red chloride (30) took place under Friedel–Crafts reaction conditions, whereby a phenyl group was introduced at the 14b-bridgehead to give the same lactam (7) as that obtained previously by a different route. This phenylation must involve attack on the 10-oxoisoindolo[2,1-*f*]phenanthridinylium ion (30), which is stabilised in the presence of aluminium chloride. The result provides confirmation of the structure (7) and an alternative route to this fused heterocyclic system, which we shall develop in future work.

† Paul and Chadha [9] report carbonyl absorptions at 2 100 and 2 000 cm^{-1} for the pyridine–benzoyl chloride complex. However, these authors represent the structure of the cation confusingly as [R–C≡O→py]$^+$, and not as *N*-benzoylpyridinium, which would be analogous to the more extensively conjugated cation (30).

‡ The carbonyl absorption of aromatic acid chlorides is typically >1 770 cm^{-1}, but with a weaker band at lower frequency which is ascribed to Fermi resonance.[10]

EXPERIMENTAL

I.r. spectra of solids were recorded for Nujol mulls and calibrated with polystyrene; absorptions are recorded only for the regions 3 500—3 000 and 2 000—1 500 cm^{-1}. ^1H N.m.r. spectra were recorded at 60 MHz for solutions in deuteriochloroform, or in other solvents specified, with tetramethylsilane as internal standard. Mass spectra were recorded with an A.E.I. MS12 instrument operating at 70 eV.

We have described elsewhere [4,6] the preparation of compounds (1)—(4), (19), (25), and (26).

11,14-*Dimethyl*-14b-*phenylisoindolo*[2,1-f]*phenanthridin*-10(14bH)-*one* (5).—The 3-*o*-biphenylylaminophthalide derivative (4) (0.31 g) in phosphoric trichloride was heated under reflux for 5 h. The phosphoric trichloride was evaporated off under reduced pressure. The residue was washed with aqueous sodium hydrogen carbonate and then extracted with ether. The extract was again washed with sodium hydrogen carbonate solution, then with water, dried (K_2CO_3), and evaporated. The residue afforded the *isoindolo*[2,1-f]*phenanthridin*-10-*one* (5) (0.11 g, 37%), m.p. 220—221° [from benzene–light petroleum (b.p. 60—80 °C)] (Found: C, 86.5; H, 5.8; N, 3.5. $C_{28}H_{21}NO$ requires C, 86.8; H, 5.5; N, 3.6%), $\nu_{max.}$ 1 698, 1 606, 1 590, and 1 510 cm^{-1}, τ (CCl_4) 2.0—3.1 (15 H, m, ArH) and 7.2 and 8.0 (each 3 H, s, CH_3), *m/e* 387 (M^+, 30%), 311 (26), 310 (*M* − Ph, 100), and 193.5 (4), *m** 248.3 (387 ⟶ 310).

Isoindolo[2,1-f]*phenanthridin*-10(14bH)-*one* (6).—Attempts to prepare compound (6) by the above method were unsuccessful. When either of the isomeric phthalaldehydic acid derivatives (1a and c) was heated in phosphoric trichloride, the solution rapidly turned dark red, then black, and no identified product was obtained on work-up.

Instead 3-*o*-biphenylylaminophthalide (1a) (3.0 g) in polyphosphoric acid (70 g) was heated at 110—120 °C for 2.5 h. After cooling, ice was added, and the mixture was extracted with ether. The ether layer was separated, washed repeatedly with aqueous sodium hydrogen carbonate and with water, dried ($MgSO_4$), and evaporated. The residue was recrystallised (chloroform–methanol) to give *isoindolo*[2,1-f]*phenanthridin*-10(14bH)-*one* (6) (0.3 g, 11%) as needles, m.p. 178—181° (Found: C, 84.7; H, 4.8; N, 4.9. $C_{20}H_{13}NO$ requires C, 84.8; H, 4.6; N, 4.9%), $\nu_{max.}$ 1 690, 1 600, and 1 588 cm^{-1}, τ 1.6—2.8 (12 H, m, ArH) and 4.18 (1 H, s, 14b-H), *m/e* 284 (12%), 283 (M^+, 65), 282 (*M* − H, 100), 255 (11), 254 (32), 253 (16), 252 (11), 251 (6), 149 (16), 141.5 (6), 133 (13), 127 (14), 121 (53), 120 (65), 105 (11), 97 (11), 95 (16), 93 (22), 92 (35), 91 (15), 83 (15), 81 (18), 69 (22), 67 (15), 65 (31), 57 (25), and 55 (30).

14b-*Phenylisoindolo*[2,1-f]*phenanthridin*-10(14bH)-*one* (7).—(i) *N*-*o*-Biphenylyl-*o*-benzoylbenzamide (2b) (1.5 g) in phosphoric trichloride was heated under reflux for 5.5 h. The excess of phosphoric trichloride was removed under reduced pressure, the residue was added to aqueous sodium hydrogen carbonate, and the mixture was stirred vigorously for 0.5 h. The solid product was filtered off, thoroughly washed with water, and dried. Recrystallisation (chloroform–ethanol) afforded the *isoindolo*[2,1-f]*phenanthridin*-10-*one* (7) (0.8 g, 56%), m.p. 222—225° (Found: C, 86.75; H, 4.9; N, 3.9. $C_{26}H_{17}NO$ requires C, 86.9; H, 4.8; N,

[9] R. C. Paul and S. L. Chadha, *Spectrochim. Acta*, 1966, **22**, 615.

[10] *Cf.* H. N. Al-Jallo and M. G. Jahloom, *Spectrochim. Acta*, 1972, **28A**, 1655; L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' 3rd edn., Chapman and Hall, London, 1975, p. 141.

3.9%), $\nu_{max.}$ 1 703 and 1 602 cm^{-1}, *m/e* 359 (M^+, 17%), 283 (24), 282 (M − Ph, 100), 254 (17), 253 (15), 252 (10), 251 (6), 179.5 (3), and 77 (10), *m** 228.8 (282 ⟶ 254) and 221.5 (359 ⟶ 282). The n.m.r. spectrum showed only absorptions at $\tau < 3.0$ (ArH).

(ii) The product (7) was also obtained (76% yield) by the same method but from 3-*o*-biphenylylamino-3-phenylphthalide (2a); its m.p. and i.r. spectrum were the same as those of the previous sample (Found: C, 86.6; H, 4.9; N, 3.8%).

(iii) Alternatively, *o*-benzoylbenzoic acid (3.0 g) and *o*-aminobiphenyl (2.24 g) in polyphosphoric acid (45 g) were heated at 200 °C for 45 min. After cooling, the mixture was stirred with ice and water; the water was decanted from a gum, which was then stirred with aqueous sodium hydrogen carbonate until there was obtained a solid removable by filtration. This solid was collected, washed, dried, and recrystallised to give the same product (7) (0.95 g, 20%), identified by comparison (m.p. and i.r. spectrum) with the previous sample.

(iv) The red chloride (30) obtained from 2-(6-phenanthridyl)benzoic acid (26) (5.0 g) with thionyl chloride (see below) was added in portions to a stirred mixture of anhydrous aluminium chloride (9.0 g) and dry benzene at 60 °C. Hydrogen chloride was evolved copiously. After addition was complete, the mixture was stirred for 1 h without being heated and then for 1 h at reflux temperature. It was cooled, and poured into ice and concentrated hydrochloric acid (4 ml). After thorough stirring, the organic layer was separated and washed with aqueous sodium hydrogen carbonate and with water and dried ($MgSO_4$). The benzene was evaporated off, and the residue was redissolved in hot methanol, from which compound (7) (1.8 g, 30%) crystallised on cooling; m.p. 220—223°, undepressed on admixture with the material obtained by method (i) (Found: C, 86.6; H, 5.0; N, 3.9%), i.r. spectrum identical with that of the previous sample.

10,14b-*Dihydro*-14b-*phenylisoindolo*[2,1-f]*phenanthridine* (11).—Compound (7) (1.0 g) and aluminium lithium hydride (0.2 g) in dry tetrahydrofuran were heated under reflux for 17 h. The mixture was cooled, and unchanged hydride was destroyed by careful addition of aqueous ammonium chloride (10%). The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue on recrystallisation (chloroform–methanol) afforded 10,14b-*dihydro*-14b-*phenylisoindolo*[2,1-f]*phenanthridine* (11) (0.3 g, 30%), m.p. 172° (Found: C, 90.2; H, 5.7; N, 4.0. $C_{26}H_{19}N$ requires C, 90.4; H, 5.5; N, 4.05%), $\nu_{max.}$ (C=O absent) 1 605 and 1 581 cm^{-1}, τ 2.1—3.3 (17 H, m, ArH) and 4.74 and 5.29 (each 1 H, d, J 13 Hz, AB pattern of CH_2), *m/e* 345 (M^+, 4%), 269 (21), 268 (M − Ph, 100), 267 (26), 266 (14), 265 (5), 239 (5), 172.5 (1), and 77 (4), *m** 208 (345 ⟶ 268) and 214.7 (266 ⟶ 239). The material turned pink on exposure to light.

10,14b-*Dihydro*-10,14b-*diphenylisoindolo*[2,1-f]*phenanthridin*-10-*ol* (12).—A solution of phenyl-lithium [prepared from redistilled bromobenzene (1.4 g) and lithium (0.1 g) in dry ether, under nitrogen] was filtered through glass wool to remove unchanged lithium and added slowly to a stirred suspension of compound (7) (1.57 g) in dry ether. The mixture was then heated under reflux for 1.5 h and cooled. Water was added cautiously to destroy unchanged phenyllithium; then the ether layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue was fractionally recrystallised (chloroform–methanol and dioxan–methanol) to separate starting material (7) (0.57 g), m.p. and mixed m.p. 220—223°, from the *carbinolamine* (12) (0.36 g, 30%), m.p. 237—239° (Found: C, 88.1; H, 5.2; N, 3.2. $C_{32}H_{23}O$ requires C, 87.8; H, 5.3; N, 3.2%), $\nu_{max.}$ 3 400 (O–H) (C=O absent) and 1 598 cm^{-1}, *m/e* 437 (M^+, 12%), 421 (8), 420 (10), 373 (33), 361 (25), 360 (M − Ph, 100), 345 (25), 344 (98), 343 (24), 342 (9), 341 (14), 282 (19), 267 (17), 266 (17), 256 (27), 254 (13), 105 (37), and 77 (23), *m** 296.5 (437 ⟶ 360).

2-o-*Biphenylyl*-3-*methoxy*-3-*phenylphthalimidine* (21).—A solution of 2-*o*-biphenylyl-3-phenylphthalimidine (19) (0.5 g) and bromine (0.4 g) in carbon disulphide (110 ml) was irradiated (water-cooled Hanovia medium-pressure mercury arc in Pyrex jacket) for 4.5 h. Unchanged bromine was removed by shaking with aqueous sodium sulphite, and the carbon disulphide layer was separated, washed with water, dried (K_2CO_3), and evaporated. The residue was triturated with ether and recrystallised (chloroform–methanol) to give the 3-*methoxyphthalimidine* (21) (0.2 g, 37%), m.p. 197—200° (Found: C, 82.3; H, 5.5; N, 3.6. $C_{27}H_{21}NO_2$ requires C, 82.8; H, 5.4; N, 3.6%), $\nu_{max.}$ 1 694 (lactam C=O), 1 611, 1 600, and 1 509 cm^{-1}, *m/e* 392 (18%), 391 (M^+, 62), 361 (29), 360 (M − OMe, 100), 314 (9), 282 (31), 254 (8), 225 (22), 209 (44), 195.5 (6), 165 (19), 153 (10), 152 (27), 151 (8), 105 (22), and 77 (16), *m** 331.5 (391 ⟶ 360), 229 (282 ⟶ 254), 221 (360 ⟶ 282), 129.5 (391 ⟶ 225), and 52.5 (105 ⟶ 77).

Concentrated hydrochloric acid was added dropwise to a solution of *N*-*o*-biphenylyl-*o*-benzoylbenzamide (2c) in chloroform–methanol, which was heated under reflux. On cooling this solution, the same product (21) was obtained (30% yield); m.p. 199—201°; its i.r. spectrum was identical with that of the previous sample (mixed m.p. 197—200°).

Attempted Cyclisation of 2-o-*Biphenylyl*-3-*phenylphthalimidine* (19).—The phthalimidine (19) (1.0 g) was heated in phosphoric trichloride and the mixture was worked up as described for the conversion of compounds (2a) and (2b) into compound (7). The crude solid product was redissolved in benzene and chromatographed on alumina (Laporte type H; deactivated with 10% of its weight of aqueous 10% acetic acid). Elution with benzene gave material which was recrystallised (ether, then methanol) to yield 2-(6-phenanthridyl)benzophenone (25) (30 mg, 3%), m.p. 158.5—161° (lit.,[6] 160—162°); its i.r. spectrum was identical with that of an authentic specimen of the ketone (25) and a mixed m.p. was undepressed.

Chloride of 2-(6-*Phenanthridyl*)*benzoic Acid*.—2-(6-Phenanthridyl)benzoic acid (26) (1.0 g) in redistilled thionyl chloride was heated under reflux for 3 h. The deep red solution was cooled, and thionyl chloride was evaporated off under reduced pressure, leaving red crystals of 10-*oxoisoindolo*[2,1-f]*phenanthridinylium chloride* (30) (1.0 g), m.p. 275°. Residual traces of thionyl chloride were removed by several times adding carbon tetrachloride (spectroscopic grade) and evaporating again under reduced pressure. The product (30) was stored in a desiccator; it decomposed on exposure to moisture or on attempted recrystallisation from a variety of solvents [Found: Cl, 11.0 (by titration, see below). $C_{20}H_{12}ClNO$ requires Cl, 11.2%], $\nu_{max.}$ 1 805s, 1 702w, and 1 611 cm^{-1}.

The red chloride (30) reacted with water to give the acid (26), m.p. and mixed m.p. 270—272°. After hydrolysis of (30) (72 mg) with distilled water, the precipitated acid (26) was filtered off and washed with more water. The combined filtrate and washings were neutralised with sodium

hydrogen carbonate, and the chloride ion content was estimated with silver nitrate (8.9 ml of 0.010N-solution).

The red colour of (30) survived one recrystallisation from dry dioxan, but attempted further recrystallisation from dioxan or acetonitrile gave colourless material, 14b-*chloro-isoindolo*[2,1-f]*phenanthridin*-10(14bH)-*one* (8), m.p. 268—271° (softening from 230°) [Found: Cl, 10.7% (by hydrolysis and titration, as described above)], $\nu_{max.}$ 1 925br, 1 698s, 1 638, 1 608, 1 515w, and 1 500w cm^{-1}. The m.p. of the chloride (8) and that of the acid (26) are very similar, and the i.r. spectrum recorded for (8) suggests that the sample may contain (26); however, the two compounds are clearly distinguished by the ionisable chlorine in (8) and by testing with concentrated sulphuric acid, in which only the chloride (8) dissolves to give an intense red colouration.

Methyl 2-(6-*Phenanthridyl*)*benzoate* (28).—The red chloride (30) (1.3 g) in methanol (15 ml) was set aside at room temperature until the colour faded to pale yellow. Methanol was removed under reduced pressure, the residue was redissolved in chloroform, and this solution was shaken with aqueous sodium hydrogen carbonate and with water, then dried ($MgSO_4$) and evaporated. The residue was recrystallised (methanol) to give the methyl ester (28) (0.8 g, 64%), m.p. 148.5—150° (lit.,[11] 150—151°) (Found: C, 80.7; H, 5.0; N, 4.4. Calc. for $C_{21}H_{15}NO_2$; C, 80.5; H, 4.8; N, 4.5%), $\nu_{max.}$ 1 715, 1 611, and 1 565br cm^{-1}, τ (CD_3OD) 0.8—2.2 (12 H, m, ArH) and 6.4 (3 H, s, CH_3), *m/e* 313 (M^+, 47%), 283 (26), 282 (M — OMe, 94), 255 (30), 254 (M — CO_2Me, 100), 253 (37), 252 (28), 251 (17), 128 (15), and 127 (12), *m** 228.8 (282 ⟶ 254) and 206 (313 ⟶ 254).

2-(6-*Phenanthridyl*)*phenyl*(*diphenyl*)*methanol* (29).—(i) A solution of phenyl-lithium [prepared from redistilled bromobenzene (0.9 g) and lithium (0.1 g) in dry ether] was filtered through glass wool to remove unchanged lithium and added slowly to a stirred suspension of 2-(6-phenanthridyl)benzophenone (25) (1.0 g) in dry ether. The light yellow solution was then heated under reflux for 1.5 h, and cooled; water was added and the ether layer was separated, washed again with water, dried ($MgSO_4$), and evaporated. The residue was recrystallised (chloroform–methanol) to give the *carbinol* (29) (0.87 g, 72%), m.p. 186—188° (Found: C, 87.75; H, 5.5; N, 3.1. $C_{32}H_{23}O$ requires C, 87.8; H, 5.3; N, 3.2%), $\nu_{max.}$ 3 200 (O–H) (C=O absent), 1 612, 1 600, 1 580, and 1 530 cm^{-1}, *m/e* 438 (20%), 437 (M^+, 58), 360 (M — Ph, 52), 344 (10), 282 (10), 256 (25), 255 (48), 254 (M — CPh_2OH, 100), 253 (13), 218.5 (3), 205 (7), 127 (5), 105 (23), and 77 (20), *m** 296.5 (437 ⟶ 360).

(ii) A solution of phenyl-lithium [from bromobenzene (2.3 g) and lithium (0.3 g) in dry ether] was added slowly to a stirred suspension of the red chloride (30) (4.0 g) in dry ether. The mixture was then stirred for 2 h at room temperature and heated under reflux for 1 h. It was filtered from some unchanged red chloride (30), and the filtrate was shaken with water; the ether layer was separated, dried ($MgSO_4$), and evaporated. The residue was recrystallised (methanol, then chloroform) to give the same carbinol (29) (0.54 g, 10%), m.p. 181—184°, with i.r. and mass spectra very similar to those of the sample obtained above; mixed m.p. 184—187°.

[6/1043 *Received*, 2*nd June*, 1976]

[11] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1936, **58**, 1325.