Photocyclisation of Enamides. Part IX.[1] Syntheses of Benzonaphthyridines by Photocyclisation of *N*-Pyridylcyclohex-1-enecarboxamides and Pyridine-(*N*-cyclohex-1-enyl)carboxamides

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The *N*-pyridylenamides (Ia—c) were photocyclised to afford equimolar mixtures of *cis*- and *trans*-lactams (IIa—d). Photocyclisation of the *N*-(pyridylcarbonyl)enamines (VIII)—(IX) gave products (X)—(XVI) with incorporation of solvent alcohol.

PREVIOUSLY we have described the stereoselective photocyclisation of *N*-acylanilides [2] as part of a study of enamide photochemistry. We now report an extension of this photocyclisation to *N*-pyridylenamides and *N*-(pyridylcarbonyl)enamine, thus providing a convenient route to a variety of benzonaphthyridine systems.

Photocyclisation of N-*Pyridylenamides.*—The *N*-pyridylenamides (Ia—c) were readily prepared by acylation of aminopyridines with cyclohex-1-enecarbonyl chloride.[5] Their structures were readily determined from their n.m.r. spectra, particularly from the presence of an olefinic proton signal at δ *ca.* 6.7—7.0 (this peak was used for checking whether photocyclisation had occurred). Ogata has reported the related photocyclisation of *N*-pyridylacrylamides.[3]

Irradiation of the *N*-pyridylenamides (Ia—c) was carried out in solution, as described previously,[2] with a 120 W low-pressure mercury lamp at room temperature. The reaction was monitored by t.l.c. and g.l.c. The

[1] Part VIII, I. Ninomiya, T. Naito, and H. Takasugi, *J.C.S. Perkin I*, 1975, 1791.

[2] I. Ninomiya, S. Yamauchi, T. Kiguchi, A. Shinohara, and T. Naito, *J.C.S. Perkin I*, 1974, 1747.

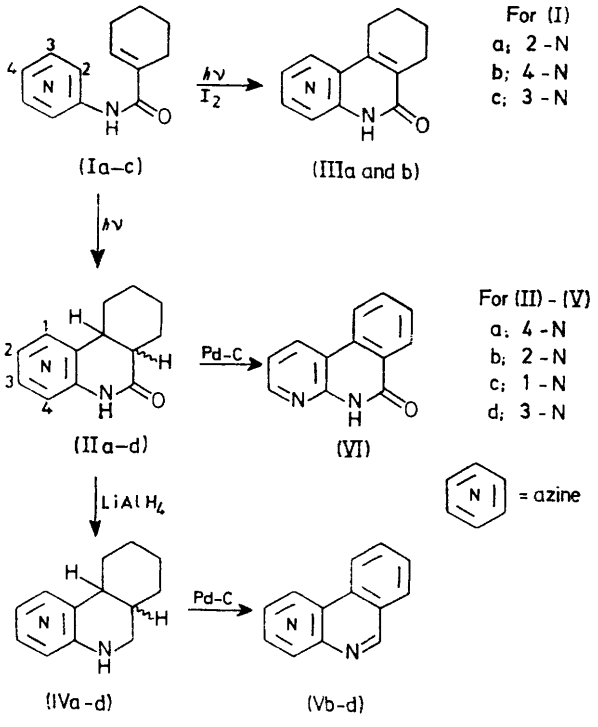
[3] M. Ogata and H. Matsumoto, *Chem. and Pharm. Bull. (Japan)*, 1972, **20**, 2264.

crude photoproduct showed one spot on t.l.c. but two peaks on g.l.c., suggesting the formation of two stereoisomers. This was confirmed by the analyses of the products and by dehydrogenation which afforded a single product.

Contrary to the photocyclisations of *N*-acylanilides,[2] in which ratios of *cis*- and *trans*-products were influenced by the solvent, the ratios of the present photocyclisation products were not affected by the solvent; in methanol, benzene, or ether equimolar mixtures of isomers were formed. Further, thermal interconversion of the isomers was not observed. The structures of the photoproducts were established from analyses and n.m.r. data, which however gave no hint of the stereochemistry at the ring junction.

Oxidative photocyclisations of the enamides (Ia and b) afforded in each case a single product (IIIa or b), with a double bond at the ring junction.

Whereas photocyclisation of the enamides (Ia and b) proceeded regiospecifically, the enamide (Ic) from 3-



aminopyridine afforded a mixture of two products (IIc and d) corresponding to the two possible directions of cyclisation.

Dehydrogenation of the product (IIa) afforded the corresponding aromatic lactam (VI) in good yield, identical with an authentic sample.[4] Reduction of the products (IIa—d) (as equimolar mixtures of *cis*- and *trans*-isomers) with lithium aluminium hydride afforded stereoisomeric mixtures of the tertiary amines (IVa—d).

Heating the tertiary amines (IVb—d) with palladium–charcoal yielded the corresponding aromatic benzonaphthyridines (Vb—d)[6,7] as sole products.

Photocyclisation of 7-(Pyridylcarbonyl)enamides.—It has been reported that photocyclisation of pyridinecarboxanilide does not occur.[4,8] Further, the preparation of benzonaphthyridines by photocyclisation [6] of both benzylideneaminopyridine and *N*-pyridylmethyleneaniline has been described. However, these reports have been limited to the formation of the aromatic ring systems. For comparison with the results of photocyclisation of the *N*-pyridylenamides, we have investigated the photocyclisation of *N*-(pyridylcarbonyl)-enamines, which were readily prepared by acylation of *N*-cyclohexylidenebenzylamine with pyridinecarbonyl chlorides in good yields. The products (VII)—(IX) again showed characteristic olefinic proton signals in their n.m.r. spectra.

Methanolic 0.02M-solutions of the *N*-(pyridylcarbonyl)-enamines (VII)—(IX) were irradiated with a 120 W low-pressure mercury lamp at room temperature. The reaction proceeded very slowly, and prolonged irradiation only caused decomposition of the product. Therefore, the irradiation was stopped at a point where a considerable amount of starting enamides still remained (t.l.c.); this was readily removed by chromatography. Although methanol was the solvent of choice for cyclisation, addition of a small amount of benzene was very effective in raising the yield. Thus, from irradiation of the enamide (VII) in methanol, the photoproduct (X) was obtained in 9% yield along with the unchanged enamide (VII) (17%). However, in benzene–methanol (1 : 3) the yield of (X) was raised to 25%. When ethanol was used as solvent for photocyclisation, an ethanol adduct was obtained. Oxidative photocyclisation gave the didehydro-lactam (XI) (16%).

Similarly, the enamide (VIII) afforded the photocyclisation products (XII) and (XIII), albeit in poor yields.

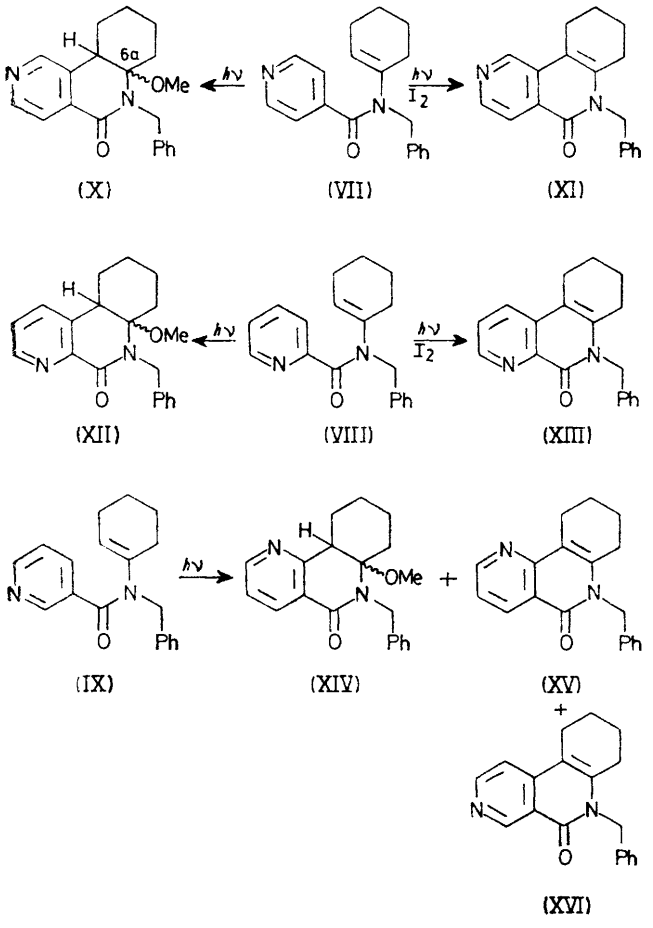
The presence of an alkoxy-group at the ring junction in the photoproducts (X) and (XII) was deduced as follows. The n.m.r. spectra contained a methoxy-singlet at δ 3.00. Further, compounds (X) and (XII), when heated, were readily converted into the corresponding didehydrolactams (XI) and (XIII), respectively, identical with the products of oxidative photocyclisation. The n.m.r. spectra of compounds (XI) and (XIII) showed signals for eight aliphatic protons, and the aromatic proton signals clearly determined the orientation of substitution on the pyridine ring, and thus the direction of cyclisation.

The methoxy-group in structures (X) and (XII) presumably arises from the solvent. Mechanistic considerations [9] and the n.m.r. analysis indicate its location as C-6a.

Photocyclisation of the nicotinoylenamine (IX), which

[4] K. Ito and Y. Kanaoka, *Chem. and Pharm. Bull. (Japan)*, 1974, **22**, 1431.
[5] G. H. Alt and A. J. Speziale, *J. Org. Chem.*, 1966, **31**, 1340.
[6] H. H. Perkampus and B. Behjati, *J. Heterocyclic Chem.*, 1974, **11**, 511.
[7] S. V. Kessar, M. Singh, P. Jit, G. Singh, and A. K. Lumb., *Tetrahedron Letters*, 1971, 471.
[8] M. T. LeGoff and P. Beugelmans, *Bull. Soc. chim. France*, 1972, (*a*) p. 1106; (*b*) p. 1115.
[9] I. Ninomiya, T. Naito, and T. Mori, *J.C.S. Perkin I*, 1973, 505.

could afford two geometrical isomers of each of two types of photoproduct (corresponding to the two modes of cyclisation), was carried out. The isolated photoproducts were the two types of didehydro-lactam, (XVI) (21%) and (XV) (1%), and the methoxy-incorporated lactam (XIV) (2%). The structures of the didehydro-lactams (XVI) and (XV) were deduced from their n.m.r. spectra, in particular the aromatic proton signals which determined the direction of cyclisation. The product (XIV),



which underwent ready conversion into (XV) upon heating, exhibited a methoxy-singlet at δ 3.00. Further, oxidative photocyclisation of (IX) afforded two didehydro-lactams, (XVI) (4%) and (XV) (24%). The ratio of yields of the didehydro-lactams (XV) and (XVI) was the converse of that obtained from non-oxidative cyclisation.

In conclusion, the photocyclisation of *N*-(pyridylcarbonyl)enamines proceeded very slowly and afforded an alkoxy-incorporated lactam susceptible to decomposition under irradiation conditions, whereas the *N*-pyridylenamides underwent smooth photocyclisation to afford equimolar mixtures of *cis*- and *trans*-lactams, irrespective of the solvent employed.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured for solutions in deuteriochloroform with tetramethylsilane as internal reference. I.r. spectra were taken for chloroform solutions unless otherwise stated. Mass spectra were measured on a JEOL-JMS-01SG machine. M.p.s were determined with a Kofler-type hot-stage apparatus. Photochemical reactions were carried out as described in Part I.[9]

Acylation of 2-Aminopyridine.—To a stirred solution of 2-aminopyridine (8.0 g) and triethylamine (15 g) in anhydrous benzene (300 ml) cooled in ice, a solution of cyclohex-1-enecarbonyl chloride (15 g) in anhydrous benzene (60 ml) was added dropwise. The resulting solution was heated under reflux for 2 h, then washed with water, dried, and evaporated. The residue was chromatographed on alumina. Elution with benzene afforded N-(2-*pyridyl*)*cyclohex*-1-*enecarboxamide* (Ia) (7.4 g, 46%), crystals, m.p. 64—66 °C (from n-hexane), $\nu_{max.}$ 3 180 (NH), 1 678 (NCO), and 1 639 cm^{-1} (C=C), δ 8.37br (1 H, s, NH), 8.30 (2 H, m, 3′- and 5′-H), 7.75 (1 H, td, *J* 7.8 and 2.0 Hz, 4′-H), and 6.90 (2 H, m, 6′-H, C=CH) (Found: C, 71.0; H, 7.0; N, 13.95. $C_{12}H_{14}N_2O$ requires C, 71.25; H, 7.0; N, 13.85%). Elution with benzene–chloroform afforded N-(2-*pyridyl*)-2-(2-*pyridylamino*)*cyclohexanecarboxamide* (2.7 g, 16%), m.p. 199—201°, as crystals (from methanol), $\nu_{max.}$ 3 360 (NH), 3 150 (NH), and 1 678 cm^{-1} (NCO), δ 10.27br (1 H, s, CONH), 6.10 (1 H, d, *J* 9 Hz, NH), 4.55 (1 H, m, N·CH), and 3.00 (1 H, m, CO·CH) (Found: C, 68.85; H, 6.8; N, 19.0. $C_{17}H_{20}N_4O$ requires C, 68.9; H, 6.8; N, 18.9%).

N-(4-*Pyridyl*)*cyclohex*-1-*enecarboxamide* (Ib).—A similar reaction of 4-aminopyridine (3.5 g) with cyclohex-1-enecarbonyl chloride (6.0 g) afforded the *enamide* (Ib) (6.7 g, 90%), b.p. 190° (bath temp.) at 6 × 10^{-3} mmHg, $\nu_{max.}$ 3 490 (NH), 1 685 (NCO), and 1 640 cm^{-1} (C=C), δ 8.58br (1 H, s, NH), 8.49 (2 H, dd, *J* 5 and 1.5 Hz, 2′- and 6′-H), 7.61 (2 H, dd, *J* 5 and 1.5 Hz, 3′- and 5′-H), and 6.75 (1 H, m, HC=C) (Found: C, 71.25; H, 6.95; N, 13.45%).

N-(3-*Pyridyl*)*cyclohex*-1-*enecarboxamide* (Ic).—A similar reaction of 3-aminopyridine (3.8 g) with cyclohex-1-enecarbonyl chloride (5.0 g) afforded the *enamide* (Ic) (6.1 g, 75%), b.p. 180° (bath temp.) at 6 × 10^{-3} mmHg, $\nu_{max.}$ 3 470 (NH), 1 679 (NCO), and 1 639 cm^{-1} (C=C), δ 8.18br (1 H, s, NH) and 6.78 (1 H, m, HC=C) (Found: C, 71.4; H, 7.15; N, 13.95%).

cis- *and* trans-6a,7,8,9,10,10a-*Hexahydrobenzo*[c][1,8]*naphthyridin*-6(5H)-*one* (IIa).—A 0.02M-solution of the enamide (Ia) (370 mg) in methanol, ether, or benzene (100 ml) was irradiated with a low-pressure mercury lamp at room temperature for 49 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with chloroform afforded the *lactam* (IIa) (38—41%), m.p. 194—198° (from ether), $\nu_{max.}$ 3 440 (NH) and 1 685 cm^{-1} (NCO), δ 10.10br (1 H, s, NH), 8.31 (1 H, dd-like, 3-H), 7.55 (1 H, m, 1-H), and 7.00 (1 H, m, 2-H) (Found: C, 70.95; H, 6.75; N, 13.7. $C_{12}H_{14}N_2O$ requires C, 71.25; H, 7.0; N, 13.85%), shown to be a mixture of *cis*- and *trans*-isomers (*ca.* 1 : 1) by g.l.c. and n.m.r.

cis- *and* trans-6a,7,8,9,10,10a-*Hexahydrobenzo*[c][1,6]*naphthyridin*-6(5H)-*one* (IIb).—By the procedure given for (Ia), irradiation of the enamide (Ib) (400 mg) in methanol, ether, or benzene for 19—20 h afforded, after chromatography on silica gel with chloroform as eluant, the *lactam* (IIb) (72.5—87.5%), m.p. 240—244°, as crystals (from methanol), $\nu_{max.}$ 3 430 (NH) and 1 693 cm^{-1} (NCO), δ 9.20 (1 H, m, NH) and 6.80 (1 H, d, *J* 6 Hz, 4-H) (Found: C, 71.55; H, 7.25; N, 13.75%), shown to be a mixture of *cis*- and *trans*-isomers (*ca.* 1 : 1) by g.l.c. and n.m.r.

Photocyclisation of the Enamide (Ic).—By the procedure

given for (Ia), irradiation of the enamide (Ic) (3.0 g) in ether for 20 h afforded, after chromatography on silica gel with chloroform, *cis-* and *trans*-6a,7,8,9,10,10a-*hexahydrobenzo*[c][1,5]*naphthyridin*-6(5H)-*one* (IIc) (0.32 g, 11%), m.p. 236—237° (from methanol), $\nu_{max.}$ 3 440 (NH) and 1 684 cm^{-1} (NCO), δ 9.48 (1 H, m, NH) (Found: C, 71.15; H, 6.9%), and cis- and trans-6a,7,8,9,10,10a-*hexahydrobenzo*[c][1,7]*naphthyridin*-6(5H)-*one* (IId) (0.54 g, 18%), m.p. 236—240° (from methanol), $\nu_{max.}$ 3 440 (NH) and 1 689 cm^{-1} (NCO), δ 9.48br (1 H, s, NH) (Found: C, 71.35; H, 6.9; N, 13.7%) (each *ca.* 1 : 1 by g.l.c. and n.m.r.). Irradiation of the enamide (Ic) in benzene gave the same lactams, but with methanol as solvent only decomposition took place.

7,8,9,10-*Tetrahydrobenzo*[c][1,8]*naphthyridin*-6(5H)-*one* (IIIa).—The enamide (Ia) (400 mg) in methanol (100 ml) was irradiated in the presence of iodine (250 mg) for 35 h. The solvent was removed and the residue was dissolved in chloroform and washed with aqueous sodium hydrogen sulphate and water, dried, and evaporated. The residue was chromatographed on silica gel; elution with chloroform gave the *didehydro-lactam* (IIIa) (40 mg, 10%), m.p. 236—237° (from methanol), $\nu_{max.}$ 3 450 (NH) and 1 649 cm^{-1} (NCO), δ 12.47br (1 H, s, NH), 8.75 (1 H, dd, *J* 5 and 1.8 Hz, 3-H), 8.00 (1 H, dd, *J* 8 and 1.8 Hz, 1-H), and 7.15 (1 H, dd, *J* 8 and 5 Hz, 2-H) (Found: C, 72.05; H, 5.9; N, 13.7. $C_{12}H_{12}N_2O$ requires C, 72.0; H, 6.05; N, 14.0%).

7,8,9,10-*Tetrahydrobenzo*[c][1,6]*naphthyridin*-6(5H)-*one* (IIIb).—By the procedure given for (Ia), irradiation of the enamide (Ib) (400 mg) in the presence of iodine (130 mg) afforded the *didehydro-lactam* (IIIb) (310 mg, 77.5%) as crystals (from methanol), m.p. 262—264°, $\nu_{max.}$ 3 440 (NH) and 1 654 cm^{-1} (NCO), δ (C_5D_5N) 9.02br (1 H, s, 1-H), 8.70 (1 H, d, *J* 6 Hz, 3-H), and 7.43 (1 H, d, *J* 6 Hz, 4-H) (Found: C, 72.2; H, 6.25; N, 13.5%).

cis- *and* trans-5,6,6a,7,8,9,10,10a-*Octahydrobenzo*[c][1,8]*naphthyridine* (IVa).—To a solution of the lactam (IIa) (500 mg) in anhydrous ether–tetrahydrofuran (10 : 3; 130 ml), lithium aluminium hydride (500 mg) was added carefully in small portions. The mixture was refluxed for 1 h. The excess of hydride was decomposed by adding water with cooling. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried (Na_2SO_4), and evaporated to give the secondary *amine* (IVa) (206 mg, 55%), as crystals (from n-hexane), m.p. 89—90°, $\nu_{max.}$ 3 440 cm^{-1} (NH), δ 7.88br (1 H, d, 3-H), 7.25 (1 H, m, 1-H), 6.49 (1 H, dd, *J* 7.5 and 5 Hz, 2-H), and 5.25br (1 H, s, NH) (Found: C, 76.7; H, 8.4; N, 14.85. $C_{12}H_{16}N_2$ requires C, 76.55; H, 8.55; N, 14.9%).

cis- *and* trans-5,6,6a,7,8,9,10,10a-*Octahydrobenzo*[c][1,6]*naphthyridine* (IVb).—A similar reaction of the lactam (IIb) (310 mg) with lithium aluminium hydride (290 mg) afforded the secondary *amine* (IVb) (130 mg, 45%) as crystals (from ether), m.p. 174—176°, $\nu_{max.}$ 3 500 cm^{-1} (NH), δ 6.25 (1 H, d, *J* 5.5 Hz, 4-H) and 3.25br (1 H, s, NH) (Found: C, 76.55; H, 8.55; N, 14.75%).

cis- *and* trans-5,6,6a,7,8,9,10,10a-*Octahydrobenzo*[c][1,5]*naphthyridine* (IVc).—A similar reaction of the lactam (IIc) (320 mg) with lithium aluminium hydride (300 mg) afforded the secondary *amine* (IVc) (160 mg, 29%) as crystals (from n-hexane), m.p. 92—93°, $\nu_{max.}$ 3 450 cm^{-1} (NH), δ 7.90 (1 H, dd, *J* 1.5 and 4.5 Hz, 2-H), 6.90 (1 H, dd, *J* 4.5 and 8 Hz, 3-H), 6.68 (1 H, dd, *J* 8 and 1.5 Hz, 4-H), and 3.20br (1 H, s, NH) (Found: C, 76.4; H, 8.4; N, 14.95%).

cis- *and* trans-5,6,6a,7,8,9,10,10a-*Octahydrobenzo*[c][1,7]*naphthyridine* (IVd).—A similar reaction of the lactam (IId) (500 mg) with lithium aluminium hydride (500 mg) afforded the secondary *amine* (IVd) (330 mg, 77%) as crystals (from n-hexane), m.p. 89—90°, $\nu_{max.}$ 3 470 cm^{-1} (NH), δ 6.95 (1 H, m, 1-H), and 3.75br (1 H, s, NH) (Found: C, 76.75; H, 8.45%).

Benzo[c][1,8]*naphthyridin*-6(5H)-*one* (VI).—A mixture of the lactam (IIa) (200 mg) and 10% palladium–charcoal (200 mg) was heated at 220—240 °C (metal bath) for 5 h, then extracted with hot chloroform. The chloroform layer was filtered and evaporated and the residue was recrystallised from chloroform to give the lactam (VI) (140 mg, 70%) as crystals, m.p. 268° (lit.,[4] 274—276°), identical with an authentic sample.

Benzo[c][1,6]*naphthyridine* (Vb).—A similar reaction of the secondary amine (IVb) (320 mg) at 250 °C for 7 h afforded the benzonaphthyridine (Vb) (116 mg, 37%) as crystals (from ether), m.p. 93—95° (lit.,[6] 104—106°) (Found: C, 79.85; H, 4.65; N, 15.5. Calc. for $C_{12}H_8N_2$: C, 80.0; H, 4.5; N, 15.55%).

Benzo[c][1,5]*naphthyridine* (Vc).—A similar reaction of the secondary amine (IVc) (140 mg) and 10% palladium–charcoal (140 mg) afforded the benzonaphthyridine (Vc) (120 mg, 90%) as crystals (from ether), m.p. 92—93.5° (lit.,[6] 95—97°) (Found: C, 79.7; H, 4.55; N, 15.35%).

Benzo[c][1,7]*naphthyridine* (Vd).—By the procedure given for (IVb), the secondary amine (IVd) (160 mg) afforded the benzonaphthyridine (Vd) (140 mg, 91%) as crystals (from ether), m.p. 98—100° (lit.,[7] 102°) (Found: C, 79.7; H, 4.5; N, 15.65%).

Preparation of the Enamides (VII)—(IX).—N-*Benzyl*-N-*cyclohex*-1-*enylnicotinamide* (IX). A solution of cyclohexanone (9.82 g) and benzylamine (9.63 g) in benzene (200 ml) was refluxed for 5 h with removal of water as formed, then evaporated under reduced pressure. A solution of the resulting imine and triethylamine (23 g) in anhydrous benzene (100 ml) was added dropwise to a cooled suspension of an excess of nicotinoyl chloride. After stirring at room temperature for 2 h, the mixture was washed with water, dried (Na_2SO_4), and evaporated to give an oil, which was chromatographed on alumina with benzene–chloroform as eluant. Distillation of the eluted oil afforded the *enamide* (IX) (11 g, 46%) as an oil, b.p. 205° (bath temp.) at 7×10^{-3} mmHg, $\nu_{max.}$ 1 631 cm^{-1} (NCO), δ 8.81 (1 H, dd, *J* 1.5 and 1 Hz 2-H), 8.63 (1 H, dd, *J* 5 and 1.5 Hz, 4-H), 7.91 (1 H, dt, *J* 7 and 1.5 Hz, 6-H), 5.31 (1 H, t-like, C=CH), and 4.85 (2 H, s, N·CH_2Ph) (Found: C, 77.9; H, 6.8; N, 9.45. $C_{19}H_{20}N_2O$ requires C, 78.05; H, 6.9; N, 9.6%).

Similarly, N-*benzyl*-N-*cyclohex*-1-*enylisonicotinamide* (VII) was prepared in 26% yield as crystals (from ether), m.p. 81—82°, $\nu_{max.}$ 1 635 cm^{-1} (NCO), δ 8.63 (2 H, m, 2- and 6-H), 5.26 (1 H, approx. t, HC=C), and 4.81 (2 H, s, NCH_2Ph) (Found: C, 78.1; H, 6.95; N, 9.6%).

N-*Benzyl*-N-*cyclohex*-1-*enylpicolinamide* (VIII) was also prepared similarly in 68.5% yield, as crystals (from n-hexane), m.p. 56—57.5°, $\nu_{max.}$ 1 635 cm^{-1} (NCO), δ 5.10 (1 H, m, HC=C) and 4.81 (2 H, s, NCH_2Ph) (Found: C, 78.25; H, 6.8; N, 9.6%).

Photocyclisation of the Enamides (VII)—(IX).—Reactions were carried out as described previously with 0.02M-solutions of the enamides in an appropriate solvent, such as methanol or ethanol.

The enamide (VII) *in methanol.* The enamide (VII) (3.9 g) was irradiated in methanol for 11 h. (Prolonged irradiation caused decomposition of the products.) The solvent was removed and the residue was chromatographed

on alumina. Elution with benzene afforded first N-*benzyl*-6a,7,8,9,10,10a-*hexahydro*-6a-*methoxybenzo*[c][2,6]*naphthyridin*-5(6H)-*one* (X) (350 mg, 9%) as crystals (from methanol), m.p. 165—167°, $\nu_{max.}$ 1 657 (NCO) and 1 066 cm^{-1}, δ 8.66 (2 H, m, 1- and 3-H), 7.97 (1 H, d, *J* 5.5 Hz, 4-H), 5.63 and 4.50 (2 H, ABq, *J* 16 Hz, NCH_2Ph), and 3.01 (3 H, s, OCH_3) (Found: M^+, 322.168 324. $C_{20}H_{22}N_2O_2$ requires *M*, 322.168 13), then the starting enamide (VII) (650 mg, 17%).

The enamide (VIII) *in methanol.* The enamide (VIII) (4.8 g) in methanol (800 ml) for 80 h afforded, upon repeated chromatography, 6-benzyl-6a-methoxy-6a,7,8,9,10,10a-hexahydrobenzo[*f*][1,7]naphthyridin-5(6*H*)-one (XII) (30 mg, 0.6%) as a pale brown oil, $\nu_{max.}$ 1 660 (NCO) and 1 065 cm^{-1}, δ 8.71 (1 H, m, 3-H), 7.67 (1 H, m, 1-H), 7.45 (1 H, m, 3-H), 5.71 and 4.53 (2 H, ABq, *J* 11 Hz, NCH_2Ph), and 3.02 (3 H, s, OCH_3).

The enamide (IX) *in methanol.* The enamide (IX) (4.67 g) was irradiated for 7—8 h. Benzene eluted 6-benzyl-6a,7,8,9,10,10a-hexahydro-6a-methoxybenzo[*h*][1,6]naphthyridin-6(5*H*)-one (XIV) (50 mg, 1%) as an amorphous solid (from ether), $\nu_{max.}$ 1 647 (NCO) and 1 063 cm^{-1}, δ 8.70 (1 H, dd, *J* 5 and 2 Hz, 2-H), 8.43 (1 H, dd, *J* 8 and 2 Hz, 4-H), 5.61 and 4.50 (2 H, ABq, *J* 16 Hz, NCH_2Ph), 3.21 (1 H, m, 10a-H), and 3.00 (3 H, s, OCH_3), followed by 5-*benzyl*-7,8,9,10-*tetrahydrobenzo*[h][1,6]*naphthyridin*-6(5H)-*one* (XV) (100 mg, 2%) as pale yellow crystals (from methanol), m.p. 172—174°, $\nu_{max.}$ 1 650 (NCO), 1 613, and 1 590 cm^{-1}, δ 8.96 (1 H, dd, *J* 4.5 and 2 Hz, 2-H), 8.76 (1 H, dd, *J* 8 and 2 Hz, 4-H), and 5.47 (2 H, s, NCH_2Ph) (Found: C, 78.7; H, 6.05; N, 9.5. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%), and finally the enamide (IX) (1.68 g, 36%). Elution with benzene–chloroform then afforded 6-*benzyl*-7,8,9,10-*tetrahydrobenzo*[c][2,7]*naphthyridin*-5(6H)-*one* (XVI) (1 g, 21%) as pale yellow crystals (from methanol), m.p. 189—191°, $\nu_{max.}$ 1 657 (NCO) and 1 612 cm^{-1}, δ 9.65 (1 H, s, 4-H), 8.71 (1 H, d, *J* 6 Hz, 2-H), and 5.43 (2 H, s, NCH_2Ph) (Found: C, 78.5; H, 6.15; N, 9.65. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%).

Oxidative Photocyclisation of the Enamide (VII).—The enamide (VII) (1.26 g) in methanol (200 ml) in the presence of iodine (1 g) was irradiated for 27 h. The solution was evaporated and the residue was dissolved in chloroform. This solution was washed with aqueous sodium hydrogen sulphate and water, dried, and evaporated. The residue was chromatographed on alumina. Elution with benzene gave the enamide (VII) (600 mg, 48%), followed by 6-*benzyl*-7,8,9,10-*tetrahydrobenzo*[c][2,6]*naphthyridin*-5(6H)-*one* (XI) (200 mg, 16%), as needles (from ether–methanol), m.p. 139—141°, $\nu_{max.}$ 1 652 (NCO) and 1 614 cm^{-1}, δ 9.12 (1 H, s, 1-H), 8.70 (1 H, d, *J* 5 Hz, 3-H), 8.23 (1 H, d, *J* 5 Hz, 4-H), and 5.42 (2 H, s, NCH_2Ph) (Found: C, 78.3; H, 6.3; N, 9.4. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%).

Oxidative Photocyclisation of the Enamide (VIII).—By the procedure given for (VII), the enamide (VIII) (2.34 g) afforded 6-*benzyl*-7,8,9,10-*tetrahydrobenzo*[f][1,7]*naphthyridin*-5(6H)-*one* (XIII) (12 mg, 0.5%) as a pale brown amorphous substance, $\nu_{max.}$ 1 657 (NCO) and 1 613 cm^{-1}, δ 8.91 (1 H, m, 3-H), 8.03 (1 H, m, 1-H), 7.60 (1 H, m, 2-H), and 5.51 (2 H, s, NCH_2Ph) (Found: M^+, 290.141 45. $C_{19}H_{18}N_2O$ requires *M*, 290.141 91).

Oxidative Photocyclisation of the Enamide (IX).—By the procedure given for (VII), the enamide (IX) (1.26 g) afforded the didehydro-lactam (XV) (300 mg, 24%), the enamide (IX) (150 mg, 12%), and the didehydro-lactam (XVI) (50 mg, 4%).

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