Photocyclisation of Enamides. Part II.[1] Photocyclisation of *N*-Benzoyl Enamines of 1-Tetralone to Benzo[*c*]phenanthridines[2]

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Irradiation of methanolic solutions of the *N*-benzoyl enamines (Ia—d) of 1-tetralone with a low-pressure mercury lamp caused stereoselective cyclisation to give the *trans*-tetrahydrobenzo[*c*]phenanthridones (IIIa—d), two of which were converted into the corresponding *cis*-isomers (VIIa and b) by heating with selenium. Further conversion into the BC *cis*-hexahydrobenzo[*c*]phenanthridine (XI) represents a potential route to natural products.

In Part I[1] a novel stereoselective photocyclisation of *N*-benzoyl enamines of 2-tetralone was described. We now report a similar photocyclisation of the enamides (Ia—d) of 1-tetralone to afford benzo[*c*]phenanthridones (IIIa—d) stereoselectively.

Benzoylation as previously described[1] of the imine prepared from 1-tetralone and benzylamine, with benzoyl chloride, afforded the *N*-benzoyl enamine (Ia) in 80% yield [$\nu_{max.}$ 1630 cm^{-1} (amide CO), δ 5·26 (t, J 5 Hz, olefinic) and 7·55—7·00 (14H, aromatic)]. A

[1] Part I, I. Ninomiya, T. Naito, and T. Mori, *J.C.S. Perkin I*, 1973, 505.

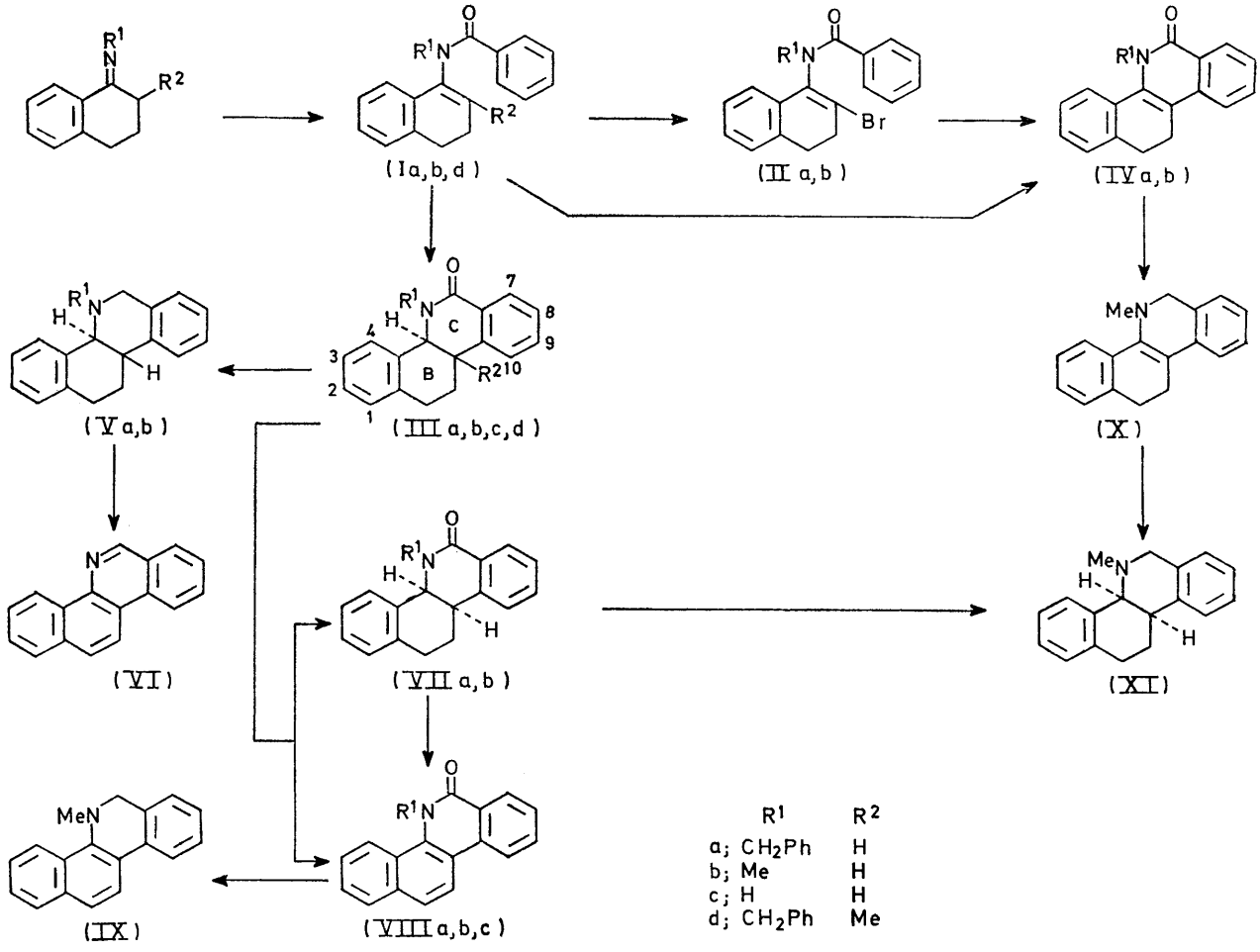
[2] Preliminary report, I. Ninomiya, T. Naito, and T. Mori, *Tetrahedron Letters*, 1969, 3643.

0·02M-solution of the product in methanol was irradiated with a low-pressure mercury lamp as described previously.[1] After 40 h a crystalline product was obtained (55% yield) which was shown to be homogeneous by both t.l.c. and g.l.c., suggesting the stereoselectivity of the photocyclisation. This photoproduct (IIIa) showed $\nu_{max.}$ 1640 cm^{-1} (six-membered lactam CO), and δ 7·5—6·60 (12H, aromatic), 8·10 (1H, aromatic), and 4·85 (d, J 11·5 Hz, 4b-H); the olefinic proton signal from the enamide had disappeared.

A similar result was obtained with the *N*-methyl enamide (Ib); the photoproduct (IIIb), also homogeneous (t.l.c. and g.l.c.), was obtained in 51% yield. Its n.m.r. and i.r. spectra closely resembled those of (IIIa), particularly the former, which showed δ 4·78 (d, J 12 Hz, 4b-H).

The *N*-benzyl photoproduct (IIIa) was debenzylated[3] with sodium in liquid ammonia to give the lactam (IIIc), which was methylated to give material identical with the photoproduct (IIIb).

The photoproduct (IIIa) was reduced with lithium aluminium hydride to give the tertiary amine (Va), which was then converted into benzo[*c*]phenanthridine (VI)[4] by heating with palladium–charcoal. Thus the skeletal structure of the photoproducts (IIIa and b) was established. The n.m.r. spectra of the photoproducts (IIIa and b) also support the benzo[*c*]phenanthridone structure, and the coupling constant shown by the 4b-proton suggested that the BC ring junction was *trans* (from use of a Dreiding model and calculation by the Karplus equation[5]).



The photoproducts (IIIa and b) were heated with selenium to convert them into the fully aromatised lactams (VIIIa and b), which, however, were obtained only in small amounts; the major products were the BC-*cis* isomers (VIIa and b) of (IIIa and b) (43—49% yields). The n.m.r. spectrum of (VIIb) showed a doublet at δ *ca.* 4·78 (4b-H), but with a smaller coupling constant (4·5 Hz) than in the photoproduct (IIIb). Reduction of the *cis*-lactam (VIIb) with lithium aluminium hydride afforded the tertiary amine (XI), which also showed a doublet due to the 4b-proton, at δ 3·65 (J 4 Hz). Structure (XI) is similar to that of

[3] S. Sugasawa and T. Fujii, *Chem. and Pharm. Bull. Japan*, 1958, **6**, 587.

[4] R. A. Abramovitch and G. Tertzakin, *Canad. J. Chem.*, 1963, **41**, 2265.

[5] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

chelidonine,[6] a major alkaloid of *Chelidonium majus*; thus this series of reactions may well be a useful route to this group of alkaloids.

A similar photocyclisation was also observed with the enamide (Id), prepared from 2-methyl-1-tetralone, to yield the lactam (IIId). The photocyclisations so far described are non-oxidative, providing saturated products (IIIa—d); these results resemble the photocyclisations of *N*-(unsaturated acyl)anilides.[7] However when the enamide (Ib) was irradiated in the presence of an oxidising agent, *i.e.* iodine, as used for benzanilides,[8] the product was the corresponding didehydrolactam (IVb). The didehydro-lactam (IVa) was also obtained from the photocyclisation of the bromoenamide (IIa), prepared readily by bromination[9] of the enamide (Ia) with *N*-bromosuccinimide. The

N.m.r. data (δ values; *J* in Hz) for the photoproducts and related compounds *

Compd.	Aromatic	4b-H	BC ring junction
(IIIa)	8·10 (1H, m), 7·50—6·60 (12H, m)	4·85 (d, *J* 11·5)	*trans*
(IIIb)	8·16 (1H, m), 7·60—7·15 (7H, m)	4·78 (d, *J* 12)	*trans*
(IIIc)	8·20 (1H, m), 7·75—7·10 (7H, m)	4·60 (*d*, *J* 12·5)	*trans*
(Va)	7·90 (1H, m), 7·60—6·80 (12H, m)	3·97 (d, *J* 11·5)	*trans*
(Vb)	7·75 (1H, m), 7·50—7·00 (7H, m)	4·05 (d, *J* 11)	*trans*
(VIIa)	8·15 (1H, m), 7·55—6·85 (12H, m)	4·80 (d, *J* 4·5)	*cis*
(VIIb)	8·05 (1H, m), 7·50—7·10 (7H, m)	4·75 (d, *J* 4·5)	*cis*
(XI)	7·50—6·90 (8H, m)	3·65 (d, *J* 4)	*cis*

* Solutions in [^{2}H]chloroform.

n.m.r. spectra of these didehydro-lactams (IVa and b) showed no peaks due to 4b- and 10b-protons. Reduction of the didehydro-lactam (IVb) with lithium aluminium hydride afforded the enamine (X), which was hydrogenated over platinum oxide to give the *cis*-amine (XI), identical with that obtained by the selenium treatment.

The n.m.r. spectra of the photoproducts and related compounds are summarised in the Table, which clearly shows the connection between the BC-ring junction stereochemistry and the magnitude of the coupling constant $J_{4b,10b}$. These conclusions agreed with the data reported for the octahydrophenanthrenes.[10] It is therefore firmly established that the photocyclisation proceeds stereoselectively giving only *trans*-products.

The n.m.r. spectra of the *trans*-amines (Va and b) showed one aromatic proton signal at lower field (δ *ca.* 7·82) than the others. This can be explained by assuming that the *N*-alkyl group is in a *pseudo*-axial orientation, owing to steric interference with the 4-proton; thus this proton will be deshielded (Figure 1).[11]

In the case of the *cis*-amine (XI) there appear to be two possible conformations, a stable form, with the

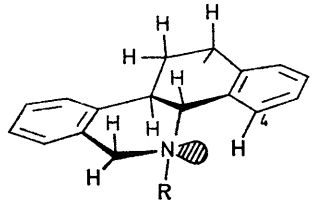


FIGURE 1

4b-proton *pseudo*-equatorial with respect to ring B and an unstable form, with the 4b-proton *pseudo*-axial (Figure 2). In the latter form, the *N*-methyl group must have a *pseudo*-axial orientation owing to inter-

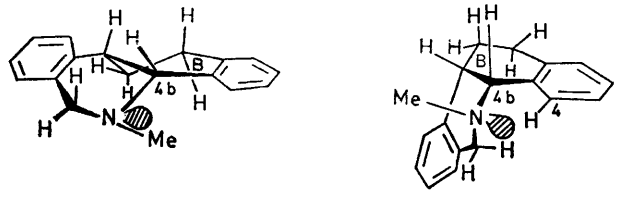


FIGURE 2

ference with the 4-proton; this proton should therefore be deshielded by the nitrogen lone-pair. However, the absence of this effect shows that the latter conformation is not present.

EXPERIMENTAL

N.m.r. spectra were determined for solutions in deuteriochloroform with a Varian A-60D instrument (tetramethylsilane as internal reference). M.p.s were determined with a Kofler hot-stage apparatus. The photochemical reactions were carried out by irradiation at room temperature, either with an external, low-pressure (120 W) quartz, spiral mercury lamp (principal emission at 253·7 nm) through quartz, or with an internal, quartz, pencil-shaped mercury lamp, of a 0·02M-solution of the enamide in ether, benzene, or methanol.

N-(3,4-*Dihydro*-1-*naphthyl*)-N-*methylbenzamide* (Ib).—Anhydrous methylamine gas was bubbled into a boiling solution of 1-tetralone (10 g) and toluene-*p*-sulphonic acid (a small amount) in toluene (60 ml) for 5 h; water was removed as it was formed. The mixture was evaporated to yield a pale yellow oil. To an ice-cooled solution of the resulting oil and triethylamine (9·5 g) in anhydrous chloroform, a solution of benzoyl chloride (12 g) in anhydrous chloroform (15 ml) was added dropwise. The mixture was left at room temperature overnight, the solvent was removed, and the residue was extracted with ether. The extract

[6] C. Y. Chen and D. B. MacLean, *Canad. J. Chem.*, 1967, **45**, 3001.

[7] (*a*) P. G. Cleveland and O. L. Chapman, *Chem. Comm.*, 1967, 1064; (*b*) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 4243; (*c*) O. L. Chapman, and W. R. Adams, *ibid.*, 1968, **90**, 2333; (*d*) Y. Ogata, K. Takagi, and I. Ishino, *J. Org. Chem.*, 1971, **36**, 3975.

[8] (*a*) B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Comm.*, 1967, 614; (*b*) E. Winterfeldt and H. J. Altmann, *Angew. Chem.*, 1968, **80**, 486; (*c*) D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc.* (*C*), 1971, 116; (*d*) A. Mondon and K. Krohn, *Chem. Ber.*, 1972, **105**, 3726.

[9] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, 1968, **90**, 2432.

[10] Z. G. Hajos, K. J. Doebel, and M. W. Goldberg, *J. Org. Chem.*, 1964, **29**, 2527.

[11] Y. Hamada, K. Aono, K. Tori, and K. Kotera, Abstracts, 20th Annual Meeting of the Chemical Society of Japan, 1967, *III*, 145.

was washed with brine, dried (Na_2SO_4), and evaporated to give a solid. Recrystallisation from n-hexane afforded the *enamide* (Ib) (10 g, 56%), m.p. 108·5—109°, $\nu_{max.}$ (Nujol) 1645 cm^{-1} (C=C–NBz), $\delta(CDCl_3)$ 5·60 (1H, t, *J* 4·5 Hz, HC=C–N), and 3·26 (3H, s, NMe) (Found: C, 82·6; H, 6·65; N, 5·5. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%).

N-*Benzyl*-N-(3,4-*dihydro*-1-*naphthyl*)*benzamide* (Ia).—A similar reaction of the imine formed from 1-tetralone and benzylamine with benzoyl chloride afforded the *enamide* (Ia) (80%), m.p. 147—148° (from n-hexane), $\nu_{max.}$ (Nujol) 1630 cm^{-1} (C=C–NBz), $\delta(CDCl_3)$ 5·67 and 4·12 (2H, ABq, *J* 14 Hz, N·CH_2Ph) and 5·26 (1H, t, *J* 5 Hz, HC=C–N) (Found: C, 85·1; H, 6·2; N, 4·4. $C_{24}H_{21}NO$ requires C, 84·9; H, 6·25; N, 4·15%).

trans-4b,10b,11,12-*Tetrahydro*-5-*methylbenzo*[c]*phenanthridin*-6(5H)-*one* (IIIb).—A 0·02M-solution of the *N*-benzoyl enamine (Ib) (2·4 g) in methanol (460 ml) was irradiated for *ca.* 40 h (t.l.c. then showed complete disappearance of the starting enamide). The solvent was removed and the residue was chromatographed on alumina. Elution with benzene gave a solid which was recrystallised from methanol–ether to give the *lactam* (IIIb) (1·2 g, 51%) as plates, m.p. 164—165°, $\nu_{max.}$ (Nujol) 1645 cm^{-1} (N–CO), $\delta(CDCl_3)$ 8·16 (1H, m, 7-H), 4·78 (1H, d, *J* 12 Hz, 4b-H), and 3·12 (3H, s, NMe) (Found: C, 82·4; H, 6·45; N, 5·2. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%).

trans-5-*Benzyl*-4b,10b,11,12-*tetrahydrobenzo*[c]*phenanthridin*-6(5H)-*one* (IIIa).—Similar irradiation of the enamide (Ia) afforded the *lactam* (IIIa) (55%), m.p. 123·5—125° (from petroleum), $\nu_{max.}$ (Nujol) 1640 cm^{-1} (N–CO), $\delta(CDCl_3)$ 8·10 (1H, m, 4-H), 5·30 and 4·48 (2H, ABq, *J* 15 Hz, N·CH_2Ph), and 4·85 (1H, d, *J* 11·5 Hz, 4b-H) (Found: C, 85·25; H, 6·1; N, 4·05. $C_{24}H_{21}NO$ requires C, 84·9; H, 6·25; N, 4·15%).

trans-4b,10b,11,12-*Tetrahydrobenzo*[c]*phenanthridin*-6-(5H)-*one* (IIIc).—To a solution of the *N*-benzyl lactam (IIIa) (325 mg) in liquid ammonia (*ca.* 20 ml), sodium (200 mg) was added in small portions. The blue mixture was stirred for 30 min then decomposed with an excess of ammonium chloride. Ammonia was evaporated off and the residue was treated with water and ether. The aqueous layer was extracted with ether. The combined ether layers were washed with brine, dried (Na_2SO_4), and evaporated to give a solid. Recrystallisation from methanol afforded pale yellow *crystals* (IIIc) (190 mg, 82%), m.p. 214—215°, $\nu_{max.}$ (Nujol) 3300sh, 3220 (NH), and 1660 cm^{-1} (N–CO), $\delta(CDCl_3)$ 8·20 (1H, m, 7-H) and 4·60 (1H, d, *J* 12·5 Hz, 4b-H) (Found: C, 81·9; H, 6·05; N, 5·4. $C_{17}H_{15}NO$ requires C, 81·9; H, 6·05; N, 5·6%).

Methylation of the Lactam (IIIc).—A mixture of the lactam (IIIc) (130 mg), methyl iodide (360 mg), potassium hydroxide (140 mg), and anhydrous acetone (20 ml) was refluxed for 48 h, cooled, filtered, and evaporated. The residue was extracted with chloroform and the extract was washed with water, dried (Na_2SO_4), and evaporated to give a viscous oil which was chromatographed on silica gel. Elution with chloroform gave a solid which was recrystallised from ether to give the *N*-methyl lactam (IIIb) (11 mg, 7%), m.p. 157—159°, identical with that obtained earlier (t.l.c., i.r. spectrum, and mixed m.p.).

Dehydrogenation of the trans-*Lactam* (IIIb).—(a) *By* 10% *palladium–charcoal.* A mixture of the *trans*-lactam (IIIb) (840 mg) and 10% palladium–charcoal (840 mg) was heated at 220—250° for 3 h. After cooling, hot methanol was added and the catalyst was filtered off. Evaporation of the filtrate gave a solid (805 mg, 97%), which was recrystallised from methanol to give 5-methylbenzo[*c*]-phenanthridin-6(5*H*)-one (VIIIb), as needles, m.p. 148—149° (lit.,[12] 145°), $\nu_{max.}$ (Nujol) 1650 (N–CO), 1610, and 755 cm^{-1}, $\delta(CDCl_3)$ 8·63—8·40 (1H, m), 8·35—8·00 (3H, m), 7·90—7·25 (6H, m), and 3·92 (3H, s, NMe) (Found: C, 83·65; H, 5·35; N, 5·2. Calc. for $C_{18}H_{13}NO$: C, 83·35; H, 5·05; N, 5·4%).

(b) *By selenium.* A mixture of the *trans*-lactam (IIIb) (1·1 g) and selenium (1·7 g) was heated at 220—250° for 3 h. Treatment as described in (a) gave crude crystals (1·1 g); g.l.c. showed three components but no *trans*-lactam (IIIb). The mixture was chromatographed repeatedly on alumina with benzene as eluant. The residue from the first fraction was recrystallised from methanol to give needles of cis-4b,10b,11,12-*tetrahydro*-5-*methylbenzo*-[c]*phenanthridin*-6(5H)-*one* (VIIb) (490 mg, 43%), m.p. 161—162°, $\nu_{max.}$ (Nujol) 1645 cm^{-1} (N–CO), $\delta(CDCl_3)$ 8·05 (1H, m, 4-H), 4·75 (1H, d, *J* 4·5 Hz, 4b-H), and 3·10 (3H, s, NMe) (Found: C, 82·35; H, 6·35; N, 5·4. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%). The second fraction yielded crystals of the aromatised product (VIIIb) (102 mg, 9%), m.p. 148—149° (from methanol), identical with the sample obtained in (a) (t.l.c. and i.r. spectrum). Dehydrogenation of the *cis*-lactam (VIIb) with 10% palladium–charcoal gave only (VIIIb) (75%), also identical with the sample obtained in (a).

Dehydrogenation of the trans-*Lactam* (IIIa).—(a) *By* 10% *palladium–charcoal.* Treated as for (IIIb), the *trans*-lactam (IIIa) (100 mg) with 10% palladium–charcoal (100 mg) afforded the *benzo*[c]*phenanthridin*-6(5H)-*one* (VIIIc) (5 mg, 7%), identical with a sample prepared by dehydrogenation of (IIIc) (t.l.c. and i.r. spectrum).

(b) *By selenium.* By a procedure similar to that described for (IIIb), the *trans*-lactam (IIIa) (500 mg) with selenium (750 mg) afforded two products. The first fraction from chromatography crystallised from ethanol to afford 5-benzylbenzo[*c*]phenanthridin-6(5*H*)-one (VIIIa) (40 mg, 8%), m.p. 151—153° (lit.,[13] 252°), $\nu_{max.}$ (Nujol) 1655 (N–CO), 1610, and 757 cm^{-1} (Found: C, 85·65; H, 5·05; N, 4·4. Calc. for $C_{24}H_{17}NO$: C, 85·95; H, 5·1; N, 4·2%). The second fraction afforded cis-5-*benzyl*-4b,10b,-11,12-*tetrahydrobenzo*[c]*phenanthridin*-6(5H)-*one* (VIIa) (240 mg, 49%), m.p. 141—142·5° (from methanol), $\nu_{max.}$ (Nujol) 1645 cm^{-1} (N–CO), $\delta(CDCl_3)$ 8·15 (1H, m, 4-H), 5·50 and 4·35 (2H, ABq, *J* 15·5 Hz, N·CH_2Ph), and 4·80 (1H, d, *J* 4·5 Hz, 4b-H) (Found: C, 84·75; H, 6·35; N, 3·95. $C_{24}H_{21}NO$ requires C, 84·9; H, 6·25; N, 4·15%).

Benzo[c]*phenanthridin*-6(5H)-*one* (VIIIc).—A mixture of the lactam (IIIc) (420 mg) and 10% palladium–charcoal (420 mg) was heated at 230—280° for 20 min. After cooling, hot dimethylformamide was added and the catalyst was filtered off. The filtrate was evaporated and the residue was recrystallised from dimethylformamide to give the product (VIIIc) (370 mg, 90%), as needles, m.p. 314—315° (lit.,[14] 330°), $\nu_{max.}$ (Nujol) 3140 (NH), 1660 (N–CO), 1612, and 758 cm^{-1} (Found: C, 83·25; H, 4·7; N, 5·85. Calc. for $C_{17}H_{11}NO$: C, 83·25; H, 4·5; N, 5·7%).

[12] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 105.

[13] K. K. Mathew, B. S. Pai, and K. N. Menon, *Current Sci.*, 1955, **24**, 193 (*Chem. Abs.*, 1956, **50**, 8645a).

[14] D. N. Brown, D. H. Hey, and C. W. Rees, *J. Chem. Soc.*, 1961, 3873.

trans-5-*Benzyl*-4b,5,6,10b,11,12-*hexahydrobenzo*[c]*phenanthridine* (Va).—To a solution of the *trans*-lactam (IIIa) (1 g) in anhydrous ether (120 ml), lithium aluminium hydride (580 mg) was added in small portions with cooling. The mixture was stirred at room temperature for 1 h, then the excess of lithium aluminium hydride was decomposed by adding water (with cooling). The aqueous layer was extracted with ether. The combined ether layers were washed with brine, dried (Na_2SO_4), and evaporated to give a viscous syrup, which crystallised from methanol to afford the tertiary *amine* (Va) (850 mg, 89%) as needles, m.p. 170—171°, δ($CDCl_3$) 7·90 (1H, m, 4-H) and 3·97 (1H, d, *J* 11·5 Hz, 4b-H) (Found: C, 88·4; H, 7·1; N, 4·15. $C_{24}H_{23}N$ requires C, 88·55; H, 7·1; N, 4·3%).

trans-4b,5,6,10b,11,12-*Hexahydro*-5-*methylbenzo*[c]*phenanthridine* (Vb).—Treated as for (Va), the *trans*-lactam (IIIb) (290 mg) with lithium aluminium hydride (200 mg) afforded the tertiary *amine* (Vb) (240 mg, 87%) as pale yellow needles (from methanol), m.p. 97·5—98·5°, δ($CDCl_3$) 7·75 (1H, m, 4-H), 4·55 and 3·85 (2H, ABq, *J* 16·5 Hz, 6-H_2), 4·05 (1H, d, *J* 11 Hz, 4b-H), and 2·25 (3H, s, NMe) (Found: C, 87·05; H, 7·5; N, 5·55. $C_{18}H_{19}N$ requires C, 86·7; H, 7·7; N, 5·6%).

cis-4b,5,6,10b,11,12-*Hexahydro*-5-*methylbenzo*[c]*phenanthridine* (XI).—(a) *From the* cis-*lactam* (VIIb). Treated as for (Va), the *cis*-lactam (VIIb) (280 mg) with lithium aluminium hydride (240 mg) afforded a yellow oil (270 mg), which was chromatographed on silica gel with benzene as an eluant. The product was distilled to give the *cis*-tertiary amine (XI) (225 mg, 85%) as a pale yellow oil, b.p. 150—160° (bath temp.) at 1 mmHg, δ($CDCl_3$) 4·00 and 3·55 (2H, ABq, *J* 15·5 Hz, 6-H_2), 3·65 (1H, d, *J* 4 Hz, 4b-H), and 2·30 (3H, s, NMe). Recrystallisation of the *perchlorate* from isopropyl alcohol afforded crystals, m.p. 199—200·5° (Found: C, 62·15; H, 5·9; N, 4·1. $C_{18}H_{20}ClNO$ requires C, 61·8; H, 5·75; N, 4·0%).

(b) *From the enamine* (X). A solution of the enamine (X) (50 mg) in anhydrous ethanol (20 ml) was hydrogenated over platinum oxide (10 mg) at room temperature for *ca.* 10 h. Filtration and evaporation gave an oil which contained no *trans*-amine (Vb) (t.l.c.). Preparative t.l.c. on silica gel afforded the amine (XI) (7 mg), identical with that prepared in (a) (t.l.c. and i.r. spectrum).

5,6,11,12-*Tetrahydro*-5-*methylbenzo*[c]*phenanthridine* (X).—By the procedure given for (Va), reduction of the 4b,10b-didehydro-lactam (IVb) (200 mg) with lithium aluminium hydride gave the *enamine* (X) (180 mg, 87%) as pale yellow crystals, m.p. 104—105° (from methanol), $\nu_{max.}$ (Nujol) 1595 and 1545 cm^{-1}, δ($CDCl_3$) 4·11 (2H, s, 6-H_2) and 2·48 (3H, s, NMe) (Found: C, 87·5; H, 6·8; N, 5·55. $C_{18}H_{17}N$ requires C, 87·4; H, 6·95; N, 5·65%).

5,6-*Dihydro*-5-*methylbenzo*[c]*phenanthridine* (IX).—By the procedure given for (Va), reduction of the lactam (VIIIb) (500 mg) with lithium aluminium hydride gave *compound* (IX) (380 mg, 80%) as pale yellow plates (from methanol), m.p. 123—124·5°, δ($CDCl_3$) 4·21 (2H, s, 6-H_2) and 2·67 (3H, s, NMe) (Found: C, 87·85; H, 6·3; N, 5·5. $C_{18}H_{15}N$ requires C, 88·15; H, 6·15; N, 5·7%).

Benzo[c]*phenanthridine* (VI).—By the procedure described for the preparation of (VIIIb), the reaction of the *trans*-amine (Va) (200 mg) with 10% palladium–charcoal (200 mg) afforded compound (VI) (90 mg, 71%) as plates (from ethanol), m.p. 135·5—137·5° (lit.,[4] 135—135·5°) (Found: C, 89·1; H, 4·85; N, 6·2. $C_{17}H_{11}N$ requires C, 89·05; H, 4·85; N, 6·1%). The picrate had m.p. 250—251° (decomp.) (from ethanol) [lit.,[15] 256—257° (decomp.)], identical with an authentic sample (i.r. spectrum and mixed m.p.).

N-*Benzyl*-N-(3,4-*dihydro*-2-*methyl*-1-*naphthyl*)*benzamide* (Id).—By the procedure given for (Ia), the reaction of the imine prepared from 2-methyl-1-tetralone (10 g) and benzylamine, with benzoyl chloride afforded the *enamide* (Id) (8·3 g, 38%) as plates (from n-hexane), m.p. 113—114°, $\nu_{max.}$ (Nujol) 1630 cm^{-1} (C=C–NBz), δ($CDCl_3$) 5·65 and 4·00 (2H, ABq, *J* 14 Hz, N·CH_2Ph) and 0·90 (3H, s, C=C–CH_3) (Found: C, 85·0; H, 6·7; N, 4·0. $C_{25}H_{23}NO$ requires C, 84·95; H, 6·55; N, 4·0%).

trans-5-*Benzyl*-4b,10b,11,12-*tetrahydro*-10b-*methylbenzo*-[c]*phenanthridin*-6(5H)-*one* (IIId).—A solution of the enamide (Id) (3·5 g) in methanol (500 ml) was irradiated for 106 h. The solvent was removed and the residue was chromatographed on silica gel with benzene as eluant. The first fraction yielded a small amount of the starting enamide (Id). The second fraction, after recrystallisation from n-hexane, yielded pale yellow crystals of *compound* (IIId) (700 mg, 20%), m.p. 147—148°, $\nu_{max.}$ (Nujol) 1655 cm^{-1} (N–CO), δ($CDCl_3$) 8·15 (1H, m, 7-H), 5·16br (1H, s, 4b-H), 5·13 and 4·40 (2H, ABq, *J* 16 Hz, N·CH_2Ph), and 1·06 (3H, s, CMe) (Found: C, 85·25; H, 6·3; N, 3·8. $C_{25}H_{23}NO$ requires C, 84·95; H, 6·55; N, 4·0%).

N-*Benzyl*-(2-*bromo*-3,4-*dihydro*-1-*naphthyl*)*benzamide* (IIa).—To a solution of the enamide (Ia) (6·8 g) in carbon tetrachloride (280 ml), *N*-bromosuccinimide (4 g) was added in portions with stirring, and stirring was continued for a further 30 min at room temperature. The crystals were collected and the filtrate was evaporated to dryness under reduced pressure at low temperature. The residue was recrystallised from n-hexane to give the *bromo-enamide* (IIa) (5·2 g, 71%), m.p. 132—134°, $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (C=C–NBz), δ($CDCl_3$) (no olefinic proton) 4·55 and 5·30 (2H, ABq, *J* 14 Hz, N·CH_2Ph) (Found: C, 68·75; H, 4·6; N, 3·15. $C_{24}H_{20}BrNO$ requires C, 68·9; H, 4·8; N, 3·35%).

N-(2-*Bromo*-3,4-*dihydro*-1-*naphthyl*)-N-*methylbenzamide* (IIb).—By the procedure given for (IIa), the reaction of (Ib) with *N*-bromosuccinimide afforded the *bromo-enamide* (IIb) (42%), m.p. 131·5—132° (from n-hexane), $\nu_{max.}$ ($CHCl_3$) 1645 cm^{-1} (C=C–NBz), δ($CDCl_3$) (no olefinic protons) 3·30 (3H, s, NMe) (Found: C, 62·95; H, 4·9; N, 3·95. $C_{18}H_{16}BrNO$ requires C, 63·15; H, 4·7; N, 4·1%). The bromo-enamide (IIb) was also obtained by bromination with bromine in carbon tetrachloride, in 74% yield.

11,12-*Dihydro*-5-*methylbenzo*[c]*phenanthridin*-6(5H)-*one* (IVb).—A solution of the *N*-benzoyl enamine (Ib) (263 mg) and iodine (127 mg) in methanol (50 ml) was irradiated for 40 h. Evaporation left a residue, which was extracted with chloroform. The extract was washed with aqueous sodium thiosulphate and water, dried (Na_2SO_4), and evaporated to give a black oil, which was chromatographed on silica gel. Elution with chloroform gave crystals, which afforded *compound* (IVb) (55 mg, 21%) as pale yellow crystals, m.p. 143—145° (from ether), $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1}, δ($CDCl_3$) 8·52 (1H, m, 7-H), 3·75 (3H, s, NMe), and 2·82 (4H, s, CH_2·CH_2) (Found: C, 83·0; H, 5·75; N, 5·25. $C_{18}H_{15}NO$ requires C, 82·75; H, 5·8; N, 5·35%).

5-*Benzyl*-11,12-*dihydrobenzo*[c]*phenanthridin*-6(5H)-*one* (IVa).—A solution of the bromo-enamide (IIa) (4·8 g) in methanol (575 ml) was irradiated with cooling for 15 h.

[15] W. M. Whaley and M. Meadow, *J. Org. Chem.*, 1954, **19**, 661.

Potassium hydroxide in methanol was added dropwise with cooling and the resulting solution was stirred under reflux for 1·5 h, then evaporated to one third of its volume. Water was added and the mixture was extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated to give a red oil, which was chromatographed on alumina. Elution with benzene–chloroform (1 : 1) gave crystals, which afforded *compound* (IVa) (1·1 g, 28%), m.p. 129—131° (from ether), $\nu_{max.}$ ($CHCl_3$) 1645 cm^{-1}, δ($CDCl_3$) 8·48 (1H, m, 4-H), 5·58 (2H, s, $N{\cdot}CH_2Ph$), and 2·80 (4H, s, $CH_2{\cdot}CH_2$) (Found: C, 85·65; H, 5·4; N, 4·3. $C_{24}H_{19}NO$ requires C, 85·45; H, 5·7; N, 4·15%).

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