Photocyclisation of Enamides. Part III.[1] Photocyclisation of *N*-Benzoylenamines of Cyclohexanone and 2-Substituted Cyclohexanones[2]

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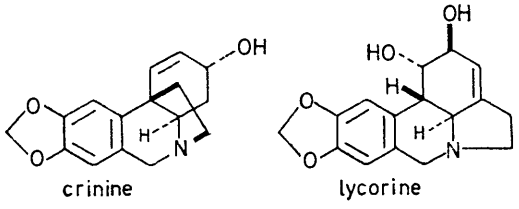
Irradiation of methanolic solutions of *N*-benzoylenamines [(I), (VIII), and (IX)] of cyclohexanone and 2-substituted cyclohexanones (R = Me or CO_2Et) resulted in stereoselective photocyclisation to give *trans*-octahydrophenanthridones [(II), (X), and (XI)]. However irradiation of the enamide (Ia) in the presence of iodine afforded the hexahydrophenanthridone (V), which was also obtained from the 6-bromo-enamide (VI) upon irradiation. The conjugated oxo-enamides (XIV) afforded the hexahydrophenanthridones (XV) even under non-oxidative conditions.

trans-OCTAHYDROPHENANTHRIDINE constitutes part of the skeleton of many alkaloids[3] such as crinine and



lycorine. As an extension of the photocyclisation of enamides,[1] we now report that *N*-benzoylenamines of cyclohexanones undergo stereoselective photocyclisation to form *trans*-octahydrophenanthridones; this phenanthridine synthesis *via* a stable intermediate enamide seems to have advantages over previously established methods,[4] which mostly involve a Diels–Alder reaction of a butadiene with a nitrostyrene.

The imines, prepared from cyclohexanone and primary amines, were readily benzoylated as described previously,[1] to afford the *N*-benzoylenamines (Ia and b) in 72—74% yields [$\nu_{max.}$ 1625 cm^{-1}; δ *ca.* 5·34 (=CH)].

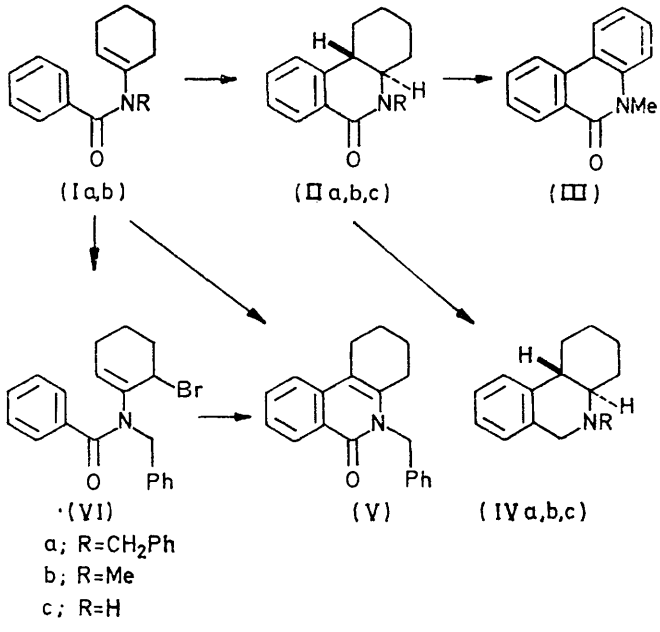
Irradiation with a low-pressure mercury lamp of a methanolic solution of the *N*-benzoylenamine (Ia) for 40 h afforded a crystalline photoproduct (IIa) (35% yield), identified by i.r. absorption at 1640 cm^{-1}, an isolated low-field aromatic proton signal at δ 8·20 (7-H), and the lack of an olefinic proton signal. The *N*-methylenamide (Ib) similarly gave the lactam (IIb) in 15% yield.

The *N*-benzyl-lactam (IIa) was debenzylated with sodium in liquid ammonia to give the lactam (IIc), which was then methylated with methyl iodide to afford the *N*-methyl-lactam, identical with the photoproduct (IIb).

The skeletal structure of the photoproducts (IIa and b) was confirmed by the conversion of (IIb), by dehydrogenation with palladium–charcoal, into *N*-methylphenanthridone (III), identical with an authentic sample.[5]

The stereochemistry of the photoproducts was deduced from the 4a-proton n.m.r. signals [δ 3·35 (td, J 11 and 3·5 Hz), and unequivocally established by conversion into the known compounds (IVb and c).[6] The photoproduct (IIb) and the lactam (IIc) were reduced with lithium aluminium hydride to the corresponding amines (IVb and c); the latter was identical with an authentic sample[6] of B/C-*trans*-compound.

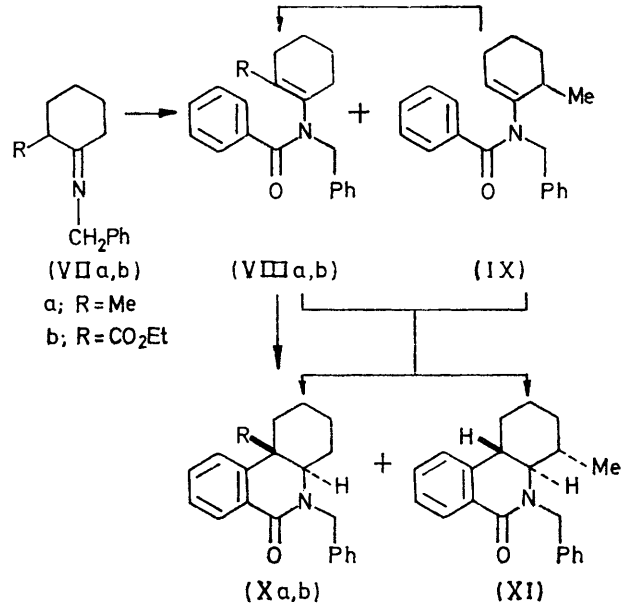
When irradiation of the enamide (Ia) was carried out in the presence of iodine, the hexahydrophenanthridone (V) was obtained as the sole product in 54% yield. Thus photocyclisation of *N*-benzoylenamines of cyclic ketones is non-oxidative and proceeds stereoselectively to afford the *trans*-fused photoproduct.



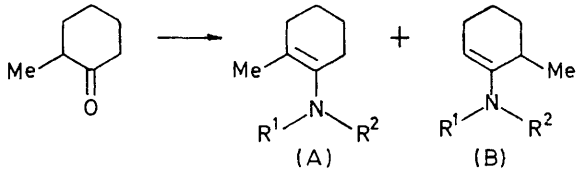
Further examples of the photocyclisation were observed with substituted enamides, to provide information on the orientation of the ring closure. When the imine prepared from 2-methylcyclohexanone and benzylamine was treated with benzoyl chloride, a mixture of two isomeric enamides [(VIIIa) and (IX)] was obtained in 65% yield. Attempted separation was unsuccessful.

[1] Part II, I. Ninomiya, T. Naito, and T. Kiguchi, *J.C.S. Perkin I*, 1973, 1696.
[2] I. Ninomiya, T. Naito, and T. Kiguchi, *Tetrahedron Letters*, 1970, 4451.
[3] T. Kametani, ' The Chemistry of the Isoquinoline Alkaloids,' Hirokawa, Tokyo, 1968, pp. 176—212.
[4] J. A. Van Allan, ' The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1958, vol. 12, p. 281.
[5] T. Hase, *Acta Chem. Scand.*, 1964, **18**, 1806; C. B. Reese, *J. Chem. Soc.*, 1958, 895.
[6] T. Masamune, M. Ohno, M. Koshi, S. Ohuchi, and T. Iwadare, *J. Org. Chem.*, 1964, **29**, 1419; T. Nomura, *J. Pharm. Soc. Japan*, 1957, **77**, 270.

However, when the mixture was directly irradiated with a high pressure mercury lamp, or heated at 200 °C for 2h,



the enamide (IX) was converted into the minor component (VIIIa) [δ 4·90 and 4·70 (ABq, PhCH_2) and 1·20 (s, Me); no olefinic signal]. The n.m.r. spectrum of the

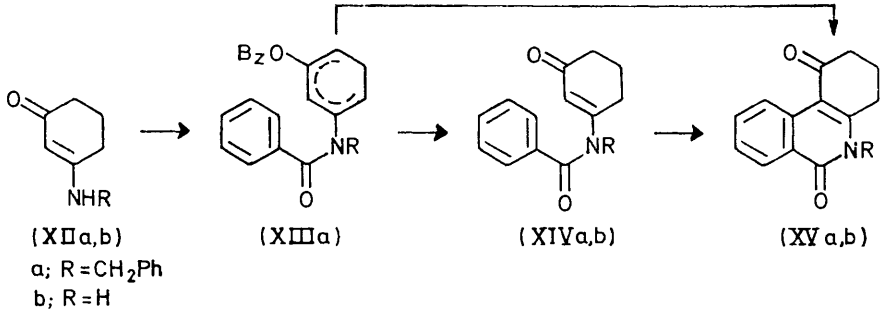


mixture showed peaks at δ 5·37 (0·8H, t, olefinic), 5·10 and 4·60 (1·6H, PhCH_2), 0·95 (2·4H, d, Me), and 4·90 and 4·70 (0·4H, PhCH_2), in agreement with the presence of a mixture of (VIIIa) and (IX) in the ratio 1 : 4. Gurowitz,[7] in discussing the stability of enamines derived from 2-substituted ketones, showed that the product ratio is affected by whether the nitrogen lone pair is conjugated with the double bond or the amine substituent, *i.e.* the enamine formed from 2-methylcyclohexanone and *N*-methylaniline apparently exists mostly in form (A), whereas that formed from pyrrolidine exists predominantly in form (B). In our case conjugation of the nitrogen lone-pair with the benzoyl group would be preferable to conjugation with the double bond. Thus, thermal or photoinduced isomerisation of the trisubstituted enamide (IX) to the tetrasubstituted enamide (VIIIa) might be expected. Photocyclisation of the enamide (VIIIa) in methanol proceeded smoothly to afford the lactam (Xa) as the sole product, whereas irradiation of the mixture of enamides (VIIIa and IX) afforded the corresponding mixture of lactams (Xa and XI), but in a ratio of 3 : 2, which suggested that partial isomerisation occurred competitively during the course of the photocyclisation.

The structures of the two photoproducts (Xa and XI) were deduced mainly from the n.m.r. spectra. That of compound (Xa) exhibited signals at δ 1·15 (s, Me) and 3·65 (dd, *J* 11 and 4 Hz, 4a-H), in agreement with the B/C-*trans* structure, with an angular methyl group. The spectrum of the photoproduct (XI) exhibited a doublet at δ 1·10 (Me) and a double doublet at δ 3·30 (*J* 11·3 and 9·5 Hz), in agreement with a B/C-*trans* structure with a C-4 equatorial methyl group.

Treatment of ethyl 2-oxocyclohexanecarboxylate with benzylamine afforded the corresponding imine in good yield, which was benzoylated smoothly to afford only the enamide (VIIIb), in 82% yield, which showed no olefinic proton signal in the n.m.r. spectrum. Photocyclisation of the enamide (VIIIb) in methanol proceeded smoothly to afford the product (Xb) in 40% yield. This photoproduct (Xb) showed i.r. absorption at 1720 (isolated CO_2Et) and 1640 cm^{-1} (lactam CO) and the n.m.r. signal of the 4a-proton at δ 3·85 as a double doublet (*J* 10 and 5 Hz).

The imine (XIIa), prepared from dihydroresorcinol and benzylamine, was treated with benzoyl chloride to



afford the dibenzoyl derivative (XIIIa), which was then carefully hydrolysed with sodium hydroxide to give the enamide (XIVa). The corresponding enamide (XIVb) was obtained directly from 3-aminocyclohex-2-enone and benzoyl chloride.

Although irradiation of these conjugated oxo-enamides (XIVa and b) was carried out nonoxidatively in degassed methanol, the products were the hexahydrophenanthridones (XVa and b), respectively. Oxidative photocyclisation of (XIVa) in the presence of iodine also

[7] W. D. Gurowitz, and M. A. Joseph, *J. Org. Chem.*, 1967, **32**, 3289.

afforded the hexahydrophenanthridone (XVa), and *N*-benzylbenzamide [8] and dihydroresorcinol monomethyl ether [9] as decomposition products. In addition, irradiation of the dibenzoate (XIIIa) afforded the hexahydrophenanthridone lactam (XVa), though in a poor yield. These results suggest that the formation of the hexahydrophenanthridone depends not only on the reaction conditions, but also on the structure of the enamide.

Bromination [10] of the enamide (IIa) afforded the bromo-enamide (VI) in good yield [δ 5·51 (=CH)]. Photocyclisation of this compound (VI) proceeded analogously, but was accompanied by elimination of hydrogen bromide to afford the hexahydrophenanthridone (V), identical with the product (V) from the oxidative photocyclisation of the enamide (Ia).

Photocyclisations of enamides with substituents on the benzene ring have been studied, and these reactions have been applied to natural products.[11]

EXPERIMENTAL

N.m.r. spectra were determined for solutions in deuteriochloroform with Varian A-60D and HA-100 instruments (tetramethylsilane as internal reference). M.p.s were determined with a Kofler hot-stage apparatus. The photochemical reactions were carried out as described in Part II.[1]

N-Benzyl-N-cyclohex-1-enylbenzamide (Ia).—A solution of cyclohexanone (24 g) and benzylamine (27·5 g) in benzene was refluxed for 3 h; water was removed as formed. The resulting yellow solution was evaporated under reduced pressure. The residual oil was distilled *in vacuo* to give *N*-cyclohexylidenebenzylamine (38·5 g) as a pale yellow oil, b.p. 130° at 5 mmHg. To a cooled solution of the imine and triethylamine (23 g) in anhydrous benzene (200 ml), a solution of benzoyl chloride (29 g) in anhydrous benzene (150 ml) was added dropwise with stirring. After refluxing for 1 h, the mixture was diluted with benzene and the organic layer was washed with water, dried (Na_2SO_4), and evaporated to give a solid, which was crystallised from n-hexane to afford the *enamide* (Ia) (53 g, 74%), m.p. 73—74°, $\nu_{max.}$ ($CHCl_3$) 1625 cm^{-1} (C=C–NBz), δ ($CDCl_3$) 5·27 (1H, m, HC=C–N) and 4·80 (2H, s, N·CH_2Ph) (Found: C, 82·45; H, 7·15; N, 4·75. $C_{20}H_{21}NO$ requires C, 82·45; H, 7·25; N, 4·8%).

N-Cyclohex-1-enyl-N-methylbenzamide (Ib).—The similar reaction of *N*-cyclohexylidenemethylamine with benzoyl chloride afforded the *enamide* (Ib) (72%) as an oil, b.p. 125° (bath temp.) at 3×10^{-3} mmHg, $\nu_{max.}$ ($CHCl_3$) 1625 cm^{-1} (C=C–N·COPh), δ ($CDCl_3$) 5·40 (1H, m, HC=C–N) and 3·15 (3H, s, NMe) (Found: C, 77·8; H, 7·9; N, 6·55. $C_{14}H_{17}NO$ requires C, 78·1; H, 7·95; N, 6·5%).

trans-5-*Benzyl*-1,2,3,4,4a,10b-*hexahydrophenanthridin*-6(5H)-*one* (IIa).—A 0·02M-solution of the *N*-benzylenamide (Ia) (4·7 g) in methanol (800 ml) was irradiated for 40 h. T.l.c. showed the complete disappearance of the starting material. Removal of the solvent and recrystallisation from methanol afforded the *lactam* (IIa) (1·6 g, 35%), m.p. 154—155°, $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (N–CO), δ (100 MHz; $CDCl_3$) 8·20 (1H, m, 7-H), 5·35 and 4·55 (2H, ABq, *J* 16 Hz, N·CH_2Ph), and 3·35 (1H, td, *J* 11 and 3·5 Hz, 4a-H) [irradiation at 1·47 caused collapse of td at 3·35 to dd (*J* 11 and 3·5 Hz); irradiation at 1·76 caused collapse of td at 3·35 to a doublet (*J* 11 Hz)] (Found: C, 82·1; H, 6·95; N, 4·75. $C_{20}H_{21}NO$ requires C, 82·45; H, 7·25; N, 4·8%).

trans-1,2,3,4,4a,10b-*Hexahydro-5-methylphenanthridin*-6(5H)-*one* (IIb).—Similar irradiation of the enamide (Ib) (14·2 g) in methanol afforded the *lactam* (IIb) (2·1 g, 15%) as needles (from n-hexane), m.p. 141—143°, $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (N·CO), δ ($CDCl_3$) 8·10 (1H, m, 7-H) and 3·10 (3H, s, NMe) (Found: C, 78·35; H, 8·0; N, 6·5. $C_{14}H_{17}NO$ requires C, 78·1; H, 7·95; N, 6·5%).

trans-1,2,3,4,4a,10b-*Hexahydrophenanthridin*-6(5H)-*one* (IIc).—To a solution of the *N*-benzyl-lactam (IIa) (7·1 g) in liquid ammonia (*ca.* 200 ml), sodium (2·7 g) was added carefully in small portions. The blue mixture was stirred for 30 min, before decomposition with an excess of ammonium chloride. The ammonia was evaporated off and the residue was treated with water and chloroform. The chloroform layer was separated and the aqueous layer was extracted with chloroform. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated. Recrystallisation from chloroform afforded the lactam (IIc) (2·5 g, 52%), m.p. 218—219° (sealed tube), $\nu_{max.}$ ($CHCl_3$) 3400 (NH) and 1665 cm^{-1} (N·CO) (Found: C, 77·65; H, 7·25; N, 6·75. $C_{13}H_{15}NO$ requires C, 77·6; H, 7·5; N, 6·95%).

Methylation of the Lactam (IIc).—A mixture of the lactam (IIc) (201 mg), methyl iodide (710 mg), potassium hydroxide (280 mg), and anhydrous acetone (40 ml) was refluxed for 14 h. The mixture was cooled and filtered, and the filtrate was evaporated. The residue was extracted with chloroform and the extract was washed with water, dried (Na_2SO_4), and evaporated to give a solid (210 mg), which was chromatographed on silica gel. Elution with chloroform gave crystals which were recrystallised from n-hexane to give the *N*-methyl-lactam (IIb) (100 mg, 47%), m.p. 141—143°, identical (t.l.c., i.r. spectrum, and mixed m.p.) with the photoproduct (IIb) from (Ib).

5-*Methylphenanthridin*-6(5H)-*one* (III).—A mixture of the lactam (IIb) (50 mg) and 10% palladium–charcoal (50 mg) was heated at 220—250° for 3 h. After cooling, hot methanol was added and the catalyst was filtered off. Evaporation of the solution gave a solid, which was chromatographed on silica gel with chloroform as an eluant to give the phenanthridone (III), as needles (from n-hexane), m.p. 107—109° (lit.,[5] 107—108°), identical (i.r. and u.v. spectra) with an authentic sample.[5]

trans-1,2,3,4,4a,5,6,10b-*Octahydro-5-methylphenanthridine* (IVb).—To a solution of the lactam (IIb) (1·1 g) in anhydrous ether–tetrahydrofuran (5 : 1; 100 ml), lithium aluminium hydride (950 mg) was added carefully in small portions. The mixture was refluxed for 1 h, then 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 amine (IVb) (900 mg, 89%) as a pale yellow oil. The picrate afforded yellow crystals, m.p. 170—171° (from ethanol) (lit.,[6] 167—168°) (Found: C, 56·2; H, 5·05; N, 12·85. Calc. for $C_{20}H_{22}N_4O_7$: C, 55·8; H, 5·15; N, 13·0%).

trans-5-*Benzyl*-1,2,3,4,4a,5,6,10b-*octahydrophenanthridine* (IVa).—Similar reaction of the lactam (IIa) (500 mg) with

[8] E. Beckmann, *Ber.*, 1904, **37**, 4136.
[9] H. Stetter and W. Dierichs, *Chem. Ber.*, 1952, **85**, 61.
[10] R. A. Henry, A. T. Nielsen, and D. W. Moore, *J. Org. Chem.*, 1972, **37**, 3206.
[11] I. Ninomiya, T. Naito, T. Kiguchi, *Chem. Comm.*, 1970, 1669; *J.C.S. Chem. Comm.*, 1973, in the press; *J.C.S. Perkin I*, following paper.

lithium aluminium hydride afforded the tertiary *amine* (IVa) (380 mg, 80%) as a pale yellow oil, b.p. 180—190° at 1 mmHg (Found: C, 86·35; H, 8·45; N, 5·1. $C_{20}H_{23}N$ requires C, 86·6; H, 8·35; N, 5·05%).

trans-1,2,3,4,4a,5,6,10b-*Octahydrophenanthridine* (IVc).—Similar reaction of the lactam (IIc) (2 g) with lithium aluminium hydride afforded the secondary amine (IVc) (1·6 g, 87%), m.p. 87° (from petroleum) (lit.,[6] 88—90°; 86·5—87·5°), $\nu_{max.}$ (Nujol) 3150 cm^{-1} (NH), identical (t.l.c., i.r. spectrum, and mixed m.p.) with an authentic sample [6] (Found: C, 83·65; H, 9·15; N, 7·25. Calc. for $C_{13}H_{17}N$: C, 83·35; H, 9·15; N, 7·5%).

Benzoylation of N-(2-*Methylcyclohexylidene*)*benzylamine* (VIIa).—According to the procedure given for (Ia), acylation of the imine prepared from 2-methylcyclohexanone (25 g) and benzylamine with benzoyl chloride afforded an oil, which was chromatographed several times on silica gel and alumina with benzene and chloroform. A colourless oil (43·8 g, 64%), homogeneous on t.l.c., was obtained; however, it was found to be a mixture of *N*-benzyl-*N*-(2-methylcyclohex-1-enyl)benzamide (VIIIa) and *N*-benzyl-*N*-(6-methylcyclohex-1-enyl)benzamide (IX) in a ratio of *ca.* 1 : 4 (n.m.r.). Rapid distillation of the oil gave a sample which showed $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–N·COPh), δ ($CDCl_3$) 5·37 (*ca.* 0·8H, approx. t, HC=CN), 5·10 and 4·60 (*ca.* 1·6H, ABq, *J* 15 Hz, N·CH_2Ph), 4·90 and 4·70 (*ca.* 0·4H, ABq, *J* 14 Hz, N·CH_2Ph), and 0·95 (*ca.* 2·4H, d, *J* 6·5 Hz, CH·CH_3) (Found: C, 82·3; H, 7·6; N, 4·5. Calc. for $C_{21}H_{23}NO$: C, 82·6; H, 7·6; N, 4·6%).

N-*Benzyl*-N-(2-*methylcyclohex*-1-*enyl*)*benzamide* (VIIIa).—The 1 : 4 mixture (4 g) of the enamides (VIIIa) and (IX) was irradiated with a 1 kW high-pressure mercury lamp for 20 min; isomerisation was monitored by observing the i.r. spectrum. The resulting oil was chromatographed on alumina with benzene as eluant to give the *enamide* (VIIIa), b.p. 150—160° (bath temp.) at 2 × 10^{-3} mmHg, homogeneous on t.l.c., $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–N·COPh), δ ($CDCl_3$) 4·90 and 4·70 (2H, ABq, *J* 14 Hz, N·CH_2Ph) and 1·20 (3H, s, C=C–CH_3) (Found: C, 82·65; H, 7·55; N, 4·3. $C_{21}H_{23}NO$ requires C, 82·6; H, 7·6; N, 4·6%). The isomerisation also occurred on heating at 200 °C without solvent.

trans-5-*Benzyl*-1,2,3,4,4a,10b-*hexahydro*-10b-*methylphenanthridin*-6(5H)-*one* (Xa).—According to the procedure given for (Ia), irradiation of the *N*-benzoylenamine (VIIIa) (3 g) in methanol and chromatography of the crude photoproduct on alumina with benzene as eluant afforded the *lactam* (Xa) (1·6 g, 55%) as plates (from n-hexane), m.p. 90—92°, $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (N·CO), δ ($CDCl_3$) 8·25 (1H, m, 7-H), 3·65 (1H, dd, *J* 11 and 4 Hz, 4a-H), and 1·15 (3H, s, CMe) (Found: C, 82·7; H, 7·4; N, 4·6. $C_{21}H_{23}NO$ requires C, 82·6; H, 7·6; N, 4·6%).

Irradiation of the 1 : 4 *Mixture of* N-*Benzoylenamines* (VIIIa) *and* (IX).—Similar irradiation of the 1 : 4 mixture (1 g) of enamides in methanol was followed by repeated chromatography of the crude photoproducts on alumina with benzene as eluant. The residue from the first fraction was recrystallised from n-hexane to give the enamide (Xa) as plates (395 mg, 40%), m.p. 90—92°, identical (t.l.c. and i.r. spectrum) with the sample obtained from the photo-induced isomerisation already described. Distillation of the second fraction afforded a viscous oil, b.p. 170° (bath temp.) at 2 × 10^{-3} mmHg, which slowly crystallised, and was recrystallised from ether to give 5-*benzyl*-1,2,3,4,c-4a,t-10b-*hexahydro*-r-4-*methylphenanthridin*-6(5H)-*one* (XI) (228 mg, 23%), m.p. 101—103°, $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (N·CO), δ ($CDCl_3$) 8·10 (1H, m, 7-H), 5·30 and 4·75 (2H, ABq, *J* 16 Hz, N·CH_2Ph), 3·30 (1H, dd, *J* 11·3 and 9·5 Hz, 4a-H), and 1·10 (3H, d, *J* 5·5 Hz, CH*Me*) (Found: C, 82·1; H, 7·85. $C_{21}H_{23}NO$ requires C, 82·6; H, 7·6%).

Ethyl 2-(N-*Benzylbenzamido*)*cyclohex*-1-*enecarboxylate* (VIIIb).—According to the procedure given for (Ia), acylation of the imine prepared from ethyl 2-oxocyclohexanecarboxylate (17 g) with benzoyl chloride afforded the *enamide* (VIIIb) (29·6 g, 82%), b.p. 185° (bath temp.) at 2 × 10^{-3} mmHg, $\nu_{max.}$ ($CHCl_3$) 1705 (CO_2Et) and 1635 cm^{-1} (N·CO), δ ($CDCl_3$) 4·18 (2H, q, *J* 7 Hz, O·CH_2Me) and 1·30 (3H, t, *J* 7 Hz, O·CH_2*Me*) (Found: C, 75·8; H, 6·8; N, 3·9. $C_{23}H_{25}NO_3$ requires C, 76·0; H, 6·95; N, 3·85%).

Ethyl trans-5-*Benzyl*-1,2,3,4,4a,5,6,10b-*octahydro*-6-*oxophenanthridine*-10b-*carboxylate* (Xb).—According to the procedure given for (Ia), irradiation of the enamide (VIIIb) (5·3 g) in methanol for 7·5 h, and chromatography of the crude product on alumina with benzene as eluant, afforded the *lactam* (Xb) (2·1 g, 40%), m.p. 108—109° (from ether), $\nu_{max.}$ ($CHCl_3$) 1720 (CO_2Et) and 1640 cm^{-1} (NCO), δ ($CDCl_3$) 8·20 (1H, m, 7-H), 5·65 and 4·40 (2H, ABq, *J* 16·5 Hz, N·CH_2Ph), 4·05 (2H, q, *J* 7 Hz, O·CH_2Me), 3·85 (1H, dd, *J* 10 and 5 Hz, 4a-H), and 1·14 (3H, t, *J* 7 Hz, O·CH_2*Me*) (Found: C, 76·15; H, 6·9; N, 3·95. $C_{23}H_{25}NO_3$ requires C, 76·0; H, 6·95; N, 3·85%).

N-*Benzyl*-N-(6-*bromocyclohex*-1-*enyl*)*benzamide* (VI).—To a solution of the enamide (Ia) (590 mg) in carbon tetrachloride (30 ml), *N*-bromosuccinimide (534 mg) was added in portions with stirring, and stirring was continued for 1 h at room temperature. The precipitate was collected and the filtrate was evaporated at low temperature; the residue was recrystallised from n-hexane to give the *bromo-enamide* (VI) (410 mg, 73%), m.p. 88—89°, $\nu_{max.}$ ($CHCl_3$) 1633 cm^{-1} (N·CO), δ ($CDCl_3$) 5·51 (1H, t, *J* 4 Hz, HC=C), 5·45, 4·55 (2H, ABq, *J* 15 Hz, N·CH_2Ph), and 4·57br (1H, CHBr) (Found: C, 64·95; H, 5·4; N, 3·65. $C_{20}H_{20}BrNO$ requires C, 64·9; H, 5·4; N, 3·8%).

5-*Benzyl*-1,2,3,4-*tetrahydrophenanthridin*-6(5H)-*one* (V).—(a) *From the bromo-enamide* (VI). According to the procedure given for (Ia), irradiation of the bromo-enamide (VI) (5·3 g) in methanol with an external cooling for 16·5 h afforded the *hexahydrophenanthridone* (V) (200 mg, 5%), m.p. 156—157° (from ether), $\nu_{max.}$ ($CHCl_3$) 1647 cm^{-1} (N·CO), δ ($CDCl_3$) 5·46 (2H, s, N·CH_2Ph) (Found: C, 83·2; H, 6·3; N, 4·85. $C_{20}H_{19}NO$ requires C, 83·0; H, 6·6; N, 4·85%).

(b) *From the enamide* (Ia). A solution of the *N*-benzoylenamine (Ia) (290 mg) and iodine (127 mg) in methanol (50 ml) was irradiated for 30 h. Removal of the solvent and extraction of the residue with chloroform, followed by washing the extract with aqueous sodium thiosulphate and water, drying (Na_2SO_4), and evaporation, gave a viscous oil, which was triturated with ether. Recrystallisation from ether afforded the hexahydrophenanthridone (V) (156 mg, 54%) as pale brown crystals, m.p. 159—161°, identical with the photoproduct (V) obtained in (a) (t.l.c., i.r. spectrum, and mixed m.p.).

N-(3-*Oxocyclohex*-1-*enyl*)*benzamide* (XIVb).—To a solution of 3-aminocyclohex-2-enone (XIIb) (4·5 g) (prepared [12] by bubbling ammonia gas into a boiling solution of dihydroresorcinol in benzene with removal of water as it formed), and pyridine (2·76 g) dissolved in 1,2-dimethoxyethane (175 ml), a solution of benzoyl chloride (5·64 g) in dimethoxy-

[12] F. Zymalkowski and H. Rimek, *Arch. Pharm.*, 1961, **294**, 759.

ethane (35 ml) was added dropwise (20 min).[13] The resulting solution was refluxed for 1 h and left at room temperature overnight. The supernatant layer was separated and evaporated The residue was purified by chromatography on silica gel. Elution with chloroform–methanol (9 : 1) afforded material which crystallised from ethyl acetate to give the *enamide* (XIVb) as pale yellow crystals, m.p. 178—179° (1·2 g, 14·2%), $\nu_{max.}$ ($CHCl_3$) 1690 (CO), 1650 (CO·N), and 1610 cm^{-1} (C=C), δ ($CDCl_3$) 8·63br (1H, s, NH) and 6·78 (1H, s, HC=C) (Found: C, 72·75; H, 6·05; N, 6·35. $C_{13}H_{13}NO_2$ requires C, 72·55; H, 6·1; N, 6·5%).

Benzoylation of 3-*Benzylaminocyclohex-2-enone* (XIIa).—To a cooled solution of 3-benzylaminocyclohex-2-enone (XIIa) (6·03 g) (prepared in 68·2% yield by refluxing a solution of dihydroresorcinol and benzylamine in benzene with removal of water as it formed) and triethylamine (6·06 g) in anhydrous benzene (300 ml), a solution of benzoyl chloride (8·5 g) in anhydrous benzene (50 ml) was added dropwise and the resulting solution was refluxed for 1 h. Water was added and the organic layer was washed with water, dried (Na_2SO_4), and evaporated to yield a viscous oil. Chromatography on silica gel afforded the dibenzoyl derivative (XIIIa) as a viscous oil (10·8 g, 91·5%), b.p. 230—250° (bath temp.) at 3×10^{-3} mmHg, $\nu_{max.}$ ($CHCl_3$) 1732 (O·COPh), 1638 (CO·N), and 1257 and 1133 cm^{-1} (ester), δ ($CDCl_3$) 5·83 (1H, diffused s, C=C–CH=C), 4·98 (1H, approx. t, HC=C), and 4·86 (2H, s, NCH_2Ph) (Found: C, 79·2; H, 5·65; N, 3·4. Calc. for $C_{27}H_{23}NO_3$: C, 79·1; H, 5·55; N, 3·5%).

N-*Benzyl*-N-(3-*oxocyclohex*-1-*enyl*)*benzamide* (XIVa).—Compound (XIIIa) (7·3 g) was dissolved in methanol (100 ml) containing 0·5 mol. equiv. of potassium hydroxide, and the resulting solution was stirred at room temperature. The reaction was monitored by t.l.c. Extraction with chloroform followed by washing with water, drying (Na_2SO_4) and evaporation afforded a pale brown solid, which was recrystallised from ether to give the N-*benzylenamide* (XIVa) as pale brown crystals (1·9 g, 35%), m.p. 127—127·5°, $\nu_{max.}$ ($CHCl_3$) 1655 cm^{-1} (CO), δ ($CDCl_3$) 5·80 (1H, s, HC=C) and 5·03 (2H, s, N·CH_2Ph) (Found: C, 78·5; H, 6·2; N, 4·45. $C_{20}H_{19}NO_2$ requires C, 78·65; H, 6·25; N, 4·6%).

2,3,4,5-*Tetrahydrophenanthridine*-1,6-*dione* (XVb).—Irradiation of the enamide (XIVb) (1·2 g) in methanol (260 ml) for 150 h afforded the *lactam* (XVb) (100 mg, 8%), m.p. 263—264° (from methanol), $\nu_{max.}$ (Nujol) 1650 cm^{-1} (CO), δ [$(CD_3)_2SO$] 11·80br (1H, s, NH), 9·20 (1H, dd, *J* 2 and 8 Hz, aromatic), and 8·25 (1H, dd, *J* 2 and 8 Hz, aromatic) (Found: C, 72·9; H, 5·4; N, 6·40. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·55%). The lactam (XVb) was also obtained from irradiation of the enamide (XIVb) in benzene for 43·5 h in 30% yield and from irradiation of the dibenzoyl derivative (XIIIa) in methanol, though in poor yield. Irradiation in degassed methanol afforded the same result.

5-*Benzyl*-2,3,4,5-*tetrahydrophenanthridine*-1,6-*dione* (XVa).—Irradiation of the *N*-benzylenamide (XIVa) (460 mg) in methanol (75·4 ml) for 6 h, followed by chromatography on silica gel afforded the *dione* (XVa) (270 mg, 60%), which formed yellow crystals, m.p. 165—166° (from methanol), $\nu_{max.}$ ($CHCl_3$) 1650 cm^{-1} (CO), δ ($CDCl_3$) 8·46 (1H, dd, *J* 2 and 8 Hz, aromatic), 7·77 (1H, dt, *J* 2 and 8 Hz, aromatic), 7·55 (1H, dd, *J* 8 and 2 Hz, aromatic), and 5·50 (2H, s, N·CH_2Ph) (Found: C, 79·05; H, 5·5; N, 4·45. $C_{20}H_{17}NO_2$ requires C, 79·2; N, 5·65; N, 4·6%).

Irradiation of the N-*Benzylenamide* (XIVa) *in the Presence of Iodine*.—Irradiation of a methanolic solution of the *N*-benzylenamide (XIVa) in the presence of iodine afforded three products (t.l.c.); 3-methoxycyclohex-2-enone,[9] *N*-benzylbenzamide,[8] and the *N*-benzyl-lactam (XVa), identified by direct comparison with authentic samples.

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[13] *Cf.* D. L. Ostercamp, *J. Org. Chem.*, 1970, **35**, 1632.