Photocyclisation of Enamides. Part I. Photochemical Reactions of *N*-Acyl Enamines [1]

By **Ichiya Ninomiya,* Takeaki Naito,** and **Takako Mori,** Kobe Women's College of Pharmacy, Motoyama, Higashinada, Kobe, Japan

Irradiation of ethereal solutions of the *N*-benzoyl enamines (8a—d) of 2-tetralone with a low pressure mercury lamp afforded benzo[*a*]phenanthridones (10a—d) as the major products along with the acyl-migration product (9). The structure and stereochemistry of the photoproducts have been established. Similar irradiation of the corresponding *N*-acetyl enamines (1) and (5a—d), however. afforded only acyl-migration products which on hydrolysis provided 2-acetyl ketones in comparable yields. The transformation of the *trans*-photoproduct (10b) into the *cis*-isomer (12) was observed when the former was heated with selenium at an elevated temperature.

ACYL migration [2] has been regarded as the only behaviour exhibited by *N*-acyl enamines (or enamides) under u.v. irradiation. For example, *N*-acyl anilides undergo an acyl migration to give *ortho*- and *para*-substituted compounds.[3] However, Chapman and his co-workers have reported a non-oxidative photocyclisation of *N*-acryloyl anilides to dihydroisoquinoline derivatives.[4]

During the syntheses of ring systems related to azasteroids, we prepared the *N*-acetyl and *N*-benzoyl enamines of cyclohexanone and 2-tetralone and subjected them to u.v. irradiation. We found that the *N*-acetyl enamines underwent an acetyl migration analogous

[1] I. Ninomiya, T. Naito, and T. Mori, *Tetrahedron Letters*, 1969, 2259.

[2] (*a*) N. C. Yang and G. R. Lenz, *Tetrahedron Letters*, 1967, 4897; (*b*) P. T. Izzo and A. S. Kende, *ibid.*, 1966, 5731; (*c*) R. W. Hoffmann and K. R. Eicken, *ibid.*, 1968, 1759; (*d*) R. W. Hoffmann and K. R. Eicken, *Chem. Ber.*, 1969, **102**, 2987.

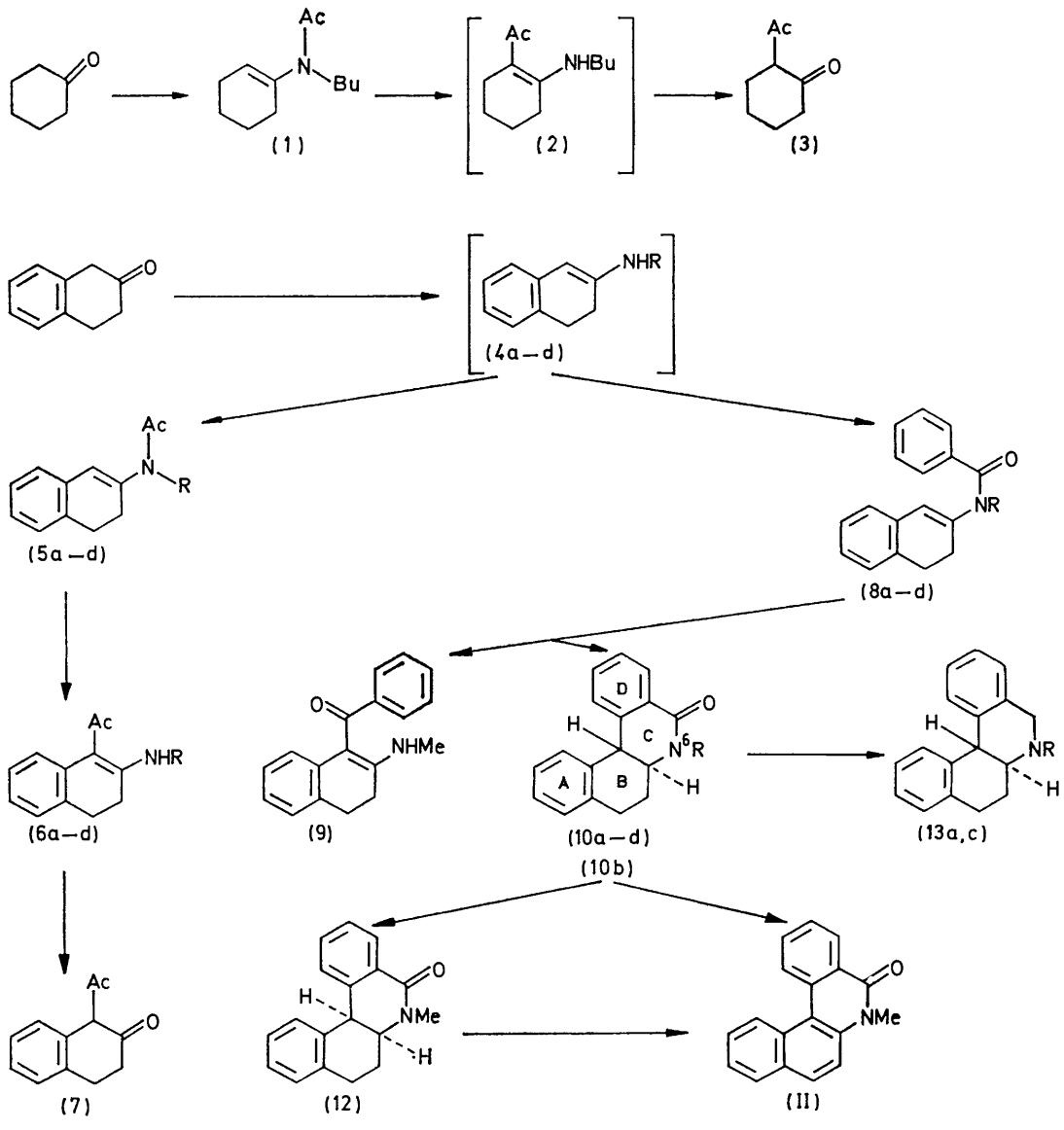
[3] (*a*) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, 1965, **30**, 3252; (*b*) M. Fischer, *Chem. Ber.*, 1969, **102**, 342.

[4] (*a*) P. G. Cleveland and O. L. Chapman, *Chem. Comm.*, 1967, 1064; (*b*) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 2333.

to those in the literature [2,3] but the *N*-benzoyl enamines underwent a hitherto unknown stereospecific, non-oxidative photocyclisation to give saturated heterocyclic systems.

The *N*-acetyl enamines (1) and (5a—d) of cyclohexanone and 2-tetralone were readily prepared by acetylation of the corresponding imines with acetic anhydride in the presence of pyridine. The structures of the enamides were assigned from spectral data, particularly from i.r. spectra, which contained absorptions characteristic of an enamide at *ca.* 1635 cm^{-1}.

The irradiation of the enamide (1) (0·02M in ether) was carried out using a low pressure mercury lamp over 66 h. The product exhibited i.r. absorptions at 1595 and 1560 cm^{-1} characteristic of a vinylogous amide. Because of its instability, it was hydrolysed with dilute hydrochloric acid to yield 2-acetyl cyclohexanone (3) [5] (26%). A similar acetyl migration was observed for the enamides (5a—d), and on hydrolysis 1-acetyl-2-tetralone (7) [6] was obtained in *ca.* 40% yield. This photo-induced acyl migration of the *N*-acetyl enamines of cyclic ketones is useful means of preparing 2-acetyl ketones.[2a]



SCHEME 1

The *N*-benzoyl enamines (8a—d) of 2-tetralone were prepared by treatment of the imines (4) with benzoyl

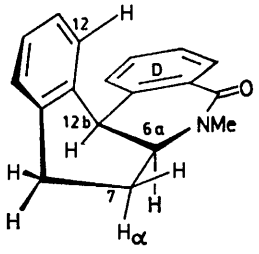
[5] J. Szmusszkovicz, in 'Advances in Organic Chemistry; Methods and Results,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, 1963, vol. IV, p. 57.

[6] W. Herz and G. Caple, *J. Org. Chem.*, 1964, **29**, 1691.

chloride in the presence of triethylamine. Similar irradiation of the *N*-benzoyl enamine (8b) was carried out until the starting enamide disappeared (t.l.c.; 40 h). Chromatography of the mixture gave the expected benzoyl-migration product (9) in small amounts only. The major component was the photocyclised product (10b) (40%), m.p. 160—163°, which was homogeneous on t.l.c. and exhibited an i.r. absorption at 1650 cm^{-1} due to a six-membered lactam carbonyl group. The n.m.r. spectrum contained peaks for eight aromatic protons and a proton at C-12b (d, J 11·3 Hz). The product (10b) was shown to be a benzo[*a*]phenanthridone by conversion with 10% palladium–charcoal or selenium into the fully aromatised lactam (11), m.p. 121—122°, which was identical with an authentic sample [7] (see Scheme 1).

Photocyclisation of the enamides (8a, c, d) afforded the products (10a, c, d) in comparable yields. Lithium aluminium hydride reduction of products (10a and c) afforded the amines (13a and c), which also exhibited a peak at δ *ca.* 4·00 (d, J 10 Hz) in the n.m.r. spectrum.

When the phenanthridone (10b) was heated with selenium at 250° for 3 h using the conventional dehydrogenation procedure compound (12), m.p. 175—178 °C, which had the same elemental composition as (10b), was obtained in 41% yield. Compound (12) was homogeneous on t.l.c. and g.l.c. and exhibited a similar i.r.



(12)

FIGURE

absorption at 1650 cm^{-1} to that of (10b). The n.m.r. spectrum [δ 4·47 (1H, d, J 5·5 Hz, 12b-H)] established that it was the epimer of compound (10b).

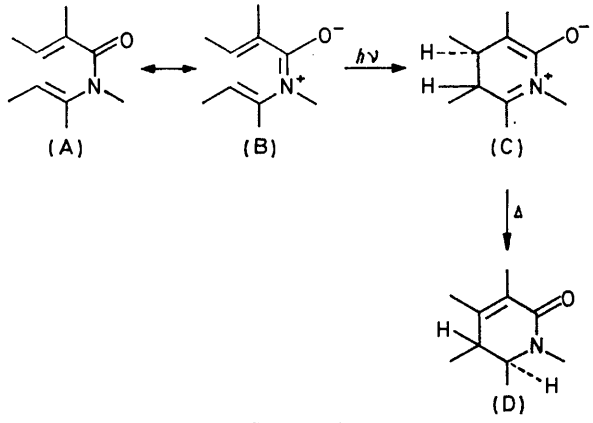
The stereochemistries of the photoproducts (10a—d) and related compounds (12) and (13a and c) were established as follows. In the n.m.r. spectra of (10b) and (12), the signal for 12b-H at the B/C ring junction was a doublet with J 11·3 for (10b) and 5·5 Hz for (12). Inspection of Dreiding models suggests that the B/C junction is *trans*-fused in (10b) and *cis*-fused in (12).[8,9] Data for the other compounds supports these conclusions. The 12-H peak for compound (12) appeared at considerably higher field than expected (δ 6·80), owing to the anisotropy of ring D, and the signal for 6a-H was a doublet of triplets (J 11 and 5·5 Hz) at δ 3·67, implying that 6a- and 7α-H are in an eclipsed conformation. The conformation of compound (12) is shown in the Figure.

[7] B. R. T. Keene and K. Schofield, *J. Chem. Soc.*, 1958, 2609.

[8] (*a*) Z. G. Hajos, K. J. Doebel, and M. W. Goldberg, *J. Org. Chem.*, 1964, **29**, 2527; (*b*) L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, Oxford, 1969, p. 280.

Therefore, the photocyclisation of the unsaturated enamides (8a—d) proceeded stereospecifically giving only the *trans*-fused benzo[*a*]phenanthridones (10a—d).

Photocyclisation in the presence of other solvents such as methanol and benzene was examined with less success.



SCHEME 2

The photocyclisation may be explained by invoking an electrocyclic mechanism [10] (Scheme 2), that is, the unsaturated enamide after excitation [(A) ⇄ (B)] would undergo photochemical cyclisation to the intermediate (C), followed by a [1,5] suprafacial, thermal hydrogen shift to the product (D). The thermal isomerisation of the *trans*-isomer (10b) to the *cis*-isomer (12) by the action of selenium may be due to a process similar to catalytic hydrogenation, that is, a 6a,12b-didehydro-intermediate is formed which then reacts in two ways. One pathway gives the aromatic compound (11) and in the other the partially reduced selenium acts as a hydrogenating agent to afford the B/C *cis*-isomer (12). This type of hydrogen transfer was also observed with palladium–charcoal though to a much lesser extent.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in deuteriochloroform with a Varian A-60D instrument with tetramethylsilane as internal reference. I.r. spectra were taken with a Hitachi EPI-S_2 spectrometer. A Shimadzu gas chromatograph GC-3APF with an SE-52 column was used for g.l.c. M.p.s were determined with a Kofler hot-stage apparatus. The photochemical reactions were carried out by irradiation at room temperature either by an external, low pressure (120 W), quartz, spiral mercury lamp (principal emission at 253·7 nm) through quartz or by an internal, quartz, pencil-shaped mercury lamp, using a 0·02M solution of the enamide in ether, benzene, or methanol.

N-Butyl-N-cyclohex-1-enylacetamide (1).—A mixture of cyclohexanone (4·9 g) and n-butylamine (4·4 g) was dissolved in benzene (50 ml). The solution was refluxed for 8 h and water was removed as it formed. The resulting yellow solution was evaporated quickly under reduced pressure. To a solution of the residue in pyridine (30 ml) was added acetic anhydride (30 ml). The mixture was left

[9] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[10] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

at room temperature overnight and evaporation left an oil which was distilled *in vacuo* to give the *amide* (1) (7·8 g, 80%), b.p. 120° at 5 mmHg, $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–N–CO) (Found: C, 73·75; H, 10·95; N, 7·15. $C_{12}H_{21}NO$ requires C, 73·8; H, 10·85; N, 7·15%).

Photolysis of the N-*Acetyl Enamine* (1) *and Hydrolysis of the Product.*—A solution of the *N*-acetyl enamine (1) (1·2 g) in ether (250 ml) was irradiated at room temperature for 66 h. Removal of the solvent left an oil which could not be purified by chromatography due to its instability. The presence of 2-acetyl-*N*-butylcyclohex-1-enylamine (2) as the main component was confirmed by its i.r. spectrum, $\nu_{max.}$ ($CHCl_3$) 1595 and 1560 cm^{-1} (N–C=C–CO). The oil was dissolved in 10% hydrochloric acid (10 ml) and the resulting solution was heated on a steam-bath for 5 min. After cooling, the aqueous layer was extracted with ether. The extract was washed with brine, dried (Na_2SO_4), and evaporated to give an oil, which was chromatographed on silica gel. Elution with benzene gave a yellow oil which was distilled to give 2-acetylcyclohexanone (3) (224 mg, 26%) as a pale yellow oil, b.p. 85—88° at 11 mmHg, identical with an authentic sample.[5] Compound (3) gave a red-purple colour with alcoholic ferric chloride.

Preparation of N-*Acetyl Enamines*(5a—d).—The preparation of the *N*-acetyl enamines (5a—d) is described for the typical example, *N*-butyl-*N*-(3,4-dihydro-2-naphthyl)acetamide (5d). A mixture of 2-tetralone (10 g), n-butylamine (10 g), toluene-*p*-sulphonic acid (small amount), and toluene (60 ml) was refluxed for 4·5 h, water being removed as it formed. Evaporation of the solvent under reduced pressure and distillation of the residual oil gave a pale yellow oil (4d) (11·2 g, 82%), $\nu_{max.}$ ($CHCl_3$) 3460 (NH) and 1630 cm^{-1} (C=C–N). To a solution of the enamine (4d) (3·3 g) in anhydrous pyridine (10 ml) was added acetic anhydride (10 ml). The mixture was left overnight at room temperature and evaporation left a residue which was distilled *in vacuo* to give the pale yellow *amide* (5d) (3·9 g, 80%), b.p. 160—165° at 1 mmHg (bath temp.), $\nu_{max.}$ 1655sh and 1633 cm^{-1} (C=C–N–CO), δ ($CDCl_3$) 6·23 (1H, nearly s, HC=C–N), 3·48 (2H, t, *J* 8 Hz, NCH_2CH_2), 2·05 (3H, s, Ac), and 0·90 (3H, t, *J* 6 Hz, CH_2CH_3) (Found: C, 78·8; H, 8·65; N, 5·7. $C_{16}H_{21}NO$ requires C, 78·95; H, 8·7; N, 5·75%).

Data for the other *N*-acetyl enamines were: N-*allyl*-N-(3,4-*dihydro*-2-*naphthyl*)*acetamide* (5a) (61%), b.p. 133—134° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1655sh and 1635c m^{-1} (C=C–N–CO), δ ($CDCl_3$) 6·31 (1H, nearly s, HC=C–N) and 2·13 (3H, s, Ac) (Found: C, 78·6; H, 7·75; N, 6·05. $C_{15}H_{17}NO$ requires C, 79·25; H, 7·55; N, 6·15%); N-*benzyl*-N-(3,4-*dihydro*-2-*naphthyl*)*acetamide* (5c) (63%), b.p. 160—165° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1660sh and 1640 cm^{-1} (C=C–N–CO) (Found: C, 82·0; H, 6·9; N, 4·85. $C_{19}H_{19}NO$ requires C, 82·3; H, 6·9; N, 5·05%); and N-(3,4-*dihydro*-2-*naphthyl*)-N-*methylacetamide* (5b) (87%), b.p. 123° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1655sh and 1640 cm^{-1} (C=C–N–CO) (Found: C, 76·95; H, 7·6; N, 6·85. $C_{13}H_{15}NO$ requires C, 77·6; H, 7·5; N, 6·95%).

N-*Benzoyl Enamines* (8a—d).—The preparation of the *N*-benzoyl enamines (8a—d) is described for *N*-butyl-*N*-(3,4-dihydro-2-naphthyl)benzamide (8d). To a solution of a mixture of the enamine (4d) (11·2 g), obtained as before, and triethylamine (6·2 g) in anhydrous chloroform (50 ml), a solution of benzoyl chloride (7·8 g) in anhydrous chloroform (15 ml) was added dropwise with stirring and cooling. The mixture was left at room temperature overnight, the solvent was removed, and the residue was extracted with ether. The extract was washed with brine, dried (Na_2SO_4), and evaporated to give an oil which was distilled to afford the pale yellow *amide* (8d) (14·3 g, 80%), b.p. 158—161° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1628 cm^{-1} (C=C–NBz) (Found: C, 82·7; H, 7·45; N, 4·75. $C_{21}H_{23}NO$ requires C, 82·6; H, 7·6; N, 4·6%).

Data for the other *N*-benzoyl enamines were: N-*allyl*-N-(3,4-*dihydro*-2-*naphthyl*)*benzamide* (8a) (63%), b.p. 185—190° (bath temp.) at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–NBz), δ ($CDCl_3$) 7·60 (2H, m, 2 × *o*-H on the benzene ring) and 6·20 (1H, nearly s, HC=C–N) (Found: C, 82·95; H, 6·75; N, 4·75. $C_{20}H_{19}NO$ requires C, 83·0; H, 6·6; N, 4·85%); N-*benzyl*-N-(3,4-*dihydro*-2-*naphthyl*)*benzamide* (8c) (35%), b.p. 190° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–NBz) (Found: C, 85·25; H, 5·9; N, 4·05. $C_{24}H_{21}NO$ requires C, 84·9; H, 6·25; N, 4·15%); and N-(3,4-*dihydro*-2-*naphthyl*)-N-*methylbenzamide* (8b) (70%), b.p. 172° at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1630 cm^{-1} (C=C–NBz) (Found: C, 82·55; H, 6·3; N, 5·2. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%).

Photolysis of the N-*Acetyl Enamines* (5a—d).—A solution of the *N*-acetyl enamine (5b) (1 g) in ether (200 ml) (thus 0·02M) was irradiated for 24 h when the starting enamide had disappeared completely (t.l.c.). The solvent was removed and the residue was chromatographed on alumina with n-hexane–benzene (1 : 1) to give 3,4-*dihydro*-2-*methylamino*-1-*naphthyl methyl ketone* (6b) as plates (670 mg, 67%), m.p. 122—123·5° (from n-hexane), $\nu_{max.}$ ($CHCl_3$) 1605sh, 1590, and 1560 cm^{-1} (N–C=C–CO), δ ($CDCl_3$) 11·80br (1H, NH), 2·98 (3H, d, *J* 5 Hz, NMe), and 2·32 (3H, s, Ac) (Found: C, 77·35; H, 7·45; N, 6·85. $C_{13}H_{15}NO$ requires C, 77·6; H, 7·5; N, 6·95%).

Data for the other ketones were: *ketone* (6a) (60%), m.p. 72·5—73·5° (from ether), $\nu_{max.}$ ($CHCl_3$) 1650w (C=C), 1610sh, and 1590 cm^{-1} (N–C=C–CO), δ ($CDCl_3$) 11·90br (1H, NH) and 2·34 (3H, s, Ac) (Found: C, 79·5; H, 7·7; N, 6·2. $C_{15}H_{17}NO$ requires C, 79·25; H, 7·55; N, 6·15%); *ketone* (6c) (46%), m.p. 85—86° (from n-hexane), $\nu_{max.}$ ($CHCl_3$) 1605sh, 1590, and 1575sh cm^{-1} (N–C=C–CO), δ ($CDCl_3$) 12·20br (1H, NH), 4·50 (2H, d, *J* 6 Hz, $NHCH_2Ph$), and 2·35 (3H, s, Ac) (Found: C, 82·2; H, 6·8; N, 5·25. $C_{19}H_{19}NO$ requires C, 82·3; H, 6·9; N, 5·05%); and *ketone* (6d) (50%), m.p. 49·5—50·5° (from n-hexane), $\nu_{max.}$ ($CHCl_3$) 1605sh and 1585 cm^{-1} (N–C=C–CO), δ ($CDCl_3$) 12·00br (1H, NH), 3·35 (2H, d-t, *J* 5·5 and 6 Hz, $NHCH_2CH_2$), 2·34 (3H, s, Ac), and 0·98 (3H, t, *J* 6 Hz, CH_2CH_3).

1-*Acetyl*-3,4-*dihydronaphthalen*-2(1H)-*one* (7).—A solution of one of the amides (6a—d) in 10% hydrochloric acid was warmed on a steam-bath for 10 min. After cooling, the aqueous layer was extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated to give an oil which was distilled to give the ketone (7) as an oil, b.p. 125—130° at 1 mmHg (55—70%), identical with an authentic sample.[6]

Photolysis of the N-*Benzoyl Enamines* (8a—d).—A 0·02M solution of the *N*-benzoyl enamine (8b) (2·2 g) in ether (420 ml) was irradiated for *ca.* 40 h when no starting enamide remained (t.l.c.). The solvent was removed and the residue was chromatographed on silica gel with chloroform as eluant. The pale green residue from the first fraction was recrystallised from ether, giving pale green plates of 3,4-*dihydro*-2-*methylamino*-1-*naphthyl phenyl ketone* (9) (200 mg, 9%), m.p. 161—162°, $\nu_{max.}$ (Nujol) 1600sh, 1585, and 1575sh cm^{-1} (N–C=C–CO) (Found: C, 82·3; H, 6·65; N, 5·45. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%).

Upon recrystallisation from ether the second fraction yielded *trans*-6a,7,8,12b-*tetrahydro*-6-*methylbenzo*[a]*phenanthridin*-5(6H)-*one* (10b) (880 mg, 40%) as plates, m.p. 160—163°, $\nu_{max.}$ (Nujol) 1650 cm^{-1} (N–CO), δ ($CDCl_3$) 8·08 (1H, m, 4-H), 4·26 (1H, d, *J* 11·3 Hz, 12b-H), 3·63 (1H, t-d, *J* 11·3 and 3·5 Hz, 6a-H), and 3·20 (3H, s, NMe) (Found: C, 82·25; H, 6·5; N, 5·35. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%). Yields and quality of the photoproduct (10b) varied depending upon the amount of enamide employed. The best result was obtained when a solution of *N*-benzoyl enamine (8b) (1·05 g) in ether (200 ml) was irradiated for 24 h. Evaporation of the solvent and trituration of the residue with ether gave crystals (550 mg, 53%), homogeneous on g.l.c.

Data for the other photoproducts were: *phenanthridinone* (10a), b.p. 180—190° (bath temp.) at 1 mmHg, $\nu_{max.}$ ($CHCl_3$) 1644 cm^{-1} (N–CO), δ ($CDCl_3$) 8·14 (1H, m, 4-H), 4·35 (1H, d, *J* 12 Hz, 12b-H), and 3·75 (1H, t-d, *J* 12 and 4 Hz, 6a-H) (Found: C, 82·5; H, 7·05; N, 4·75. $C_{20}H_{19}NO$ requires C, 83·0; H, 6·6; N, 4·85%); *phenanthridinone* (10c) (47%), m.p. 143—144° (from ether), $\nu_{max.}$ ($CHCl_3$) 1644 cm^{-1} (N–CO) (Found: C, 85·25; H, 6·25; N, 4·1. $C_{24}H_{21}NO$ requires C, 84·9; H, 6·25; N, 4·15%); and *phenanthridinone* (10d) (63%), m.p. 113·5—114·5° (from ether), $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1} (N–CO), δ ($CDCl_3$) 8·10 (1H, m, 4-H), 4·30 (1H, d, *J* 12 Hz, 12b-H), 3·69 (1H, td, *J* 12 and 4 Hz, 6a-H), and 0·98 (3H, diffuse t, CH_2CH_3) (Found: C, 82·55; H, 7·5; N, 4·45. $C_{21}H_{23}NO$ requires C, 82·6; H, 7·6; N, 4·6%).

Dehydrogenation of the trans-*Photoproduct* (10b).—(a) *By selenium*. A mixture of the *trans*-lactam (10b) (500 mg) and selenium (750 mg) was heated at 250° for 3 h. After cooling, hot methanol was added and the selenium was removed by filtration. The solvent was evaporated and the residue, which showed two components on t.l.c., was chromatographed on alumina with benzene as eluant. The residue from the first fraction was recrystallised from ether to give cis-*isomer* (12) (203 mg, 41%), as plates, m.p. 175—178°, $\nu_{max.}$ (Nujol) 1650 cm^{-1} (N–CO), δ ($CDCl_3$) 8·08 (1H, m, 4-H), 6·80 (1H, m, 12-H), 4·47 (1H, d, *J* 5·5 Hz, 12b-H), 3·67 (1H, d-t, *J* 11 and 5·5 Hz, 6a-H), and 3·18 (3H, s, NMe) (Found: C, 82·3; H, 6·5; N, 5·3. $C_{18}H_{17}NO$ requires C, 82·1; H, 6·5; N, 5·3%). Recrystallisation from ether of the residue from the second fraction yielded 6-methylbenzo[*a*]phenanthridin-5(6*H*)-one (11) (40 mg, 8%), as needles, m.p. 120—121° (lit.,[7] m.p. 121—122°), identical with an authentic sample. Heating the *trans*-lactam (10b) without selenium at 250° for 3 h did not give the *cis*-lactam (12) but three decomposition products were detected by t.l.c. but they were not investigated further.

(b) *By* 10% *palladium–charcoal*. A mixture of the *trans*-lactam (10b) (200 mg) and 10% palladium–charcoal (200 mg) was heated at 250° for 1·5 h. After cooling, hot methanol was added and the catalyst was removed by filtration. The solvent was evaporated and the residue, which showed the presence of a trace of the *cis*-lactam (12) on t.l.c., was chromatographed as in (a). Recrystallisation of the residue from light petroleum afforded (11) (132 mg, 67%), m.p. 121—122°, identical with the sample obtained in (a). Dehydrogenation of the *cis*-lactam (12) by 10% palladium–charcoal at 250° for 3 h gave only (11).

trans-6-*Benzyl*-5,6,6a,7,8,12b-*hexahydrobenzo*[a]*phenanthridine* (13c).—To a solution of the *trans*-lactam (10c) (230 mg) in anhydrous ether (30 ml), lithium aluminium hydride (260 mg) was carefully added in small portions with cooling. The mixture was stirred at room temperature for 1 h before decomposing the excess of lithium aluminium hydride by adding water with cooling. The ether layer was separated and the aqueous layer was extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and evaporated. The residue was chromatographed on alumina using benzene as eluant to give compound (13c) as a semi-solid (200 mg, 89%), characterised as the *perchlorate*, which was recrystallised from ethanol as plates, m.p. 232—233° (decomp.) (Found: C, 67·65; H, 5·75; N, 3·25. $C_{24}H_{24}ClNO_4$ requires C, 67·8; H, 5·7; N, 3·3%).

trans-6-*Allyl*-5,6,6a,7,8,12b-*hexahydrobenzo*[a]*phenanthridine* (13a).—Reduction of the *trans*-lactam (10a) (310 mg) with lithium aluminium hydride was carried out as described for (10c) to give compound (13a) (237 mg, 80%), δ ($CDCl_3$) 4·00 (1H, d, *J* 10 Hz, 12b-H) and 3·95 and 3·50 (2H, ABq, *J* 15 Hz, 5-H_2). Recrystallisation of the *perchlorate* from ethanol afforded pale yellow crystals, m.p. 199·5—200·5° (Found: C, 63·6; H, 5·95; N, 3·7. $C_{20}H_{22}ClNO_4$ requires C, 63·9; H, 5·9; N, 3·75%).

[2/1939 *Received*, 14*th August*, 1972]