Photocyclisation of Enamides. Part 13.[1] Substituent Effects in the Photocyclisation of *N*-Benzoylenamines [2]

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trans-Hexahydrophenanthridones (IIa—g) and *trans*-tetrahydrobenzo[*c*]phenanthridones (VIa—e) were prepared by stereospecific photocyclisation of a variety of *N*-benzoylenamines (Ia—n) and (Va—g) bearing either electron-donating or -attracting substituents on the benzoyl group. Suprafacial [1,5] migration of an *o*-methoxy-group upon cyclisation and photoinduced *trans–cis*-isomerisation of some benzo[*c*]phenanthridones (VIa—c) were observed.

ENAMIDES (Ia) and (Va) of the *N*-benzoylenamine type have been shown to undergo ready stereospecific photocyclisation to afford the *trans*-lactams (IIa) and (VIa) [3] respectively. As an extension of the study of this photocyclisation aiming at the evaluation of this reaction as a useful synthetic tool, the present investigation of the effect of the substituents on the benzoyl group was undertaken. Some interesting and useful reactions applicable to the synthesis of heterocyclic compounds have been found.

Acylation of the imines, prepared from cyclohexanone or 1-tetralone and primary amines, with substituted benzoyl chlorides afforded a variety of the substituted enamides (Ib—n) and (Vb—g) in good yields, respectively. The structures of these enamides were readily assigned from their spectral data [$\nu_{max.}$ 1 610—1 640 cm^{-1} (NCO); δ 5.30—5.45 (m, HC=C)].

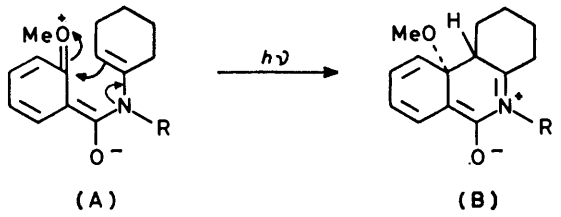
A 0.02M solution of the enamide in a solvent such as methanol, benzene, or ether was irradiated with a low-pressure mercury lamp at room temperature as described previously.[3] Thus, the photocyclisation of the *p*- and *m*-methoxy-substituted enamides (Ib and c) proceeded smoothly to afford the *trans*-lactams (IIb) (29%) and (IIc) (36%), of which the latter (IIc) was formed as a result of a regiospecific cyclisation to the *para*-position of a methoxy-group. The *para*-ester-substituted enamide (Ie) underwent photocyclisation to afford the didehydrolactam (IIIc) under normal conditions, while the *trans*-lactam (IId) (10%) was obtained under nitrogen.

Irradiation of the enamide (If) bearing an *o*-methoxy-group in ether yielded the methoxy-migrated lactam (IV) (30%), homogeneous on t.l.c. and n.m.r., together with the didehydrolactam (IIIa) (18%), which was also obtained by heating (IV), thus suggested migration of the *o*-methoxy-group to the 4a-position. The n.m.r. spectrum of the lactam (IV), particularly the coupling constant of the 10b-proton signal and the presence of a long-range coupling between the 10- and 10b-protons confirmed its B–C-*trans*-structure.

Furthermore, the *o*-methoxy-substituted enamides (Ig and h) gave regiospecifically the didehydrolactams (IIId and e) which lost one methoxy-group.[4]

The most likely explanation for this regiospecific cyclisation would be explained as shown in Scheme 1; because of the contribution of the excited state form (A) of an enamide, conrotatory photocyclisation would occur specifically at the *o*-methoxy-group to yield the *trans*-intermediate (B) and a thermally allowed suprafacial [1,5] shift of the methoxy-group would follow to give product (IV) which therefore holds a B–C-*trans*-structure and is susceptible to elimination of a methanol molecule to give the corresponding didehydrolactam (IIIa). The fact that the *trans*-methoxy-lactam (IV) was isolated was unambiguous evidence for an electrocyclic mechanism and the thermal [1,5] sigmatropic shift in the photocyclisation of the 6π-electron system in compliance with the Woodward–Hoffmann rule.

Similar examples of the photochemical cyclisation at the *o*-methoxy-group in 6π-electron systems have been reported.[5]



(A) (B)

SCHEME 1

The photocyclisation of the enamide (Ii) with an *o*-methylenedioxy-group also proceeded smoothly only at the substituent, which then underwent spontaneous cleavage and elimination of a C_1 unit to afford a phenolic lactam (IIIf) (14%), which was identified by methylation with methyl iodide to give the known *o*-methoxy-lactam (IIIe).

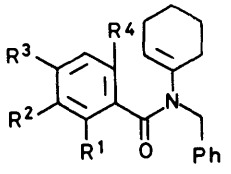
The enamide (In) with an *o*-amino-group underwent smooth photocyclisation to afford the normally cyclised lactam (IIg) (71%) homogeneously, presumably due to hydrogen bonding between the amino and carbonyl groups which would fix the conformation of the enamide in a form favourable to cyclisation [6] at the opposite site of an amino group.

The photocyclisation of enamides (Ij—m) with other *ortho*-substituents gave a mixture of two types of products respectively, thus showing non-specificity on the orientation of cyclisation as shown in Table 3.

The stereochemistry of the photoproducts (IIb—g) was deduced as B–C-*trans* from the n.m.r. signals of the

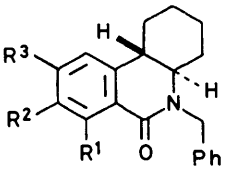
4a-protons (dt, J 4 and 11 Hz), thus establishing the stereochemistry of the photocyclisation of enamides (I).

Prolonged irradiation was required for some enamides (Vb—d), which were prepared from 1-tetralone, to complete cyclisation. However the products obtained were the B–C-*cis*-lactams (VIIb—d), which were presum-



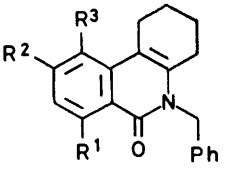
(I)

a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^3 = OMe, R^1 = R^2 = R^4 = H$
c; $R^2 = OMe, R^1 = R^3 = R^4 = H$
d; $R^3 = NO_2; R^1 = R^2 = R^4 = H$
e; $R^3 = CO_2Me, R^1 = R^2 = R^4 = H$
f; $R^1 = OMe, R^2 = R^3 = R^4 = H$
g; $R^1 = R^4 = OMe, R^2 = R^3 = H$
h; $R^1 = R^2 = OMe, R^3 = R^4 = H$
i; $R^1 = R^2 = OCH_2O, R^3 = R^4 = H$
j; $R^1 = Me, R^2 = R^3 = R^4 = H$
k; $R^1 = Cl, R^2 = R^3 = R^4 = H$
l; $R^1 = OAc, R^2 = R^3 = R^4 = H$
m; $R^1 = CO_2Me, R^2 = R^3 = R^4 = H$
n; $R^1 = NH_2, R^2 = R^3 = R^4 = H$



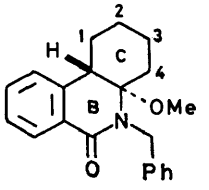
(II)

a; $R^1 = R^2 = R^3 = H$
b; $R^3 = OMe, R^1 = R^2 = H$
c; $R^2 = OMe, R^1 = R^3 = H$
d; $R^3 = CO_2Me, R^1 = R^2 = H$
e; $R^1 = Me, R^2 = R^3 = H$
f; $R^1 = OAc, R^2 = R^3 = H$
g; $R^1 = NH_2, R^2 = R^3 = H$

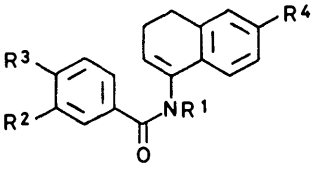


(III)

a, $R^1 = R^2 = R^3 = H$
b; $R^2 = NO_2, R^1 = R^3 = H$
c; $R^2 = CO_2Me, R^1 = R^3 = H$
d; $R^1 = OMe, R^2 = R^3 = H$
e; $R^3 = OMe, R^1 = R^2 = H$
f; $R^3 = OH, R^1 = R^2 = H$
g; $R^1 = Cl, R^2 = R^3 = H$
h; $R^1 = CO_2Me, R^2 = R^3 = H$

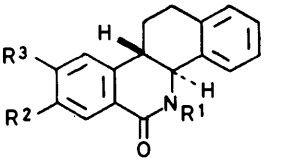


(IV)



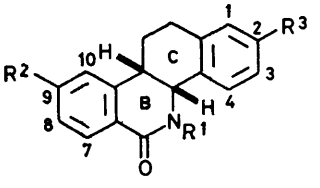
(V)

a $R^1 = Me, R^2 = R^3 = R^4 = H$
b; $R^1 = Me, R^3 = CO_2Me, R^2 = R^4 = H$
c; $R^1 = Me, R^3 = CO_2Me, R^4 = OMe, R^2 = H$
d; $R^1 = CH_2Ph, R^3 = CN, R^2 = R^4 = H$
e; $R^1 = Me, R^2 = CO_2Me, R^3 = R^4 = H$
f; $R^1 = CH_2Ph, R^3 = OMe, R^2 = R^4 = H$
g; $R^1 = Me, R^3 = OAc, R^2 = R^4 = H$



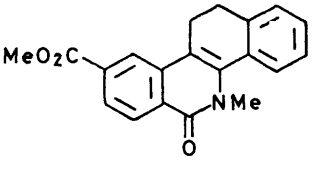
(VI)

a; $R^1 = Me, R^2 = R^3 = H$
b; $R^1 = Me, R^3 = CO_2Me, R^2 = H$
c; $R^1 = Me, R^2 = CO_2Me, R^3 = H$
d; $R^1 = CH_2Ph, R^3 = OMe, R^2 = H$
e; $R^1 = Me, R^3 = OAc, R^2 = H$



(VII)

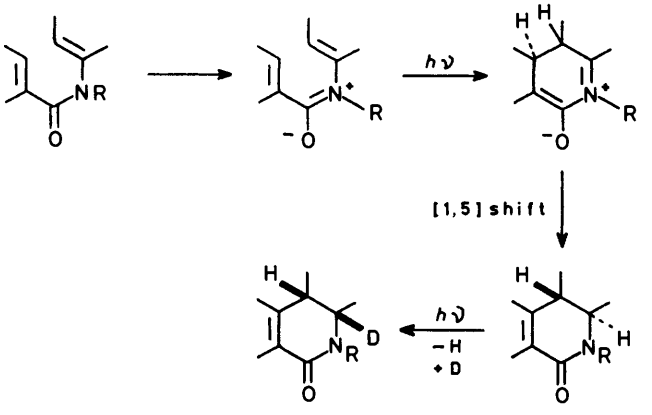
a; $R^1 = Me, R^2 = R^3 = H$
b; $R^1 = Me, R^2 = CO_2Me, R^3 = H$
c; $R^1 = Me, R^2 = CO_2Me, R^3 = OMe$
d; $R^1 = CH_2Ph, R^2 = CN, R^3 = H$



(VIII)

ably formed as a result of photoisomerisation occurring during the course of prolonged irradiation.

Thus, the enamide (Vb) first yielded the homogeneous *trans*-lactam (VIb) upon irradiation in methanol for a



SCHEME 2

short time when most of the starting enamide remained unchanged. Prolonged irradiation of the mixture until the starting enamide (Vb) disappeared completely on t.l.c. afforded the homogeneous *cis*-lactam (VIIb) in 20% yield. The structures of these products were established mainly from their n.m.r. spectra, of which the *trans*-lactam (VIb) exhibited a peak for 4b-H at δ 4.80 (d, *J* 12 Hz) and the *cis*-lactam (VIIb) at δ 4.77 (d, *J* 4.5 Hz). Further, the *trans*-lactam (VIb) was quantitatively isomerised to the *cis*-isomer (VIIb) upon irradiation in methanol under the same conditions as above.

However, this isomerisation was not observed when an aprotic solvent such as benzene, ether, or dioxan was employed. Similar results for photocyclisation and isomerisation were also observed for the enamide (Vd) which carries a nitrile group at the *para*-position. On

TABLE 1

Enamides (Ib—n) and (Vb—g)

Compound	Yield (%)	M.p. [B.p.] (°C) (solvent)	Formula	Analysis (%) [a] C	H	N
(Ib)	48	[205; 7 × 10^{-3} mmHg]	$C_{21}H_{23}NO_2$	78.45 (78.45	7.15 7.2	4.65 4.35)
(Ic)	93	48—49 (Et_2O–C_6H_{14})	$C_{21}H_{23}NO_2$	78.65 (78.45	7.2 7.2	4.45 4.35)
(Id)	98	142—143 (MeOH)	$C_{20}H_{20}N_2O_3$	71.1 (71.4	5.95 6.0	8.4 8.35)
(Ie)	95		$C_{22}H_{23}NO_3$	*b*		
(If)	31	61.5—62 (petrol)	$C_{21}H_{23}NO_2$	78.3 (78.45	7.35 7.2	4.5 4.35)
(Ig)	92	132—135 (Et_2O–MeOH)	$C_{22}H_{25}NO_3$	74.75 (75.2	7.1 7.15	4.0 4.0)
(Ih)	60	[220; 7 × 10^{-3} mmHg]	$C_{22}H_{25}NO_3$	75.4 (75.2	7.2 7.15	4.1 4.05)
(Ii)	57	113—116 (petrol)	$C_{21}H_{21}NO_3$	75.05 (75.2	6.15 6.3	4.35 4.2)
(Ij)	95	57—58 (C_6H_{14})	$C_{21}H_{23}NO$	82.4 (82.6	7.6 7.6	4.55 4.6)
(Ik)	95	[210; 13 × 10^{-3} mmHg]	$C_{20}H_{20}NOCl$	73.45 (73.7	6.15 6.2	4.3 4.3)
(Il)	52	[210; 13 × 10^{-3} mmHg]	$C_{22}H_{23}NO_3$	75.35 (75.6)	6.6 6.65	4.2 4.0)
(Im)	90	Viscous oil	$C_{22}H_{23}NO_3$	*b*		
(In)	79	88—91 (C_6H_{14})	$C_{20}H_{22}N_2O$	78.25 (78.4	7.3 7.25	8.9 9.15)
(Vb)	93	126—127 (Et_2O)	$C_{20}H_{19}NO_3$	74.7 (74.75	5.95 5.95	4.3 4.35)
(Vc)	95	Viscous oil	$C_{21}H_{21}NO_4$	*b*		
(Vd)	75	142—144 (MeOH)	$C_{25}H_{20}N_2O$	82.45 (82.4	5.7 5.55	7.7 7.7)
(Ve)	95	Viscous oil	$C_{20}H_{19}NO_3$	*b*		
(Vf)	93	83—85 (MeOH)	$C_{25}H_{23}NO_2$	81.3 (81.25	6.35 6.3	3.55 3.8)
(Vg)	57	110.5—112 (Et_2O)	$C_{20}H_{19}NO_3$	74.9 (74.75	5.85 5.95	4.5 4.35)

[a] Required values in parentheses. [b] Because of its instability, the compound was not obtained pure.

TABLE 2

Spectral data for enamides (Ib—n) and (Vb—g)

Compound	$\nu_{max.}$($CHCl_3$)/ cm^{-1} (C=C–N–CO)	δ($CDCl_3$)
(Ib)	1 610	7.57 (2 H, d, *J* 9 Hz, 2- and 6-H), 6.83 (2 H, d, *J* 9 Hz, 3- and 5-H), 5.33 (1 H, m, HC=C), 4.82 (2 H, s, NCH_2Ph), 3.78 (3 H, s, OMe)
(Ic)	1 640	5.31 (1 H, m, HC=C), 4.81 (2 H, s, NCH_2Ph), 3.75 (3 H, s, OMe)
(Id)	1 635 1 525, 1 350 (NO_2)	
(Ie)	1 720 (CO_2Me) 1 630	
(If)	1 630	5.35 (1 H, m, HC=C), 4.83 (2 H, s, NCH_2Ph), 3.78 (3 H, s, OMe)
(Ig)	1 625	6.50 (2 H, d, *J* 8 Hz, 3- and 5-H), 5.45 (1 H, m, HC=C), 4.86 (2 H, s, NCH_2Ph), 3.77 (6 H, s, 2 × OMe)
(Ih)	1 630	5.43 (1 H, m, HC=C), 4.83 (2 H, s, NCH_2Ph), 3.91 and 3.88 (each 3 H, s, 2 × OMe)
(Ii)	1 625	5.92 (2 H, s, OCH_2O), 5.32 (1 H, m, HC=C), 4.80 (2 H, s, NCH_2Ph)
(Ij)	1 630	5.30 (1 H, m, HC=C), 4.80 (2 H, s, NCH_2Ph), 2.33 (3 H, s, Me)
(Ik)	1 630	5.45 (1 H, m, HC=C), 4.45 (2 H, s, NCH_2Ph)
(Il)	1 770 (OAc) 1 635	5.35 (1 H, m, HC=C), 4.78 (2 H, s, NCH_2Ph), 2.18 (3 H, s, OAc)
(Im)	1 730 (CO_2Me) 1 635	5.43 (1 H, m, HC=C), 4.85 (2 H, s, NCH_2Ph), 3.78 (3 H, s, CO_2Me)
(In)	3 500, (NH_2) 3 400 1 625	5.42 (1 H, m, HC=C), 4.83 (2 H, s, NCH_2Ph), 4.43br (2 H, s, NH_2)
(Vb)	1 710 (CO_2Me) 1 620	7.87 (2 H, d, *J* 8.5 Hz, 3- and 5-H), 7.50 (2 H, d, *J* 8.5 Hz, 2- and 6-H), 5.60 (1 H, t, *J* 4.5 Hz, HC=C), 383 (3 H, s, CO_2Me), 3.25 (3 H, s, NMe)
(Vc)	1 720 (CO_2Me) 1 630	
(Vd)	2 250 (CN) 1 640	
(Ve)	1 725 (CO_2Me) 1 630	
(Vf)	1 620	
(Vg)	1 775 (OAc) 1 630	7.47 (2 H, d, *J* 8.5 Hz, 2- and 6-H), 6.93 (2 H, d, *J* 8.5 Hz, 3- and 5-H), 5.59 (1 H, t, *J* 4.5 Hz, HC=C), 3.22 (3 H, s, NMe), 2.20 (3 H, s, OAc)

the other hand, the enamides (Ve—g) which are substituted with either an ester group at the *meta*-position, or a methoxy- or an acetoxy-group at the *para*-position afforded only the *trans*-lactams (VIc—e) even after prolonged irradiation. Further irradation of the didehydrolactams (VIII) and (IIIa—h) and the *trans*-phenanthridones (IIa—g) caused only decomposition of the lactams.

Therefore, with the results so far obtained, it can be noted that this photoinduced isomerisation is specific to the tetrahydrobenzo[*c*]phenanthridone ring systems, particularly where an electron-attracting group is present at C-9.

However, unsubstituted *trans*-tetrahydrobenzo[*c*]-phenanthridone (VIa) underwent very slow isomerisation which took over 10 days to give the corresponding *cis*-isomer (VIIa) in only 10% yield.

We then carried out experiments with deuterium methoxide in order to examine the possibility of solvent incorporation in these photocyclisation and isomerisation. Irradiation of the enamide (Vb) in a deuterium methoxide solution afforded two isomeric lactams (VIb) and (VIIb); the *trans*-lactam (VIb) contained no deuterium while the *cis*-isomer (VIIb) showed almost quantitatively incorporation of an equivalent of deuterium exclusively at the 4b-position. The normal *trans*-lactam (VIb) was irradiated in deuterium methoxide to afford the *cis*-lactam (VIIb) which had deuterium incorporated at the 4b-position. This marked contrast suggests the mechanism for the photocyclisation and the following isomeris-

TABLE 3

Cyclisation products (II)—(IV) and (VI)—(VIII)

Compound	Yield (%) (starting enamide)	M.p. (°C) (solvent)	Formula	Analysis (%) [f] C	H	N
(IIb)	29 [a] (Ib)	144—145 (MeOH)	$C_{21}H_{23}NO_2$	78.75 (78.45	6.9 7.2	4.25 4.35)
(IIc)	36 [a] (Ic)	141—143 (Et_2O–MeOH)	$C_{21}H_{23}NO_2$	78.15 (78.45	7.05 7.2	4.4 4.35)
(IId)	10 [a] (Ie)	133—134.5 (Et_2O–MeOH)	$C_{22}H_{23}NO_3$	75.35 (75.6	6.45 6.65	4.0 4.0)
(IIe)	22 [a] (Ij)	143—144 (Et_2O)	$C_{21}H_{23}NO$	82.5 (82.6	7.6 7.6	4.45 4.6)
(IIf)	13 [b] (Il)	162—163 (MeOH)	$C_{22}H_{23}NO_3$	75.45 (75.6	6.65 6.65	4.05 4.0)
(IIg)	71 [b] (In)	182—183.5 (MeOH)	$C_{20}H_{22}N_2O$	78.45 (78.4	7.2 7.25	9.0 9.15)
(IIIa)	18 (If),[b] 1 (Ij),[a] 14 (Ik),[a] 7 (Il),[b] 1.5 (Im) [c]	157—159 lit.,[3b] 156—159°) (Et_2O)				
(IIIb)	13.5 [a] (Id)	210—212 (MeOH)	$C_{20}H_{18}N_2O_3$	71.7 (71.85	5.3 5.45	8.4 8.4)
(IIIc)	15 [a] (Ie)	162—164 (MeOH)	$C_{22}H_{21}NO_3$	76.1 (76.05	6.1 6.1	4.25 4.05)
(IIId)	10 [b] (Ig)	174.5—176 (MeOH)	$C_{21}H_{21}NO_2$	79.15 (78.95	6.7 6.65	4.35 4.4)
(IIIe)	15 [a] (Ih)	174—175 (Et_2O)	$C_{21}H_{21}NO_2$	79.0 (79.95	6.6 6.65	4.55 4.4)
(IIIf)	14 [b] (Ii)	240—243 (MeOH)	$C_{20}H_{19}NO_2$	78.85 (78.65	6.35 6.25	4.4 4.6)
(IIIg)	4 [a] (Ik)	177—178.5 (MeOH)	$C_{20}H_{18}ClNO$	74.35 (74.15	5.7 5.6	4.15 4.15)
(IIIh)	2.5 [c] (Im)	193—195 (MeOH)	$C_{22}H_{21}NO_3$	76.05 (76.05	6.0 6.1	4.1 4.05)
(IV)	30 [b] (If)	124—125 (MeOH)	$C_{21}H_{23}NO_2$	78.9 (78.45	7.15 7.2	4.5 4.35)
(VIb)	13 [d,g] (Vb)	134—135 (EtO_2–MeOH)	$C_{20}H_{19}NO_3$	74.55 (74.75	6.0 5.95	4.2 4.35)
(VIc)	24 [a] (Ve)	152—153 (Et_2O–MeOH)	$C_{20}H_{19}NO_3$	75.05 (74.75	5.55 5.95	4.45 4.35)
(VId)	30 [a] (Vf)	Viscous oil	$C_{25}H_{23}NO_2$	80.85 (81.25	6.15 6.3	3.65 3.8)
(VIe)	33 [a] (Vg)	150—152 (Et_2O)	$C_{20}H_{19}NO_3$	74.95 (74.75	5.95 5.95	4.55 4.35)
(VIIb)	20 [a] (Vb)	173—174 (Et_2O–MeOH)	$C_{20}H_{19}NO_3$	74.55 (74.75	6.00 5.95	4.3 4.35)
(VIIc)	5 [a] (Vc)	191—192 (MeOH)	$C_{21}H_{21}NO_4$	71.75 (71.8	5.95 6.0	4.05 4.0)
(VIId)	14 [a] (Vd)	175—176 (MeOH)	$C_{25}H_{20}N_2O$	82.3 (82.4	5.65 5.55	7.6 7.7)
(VIII)	23 [e] (Vb)	157—158 (Et_2O–MeOH)	$C_{20}H_{17}NO_3$	75.05 (75.2	5.5 5.35	4.2 4.4)

[a] Solvent methanol. [b] Ether. [c] Benzene. [d] Benzene–methanol. [e] Methanol in the presence of I_2. [f] Required values in parentheses. [g] Starting material recovered in 56% yield.

TABLE 4

Spectral data for the photocyclisation products

Compound	$\nu_{max.}$(CHCl$_3$)/cm^{-1} (C=C–N–CO)	δ(CDCl$_3$)
(IIb)	1 638	8.13 (1 H, dd, *J* 8 and 1.5 Hz, 7-H), 5.37 and 4.60 (2 H, ABq, *J* 16 Hz, NC*H*$_2$Ph), 3.82 (3 H, s, OMe), 3.33 (1 H, dt, *J* 4 and 11 Hz, 4a-H)
(IIc)	1 640	7.79 (1 H, d, *J* 2.5 Hz, 7-H), 5.40 and 4.62 (2 H, ABq, *J* 16 Hz, NC*H*$_2$Ph), 3.88 (3 H, s, OMe), 3.33 (1 H, dt, *J* 4, 11 Hz, 4a-H)
(IId)	1 720 (CO_2Me) 1 640	8.24 (1 H, d, *J* 9.5 Hz, 7-H), 8.01 (1 H, dd, *J* 9.5, 2 Hz, 8-H), 5.66 and 4.62 (2 H, ABq, *J* 16 Hz, NC*H*$_2$Ph), 3.92 (3 H, s, CO_2Me), 3.37 (1 H, dt, *J* 4 and 11 Hz, 4a-H)
(IIe)	1 640	5.32 and 4.62 (2 H, ABq, *J* 16 Hz, NC*H*$_2$Ph), 3.28 (1 H, dt, *J* 4 and 11 Hz, 4a-H), 2.76 (3 H, s, Me)
(IIf)	1 763 (OAc) 1 640	5.37 and 4.55 (2 H, ABq, *J* 16.5 Hz, NC*H*$_2$Ph), 2.33 (3 H, s, OAc) 3.35 (1 H, dt, *J* 4, 11 Hz, 4a-H)
(IIg)	3 500, 3 350 (NH_2) 1 640	6.60br (2 H, d, *J* 8 Hz, 8- and 10-H), 6.17br (2 H, s, NH_2), 5.25 and 4.62 (2 H, ABq, *J* 16.5 Hz, NC*H*$_2$Ph), 3.29 (1 H, dt, *J* 4, 11 Hz, 4a-H)
(IIIb)	1 650 1 530, 1 350 (NO_2)	8.65 (1 H, d, *J* 9 Hz, 7-H), 8.50 (1 H, d, *J* 2 Hz, 10-H), 8.20 (1 H, dd, *J* 9, 2 Hz, 8-H), and 5.47 (2 H, s, NC*H*$_2$Ph)
(IIIc)	1 710 (CO_2Me) 1 650	8.55 (1 H, d, *J* 9.5 Hz, 7-H), 8.33 (1 H, d, *J* 1.5 Hz, 10-H), 8.10 (1 H, dd, *J* 9.5, 1.5 Hz, 8-H), 5.44 (2 H, s, NC*H*$_2$Ph), 4.00 (3 H, s, CO_2Me)
(IIId)	1 645	7.55 (1 H, t, *J* 8 Hz, 9-H), 7.18br (1 H, d, *J* 8 Hz, 10-H), 6.92br (1 H, d, *J* 8 Hz, 8-H), 5.42 (2 H, s, NC*H*$_2$Ph), 3.97 (3 H, s, OMe)
(IIIe)	1 640	8.21 (1 H, dd, *J* 8, 2 Hz, 7-H), 5.47 (2 H, s, NC*H*$_2$Ph), 3.87 (3 H, s, OMe)
(IIIf)	1 620 [a]	9.87 (1 H, s, OH), 7.88 (1 H, dd, *J* 7, 2.5 Hz, 7-H), 5.39 (2 H, s, NC*H*$_2$Ph) [b]
(IIIg)	1 650	5.38 (2 H, s, NC*H*$_2$Ph)
(IIIh)	1 725 (CO_2Me) 1 650	5.42 (2 H, s, NC*H*$_2$Ph), 3.98 (3 H, s, CO_2Me)
(IV)	1 650	8.62 (1 H, m, 7-H), 5.84 and 4.16 (2 H, ABq, *J* 16 Hz, NC*H*$_2$Ph), 2.72 (1 H, ddd, *J* 12, 4, 2 Hz, 10b-H, which changed to dd, *J* 12, 4 Hz upon irradiation at δ 7.07), 2.64 (3 H, s, OMe) [c]
(VIb)	1 720 (CO_2Me) 1 640	4.80 (1 H, d, *J* 12 Hz, 4b-H), 3.93 (3 H, s, CO_2Me), 3.20 (3 H, s, NMe)
(VIc)	1 720 (CO_2Me) 1 640	8.72 (1 H, d, *J* 2 Hz, 7-H), 8.13 (1 H, dd, *J* 7, 2 Hz, 9-H), 4.77 (1 H, d, *J* 11.5 Hz, 4b-H), 3.75 (3 H, s, CO_2Me), 3.12 (3 H, s, NMe)
(VId)	1 640	8.13 (1 H, d, *J* 8.5 Hz, 7-H), 5.38 and 4.59 (2 H, ABq, *J* 15 Hz, NC*H*$_2$Ph), 4.92 (1 H, d, *J* 11 Hz, 4b-H), 3.81 (3 H, s, OMe)
(VIe)	1 755 (OAc) 1 640	8.13 (1 H, d, *J* 9 Hz, 7-H), 4.82 (1 H, d, *J* 11.5 Hz, 4b-H), 3.07 (3 H, s, NMe), and 2.30 (3 H, s, OAc)
(VIIb)	1 720 (CO_2Me) 1 640	4.77 (1 H, d, *J* 4.5 Hz, 4b-H), 3.88 (3 H, s, CO_2Me), 3.13 (3 H, s, NMe)
(VIIc)	1 720 (CO_2Me) 1 640	8.18 (1 H, d, *J* 8 Hz, 7-H), 7.18 (1 H, dd, *J* 8, 2 Hz, 8-H), 4.78 (1 H, d, *J* 4 Hz, 4b-H), 3.96 and 3.80 (each 3 H, s, OMe and CO_2Me), 3.12 (3 H, s, NMe)
(VIId)	2 250 (CN) 1 650	8.50 (1 H, d, *J* 8.5 Hz, 7-H), 7.57 (1 H, d, *J* 2 Hz, 10-H), 5.50 and 4.38 (2 H, ABq, *J* 15 Hz, NC*H*$_2$Ph), 4.83 (1 H, d, *J* 4.5 Hz, 4b-H)
(VIII)	1 720 (CO_2Me) 1 635	8.50 (1 H, d, *J* 1.5 Hz, 10-H), 8.01 (1 H, dd, *J* 8.5, 1.5 Hz, 8-H), 3.93 (3 H, s, CO_2Me), 3.71 (3 H, s, NMe), 2.83 (4 H, s, [CH_2]$_2$)

[a] In Nujol. [b] In (CD$_3$)$_2$SO. [c] In C$_6$D$_6$.

ation shown in Scheme 2; first, the photochemical electrocyclic ring closure of 6π-electron system followed by a thermally converted [1,5] shift would occur to afford the *trans*-lactam homogeneously, which would then in some cases undergo irreversible photoinduced isomerisation to yield the *cis*-lactam by involving incorporation of a protic solvent at the 4b-position of the *trans*-lactam.

EXPERIMENTAL

I.r. spectra were recorded for solutions in chloroform and ^{1}H n.m.r. spectra for solutions in deuteriochloroform on Varian A–60D and NEVA NV–21 (90 MHz) instruments (tetramethylsilane as internal reference). M.p.s were determined with a Kofler-type hot-stage apparatus. Photochemical reactions were carried out as described previously.[3]

General Procedure for the Preparation of Enamides (Ib—m) *and* (Vb—g).—To a solution of the imines (0.1 mol) prepared from cyclohexanone or 1-tetralone and primary amines, and triethylamine (0.12 mol) in anhydrous benzene (100 ml), a solution of the appropriate substituted benzoyl chloride (0.1 mol) in anhydrous benzene (50 ml) was added dropwise with stirring. After refluxing for 2 h, the mixture was cooled and filtered to remove triethylamine hydrochloride. Evaporation left a residue, which was either distilled or recrystallised to give the enamides (Tables 1 and 2).

2-*Amino*-N-*benzyl*-N-*cyclohex*-1-*enylbenzamide* (In).—The similar reaction of *N*-cyclohexylidenebenzylamine with 2-nitrobenzoyl chloride afforded N-*benzyl*-N-*cyclohex*-1-*enyl*-2-*nitrobenzamide* as needles (from ether), m.p. 89—90.5° (Found: C, 71.45; H, 5.9; N, 8.35. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.35%). The enamide (12 g) was reduced with Raney nickel (2.5 g) and hydrazine hydrate (7.2 ml) in methanol (200 ml) to afford the enamide (In) (8.7 g, 79%) (Tables 1 and 2).

General Procedure for Irradiation of Enamides (Ib—n) *and* (Vb—g).—A 0.02M solution of an enamide (Ib—n) or (Vb—g) in methanol, benzene, or ether was irradiated at room temperature for several hours in a quartz vessel until disappearance of the starting enamide was indicated by t.l.c. The solvent was removed and the residue was purified, either by recrystallisation or chromatography, to afford the photocyclised products (Tables 3 and 4).

Methylation of the Phenolic Lactam (IIIf).—A mixture of the lactam (IIIf) (30 mg), potassium carbonate (1 g), and methyl iodide (2 ml) in acetone (5 ml) was refluxed for 8 h. After cooling, the mixture was filtered, the filtrate was evaporated, and the residue was chromatographed on alumina. The first fraction eluted by benzene and chloroform was recrystallised from ether to give the lactam (IIIe) (15 mg, 50%), identical with the photoproduct of the enamide (Ih).

Oxidative Photocyclisation of the Enamide (Vb).—The enamide (Vb) (600 mg) in methanol (100 ml) was irradiated in the presence of iodine (530 mg) for 20 h. The solvent

was evaporated off and the residue dissolved in chloroform, washed with aqueous sodium thiosulphate and water, and dried. Evaporation of the solvent gave a residue which was crystallised from ether to afford the lactam (VIII) (Tables 3 and 4).

Photoisomerisation of the trans-*Lactam* (VIb).—The lactam (VIb) (100 mg) in methanol (10 ml) was irradiated over 10 h until the disappearance of the starting *trans*-lactam (VIb) was indicated on g.l.c. The solvent was removed and the compound was recrystallised from ether–methanol to afford the *cis*-lactam (VIIb) (70 mg, 70%) (Tables 3 and 4).

Photoisomerisation of the trans-*Lactam* (VIa).—Similar irradiation of the *trans*-lactam (VIa) (520 mg) in methanol for 10 days afforded the *cis*-lactam (VIIa) (50 mg, 10%), m.p. 157—159° (lit.,[3a] 161—162°).

Photocyclisation of the Enamide (Vb) *in Deuterium Methoxide*.—The enamide (Vb) (200 mg) was irradiated in CH_3OD (10 ml) over 46 h. The solvent was evaporated to afford a residue which was recrystallised from ether to give the *cis*-lactam (VIIb) (20 mg, 10%). The n.m.r. spectrum of the *cis*-lactam (VIIb) showed the disappearance of the 4b-H signal. Analysis of deuterium incorporation demonstrated that deuterium was 100% incorporated at the 4b-position. Similar irradiation of the enamide (Vb) (180 mg) for a short time (12 h) afforded a mixture of the unchanged enamide and the *trans*-lactam (VIb), whose n.m.r. spectrum showed no decrease of the 4b-H signal.

Photoisomerisation of the trans-*Lactam* (VIb) *in Deuterium Methoxide*.—Irradiation of the *trans*-lactam (VIb) (10 mg) in CH_3OD (1 ml) for 5 h afforded the *cis*-lactam (VIIb) quantitatively, with one deuterium atom at the 4b-position.

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