Photocyclisation of Enamides. Part 14.[1] Substituent Effects in the Photocyclisation of *N*-α,β-Unsaturated Acylanilides [2]

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Irradiation of *N*-α,β-unsaturated acylanilides [(1a—d and 1i) and (2a—f and 2h)] having various substituents on the benzene ring yielded a mixture of *cis*- and *trans*-octahydrophenanthridones (3a—f) and dihydroquinolones (5a, e, and f). The *N*-alkylanilides [(1e—h) and (2b—d)] having an *ortho*-electron-attracting group, such as CO_2Me, Ac, CN, or $CONH_2$, brought about [1,5] migration of the group to afford the *trans*-lactams (4a—d) and dihydroquinolones (5b—d), while anilides [(1j), (2g), and (8a—c)] having an *ortho*-carboxy-group afforded the decarboxylactams [(3a), (5a), (9a—c), and (10b and c)].

THOUGH non-oxidative photocyclisation of simple *N*-α,β-unsaturated acylanilides was first reported by Chapman [3] and then by Ogata *et al.*,[4,5] the stereochemistry of the photocyclisation remained unexploited until our previous work [6] on the photocyclisation to tricyclic lactams provided evidence on the stereochemical aspects of the photocyclisation and the solvent effect. In order to elevate this type of photocyclisation to the level of a useful preparative reaction, it is necessary to establish the substituent effect which could control a regioselectivity of the cyclisation and give a satisfactory yield of cyclisation. The present paper gives full details of a study on the substituent effects of the acylanilide photocyclisation, and includes some interesting reactions of cyclisation–decarboxylation, cyclisation with ester-group migration, and regioselectivity by hydrogen bonding, thus establishing this type of photocyclisation as a useful preparative tool.

RESULTS AND DISCUSSION

As described previously,[6] acylation of the *N*-alkylanilines with cyclohex-1-enecarbonyl chloride or methacryloyl chloride afforded the corresponding *N*-α,β-unsaturated acylanilides [(1b—i) and (2b—f)], respectively, in good yields. Their structures were established from their spectral data [i.r., $\nu_{max.}$ 1 620—1 670 cm^{-1} (NCO); n.m.r. δ 4.97—6.90 (HC=C–CO)].

A 0.02M solution of the acylanilide in a solvent such as methanol, benzene, ether, or acetic acid was irradiated with a low-pressure mercury lamp at room temperature as described previously.[6]

TABLE 1

Solvent effect on the value of (*trans*)/(*cis*) of isomeric photocyclisation products

Anilide	Et_2O	C_6H_6	MeOH
(1a)	15.6	1.6	0.4
(1b)	9.2	1.2	0.2
(1c)	34.5	8.7	0.5
(1d)	20.8	1.9	0.3
(1h)	3.0	2.0	0.07
(1i)	2.0	0.5	
(1j)	0.2	0.13	0.1

TABLE 2

Solvent effect on the proportions of photocyclisation products

Anilide	Products	Et_2O	C_6H_6	MeOH
(1h)	[(4d)]/[(3a)]	3.8	1.3	(3a) only
(2d)	[(5d)]/[(5a)]		5.0	1.0

Irradiation of the *para*-substituted anilides (1b and c) with a methoxy or an ester group yielded mixtures of *cis*- and *trans*-lactams (3b and c), respectively, in 50—65% yields, whose ratios were also dependent on the solvent used, as is the case for the unsubstituted anilides (1a) [6] (Table 1). The stereochemistry of the lactams was deduced by the comparisons of their n.m.r. spectra with those of the *cis*- and *trans*-lactams (3a).[6]

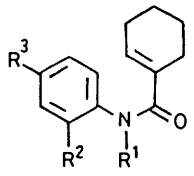
In contrast to the enamides of the *N*-benzoylenamine type,[1] the *ortho*-methoxy-substituted anilide (1d) underwent photocyclisation to the *ortho*-position opposite to the methoxy-group, thus affording a mixture of the *cis*- and *trans*-lactams (3d) in 52—65% yields (Tables 1 and 5), the *cis* : *trans* ratio depending on the solvent employed.

On the other hand, the *ortho*-ester-substituted anilide (1e) underwent smooth photocyclisation followed by [1,5] migration of the substituent to afford the lactam (4a), which carries an ester group on the 6a-position, in 71% yield, accompanied by a small amount of the lactam (3e) (1.8% yield). This ester migration was also observed in methanol, benzene, and ether.

The stereochemistry and structure of the lactam (4a) were deduced from its n.m.r. spectrum, particularly signals at δ 2.89 (dd, *J* 10 and 6 Hz, 10a-H) and 7.25—6.75 (9 Ar-H) and the following reactions. The photoproduct (4a) was dehydrogenated with *N*-bromosuccinimide under irradiation with a high-pressure mercury lamp to afford the didehydrolactam (7) in 22% yield, which was then reduced with 40% palladium–charcoal to give the *trans*-lactam (4a) in 65% yield, identical with the photocyclised product from the anilide (1e).

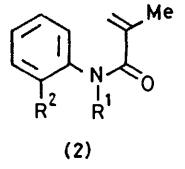
Similarly, the other cyclohexenoylanilides (1f and g) and methacryloylanilides (2b and c) having electron-attracting substituents such as ester, acetyl, and nitrile groups, were readily photocyclised to give the acyl-migrated lactams (4b and c) and (5b and c), each of which was shown to be homogeneous by t.l.c. and n.m.r. spectra. The B/C-*trans*-ring juncture of the lactams (4b and c) was deduced from the close similarity between the n.m.r. signals of the 10a-proton and the corresponding

signal in (4a), as shown in Table 6. Furthermore, the n.m.r. signal of the methyl protons (δ 1.50—1.60) located the migrated group at the 3-position in the photocyclised lactams (5b and c) (Table 6). A similar migration of the



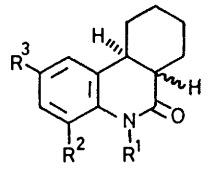
(1)

a; $R^1 = CH_2Ph, R^2 = R^3 = H$
b; $R^1 = CH_2Ph, R^2 = H, R^3 = OMe$
c; $R^1 = CH_2Ph, R^2 = H, R^3 = CO_2Me$
d; $R^1 = CH_2Ph, R^2 = OMe, R^3 = H$
e; $R^1 = CH_2Ph, R^2 = CO_2Me, R^3 = H$
f; $R^1 = CH_2Ph, R^2 = Ac, R^3 = H$
g; $R^1 = CH_2Ph, R^2 = CN, R^3 = H$
h; $R^1 = CH_2Ph, R^2 = CONH_2, R^3 = H$
i; $R^1 = H, R^2 = CO_2Me, R^3 = H$
j; $R^1 = CH_2Ph, R^2 = CO_2H, R^3 = H$



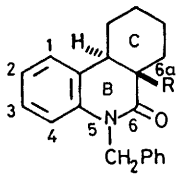
(2)

a; $R^1 = CH_2Ph, R^2 = H$
b; $R^1 = CH_2Ph, R^2 = CO_2Me$
c; $R^1 = CH_2Ph, R^2 = Ac$
d; $R^1 = CH_2Ph, R^2 = CONH_2$
e; $R^1 = CH_2Ph, R^2 = Cl$
f; $R^1 = H, R^2 = CO_2Me$
g; $R^1 = CH_2Ph, R^2 = CO_2H$
h; $R^1 = H, R^2 = CO_2H$



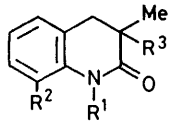
(3)

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



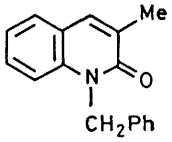
(4)

a; R = CO_2Me
b; R = Ac
c; R = CN
d; R = $CONH_2$
e; R = CO_2H

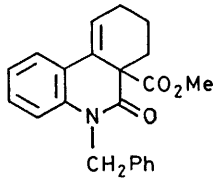


(5)

a; $R^1 = CH_2Ph, R^2 = R^3 = H$
b; $R^1 = CH_2Ph, R^2 = H, R^3 = CO_2Me$
c; $R^1 = CH_2Ph, R^2 = H, R^3 = Ac$
d; $R^1 = CH_2Ph, R^2 = H, R^3 = CONH_2$
e; $R^1 = H, R^2 = CO_2Me, R^3 = H$
f; $R^1 = H, R^2 = CO_2H, R^3 = H$



(6)



(7)

ortho-substituted group such as benzoyl and formyl in the photocyclisation of the hexatriene system has recently been reported.[7]

However, the anilides having an *ortho*-substituent such as nitro, phenyl, and methyl groups afforded no isolable products upon irradiation. But the *ortho*-chloro-substituted anilide (2e) was photocyclised to afford the didehydrolactam (6).

Next, we investigated the behaviour of the anilides (1h) and (2d) having an *ortho*-carbamoyl group. Irradiation of (1h) and (2d) yielded a mixture of the acyl-migrated lactams (4d) and (5d) and the saturated lactams (3a) and (5a), which lost a carbamoyl group, with ratios as described in Table 2. The product (3a) was a mixture of *cis*- and *trans*-lactams whose ratios were as shown in Table 1. The structure of the lactam (4d) was established by comparison with the compound prepared by amidation of the carboxylic acid (4e), obtained from the photoproduct (4a) by hydrolysis. The structures of the compounds (3a) and (5a) were established by direct comparison with authentic samples.[5,6] Further, these two products (3a) and (5a) were also obtained by irradiation of the *ortho*-carboxy-substituted anilides (1j) and (2g).

Irradiation of the *ortho*-carboxy-substituted anilides (1j) and (2g) brought about cyclisation and decarboxylation to afford the saturated lactams (3a) and (5a). The ratio of *cis*- and *trans*-isomers in the lactam (3a) was

TABLE 3

Physical properties and analyses of anilides (1b—j), (2b—h), and (8a—c)

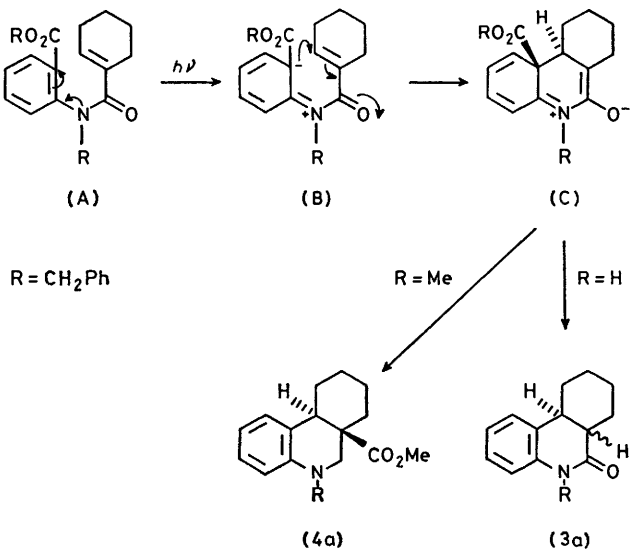
Compd.	Yield (%)	M.p. [B.p.] (°C) (solvent)	Formula	Analysis (%) * C	H	N
(1b)	45	Viscous oil	$C_{21}H_{23}NO_2$	78.1 (78.45	7.45 7.2	4.2 4.35)
(1c)	80	97.5—98.5 (C_6H_{14})	$C_{22}H_{23}NO_3$	75.55 (75.6	6.65 6.65	4.1 4.0)
(1d)	50	89—90 (C_6H_{14})	$C_{21}H_{23}NO_2$	78.5 (78.45	7.2 7.2	4.35 4.35)
(1e)	87	124.5—125.5 (MeOH)	$C_{22}H_{23}NO_3$	75.45 (75.6	6.35 6.65	4.05 4.0)
(1f)	50	165—167 (MeOH)	$C_{22}H_{23}NO_2$	78.95 (79.25	6.9 6.95	4.15 4.2)
(1g)	60	156—157 (Et_2O)	$C_{21}H_{20}N_2O$	79.8 (79.7	6.45 6.35	8.95 8.95)
(1h)	42	131—132 (PhH–C_6H_{14})	$C_{21}H_{22}N_2O_2$	75.2 (75.4	6.65 6.65	8.3 8.4)
(1i)	63	83—85 (MeOH)	$C_{15}H_{17}NO_3$	69.4 (69.5	6.65 6.6	5.4 5.4)
(1j)	50	162—165 (Et_2O)	$C_{21}H_{21}NO_3$	75.2 (75.2	6.35 6.3	4.2 4.2)
(2b)	64	56—57.5 (C_6H_{14})	$C_{19}H_{19}NO_3$	74.0 (73.75	6.2 6.2	4.65 4.55)
(2c)	42	95—97 (MeOH–Et_2O)	$C_{19}H_{19}NO_2$	77.6 (77.5	6.65 6.55	5.05 4.75)
(2d)	70	123—124 (Et_2O–PhH)	$C_{18}H_{18}N_2O_2$	73.65 (73.45	6.0 6.15	9.45 9.5)
(2e)	70	[185; 13×10^{-3} mmHg]	$C_{17}H_{16}ClNO$	71.55 (71.45	5.65 5.65	4.85 4.9)
(2f)	75	75—77 (C_6H_{14}–Et_2O)	$C_{12}H_{13}NO_3$	66.05 (65.75	6.0 6.0	6.3 6.4)
(2g)	73	137—139 (Et_2O)	$C_{18}H_{17}NO_3$	73.5 (73.2	5.75 5.8	4.95 4.75)
(2h)	66	170—171 (Et_2O)	$C_{11}H_{11}NO_3$	64.1 (64.4	5.35 5.4	6.9 6.85)
(8a)	70	164—165.5 (Et_2O–EtOH)	$C_{15}H_{13}NO_3$	70.6 (70.6	5.05 5.15	5.55 5.5)
(8b)	83	120—130 (Et_2O)	$C_{19}H_{15}NO_3$	74.5 (74.75	4.9 4.95	4.45 4.5)
(8c)	77	199—200 (EtOH)	$C_{19}H_{15}NO_3$	74.55 (74.75	4.9 4.95	4.6 4.5)

* Required values in parentheses.

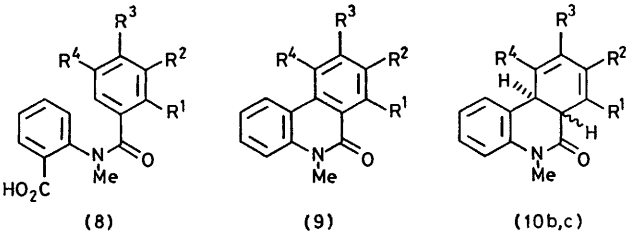
apparently not affected by the solvent employed. (Table 1).

The most likely explanation for this photocyclisation, and the following acyl migration [in the case of (1e)] or decarboxylation [in the case of (1j)] would be as shown in the Scheme. The anilide (A) (R = Me) having an *ortho*-ester group (1e), after excitation to the zwitterion (B) (R = Me), would undergo a conrotatory cyclisation to the *trans*-intermediate (C) (R = Me), which would then undergo a thermally allowed [1,5] shift of the ester group suprafacially thus giving the *trans*-product (4a) with the ester group on the 6a-position. As in the case of the anilide (A) (R = H) (1j), from the *trans*-intermediate (C) (R = H), decarboxylation occurred to give the product (3a). In fact, the lactam (4e), having a carboxy-group at the 6a-position, did not undergo decarboxylation under similar conditions.

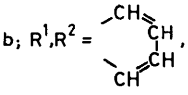
As an application of this cyclisation–decarboxylation reaction, irradiation of the *ortho*-carboxy-substituted aromatic anilides was carried out in acetic acid under non-oxidative conditions, since it is known that the aromatic anilides undergo photocyclisation only under



oxidative conditions.[8] By introducing an *ortho*-carboxy-group, the benzanilide (8a) underwent smooth photocyclisation to afford the known phenanthridone (9a) [9] in 22% yield. Similarly, the naphthalenecarboxanilides



a; $R^1 = R^2 = R^3 = R^4 = H$

b; R^1,R^2 =  , $R^3 = R^4 = H$

c; $R^1 = R^2 = H$, R^3,R^4 = 

(8b and c) yielded the corresponding benzophenanthridones [(9b; 12%) and (9c; [10] 1.5%)], respectively, together with the dihydrolactams (10b and c), as summarised in Tables 5 and 6. Thus, a convenient route for the photocyclisation of some benzanilides even under non-oxidative condition was established by the introduction of an *ortho*-carboxy-group.

Photocyclisation of the *N*-noranilides [(1i) and (2f and h)] proceeded smoothly to afford the normally cyclised lactams [(3f) and (5e and f) as in Tables 1, 5, and 6, presumably due to hydrogen bonding [11] between the NH and carboxy-groups, as in the case of *N*-(2-amino-

TABLE 4

Spectral data for anilides

Compd.	$\nu_{max.}$(CHCl$_3$)/cm^{-1} (–N–CO–C=C)	N.m.r. [δ(CDCl$_3$)]
(1b)	1 620	5.87 (1 H, m, HC=C), 4.93 (2 H, s, NCH_2Ph), 3.73 (3 H, s, OMe)
(1c)	1 720 (CO_2Me) 1 630	5.90 (1 H, m, HC=C), 5.02 (2 H, s, NCH_2Ph), 3.89 (3 H, s, CO_2Me)
(1d)	1 620	5.78 (1 H, m, HC=C), 3.73 (3 H, s, OMe)
(1e)	1 720 (CO_2Me) 1 630	7.91 (1 H, m, 3-H), 6.90 (1 H, m, 6-H), 5.78 (1 H, m, HC=C), 3.83 (3 H, s, CO_2Me)
(1f)	1 700 (Ac) 1 635	
(1g)	2 250 (CN) 1 655	5.87 (1 H, m, HC=C), 5.06 (2 H, s, NCH_2Ph)
(1h)	3 620, 3 500 (NH_2) 1 675 ($CONH_2$) 1 625	6.90 (1 H, m, 6-H), 5.93 (1 H, m, HC=C)
(1i)	3 325 (NH) 1 695 (CO_2Me) 1 670	11.36 (1 H, br s, NH), 8.85 (1 H, dd, *J* 8.5 and 1 Hz, 3-H), 8.03 (1 H, dd, *J* 8.5 and 2 Hz, 6-H), 6.91 (1 H, m, HC=C), 3.91 (3 H, s, CO_2Me)
(1j)	1 700 (CO_2H) 1 630	
(2b)	1 725 (CO_2Me) 1 645	5.55 and 4.30 (2 H, AB q, *J* 15 Hz, NCH_2Ph), 4.97 (2 H, br s, H_2C=C), 3.83 (3 H, s, CO_2Me), 1.78 (3 H, br s, CMe)
(2c)	1 695 (Ac) 1 650	
(2d)	3 570, 3 470 (NH_2) 1 690—1 660 ($CONH_2$ + NCO)	6.25 (2 H, br s, NH_2), 5.12 (2 H, br s, H_2C=C), and 1.87 (3 H, br s, CMe)
(2e)	1 650	
(2f)	3 400 (NH) 1 700 (CO_2Me) 1 680	
(2g)	1 705 (CO_2H) 1 650	11.1 (1 H, s, CO_2H), 5.07 (2 H, br s, H_2C=C), 1.84 (3 H, br s, CMe)
(2h)	3 300 (NH) 1 695 (CO_2H) 1 675	
(8a)	1 710 (CO_2H) 1 640	
(8b)	1 695 (CO_2H) 1 640	
(8c)	1 710 (CO_2H) 1 640	

TABLE 5

Cyclisation products (3)—(6), (9), and (10)

Compound	Yield (%) (Starting anilide)	B/C ring juncture	M.p. (°C) (solvent)	Formula	Analyses (%) [a]		
(3a)	53 [b] (1j)	*cis*	109—111 (lit.,[6] 109—111 °C) (C_6H_{14})				
	70,[b] 80 [c] (1h)	*trans*	116—117 (lit.,[6] 118—119 °C) (C_6H_{14})				
(3b)	60—65 [d] (1b)	*cis*	87—90 (Et_2O)	$C_{21}H_{23}NO_2$	78.65	7.35	4.35
		trans	130—131 (Et_2O)		78.3 (78.45	7.3 7.2	4.5 4.35)
(3c)	50—60 [d] (1c)	*cis*	151—155 (MeOH)	$C_{22}H_{23}NO_3$	75.7	6.7	4.0
		trans	183—185 (MeOH–PhH)		75.55 (75.6	6.65 6.65	4.0 4.0)
(3d)	52—65 [d] (1d)	*cis*	113—116 (C_6H_{14})	$C_{21}H_{23}NO_2$	78.45	7.3	4.45
		trans	137—138 (C_6H_{14}–Et_2O)		78.45 (78.45	7.2 7.2	4.5 4.35)
(3e)	1.8 [b] (1e)	*cis* + *trans* (1 : 1)	[b.p. 245 °C; 13×10^{-3} mmHg]	$C_{22}H_{23}NO_3$ [e]			
(3f)	60 [d] (1i)	*cis*	112—113 (Et_2O)	$C_{15}H_{17}NO_3$ +1/5H_2O	68.35 (68.5	6.65 6.65	5.15 5.35)
		trans	143—146 (MeOH)	$C_{15}H_{17}NO_3$	69.25 (69.5	6.65 6.6	5.4 5.4)
(4a)	71 [b] (1e)		116—117 (PhH)	$C_{22}H_{23}NO_3$	75.45 (75.6	6.4 6.65	4.05 4.0)
(4b)	45 [b] (1f)		125—127 (Et_2O)	$C_{22}H_{23}NO_2$	79.5 (79.25	7.0 6.95	4.25 4.2)
(4c)	40 [b] (1g)		146—148 (Et_2O)	$C_{21}H_{20}N_2O$	79.85 (79.7	6.35 6.35	8.85 8.95)
(4d)	55 [f] (1h)		172—173 (PhH)	$C_{21}H_{22}N_2O_2$	75.6 (75.4	6.65 6.65	8.35 8.4)
(5a)	15 [b] (2d)		85—86 (C_6H_{14})	$C_{17}H_{17}NO$	81.45 (81.25	7.0 6.8	5.5 5.55)
	41,[b] 70 [c] (2g)						
(5b)	40 [b] (2b)		98.5—100 (Et_2O)	$C_{19}H_{19}NO_3$	73.45 (73.45	6.15 6.2	4.65 4.55)
(5c)	25 [b] (2c)		102—103 (Et_2O)	$C_{19}H_{19}NO_2$	77.6 (77.8	6.65 6.55	4.85 4.75)
(5d)	54 [g] (2d)		134—135 (Et_2O–MeOH)	$C_{18}H_{18}N_2O_2$ +3/2H_2O	67.65 (67.25	6.35 6.55	8.65 8.7)
(5e)	61 [g] (2f)		150.5—152 (MeOH)	$C_{12}H_{13}NO_3$	65.8 (65.75	5.75 6.0	6.3 6.4)
(5f)	33 [g] (2h)		202—203 (PhH–$CHCl_3$)	$C_{11}H_{11}NO_3$	64.4 (64.4	5.4 5.4	6.5 6.85)
(6)	15 [b] (2e)		154—155 (Et_2O)	$C_{17}H_{15}NO$	82.3 (81.9	6.15 6.05	5.5 5.6)
(9a)	22 [c] (8a)		105—108 (lit.,[9] 107—109) (C_6H_{14})				
(9b)	12 [c] (8b)		159—161 (Et_2O)	$C_{18}H_{13}NO$	83.25 (83.35	5.1 5.05	5.35 5.4)
(9c)	1.5 [c] (8c)		142—144.5 (lit.,[10] 140—141 °C) (MeOH)				
(10b)	4 [c] (8b)		126—129 (Et_2O)	$C_{18}H_{15}NO$	83.0 (82.75	5.7 5.8	5.35 5.35)
(10c)	16 [c] (8c)	*cis*	143—145 (Et_2O)	$C_{18}H_{15}NO$	83.0	6.0	5.3
		trans	158—159 (Et_2O)		82.55 (82.75	5.75 5.8	5.45 5.4)

[a] Required values in parentheses. [b] Yield in methanol. [c] Yield in acetic acid. [d] Yield of photoirradiation in ether, benzene, and methanol. Solvent effect on the value (*trans*)/(*cis*) was shown in Table 1. [e] Because of its instability, the compound was not obtained in pure state. [f] Yield in ether. [g] Yield in benzene.

benzoyl)enamine.[1] The photoproduct (5f) was treated with methanol in the presence of hydrogen chloride to afford the corresponding ester (5a), which was found to be identical with that obtained from the photocyclisation of the *ortho*-ester-substituted anilide (2f).

In conclusion, the photocyclisation of *N*-α,β-unsaturated acylanilides proceeds smoothly, irrespective of the substituent on the benzene ring, to afford a mixture of *cis*- and *trans*-lactams in good yield, of which the *cis*-isomer is predominant when a protic solvent is employed while the *trans*-isomer is predominant in an aprotic solvent. However, the photocyclisation proceeds stereo-

TABLE 6

Spectral data for photocyclisation products

Compd.	B/C	$\nu_{max.}$(CHCl$_3$)/cm^{-1} (N–CO)	N.m.r. [δ(CDCl$_3$)]
(3b)	*cis*	1 660	5.17 (2 H, br s, NCH_2Ph), 3.72 (3 H, s, OMe)
	trans	1 660	5.40 and 4.95 (2 H, AB q, *J* 16.5 Hz, NCH_2Ph), 3.73 (3 H, s, OMe)
(3c)	*cis*	1 715 (CO_2Me) 1 675	5.23 (2 H, s, NCH_2Ph), 3.87 (3 H, s, CO_2Me)
	trans	1 710 (CO_2Me) 1 675	5.45 and 5.05 (2 H, AB q, *J* 16 Hz, NCH_2Ph), and 3.87 (3 H, s, CO_2Me)
(3d)	*cis*	1 660	5.33 (2 H, br s, NCH_2Ph) and 3.67 (3 H, s, OMe)
	trans	1 660	5.52 and 5.13 (2 H, AB q, *J* 14.5 Hz, NCH_2Ph), and 3.68 (3 H, s, OMe)
(3e)	*cis* + *trans* (1 : 1)	1 720 (CO_2Me) 1 675	7.57 (1 H, dd, *J* 7 and 2.5 Hz, 3-H), 5.63 and 4.30 (1 H), 5.43 and 4.50 (1 H) (each ABq, *J* 15 Hz, NCH_2Ph), 3.88 and 3.83 (each 1.5 H, s, CO_2-Me)
(3f)	*cis*	3 450 (NH) 1 700—1 675 (CO_2Me + NCO)	10.42 (1 H, br s, NH), 7.79 (1 H, dd, *J* 8 and 2 Hz, 3-H), 7.35 (1 H, dd, *J* 8 and 2 Hz, 1-H), 6.98 (1 H, t, *J* 8 Hz, 2-H), 3.90 (3 H, s, CO_2Me)
	trans	3 400 (NH) 1 700—1 675 (CO_2Me + NCO)	10.48 (1 H, br s, NH), 7.90 (1 H, dd, *J* 8 and 2 Hz, 3-H), 7.02 (1 H, t, *J* 8 Hz, 2-H), and 3.90 (3 H, s, CO_2Me)
(4a)		1 745 (CO_2Me) 1 670	5.60 and 4.80 (2 H, AB q, *J* 16 Hz, NCH_2Ph), 3.45 (3 H, s, CO_2Me), 2.89 (1 H, dd, *J* 10 and 6 Hz, 10a-H)
(4b)		1 710 (Ac) 1 665	5.40 and 4.98 (2 H, AB q, *J* 16 Hz, NCH_2Ph), 2.89 (1 H, dd, *J* 9 and 7 Hz, 10a-H), 2.02 3 H, s, Ac)
(4c)		2 250 (CN) 1680	5.50 and 4.90 (2 H, AB q, *J* 16 Hz, NCH_2Ph), 2.89 (1 H, dd, *J* 11.5 and 3.5 Hz, 10a-H)
(4d)		3 560, 3 450 (NH_2) 1 695 ($CONH_2$) 1 660	5.85 (2 H, br s, NH_2), 5.30 and 4.90 (2 H, AB q, *J* 16 Hz, NCH_2Ph), 2.89 (1 H, dd, *J* 10 and 6 Hz, 10a-H)
(5a)		1 665	5.27 and 5.10 (2 H, AB q, *J* 16 Hz, NCH_2Ph) and 1.35 (3 H, d, *J* 7 Hz, 3-Me)
(5b)		1 740 (CO_2Me) 1 675	5.43 and 4.92 (2 H, AB q, *J* 16 Hz, NCH_2Ph), 3.63 (3 H, s, OMe), 3.42 and 2.97 (2 H, AB q, *J* 16 Hz, 4-H_2) 1.60 (3 H, s, 3-Me)
(5c)		1 715 (Ac) 1 665	5.30 and 5.10 (2 H AB q, *J* 16 Hz, NCH_2Ph), 3.40 and 2.90 (2 H, AB q, *J* 16 Hz, 4-H_2), 2.17 (3 H, s, Ac), and 1.50 (3 H, s, 3-Me)
(5d)		3 550, 3 450 (NH_2) 1 690—1 660 ($CONH_2$ + NCO)	3.43 and 3.05 (2 H, AB q, *J* 16 Hz, 4-H_2), 1.56 (3 H, s, 3-Me)
(5e)		3 380 (NH) 1 680 (CO_2Me + NCO)	10.33 (1 H, br s, NH), 7.87 (1 H, dd, *J* 8 and 2 Hz, 7-H), 7.33 (1 H, dd, *J* 8 and 2 Hz, 5-H), 6.98 (1 H, t, *J* 8 Hz, 6-H), 3.88 (3 H, s, CO_2Me), 1.30 (3 H, d, *J* 6 Hz, 3-Me)
(5f)		(Nujol) 3 350 (NH) 1 680 (CO_2H + NCO)	
(6)		1 645	7.62 (1 H, d, *J* 1 Hz, 4-H), 5.58 (2 H, s, NCH_2Ph), 2.32 (3 H, d, *J* 1 Hz, 3-Me)
(9a)		1 635	
(9b)		1 635	
(9c)		1 635	
(10b)	*cis*	1 665	6.62 (1 H, dd, *J* 9.5 and 2 Hz, 12-H), 5.90 (1 H, ddd, *J* 9.5, 3, and 1 Hz, 11-H), 3.93 (1 H, ddd, *J* 7, 3, and 2 Hz, 10b-H), 3.52 (1 H, br d, *J* 7 Hz, 4b-H), 3.43 (3 H, s, NMe)
(10c)	*cis*	1 650	6.20 (1 H, dd, *J* 11.5 and 2 Hz, 8-H), 5.87 (1 H, dd, *J* 11.5 and 7 Hz, 7-H), 4.95 (1 H, d, *J* 5.5 Hz, 12b-H), 4.59 (1 H, ddd, *J* 7, 5.5, and 2 Hz, 6a-H), 2.50 (3 H, s, NMe)
	trans	1 660	6.60 (1 H, dd, *J* 9.5 and 2 Hz, 8-H), 6.00 (1 H, dd, *J* 9.5 and 4 Hz, 7-H), 4.25 (1 H, d, *J* 7 Hz, 12b-H), 3.60 (1 H, ddd, *J* 7, 4, and 2 Hz, 6a-H), 3.33 (3 H, s, NMe)

selectively to give only *trans*-lactam when an *ortho*-electron-withdrawing substituent is present. Introduction of *ortho*-carboxy and ester groups, and thus formation of hydrogen bonding with the *ortho*-substituent, leads to regiospecificity of the photocyclisation.

EXPERIMENTAL

I.r. spectra were recorded for solutions in chloroform; ^{1}H n.m.r. spectra were recorded 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.[6]

General Procedure for the Preparation of the Anilides (1b—i) *and* (2b—f).—To a solution of the substituted aniline (0.1 mol) and triethylamine (0.12 mol) in anhydrous benzene (100 ml), a solution of cyclohex-1-enecarbonyl chloride or methacryloyl 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. The filtrate was evaporated to give a residue which was either distilled or recrystallised to afford the corresponding anilides (1b—i) and (2b—f), respectively (Tables 3 and 4).

The Preparation of the Anilides (1j), (2g *and* h), *and* (8a—c) *by Hydrolysis*.—A mixture of the anilide (with an *ortho*-ester group) (1 mmol) and potassium hydroxide (1—5 mmol) in methanol (20 ml) was refluxed for several hours. The solvent was evaporated and the residue was dissolved in water and extracted with ether. The aqueous layer was acidified and the crystals were collected, or extracted with ether to afford the corresponding anilides [(1j), (2g and h), and (8a—c)] (Tables 3 and 4).

General Procedure for Irradiation of the Anilides (1b—j), (2b—h) *and* (8a—c).—A 0.02M solution of the anilide [(1b—j), (2b—h), and (8a—c)] in a solvent (methanol, benzene, ether, or acetic acid) was irradiated at room temperature for several hours in a quartz vessel until the disappearance of the starting anilide was indicated by t.l.c.

The solvent was removed and the residue was chromatographed on alumina or silica gel to give the photocyclised products (3a—f), (4a—d), (5a—f), (6), (9a—c), and (10b and c), respectively (see Tables 5 and 6).

Dehydrogenation of the Lactam (4a).—To a solution of the lactam (4a) (750 mg) in carbon tetrachloride (140 ml), *N*-bromosuccinimide (350 mg) was added and the mixture was irradiated with a high-pressure mercury lamp, with stirring under nitrogen, for 2 h. The crystals were filtered off and the filtrate was washed with aqueous sodium hydrogencarbonate, water, and dried. The solvent was evaporated to give a residual oil, which was chromatographed on alumina. The fraction with benzene gave the didehydrolactam (7) (165 mg, 22%) as colourless crystals from ether, m.p. 206—208 °C; $\nu_{max.}$ 1 735 (CO_2Me) and 1 670 cm^{-1} (NCO); δ 6.38 (1 H, t, *J* 4 Hz, 10-H), 5.63 and 4.70 (2 H, ABq, *J* 16 Hz, NCH_2Ph), and 3.57 (3 H, s, CO_2Me) (Found: C, 75.75; H, 5.9; N, 4.05. $C_{22}H_{21}NO_3$ requires C, 76.05; H, 6.1; N, 4.05%).

Reduction of the Didehydrolactam (7).—A solution of the didehydrolactam (7) (100 mg) in acetic acid (10 ml) was hydrogenated over 40% palladium–charcoal under atmospheric pressure. Filtration and evaporation gave the lactam (4a), (65 mg, 65%), identical with the photocyclised product obtained from the anilide (1e).

N-Benzyl-5,6,6a,7,8,9,10,10a-octahydro-6-oxophenanthridine-6a-carboxylic Acid (4e).—A mixture of the lactam (4a, 700 mg) and potassium hydroxide (320 mg) in methanol (50 ml) was refluxed for 5 h. The solvent was removed, and the residue dissolved in water, and washed with ether. The aqueous layer was acidified and extracted with ether. The ethereal extract was washed with brine, dried, and the solvent evaporated to afford the lactam (4e) (350 mg, 50%) as crystals from ether–methanol, m.p. 157—160°; $\nu_{max.}$ 1 710 (CO_2H) and 1 675 cm^{-1} (NCO) (Found: C, 71.85; H, 6.7; N, 3.95. $C_{21}H_{21}NO_3 \cdot 0.5MeOH$ requires C, 71.75; H, 6.6; N, 4.0%).

N-Benzyl-5,6,6a,7,8,9,10,10a-octahydro-6-oxophenanthridine-6a-carboxamide (4d).—A solution of the lactam (4e) (300 mg) in thionyl chloride (2 ml) was refluxed for 1 h. The reagent was removed under reduced pressure, the residual oil was dissolved in benzene, and then the solution was refluxed for 0.5 h under ammonia bubbling. The solvent was evaporated off to give the lactam (4d) (150 mg, 50%), identical with the photocyclised product obtained from the anilide (1h).

Methyl 3-Methyl-2-oxo-1,2,3,4-tetrahydroquinoline-3-carboxylate (5e).—The crude oil (200 mg), obtained by irradiation of the anilide (2h) followed by evaporation of the solvent, was dissolved in absolute methanol. The resulting solution was saturated with dry hydrogen chloride gas and then refluxed for 2 h. The solvent was removed to give a residue which was treated with 10% sodium hydroxide solution to afford crystals of (5e) (65 mg, 33%), identical with the photocyclised product obtained from the anilide (2f).

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