N-Iodo-amides: Mechanism of Intramolecular Reactions with Aromatic Rings of Amido-radicals in Σ- and Π-Electronic States

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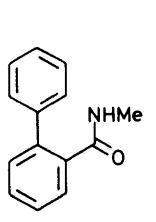
Intramolecular cyclisations of amido-radicals generated by homolysis of *N*-iodo-amides onto aromatic systems gives γ- and δ-lactams, in cases where the aromatic rings can rotate, and only δ-lactams in rigid planar systems. Kinetic studies of the cyclisation of *N*-methylbiphenyl-2-carboxamide with t-butyl hypoiodite under irradiation have shown that γ- and δ-cyclisation products are formed in parallel and that the reactions have different activation energies and entropies. Reactions of *N*-methyl derivatives of 1,2,3,4-tetrahydro- and 1,2-dihydro-phenanthrene-4-carboxamides with t-butyl hypoiodite under irradiation have provided evidence that Π-conjugation is a prerequisite for δ-lactam formation. From a consideration of the molecular orbitals involved it is suggested that γ- and δ-cyclisation reactions occur with amidyls in the Σ- and Π-electronic states.

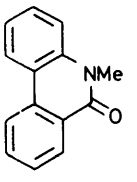
THE amido-radical has been the subject of extensive investigations.[1,2] Recently it was reported[3] that *N*-methylbiphenyl-2-carboxamide (1) in t-butyl alcohol cyclised when irradiated in the presence of t-butyl hypoiodite to give *N*-methylphenanthridone (2) and the γ-lactams 4′-t-butoxy- (3) and 4′-oxo-isoindoline-1-spiro-1′-cyclohexa-2′,5′-dien-3-ones (5). In extending this cyclisation reaction to other systems it was found that *cis*-cinnamamide (10), prepared from the *trans*-isomer by optical 'pumping,' *cis*-N-methylcinnamamide (11), and *N*-methylphenanthrene-4-carboxamide (20) gave mixtures which contained δ-lactam products [(14), (15), and (21) and (22), respectively]. Only the reaction mixture from *cis*-cinnamamide contained γ-lactam (spiro) components (as shown by n.m.r. and i.r. spectra), and these were present in low yield as an intractable mixture.

The thermal reactions of *N*-methyl-*cis*-cinnamamide and *N*-methylphenanthrene-4-carboxamide produced mixtures which likewise did not contain γ-lactam (spiro) components (Table 1).

The almost exclusive formation of δ-lactam products from the reactions of *cis*-cinnamamides contrasted markedly with the reactions of biphenyl-2-carboxamides, which gave γ-lactams (spiro cyclisation) as the major products. In attempts to induce γ-lactam formation, *cis-o-* and *cis-p*-methoxy-*N*-methyl-*cis*-cinnamamides were irradiated in the presence of t-butyl hypoiodite. In contrast to a similar reaction with 4′-methoxybiphenyl-2-carboxamide which afforded predominantly spiro cyclisation,[4] *cis-p*-methoxy-*N*-methylcinnamamide reacted spontaneously and exothermally with t-butyl hypoiodite in t-butyl alcohol in the dark to give the addition product 2-iodo-3-(*p*-methoxyphenyl)-*N*-methyl-3-t-butoxypropionamide (18), presumably owing to activation of the olefin towards electrophilic iodonium ion attack. This is in accord with a favourable planar conformation of *cis*-cinnamamides. The reaction with *cis-o*-methoxy-*N*-methylcinnamamide gave the γ-lactam (19) as major product. The formation of these products indicates that olefin activation by the *o*-methoxy-substituted phenyl ring is not a major effect in *cis-o*-methoxy-*N*-methylcinnamamide and that, owing to steric hindrance by the *o*-methoxy-group, it prefers to assume a non-



(1)



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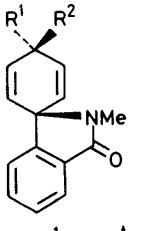
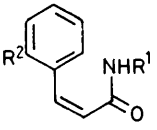
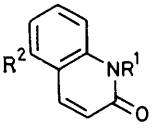


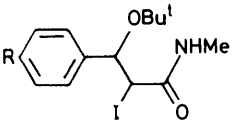
(3) R^1 = OBu^t, R^2 = H
(4) R^1 = H, R^2 = OBu^t
(5) R^1 R^2 = O
(6) R^1 = I, R^2 = H
(7) R^1 = H, R^2 = I
(8) R^1 = OMe, R^2 = H
(9) R^1 = H, R^2 = OMe



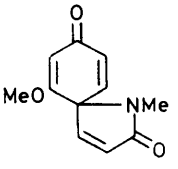
(10) R^1 = R^2 = H
(11) R^1 = Me, R^2 = H
(12) R^1 = Me, R^2 = OMe
(13) R^1 = CH_2·OBu^t, R^2 = H



(14) R^1 = R^2 = H
(15) R^1 = Me, R^2 = H
(16) R^1 = Me R^2 = OMe



(17) R = H
(18) R = OMe



(19)

[1] R. S. Neale, *Synthesis*, 1971, **1**, 1.
[2] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 118; A. R. Forrester, A. S. Ingram, and R. H. Thomson, *ibid.*, p. 2847; M. E. Kuehne and D. A. Horne, *J. Org. Chem.*, 1975, **40**, 1287; Y. L. Chow, J. N. S. Tam, and A. C. H. Lee, *Canad. J. Chem.*, 1969, **47**, 2441.
[3] S. A. Glover and A. Goosen, *J.C.S. Perkin I*, 1974, 2353.
[4] S. A. Glover and A. Goosen, unpublished result.

planar conformation which facilitates attack at the 1′-position by the electronegative amido-radical.[1]

In reinvestigating the cyclisation of *N*-methylbiphenyl-2-carboxamide (1) with t-butyl hypoiodite in carbon tetrachloride it was found that irradiation for a relatively short period gave a mixture which contained the iodo-γ-lactams (6) and (7); methanolysis with methanol–silver nitrate gave silver iodide and the isomeric methoxy-dienes (8) and (9), identical (n.m.r. data and t.l.c.) with an authentic mixture of isomers prepared by an alternative procedure. When the reaction under irradiation was carried out in t-butyl alcohol as solvent the mixture contained *N*-methylphenanthridone (2), the spirocyclohexadienone (5), and only one 4′-t-butoxy-spirocyclohexadiene [(3) or (4)].[3]

In contrast, the thermal reaction of the same reactant mixture differed in that negligible quantities of the spirocyclohexadienone (5) and both 4′-t-butoxy-spirodienes [(3) and (4)] were formed. This difference is due to one of the isomeric ethers reacting faster than the other upon irradiation in the presence of t-butyl hypoiodite to form the spirocyclohexadienone (5).

On the basis of a previous assignment [5] of the high field *N*-methyl singlet to the *trans*-*N*-methyl-4′-hydroxy-spirocyclohexadiene it is concluded that the *cis*-4′-t-butoxy-spirocyclohexadiene (4) is more readily converted by hydrogen abstraction with a t-butoxyl radical [3] into the spirocyclodienone (5). The difference in reactivity accounts for the formation of only one isomer of the spirocyclohexadienyl ether in the irradiative reaction of *N*-methylbiphenyl-2-carboxamide with t-butyl hypoiodite in t-butyl alcohol. Hence it is concluded that below 71 °C, in the dark, t-butyl hypoiodite must, surprisingly, be a poor source of t-butoxyl radicals.

In order to determine whether the phenanthridone (2) was being formed from spirocyclohexadienyl species when *N*-methylbiphenyl-2-carboxamide was irradiated in the presence of t-butyl hypoiodite, a kinetic study was undertaken. An excess of t-butyl hypoiodite was used in order to ensure complete conversion of the amide into its *N*-iodo-derivative, and a constant light source was employed. A plot of ln[amide] against time gave a straight line (Figure 1), slope (k_{obs}) 1.512×10^{-4} s^{-1}, in accord with first-order kinetics. Furthermore plots of [phenanthridone] and [total spiro products] against $(1 - e^{-k_{obs}t})$ also gave straight lines (Figure 2), in accord with product formation by a parallel reaction, with slopes $k^{p}_{obs}A_0/k_{obs} = 0.031\,28$ and $k^{s}_{obs}A_0/k_{obs} = 0.062\,91$, where k^{s}_{obs} and k^{p}_{obs} are the observed rates of formation of spiro products and phenanthridone, respectively, and A_0 is the initial concentration of *N*-methylbiphenyl-2-carboxamide or its *N*-iodo-derivative. Hence $k^{p}_{obs} = 0.5 \times 10^{-4}$ s^{-1} and $k^{s}_{obs} = 1.0 \times 10^{-4}$ s^{-1}, and in confirmation of the occurrence of a parallel reaction, $k^{s}_{obs} + k^{p}_{obs} = 1.5 \times 10^{-4}$ s^{-1} $= k_{obs}$. It is thus concluded that the spirodienyl trapping process takes place readily and that the γ- and δ-lactam products or intermediates are not interconvertible. This result is in

TABLE 1

Products from the reactions of amides with t-butyl hypochlorite–iodine–potassium t-butoxide in t-butyl alcohol

Amide	Conditions	Time (h)	γ-Lactams [%]	δ-Lactams [%]	Other [%]
(1)	*hν* [a]	1.5	(6) + (7) [19]	(2) [71]	(1) [10]
(1)	Heat	Rate studies	(3) + (4) + (5)	(2)	(1)
(10)	*hν*	3.45	Trace	(14) [64]	(10)
(11)	*hν*	6		(15) [24]	(13) (*cis* and *trans*) [18] (11) (*cis* and *trans*) [40]
(11)	Heat	8.5		(15) [17]	(13) (*cis* and *trans*) [6.5] (11) (*cis* and *trans*) [30] (17) [14]
p-OMe-(11)		Instantaneous			(18) [33]
o-OMe-(11)	*hν*	6.5	(19) [49]	(16) [14]	*trans*-(12) [31] *o*-OMe-(17) [Trace]
(20)	*hν*	4.5		(21) [37] (22) [45]	(20) (23) [1] (24) [2]
(20)	Heat	6		(22) [53]	(20) [33]

[a] Reaction carried out with iodine chloride–potassium t-butoxide in carbon tetrachloride.

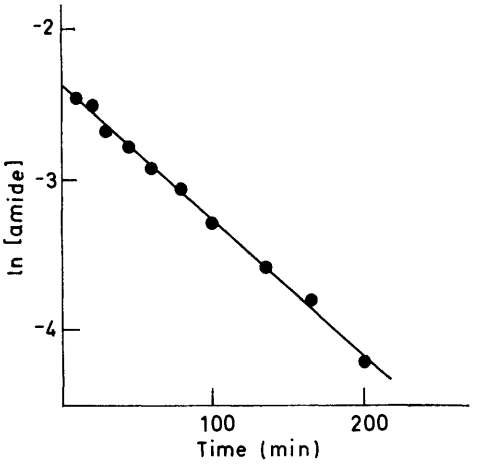


FIGURE 1 Graph of ln[*N*-methylbiphenyl-2-carboxamide] against time (26 °C)

[5] S. A. Glover, A. Goosen, and H. A. H. Laue, *J.C.S. Perkin I*, 1973, 1647.

accord with the abstraction reactions of spirocyclohexadienes, which produce only dimers at 60 °C.[6]

In order to gain information about the transition states for the cyclisation processes the effect of heat on the rate of cyclisation of *N*-methylbiphenyl-2-carboxamide under irradiation in the presence of t-butyl hypoiodite was investigated at temperatures at which

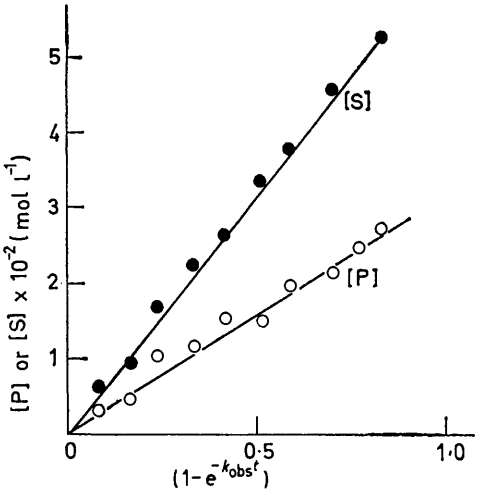


FIGURE 2 Graphs of [*N*-methylphenanthridone] ([P]) and [spiro-product] ([S]) against ($1 - e^{-k_{obs}t}$)

the N–I bond is thermally stable (<50 °C).[4] First-order plots of ln[amide] against time at various temperatures gave satisfactory straight lines from which the observed rate constants were derived (Table 2). An

TABLE 2

Rate constants for cyclisation of *N*-methylbiphenyl-2-carboxamide under irradiation in the presence of t-butyl hypoiodite

T/K	299.4	309.4	313.6	316.1
$10^4 k_{obs}$/s^{-1}	1.3	2.33	3.15	5.05

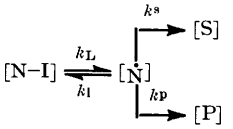
Arrhenius plot (correlation coefficient −0.993) gave the following activation parameters at 25 °C (estimated standard deviations for the last significant figure in parentheses): $\Delta H^{\ddagger}$ 12(1) kcal mol^{-1}; $\Delta S^{\ddagger}$ −35(3) cal K^{-1} mol^{-1}. The observed rate constants for the formation of γ- (k^{s}_{obs}) and δ-lactams (k^{p}_{obs}) also gave linear plots (correlation coefficients −0.999 and −0.992,

TABLE 3

	Spiro cyclisation (γ-lactam)	Phenanthridone formation (δ-lactam)
$E_a^{\ddagger}$/kcal mol^{-1}	15.0 (2)	10 (1)
$\Delta H^{\ddagger}$/kcal mol^{-1}	15.0 (2)	9 (1)
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−28 (1)	−48 (3)

respectively) from which the following activation parameters at 25 °C (estimated standard deviations for the last significant figure in parentheses) for the two cyclisation processes were obtained (Table 3). These parameters show not only that the activation energies are different for γ- and δ-cyclisation but also that the entropies of activation differ by *ca.* 20 cal K^{-1} mol^{-1}, which is evidence that the amido-radical does not interact with the aromatic ring *via* a common species (25) in the formation of γ- and δ-lactams.

The kinetic scheme in accord with the observed first-order results is based on the special nature of the reaction. The irradiation of the *N*-iodo-amide is carried out in the presence of a nine molar excess of t-butyl hypoiodite which, like the *N*-iodo-amide itself under irradiation, is a source of iodine atoms. Further iodide produced in the reaction mixture when cyclisation occurs reacts with any positive species to produce iodine, which also is a source of iodine atoms. The amido-radicals are thus generated in the presence of a fairly constant concentration of iodine radicals or iodine, and thus they are either trapped or undergo intramolecular cyclisation reactions. In Scheme 1,



SCHEME 1

[N–I], [Ṅ], [S], and [P] represent the concentrations of *N*-iodo-amide, amido-radicals, spiro products (γ-lactam), and phenanthridone, respectively, k_L is the rate constant for the excitation process which is *T*-independent, k_l is the rate constant for the activationless radical trapping reaction which is known to be large (10^9), and k^s and k^p are the rate constants for cyclisation at the 1′- and 2′-positions, respectively. We can then derive equations (i) and (ii). Substituting (ii) in (i) gives

$$-d[N\text{–}I]/dt = k_L[N\text{–}I] - k_l[\dot{N}][\dot{I}] \quad (i)$$

$$-d[\dot{N}]/dt = -k_L[N\text{–}I] + k_l[\dot{N}][\dot{I}] + k^s[\dot{N}] + k^p[\dot{N}] = 0 \quad (ii)$$

equation (iii). However, [Ṅ] can be expressed as in

$$-d[N\text{–}I]/dt = k^s[\dot{N}] + k^p[\dot{N}] \quad (iii)$$

equation (iv). Further, $k_l[\dot{I}] \gg k^s + k^p$ because of the

$$[\dot{N}] = k_L[N\text{–}I]/(k_l[\dot{I}] + k^s + k^p) \quad (iv)$$

large [İ], and the large excess of Bu^{t}OI in the reaction mixture buffers changes in [İ]. Hence $k_l[\dot{I}]$ is constant. We may then introduce a parameter K [equation (v)],

$$K = k_L/k_l[\dot{I}] \quad (v)$$

enabling us to rewrite (iii) as (vi), where $K(k^s + k^p) =$

$$-d[N\text{–}I]/dt = Kk^s[N\text{–}I] + Kk^p[N\text{–}I] = K(k^s + k^p)[N\text{–}I] \quad (vi)$$

k_{obs}. Hence $[N\text{–}I] = [N\text{–}I]_0 e^{-k_{obs}t}$. For parallel kinetics, $d[S]/dt = k^s[\dot{N}]$ and from (iv) and (v) equations (vii) and (viii), and similarly equation (ix), follow.

$$d[S]/dt = k^sK[N\text{–}I] = k^sK[N\text{–}I]_0 e^{-k_{obs}t} \quad (vii)$$

[6] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113.

Hence $k^s_{obs} = k^sK$ and $k^p_{obs} = k^pK$, and plots of ln k^p_{obs} and ln k^p_{obs} against $1/T$ give the relative E_a and $\Delta H^\ddagger$ values for the 1'- and 2'-cyclisation processes. The intercepts thus give the relative entropies of activation

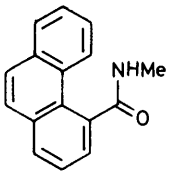
$$[S] = -k^sK[N\text{-}I]_0(1 - e^{-k_{obs}t})/k_{obs} \quad \text{(viii)}$$

$$[P] = -k^pK[N\text{-}I]_0(1 - e^{-k_{obs}t})/k_{obs} \quad \text{(ix)}$$

for the two cyclisation processes, which were found to differ by *ca.* 20 cal K^{-1} mol^{-1}.

A similar kinetic study was undertaken for *N*-methylphenanthrene-4-carboxamide (20), which afforded only δ-lactam products and likewise also gave first-order plots. In order to gain insight into the factors which facilitated γ-lactam formation (spiro cyclisation) and why other systems in which the amido-radical could approach within bonding distance of the aromatic ring failed to undergo the intramolecular reaction to form γ- or δ-lactams, the structure of the amido-radical and the conformations of the molecules in the transition state were considered.

E.s.r. evidence [7,8] suggests that amido-radicals exist



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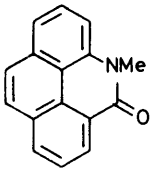

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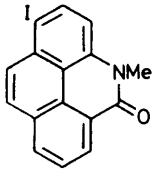

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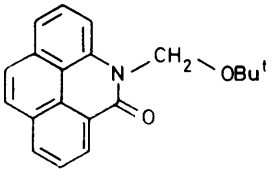

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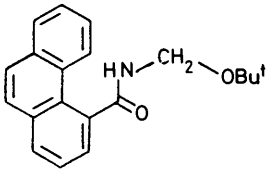

(24)

in the Π-ground state (26); even though reaction through oxygen has been reported,[9] they react mainly through nitrogen.[10] Theoretical studies [7] by use of the INDO approximation also predict that the Π-state has the lowest energy. Irrespective of the actual state of the amido radical, which must initially be generated in the Σ-state (27), reaction to form γ-lactams (spiro cyclisation) must occur with orbitals of the aromatic ring which have Π-symmetry. The nearest approach of the nitrogen atom in the Π-state amidyl and the 1'-position would lead to zero overlap if the nitrogen *p*-orbital is conjugated with the amide carbonyl and the carbonyl is coplanar with the aromatic ring (28). In contrast, reaction of a Σ-state amidyl would have maximum overlap if the aromatic rings were orthogonal (29). On the same basis, if the aromatic rings were coplanar, as in the reaction of phenanthrene-4-carboxamide, best orbital overlap for δ-lactam formation would be with the amidyl in the Π-state (30) as opposed to the Σ-state (31). These concepts would thus account for the large difference in $\Delta S^\ddagger$, since for δ-lactam formation, a sterically hindered rotation would be required to attain the less favoured coplanar conformation. These concepts would also explain the failure of a Σ-state *N*-methyl-α-naphthamido-radical (32) to cyclise under the reaction conditions.

In contrast to successful cyclisations of *cis*-cinnamamides, the dihydro-analogue of *N*-methyl-*cis*-cinnamamide (*N*-methyl-3-phenylpropionamide) as well as *N*-methylphenoxyacetamide failed to undergo cyclisation under the reaction conditions. It was established that conjugation and not restriction of rotation was essential for δ-lactam formation by investigating the reactions, under irradiation in the presence of t-butyl hypoiodite, of *N*-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxamide (33) and *N*-methyl-1,2-dihydrophenanthrene-4-carboxamide (34).

Although a sample from the reaction mixture of the tetrahydrophenanthrene-4-carboxamide (33) showed an intense γ-lactam i.r. absorption band at 1 695 cm^{-1} and an $N\text{-}CH_3$ singlet in the n.m.r. spectrum at δ 2.79, work-up gave only starting material and a crystalline solid whose n.m.r. spectrum was consistent with structure (35). In a repeat experiment, analysis of samples of the irradiated reaction mixture showed that the γ-lactam species was rapidly formed at 50 °C but was unstable to prolonged irradiation at this temperature and reverted to starting material. No evidence for any δ-lactam species was found, even though the nitrogen nucleus can approach within 1.2 Å of the 5-position in a relatively unstrained conformation. In contrast the reaction of *N*-methyl-1,2-dihydrophenanthrene-4-carboxamide (34) did not proceed satisfactorily under irradiation at 26 °C, but irradiation at higher temperatures afforded *N*-methylphenanthrene-4-carboxamide (20), *N*-methylthebenidinone (21), and a yellow crystalline δ-lactam component which was assigned

[7] T. Koenig, J. A. Hoobler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russel, *J. Amer. Chem. Soc.*, 1974, **96**, 4573.

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[9] A. R. Forrester, A. S. Ingram, and R. H. Thomson, *J.C.S. Perkin I*, 1972, 2847.

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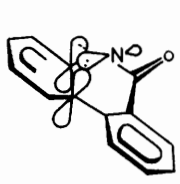
structure (36).* Since *N*-methylthebenidinone (21) could have been formed subsequent to aromatisation of the non-aromatic ring, no conclusions could be drawn from its formation. However the formation of the



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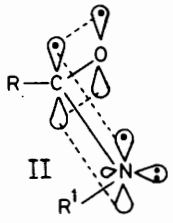

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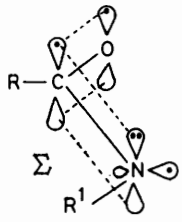

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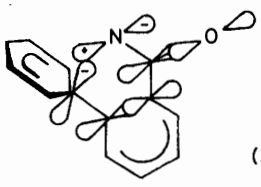

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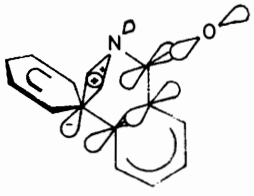

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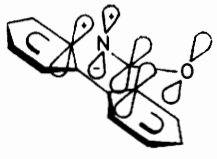

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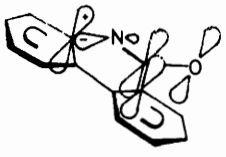

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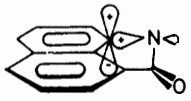
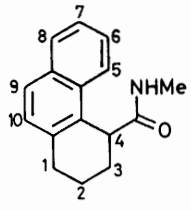


(32)

δ-lactam epoxide (36) supports our proposal that conjugation is essential for δ-lactam formation. Functionalisation of the olefin prior to cyclisation is excluded on the following grounds: (*a*) the tetrahydro-analogue (33), in which cross conjugation was destroyed, did not produce δ-lactam products; and (*b*) no uncyclised olefin addition species were detected from the reaction with the *N*-methyldihydrophenanthrene-4-carboxamide (34) either after irradiation for 3 h at 26 °C or after heating at 50 °C for 3 h in the dark. Since aromatisation



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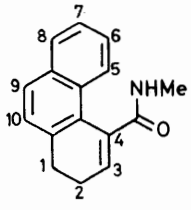

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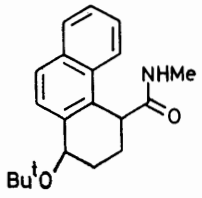

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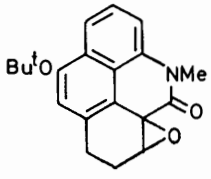
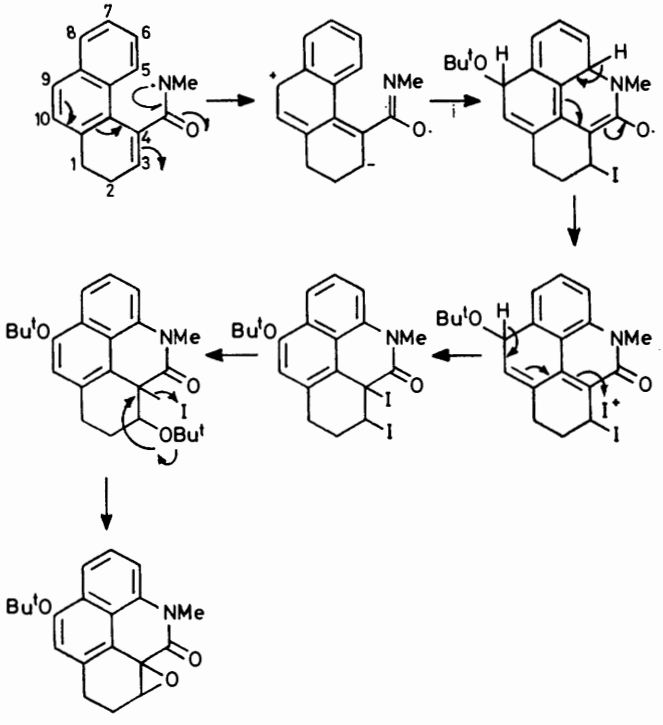


(36)

is the major process in the reaction it would be expected that the δ-lactam (*N*-methyl-7,8-dihydrothebenidinone) if formed would be readily converted into *N*-methylthebenidinone. Hence it is proposed that functionalisation occurs in conjunction with the cyclisation process as outlined in Scheme 2.



SCHEME 2 Reagents: i, $Bu^tOH + Bu^tOI$

The participation of nitrogen in electrocyclic reactions has been well documented [11] and a close analogy exists in the concerted photocyclisation of enamides [12] and

* Details of the structural elucidation are available as Supplementary Publication No. SUP 22030 (9 pp.) (see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue).

[11] R. B. Woodward and R. Hoffmann, 'Conservation of Orbital Symmetry,' Akademische Verlag, Weinheim, 1970; O. L. Chapman and G. L. Eian, *J. Amer. Chem. Soc.*, 1968, **90**, 5329.

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αβ-unsaturated anilides [13] to give hexahydrophenanthridones. These results encourage us to propose that the δ-lactams are formed by an electrocyclic reaction of the conjugated amido-radical.

On the basis of these results we suggest that the energy profile for the reaction of *N*-methylbiphenyl-2-carboxamide under irradiation in the presence of t-butyl

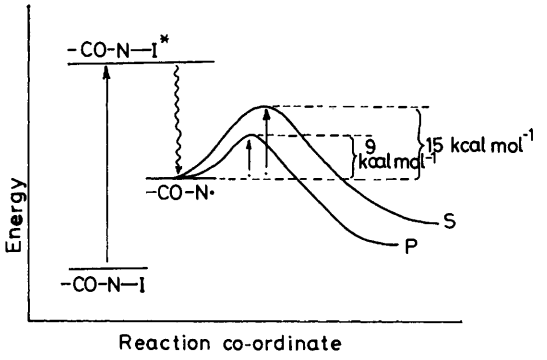

FIGURE 3 Energy profile for the reaction of the amide (1) under irradiation in the presence of t-butyl hypoiodite

hypoiodite is as illustrated in Figure 3. Irradiation of the *N*-iodo-amide excites the molecule which dissipates its energy by homolysis of the N–I bond to form an amido-radical which can exist in the Π- or Σ-state or a hybrid of the two. In order to produce γ-lactams the transition state involves orbital reorganisation to a Σ-state amidyl, which gives best orbital overlap with an orthogonal aromatic system at the 1′-position. δ-Lactams are produced in a concerted electrocyclic process in which conjugation is essential and in the transition state the amidyl participates in the Π-state.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were run on Unicam SP 200G and SP 1000 spectrometers. ^{1}H N.m.r. spectra (60 MHz) were recorded with a Perkin-Elmer R12A spectrometer, with tetramethylsilane as internal standard; 100 MHz ^{1}H n.m.r. (Varian XL-100), ^{13}C n.m.r. (Varian CFT-20), and mass spectra (A.E.I. MS9 instrument) were recorded at the N.C.R.L./C.S.I.R. laboratories in Pretoria. Silica gel for preparative t.l.c. was Merck HF 254 + 366 type 60 (nach Stahl). Irradiations were performed with a 1 000 W tungsten bulb unless otherwise specified. U.v. irradiations were carried out with either a Phillips 125 W low-pressure mercury lamp or a Hanovia medium-pressure photochemical lamp.

cis-*Cinnamamides.—General procedure.* The amides, synthesised by standard procedures, in methanol, were irradiated with a medium pressure u.v. lamp for 24 h. The mixtures of *cis*- and *trans*-isomers were separated by chromatography on silica gel. *cis*-Cinnamamide was a semisolid, δ ($CDCl_3$) 4.67br (2 H, s), 5.98 and 6.78 (2 H, 2 × d, J_{AB} 13 Hz), and 7.15—8.1 (5 H, m); $\nu_{max.}$ 1 675, 3 415, and 3 540 cm^{-1}. *cis*-N-Methylcinnamamide distilled at 132—136° and 0.4 mmHg; δ ($CDCl_3$) 2.56 (3 H, d), 5.83 and 6.52 (2 H, 2 × d, J_{AB} 13 Hz), 7.1—7.7 (5 H, m), and 6.85br (1 H, s). *cis-p*-Methoxy-*N*-methylcinnamamide was an oil, δ ($CDCl_3$) 2.79 (3 H, d), 3.8 (3 H, s), 5.855 and 6.69 (2 H, 2 × d, J_{AB} 13 Hz), 6.86 and 7.51 (4 H, 2 × d, $J_{o,m}$ 9 Hz), and 6.0br (1 H, s).

cis-o-*Methoxycinnamic Acid.*—Coumarin (15 g, 0.1027 mol) was refluxed in aqueous potassium hydroxide (20 g in 150 ml) for 1 h, and the solution was then stirred with dimethyl sulphate (11 ml) for 1.5 h. After refluxing for 0.5 h, the solution was acidified with hydrochloric acid and extracted with chloroform (3 × 50 ml); the extract was washed with saturated sodium carbonate solution (30 g in 100 ml; 2 × 50 ml). The basic extracts were combined, washed with chloroform (2 × 50 ml), acidified with hydrochloric acid, and extracted with ether (3 × 50 ml), and the ethereal solution was dried (Na_2SO_4) and concentrated to an oil (8 g, 0.0449 mol) which solidified on cooling; δ ($CDCl_3$) 3.79 (3 H, s), 5.97 and 7.06 (2 H, 2 × d, J_{AB} 13 Hz), 6.8—7.71 (4 H, m), and 11.5 (1 H, s).

Conversion into the *N*-methylamide was accompanied by isomerisation to trans-o-*methoxy*-N-*methylcinnamamide*, which crystallised from benzene as plates, m.p. 122°; M^+ 191; δ ($CDCl_3$) 2.91 (3 H, d), 3.75 (3 H, s), 6.64 and 7.95 (2 H, 2 × d, J_{AB} 16 Hz), and 6.7—7.6 (4 H, m) (Found: C, 68.6; H, 6.8; N, 7.3. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%).

Irradiation for 4 h as above afforded a mixture of *cis*- and *trans*-amides in the ratio 60 : 40 (n.m.r.), which was chromatographed on silica gel plates (12 × 200 × 2 mm) developed with chloroform (2 runs) and 6% ethanol–chloroform (2 runs). The band with higher R_F value was collected and extracted with ethanol; concentration gave a gum which crystallised on lixiviation with ether as low-melting prisms (1.12 g, 0.0059 mol) of *cis-o*-methoxy-*N*-methylcinnamamide, δ ($CDCl_3$) 2.69 (3 H, d), 3.8 (3 H, s), 5.96 and 6.95 (2 H, 2 × d, J_{AB} 13 Hz), and 6.78—7.6 (4 H, m); $\nu_{max.}$ ($CHCl_3$) 1 668 and 3 465 cm^{-1}.

1,2-*Dihydrophenanthrene*-4-*carboxylic Acid.*—4-(5,6,7,8-Tetrahydro-2-naphthyl)butanoic acid (340 g), m.p. 47—49° (lit.,[14] 49.5°), was synthesised, and upon treatment with ethanol (1 l) and concentrated sulphuric acid (40 ml) gave ethyl 4-(5,6,7,8-tetrahydro-2-naphthyl)butanoate (382 g), δ ($CDCl_3$) 1.23 (3 H, t), 1.6—2.9 (14 H, m), 4.13 (2 H, q), and 6.8—7.2 (3 H, m); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}. The ester (380 g) was heated at 200 °C with sulphur (100 g) for 8 h with constant stirring. Distillation afforded ethyl 4-(2-naphthyl)butanoate (255 g), b.p. 178—181° at 3 mmHg. Saponification of a portion in aqueous ethanolic potassium hydroxide gave, after crystallisation from benzene, 4-(2-naphthyl)butanoic acid, m.p. 96—98° (lit.,[14] 98.5°).

Ethyl 4-(2-naphthyl)butanoate (242 g) was converted [15] into 1,2-dihydrophenanthrene-4-carboxylic acid (220 g), which was crystallised twice from acetone–light petroleum (b.p. 40—60°) to give needles, m.p. 234—235° (lit.,[15] 234—234.5°).

1,2-*Dihydro*-N-*methylphenanthrene*-4-*carboxamide.*— The N-*methylamide* sublimed at 150° and 1 mmHg as needles, m.p. 173—175°; M^+ 237; δ ($CDCl_3$) 2.05—3.1 (4 H, m), 2.82 (3 H, d), 5.6br (1 H, s), 6.93 (1 H, t), and 7.28—8.0 (6 H, m); $\nu_{max.}$ 820, 1 613, 1 663, and 3 455 cm^{-1} (Found: C, 81.05; H, 6.4; N, 6.0. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%).

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[15] K. G. Rutherford and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 213.

1,2,3,4-Tetrahydrophenanthrene-4-carboxylic Acid.—1,2-Dihydrophenanthrene-4-carboxylic acid (8.134 g, 0.0363 mol) was hydrogenated in ethyl acetate (200 ml) over platinum oxide (0.5 g). The solvent was removed after filtration and the resultant mixture was dissolved in chloroform (100 ml), which was then extracted with 10% sodium carbonate solution (3 × 50 ml). The basic extracts were combined, acidified, and extracted with chloroform (3 × 50 ml), and the organic layer was dried (Na_2SO_4) and concentrated to a gum (6.9 g, 0.0305 mol), which crystallised on lixiviation with benzene–light petroleum (b.p. 60—80°) to give *1,2,3,4-tetrahydrophenanthrene-4-carboxylic acid*, m.p. 142—144°; M^+ 226; δ ($CDCl_3$) 1.7—3.15 (6 H, m), 4.4br (1 H, t), 7.1—8.1 (6 H, m), and 10.5 (1 H, s); $\nu_{max.}$ 1 713 and 3 500br cm^{-1} (Found: C, 79.5; H, 6.5. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%). *1,2,3,4-Tetrahydro-N-methylphenanthrene-4-carboxamide* had m.p. 188—189.5°; M^+ 239; δ ($CDCl_3$) 1.65—2.9 (4 H, m), 2.62 (3 H, d), 2.98br (2 H, t), 4.3br (1 H, t), 5.2br (1 H, s), and 7.2—8.05 (6 H, m); $\nu_{max.}$ 1 661 and 3 440 cm^{-1} (Found: C, 80.3; H, 7.1; N, 5.7. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.1; N, 5.8%).

Phenanthrene-4-carboxylic Acid.—1,2-Dihydrophenanthrene-4-carboxylic acid (28 g, 0.125 mol) was converted into the methyl ester, m.p. 69—70° (lit.,[15] 70.5—71.5°), which was heated to 260 °C with sulphur (2.7 g, 0.0844 mol) until evolution of hydrogen sulphide ceased. The mixture, after hydrolysis for 3 h with 20% potassium hydroxide, gave a solid (15.3 g, 0.0689 mol), which crystallised from chloroform–benzene–light petroleum (b.p. 40—60°) as plates of phenanthrene-4-carboxylic acid, m.p. 169—171.5° (lit.,[15] 173.5—174.5°; 169—171°; 171.5—173°). The *N-methylamide* crystallised from chloroform–light petroleum (b.p. 40—60°) as prisms, m.p. 204—205.5°; M^+ 235; δ ($CDCl_3$) 3.02 (3 H, d), 4.0br (1 H, s), 7.5—8.03 (8 H, m), and 8.45—8.62 (1 H, m); $\nu_{max.}$ ($CHCl_3$) 838, 1 660, and 3 455 cm^{-1} (Found: C, 81.1; H, 5.5; N, 6.0. $C_{16}H_{13}NO$ requires C, 81.7; H, 5.55; N, 5.95%).

Thermal Reactions of Amides in the Dark.—*N-Methylbiphenyl-2-carboxamide* (1) (*general procedure*). Iodine (6 g, 0.0237 mol) and t-butyl hypochlorite (2.55 g, 0.0237 mol) were added successively to t-butyl alcohol (50 ml) in a 100 ml flask and the mixture was shaken in the dark for 15 min. Potassium t-butoxide (2.65 g, 0.0237 mol) was then added, followed after further agitation for 10 min by *N*-methylbiphenyl-2-carboxamide (1 g, 0.004 74 mol). The mixture was then shaken in the dark for 15 min. In separate experiments at six different temperatures between 61 and 71 °C the rates of the reactions were followed by observing the change in the N·CH_3 n.m.r. signals.*

The combined mixtures from the thermal rate studies upon work-up gave a gum (5.2 g) which was separated (t.l.c.) and analysed (n.m.r.). The results are given in Table 1.

cis-N-*Methylcinnamamide* (11). Iodine (11.832 g, 4.658 × 10^{-2} mol), t-butyl hypochlorite (5.031 g, 4.658 × 10^{-2} mol), potassium t-butoxide (5.23 g, 4.658 × 10^{-2} mol), and *cis-N*-methylcinnamamide (1.5 g, 9.32 × 10^{-3} mol) were heated and stirred in t-butyl alcohol (97 ml) at 70 °C for 8.5 h as above to give a gum (1.71 g) which was separated (t.l.c.) (Table 1). The unstable *2-iodo-N-methyl-3-phenyl-3-t-butoxypropionamide*, m.p. 134—136°, exhibited no M^+ peak in the mass spectrum but strong $[M - 129]^+$ and $[M - 130]^+$; δ ($CDCl_3$) 2.61 (3 H, d), 4.36 and 4.76 (2 H, 2 × d, *J* 7 Hz), 4.45br (1 H, s), and 7.2—7.8 (5 H, m) (Found: C, 47.1; H, 5.45; N, 3.7. $C_{14}H_{20}INO_2$ requires C, 46.55; H, 5.55; N, 3.85%).

cis-p-*Methoxy-N-methylcinnamamide*. Iodine (10 g, 4.07 × 10^{-2} mol), t-butyl hypochlorite (4.3 g, 4.07 × 10^{-2} mol), potassium t-butoxide (4.55 g, 4.07 × 10^{-2} mol), and *cis-p*-methoxy-*N*-methylcinnamamide (1.56 g, 8.15 × 10^{-3} mol) were shaken in t-butyl alcohol (86 ml) in the dark for 15 min. A sample (3 ml) was processed and analysed by n.m.r., which showed total consumption of starting amide [disappearance of vinylic protons (δ 5.87 and 6.69) and appearance of doublets at δ 4.37 and 4.87].

The mixture was irradiated at room temperature for 4 h. A sample processed by the normal procedure and analysed by n.m.r. then exhibited no change in the composition of the mixture [δ 4.37 and 4.87 (2 × d)]. Work-up as before gave the unstable *2-iodo-3-(p-methoxyphenyl)-N-methyl-3-t-butoxypropionamide*, m.p. 150—152° (decomp.); M^+ 391; δ ($CDCl_3$) 1.18 (9 H, s), 2.85 (3 H, d), 3.82 (3 H, s), 4.37 and 4.87 (2 H, 2 × d, *J* 5.5 Hz), 6.89 and 7.31 (4 H, 2 × d, *J* 8 Hz), and 6.9br (1 H, s) (Found: C, 47.0; H, 6.0; N, 3.1. $C_{15}H_{22}INO_3$ requires C, 46.05; H, 5.6; N, 3.6%).

N-Methylphenanthrene-4-carboxamide (20). Iodine (12 g, 0.047 mol), t-butyl hypochlorite (5.1 g, 0.047 mol), potassium t-butoxide (5.3 g, 0.047 mol), and *N*-methylphenanthrene-4-carboxamide (2.23 g, 0.0095 mol) were heated and stirred in t-butyl alcohol (100 ml) at 70 °C in the dark for 6 h. Samples were withdrawn, processed, and analysed by n.m.r. The remaining mixture gave, after crystallisation, 1-iodo-*N*-methylphenanthridone (1.07 g, 2.98 × 10^{-3} mol), identical (i.r., n.m.r., and m.p.) with an authentic specimen, and starting material (0.741 g, 3.15 × 10^{-3} mol).

Reactions of Amides under Irradiation.—(*a*) Mixtures were prepared as in the general procedure for the thermal reaction. The products obtained after irradiation from *cis*-cinnamamide (10), *cis-N*-methylcinnamamide (11), and *cis-o-* and *-p*-methoxy-*N*-methylcinnamamide are summarised in Table 1. *cis-o*-Methoxy-*N*-methylcinnamamide afforded *2-methoxy-N-methylcyclohexa-2,5-diene-1-spiro-2′-Δ³-pyrroline-4,5′-dione* (19), m.p. 185—187° (needles from benzene); M^+ 205; δ ($CDCl_3$) 2.74 (3 H, s), 3.75 (3 H, s), 5.82 (1 H, d, J_{XA} 2 Hz), 6.18 and 6.46 (2 H, d and dd, J_{BA} 10, J_{AX} 2 Hz), 6.41 and 6.85 (2 H, 2 × d, *J* 6 Hz); $\nu_{max.}$ 1 602, 1 665, and 1 700 cm^{-1} (Found: C, 64.1; H, 5.45; N, 6.7. $C_{11}H_{11}NO_3$ requires C, 64.4; H, 5.4; N, 6.85%); and *5-methoxy-N-methylquinolin-2(1H)-one*, m.p. 129—130° (needles from ether); M^+ 189; δ ($CDCl_3$) 3.69 (3 H, s), 3.93 (3 H, s), 6.65 and 8.16 (2 H, 2 × d, *J* 10 Hz), 6.68 (1 H, dd, *J* 8 Hz), 6.95 (1 H, dd, *J* 8.5 Hz), and 7.51 (1 H, *J* 8 and 8.5 Hz); $\nu_{max.}$ 1 596 and 1 654 cm^{-1}.

(*b*) *N*-Methyl-3-phenylpropionamide, *N*-methylphenoxyacetamide, *N*-methyl-α-naphthamide, and *N*-methyl-α-naphthylacetamide were unchanged under the same conditions.

(*c*) *1,2,3,4-Tetrahydro-N-methylphenanthrene-4-carboxamide* (33). Nine h irradiation at 26 °C gave *1,2,3,4-tetrahydro-N-methyl-1-t-butoxyphenanthrene-4-carboxamide* (35), m.p. 205—207°; M^+ 311; δ ($CDCl_3$) 1.39 (9 H, s), 1.8—2.8 (4 H, m), 2.58 (3 H, d), 4.2—4.45 [1 H, t (distorted)], 4.68—4.96 [1 H, t (distorted)], 5.4—5.9br (1 H, s), and 7.35—8.1 (6 H, m); $\nu_{max.}$ 1 665 and 3 445 cm^{-1} (Found: C, 76.9; H, 8.1; N, 4.3. $C_{20}H_{25}NO_2$ requires C, 77.1; H, 8.05; N, 4.5%); and starting material.

The reaction was repeated and samples were processed after irradiation for 3.5 h at 26 °C; 3.5 h at 50 °C; and

* The results from these experiments will be reported elsewhere.

12 h at 50 °C. Analysis by n.m.r. [δ 2.79 (s) for γ-lactam; δ 2.58 (d) for 1-t-butoxy-compound; δ 2.62 (d) for starting material] showed that after 3.5 h at 26 °C the mixture contained the γ-lactam (*ca.* 10%) and starting material (*ca.* 90%); after 3.5 h at 50 °C the γ-lactam (*ca.* 35%), the 1-t-butoxy-compound (*ca.* 20%), and starting amide (*ca.* 45%); and after 12 h at 50 °C the 1-t-butoxy-compound (*ca.* 40%) and starting amide (*ca.* 60%). Repeating the reaction for 10 h at 26 °C gave a gum which contained the γ-lactam (δ 2.97; $\nu_{max.}$ 1 698 cm^{-1}; *ca.* 40%), starting material, and 1-t-butoxy-compound (δ 1.39; 10%). The gum, in ethyl acetate, was shaken with hydrogen over platinum oxide. The resultant mixture contained the 1-t-butoxy-compound (35) (δ 1.39; 10%) and starting amide.

(*d*) N-*Methylphenanthrene*-4-*carboxamide* (20). Treatment as above for 4.5 h gave N-(*t-butoxymethylene*)*thebenidinone* (23), m.p. 124—127°; M^+ 305 with loss of 56, 57, 73, 86, and 87 m.u.; δ ($CDCl_3$) 1.36 (9 H, s), 6.08 (2 H, s), 7.76—8.36 (7 H, m), and 8.83 (1 H, dd); $\nu_{max.}$ 1 650 cm^{-1}; N-(*t-butoxymethylene*)*phenanthrene*-4-*carboxamide* (24), m.p. 151—154°; M^+ 307 with loss of 56, 57, 58, 73, 74, 86, 87, 88, and 102 m.u.; δ ($CDCl_3$) 1.30 (9 H, s), 4.65br (1 H, s), 5.02 (2 H, d), 7.5—8.15 (8 H, m), and 8.75 (1 H, m); $\nu_{max.}$ 1 660 and 3 440 cm^{-1} (Found: C, 77.7; H, 6.9; N, 4.6. $C_{20}H_{21}NO_2$ requires C, 78.15; H, 6.9; N, 4.55%); N-*methylthebenidinone* (21), m.p. 234—235°; M^+ 233; δ ($CDCl_3$) 3.87 (3 H, s), 7.3—8.3 (7 H, m), and 8.77 (1 H, dd); $\nu_{max.}$ 1 595 and 1 649 cm^{-1} (Found: C, 82.3; H, 4.7; N, 6.05. $C_{16}H_{11}NO$ requires C, 82.4; H, 4.75; N, 6.0%); and 1-*iodo*-N-*methylthebenidinone* (22), m.p. 243—252°; M^+ 359 with loss of 127 m.u.; δ ($CDCl_3$) 3.9 (3 H, s), 7.2—7.4 (2 H, m), 7.95—8.5 (4 H, m), and 8.85 (1 H, dd); $\nu_{max.}$ 1 590 and 1 648 cm^{-1} (Found: C, 55.3, 51.65; H, 2.95, 2.6; N, 3.8, 3.65. $C_{16}H_{10}INO$ requires C, 53.5; H, 2.8; N, 3.9%).

(*e*) N-*Methylbiphenyl*-2-*carboxamide* (1). Iodine chloride (0.852 g, 0.005 31 mol) and potassium t-butoxide (0.681 g, 0.005 5 mol) in carbon tetrachloride (40 ml) were shaken in the dark for 5 min. Iodine (2.25 g, 0.0089 mol) and *N*-methylbiphenyl-2-carboxamide (1) (0.373 g, 0.0018 mol) were added and the mixture was stirred and irradiated for 1.5 h. The solution was shaken with an excess of aqueous sodium thiosulphate, dried (Na_2SO_4), and concentrated to a gum (0.358 g), which was a mixture (t.l.c. and n.m.r.) of starting material (9.6%) [δ 2.68 (d)], *N*-methylphenanthridone (2) (71.15%) [δ 3.67 (s)], and spirodienyl species (6) and (7) (19%) [δ 2.87 and 2.95 (2 × s) and 5.3—5.62 and 6.22—6.50 (m, olefinic H)]. The mixture, in methanol (20 ml), afforded a yellow precipitate upon treatment with an excess of methanolic silver nitrate; the mixture was filtered, diluted with water (100 ml), and extracted with dichloromethane. The extract was dried (Na_2SO_4) and concentrated to a gum which was a mixture (n.m.r.) of starting amide (1) (14%) [δ 2.68 (d)], *N*-methylphenanthridone (2) (73%) [δ 3.67 (s)], and a mixture of spirodienes (8) and (9), identical with an authentic mixture [16] (t.l.c. and n.m.r.), δ ($CDCl_3$) 2.94 and 2.84 (3 H, 2 × s), 3.40 and 3.44 (3 H, 2 × s), 4.52 (1 H, m), 5.47 (2 H, overlapping dd), and 6.32 (2 H, overlapping dd).

(*f*) The mixture of spirodienyl ethers (3) and (4) (0.5 g, *ca.* 0.0017 mol) isolated from the thermal reactions of the amide (1) was irradiated at ambient temperature in carbon tetrachloride (40 ml) with t-butyl hypoiodite [from t-butyl hypochlorite (0.57 g, 0.0053 mol), iodine (1.342 g, 0.0053 mol), and potassium t-butoxide (0.59 g, 0.0053 mol)]. Samples (2 ml) were withdrawn, washed with an excess of aqueous sodium thiosulphate, dried (Na_2SO_4), concentrated, and analysed by n.m.r. (integrals over *N*-methyl resonances). The results are in Table 4.

TABLE 4

Time (min)	Dienone (δ 2.99) (%)	Ether A (δ 2.84) (%)	Ether B (δ 2.93) (%)
0	7.06	47.65	45.0
30	17.39	46.0	36.52
75	25.0	43.5	30.77
135	38.52	40.98	21.0
225	54.17	34.72	11.11
320	73.53	22.55	3.92

(*g*) 1,2-*Dihydro*-N-*methylphenanthrene*-4-*carboxamide* (34). Iodine (4.26 g, 1.68×10^{-2} mol), t-butyl hypochlorite (1.81 g, 1.68×10^{-2} mol), potassium t-butoxide (1.88 g, 1.68×10^{-2} mol), and 1,2-dihydro-*N*-methylphenanthrene-4-carboxamide (34) (0.8 g, 3.375×10^{-3} mol) in t-butyl alcohol (36 ml) were irradiated at 26 °C for 4 h as above. A sample was processed to give only starting amide (n.m.r.). The mixture was stirred at 70 °C in the dark for 3 h; a sample was then processed and exhibited *N*-methyl resonances in the δ-lactam region (δ 3.75 and 3.91). Work-up after irradiation at 70 °C for 3 h afforded a red gum (1.313 g) which was separated (t.l.c.) into *N*-methylthebenidinone (21), *N*-methylphenanthrene-4-carboxamide (20) [δ 2.97 (d)] (66%), starting material, and 5a,6-*epoxy*-10-*t-butoxy*-5a,6,7,8-*tetrahydro*-N-*methylthebenidin*-5(4H)-*one* (36), m.p. 197—199.5°; M^+323; $\nu_{max.}$ 1 591 and 1 652 cm^{-1} (Found: C, 73.8; 73.8; H, 6.5, 6.5; N, 4.3, 4.4. $C_{20}H_{21}NO_3$ requires C, 74.3; H, 6.5; N, 4.35%) (see Supplementary Publication).

TABLE 5

Cyclisation of *N*-methylbiphenyl-2-carboxamide under irradiation

Temp. (°C)	Time (min)	Phenanthridone (%)	Spiro-products (%)	Amide (%)
26.4	0	0	0	100
	15	4.88	6.71	88.41
	30	8.51	17.73	73.76
	45	13.04	19.57	67.39
	75	17.57	29.71	52.72
	120	24.22	36.65	39.13
	185	29.17	40.63	30.2
36.4	0	0	0	100
	15	7.59	13.10	79.31
	30	13.81	19.25	66.95
	45	18.10	31.03	50.86
	75	23.21	42.86	33.93
	111	25.06	51.25	25.69
	165	28.57	62.03	9.39
40.6	0	0	0	100.0
	15	8.61	20.97	70.41
	30	14.51	33.66	51.84
	45	18.37	43.67	37.95
	75	22.98	52.76	24.25
46.1	0	0	0	100
	15	13.0	28.7	58.3
	30	18.67	42.22	39.11
	45	21.88	53.13	25.00
	75	24.37	61.39	14.24

Methanolysis of the Epoxythebenidinone (36).—The epoxythebenidinone (30 mg) in methanol (15 ml) was treated with concentrated sulphuric acid (0.75 ml). The mixture was

[16] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 1162.

refluxed for 0.75 h, then diluted with water (30 ml) and extracted with chloroform (2 × 15 ml). The extract was dried and concentrated to a solid (23 mg) which crystallised from benzene–ether as fine needles of 10-*methoxy*-N-*methylthebenidin*-5(4H)-*one*, m.p. 156—159°; M^+ 263; δ ($CDCl_3$) 3.85 (3 H, s), 4.07 (3 H, s), 7.01 (1 H, s), 7.25—8.25 (5 H, m), and 8.55 (1 H, dd); $\nu_{max.}$ 1 593, 1 610, and 1 650 cm^{-1}.

Kinetic Studies of Cyclisation Reactions.—Rates of cyclisation of N-*methylbiphenyl*-2-*carboxamide and* N-*methylphenanthrene*-4-*carboxamide; general procedure.* Iodine (6 g, 0.0237 mol) and t-butyl hypochlorite (2.55 g, 0.0237 mol) were added successively to t-butyl alcohol (50 ml) in a 100 ml flask which was shaken in the dark for 15 min. Potassium t-butoxide (2.65 g, 0.0237 mol) was added, followed after shaking for a further 10 min by the amide (0.004 74 mol; 0.095 mol l^{-1}). The mixture was then shaken in the dark for 15 min; it was then stirred in a Pyrex-walled constant temperature bath with illumination by a 1000 W tungsten lamp. Heat from the lamp was dissipated in a reservoir (between the lamp and the bath) through which cold water was circulated. Samples (2 ml) were withdrawn at intervals, poured into an excess of aqueous sodium thiosulphate (15 ml), and extracted into chloroform or methylene chloride (2 × 5 ml); the extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The product mixtures were analysed by n.m.r., the relative *N*-methyl integrals being converted into concentrations. First-order rate constants were derived from least-squares plots of ln[amide] *vs.* time, and the parallel rate constants were obtained from least-squares plots of [product] *vs.* $(1 - e^{-k_{obs}t})$. Spurious plots were omitted for least-squares calculations. The results for the amide (1) are in Table 5.

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