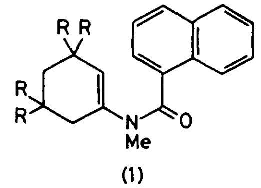
Unusual Photocyclisation of 1-(*N*-Methyl-1-naphthoylamino)tetramethylcyclohexene; *X*-Ray Crystal Structure of 4b,8,9,10,10a,10b,11,12-Octahydro-6,8,8,10-tetramethyl-10,12-methanobenzo[*i*]-phenanthridin-5(6*H*)-one

By I. NINOMIYA,* T. KIGUCHI, and T. NAITO
(*Kobe Women's College of Pharmacy, Motoyamakita, Higashinada, Kobe* 658, *Japan*)
and M. INOUE and T. ISHIDA
(*Osaka College of Pharmacy, Kawai, Matsubara, Osaka* 580, *Japan*)

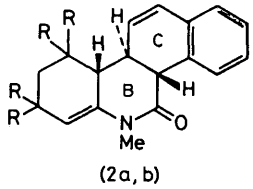
Summary Irradiation of 1-(*N*-methyl-1-naphthoylamino)-3,3,5,5-tetramethylcyclohexene (**1a**) first afforded the photocyclised B/C-*trans*-benzo[*i*]phenanthridinone (**2a**) which then underwent photoisomerisation to the corre-

sponding *cis*-isomer (**3a**) and unusual cyclisation to the cage compound (**4**), the structure of which was established by *X*-ray analysis.

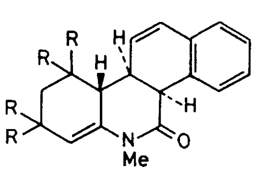
AMONG the considerable use of enamide photocyclisations in the synthesis of nitrogen-containing heterocycles,[1] the photocyclisation of *N*-naphthoylenamines has provided an efficient route to azasteroids.[2] During our study on the photocyclisation of the *N*-naphthoylenamines (**1a**) and (**1b**), prepared from cyclohexanone and its 3,3,5,5-tetramethyl congener, we found that not only a ready photoisomerisation but also a new photocyclisation involving a methyl group of the photocyclised product took place depending upon the irradiation conditions, thus yielding a new type of pentacyclic compound (**4**).†



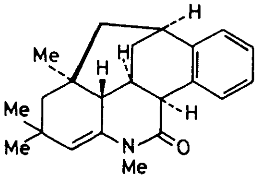
(1)
a; R = Me
b; R = H



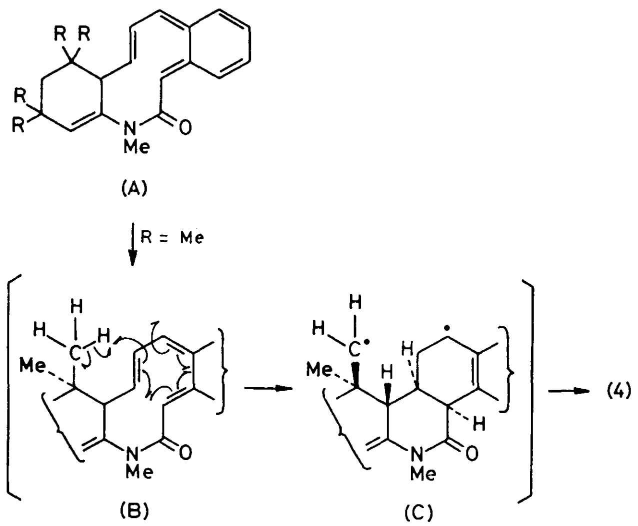
(2a, b)



(3a, b)



(4)



(A)

(B) (C) → (4)

Although irradiation of an ethereal solution of the enamine (**1a**), prepared from 3,3,5,5-tetramethylcyclohexanone[3] and 1-naphthoyl chloride, with a high-pressure mercury lamp through a Pyrex filter at room temperature for 1—2 h gave the B/C-*trans*-benzo[*i*]phenanthridinone (**2a**) predominantly, prolonged irradiation for 5 h led to the formation of two isomeric lactams (**2a**) and (**3a**) with predominant formation of the latter (Table).

TABLE. Irradiation times and isolated yields of products of irradiation of the enamines (**1a**) and (**1b**).

	% Yields of photocyclised products			
t/h	(**2a**)	(**3a**)	(**2b**)	(**3b**)
1—2	76	trace	48	10
5	10	39	6	50

Since exclusive formation of the B/C-*cis*-lactam (**3a**) without incorporation of deuterium from the solvent was observed in the irradiation of the B/C-*trans*-lactam (**2a**) under the same conditions using CD_3OD, this photoisomerisation presumably proceeds *via* a triene intermediate (A) formed by ring-opening of the B/C-*trans*-lactam (**2a**), which has a photochemically labile cyclohexadiene structure.[4]

When the enamide (**1a**) was irradiated with a high-pressure mercury lamp without a Pyrex filter for 2 h, the new pentacyclic lactam (**4**) was obtained as the sole product in 39% yield; compound (**4**) was also formed from the B/C-*trans*-lactam (**2a**) in 73% yield upon irradiation without a Pyrex filter. The structure of the pentacyclic lactam (**4**) was unambiguously determined by single-crystal *X*-ray analysis as shown in the Figure, which also made possible a rationalisation of its ^1H n.m.r. spectrum.

Crystal data: $C_{22}H_{27}NO$, $M = 321{\cdot}44$, monoclinic, space group $P2_1/a$, $a = 11{\cdot}073(3)$, $b = 12{\cdot}287(2)$, $c = 13{\cdot}320(2)$ Å, $\beta = 108{\cdot}08(2)°$, $U = 1722{\cdot}6(6)$ Å^3, $D_m = 1{\cdot}237(1)$, $D_c = 1{\cdot}239(1)$ g cm^{-3}, $Z = 4$. The structure was solved by direct methods (MULTAN 78[5]) and refined by least-squares to $R = 0{\cdot}056$ using 2938 independent reflections ($2\theta_{max} \leq 130°$).‡

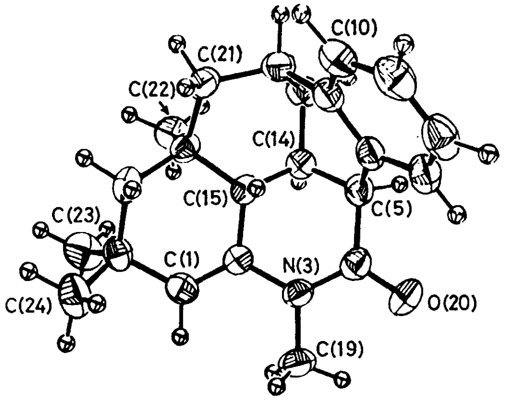


FIGURE. Molecular structure of compound (**4**).

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† All new compounds exhibited satisfactory spectroscopic and analytical data consistent with the proposed structures.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

From the above results the formation of the pentacyclic lactam (**4**) could be explained as follows; the triene (A), which would be formed from the B/C-*trans*-lactam (**2a**) by ring-opening upon irradiation with long wavelength light, would be again excited upon irradiation with short wavelength light to form the excited state (B) where hydrogen abstraction from a spatially adjacent methyl group by a triene moiety would occur[6] to give the diradical (C) which would then undergo further cyclisation to afford the pentacyclic lactam (**4**).

Irradiation of the enamine (**1b**), prepared from cyclohexanone and naphthoyl 1-chloride, with and without a Pyrex filter afforded a mixture of the B/C-*trans*-(**2b**) and B/C-*cis*- (**3b**) lactams in ratios which depend on the irradiation time (Table). Photoisomerisation of the B/C-*trans*-lactam (**2b**) to the corresponding *cis*-isomer (**3b**) was also observed under the same irradiation condition as in the case of the enamine (**1a**) described above.

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