HETEROCYCLES, Vol. 4, No. 3, 1976

PHOTOISOMERISATION OF trans-4b,10b,11,12-TETRAHYDROBENZO[c]PHENANTHRIDIN-6(5H)-ONE TO THE cis-ISOMER

Ichiya Ninomiya*, Toshiko Kiguchi, Okiko Yamamoto, and Takeaki Naito

Kobe Women's College of Pharmacy
Motoyamakita, Higashinada, Kobe, Japan

Irradiation of some B/C-trans-benzo[c]phenanthridones substituted with an electron-withdrawing group such as ester and nitrile caused isomerisation to afford the corresponding cis-lactams.

N-Benzoylenamines[1)] have been shown to undergo photocyclisation to afford the trans-lactams stereospecifically according to an electrocyclic mechanism. During the work on the photocyclisation of enamides having a substituent on the benzene ring,[2)] we found examples in which the trans-lactam was isomerised to the cis-lactam during the course of irradiation when an electron-withdrawing group such as ester and nitrile was present at the para position.

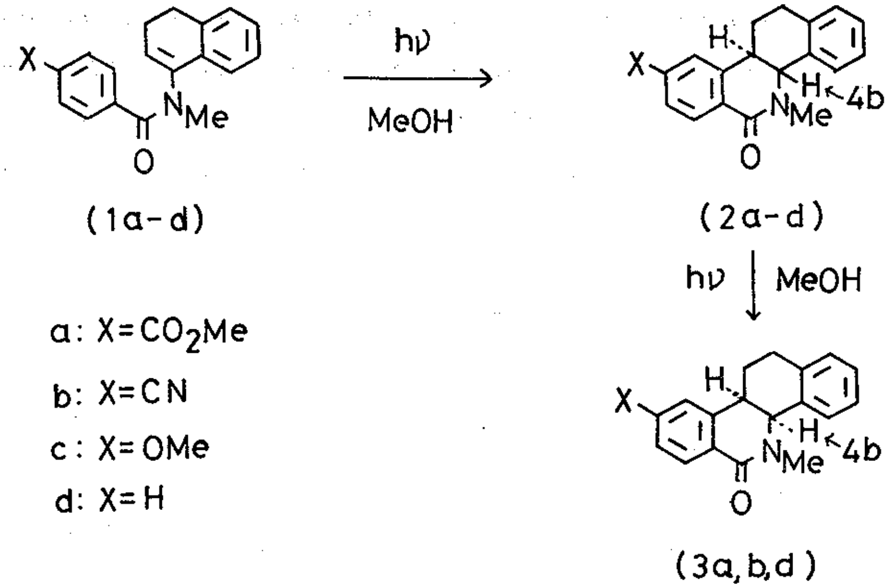
Seven hours' irradiation of a methanolic solution of the enamide (1a) with a low pressure mercury lamp afforded the trans-lactam

(2a) homogeneously. However, a prolonged irradiation (20 hr) of (1a) afforded the *cis*-lactam (3a) as a sole product in 20 % yield. The structures of these products were established mainly from their n.m.r. spectra; the *trans*-lactam (2a) exhibited peaks at δ4.80 (d, J=12Hz) for C_{4b}-H, while the *cis*-lactam (3a) at 4.85 (d, J= 4.5Hz) for the same proton.

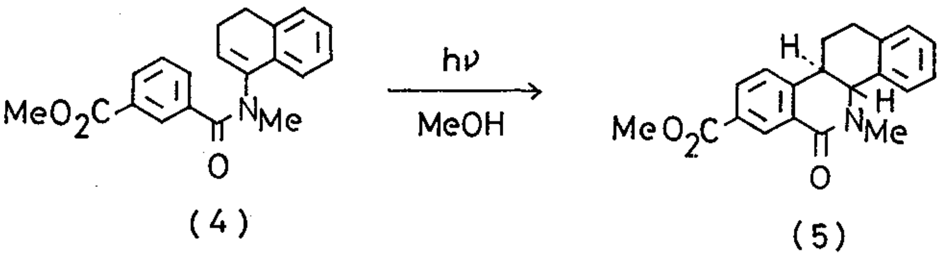
Further, the *trans*-lactam (2a) was isomerised to the *cis*-lactam (3a) quantitatively when irradiated in methanol. However, this isomerisation was not observed when an aprotic solvent such as benzene, ether or dioxane was employed.

Photocyclisation of the enamide (1b) having a nitrile group at the para position afforded the same result, while the p-methoxy-substituted enamide (1c) afforded only the *trans*-lactam (2c), which was not isomerised even upon a prolonged irradiation but decomposed. Eight hours' irradiation of the enamide (1d) afforded the *trans*-lactam (2d) homogeneously, while a prolonged irradiation (10 days) of (2d) brought about isomerisation to afford the *cis*-lactam (3d) in 10 % yield. On the other hand, irradiation of the enamide (4) which carries an ester group at the meta position, gave the homogeneous *trans*-lactam (5) which decomposed upon a prolonged irradiation.

Furthermore, irradiation of the enamide (1a) in deuterium methoxide solution was found to afford a mixture of two isomeric lactams (2a and 3a), of which the *trans*-lactam (2a) contained no deuterium while the *cis*-product (3a) was incorporated with one deuterium atom almost quantitatively, which was introduced exclusively at C_{4b}-position.



a: $X=CO_2Me$
b: $X=CN$
c: $X=OMe$
d: $X=H$



These results give not only a further support to an electrocyclic mechanism for enamide photocyclisation to afford *trans*-lactam, but also an useful synthetic means for the preparation of the epimeric lactams. The mechanism of isomerisation is now under investigation.

REFERENCES

1 a) I. Ninomiya, T. Naito, and T. Mori, *J. Chem. Soc. Perkin I*, 1973, 505

b) I. Ninomiya, T. Naito, T. Kiguchi, and T. Mori, *ibid*, 1973, 1696.

c) I. Ninomiya, T. Naito, and T. Kiguchi, *ibid*, 1973, 2257.

2 I. Ninomiya, T. Kiguchi, and T. Naito, *J. Chem. Soc. Chem. Comm.*, 1974, 81.

Received, 13th December, 1975