

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

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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-Benzoylenamines¹⁾ 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 ring²⁾ 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.

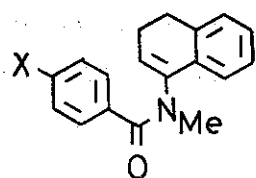
Seven hours' irradiation of a methanolic solution of the enamide (1a) with a low pressure mercury lamp afforded the trans-lactam

(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 δ 4.80 (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.



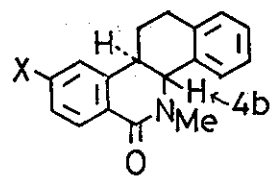
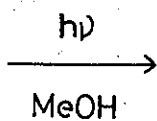
(1a-d)

a: X = CO₂Me

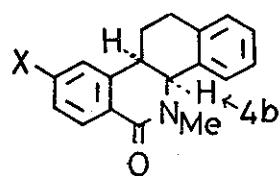
b: X = CN

c: X = OMe

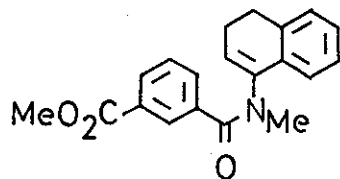
d: X = H



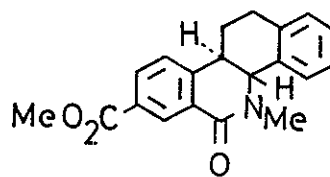
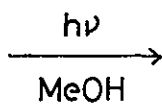
(2a-d)



(3a,b,d)



(4)



(5)

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

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