HETEROCYCLES, Vol 21, No 2, 1984

PHOTO-RING EXPANSION OF AZIDOMETHOXYQUINOLINES TO METHOXYPYRIDOAZEPINES

R.K. Smalley, E.F.V. Scriven[1] and H. Suschitzky

Dep. of Chemistry & Applied Chemistry, University of Salford, M5 4WT England

We have shown[2] that photolysis and in some cases thermolysis of bicyclic aromatic and heteroaromatic azides in amines offer a practicable route to bicyclic azepines subject to some limitations such as position of the azide group and nature of the amine. However, photochemical ring-expansion of quinolyl and isoquinolyl azides to the corresponding azepines occurs in methoxide[3] regardless of the azide position.

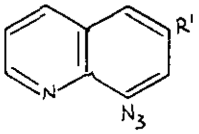
The general scope of preparing azepines by ring expansion has been further widened as the result of the following observations: The presence of a 6-methoxygroup in 8-azidoquinoline leads to a remarkable increase in the yield of singlet products azepine (2) and o-diamine (3) when this azide (1) is irradiated in primary aliphatic amines. This group also promotes azepine formation on irradiating azide (1) in secondary amines, which does not occur in absence of this substituent. Conditions for the photolytic azepine formation from 8-azidoquinoline in methanol/K-methoxide to give 9-methoxy-5H-pyrido [2,3-c] azepine (2; MeO for NR$_2^2$) have been optimised. When these are applied to 8-azido-6-methoxy-(1) and 6-azido-8-methoxy-quinoline (1; R' = N$_3$, OMe for N$_3$) the corresponding dimethoxyazepines (4 or 5) are obtained in good yield.

---

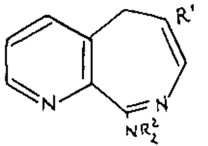
[1] Reilly Tar and Chemical Corporation, 1510 Market Square Center, 151 North Delaware St., Indianapolis, Indiana 46204, U.S.A.

[2] H. Suschitzky, Heterocyclic Lectures, 1, 5 (1980)

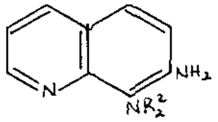
[3] F. Hollywood, Z.U. Khan, E.F.V. Scriven, R.K. Smalley, H. Suschitzky and (the late) D.R. Thomas, J. Chem. Soc. Perkin Trans; 1, 431 (1982)



(1; R'=OMe)

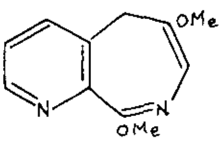


(2)



(3)

(4)



(5)