

SYNTHESES OF DIAZEPINES FROM PYRIDINE AZIDES

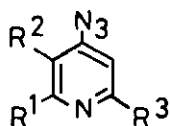
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Recently, much attention has been paid to the synthesis of new conjugated seven-membered heterocycles. As for diazepines, monocyclic 1,2-diazepines are synthesized by the photo-induced rearrangement of pyridine N-imides and 1,3-diazepines are prepared by the thermal isomerization of 1,2-diazepines, but 1,4-diazepines have not been reported. Benzodiazepines (1,2-, 1,3-, and 2,3-) and related fused diazepines condensed with aromatic heterocyclic rings have also been prepared mainly from fused pyridine N-imides or diazo compounds. We report here the syntheses of several new diazepines from pyridine azides.

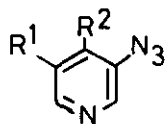
(i) Irradiation of the 4-azidopyridines (1) in the presence of methoxide ions resulted in the ring-expansion to give the 6H-1,4-diazepines (2), which afforded the 1-acyl-1H-1,4-diazepines (3) by treatment with acyl chlorides.

(ii) The 3-azidopyridines (4) gave the 5H-1,3-diazepines (5) by the photolysis under the similar conditions.

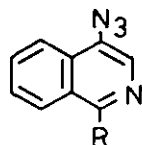
(iii) Similarly, the 4-azidoisoquinolines (6) afforded the 1H-2,4-benzodiazepines (7). The structures of the new diazepines (2, 3, 5, and 7) thus obtained were confirmed by some photochemical and thermal reactions, respectively.



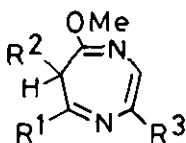
(1) R¹, R², R³ = H, Me



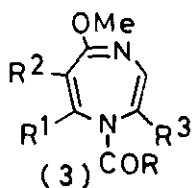
(4) R¹, R² = H, Me



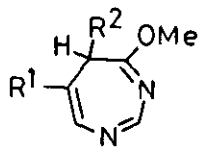
(6) R = H, OMe



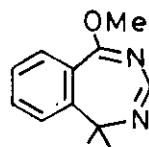
(2)



(3)



(5)



(7)