

## SYNTHESIS OF MONOCYCLIC 1,3-DIAZEPINES FROM PYRIDINES

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Previously, we have reported the first syntheses of fully unsaturated 1,2- and 1,3-diazepines condensed with aromatic rings such as benzene, pyridine, thiophen, furan, or pyrrole. As part of our studies on diazepines, we now report the synthesis of simple monocyclic 1,3-diazepines from pyridine N-imides via 1,2-diazepines.

Irradiation of the 3- or 5-substituted pyridine N-imides (1) gave the corresponding 4- or 6-substituted 1H-1,2-diazepines (2), which were heated in a solvent to give the corresponding 1,3-diazepines (3) as well as 2- or 6-ethoxycarbonylamino-pyridines. Heating of the diazabicyclo[3.2.0]heptadienes (4), which were readily obtained by further irradiation of (2), also gave the 1,3-diazepines (3). Irradiation of (3) afforded the bicyclic compounds (5), which reverted back to (3) by heating.

However, 1H-1,2-diazepines having an electron-drawing substituent such as acyl or halogen group in the 4- or 6-position, upon heating, gave the parent pyridine N-imides and 2- or 6-aminopyridines, but no 1,3-diazepines. Similarly, 3-, 5-, or 7-substituted 1,2-diazepines with either an electron-donating or -withdrawing group also gave no diazepines. These results indicate that the presence of an electron-donating substituent in the 4- and/or 6-position is essential for the thermal rearrangement of (2) into (3). The mechanism and substituent effects for the thermal reaction will be discussed in detail.

