SYNTHESES OF MONOCYCLIC 1,4-DIHETEROEPINES FROM PYRIDINES VIA 3-AZATRICYCLO[4.1.0.0]HEPTANES

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The synthesis of new conjugated seven-membered heterocyclic rings, heteroepines, have been the object of extensive study and we have already reported the syntheses of many novel diazepines such as fused 1,2-, 1,3-, 2,3-, and 2,4-diazepines condensed with aromatic rings and monocyclic 1,3-diazepines. We report here the first syntheses of 1,4-diheteroepines (3-6) from pyridines via 3-azatricyclo-[4.1.0.0]heptanes by thermal valence bond isomerization.

The starting 2-azabicyclo[2.2.0]heptanes (1) were readily prepared by photocyclisation of dihydropyridines or 2-pyridones. The bicyclic compounds (1) were treated with m-chloroperbenzoic acid, N-ethoxycarbonyl nitrene, succimide-N-sulphenyl chloride followed by $LiAlH_4$ reduction, or methylene carbene to give the corresponding 3-azatricyclo[4.1.0.0]heptanes (2).

Heating of the tricyclic compounds (2) resulted in ring-expansion to give the corresponding dihydro-1,4-diheteroepines (3)-(6) in good yields, respectively.

The reaction mechanism for the formation of the diheteroepines (3-6) from 2 and some reactions of the compounds (2-6) will be also described.