

SYNTHESIS OF 1,4-DIHETERO SEVEN-MEMBERED RINGS USING VALENCE BOND
ISOMERIZATION OF TRICYCLOHEPTANE SYSTEMS

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As part of our continuous studies on seven-membered heterocyclic ring compounds, we report that the azatricyclo[4.1.0.0^{2,5}]-heptanes (2) and -heptenes (4) are new useful synthons for novel 1,4-dihetero seven-membered ring systems.

The 2-azabicyclohexanes (1), prepared from pyridines via 1,2-dihydropyridines, were treated with m-chloroperbenzoic acid, ethoxycarbonyl nitrene, succinimide-N-sulphenyl chloride - LiAlH₄, or diazomethane to give the tricyclic compounds (2a-d).

Heating the key synthons (2a-d) in refluxing xylene or toluene resulted in valence bond isomerization with ring opening to give the corresponding seven-membered heterocycles, 1,4-oxazepines (3a), 1,4-diazepines (3b), 1,4-thiazepines (3c), and azepines (3d), in 80-90% yields. Either photolysis or thermolysis of the tricycloheptenes (4a,b) prepared from the tricycloheptanes (2) gave the fully unsaturated 1,4-oxazepines (5a) and 1,4-diazepines (5b) in good yields.

All seven-membered heterocycles thus obtained are previously unknown compounds and results of some reactions of these compounds are also presented.

