CONVERSION OF CYCLIC AMINE N-YLIDES INTO NOVEL HETEROCYCLES BY THERMAL REARRANGEMENTS

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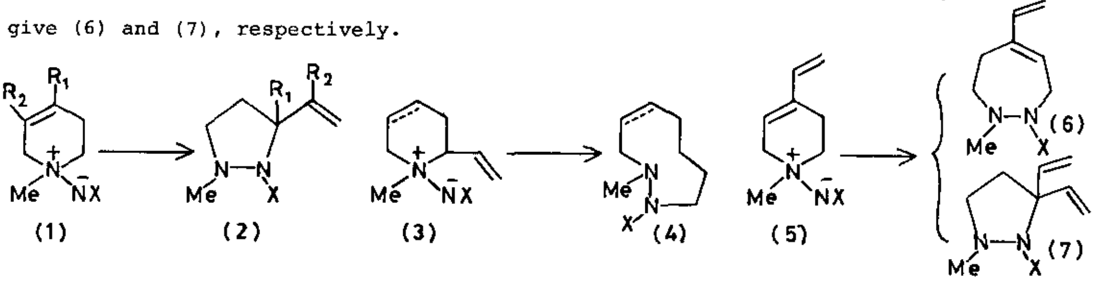
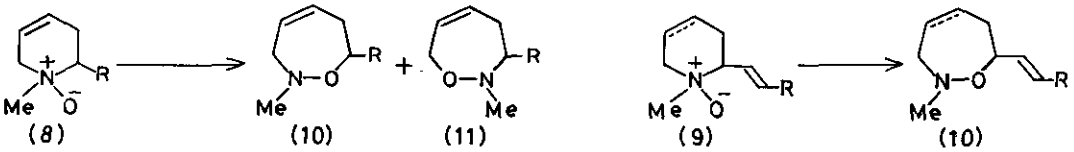
The synthetic utilization of thermal rearrangements of unsaturated cyclic amine N-ylides was examined in the synthesis of novel heterocyclic compounds.

(I) The thermolysis of the N-imides (1) underwent [2,3]-sigmatropic rearrangement to give (2), whereas the [2,3]-rearrangement with the vinyl group predominated over that with the cyclic double bond to give (4) in the thermolysis of the N-imides (3). However, the thermolysis of (5) resulted in both [1,2]- and [2,3]-rearrangement to give (6) and (7), respectively.



(II) Heating of the N-oxides (8 and 9) resulted in a Meisenheimer-type [1,2]-rearrangement to give the corresponding 1,2-oxazepines (10 and 11), in contrast to the cases of the N-imides (1 and 3).



(III) The N-imides (12) with ethynyl groups in the α-position, upon heating, underwent [2,3]rearrangement to the allene intermediates (13), followed by hydrogen shift to give the 1,2-diazonines (14). The 2-ethynylpyridines (15) gave the 3-azaindolizines (16). The mechanisms of these rearrangements will be discussed.