SYNTHESES AND REARRANGEMENTS OF 1,2-DIAZEPINES CONDENSED WITH VARIOUS HETEROCYCLIC RINGS

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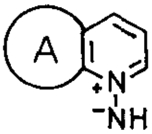
The novel heterocyclic ring systems, pyrido[2,3-c]- (2a), pyrido[3,2-c]- (2b), thieno[2,3-c]- (2c), thieno[3,2-c]- (2d), and furo[2,3-c]- (2e) 1H-1,2-diazepines, were prepared photochemically from the corresponding parent fused pyridines *via* the N-iminopyridinium ylides (1a-e), respectively. However, an analogous route for pyrrolodiazepines has not been successful.

The 1H-1,2-diazepines (2) were converted to their 3H-isomers (3) by successive lithium aluminum hydride reduction and dehydrogenation with 4-phenyl-1,2,4-triazoline-3,5-dione. The 3H-isomers (3) were readily tautomerized to the parent 1H-diazepines (2) by treatment with bases such as sodium methoxide.

The pyrido-3H-1,2-diazepines (3a,b) underwent both heat- and light-induced rearrangement to give the 3-vinyl-pyridopyrazoles (4a,b). However, photolysis of the thieno-3H-1,2-diazepines (3c,d) gave the 3-vinyl-thienopyrazoles (4c,d), whereas their thermolysis resulted in the formation of the thienylpyrazoles (5c,d) *via* a [1,5]-hydrogen shift in the diazepine ring. This mechanism has been confirmed by a deuterium-labeling experiment.

A: Heterocyclic Ring



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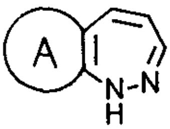

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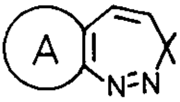

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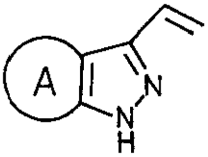

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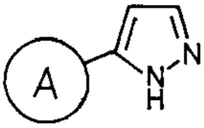

(5)