Thermal and Photochemical Rearrangements of 3*H*-Thieno-1,2-diazepines

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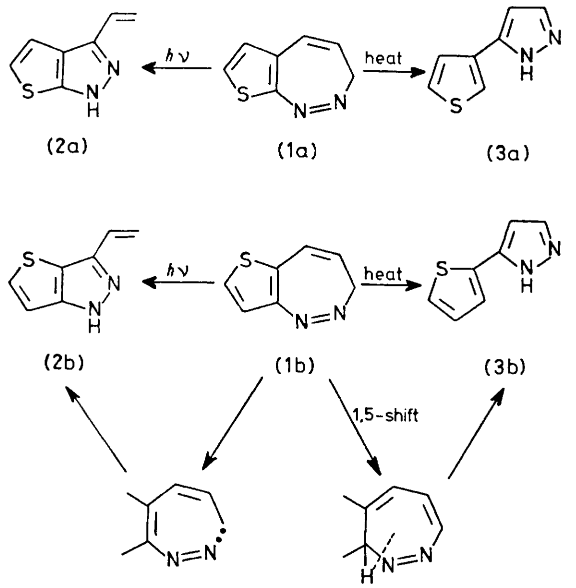
Summary Photolysis of the 3*H*-thieno-1,2-diazepines (**1**) affords the 3-vinylthienopyrazoles (**2**), whereas their thermolysis gives the thienylpyrazoles (**3**) *via* a [1,5] hydrogen shift in the diazepine ring; this mechanism has been confirmed by a deuterium-labelling experiment.

The *3H*-1,2-benzodiazepines are known to undergo both heat- and light-induced rearrangement to give 3-vinylindazoles in high yields.[1,2] Sharp recently reported that the thermolysis and photolysis of monocyclic *3H*-1,2-diazepines take quite different paths; the former gives vinylpyrazoles and the latter bicyclic compounds.[3] In connection with these studies and the similar rearrangements of other nitrogen-containing 7-membered ring systems such as triazepines[4] and oxazepines,[5] we were interested in examining analogous reactions of the recently synthesized title compounds (**1**)[6] as part of our studies on diazepines; we now report our results.

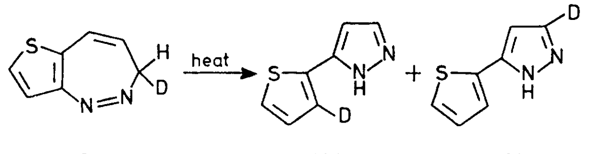


(2a) (1a) (3a)

(2b) (1b) (3b)

(4) (5)

The thienodiazepines (**1a**,**b**) were irradiated with a halogen lamp to give the corresponding 3-vinylthienopyrazoles (**2a**,**b**)† as the sole products in *ca.* 65% yields. The photolysis may involve initial C–N bond fission to the diradical intermediate (**4**) by analogy with *3H*-1,2-benzodiazepines,[1] and not tautomerization to the *5H*- or *7H*-isomers followed by $({}_{\pi}2_s + {}_{\pi}2_s)$ reaction of the azabutadiene units to the bicyclic compounds analogous to that observed for *3H*-1,2-diazepines[3] and 2,3-benzodiazepines.[7]



(6) (7) (8)

However, thermolysis of the diazepines (**1a**,**b**) in refluxing dry xylene yielded the thienylpyrazoles (**3a**,**b**)‡ in *ca.* 55% yields and no other characterized products were obtained. We assumed that the thermolysis may involve a thermally allowed [1,5] hydrogen shift in the diazepine ring to give the *7H*-isomer (**5**), followed by successive C–N bond fission and ring closure to give (**3**); this assumption was tested by the following deuterium-labelling experiment.

Thermolysis of the deuteriated diazepine (**6**)§ resulted in the formation of the labelled compounds (**7**) and (**8**) in the ratio of 1 : 3. This ratio was determined by ^{1}H n.m.r. spectral analysis and the isotope effect for the tautomerization (**6**) → (**5**) (k_H/k_D = *ca.* 3) is parallel with that for [1,5] hydrogen and deuterium migrations in other systems such as cyclopentadienes.[8] This result is clearly consistent with the foregoing mechanistic proposal.

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† Satisfactory elemental analyses and n.m.r., i.r., and mass spectral data were obtained for the new compounds (**2a**), m.p. 79—81 °C, and (**2b**), m.p. 122—124 °C.

‡ Compounds (**3a**) and (**3b**) were identified by comparison with authentic samples prepared by the literature method: S. Gronowitz, A. Hallberg, S. Liljefors, U. Forsgren, B. Sjöberg, and S.-E. Westerbergh, *Acta Pharm. Suenica*, 1968, **5**, 163.

§ Compound (**7**) was prepared from the corresponding *1H*-1,2-thienodiazepine by successive $LiAlD_4$ reduction and dehydrogenation with 4-phenyl-1,2,4-triazoline-3,5-dione, and was characterized by ^{1}H n.m.r. and mass spectroscopy.

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