

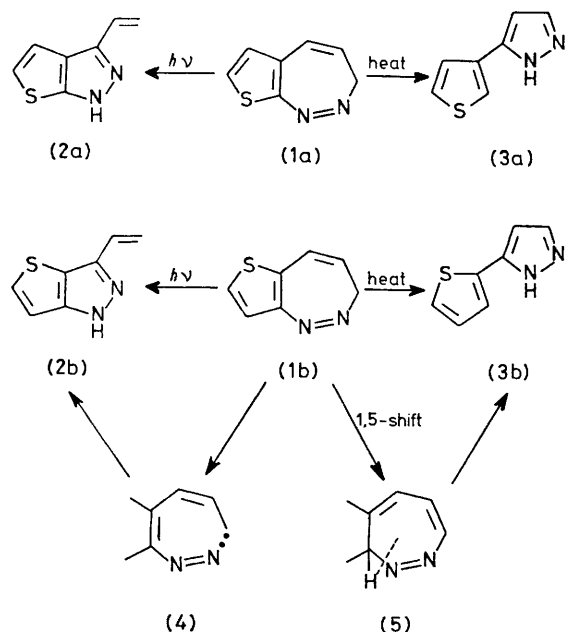
Thermal and Photochemical Rearrangements of 3*H*-Thieno-1,2-diazepines

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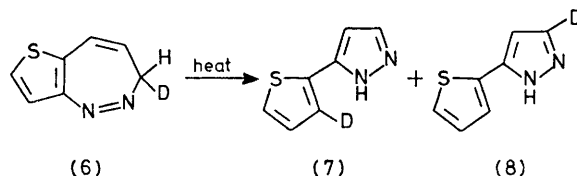
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Summary Photolysis of the 3*H*-thieno-1,2-diazepines (**1**) affords the 3-vinylthienopyrazoles (**2**), whereas their thermolysis gives the thienylpyrazoles (**3**) *via* a [1,5] hydrogen shift in the diazepine ring; this mechanism has been confirmed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

THE 3*H*-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 3*H*-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 triazepines⁴ 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.



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 3*H*-1,2-benzodiazepines,¹ and not tautomerization to the 5*H*- or 7*H*-isomers followed by ($\pi 2_s + \pi 2_s$) reaction of the azabutadiene units to the bicyclic compounds analogous to that observed for 3*H*-1,2-diazepines³ and 2,3-benzodiazepines.⁷



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 7*H*-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 deuterated diazepine (**6**)[§] resulted in the formation of the labelled compounds (**7**) and (**8**) in the ratio of 1:3. This ratio was determined by ¹H n.m.r. spectral analysis and the isotope effect for the tautomerization (**6**) \rightarrow (**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.

(Received, 29th March 1978; Com. 336.)

[†] 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 1*H*-1,2-thienodiazepine by successive LiAlD₄ reduction and dehydrogenation with 4-phenyl-1,2,4-triazoline-3,5-dione, and was characterized by ¹H n.m.r. and mass spectroscopy.

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³ C. D. Anderson, J. T. Sharp, E. Stefaniuk, and R. S. Strathdee, *Tetrahedron Letters*, 1976, 305.

⁴ G. C. Johnson and R. H. Levin, *Tetrahedron Letters*, 1974, 2303; D. J. Anderson and A. Hassner, *J.C.S. Chem. Comm.*, 1974, 45; V. Nair, *J. Heterocyclic Chem.*, 1975, **12**, 183; I. Saito, A. Yazaki, and T. Matsuura, *Tetrahedron Letters*, 1976, 4753.

⁵ T. Tezuka, O. Seshimoto, and T. Mukai, *J.C.S. Chem. Comm.*, 1974, 373; C. Kaneko and R. Kitamura, *Heterocycles*, 1977, **6**, 111.

⁶ T. Tsuchiya, M. Enkaku, and H. Sawanishi, *Heterocycles*, 1978, **9**, 621.

⁷ A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J.C.S. Perkin I*, 1973, 2544.

⁸ C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187; and refs. cited therein.