

A Vinylaziridine to Pyrroline Rearrangement

By R. S. ATKINSON and C. W. REES*

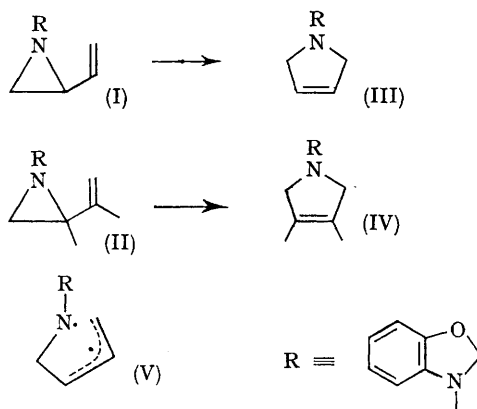
(Department of Chemistry, The University, Leicester)

A NEW thermal rearrangement, structurally analogous to that of vinylcyclopropanes to cyclopentenenes¹ but occurring under much milder conditions, has been observed with the vinylaziridines (I) and (II) described in the preceding Communication.

When (I) was heated in decalin at 180° for 40 min., the Δ^3 -pyrroline (III), m.p. 146—147° was formed (85%). Similarly (II) gave (IV), m.p. 146—148° (75%) in 12 min.; none of the isomeric 2,3-dimethyl- Δ^2 -pyrroline was detected by n.m.r. examination of the total decalin solution and thus the aziridine ring has probably opened with exclusive C–N bond fission. Analogous saturated aziridines were entirely stable in these conditions.

The vinylcyclopropane to cyclopentene rearrangement is usually considered to proceed through an alkyl-allyl diradical which collapses with allylic rearrangement,² especially where the non-allylic radical is also stabilised, e.g., by α -chlorine atoms;³ a synchronous 4-centre mechanism has also been considered. With the vinylaziridines the corresponding intermediate [e.g., (V)] is an allylic-hydrazino-diradical and the enhanced stability⁴ of this over the carbocyclic analogue explains the comparative mildness of the conditions (100—200° lower than for the vinyl cyclopropane rearrangement) and the apparently exclusive formation of the Δ^3 -pyrrolines. The faster reaction of (II) than (I), respectively 100% and 60% complete after 1 hr. at 150° in decalin, follows from the greater stability of the tertiary over the secondary allylic radical.

Scheiner⁵ has very recently attempted a thermal 2-vinylaziridine to Δ^3 -pyrroline rearrangement with an *N*-arylaziridine, but this was thwarted by faster ring closure of the vinyl group onto the aryl ring. With sodium iodide, under the conditions of the well-known *N*-acylaziridine to oxazoline rearrangement,⁶ the Δ^3 -pyrroline was formed, however. Very little (ca. 2%) of compound (I) was converted into (III) with sodium iodide in boiling acetone for 24 hr. since here opening of the aziridine ring is not facilitated by delocalisation the developing negative charge on nitrogen.



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¹ H. M. Frey, *Adv. Phys. Org. Chem.*, 1966, **4**, 155.

² M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, 1967, **89**, 723 and references therein.

³ A. D. Ketley, A. J. Berlin, E. Gorman, and J. P. Fisher, *J. Org. Chem.*, 1966, **31**, 305.

⁴ Cf., the stability of other hydrazino-radicals and the closely related nitroxide radicals reported in B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms" Interscience, London, 1965, p. 216; 1966, p. 264.

⁵ P. Scheiner, *J. Org. Chem.*, 1967, **32**, 2628.

⁶ H. W. Heine, *Angew. Chem. Internat. Edn.*, 1962, **1**, 528.