Some 1,5-Sigmatropic Shifts in Nitrogen Heterocyclics

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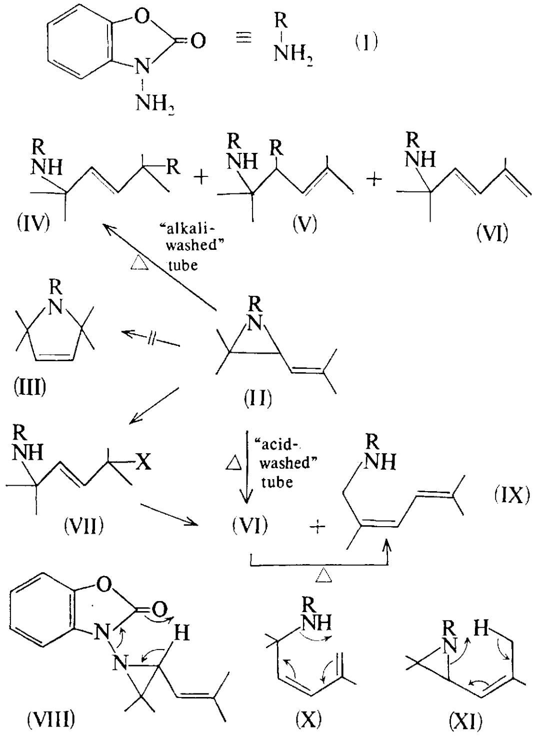
WE recently reported that oxidation of 3-aminobenzoxazolin-2-one (I) with lead tetra-acetate in the presence of mono- and di-enes gave *N*-substituted aziridines (*e.g.* II) by stereospecific 1,2-addition,[1] and the vinylaziridines formed from conjugated dienes rearranged smoothly on heating to give Δ^3-pyrrolines.[2] We now find that thermal decomposition of the tetramethyl vinylaziridine (II) gives none of the expected Δ^3-pyrroline (III) however, and that its decomposition depends strikingly upon the pH of the glass surface of the reaction vessel.

When a 20% solution of (II) in decalin was heated at 180° for 30 min. in a test-tube which had been washed with hot aqueous alkali (2N) and then repeatedly with water, and dried, it gave the bis-benzoxazolinones (IV) (33%), m.p. 112—114°, and (V) (32%), m.p. 167·5—168·5°, the diene (VI) (10%) (an oil; *N*-phenylmaleimide adduct, m.p. 195·5—197°), and starting material (8%). Analytical and spectroscopic data support these, and later, structures; in particular the *trans*-configuration of the double bond in (IV) and (VI) follows from the large coupling constant (16 c./sec.) in the n.m.r. spectra. Diene (VI) was also the product of dehydration, with phosphorus oxychloride in pyridine, of the tertiary alcohol (VII; X = OH); the latter is formed from the highly acid-sensitive vinylaziridine (II) by chromatography over silica.

Compounds (IV) and (V) were not decomposed nor interconverted at 180° in decalin; after 30 min. both could be recovered quantitatively; (VI) was 30% decomposed under these conditions (see below) but (IV) and (V) were not among the products. Thus at least two quite different decomposition paths are possible for (II).

Formation of the bis-benzoxazolinones (IV) and (V) from (II) can be most simply explained by a 1,5-hydrogen shift (VIII)[3] to give benzoxazolinone which then attacks the aziridine ring of another molecule of (II), directly to give (V) and at the allylic position to give (IV). This mechanism was supported by the complete reaction of (II) with 1·1 moles of benzoxazolinone in decalin after only 7 min. at 180°, to give (IV) (34%), (V) (27%), and (VI) (27%). The other fragment, a 2*H*-azirine, would not be expected to survive the thermolysis conditions and its polymerisation probably accounts for the red-black colour which develops (in the absence of initially added benzoxazolinone).



In contrast, the reaction mixture remained colourless when the thermolysis of (II) was repeated in a test-tube which had been washed with acetic or dilute mineral acid followed by water, and no trace of (IV) or (V) was obtained. The major product was now the diene (VI) (55%) but a second diene (IX) (15%), m.p. 87—88·5°, was also isolated; (IX) was obtained from (VI) under the same conditions, and the stereochemistry assigned to it is that which would result from a 1,5-sigmatropic nitrogen shift (X) in the *cis*-isomer of (VI).[4]

Formation of (VI) from (II) could result from a homodienyl 1,5-hydrogen shift[5] (XI) with subsequent *cis* to *trans*-isomerisation. However (II) is so sensitive to acid, being rapidly converted by cold acetic acid into the acetate (VII; X = OAc) (80%) and by hot ethanol into the ether (VII, X = OEt) (85%), that the intermolecular process, catalysed by the amphoteric benzoxazolinone, probably supervenes.

Failure of (II) to isomerise to the corresponding pyrroline, (III), as the less substituted vinylaziridines do,[2] presumably results from unfavourable steric repulsions in the transition state.[6]

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[1] R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1230.

[2] R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1232.

[3] This reaction is somewhat similar to the thermal conversion of 1-acyl-2-alkylaziridines into unsaturated amides; see D. V. Kashelikar and P. E. Fanta, *J. Amer. Chem. Soc.*, 1960, **82**, 4930.

[4] One other such shift has been reported; see H.-W. Bersch and D. Schon, *Tetrahedron Letters*, 1966, 1141; *Arch. Pharm.*, 1967, **300**, 82.

[5] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 1966, 999, and references therein.

[6] A related example of steric hindrance to ring closure was recently reported; see N. A. LeBel, T. A. Lajiness, and D. B. Ledlie, *J. Amer. Chem. Soc.*, 1967, **89**, 3076.