Pyrolysis of 4-Phenyl-2-oxa-3-azabicyclo[3,2,0]hepta-3,6-diene

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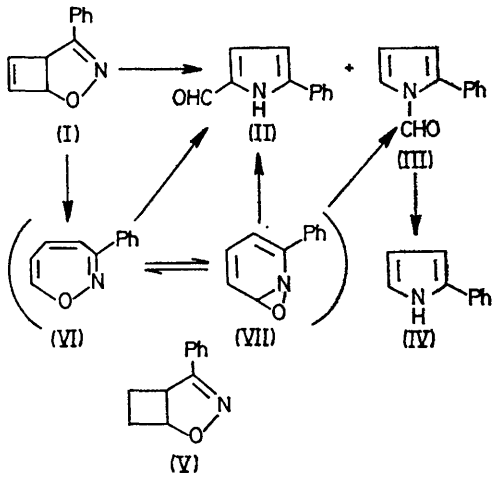
Summary Vapour-phase pyrolysis of the title compound (I) at 450 and 550° gave 2-phenylpyrrole derivatives (II), (III), and (IV); the mechanism of this rearrangement is discussed.

As a comparison with an intriguing photochemical reaction of 4-phenyl-2-oxa-3-azabicyclo[3,2,0]hepta-3,6-diene (I), in which 2-phenyl-1,3-oxazepine is formed,[1] we have studied the thermal behaviour of (I). Compound (I) was stable to heat, no change occurred below 200° in solution, and below 450° in the vapour phase. However, when a benzene solution of (I) was pyrolysed by passing through a quartz column containing Pyrex helices preheated above 450°, phenylpyrrole derivatives [(II), m.p. 139°, (III), b.p. *ca.* 70° at 1 mm and (IV), m.p. 130°] were obtained (yields: *ca.* 18%, trace, and 30% respectively at 450°; *ca.* 9, 0, and 58% at 550°). Under the same pyrolysing conditions, (III) underwent decarbonylation to give (IV) in *ca.* 50% yield, but (II) was unchanged. In addition, it should be noted that when the pyrolysis of a more concentrated solution of (I) was carried out at a higher rate at 450°, the yield of (III) was increased sharply (26%) with decrease of (IV) (5%) and recovery of (I) (37%). This suggests that (IV) is a secondary product derived from (III). The structures of 5-phenylpyrrole-2-carbaldehyde (II) and 2-phenylpyrrole (IV) were determined by comparison with authentic samples;[2] and (III) was assigned as *N*-formyl-2-phenylpyrrole on the basis of the following evidence: λ_{max} (EtOH), 234 and 282 nm (log ϵ, 4·13 and 3·95); ν_{max} (neat), 1718 cm^{-1}; *m/e*, 171 (M^+, 90%) and 143 (M − CO, 100%); δ (100 MHz; [$^2H_6$]acetone), 6·35 (3-H and 4-H), 7·48 (5–H), and 8·95 (CHO), $J_{3,4}$ 3·5, $J_{3,5}$ 1·5, and $J_{4,5}$ 3·0 Hz.



For the formation of pyrrole aldehydes (II) and (III) from (I), nitrogen–oxygen bond cleavage should be preceded by cyclobutene ring opening, because the corresponding cyclobutane derivative (V)[1] was mostly recovered when an

attempted pyrolysis was carried out under the same conditions. Thus, we may consider that the thermal rearrangement of (I) to (II) and (III) probably proceeds *via* 3-phenyl-1,2-oxazepine (VI) and/or a norcaradiene type species (VII). In the case of the photoreaction of pyridine *N*-oxides, it has been suggested that the probable intermediates, 1,2-oxazepines or norcaradiene-type isomers rearrange to 2-formyl- or-acyl-pyrroles.[3] Recently, Kaneko and others succeeded in the isolation of 1,2-oxazepine derivatives which were intermediates in the photolysis of acridine 10-oxides and found that such intermediates, under thermal conditions, are converted into 2-acyl- and *N*-acylpyrrole derivatives.[4] Their finding seems to support a reaction path *via* (VI) and (VII) for the pyrolysis of (I); however, the expected products, such as 2-phenylpyridine and 6-phenylpyridone, could not be isolated.†

A sharp contrast between the photochemical and the thermal reactions of (I) should be noted, although both reaction paths are still ambiguous.[1,5]

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† *Added in proof:* 6-Phenylpyridone (10%) could be isolated in addition to (II), (III), and (IV).

[1] T. Mukai and H. Sukawa, *Tetrahedron Letters*, 1973, 1835.
[2] G. Plancher, G. Rossi, and E. Ghigi, *Gazzetta*, 1929, **59**, 347; M. Bellas, D. B. Smith, and A. Gilbert, *Chem. Comm.*, 1967, **263**.
[3] J. Streith and C. Sigwalt, *Tetrahedron Letters*, 1966, 1347; F. Bellamy, L. G. Ruiz-Barragan, and J. Streith, *Chem. Comm.*, 1971, **456**; P. L. Kumler and O. Buchardt, *ibid.*, 1968, 1321.
[4] S. Yamada, M. Ishikawa, and C. Kaneko, *Tetrahedron Letters*, 1972, 971, 977; *J.C.S. Chem. Comm.*, 1972, 1093.
[5] A. Padwa, J. Smolanoff, and A. Tremper, *Tetrahedron Letters*, 1974, 29.