The Pyrolytic Formation and Rearrangement of 2-Quinolyl- and of 1-Isoquinolyl-nitrenes

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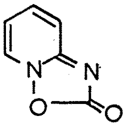
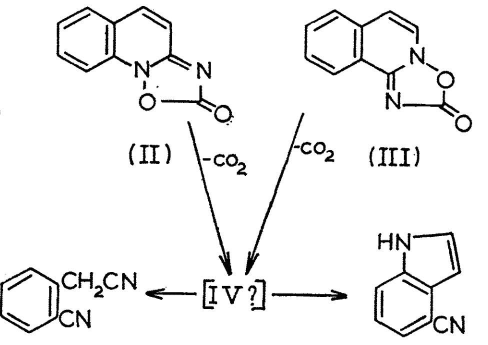
Summary Pyrolysis of quino[1,2-*b*]- and isoquino[2,1-*b*]-1,2,4-oxadiazolones gives the rearranged products, homophthalonitrile (V) and 4-cyanoindole (VI).

PYROLYSIS of the pyrido-oxadiazolone (I)[1] at 600°/0·1 mm. over silica packing gave a mixture of 2-cyano- and 3-cyanopyrrole† (1 : 1, 70% yield), in accord with the work of Crow and Wentrup[2] on the ring contraction of 2-pyridylnitrene formed by pyrolysis of tetrazolo[1,5-*a*]pyridine. However, similar pyrolysis of the corresponding quinolino-compound (II)[3] gave not the expected 2- and 3-cyanoindoles, but a mixture of homophthalonitrile[4] (V, 52% yield) and 4-cyanoindole[5] (VI, 41%). A similar mixture (V, 57%; VI, 38%) was obtained by pyrolysis of the isoquinolino-compound (III),[6] and this suggests that a common intermediate is involved. Compounds (V) and (VI) were not produced by pyrolysis of 2-cyano- or 3-cyano-indole, and they were not interconverted by pyrolysis at 600—800°. Their formation from compound (III) requires few further changes after the fission of the C-1–N-2 bond in 1-isoquinolylnitrene, but a considerable rearrangement must be involved in their formation from (II) *via* 2-quinolylnitrene.

We suggest that the common intermediate may be the nitrene (IV), and that formation of (IV) from 2-quinolylnitrene (VII) is likely to involve the ring fission and ring contraction (VII)—→(VIII). Subsequent ring expansion of (VIII) would lead to species having the skeletal arrangement of nitrene (IV). Hydrogen migration[7] in (IV) would then form the dinitrile (V), and attack of the nitrene on the *ortho*-position[8] would lead to the cyano-indole (VI). Radioactive labelling experiments designed to show the origin of the carbon atoms of the aromatic nitrile groups of (V) and (VI) are in progress.

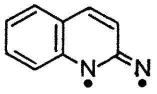


(I)

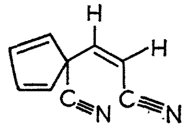


(II) (III)

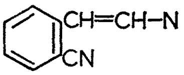
(V) (VI)



(VII)



(VIII)



(IV)

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† Pyrolytic products were isolated and identification made by comparison of m.p., where appropriate, and of i.r., n.m.r., and mass spectra; all measurements were in agreement with published data.

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