Synthesis of Some 1,3,4,6,9b-Penta-azaphenalenes

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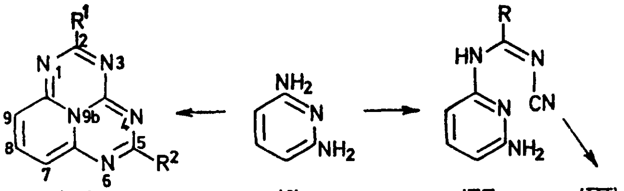
Summary Two methods for the preparation of a new nitrogen-bridged [12]annulene heterocyclic ring system, 1,3,4,6,9b-penta-azaphenalene, are reported.



(III) (I) (IV) (III)

In view of the interest in heterocyclic annulenes[1] we report results on the preparation of fused-*s*-triazino-heterocyclic ring systems.[2] We are currently studying the reactions of various substituted α-amino pyridines with *N*-cyano-imidates,[3] but the present discussion is limited to reactions of 2,6-diaminopyridine (I). Thus, refluxing of a concentrated solution of methyl *N*-cyanoacetimidate (II) (2 mol) with (I) (1 mol.) in glyme for 18 h gave the penta-azaphenalene (III; $R^1 = R^2 = Me$) (36·5%), as burgundy crystals, m.p. 275—277°.

Assignment of structure (III; $R^1 = R^2 = Me$) to this compound was based on satisfactory elemental analyses, molecular weight data (*M* 197 by vapour-phase osmometry), the absence of N–H and C$\equiv$N bands in its i.r. spectrum, its n.m.r. spectrum, and also by an alternative synthesis from (IV; R = Me) and acetic anhydride. The parent structure (III; $R^1 = R^2 = H$) was obtained similarly, as lavender crystals (77%), m.p. 258—260°, from ethyl *N*-cyanoformimidate (V) and (I).

Use of (IV) with suitable anhydrides affords unsymmetrical derivatives of (III) (see Table).

TABLE

(III)[a] R[1]	R[2]	M.p. °C	Yield[b]
Me[c]	H	249—251	48
Me[d]	Pr[n]	171—172	66
Me[e]	Ph	245—246	74

[a] [Anhydride]/[IV] = 10 in refluxing dry glyme for 18 h. [b] Crude yield. [c] From (IV; R=H) and Ac_2O; crude product purified by column chromatography (Al_2O_3–$CHCl_3$). [d] From (IV; R = Me) and butyric anhydride. [e] From (IV; R = Me) and benzoic anhydride.

The amidine (IV; R = H), m.p. 170—171° (glyme), was obtained (45%) by reaction of (I) (1 mol) with (V) (0·9 mol) in glyme for several days at room temperature; similarly, reaction of (I) with (II) gave (IV; R = Me), m.p. 179—181° (37%).

All compounds reported gave correct elemental analyses.

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[1] W. W. Paudler, R. A. VanDahm, and Y. N. Park, *J. Heterocyclic Chem.*, 1972, **9**, 81; A. B. Holmes and F. Sondheimer, *Chem. Comm.*, 1971, 1434; W. W. Paudler and E. A. Stephan, *J. Amer. Chem. Soc.*, 1970, **92**, 4468; D. Farquhar and D. Leaver, *Chem. Comm.*, 1969, 24.

[2] For the previous paper in this series see: J. T. Shaw, D. M. Taylor, F. J. Corbett, and J. D. Ballentine, *J. Heterocyclic Chem.*, 1972, **9**, 125.

[3] K. R. Huffman and F. C. Schaefer, *J. Org. Chem.*, 1963, **28**, 1816.