Tetrahedron Letters No. 21, pp 1817 - 1818, 1977. Pergamon Press. Printed in Great Britain.

HETEROCYCLIC BIPHENYLENES: SYNTHESIS OF PYRAZINE AND QUINOXALINE ANALOGUES BY THERMAL NITROGEN EXTRUSION.

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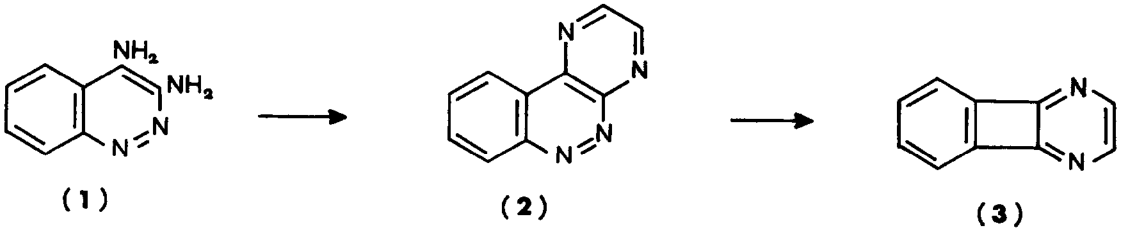
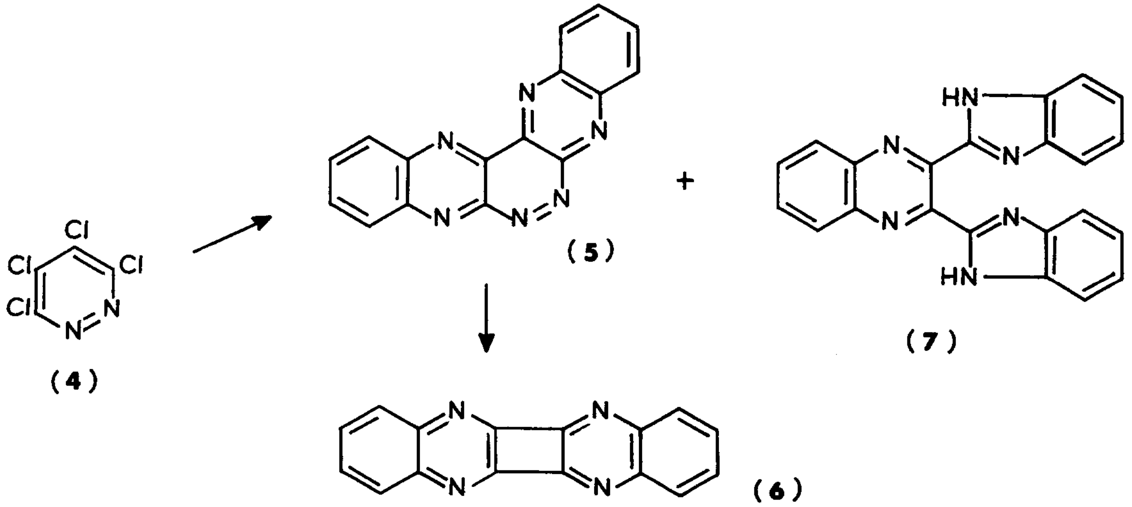
(Received in UK 28 February 1977; accepted for publication 12 April 1977)

Thermal extrusion of molecular nitrogen from benzo[c]cinnoline[1] and its aza-analogues at high temperature has proved to be the first general synthesis of the biphenylene system which can be applied to its pyridine analogues[2,3]. We now report the extension of this synthetic method to the novel pyrazine (3) and to the biquinoxalylene (6), previously obtained by Hunig and Putter[4] from squaric acid.

3,4-Diaminocinnoline (1) (prepared by the method of Baumgarten[5] but replacing sodium hydroxide by diazabicyclo-octane [1 mol, 60°, 3h] for cyclisation) was condensed with glyoxal (XS, H_2O, 100°, 15min) to give 1,4,9,10-tetra-azaphenanthrene[†] (2) (65% yield) m.p. 252-252.5° (from ethanol), λ_{max} (dioxan) 267nm (logϵ 4.08), 304(3.53), 353(3.53), 368(3.53), ν_{max} (KBr, strongest band) 1400 cm^{-1}. The mass-spectrum of (2) showed loss of N_2 from the parent followed by successive loss of CN and HCN.





Sublimation of the tetra-azaphenanthrene (2) at 0.015 torr through a silica tube loosely packed with silica wool heated to 860^o over 14 cm, extraction of the pyrolysate with ether, p.t.l.c. on silica and vacuum sublimation gave 1,4-diazabiphenylene† (3) m.p. 150.5-151^o (27% yield, allowing for 30% of recovered (2)). λ_{max} (EtOH): 221nm (logε, 4.37), 268(4.15), 358(4.04), and 373(4.08). δ($CDCl_3$): 7.42 (s, 2H and 3H) and 7.04-7.24 (AA'BB',5-8H). ν_{max} (KBr, strongest band): 755 cm^{-1}.

Reaction between tetrachloropyridazine (4) and o-phenylenediamine (2 mol, N-methylpyrrolidone, 115^o, 17h) gave a precipitate of a mixture of 2,3-bis(2'-benzimidazolyl) quinoxaline†‡ (7) m.p. 304.5-305.5^o (from acetonitrile) and the hydrochloride of 5,6,7,8,13,14-hexa-azapentaphene (5). The base † (5) (15% yield) extracted by chloroform after washing with sodium hydroxide, formed dark red needles from acetonitrile m.p. >350^o, λ_{max} (dioxan) 249nm (logε 4.60), 339(4.48), 387 infl.(3.70), and 432 infl.(3.09); ν_{max} (KBr, strongest band) 1045 cm^{-1}. The mass spectrum showed loss of N_2 from the parent ion followed by separation of the quinoxaline residues and successive loss of two CN groups.

Pyrolysis of the pentaphene (5) in the same apparatus at 800^o, 0.02 torr, extraction of the pyrolysate with ether and recrystallisation from acetonitrile gave the biquinoxalylene (6) (60% yield) m.p. 319-321^o lit.[4] 324^o, i.r. and u.v. spectra in close agreement with published data.

It is interesting that the u.v. spectra of diazabiphenylenes depend strongly on the positions of the nitrogen atoms, unlike most polycyclic aromatic systems. Thus the u.v. spectra of 2,6-[6] and 2,7-diazabiphenylenes[2] resemble that of the biphenylene itself, and so do those of the 1- and 2-mono-aza-compounds[3]. That of 1,8-diazabiphenylene[3], λ_{max}(EtOH) 228nm (logε 4.41), 233(4.36), 313(3.36), 331(3.83) and 350(4.01), shows an additional strong band obscuring the weak long-wave multiplet of the biphenylene type; the u.v. of (6) is similarly related to that of the corresponding hydrocarbon[7]. 1,4-Diazabiphenylene (3) provides a third pattern of absorption with three strong bands between 220 and 400nm.

We thank Drs. D.J. Gilman and R. Hull of I.C.I. Pharmaceuticals Division for discussion, Professor T.J. King, Nottingham University, for determining the structure of compound (7) by X-ray crystallography, the University of Durham for analyses and mass-spectra, and I.C.I. for spectra and a gift of tetrachloropyridazine.

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† Correct analyses. ‡ Further studies of this reaction to be published.

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