Synthesis of 2,7-Diazabiphenylene by Thermal Extrusion of Nitrogen from 2,7,9,10-Tetra-azaphenanthrene

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Summary 2,7,9,10-Tetra-azaphenanthrene has been obtained by reduction of 3,3′-dinitro-4,4′-bipyridyl and gives 2,7-diazabiphenylene upon vacuum pyrolysis.

Thermal extrusion of nitrogen from aromatic systems has recently proved to be a useful synthetic route to biphenylenes,[1] polyhaloacetylenes,[2] and azetes;[3] this biphenylene synthesis has now been extended to a pyridine analogue of biphenylene (bipyridylene). Attempts to obtain these compounds by dimerisation of pyridynes[4] have been generally disappointing, although Sartori and co-workers[5] obtained a mixture of hexafluoro-2,6- and -2,7-diazabiphenylene and Berry and Kramer[6] isolated a dimer of photochemically generated 3,4-pyridyne. The structure 2,6-diazabiphenylene (**1**) was infered for the apparently pure dimer by analogy with the known head-to-tail dimerisation of polarised benzynes; the present work confirms this inference by eliminating the alternative 2,7-diazabiphenylene (**5**).

The new heterocyclic system (**6**) was prepared from 4-chloro-3-nitropyridine (**2**)[7] which was converted into the cuprous chloride complex†‡ of 3,3′-dinitro-4,4′-bipyridyl by copper in dimethylformamide at 100°. The dinitrobipyridyl† (**3**) m.p. 127—128° (from EtOH), liberated by strong ammonia solution, was reduced with aqueous sodium sulphide at 20° to a mixture (*ca.* 3 : 1) of 2,7,9,10-tetra-azaphenanthrene† (**6**) m.p. 343—344° (from dioxan) λ_{max} (dioxan) 238, 252 infl., and 295 nm, and 2,7,9,10-

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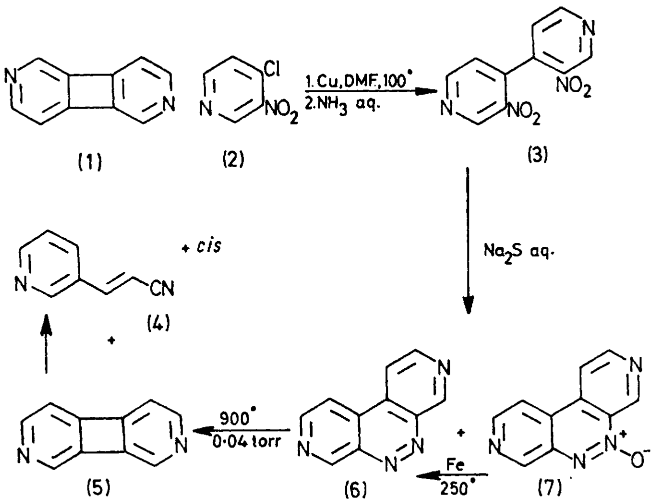
† Correct analyses and m.s. have been obtained for these compounds; the author thanks the staff of the Chemistry Department, University of Durham, for the determinations.

‡ Mass spectrum not obtained for this complex.

tetra-azaphenanthrene-9-oxide† (**7**) λ_{max} (dioxan) 241 and 333 nm. The *N*-oxide component (**7**) was deoxygenated by heating the mixture with iron powder at 250°; boiling phosphorus trichloride failed to react with the *N*-oxide (**7**).



Other reduction products of the dinitrobipyridyl (**3**) will be described elsewhere.

The tetra-azaphenanthrene (**6**) was pyrolysed by subliming it through a silica tube at 900 ± 20°, 0·04 torr, to give 2,7-diazabiphenylene (**5**)† (60%) (allowing for 60% conversion) and in smaller amount (*ca.* 15%) a liquid mixture of pyridylacrylonitrile[8] isomers, whose i.r. spectrum is most consistent with the structures (**4**). These minor products (**4**) have been shown to arise by cracking of the primary product (**5**) by pyrolysing it under the same conditions; the provisional structures (**4**) imply rearrangement upon fragmentation.

2,7-Diazabiphenylene (**5**), purified by vacuum sublimation, was obtained as pale yellow crystals, m.p. (with resublimation) 192—192·5°; λ_{max} (MeOH) 234·5 (log ϵ 4·79), 242 (4·93), 284 (3·25), 297·5 (3·26), 312 (3·17), and 326·5 nm (2·94); ν_{max} (KBr) strongest band 834 cm^{-1}; δ 8·25 (d, *J* 4·3 Hz, 3-H and 6-H), 7·90 (d, *J* 1·3 Hz, 1-H and 8-H), 6·75 (dd *J* 4·3 and 1·3 Hz, 4-H and 5-H); M^+ = 154, and prominent fragment peaks at 127, 100, and 74 corresponding to successive loss of HCN, HCN, and C_2H_2.

The m.p. and u.v. spectrum of 2,7-diazabiphenylene (**5**) distinguish it from the American workers' compound[6] m.p. 169·5—170°, which shows an additional maximum at 338 nm, and which must, therefore, be 2,6-diazabiphenylene (**1**). The i.r. (strongest band), m.s., and ^{1}H n.m.r. shifts of the two isomers are similar, although the splitting pattern of (**1**) is apparently more complex. It is interesting that the coupling constants in (**5**) are similar to the corresponding values for pyridine,[9] $J_{2,3}$ 5·5, $J_{2,5}$ 0·9 Hz.

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