

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 pyridynes⁴ have been generally disappointing, although Sartori and co-workers⁵ obtained a mixture of hexafluoro-2,6- and -2,7-diazabiphenylene and Berry and Kramer⁶ isolated a dimer of photochemically generated 3,4-pyridyne. The structure

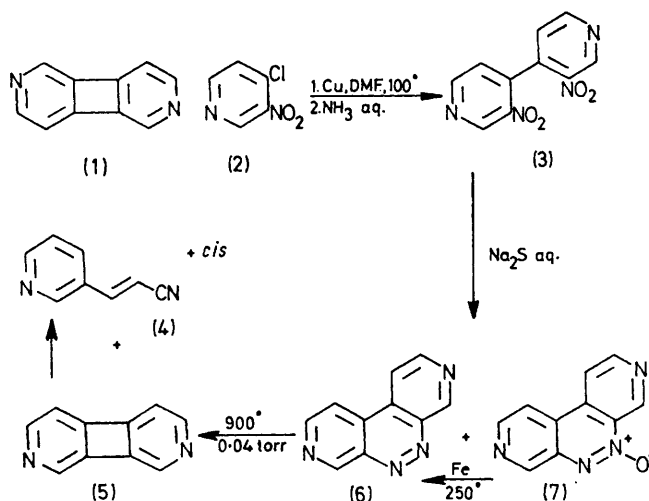
2,6-diazabiphenylene (**1**) was inferred for the apparently pure dimer by analogy with the known head-to-tail dimerisation of polarised benzyne; the present work confirms this inference by eliminating the alternative 2,7-diazabiphenylene (**5**).

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 dinitro-bipyridyl† (**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-

† 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 $900 \pm 20^\circ$, 0.04 torr, to give

2,7-diazabiphenylene (5)† (60%) (allowing for 60% conversion) and in smaller amount (*ca.* 15%) a liquid mixture of pyridylacrylonitrile⁸ 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' compound⁶ 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 ^1H 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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