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SYNTHESIS OF 1,6-DIAZABIPHENYLENE BY FLASH VACUUM PYROLYSIS OF 2,5,9,10-TETRA-AZAPHENANTHRENE; NMR EVIDENCE FOR REHYBRIDISATION IN BIPHENYLENES.

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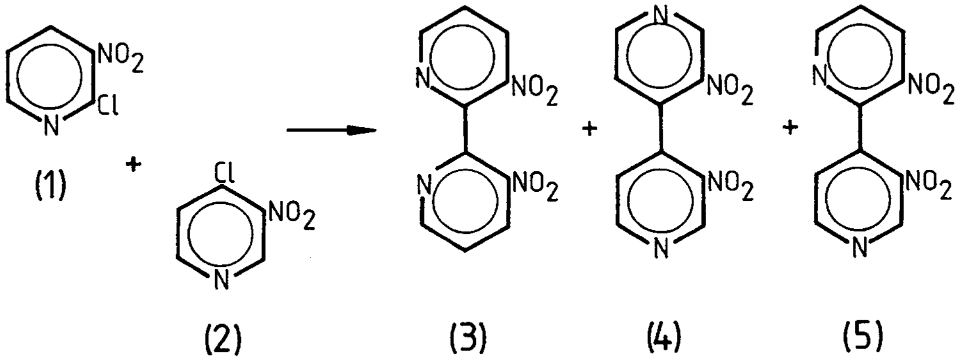
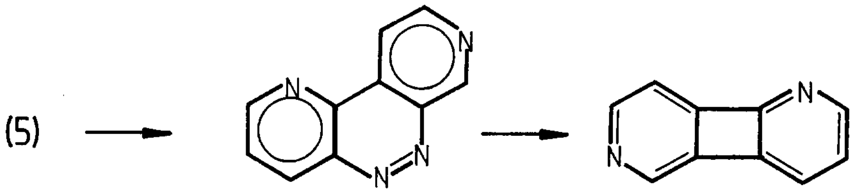
Summary: A mixed Ullmann reaction between 2- and 4-chloro-3-nitropyridines furnished 3,3'-dinitro-2,4'-bipyridyl and reduction to 2,5,9,10-tetra-azaphenanthrene followed by thermal extrusion of nitrogen gave 1,6-diazabiphenylene; different complexing abilities of the two nitrogen atoms of this compound were revealed by ^1H nmr using $Eu(fod)_3$ which are consistent with previous work on the rehybridisation in strained ring systems and the value of $^1J_{C-H}$ in biphenylene.

Extrusion of nitrogen from 9,10-diazaphenanthrenes (benzo[c]cinnolines) by flash vacuum pyrolysis has proved to be a general route to biphenylenes[1a] which has been extended to aza-, diaza-[1b], and thia-nor-analogues[1c]. We now report the application of this synthesis to the first diazabiphenylene comprising unsymmetrically fused pyridine residues.

A mixed Ullmann reaction[‡] between 2-chloro-3-nitropyridine (1) and 4-chloro-3-nitropyridine (2) (mol ratio [1]:[2]:Cu = 1.14:1:5, DMF, 130°C, 14h; work up with ammonia and dioxan[2]) gave 3,3'-dinitro-2,4'-bipyridyl (5) m.p. 112-114.5° (from methanol, light sensitive) in 4% isolated yield together with 3,3'-dinitro-4,4'-bipyridyl (4) (11%) and 3,3'-dinitro-2,2'-bipyridyl (3) (50%). Separation was achieved by chromatography (flash method[3]; silica/ethyl acetate) after crystallisation of the bulk of the major product.





(6) (7)

Reduction of the unsymmetrical dinitrobipyridyl (5) with sodium sulphide[2] (water, 21°C, 3h) gave 2,5,9,10-tetra-azaphenanthrene (6)† with a trace of its N-oxide in 94% yield, m.p. 202-203° subl. (from acetonitrile).

Sublimation of the tetra-azaphenanthrene (6) through a silica tube[4] (silica wool packing) at 850°C, 3 x 10^{-2}mBar gave 1,6-diazabiphenylene (7)† in 38% yield (allowing for recovered tetra-azaphenanthrene, 15% single pass) m.p. 106.5-108.5° subl.; λ_{max}(MeOH): 228.5nm(log ϵ 4.52), 258 (4.17), 289 infl.(3.56), 318.5(3.79) and 335.5(3.80). δ($CDCl_3$/TMS 80MHz) 8.28(d, J 4.5 Hz, 7-H), 8.00(d, J 1.5, 5-H), 7.85(dd, J 5.6 and 1.5, 2-H), 6.95(dd, J 7.1 and 1.5, 4-H), 6.88(dd, J 4.5 and 1.5, 8-H) and 6.69(dd, J 7.1 and 5.6, 3-H)ppm.

Analysis of the ^1H nmr spectrum of (7) was complicated by overlap of the 4-H and 8-H multiplets, which were resolved by adding Eu(fod)$_3$. This experiment revealed that N-6 complexes Eu(fod)$_3$ considerably more strongly than N-1 since 5-H and 7-H are shifted more than 2-H; figure 1 shows the progressive shifts with increasing Eu(fod)$_3$ concentration.

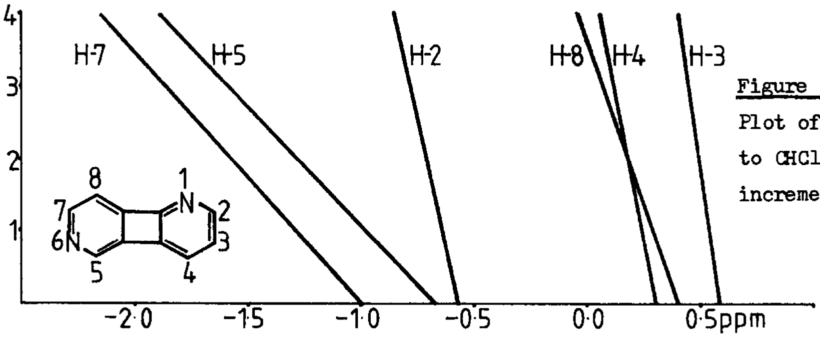


Figure 1: Plot of shift (ppm) relative to $CHCl_3$ resonance vs. arbitary increments of Eu(fod)$_3$.

Streitwieser[5] has rationalised the acidity of the α-positions of biphenylene by postulating increased p-character in the orbitals forming the four-membered ring and consequently higher s-character in the orbitals which bond the atoms ortho to the ring-junction, giving the ring-junction carbons a higher effective electronegativity. The reduced basicity of strained 2,3-cycloalkenopyridines[6] is attributed to the same effect, and we infer that the differing complexing abilities of the nitrogen atoms of 1,6-diazabiphenylene (7) provide another example. The ^{13}C-H coupling constants[7] ortho to the ring-junctions of strained cycloalkeno-benzenes and -pyridines indicate enhanced s-character in this bond as well; this effect would likewise reduce the basicity of a nitrogen atom in this position if the hybridisation of the unshared pair orbital is similarly affected. We have found that the values of $^1J_{C-H}$ in biphenylene[8] are 164.8 Hz at the α-position and 159.8 Hz at β, showing enhanced s-character for the α C-H bond in agreement with the relative complexing abilities of the α- and β-type nitrogen atoms of the diaza-analogue (7).

1,6-Diazabiphenylene (7) also allows direct comparison of J_{HH} in the pyridine rings in relation to the position of the four-membered ring. (Figure 2.)

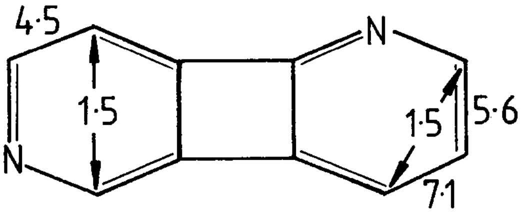


Figure 2: Observed J_{HH} in 1,6-diazabiphenylene.

Thus J_{23} (5.6 Hz) is close to that between the corresponding positions of pyridine (5.5 Hz)[9] while J_{78} is reduced to 4.5 Hz, illustrating the reduced bond orders at positions where single bonds, inherent in the biphenylene system, are drawn in (7).

The ^{13}C shifts ($CDCl_3$/TMS 20 MHz) in 1,6-diazabiphenylene are: 169.5(s, C-8b), 162.1(s, C-8a), 152.3(d, C-7), 149.7(s, C-4a), 147.3(d, C-2), 145.5(s, C-4b), 137.1(d, C-5), 124.0(d, C-4), 123.8(d, C-3), 113.5(d, C-8) ppm. These assignments were made by reference to the ^{13}C shifts in pyridine[10] and biphenylene[8] and are consistent with those obtained for 2,7- and 1,8-diazabiphenylene which will be published separately with further studies of the correlation between structures, basicities and nmr spectra of biphenylenes.

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†Satisfactory analyses and mass spectra were obtained for new compounds. The e.i. ms of (5) gave highest mass 200 ($P-NO_2$) but chemical ionisation (NH_3) gave the expected P+1 at 247.

‡Conditions not optimised for this reaction.

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