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HYDROLYSIS OF 1,8-, 2,7- AND 1,6-DIAZABIPHENYLENES BY SODIUM HYDROXIDE.

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Summary: 1,8- and 2,7-Diazabiphenylenes are hydrolysed by aqueous sodium hydroxide to 3-(3'-pyridyl)-2- and -4-pyridones respectively; 1,6-diazabiphenylene gives the former pyridone specifically.

The pyridine analogues of biphenylene are available by flash vacuum pyrolysis[1,2,3] of the corresponding tetra-azaphenanthrenes, but study of their reactions has hitherto been confined to electrophilic attack leading to quaternisation[1] of the 2,7-diaza-isomer. We now report the results of nucleophilic attack on these compounds.

Pyridine reacts with caustic alkali under forcing (and oxidising) conditions to give 2-pyridone[4] but the increased reactivity of pyridine rings constrained in the biphenylene system results in hydrolysis of each of the title compounds (1), (3) and (4) by 2.5M aqueous sodium hydroxide during 2.5h at 150°†. Attack by hydroxide ion occurs almost exclusively at the ring-junction positions: 1,8-diazabiphenylene (1) gives 1H-3(pyrid-3'-yl)pyrid-2-one (2)‡ m.p. 195-196° in 96% yield; λ_{max}(MeOH): 245(logϵ 3.86) and 321(4.05)nm; δ(DMSO-d_6/TMS:90MHz) 8.88(dd, 1H: H-2'), 8.47(dd, 1H: H-6'), 8.12(ddd, 1H: H-4'), 7.73(dd, 1H: H-6), 7.38(m, 2H: H-4 and H-5'), 6.32 (dd, 1H: H-5) ppm. Under the same conditions 2,7-diazabiphenylene (4) gives 1H-3(pyrid-3'-yl)pyrid-4-one (5)‡ m.p. 222-226° in 45% yield; λ_{max}(H_2O): 261(logϵ 4.06) and 219(4.23)nm; δ(DMSO-d_6/TMS: 90MHz) 8.8(br.s., 1H: H-2'), 8.5(dd, 1H: H-6'), 8.1(ddd, 1H: H-4'), 7.95(br.s., 1H: H-2), 7.65(dd, 1H: H-6), 7.35(dd, 1H: H-5'), 6.25(d, 1H: H-5) ppm. A second product m.p. 220-240°, M 146, was isolated in 10% yield (assuming its formation from 1 mol of DABP) and traces of two further substances were detected from hydrolysis of (4).

We postulate the mechanism exemplified by scheme 1, and analogous reaction of 2,7-DABP (4) at the indicated position, for these reactions. 1,6-DABP[3] (3) could react in the same way to give either pyridone (2) or (5), but we observed specific quantitative formation of isomer (2) corresponding to attack by hydroxide ion at C8b rather than C8a.

The infrared spectra (KBr) of compounds (2) and (3) show carbonyl and NH absorption patterns very similar to those of the corresponding unsubstituted pyridones, indicating similar tautomeric states in the solid phase.

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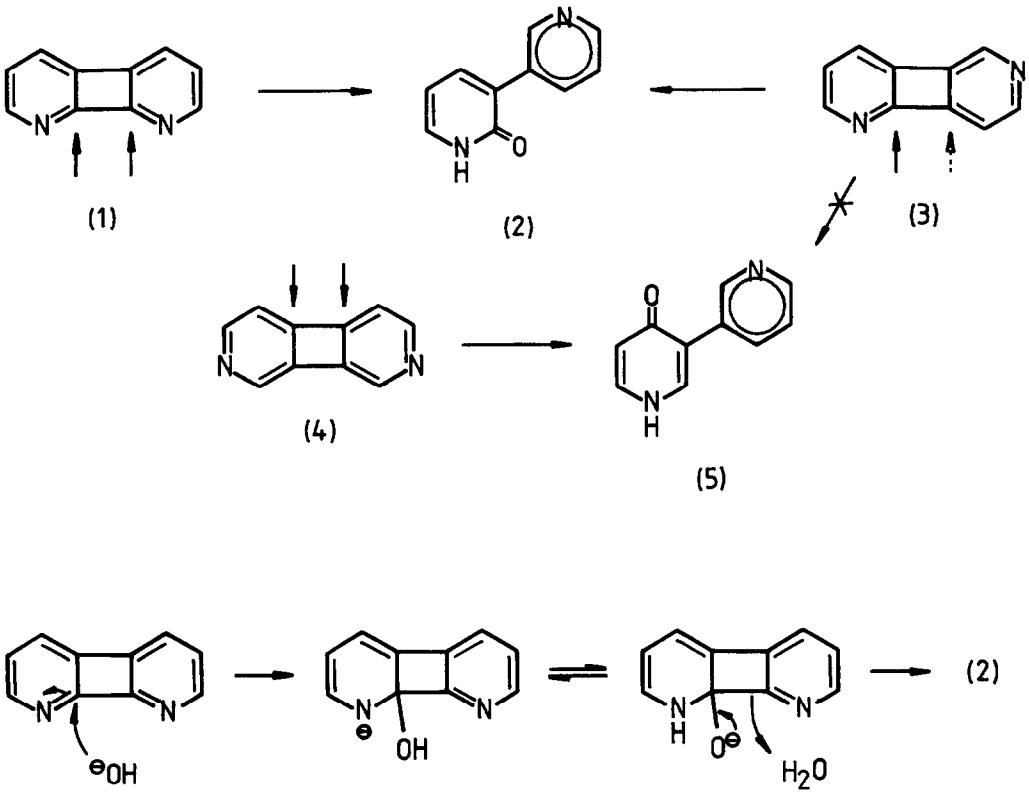

scheme 1

Footnotes:

† Teflon lined digestion vessels were used; glass ampoules gave silicic acid on neutralisation, complicating work-up.

‡ Satisfactory analytical and mass-spectrometric data were obtained for new compounds

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