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AN AZA-ANALOGUE OF N-PYRIDINIUM CYCLOPENTADIENIDE

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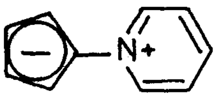
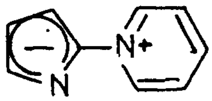
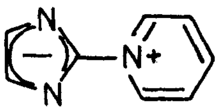
One of the most interesting derivatives of the cyclopentadienide anion is Lloyd and Sneezum's(1) pyridinium ylide I. Substitution of nitrogen for carbon in the five-membered ring should enhance the stability of this molecule, and a great many such structures, e.g. II and III, can be envisaged. A compound of this type, N-pyridinium 2-benzimidazolide V, has now been prepared.



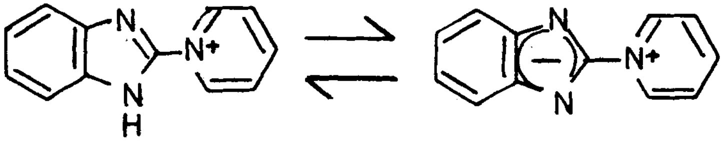
I



II



III



IV V

Prolonged heating (1 - 2 days) of an ethanolic solution of equimolecular quantities of 2-chlorobenzimidazole(2) and pyridine gave the pyridinium salt IV (36 °/o), which was isolated as the perchlorate, colourless needles (from water), m.p. 232 - 233°, NH absorption at 3200 - 3300 cm^{-1}, λ_{max} (ethanol) 345 mμ (Found: C, 48.64; H, 3.61; N, 14.11. $C_{12}H_{10}ClN_3O_4$ requires C, 48.74; H, 3.42; N, 14.21 °/o). Treatment with ammonia converted the salt into the bright yellow ylide V, needles (from water), decomposes at ca. 260°, no NH absorption (Found: C, 73.40; H, 4.85; N, 21.34. $C_{12}H_9N_3$ requires C, 73.82; H, 4.66; N, 21.53 °/o).

The new ylide, unlike the parent cyclopentadiene compound, is stable in light and air and is not affected by boiling solvents. Inorganic and organic acids regenerate the cation IV.

Dramatic changes in colour are observed(1) when pyridinium cyclopentadienide is dissolved in different solvents. This phenomenon of intramolecular charge transfer is also shown by the nitrogen analogue; there is a pronounced bathochromic shift of the first absorption band as the polarity of the solvent decreases:

Longest-wave Absorption Maxima (mμ)

	Water	Ethanol	Heptane	Benzene
I(3)	453	496	524,546	-
V	364	392	-	445

This is readily interpreted by simple molecular orbital theory. HMO calculations with the usual(4) nitrogen parameters indicate a great decrease in charge separation between the pyridinium ring and the rest of the molecule on passing from the ground state (π) to the first excited state (π^*) in these compounds:

Charges on Rings

		Pyridine ring	Five-membered ring	Benzene ring
I	π	+ 0.94	- 0.94	-
	π^*	+ 0.16	- 0.16	-
III	π	+ 0.97	- 0.97	-
	π^*	+ 0.18	- 0.18	-
V	π	+ 1.00	- 0.81	- 0.19
	π^*	+ 0.11	- 0.40	+ 0.29

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