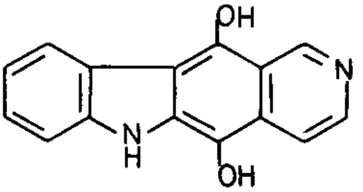
FURTHER STUDIES IN THE 6$\underline{H}$-PYRIDO [4,3b] CARBAZOLE AREA: THE CHEMISTRY OF SOME DIHYDROPYRIDINE INTERMEDIATES

Michael Driver and Malcolm Sainsbury*

School of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Abstract - The structure and reactions of dihydropyridine derivatives formed by the action of cyanide ion on certain pyridinium salts are discussed. For α-cyanodihydropyridines a ring-opening occurs.

During an attempt to prepare 5,11-dihydroxy-6$\underline{H}$-pyrido [4,3b] carbazole (1) by a modification of a synthetic procedure previously described[1], cyanide ion was added to the pyridinium salt (2) and two products isolated in about equal amounts. One is the expected 4-cyano-1,4-dihydropyridine (4) which on warming or photolysis (medium pressure lamp) affords the corresponding cyanopyridine (6).



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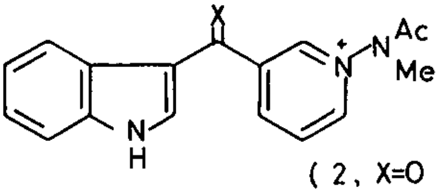
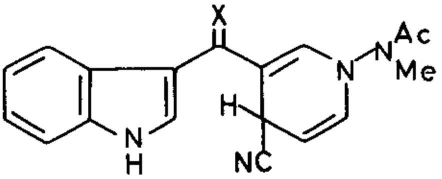
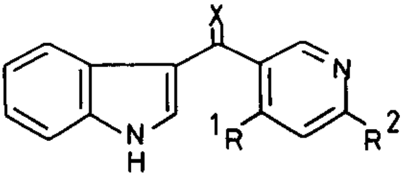


(2, X=O)
(3, X=H_2)

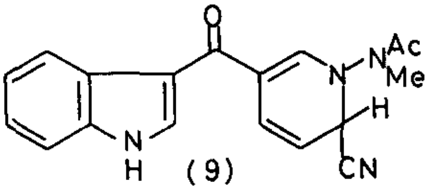


(4, X=O)
(5, X=H_2)



(6, X=O : R^1=CN : R^2= H)
(7, X=O : R^1= H : R^2=CN)
(8, X= H_2 : R^1=CN : R^2=H)

The other gives the 2-cyanopyridine(7) in low yield on strong heating but in the ^{1}H n.m.r. spectrum exhibits three one proton signals at δ 7.9(d, $\underline{J}$ = 9Hz), 7.3(d, $\underline{J}$ = 16.5Hz) and 6.7(dd, $\underline{J}_1$ = 16.5Hz, $\underline{J}_2$ = 9Hz) ppm. These signals and their chemical shift positions cannot be reconciled in terms of an α-cyanodi-hydropyridine although analytical data confirm that the product is isomeric with (4). Clearly this compound contains a unit with a trans disposition of protons about a double bond and this conclusion leads to the trienic structure (10) formed by a reverse Cope type reaction from the dihydropyridine (9).



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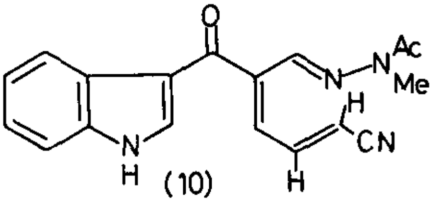
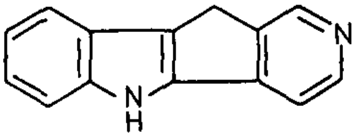


(10)

Recyclisation with concommitant loss of the pyridine N-substituent then accounts for the conversion of this product into the 2-cyanopyridine (7).

A repetition of this reaction now with the methane derivative (3) leads to the 4-cyanodihydropyridine (5) as the sole isolated product and since this appears to be a general observation[2] for salts bearing a saturated carbon atom at the pyridine β-position the influence of the carbonyl group is profound. It is probable that the extended conjugation of this function with the electrons of the pyridine nitrogen now weakens the $C_{(\alpha)}$- N bond in the relatively unstable 2-cyanodihydropyridine to allow its facile ring-opening and to disturb the normal reaction equilibrium which leads to preferential γ-substitution.

We also observe that the 4-cyanopyridine (8) cyclises directly to the tetracycle (11) in warm aqueous acid, whereas the corresponding compound (6) is unchanged under extreme hydrolytic conditions.



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