**Tetrahedron Letters No.34, pp. 3033-3035, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

CONVERSION OF A PLANCHER PYRROLENINE INTO A β CHLOROPYRIDINE

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(Received 6 July 1965)

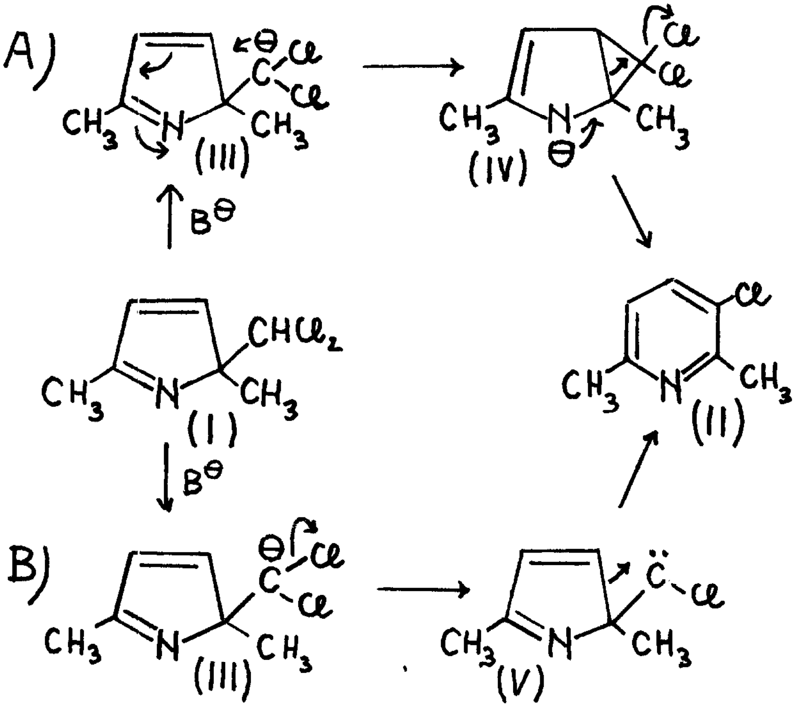
When pure pyrrolenine (I) is treated at 0° in olefin-free hexane with an excess of buthyl-lithium, an isolable amount of 2,6 dimethyl-3-chloropyridine (II) is formed (yield: ~ 5%).

This fact has been firmly established by isolation of the pyridine (II); the latter was identified by NMR Spectrum (two sharp peaks at 2,43 and 2,54 δ (two methyls); two doublets (J = 8 c/s) centered at 6.83 and 7.41 δ (β-γ hydrogen atoms); solvent CCl_4, TMS as internal reference) and by the melting point of its picrate (m.p. 142-144 (sintering from 135° C) alone or in mixture with an authentic sample).

Two mechanisms,(A) and(B), may be considered for the conversion pyrrolenine ⟶ pyridine, both involving, as first stage, anion (III).

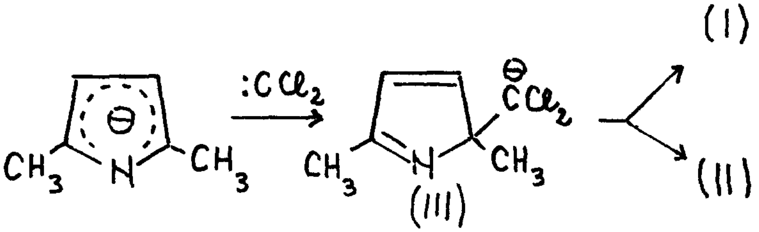
Thus, the anion (III), which is produced from (I) by the action of the strong base, might give the hypothetical bicyclic compound (IV); (IV) would eliminate Cl^- , giving (II).

Alternatively, the anion (III), might eliminate a chloride anion; the intermediate (V) containing a divalent carbon, would be capable of rearraging into the pyridine (II):



The pyrrolenine (I) is produced at the same time as the pyridine (II) in the reaction of dichlorocarbene on 2,5 dimethyl-pyrrole; it has been generally accepted that dichloromethyl-pyrrolenines (or dichloromethyl-indolenines) and β chloropyridines (or β chloroquinolines) are formed through different pathways [1] , since the compounds of the first type were believed to be not transformable into the compounds of the second type [2].

The transformability of (I) into the pyridine (II), demonstrated by us, would suggest, on the contrary, that these two compounds might be formed from the same interme=diate, the anion (III):



Further work is in progress on this subject.

REFERENCES

1) A.R.Katritzky, Advances in Heterocyclic Chemistry vol. III, p.70. Academic Press, New York 1964.

2) According to C.W.Rees and C.E.Smithen (J.Chem.Soc. 929, 1964) the 3 dichloromethyl 2,3 dimethyl--indolenine is not converted, in several conditions, into the 2,4 dimethyl 3 chloroquinoline.
On the other hand, the 2 dichloromethyl 2,5 dimethyl pyrrolenine (I) is stable under moderate basic conditions (R.Nicoletti and M.L.Forcellese, Gazz.Chim. Ital. 95, 84 (1965); however, by treatment with sodium ethoxyde, this pyrrolenine is converted into the 2 ethoxymethyl 5 methyl-pyridine and into an aziridino-pyrroline derivative (R.L.Johnson, C.W.Rees, C.E.Smithen, Proc.Chem.Soc. 217 (1964); R.Nicoletti and M.L.Forcellese, Tetrahedron Letters N° 3, 153 (1965)).