

THE MECHANISM OF THE TSCHITSCHIBABIN REACTION

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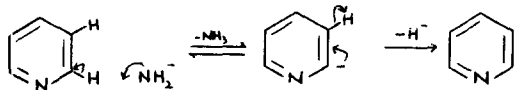
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The amination of pyriine and its derivatives has generally been discussed in terms of an addition-elimination mechanism via a  $\sigma$ -complex intermediate, but more recently the possibility that it may proceed by a mechanism involving a 2,3-pyridyne intermediate has been suggested (1). This latter proposal has been severely criticized and shown to be untenable as a general mechanism for the reaction though it might be applicable in one or two individual cases (2-5).

In spite of this, the pyridyne intermediate mechanism has been revived and bolstered by M. O. calculations in which the interesting suggestion has been made that the 2,3-dehydropyridine may be stabilized by interaction of the vacant  $sp^2$  carbon orbitals with the  $sp^2$  hybrid orbital containing the nitrogen lone-pair of electrons (6). This, it is said, would explain the lack of formation of any 3-aminopyridine derivatives (expected from the reaction of amide ion with a 2,3-pyridyne) and the fact that 4-aminopyridine is also not obtained (the latter statement is incorrect since 4-aminopyridine has been reported to be formed under more vigorous conditions). To account for substitutions at C-2 in 3-substituted pyridines it was postulated that a 2,6-dehydropyridine intermediate could be formed readily. Unfortunately, this interesting proposal goes contrary to a number of already published observations and to the present results.

Thus, the well-established amination of 5-ethyl-2-methyl- and 2-meth-

yl-5-n-propylpyridine at C-6 (3) cannot be explained either by a 2,3- or by a 2,6-dehydropyridine intermediate. On the basis of a pyriptyne intermediate mechanism in which the hydride ion elimination step is rate-determining one would expect a deuterium isotope effect in the reaction of pyridine-3d with sodamide: this was not observed (4). If, on the other hand, it is the proton-abstracting step which is rate-determining a change in the isomer ratio should have taken place when 3-picoline-2d was used instead of 3-picoline in the reaction with sodamide—again, such was not the case (4). Either of these as rate-determining steps leading to the form-



ation of a 2,6-dehydropyridine stabilized by lone-pair interaction is ruled out by the present observation that when the reaction is carried out with a pyridine-2d/pyridine mixture and interrupted before completion, the composition of recovered starting pyridine is unchanged, whereas some enrichment in pyridine-2d would have been expected on the basis of a rate-determining proton, or hydride-ion, elimination step. It is also of interest to note that when a 3-halopyridine unsubstituted at C-4 is treated with potassium amide in liquid ammonia only the 3,4-pyridyne appears to be generated (7), while the M. O. calculations including lone-pair interaction predict that the 2,3-pyriptyne would be the more stable intermediate. The above evidence seems to rule out the formation of such intermediates as a general mechanism for the Birch reduction.

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