

REACTIONS OF N-AMINOPYRIDINIUM SALTS AND THEIR REDUCTION PRODUCTS
 ——— THEIR FUNCTION AS A NEW NAD⁺-NADH MODEL COMPOUND ———

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1,4-Dihydropyridine ring system is biologically important since it occurs in the reduced form of NAD⁺. And 1,4-dihydropyridine should also be proved useful in the preparation of interesting heterocyclic compounds.

In this paper, we wish to make a report of a new NADH model compound which has N-amino group.

The reduction of N-methylacetamidopyridinium derivatives **1** with Na₂S₂O₄ gave dihydropyridines **2**, which were reversibly oxidized to pyridinium salts **1** with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), 2,6-dichlorophenolindophenol, etc. in quantitative yields.

Dihydropyridines **2** were transformed into pyridines **3** in quantitative yields by heating or irradiation with 400W high pressure mercury lamp.

Reaction of dihydropyridines **2** (also NADH) in acid have been difficult to study because a complex mixture of compounds was formed. In order to investigate this problem, we examined the reaction of α-substituted dihydropyridines **2** in acid and found that it gave ring opening products **4**.

1,4-Dihydropyridines are expected to have an enamine-like reactivity, so we examined the reaction of dihydropyridines **2** with electrophiles. For example, the reaction of **2** with 2,4-dinitrobenzenesulfonylchloride afforded 3,5-disubstituted dihydropyridine **5**, which was transformed into 3,5-disubstituted pyridine **6** by heating.

Finally, we also discuss about biological effects of these compounds by using E. Coli inner membrane.

