

acid, made by oxidation of 2-methyl-5-ethylpyridine, we observed a novel transformation of this pyridine dicarboxylic acid to variously 6-substituted nicotinic acids.

When isocinchomeric acid-N-oxide was reacted with acetic anhydride/triethylamine in methylenechloride 6-chloronicotinic acid was obtained in 50% yield, the chlorine originating from the solvent. 6-Hydroxynicotinic acid was identified as a side product in 40% yield. This unusual and unexpected chlorination with methylenechloride was also tried successfully on other pyridine carboxylic acids bearing a carboxyl group in the 2 position to the nitrogen. The carboxyl group was invariably replaced by chlorine.

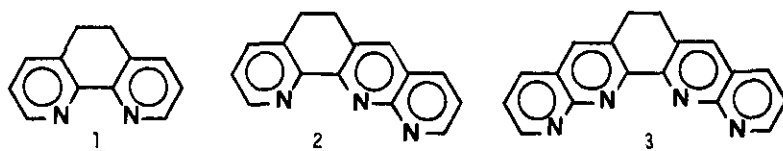
When in the system isocinchomeric acid-N-oxide/acetic anhydride/triethylamine the methylenechloride was replaced by another solvent, a radical of this solvent was found as substituent in the 2 position. In acetonitrile as solvent 6-aminonicotinic acid was isolated in 80% yield. In ethylacetate 6-hydroxynicotinic acid was formed in 80-86% yield. The benzene- and toluene-radical was also introduced into the 2 position.

We are continuing to study the scope of this reaction, which gives easy access to 6-substituted nicotinic acids hitherto available only on very cumbersome routes.

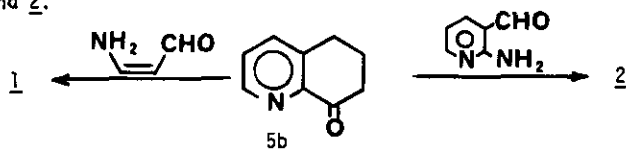
#### Annulated Derivatives of 2,2'-Bipyridine and 2,2'-Bi(1,8)naphthyridine

Randolph P. Thummel\*, Ramanathan Mahadevan, Agha S. Saleem, and David Cantu

Department of Chemistry, University of Houston, Houston, Texas 77004



The series of ethano-bridged bi-aryl compounds 1-3 has been synthesized by application of the Friedlander Condensation method. Thus the reaction of 8-oxo-5,6,7,8-tetrahydroquinoline (5b) with  $\beta$ -aminoacrolein leads to the formation of 1 while condensation with 2-aminonicotinaldehyde gives compound 2.



The 2-oxocycloalkenopyridines (5 a-c) are readily prepared by a two step route from the corresponding commercially available cycloalkenopyridines.

