SYNTHESES OF TRIAZOLOPYRIDINE DERIVATIVES WITH NICKEL PEROXIDE

Haruo Ogura and Satoshi Mineo School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108, Japan

Nickel Peroxide(Ni-PO) has been used as an oxidizing agent for many functional groups. Previously, Nakagawa <u>et al</u>. reported that the oxidation of hydrazones afforded azo compounds, while diphenylacetylene was obtained when benzil dihydrazone was oxidized with Ni-PO in ether solution. Oxidation of 2-pyridil dihydrazone with Ni-PO gave cyclized product 3,3'-bis(1,2,3-triazolo[1,5-<u>a</u>]pyridine) in 64.3% yield instead of acetylenic compound.

Now we wish to report the oxidation of pyridine-2-carbaldehyde and 2-pyridyl ketone hydrazones. The starting substituted phenyl-2-pyridyl ketones were obtained from the corresponding alcohols with Ni-PO oxidation in good yields. Though, when the substituent was \underline{p} -NO₂ or \underline{m} -NO₂ on phenyl group, the Ni-PO oxidation could not afford the ketones and the starting alcohols were recovered.

The reaction of pyridine-2-carbaldehyde and $NH_2NH_2H_2O$ afforded <u>syn</u> and <u>anti</u> isomers, both isomers were reacted with <u>p</u>-nitrobenzaldehyde to the same benzylidene compound. Hydrazones which were obtained from the corresponding ketones and aldehydes were oxidized with Ni-PO in benzene solution at room temperature to yield 1,2,3triazolo[1,5-<u>a</u>]pyridines in excellent yields(84.6-97.4%). N-Oxidation, nitration and halogenation of 1,2,3-triazolo[1,5-<u>a</u>]pyridines were reported.