SYNTHESES OF TRIAZOLOPYRIDINE DERIVATIVES WITH NICKEL PEROXIDE

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Nickel Peroxide(Ni-PO) has been used as an oxidizing agent for many functional groups. Previously, Nakagawa et al. 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-a]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 p-NO_2 or m-NO_2 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 $NH_2NH_2{\cdot}H_2O$ afforded syn and anti isomers, both isomers were reacted with p-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 1,2,3-triazolo[1,5-a]pyridines in excellent yields(84.6-97.4%). N-Oxidation, nitration and halogenation of 1,2,3-triazolo[1,5-a]pyridines were reported.