SYNTHESIS OF SOME AZAAROMATICS USING TRANSITIONMETAL COMPLEXES AS CATALYSTS

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Alkyl- and arylpyridazines were synthesized by cross-coupling reaction between chloropyridazines and Grignard reagents in the presence of nickel-phosphine complexes (as catalysts). 3-Alkynylpyridazines were prepared by cross-coupling of 3-halopyridazines and monosubstituted acetylenes in Et_2NH with $Pd(PPh_3)_2Cl_2$-CuI as a catalyst. Though the alkynylation of 3-chloropyridazine-1-oxides afforded 3-alkynylpyridazine-1-oxides, attempts to obtain 3-alkynylpyridazine-2-oxides have been unsuccessful. 3-(Dialkylamino)indolizines were synthesized in one-step from 2-bromopyridine, propargyl alcohol, and secondary amines in the presence of $Pd(PPh_3)_2Cl_2$-CuI as a catalyst. 3-(2-Pyridyl)-2-propyn-1-ol and 3-(2-pyridyl)-2-propenal were suggested to be the intermediates of the reaction. 3-Dialkylamino derivatives of pyrrolo[1,2-a]quinoline, pyrrolo-[2,1-a]isoquinoline, and pyrrolo[1,2-b]pyridazine were obtained from corresponding α-haloazaaromatics in a similar way. Reaction of 2- or 3- substituted 3-(2-pyridyl)-2-propenals with secondary amines afforded 2- or 1-substituted 3-(dialkylamino)indolizines in the presence of titanium tetrachloride. Reaction of o-(2-pyridyl)benzaldiacetate (1) with piperidine afforded 6-piperidinopyrido-[2,1-a]isoindole (2). Treatment of 1 with HCl afforded pyrido[2,1-a]isoindol-6(2H)-one (3). Treatment of 2 with HCl also afforded 3. And reaction of 3 with piperidine in the presence of titanium tetrachloride afforded 2.