THE REACTION OF THE TRANSITION METAL COMPLEXES (Ni or Pd) WITH THE COMPOUNDS CONTAINING HETERO ATOMS

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The synthesis of heterocyclic compounds by using of organometallic complexes such as Ni or Pd has been investigated. As it is considered that the hetero atoms could play an important role as the reaction site of the ligands, the reaction of the compounds containing hetero atoms with the organometallic complexes is usually complicated, however, this field is very attractive and prospective.

1) The synthesis of heterocyclic compounds by using of organonickel complexes

When N-2-chlorophenyl-N-methyl-N-allyl amine(1) was reacted with excess EtMgBr in the presence of catalytic amount of $NiCl_2(PPh_3)_2$, 1,3-dimethylindoline was obtained though in a low yield. In this reaction, it was considered that the vinyl chloride reacted with the double bond and the intermediate was organonickel complex. Terefore, when 1 was directly refluxed with zero-valent nickel[$Ni(PPh_3)_4$] in ether under the stream of argon, intramolecular cyclization reaction occurred, and 1,3-dimethylindole was obtained in 45.6% yield. Moreover, when N-methyl-(2-chlorophenyl)acrylyl amide was reacted similarly with $Ni(PPh_3)_4$, 1,3-dimethyloxindole was obtained in 43.5% yield in addition to N-methyl-2-hydroxyquinoline (7.3%). N-Methyl-2-hydroxyindoleacetic acid (70.5%) and N-methyl-3-benzyloxindole(86.6%) were obtained in the same manner.

2) The reaction on N-allyl compounds with Pd^{II}

It was found that the N-acetyl-allyl bond could be easily cleaved by Pd^{II} in AcOH at 50°. But in same cases of the basic tertiary amines involving an N-allyl group and aromatic ring, ring closure reaction occurred instead of the fission of the N-allyl group. N-Benzyl-N-ethyl-N-allylamine was reacted with $Pd(OAc)_2$ in the presence of $Cu(OAc)_2 \cdot H_2O$ in AcOH at 100°, 2-ethyl-4-methylene-1,2,3,4-tetrahydroisoquinoline was obtained in 11.7% yield. In the same way, 2,4-dibenzyl-1,2-dihydroisoquinoline was obatained in 32.0% yield from 1-(dibenzylamino)-3-phenylprop-2-ene.