

CYCLIZATION OF α -HALOCARBONYL COMPOUND HAVING INTERNAL DOUBLE
BOND BY USE OF THE LOW-VALENT METAL COMPLEX

Miwako Mori, Yukiko Kubo, Nana Kanda, Izumi Oda and Yoshio Ban
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

An aryl or vinylmetal complex which is formed by oxidative addition of an aryl or vinyl halide to the low-valent metal complex is a useful synthetic method for the heterocyclic compound. However, in general an alkyl halide can not afford an alkylmetal complex. It was anticipated that the reaction of α -halocarbonyl compound with the low-valent metal complex would afford a fairly stable σ -alkylmetal complex. Thus, the cyclization of α -haloamide and α -haloester having internal double bond has been achieved by use of the low-valent metal complex. N-Benzyl-N-allyl- α -iodoacetamide (**1**) was warmed with an equimolar amount of $\text{Pd}(\text{PPh}_3)_4$ in DMF at 65° for 5.5 h to afford N-benzyl-3-methylene-2-pyrrolidone (**2**) and N-benzyl-3-iodomethyl-2-pyrrolidone (**3**) in the yields of 14 % and 23 %, respectively. The reaction proceeded catalytically with 10 mol% of $\text{Pd}(\text{PPh}_3)_4$ in the presence of 1,8-bis(dimethylamino)naphthalene (Proton Sponge) in HMPA to afford the desired products (59 % yield). By use of this method, piperidone **4**, oxindole **5**, indolizidine **6** and quinolizidine **7** derivatives were synthesized in fairly good yields. On the other hand, α -iodoester **8** was treated with a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ in the presence of proton sponge in HMPA at 65° for 15 min to afford a cyclized product **9** in a yield of 75 %. Similarly, piperidine **10**, indole **11** and quinoline **12** derivatives were obtained in good yields.

