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

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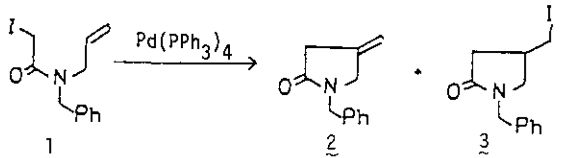
An aryl or vinylmetal complex which is formed by oxidative addition of an aryl or vinyl halide to the low-valent metal complex is a useful synthetic method for the heterocyclic compound. However, in general an alkyl halide can not afford an alkylmetal complex. It was anticipated that the reaction of 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 $Pd(PPh_3)_4$ 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 $Pd(PPh_3)_4$ 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 $Pd(PPh_3)_4$ 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.



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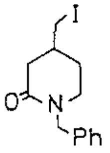

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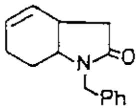

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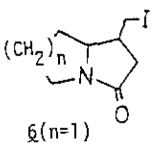
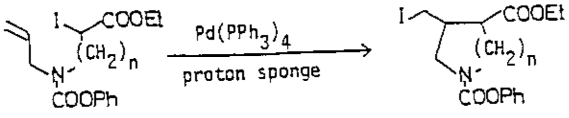
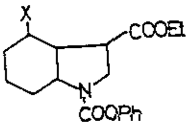


6(n=1)
7(n=2)



8 9(n=1)
10(n=2)



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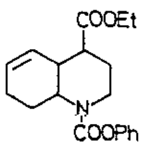

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