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THE REACTIONS AND SYNTHESES WITH ORGANOMETALLIC COMPOUNDS III.
THE SYNTHESIS OF INDOLE DERIVATIVES VIA ARYLNICKEL COMPLEXES

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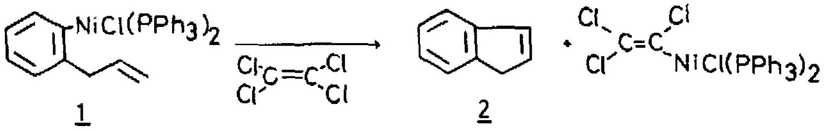
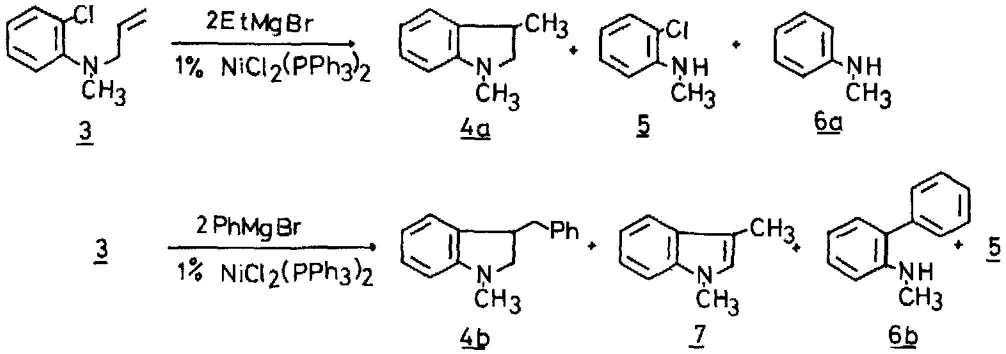
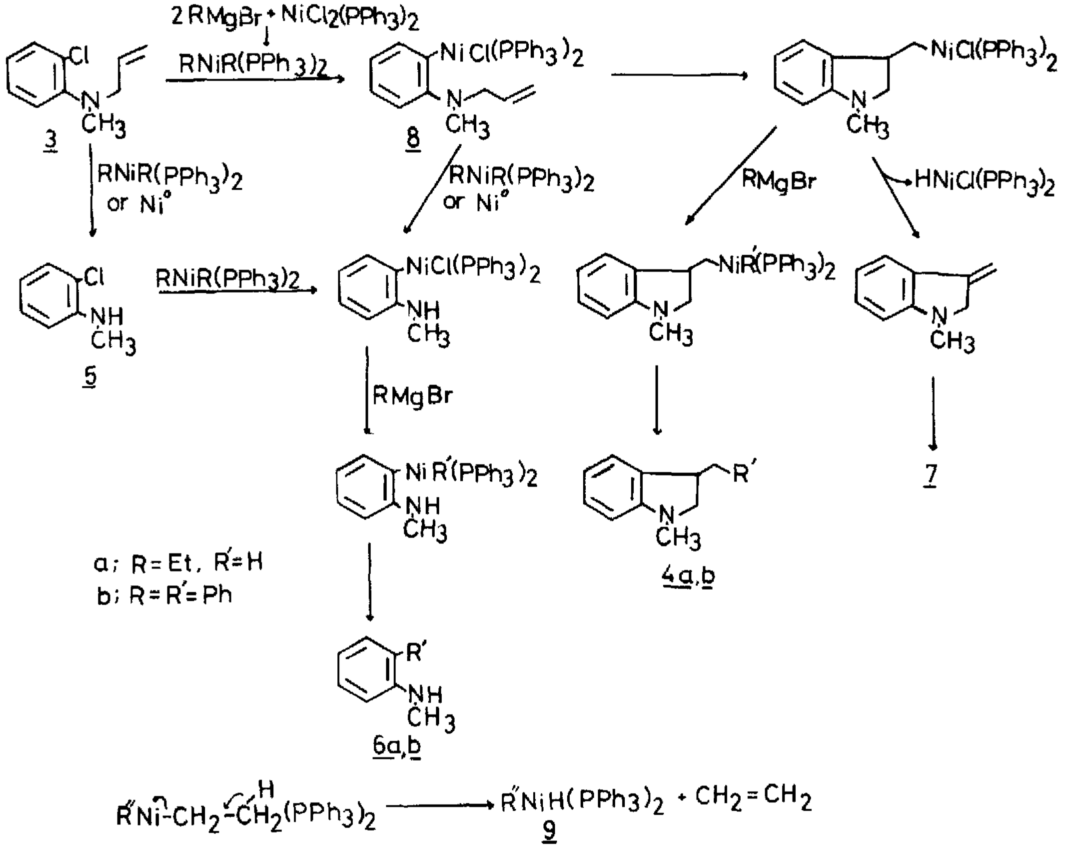
In an extention of the studies on syntheses of heterocyclic compounds by utilization of organometallic complexes,$^{1)}$ we have chosen the arylnickel complex (8) as a substrate for a novel synthesis of indole derivatives in reference to the Miller's conversion of the compound (1) into indene (2)$^{2)}$ and the other known works.$^{3)}$





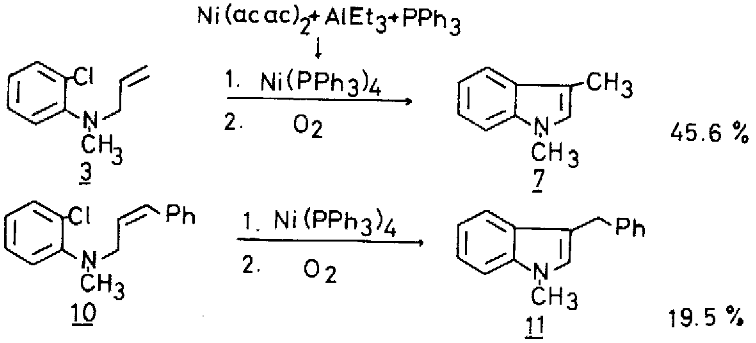
The complex (8) was prepared *in situ* by the reaction of the chloride (3) with $EtNiEt(PPh_3)_2$. Namely, when 2-chloro-N-methyl-N-allylaniline(3) was refluxed with EtMgBr (2 mol. equiv.) and a catalytic amount of $NiCl_2(PPh_3)_2$ in ether, the expected indole (7) was not obtained, but 1,3-dimethylindoline(4a) was generated though in a low yield (8.6%) in addition to 5 (54.0%) and 6a (24.6%) as a result of deallylation reactions. In the absence of $NiCl_2(PPh_3)_2$, the starting material was recovered unchanged. When PhMgBr was used in this reaction in place of EtMgBr, 1,3-dimethyl-indole (7) (5.2%) and 1-methyl-3-benzylindoline (4b) (9.0%) were obtained along with 2-phenyl-N-methylaniline (6b) (18.3%).

The reaction mechanism might presumably demonstrated in the following Chart, in which the plausible pathways for generation of the respective products (4-7) are indicated.



When EtMgBr was used to prepare an alkylnickel complex, the ethylnickel complex easily changed to the hydridonickel complex(9) accompanied by generation of ethylene, and hence the ethyl group did not remain in the resulting coupling products(4a and 6a). It is noteworthy that a catalytic amount of $NiCl_2(PPh_3)_2$ is eventually effective in this intramolecular cyclization reaction.

Based upon these results, it can be assumed that an equimolar amount of zerovalent nickel complex to 3 might be used to prevent deallylation reaction. For this purpose, tetrakis(triphenylphosphine)nickel[$Ni(PPh_3)_4$]4) was prepared *in situ* as a zerovalent nickel complex from $Ni(acac)_2$ and $AlEt_3$ in the presence of PPh_3 in ether in a current of argon, which was mixed with 3 and the whole mixture was refluxed for several hours. After oxygen was bubbled through the solution in an ice-bath to convert PPh_3 into $O\leftarrow PPh_3$ for easy handling,5) an expected 1,3-dimethylindole(7) was obtained in a far better yield of 45.6%, and was identified by comparison with the authentic sample. Similarly, 1-methyl-3-benzylindole(11) (19.5%) was obtained from 10 in a similar manner.



These results suggest that this reaction is able to be utilized for the synthesis of various indole derivatives.

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