SYNOPSIS

The dissertation entitled, 'Synthetic studies using metal catalysed organic reactions' consists of two chapters and embodies in Chapter-I : A review on Heck reaction and Chapter-II : Studies with phosphine – and PTC-free Heck reaction.

The dissertation begins with a review on Heck reaction in Chapter-I, which includes its mechanism, influencing parameters of Heck reaction and applications of Heck reaction in organic synthesis. The mechanism consists of five steps : a) preactivation, b) oxidative addition, c) migratory insertion, d) termination and e) Palladium hydride elimination. The influencing parameters are effects of base, temperature, solvent, ligand and leaving group. Some important applications mentioned are natural product synthesis, industrial applications, asymmetric synthesis, arylation of aldehydes and ketones and heteroannelation.

The Chapter-II deals with the phosphine – and PTC – free Heck reaction of p-iodoanisole, p-iodotoluene and bromobenzene in aqueous DMF. The reasons for considering phosphine – free Heck reaction are both economical and chemical. Phosphine ligands are expensive, toxic and unrecoverable. This approach would make the Heck reaction environmentally friendly (Green Chemistry). Hence, we present our work on Heck reaction under phosphine – and PTC –free conditions.

Heck reaction of p-iodoanisole with styrene was carried out in aqueous DMF using palladium chloride and potassium carbonate to yield 4'-methoxy stilbene (1.5, Chart-I, Scheme-1) in high yield. The reaction of p-iodoanisole with ethyl crotonate under the same conditions yielded ethyl 3-(4'-methoxyphenyl)-3-methyl acrylate (1.7, Chart-I, Scheme-2) in good yield.

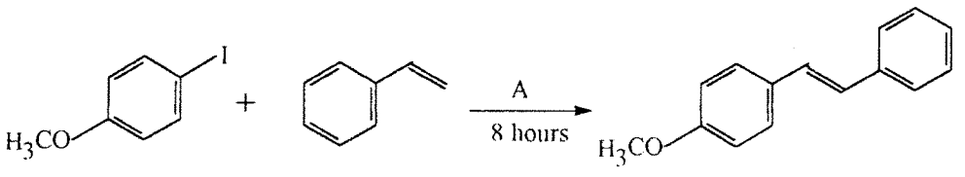
Heck reaction of p-iodotoluene with styrene under the above conditions yielded 4'-methyl stilbene (2.5 Chart-I, Scheme-3) in good yield. The Heck reaction of p-iodotoluene with methyl crotonate yielded methyl 3-(4'methylphenyl)-3-methylacrylate (2.7 Chart-I, Scheme-4). This compound has been prepared earlier by Reformatsky reaction of methyl 2-bromoacetate on p-methylacetophenone followed by dehydration and has been converted into ar-turmerone, the natural product of *Curcuma longa* Linn.

Similarly, the Heck reaction of bromobenzene with styrene yielded stilbene (3.3, Chart-II, Scheme-5) in high yield. The Heck reaction conditions developed above have been successfully applied to the synthesis of cinnamic acid (3.5) by reaction of bromobenzene and acrylic acid (Chart-II, Scheme-6).

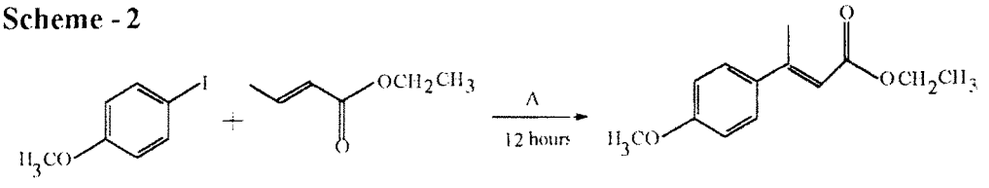
Thus, the Heck reaction under phosphine- and PTC-free conditions in DMF-H_2O gave good yields of the products. This is an environmentally friendly (Green Chemistry) approach to Heck reaction.

CHART – 1

Scheme - 1

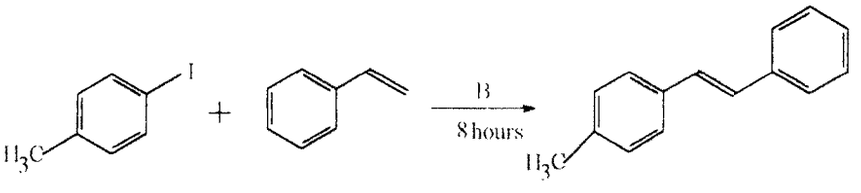


Scheme - 2

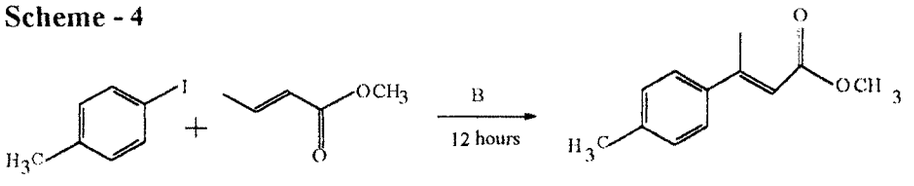


A : p-Iodoanisole (0.002 mol) $pdCl_2$(0.00002 mol), K_2CO_3 (0.002 mol)

Scheme - 3



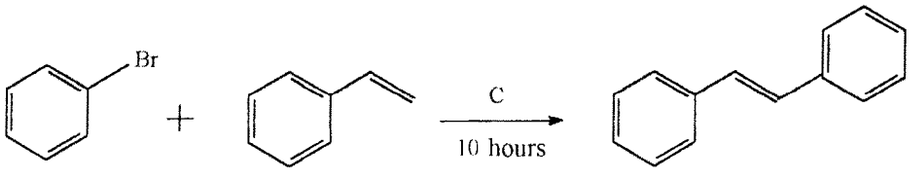
Scheme - 4



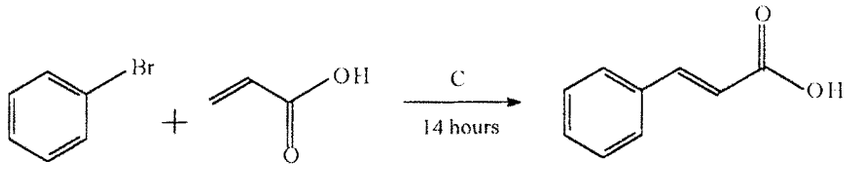
B : p-Iodotolune (0.0025 mol), $PdCl_2$ (0.000025 mol), K_2CO_3 (0.0025 mol)

CHART – II

Scheme -5



Scheme - 6



C : Bromobenzene (0.003 mol), $PdCl_2$ (0.00003 mol), K_2CO_3 (0.003 mol)