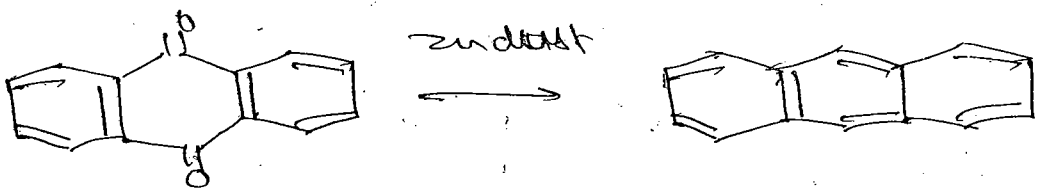
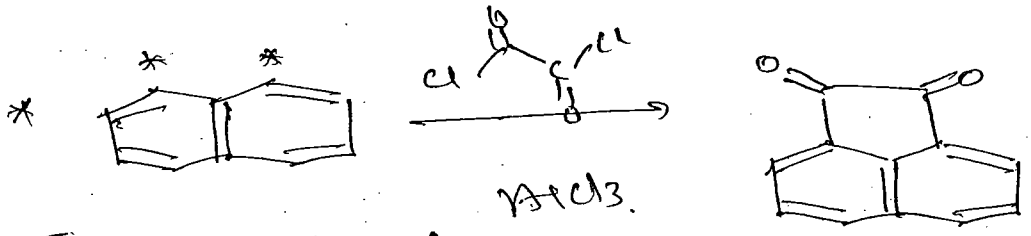




Coupling Reactions :-

* Pd catalysed reaction :- Pd^{0} | Pd^{II}

$Pd^{0}(PPh_3)_4$, $Pd^{II}(OAc)_2$, $Pd^{II}(PPh_3)_2$,

$LnPd^{0}$ $LnPd^{II}$

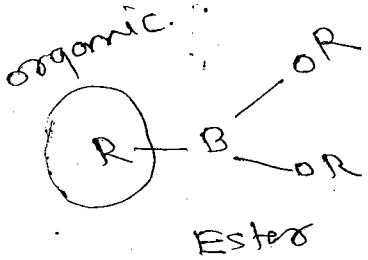
L = ligand
n = number.

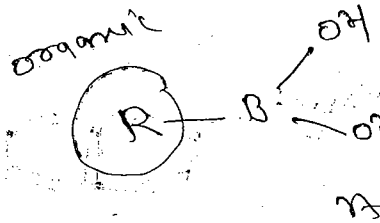
- In org. synthesis widely used in 0 and 2 oxi. sta. pd catalyst mainly for c–c bond formation reaction.

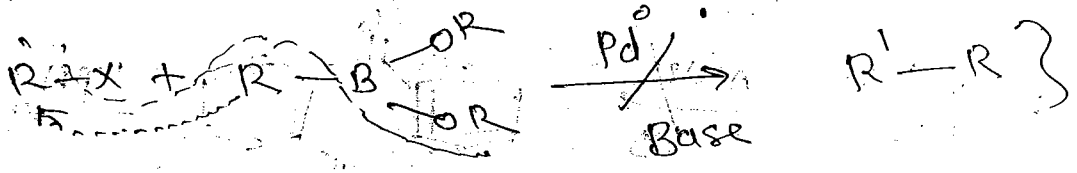
1] Suzuki cross coupling :-

organo Boromes ⟶ Acids

↘ Esters.







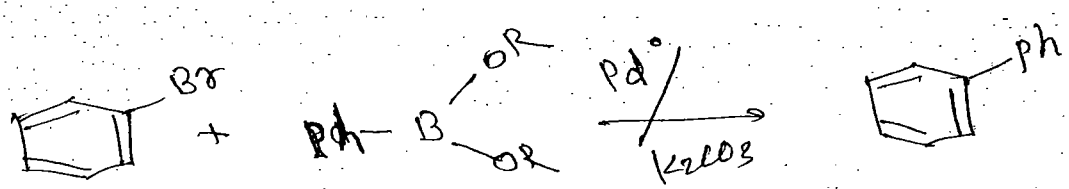
R' = Aryl, Alkyl, Alkenyl

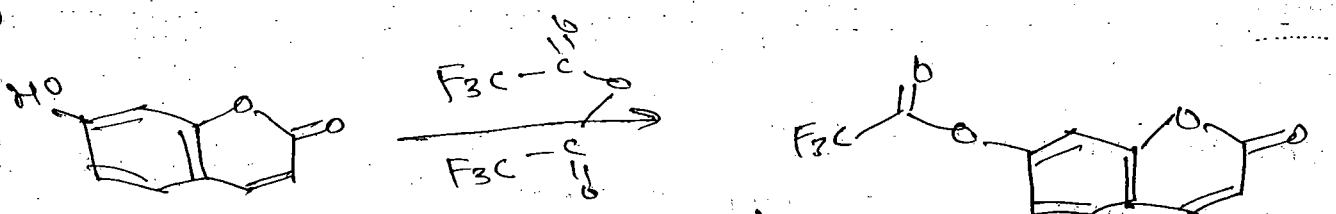
R = Heteroyl, Aryl, alkyl, Alkenyl Alkynyl *

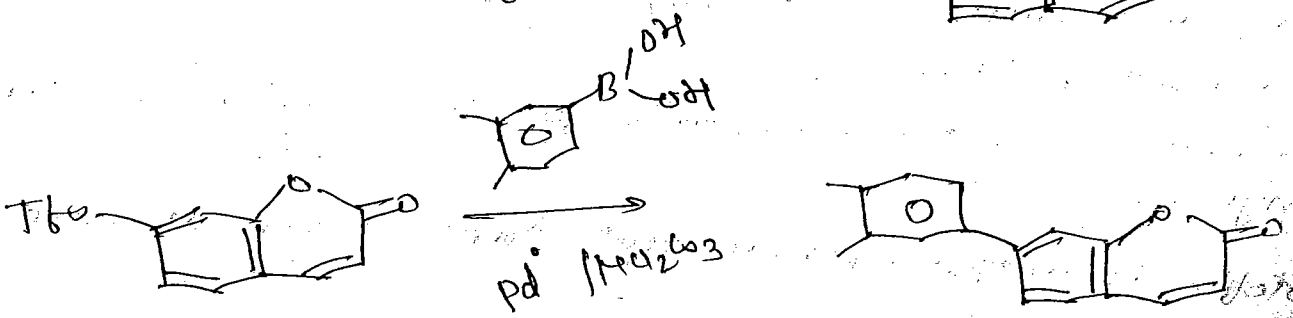
X = Halo, OTs, OTf, etc.

Cl, Br, I

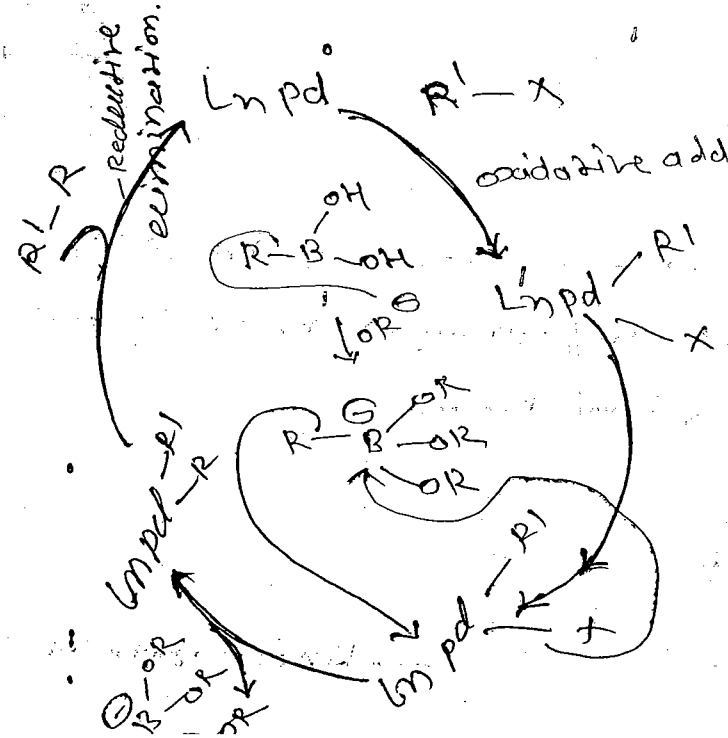
Base = Na_2CO_3, K_2CO_3, Cs_2CO_3, $RO^{\ominus}Na^{\oplus}$ etc.







Mechanism:-

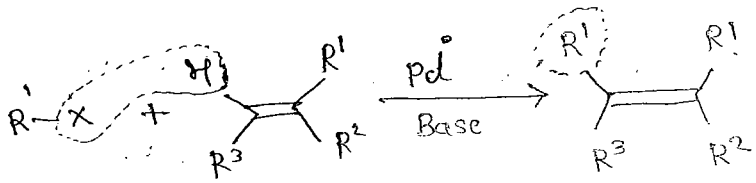


useful point:-

* It is mild (without vigorous condition)
* not sensitive to moisture (H_2O)
* If Halo or tripsylate contains any other functional group unaffected.
* high % of yields
* organo borane (cheaper and readily available

- Easy to remove by product.

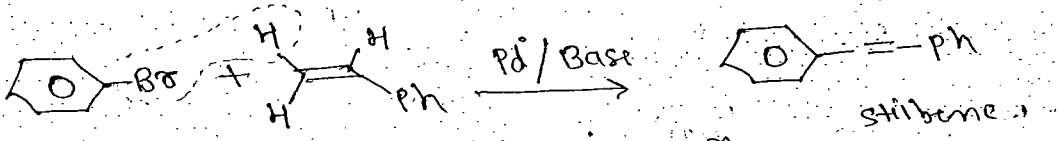
* HECK-cross coupling:-



R' = Any org. group. i.e. Aryl, Alkenyl, Alkyl.

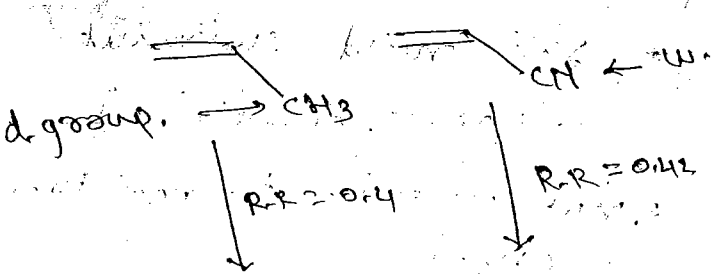
x = Halo group, OTS, OTf, $\overset{\oplus}{N_2}$

Base = Na_2CO_3, NaOH, $R\overset{\ominus}{O}\overset{\oplus}{Na}$ ($m^1 \overset{\ominus}{O}R$)



*Less substituted side 'H' participate in reaction.

- Pd catalysed coupling betn organo halo compounds are triplets and olefines cross coupling (presence of base)
- Reaction Easy to carry out. High % of yields.
- Reaction by products easy to remove. ~~Reaction~~ not sensitive at a air and moisture.
- Tolarates any other organic function. ester acid carbo-nyl etc.
- ~~olefin~~ is unsymmetrical reaction takes place at less substituted position.

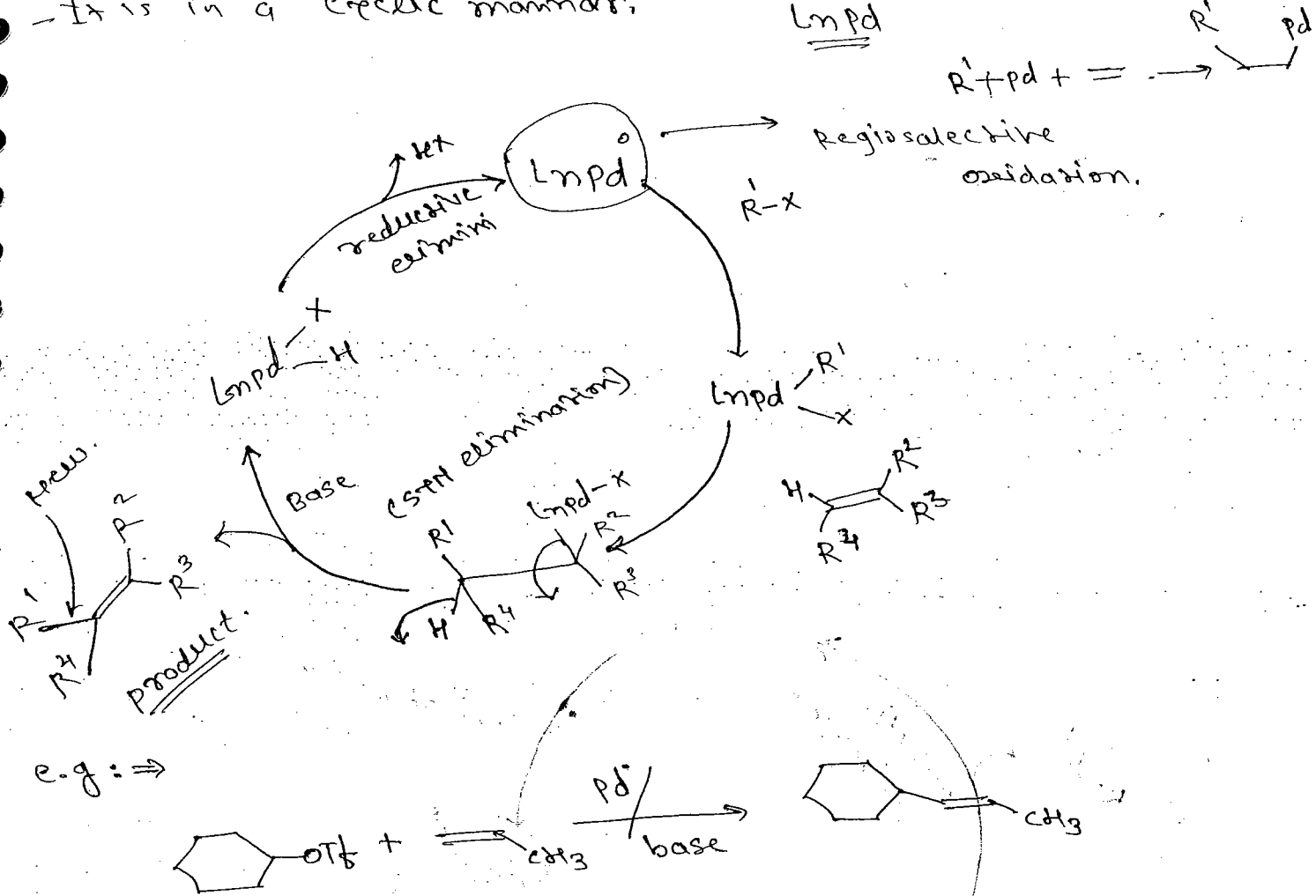


Rate of reaction unaffected by donating or withdrawing groups on olefins but is some reaction the withdrawing group increases rate of reaction compare to donating group.

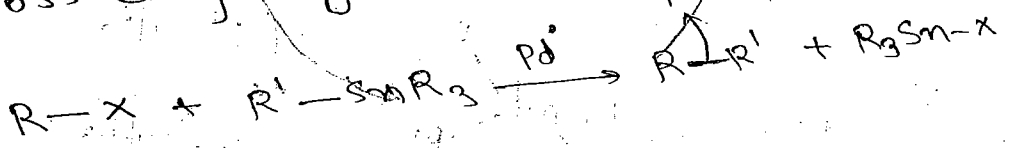
- In increasing no. of substituents on olefin rate of coupling decreases.

Pathway:-

- It is in a cyclic manner.



* STILLE CROSS-coupling: ⇒



- Pd catalysed coupling betn organo Halo comp. with organo Tin compounds STILLE CROSS coupling.
- It is similar to SUZUKI-CROSS coupling.
- Easy to carry out, high % yields of the reaction, not sensitive to the moisture and air.
- Tolerates all other organic functions i.e. acid, ester aldehyde ketone etc.
- * Tin compound expensive, environment pollutant. (Sn)

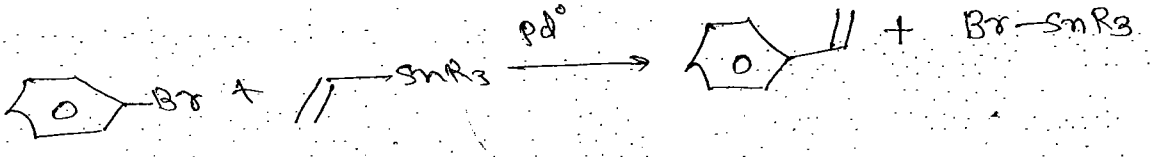
Pathway on next page ⇒

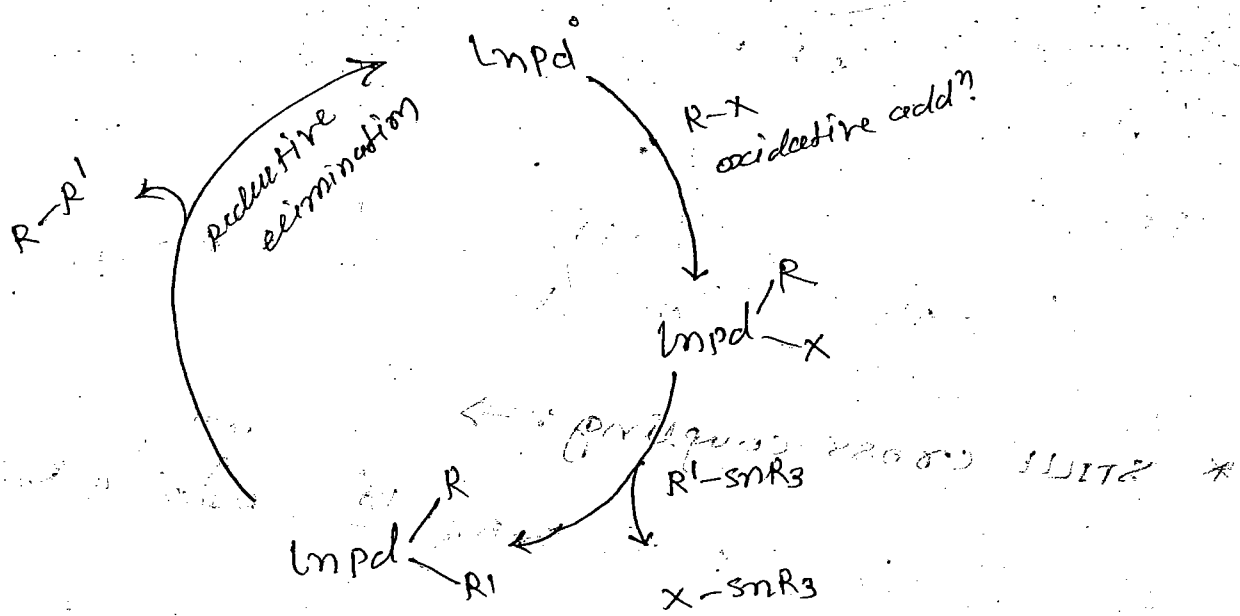
$R-X + R'-SnR_3 \xrightarrow{Pd^\circ} R-R'$

product.

- oxidative group.
- organic group

Aromatic, Alkenyls, Alkynyls, alkyls → X = Halo, OTf





✱ Sonogashira Coupling :-

$R-X + R'-\equiv-H \xrightarrow[Base/CuI]{Pd^\circ/Pd^{II}} R'-\equiv-R$

product.

- Coupling betn or Pd-Cu catalysed coupling betn organic halo comp. or triflates with terminal alkyne in basic medium sonogashira coupling.
- Terminal alkyne to internal alkyne.
- Terminal alkyne 1° convert to cusait. Copper salt.

- copper salt undergo pd - Complex.
- not sensitive air and H_2O
- Tolerate other function group. good % of yield.
- product easy to isolate.

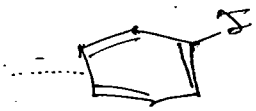
$R-X + R'-\equiv-H$

R → aryl, alkenyl, alkynyl

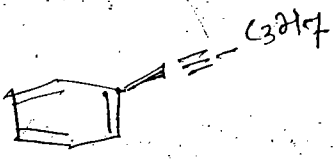
R' → organic group

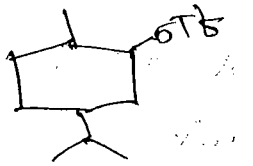
X = Halo, OTf, (Cl, Br, I)

e.g. :⇒

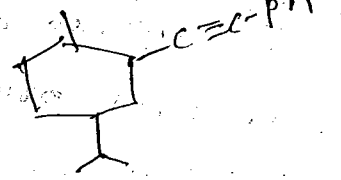


$+ C_3H_7-C\equiv C-H \xrightarrow[\text{base}]{Pd\,/\,CuI}$



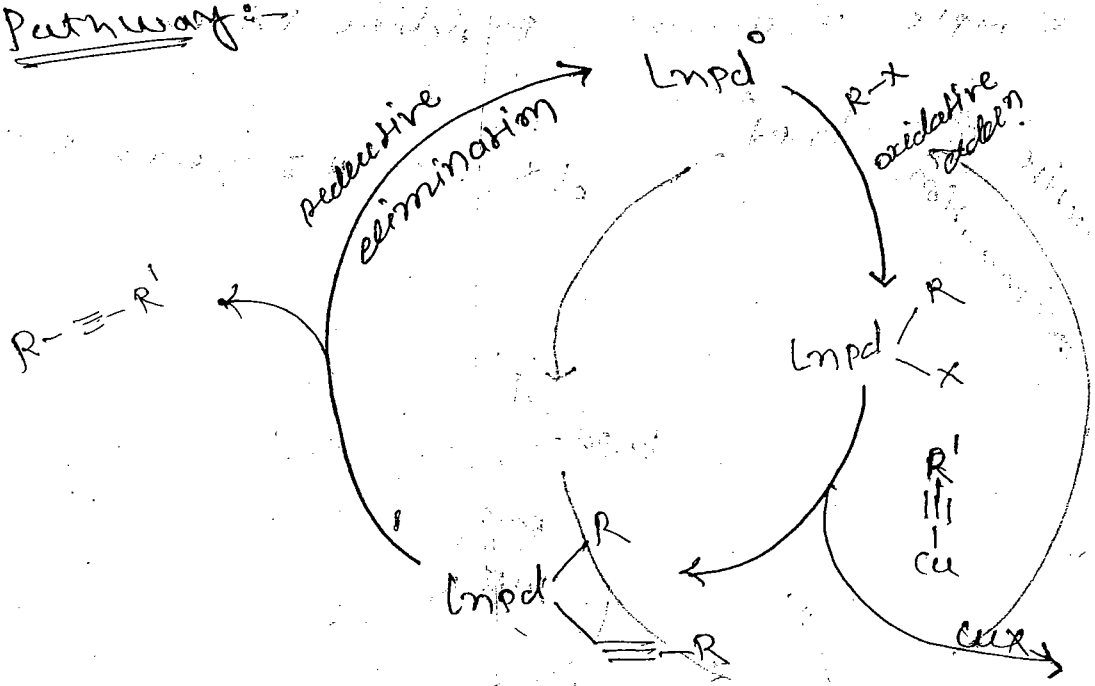


$+ Ph-C\equiv C-H \xrightarrow{\quad''\quad}$

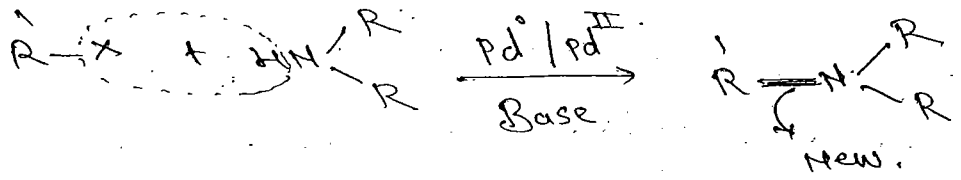


$R'-C\equiv C-H \xrightarrow{base} R'-C\equiv C^{\ominus} \xrightarrow{+Cu^{\oplus}} R'-C\equiv C-Cu$

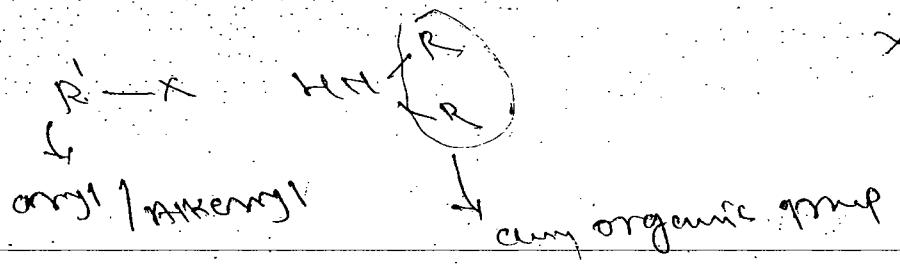
Pathway :-



* BUCHWALD - HERTWIG COUPLING : C-N bonding.

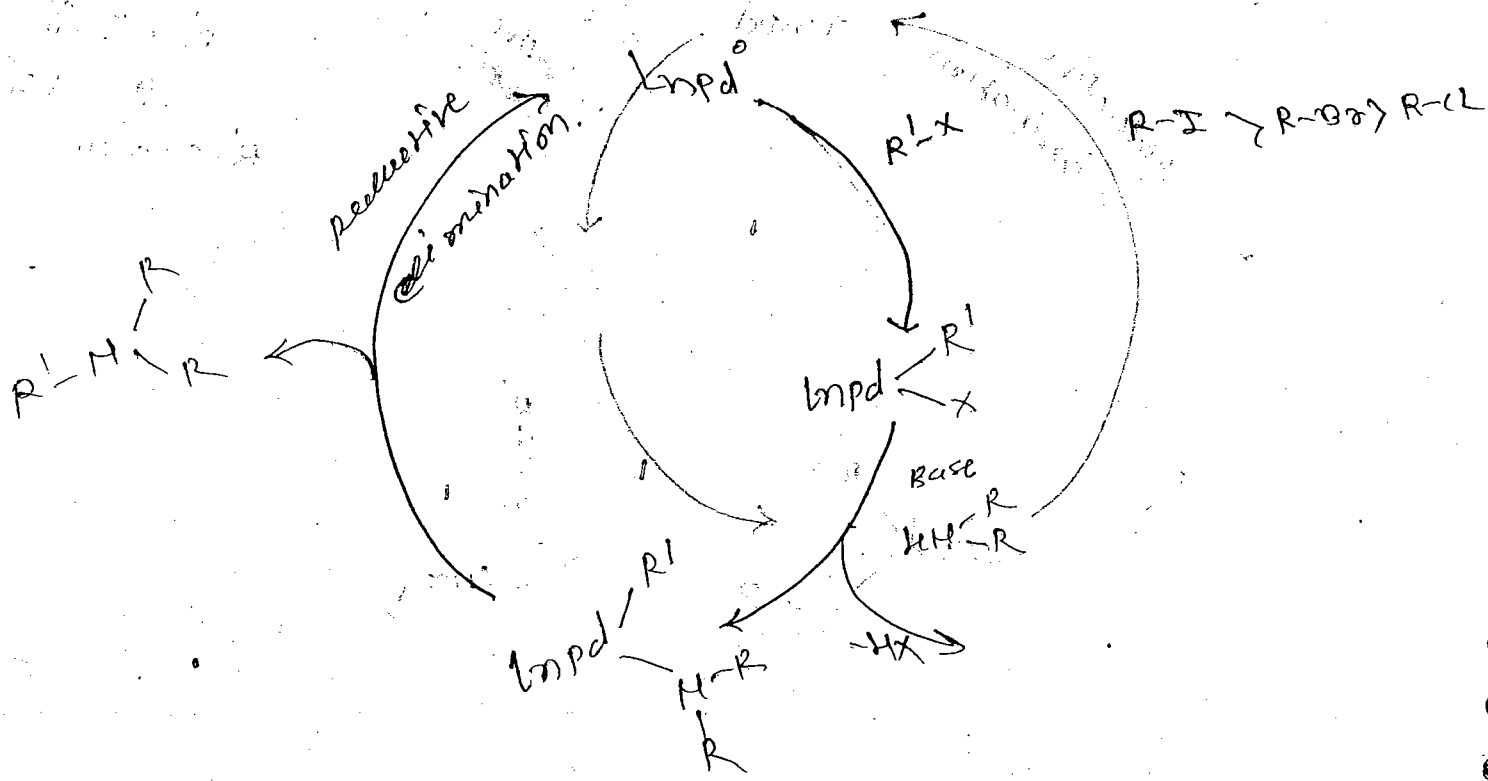


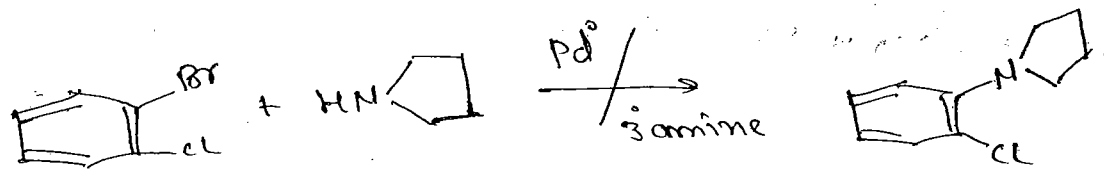
- Pd catalysed coupling betn organic Halo comp. or triflates and 1° and 2° amines in basic medium called Buchwald Hertwig coupling.

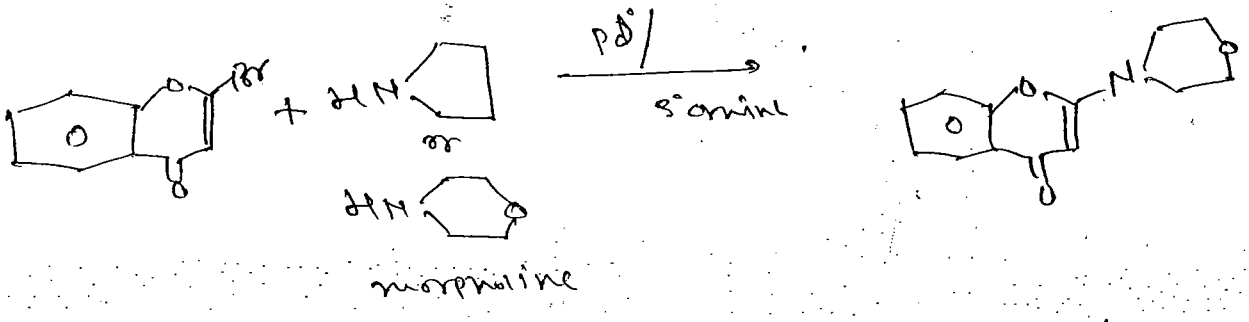


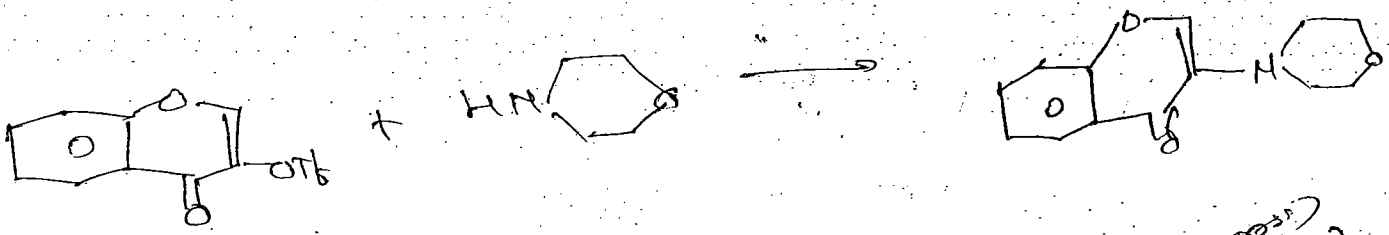
X = Cl, Br, I (Halo)
OTs,

- 2° amines are faster in coupling in compare to 1° amine.
- Preferred org. group aryl, or alkenyl.
- Good % of yield, not sensitive to air and also moisty.
- Useful for C–N bond formation even with heterocyclics common bases are hydroxides, alkoxides, simple 3° amines pyridine tri amine.

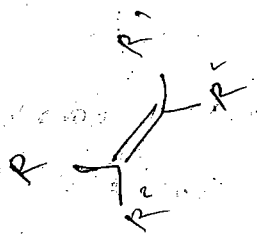






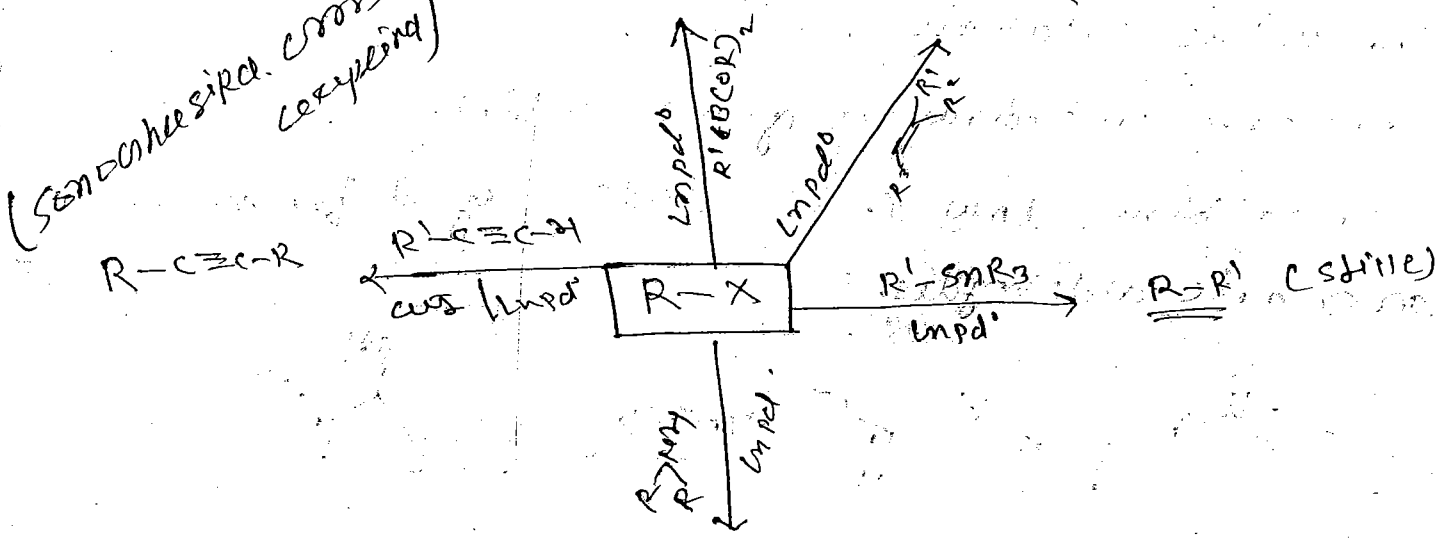


(HECK cross coupling)



R–R' (Suzuki)

(Sonogashira cross coupling)



(Buchwald)