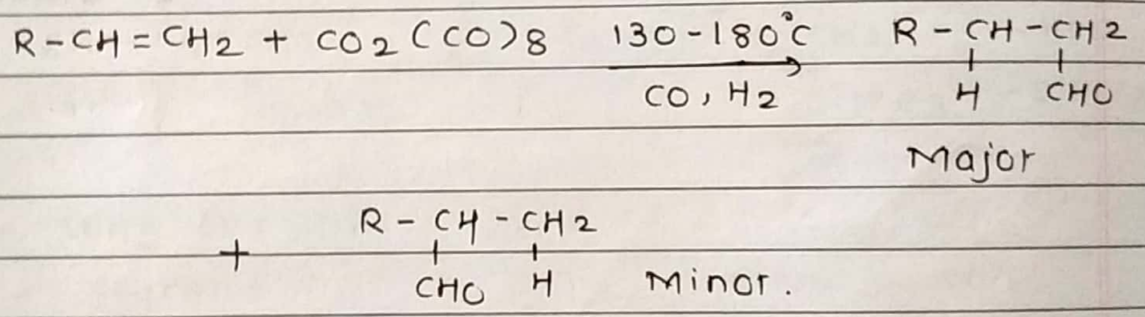
Unit-4 : Transition metal complexes in organic synthesis.

1> CO :-

- Metal carbonyls of cobalt is used in carbonylation of alkenes. For e.g. octa carbonyl cobalt. $CO_2(CO)_8$ catalyses a wide range of reactions of carbon monoxide of which the best known is probably the hydroformylation (oxo reactn) of alkenes.

- Depending on reactn condition notably CO & H_2 ratio & temperature, the products are aldehydes or alcohols (hydro methylation)



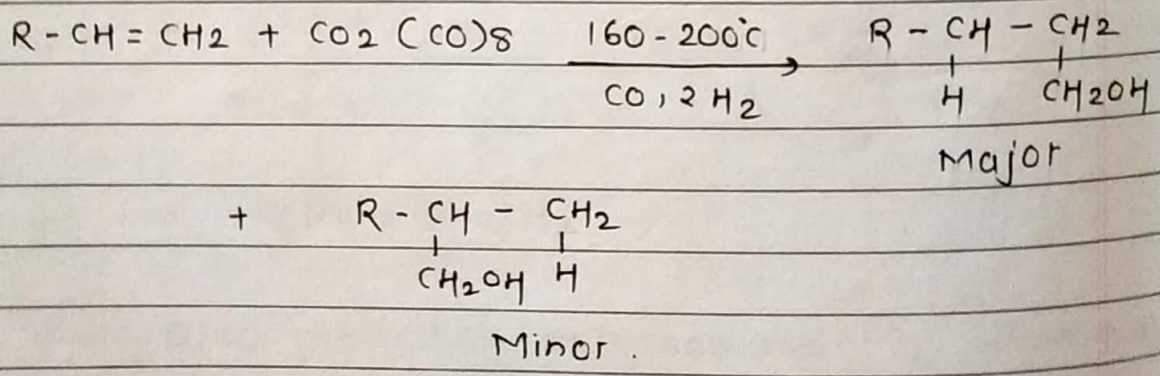
$$R-CH=CH_2 + CO_2(CO)_8 \xrightarrow[CO,\ H_2]{130-180^\circ C} R-\underset{H}{\underset{|}{CH}}-\underset{CHO}{\underset{|}{CH_2}}$$

Major

$$+\ R-\underset{CHO}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

Minor.

* For hydromethylation :-



$$R-CH=CH_2 + CO_2(CO)_8 \xrightarrow[CO,\ 2H_2]{160-200^\circ C} R-\underset{H}{\underset{|}{CH}}-\underset{CH_2OH}{\underset{|}{CH_2}}$$

Major

$$+\ R-\underset{CH_2OH}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

Minor.

* Hydro carboxylation reaction :-

Hydrogen can be replaced by protic reagents such as alcohols or amines to give a range of carbonylation product, including carboxylic acids, anhydrides, esters, amides etc.

The reactn in such case is known as hydro carboxylation reactn.

$$R-CH=CH_2 + CO + H_2O \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-COOH$$

$$R-CH=CH_2 + CO + NH_3 \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$$

$$R-CH=CH_2 + CO + R-OH \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OR.$$

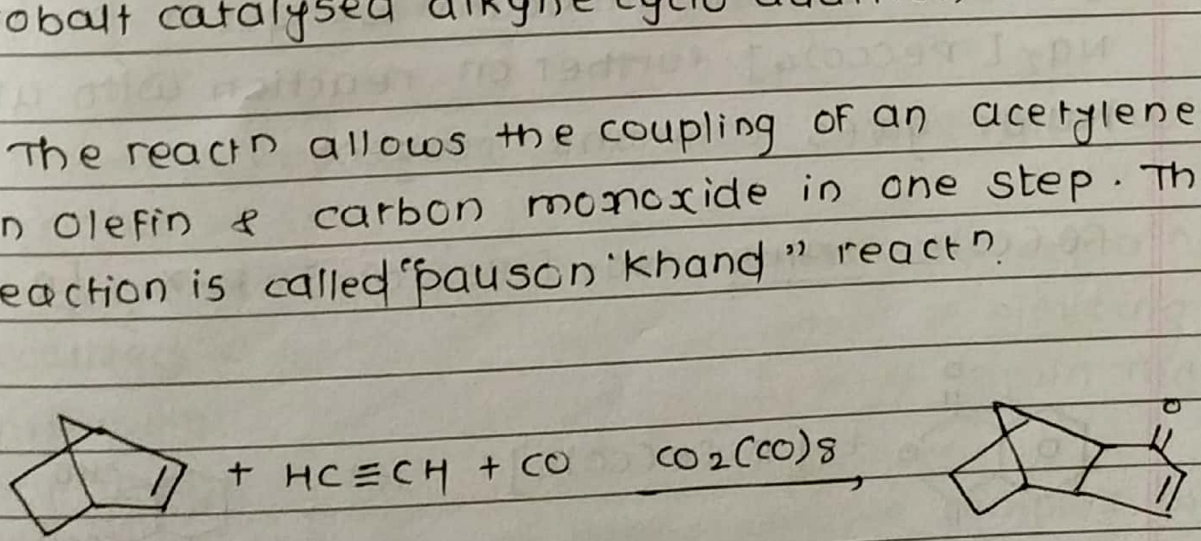
Addn of HCN with alkene :-

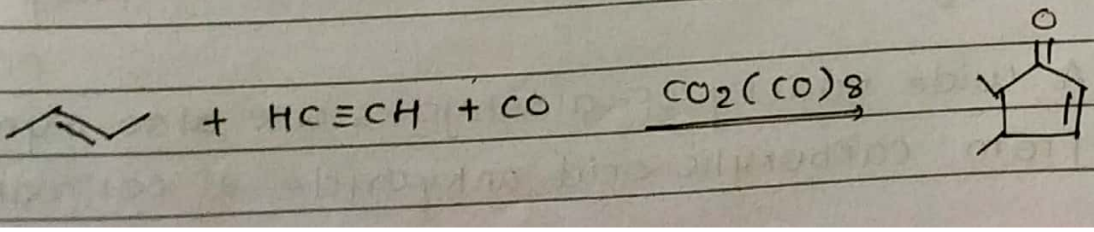
Hydrogen cynide does not add to an anactive = bond but such addition can be ~~ch~~ acheived in the presence of acid catalyzed dicobalt.

$$R-CH=CH_2 + HCN \xrightarrow{Co_2(CO)_8} R-\overset{CN}{\overset{|}{C}H}-CH_3$$

cobalt catalysed alkyne cyclo addition :

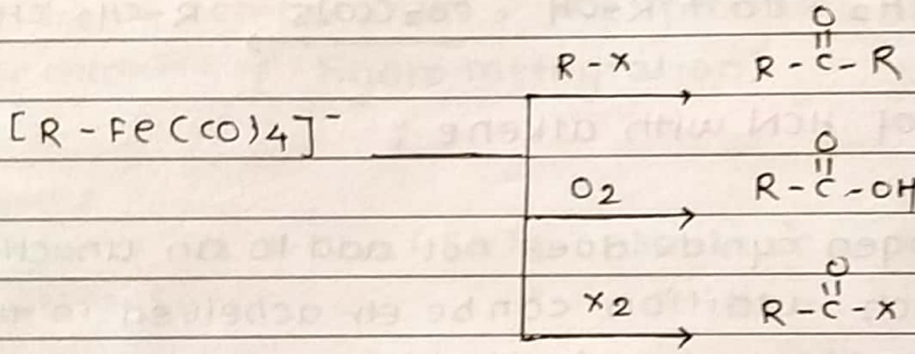
The reactn allows the coupling of an acetylene, an olefin & carbon monoxide in one step. The reaction is called "pauson khand" reactn.





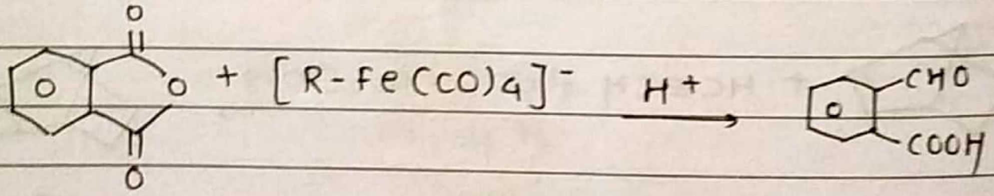
27> Fe :-

- Nucleophiles carbonyl metalates react readily with organic electrophiles gives alkyl, aryl or acyl complexes.
- A particularly convinient reagent which is easily accessable on a large scale is $Na_2[Fe(CO)_4]^{\cdot}$. It's alkyl derivatives have found numerous synthetic applications & it resembles grignard reagents. some of the imp application of $[R\text{-}Fe(CO_4)$ (collmans reagent) are as follows.



collmans reagent is prepared from penta carbonyl ion with sodium amulgum we get a complex $Na_2[Fe(CO)_4]$ further on reaction with alkyl halide gives collmans reagent.

$$Fe(CO)_5 \xrightarrow{NaHg} Na_2[Fe(CO)_4] \xrightarrow{R-X} [R\text{-}Fe(CO)_4]^-$$



A wide variety of aldehydes are also synthesized from carboxylic acid anhydride & collmans reagent

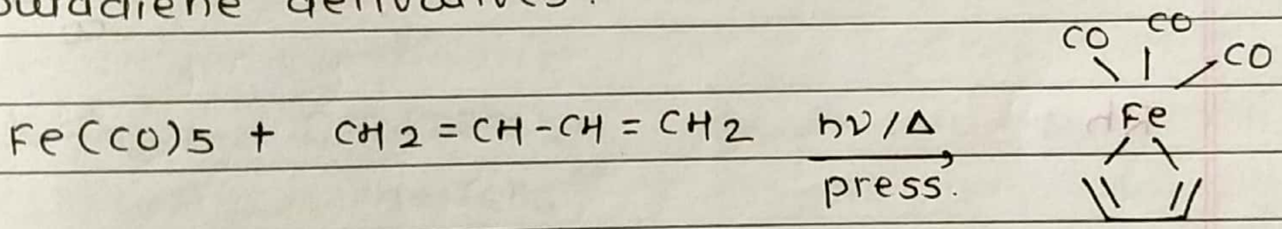
Hydromethylation of alkene :-

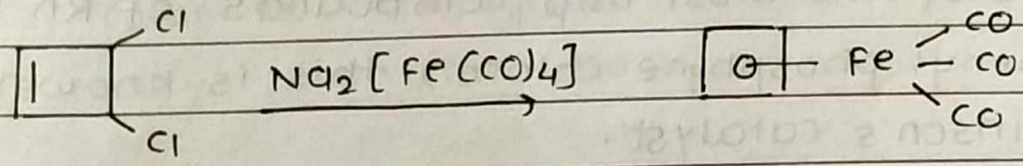
Alkenes undergo hydromethylation with CO & H_2O in the presence of Iron pentacarbonyl & an amine.

$$R-CH=CH_2 + 3CO + 2H_2O \xrightarrow[Et_3N]{Fe(CO)_5} R-CH_2-CH_2-CH_2-OH + 2CO_2$$

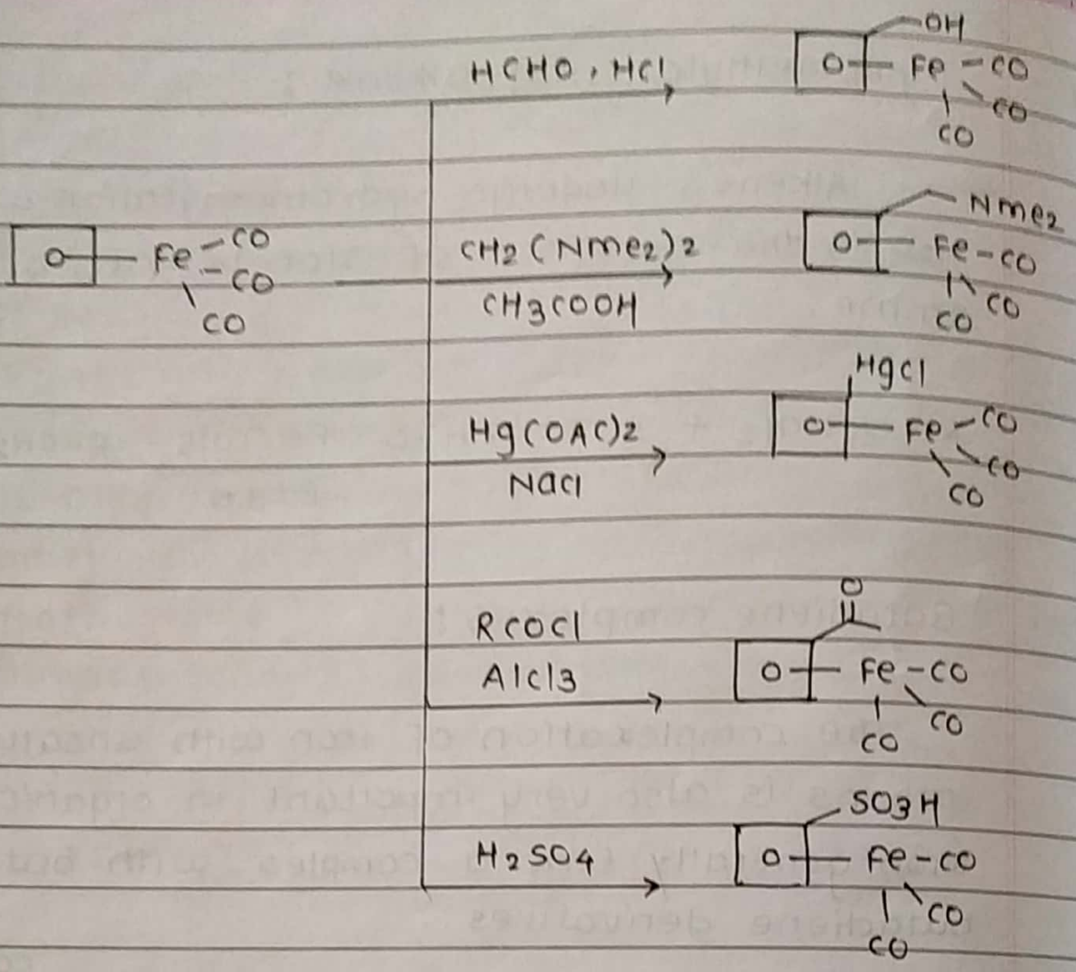
Butadiene complexes :-

The complexation of iron with unsaturated hydrocarbons is also very important in organic synthesis. Iron generally form a complex with butadiene & butadiene derivatives.





The most imp complex of this category is with cyclobutadiene.
cyclobutadiene is antiaromatic thus it contains localized d.b. this distortion while minimizing antiaromatic overlap introduces more strain than the mol. would contain.
The unstable diene form a stable complex with iron.



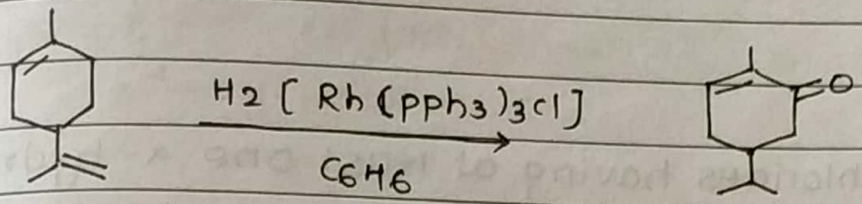
3. Rh :-

- one of the most imp compounds of Rh is tri (triphenyl phosphyne chloro) this is known as willkinson's catalyst.
- willkinson's catalyst is prepared by heating Rhodium chloride with triphenyl phosphyne in boiling ethanol

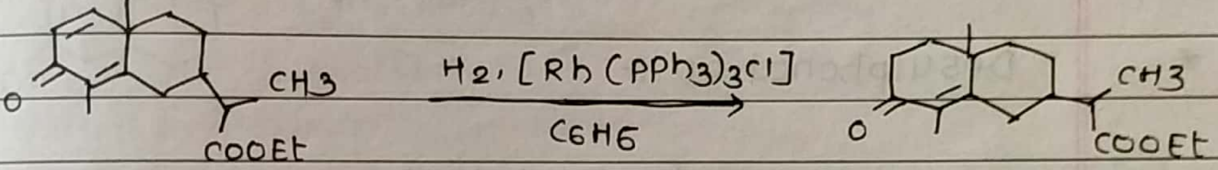
$$RhCl_3 \cdot H_2O \xrightarrow[\text{boiling ethanol}]{\text{Excess} \cdot Ph_3P} [Rh(PPh_3)_3Cl]$$

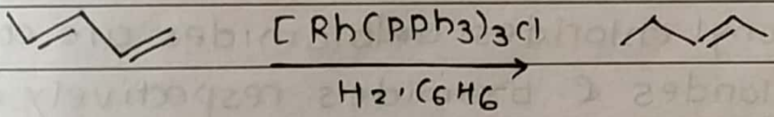
* Hydrogenation of alkenes & alkynes :-

Mono & disubstituted d. bonds are reduced much more rapidly than tri or tetra substituted d. bonds permiting the partial reductn of d·b containging diff kinds of = bonds.

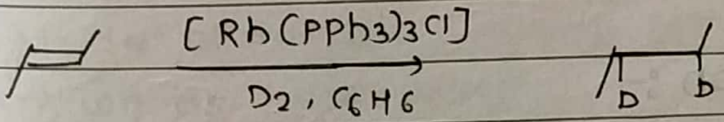
1. 

2. $C_6H_5-CH=CH-COOEt \xrightarrow[H_2,\ C_6H_6]{[Rh(PPh_3)_3Cl]} C_6H_5-CH_2-CH_2-COOEt$

3. 

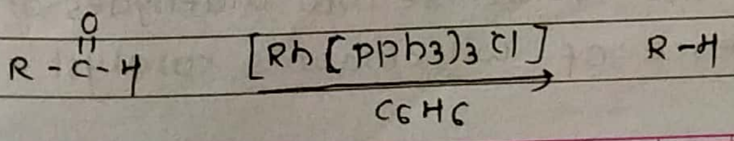
4. 

If comp. is conjugated diene then reductn is generally 1,4 - addn reactn

5. 

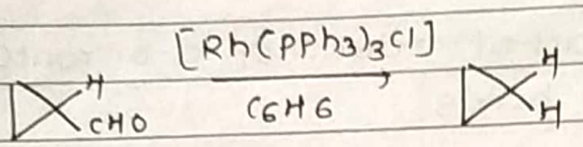
* Decarbonylation :

Aldehydes undergo decarbonylation in presence of willkinson's catalyst.



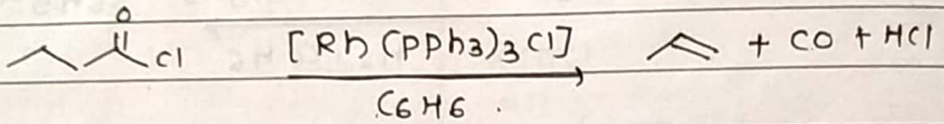
$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[C_6H_6]{[Rh[pph_3)_3Cl]} R-H$

2.



*

Acid chlorides having at least one α-hydrogen undergo decarbonylation & dehydrohalogenation on heating with willkinsons catalyst



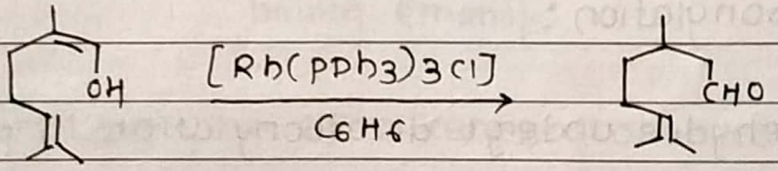
* Desulphonation :-

1. $Ar-SO_2-Cl \xrightarrow[C_6H_6]{[Rh(PPh_3)_3Cl]} Ar-Cl$

- Aryl sulphonyl chlorides and bromides are converted into aryl chlorides & bromides respectively on heating with willkinson catalyst.

2. $Ar-SO_2-Br \xrightarrow[C_6H_6]{[Rh(PPh_3)_3Cl]} Ar-Br$

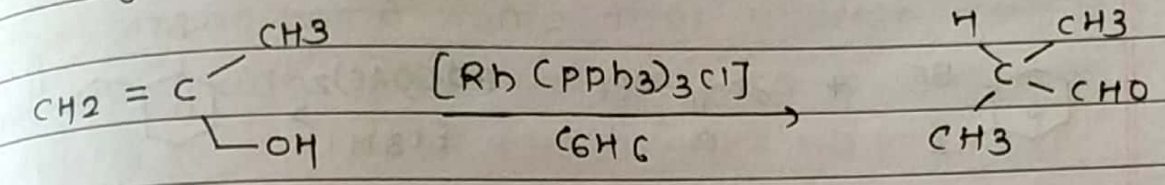
* Isomerisation :-



Allyl alcohols isomerise into aldehydes or ketones in the presence of willkinson's catalyst.

Geraniol isomerises in the presence of willkinson's catalyst.

2)



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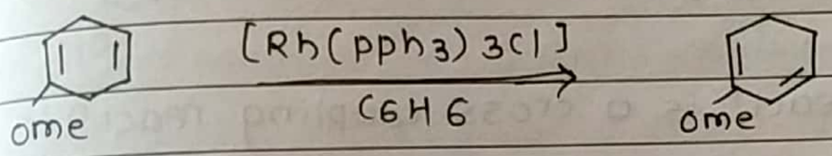

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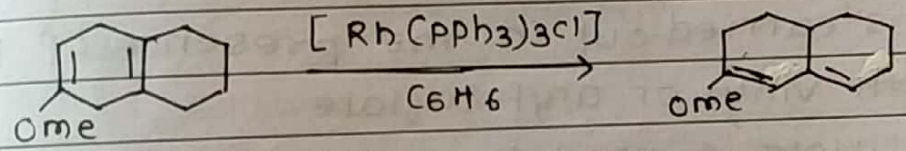
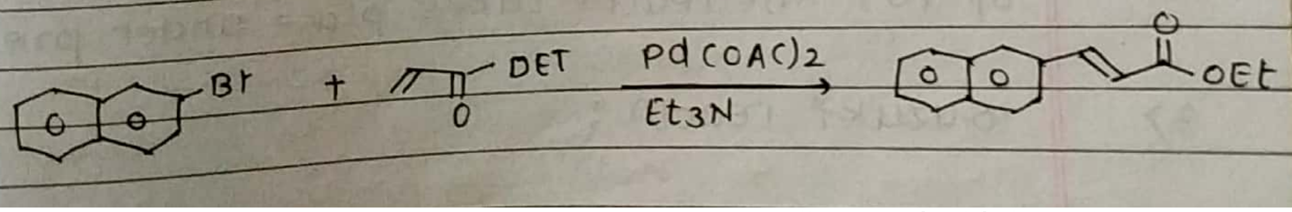


unconjugated diene Isomerise to conjugated diene in the presence of willkinsons catalyst.

4. pd :-

1. Heck reactn :- It is a coupling reactn betn halide & alkene in the presence of pd complex. oxidative addn, carbopaladation followed by β-hydride elimination which leads to an alkene is known as heck reactn.

1. $R-X + R-CH=CH_2 \xrightarrow[Base]{pd(0)} R-CH=CH-R$

2. 

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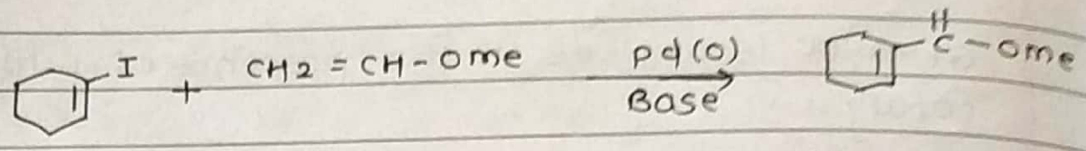

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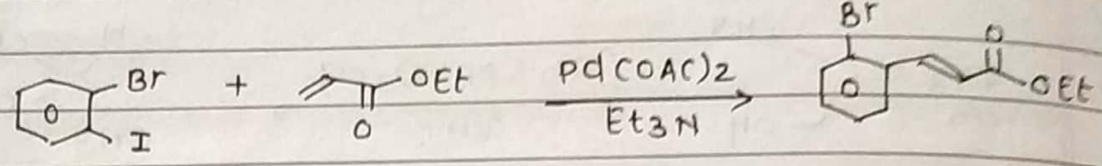
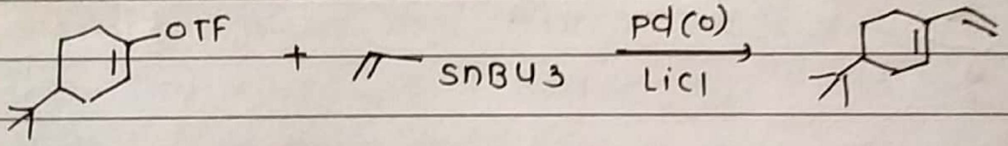


2) Stille reaction :-

Stille reactⁿ is a cross coupling reactⁿ in which the organo metallic comp is alkenyl trialkene or alkynyl trialkene stannane.

- Reactⁿ is carried out in the presence of Pd-complex with vinyl or aryl triflate.
- When triflate is used then reactⁿ is carried out in the presence of LiCl.

1.


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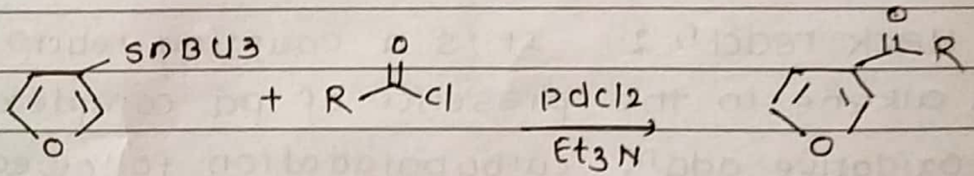

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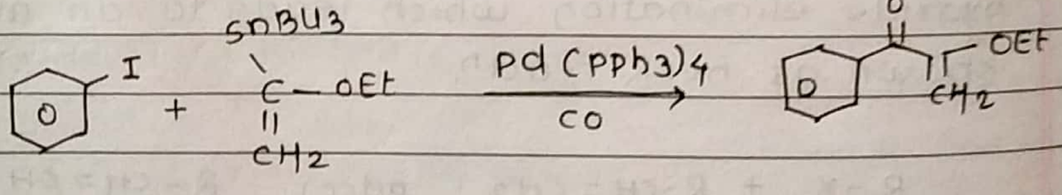
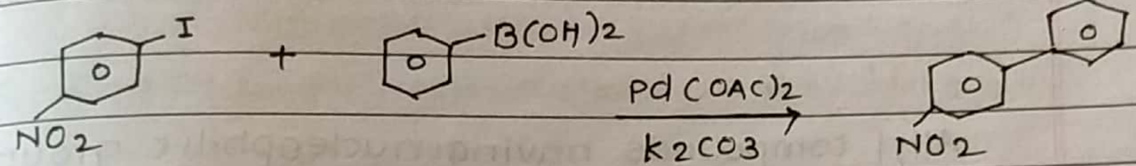


carbonylation reactⁿ also takes place in the presence of CO, the reactⁿ takes place under pressure

3) Suzuki reactⁿ :

It is a cross coupling reactn in which organometallic component is an aryl or vinyl boron compound. The organo boron comp. that undergo coupling include boronic acids, boronate esters & boranes.

1.



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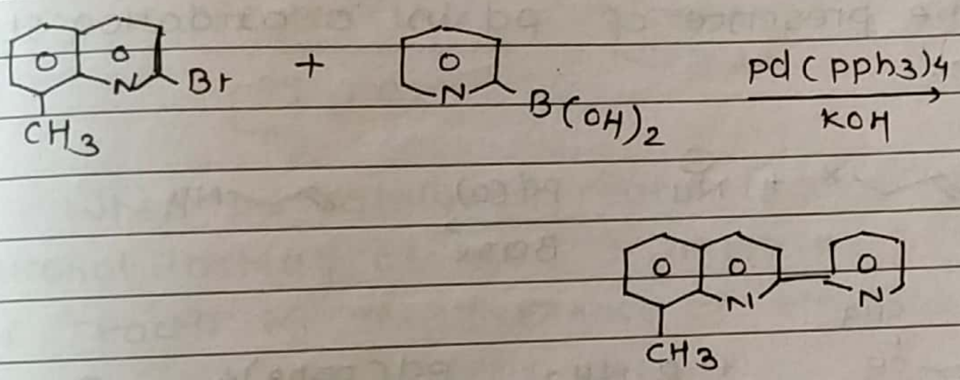


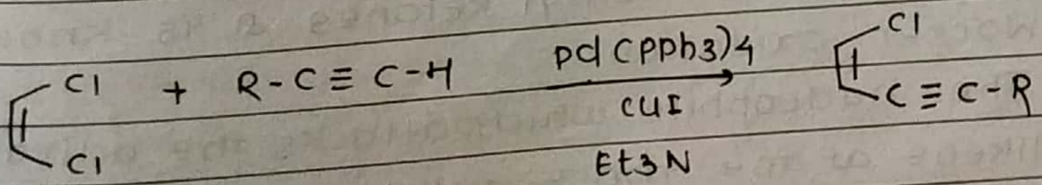
* sonogashira coupling :-

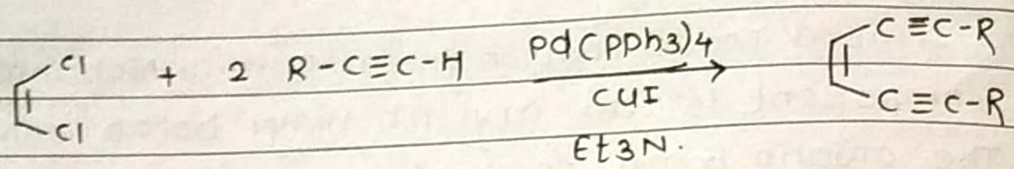
The coupling of terminal alkynes with aryl or vinyl halides in the presence of pd in 'o' oxidation state is known as sonogashira. The reactn is carried out in the presence of CuI as a co-catalyst & medium of the reactn is basic

1.

$$Ar-X + R-C\equiv C-H \xrightarrow[\substack{CuI\\Et_3N}]{pd(0)} R-C\equiv C-Ar$$

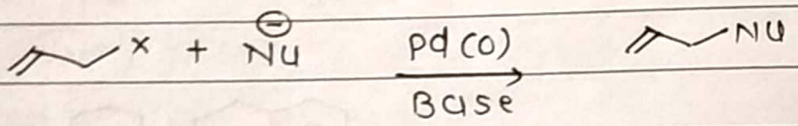
2.

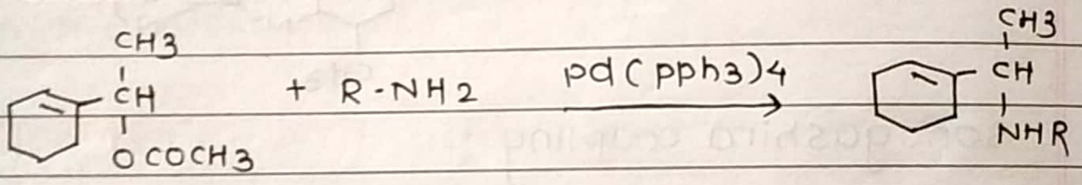


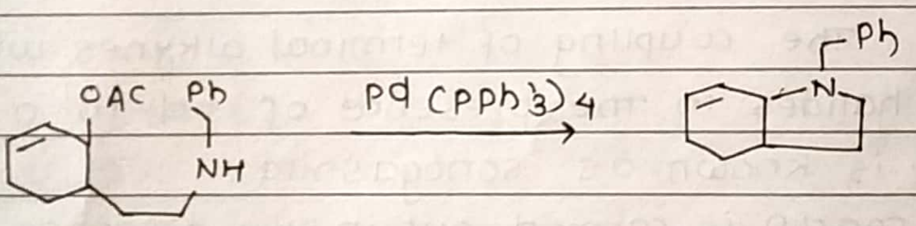


Nucleophilic substitution reaction of allylic

Allyl compounds having nucleophilic group as leaving grp gives nucleophilic substitution reactn in the presence of pd in 'o' oxidation state & base.



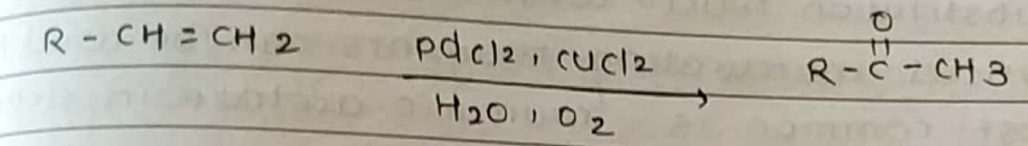




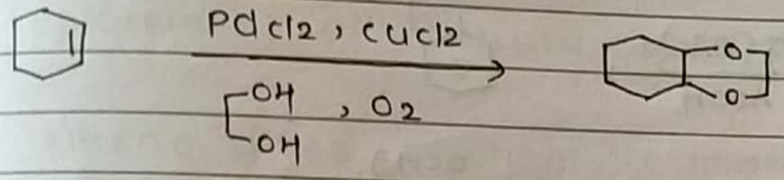
Wacker oxidation :-

The combination of reagents pdcl2, cucl2, H2O & O2 has been used to oxidised terminal vinyl grps to methyl ketones & is known as wacker oxidation.

The nucleophile which attacks the activated alkene at the more substituted end in oxipaladation state β- hydride elimination from resulting paladium complex releases enol which is rapidly converted into carbonyl comp. Thus the wackers process involve oxidation of terminal alkene to methyl ketone.



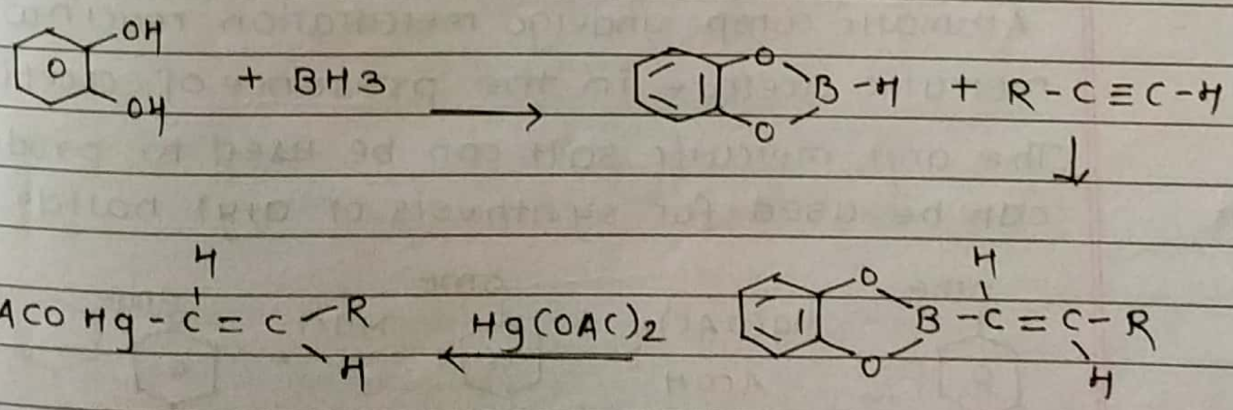
$$R-CH=CH_2 \xrightarrow[H_2O,\ O_2]{PdCl_2,\ CuCl_2} R-\overset{O}{\overset{||}{C}}-CH_3$$



When pd catalyzed reactn is carried out in alcohol instead of H_2O, vinyl ethers are formed & reactn in the presence of ethylene glycol gives cyclic acetals in good yield.

Mercury (Hg):-

Alkenyl mercury compounds can be prepared by hydro boration of an alkyne with catechol borane followed by reactn with mercury acetate.



- one of the most imp. general methods for the preparation of organo mercuric compound is mercuration 'reactn i.e formation of C-Hg bond.
- Hg + cation is electrophile & it gives electrophilic substitution reactn with aromatic comp. various murcurating reagents can be used but most common is 'murcuric acetate in acetic acid.

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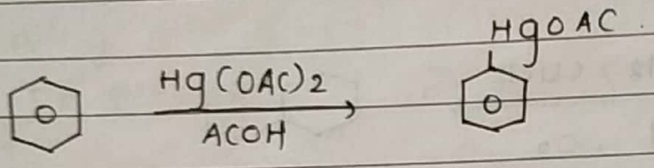

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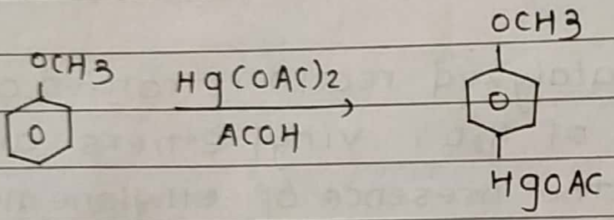
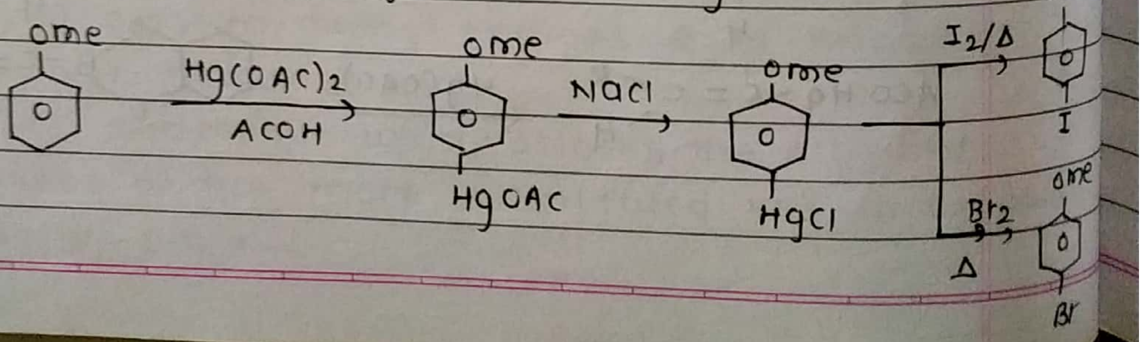
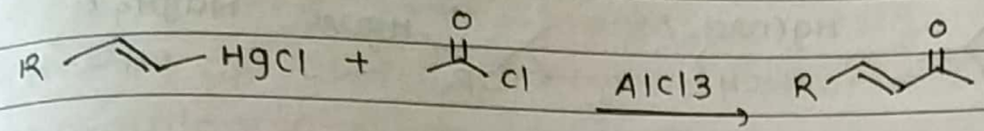


Electrophilic substitution reactn i.e by

- organo-mercuric comp. are very weak nucleophile & react only with very reactive electrophile such as $X^{\oplus}$ or $R-\overset{O}{\overset{\|}{C}}{}^{\oplus}$

- Aromatic comp. undergo mercuration reactn with mercuric acetate in the presence of acetic acid. The aryl mercuric salt can be ~~used to produced~~ can be used for synthesis of aryl halide.



2. 

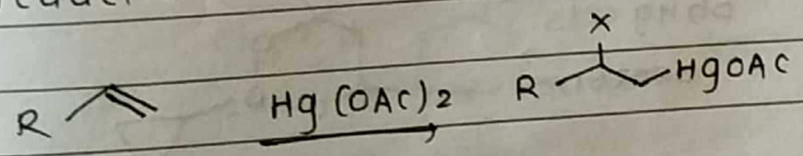
organomercury does not reacts with ketone or aldehyde but lewis acid causes reactn with acyl chloride.

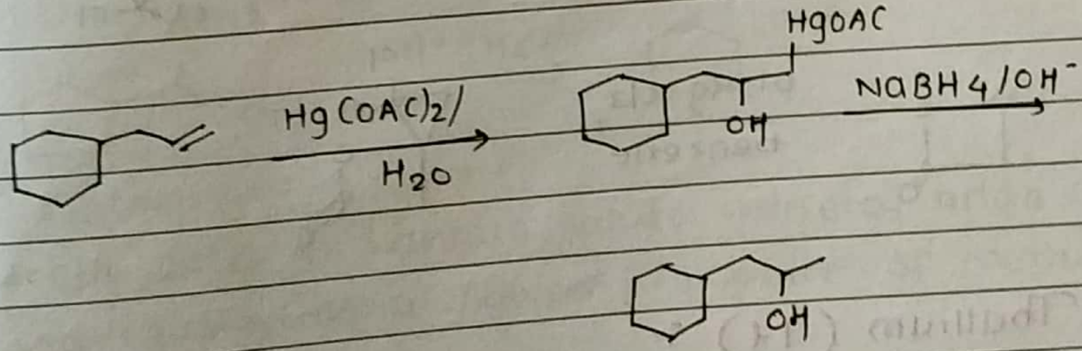
Alkenyl mercury comp gives carbonyl comp with acyl chloride

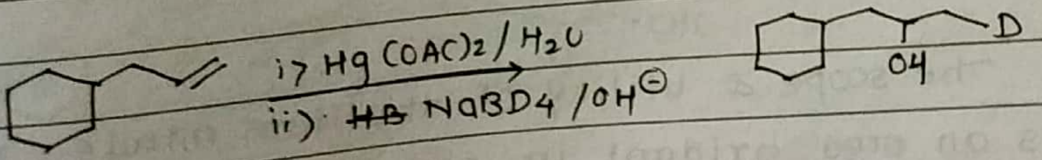
* Replacement of mercury by hydrogen :-

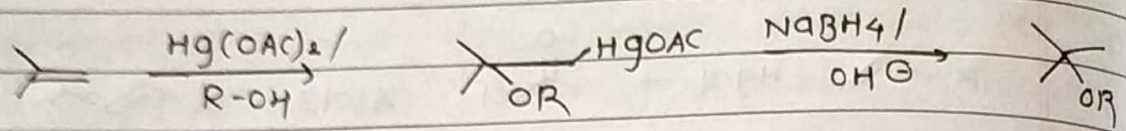
Alkene gives electrophilic addn reactn with murcuric acetate in the presence of protic solvent to give addn product.

The reactn is known as solvo mercuration. several methods are available for demercuration but most generally used are protonolysis & metal-hydride reduction.

1. 

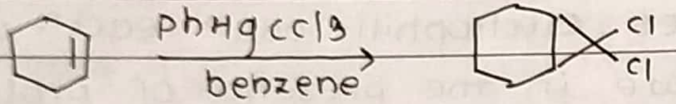
2. 

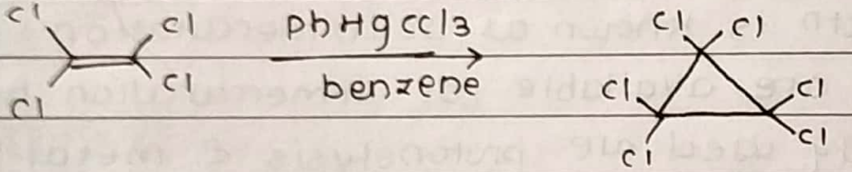
3. 

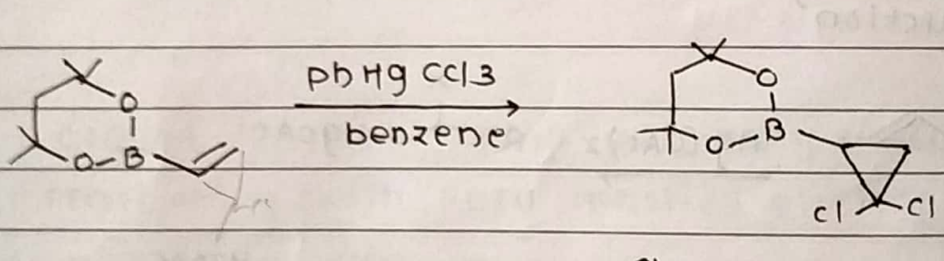
4. 

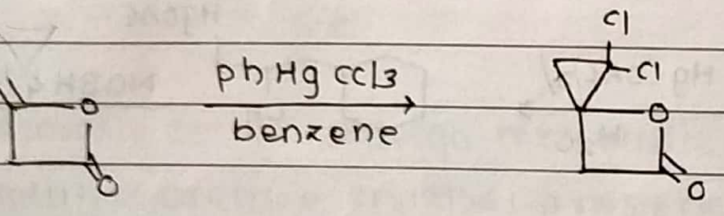
* cyclopropanation of alkenes :-

- A wide & representative set of alkene reacts with phenyl trichloromethyl mercury to afford Gem. dihalo cyclopropanes in good yield.
- Reactions are carried out using dibenzene as a solvent.

1. 

2. 

3. 

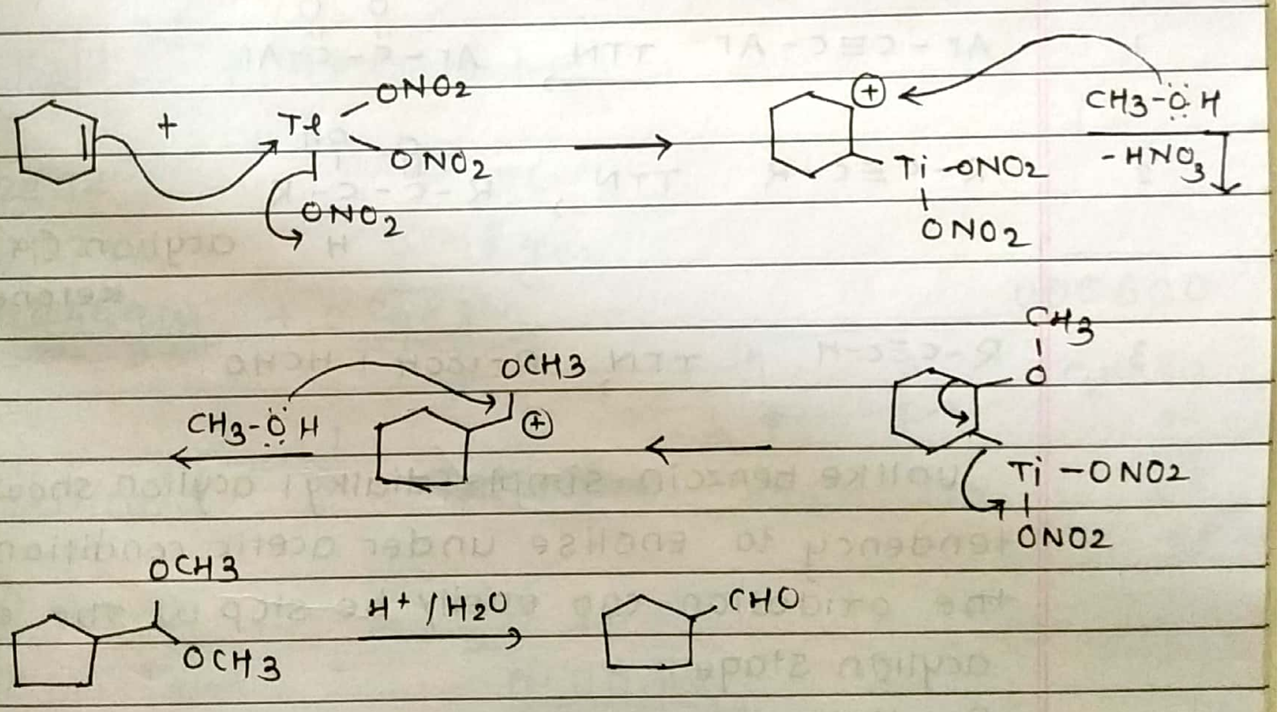
4. 

* Thallium (Tl) :-

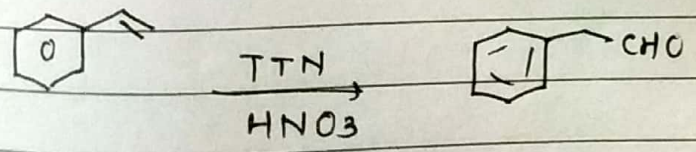
The scope & utility of thallium nitrate (TTN) as an orga oxidant in organic synthesis.

TTN is used for the oxidation & oxidative rearrangement of olefin, acetylene, ketones & comp. containing C-N double bond.

A soln of TTN in methanol is a convinient reagent for the direct oxidative rearrangement of many olefins to aldehydes & ketones.
oxidation of cyclohexene gives initially cyclopentane carboxaldehyde dimethyl acetal from which the free aldehyde may be obtain in excellent yield by acid hydrolysis.



Acetic acid & various dilute mineral acids can be used equally as a solvent in place of methanol.



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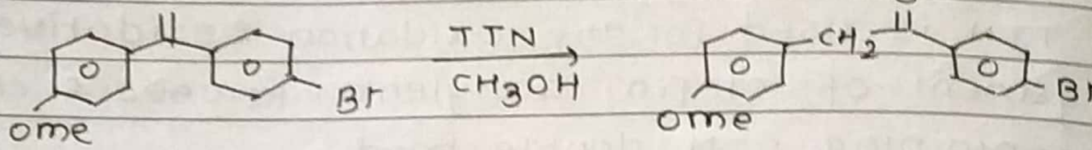
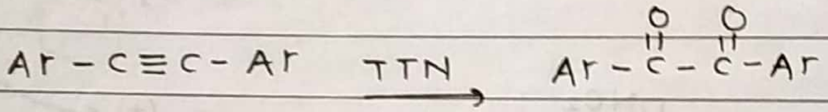


* oxidation of acetylenes :-

Thallium is Isoelectronic with mercury & therefore we expected to catalyzed the hydration of acetylene.

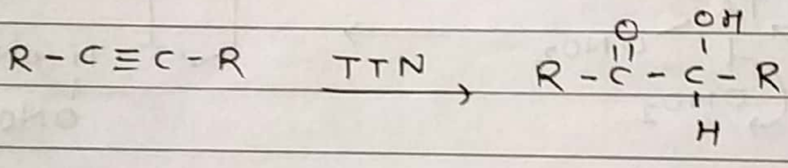
- We have examine the reactions of di aryl acetylenes, di atkyl aryl acetylenes. dialkyl acetylenes & mono alkyl acetylenes with TTN under various conditions gives diff. products.

1.



$$Ar-C\equiv C-Ar \xrightarrow{TTN} Ar-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ar$$

2.



$$R-C\equiv C-R \xrightarrow{TTN} R-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}-R$$

acylion (α-hydroxy ketone)

3. $R-C\equiv C-H \xrightarrow{TTN} R-COOH + HCHO$.

- Unlike benzoin simple dialkyl acylion show little tendency to enolise under acetic condition & hence the oxidation can easily be stop at the arylal acylion stage.

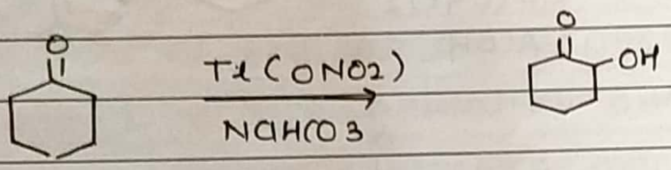
- Reactions of monoalkyl acetylenes with TTN results oxidation with overall cleavage of C-C ≡ bond & gives carboxylic acid & formaldehydes.

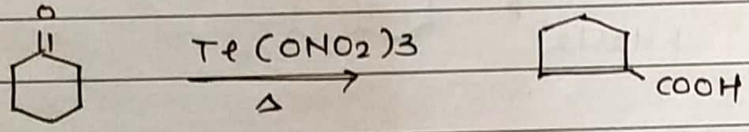
Date :

* oxidation of carbonyl :-

If oxidation is allowed to proceed untill all of the TTN is consumed & the reactn mix then treated with dil. bases acylions are obtained (α-hydroxy ketone) in high yield.

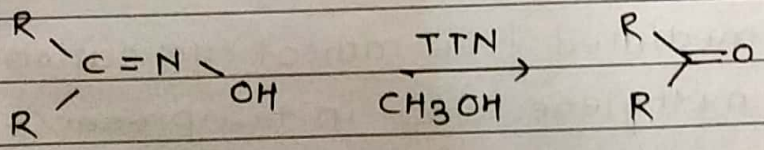
- If on the other hand the acidic reactn medium is gently heated for few min. the corresponding cyclopentane carboxylic acids are obtain.





* oxidation of comp containing C-N double bond :-

The reactions of a comp containing C-N double bonds with TTN in methanol results in the formation of parent carbonyl comp in very high yield.



* silicon (Si) :-

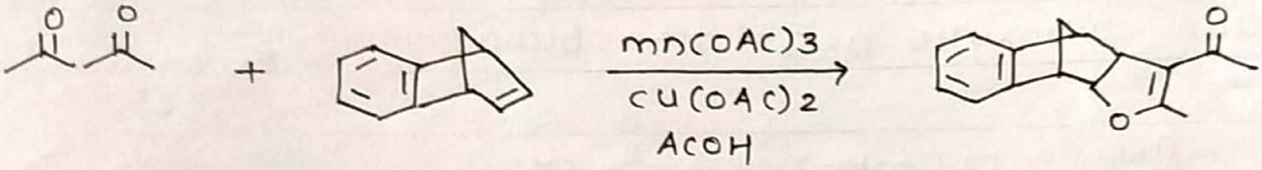
1> me3 SiI

2> peterson synthesis.

* Manganese (Mn):-

1) oxidative cyclisation of unsaturated comp with active methylene comp :-

- The oxidative cyclisation of β-dicarbonyl comp. to benzo nonbornadi in the presence of manganese acetate & $Cu(OAc)_2$ in acetic acid gives a cyclic / cyclo addition product.

i)


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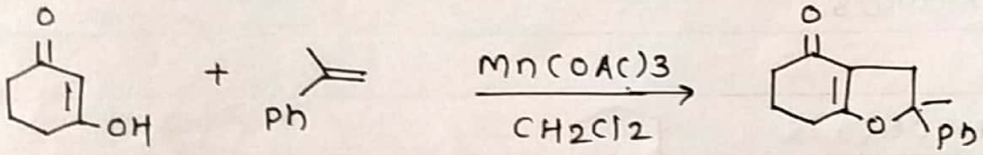

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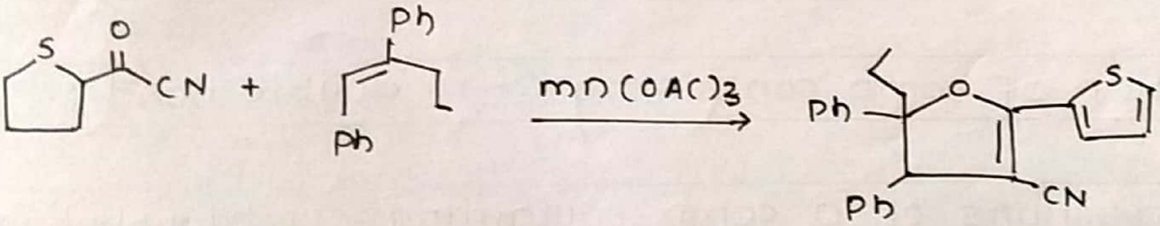
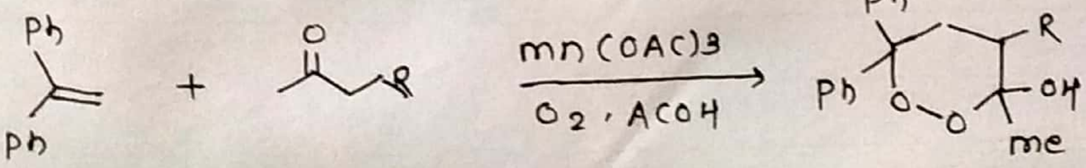


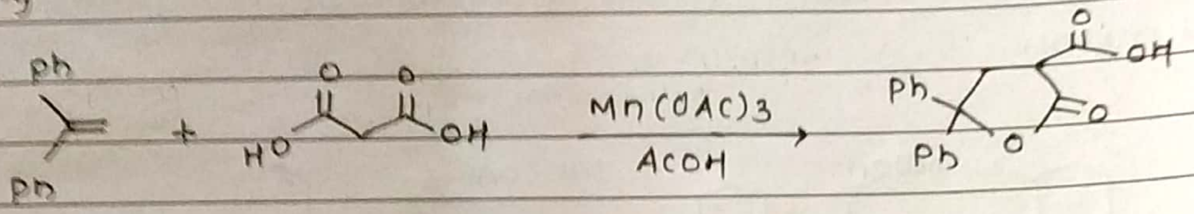
2) cycloperoxidation reaction carried out in the presence of oxygen :-

- Manganese acetate mediated free radical cyclisation of alkene with active methylene comp. in the presence of oxygen to give cyclic peroxide.



3) Manganese acetate mediated lactonisation reactⁿ :-

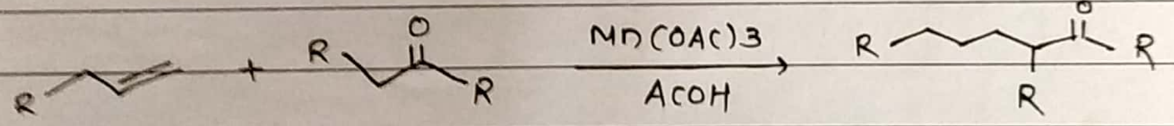
oxidative add^n of alkenes with malonic acid in the presence of manganese acetate gives a 5-mem. lactone ring.



Manganese acetate mediated alkylation react^n:-

A general e.g for manganese acetate mediated alkylation is the oxidative add^n of aldehyde & ketone to alkene, in this process manganese acetate generated α-carbon radical of the carbonyl comp is added to d.b of the alkene with proton abstraction resulting in the formation of corresponding alkylated carbonyl comp.

1.



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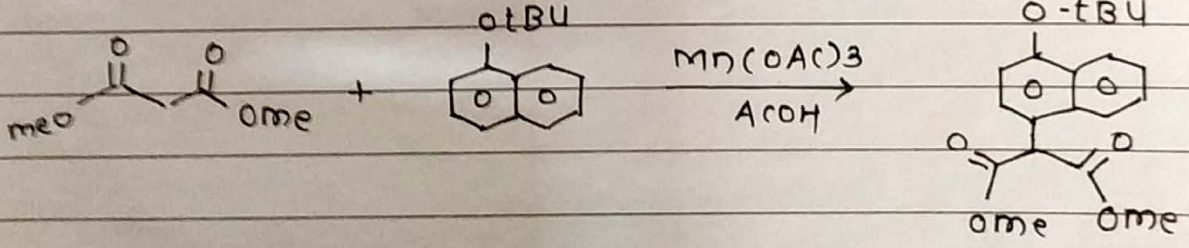

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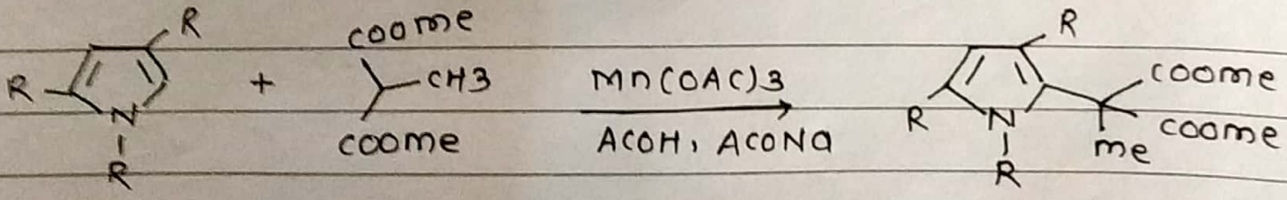

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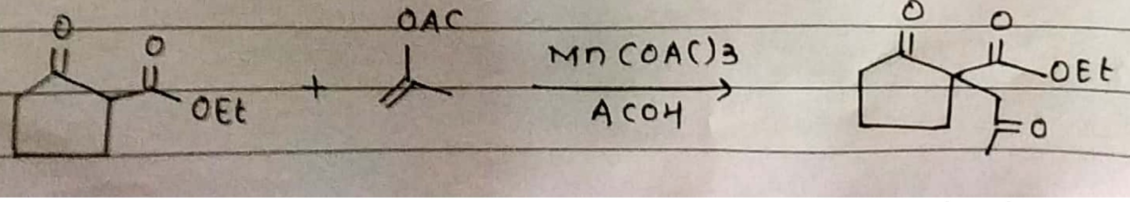
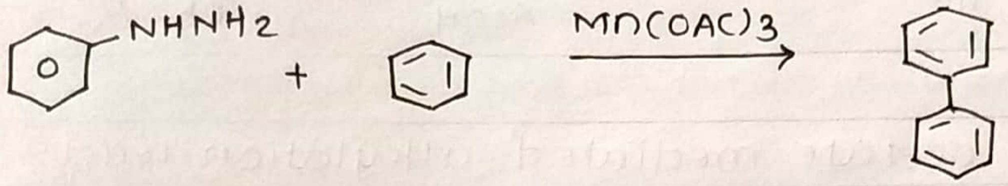


* Manganese acetate mediated coupling reactn :-

synthesis of biaryls starting from aryl hydrazine & aromatic solvent in the presence of manganese acetate.

1.



2.