

Study of

III(A)

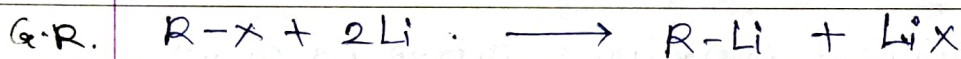
Organometallic Compound

The Organo lithium compounds characterized by a carbon lithium bond & are important in organic synthesis. Organo lithium compound shows similar reactivity as Grignard reagent, they are more reactive than Grignard reagent, Lithium is less electronegative than carbon & carbon lithium bond is polarised $\delta^- \text{C} - \text{Li}^{\delta+}$ as in Grignard reagent. The Organo lithium behaves both as nucleophile & a base.

Preparation - method of Organo lithium compounds

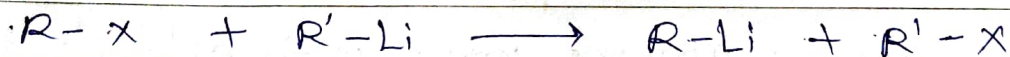
1) From alkyl or aryl halide.

The reaction of lithium metal at low temp with an alkyl or aryl halide to give alkyl lithium.



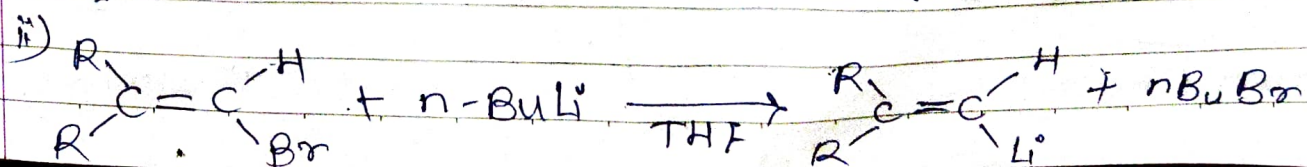
2) From halogen - metal - exchange method.

This method is useful for preparation of those Organo lithium reagent that can't be obtained from alkyl halide & metal directly. In this method an organic halide is treated with alkyl lithium.



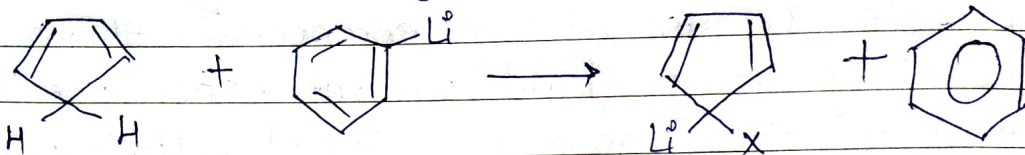
This method is useful for preparation of aryl lithium derivative.

ii) Phenyl lithium is prepared by treatment bromobenzene with n-butyl lithium.



3) From methylation

Compound containing acidic hydrogen can be easily converted into organo-lithium compounds.



Properties →

- i) Organo-lithium reagents are very reactive, powerful nucleophile & strong base.
- ii) These finds numerous applications in organic synthesis & better than grignard reagent.

Applications →

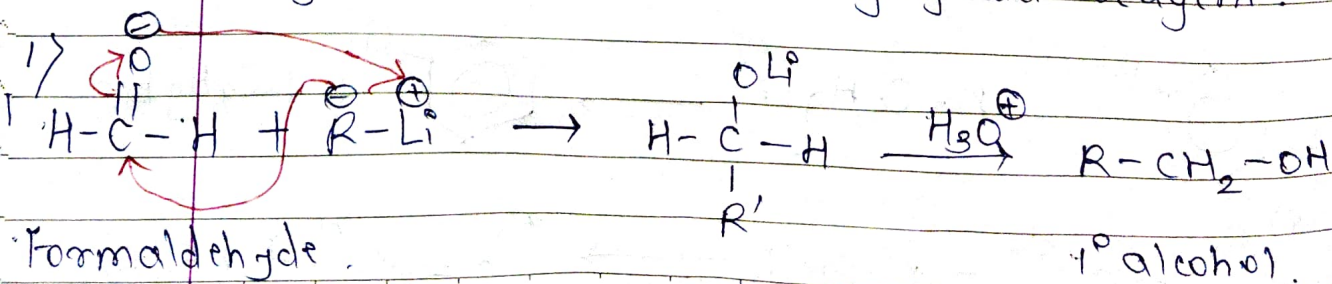
i) Synthetic applications :

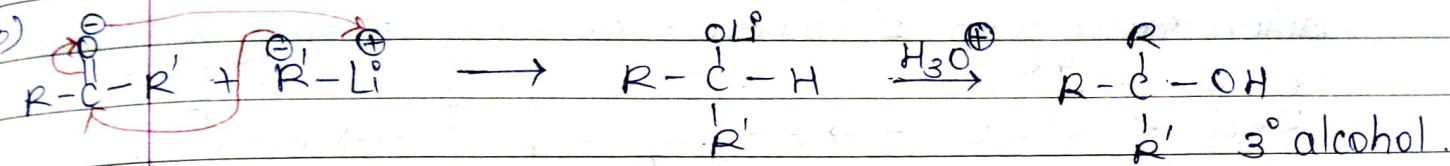
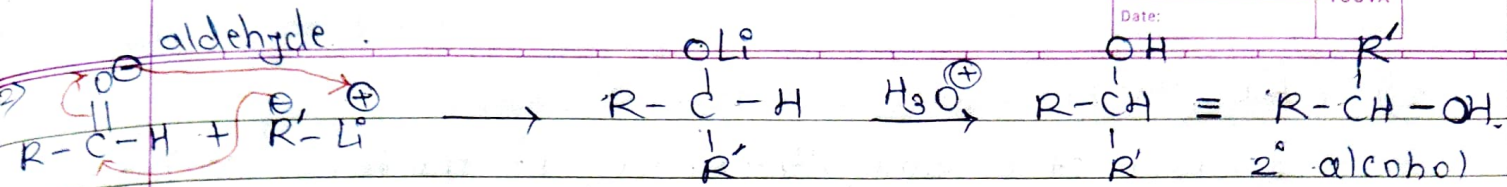
Reaⁿ with compound containing active hydrogen. Organo lithium reagent react with substrate having active hydrogen such as water, alcohol, amine (1°/2°) to give corresponding hydrocarbons.



2) Reaⁿ with carbon compounds.

Organo lithium reagent react with aldehyde to give 2° alcohol & with ketone to form 3° alcohol, & 1° alcohol are obtained by treatment with formaldehyde yields of alcohol. Organo lithium is reagent is better than grignard reagent.



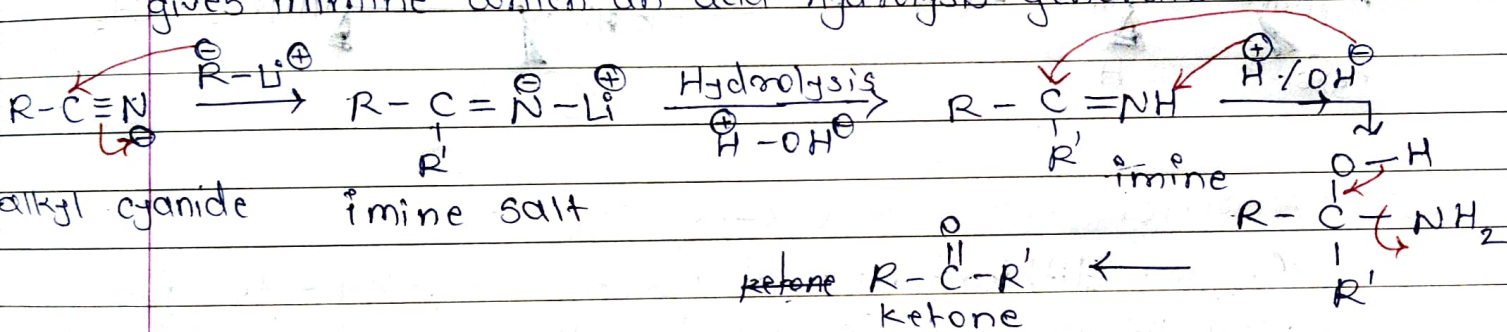


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3) Reaction with alkyl cyanide

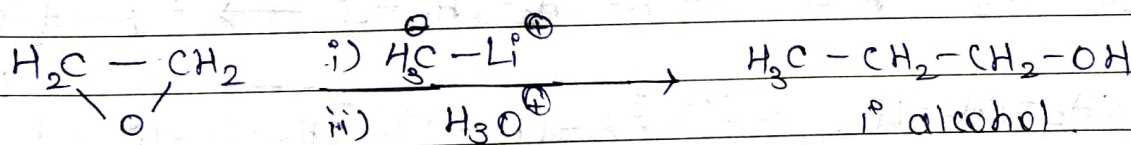
Like Grignard reagent organo lithium reagent also react with alkyl cyanide to give imine salt.

When the reagent is work up with water, protonation 1st gives imine which an acid hydrolysis generate the ketone.

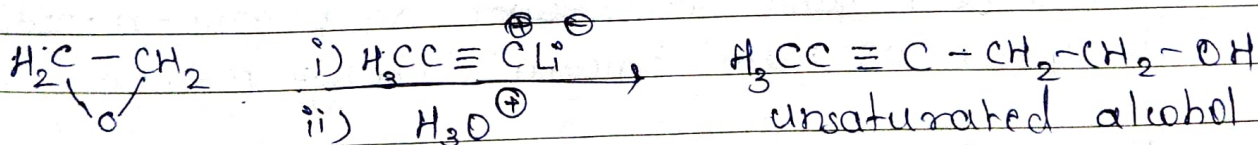


4) Reaction with epoxides

The epoxide react with organo-lithium reagent to give primary alcohol.



Use of unsaturated reagent gives unsaturated alcohol.



8) Nucleophilic displacement.

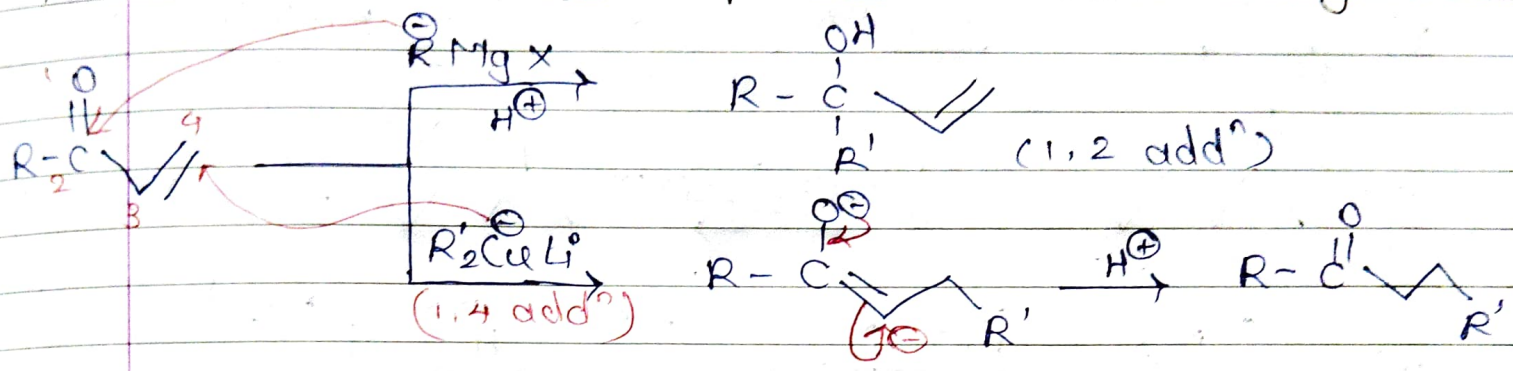
The halogen of alkyl halides can be substituted with alkyl group of the organo lithium reagent to give hydro carbon.



This reaction takes place by S_N2 mechanism as in case of Wurtz reaction.

Organometallic Compounds.

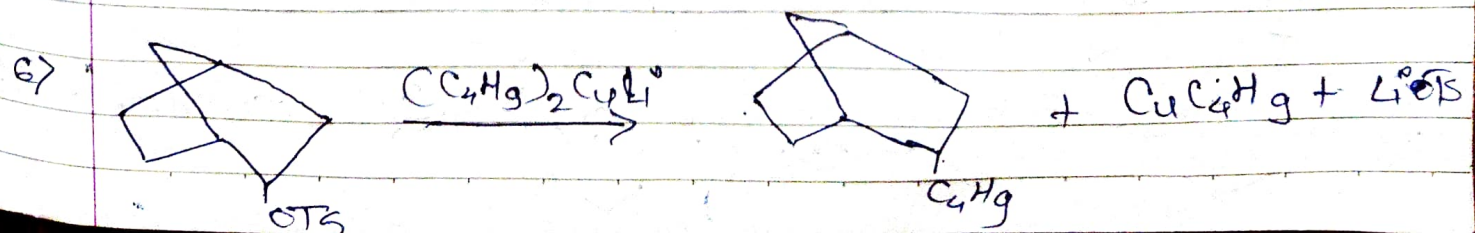
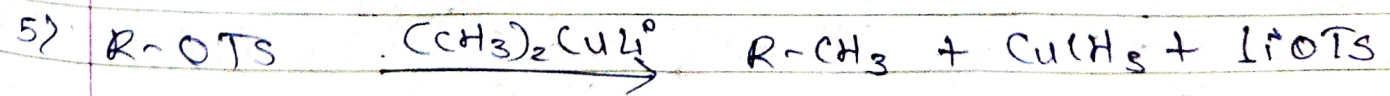
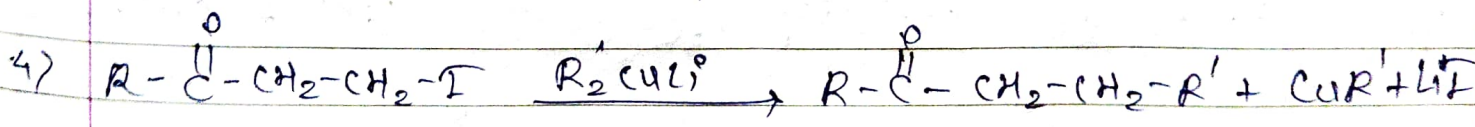
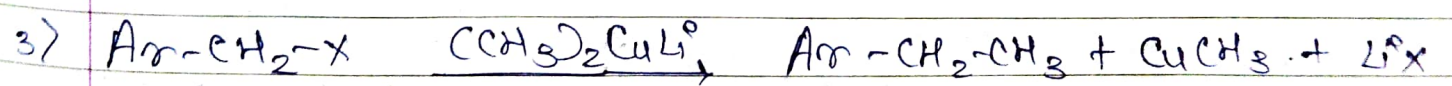
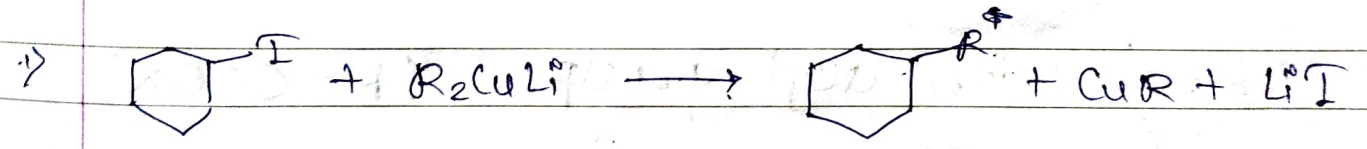
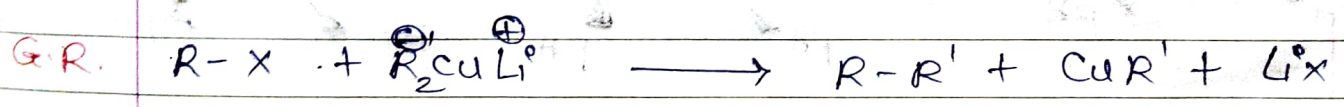
* Lithium dialkyl Cuprate (Gillman reagent)

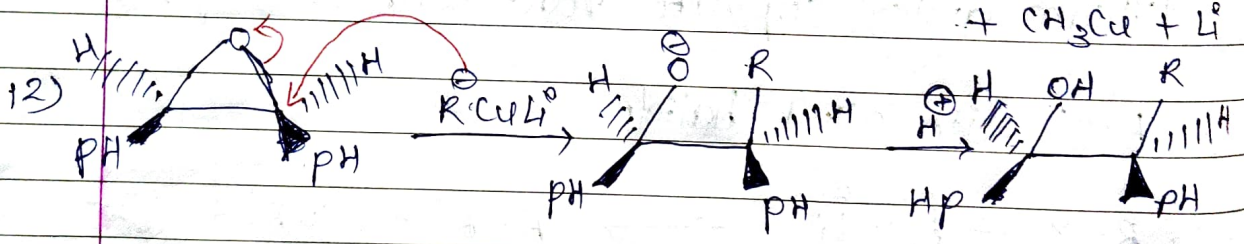
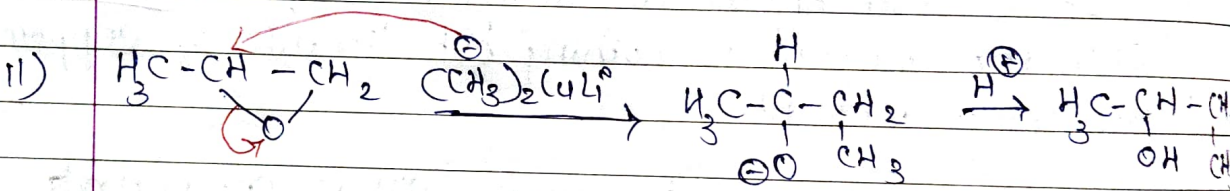
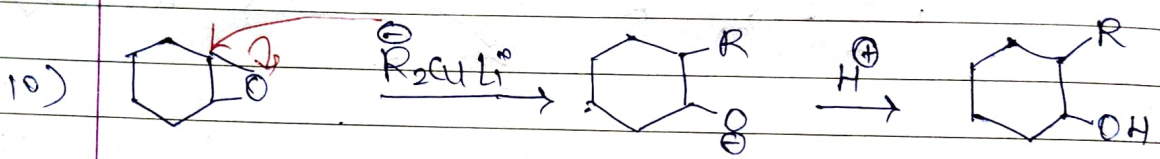
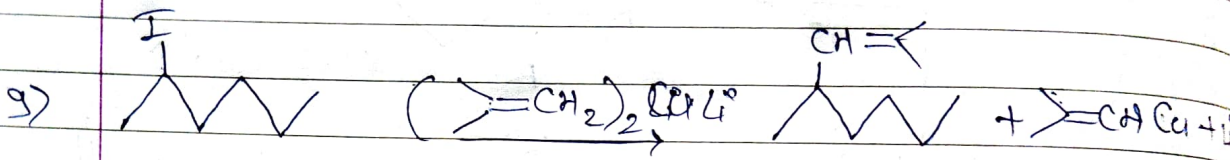
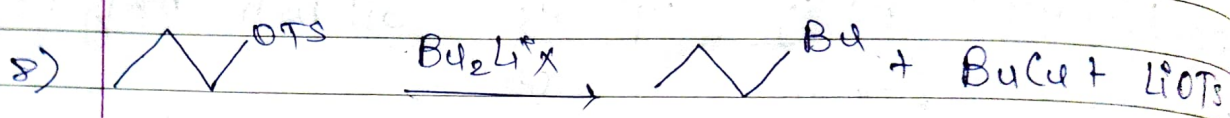
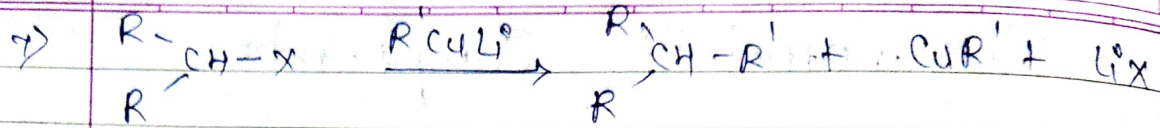


It is also known as Gillmann reagent R_2CuLi .
 Gillmann reagent is nothing but lithium & copper diorgano reagent.

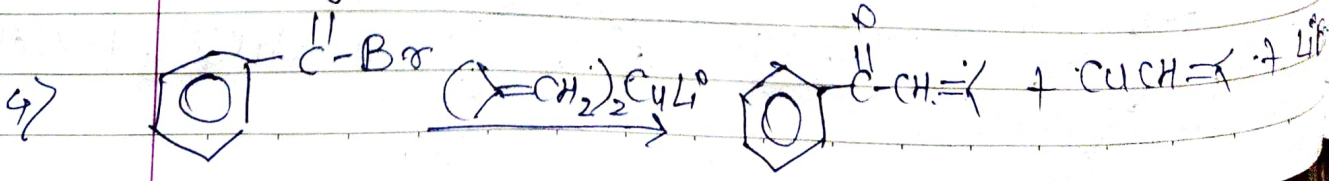
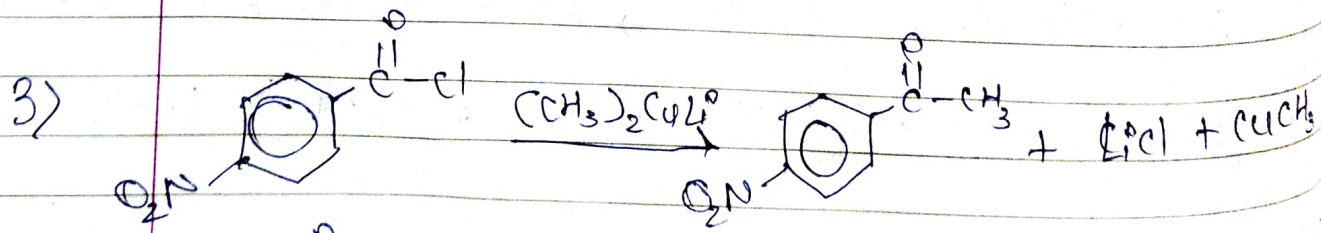
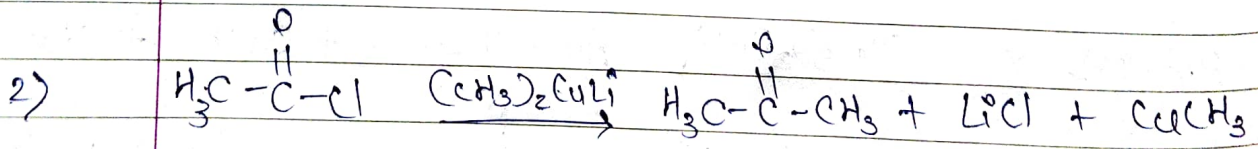
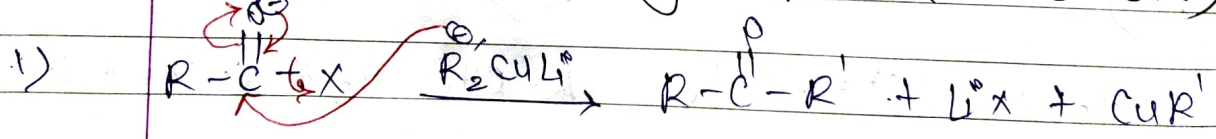
Lithium dialkyl cuprate react with γ compounds.

1) React with alkyl halide.

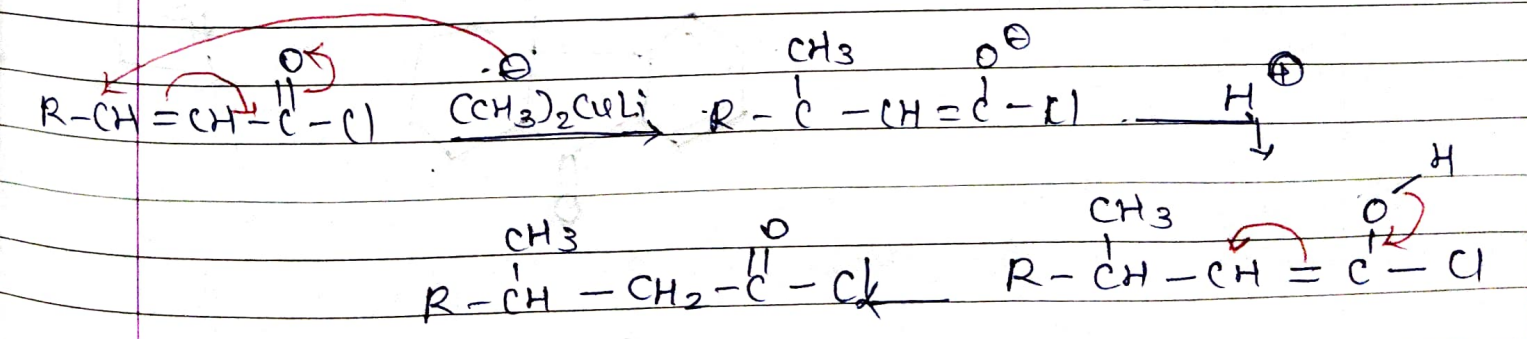
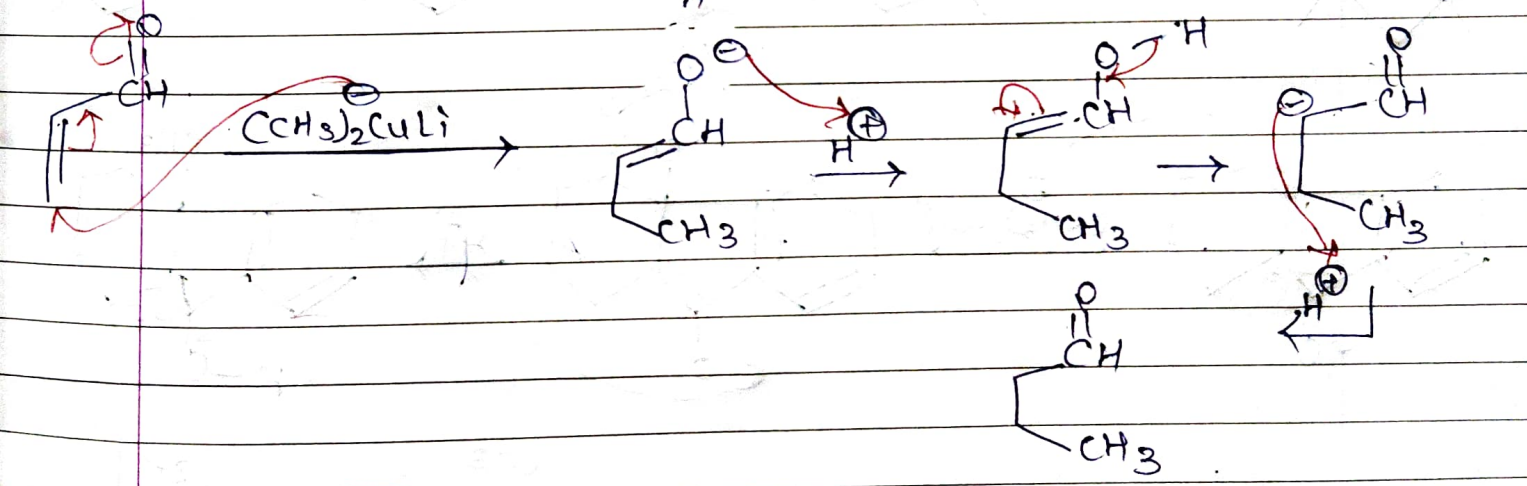
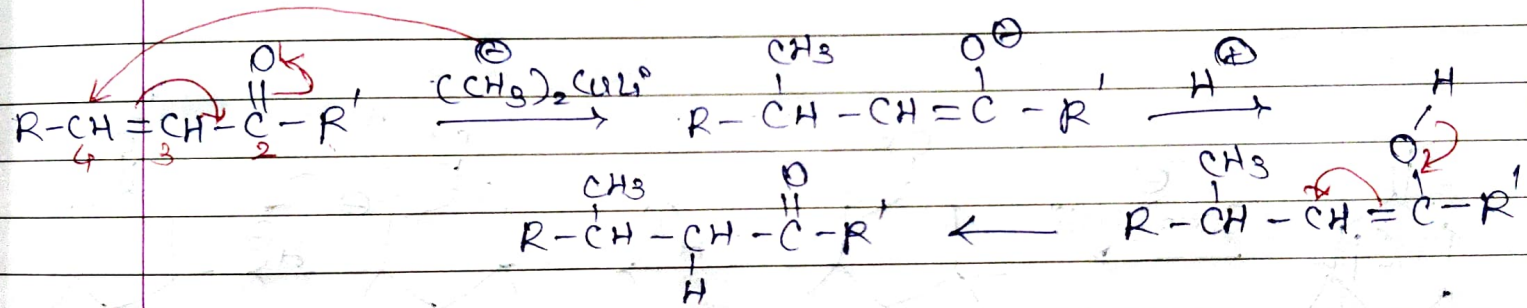
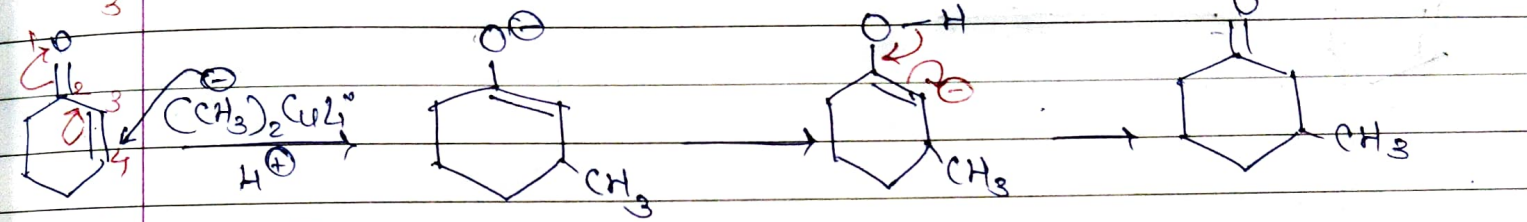
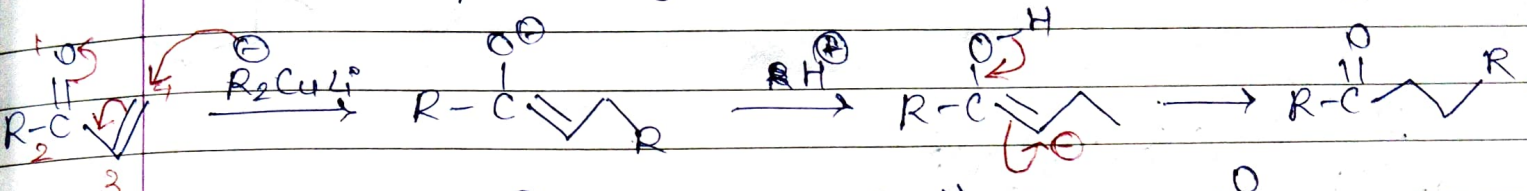


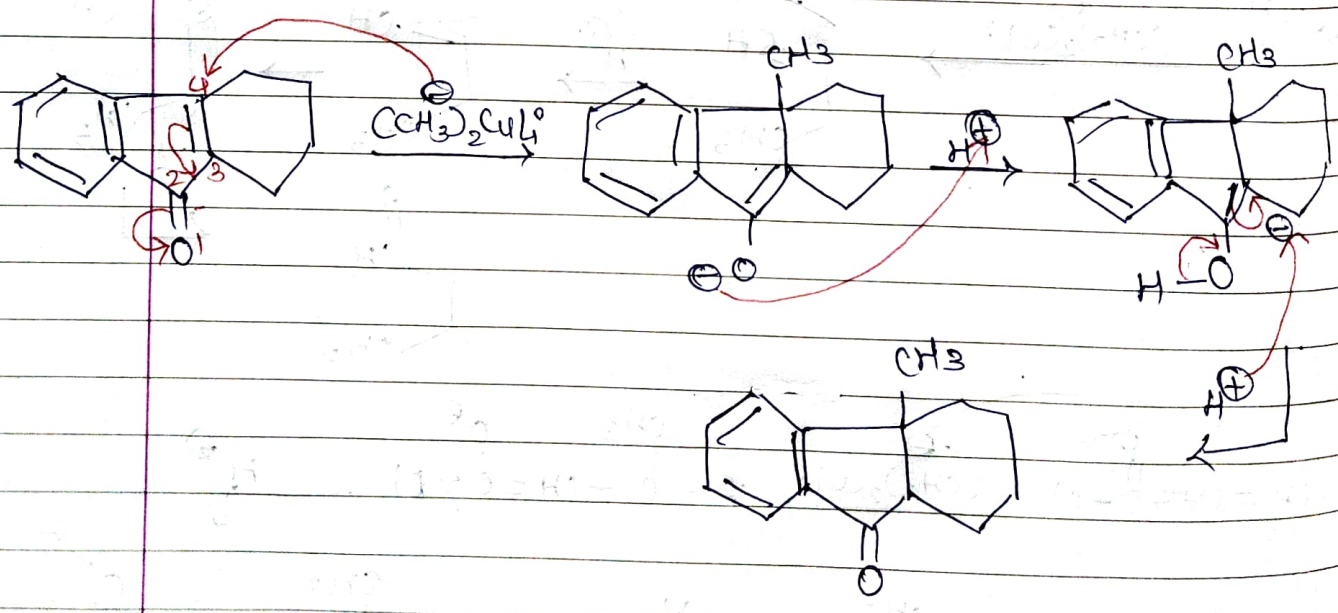
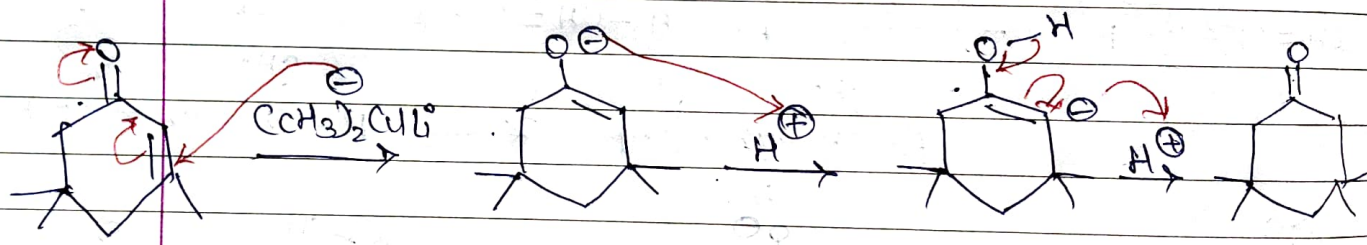
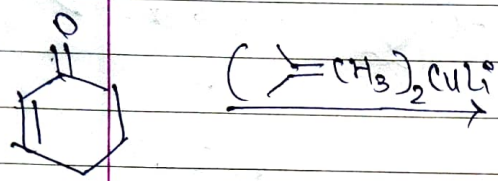
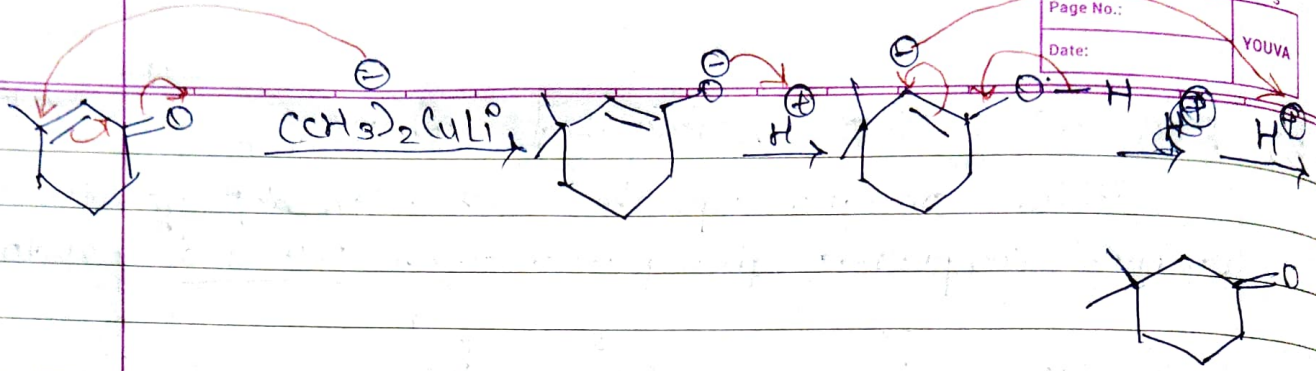


2) Redⁿ with acyl group (R-C=OX)

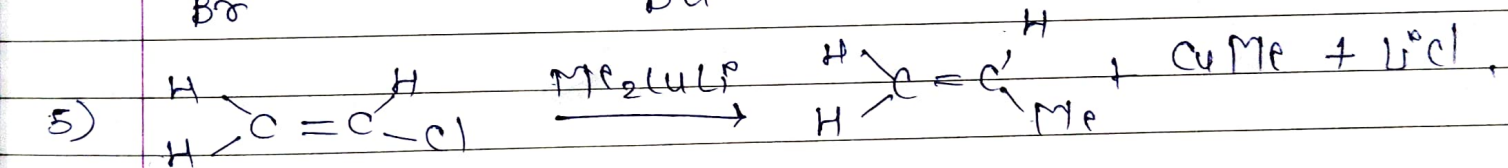
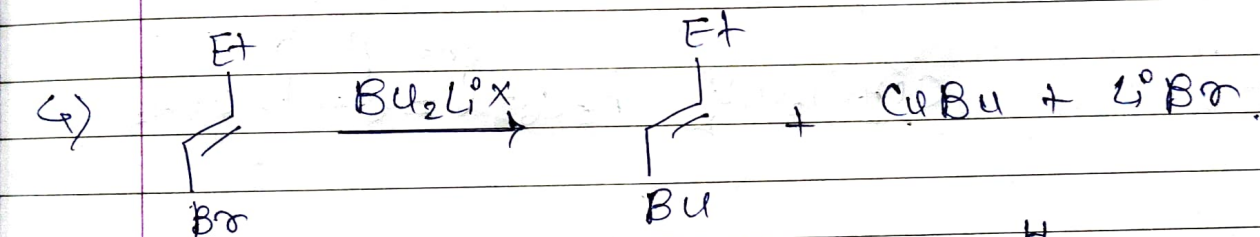
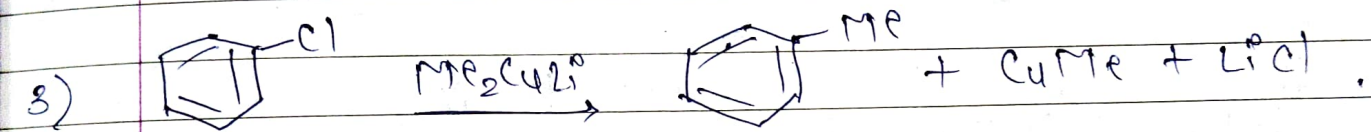
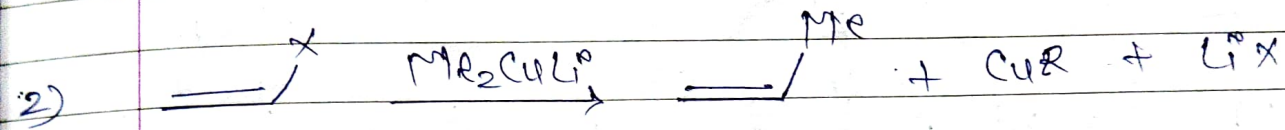
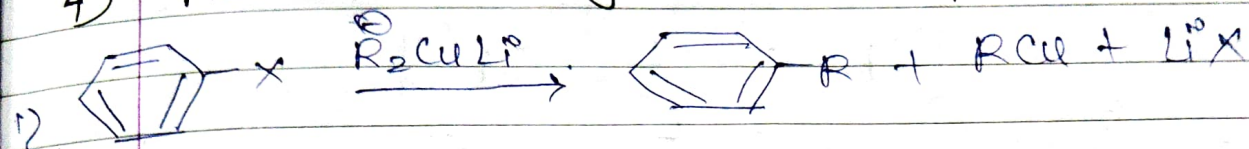


3) Redⁿ with α - β unsaturated ketone ($R-C(=O)-CH=CH-R$)
 Lithium organo cuprate react with α - β unsaturated carbonyl compounds giving exclusively 1,4 addⁿ product.

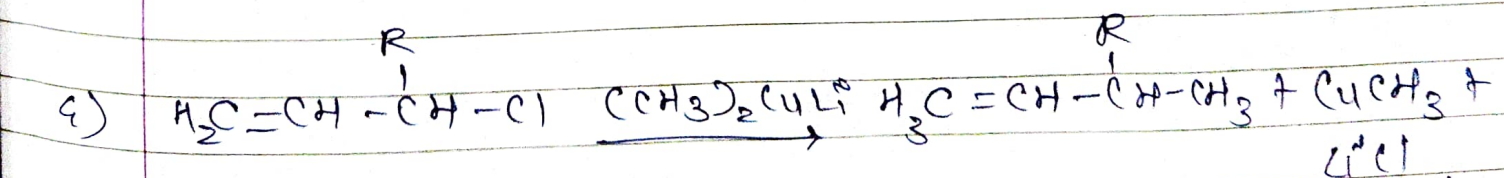
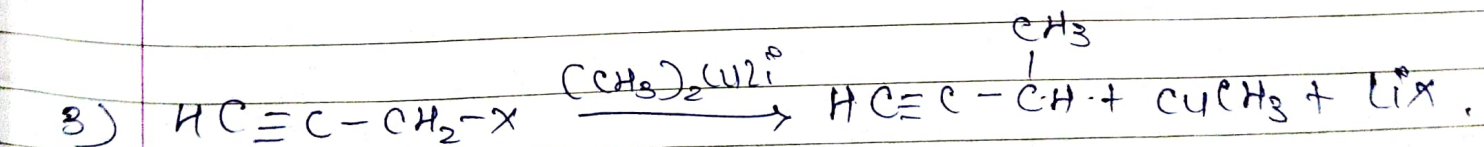
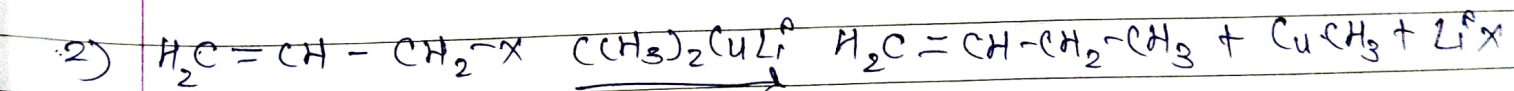
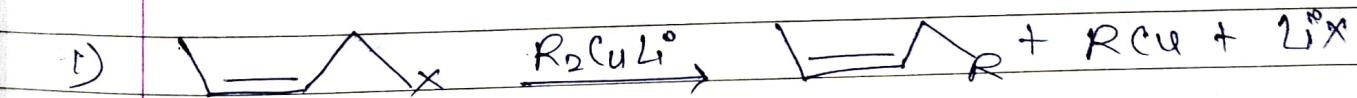




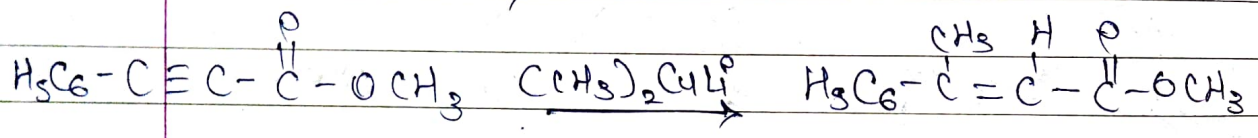
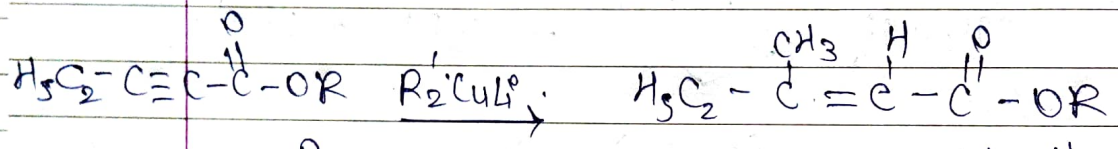
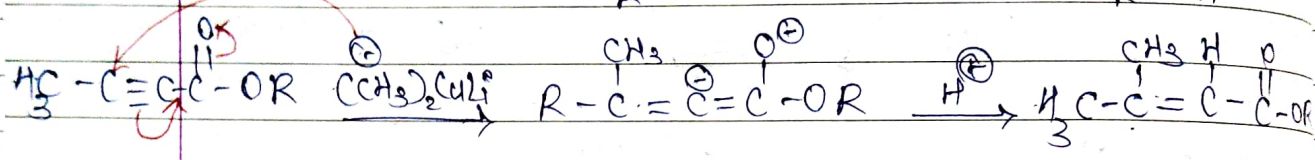
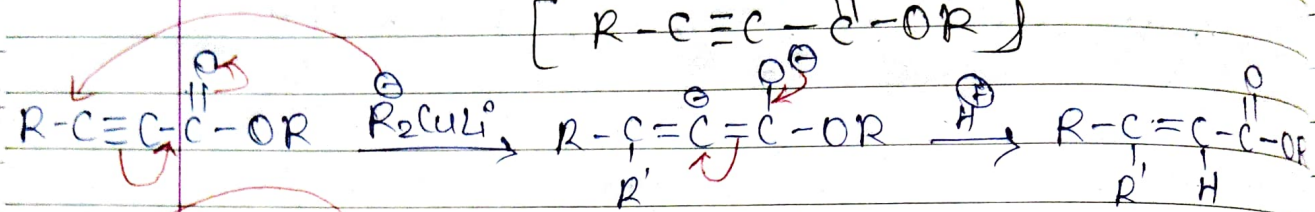
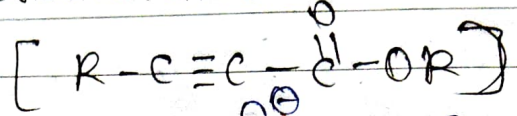
4) Reacⁿ with vinylic halide.



5) Reacⁿ with allylic halide



5) Redⁿ with Unsaturated ketone, ester



chiral centre - 4 different group.
 Anti = E-alkene - Trans
 syn = Z-alkene - cis

Allylic Organometallic of Boron, Silicon & Tin

A useful reaction in organic synthesis is the addition of allylic organometallic reagent to a carbonyl group. A number of different metals can be employed those of boron, silicon & tin have found the most use the carbon-carbon bond forming step is stereoselective & generate the versatile the homolytic alcohol unit.

Oxidative cleavage of the product alkene to the aldehyde provide the beta (β) hydroxide carbonyl compound & offers alternative stereoselective approach to the aldol-type reaction.

