

BHARAT SHIKSHAN SANSTHA

Shri Chhatrapati Shivaji College Omerga



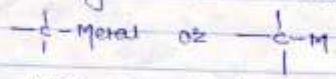
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Organometallic Compounds

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- Organometallic compounds:
 - The Grignard reagent (Alkyl Magnesium Halide, Ethyl Magnesium Bromide) Formation, structure and chemical reactions.
 - Organozinc compounds, formation and chemical reactions.
 - Organolithium compounds, formation and chemical reactions.

Introduction:- Organometallic compounds are those compounds in which metal directly attached to the carbon atom, or carbon metal bond. General presentation as follows;



where $M = Na, Li, Mg, Al, Zn, Cd$ etc.

Above metals are less electronegative than carbon so that carbon-metal bond is highly polar bond. Ionic character of the carbon metal bond order given below, or electropositive order given below, $Na > Li > Mg > Al > Zn > Cd$.

Organometallic compounds are named by simply adding the name of the metal to that of the organic group bonded to the metal, e.g.

- Ⓐ CH_3-Mg-I methyl magnesium iodide
- Ⓑ $CH_3-CH_2-Mg-Cl$ ethyl magnesium bromide.

- Ⓒ CH_3-Li methyl lithium
- Ⓓ $(CH_3-CH_2)_4Pb$ tetraethyl lead.

The carbon-lead; carbon lithium bonds are covalent & less reactive as compare to carbon-magnesium bond. Above reagent have a great importance in organic synthesis.

(A) Organomagnesium Compound

Formation of Grignard Reagents:- ($RMgX$)

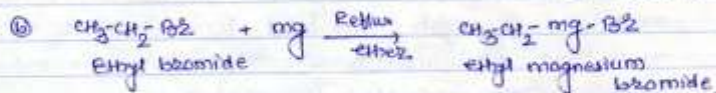
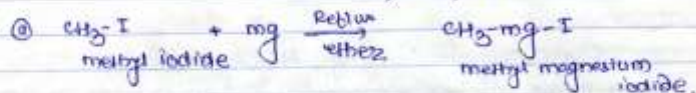
Organomagnesium halides are called as Grignard Reagents. $RMgX$ reagent discovered by the French chemist Victor Grignard in 1900. Grignard received the noble prize in 1912. So organomagnesium halides are now called as Grignard reagents in his honour. The Grignard reagent are highly reactive & used for synthesis of alkanes, alkenes, alcohols, aldehydes, ketones, carboxylic acid etc.

Grignard reagent are usually prepared by the reaction of organic halides & magnesium metal in dry ether.

General reaction:



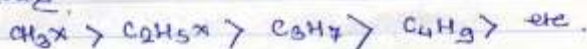
where R = alkyl; aryl etc.
X = Cl; Br; I etc.



For formation of Grignard reagent different halides are used but by considering the reactivity order of halides as follows (with magnesium metal)



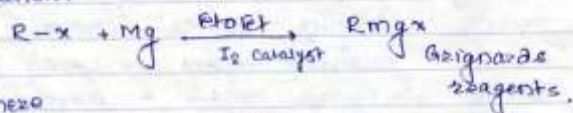
On other side for formation of Grignard reagent becomes difficult as the no. of carbon atoms in the alkyl group increases i.e. steric effect increases, or +I effect increases order as follows



Alkyl Grignard reagents are more easily prepared from alkyl bromide & alkyl iodide than from alkyl chlorides.

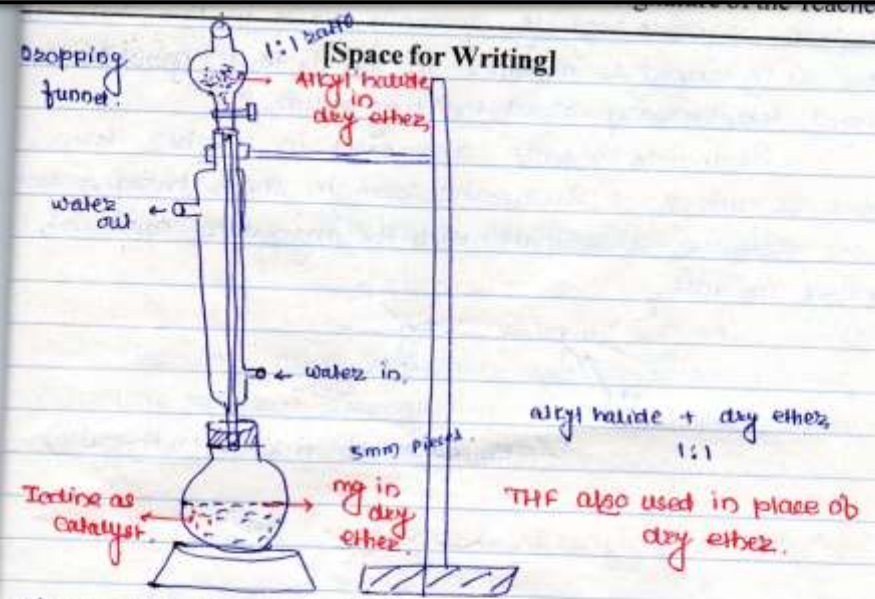
Preparation of Grignard reagents in laboratory :-

Grignard reagent prepared by taking round bottomed flask is fitted with a reflux condenser & a dropping funnel. Magnesium ribbon cut into small pieces (5mm) is suspended in dry ether placed in the round bottomed flask. Approximately 1:1 mixture of the alkyl halide & dry ether is placed in the dropping funnel. A crystal of iodine is added as catalyst to initiate the reaction.



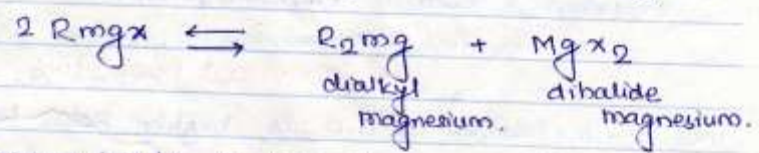
R = alkyl or aryl.

X = Cl; Br; I etc.

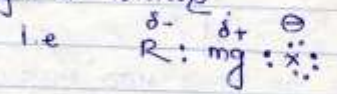


The actual structure of Grignard reagents are more complex than the general formula $Rmgx$.

The expt done by use of radio active magnesium, & he concluded the Grignard reagent eqn ~~was~~ ~~given~~ given below



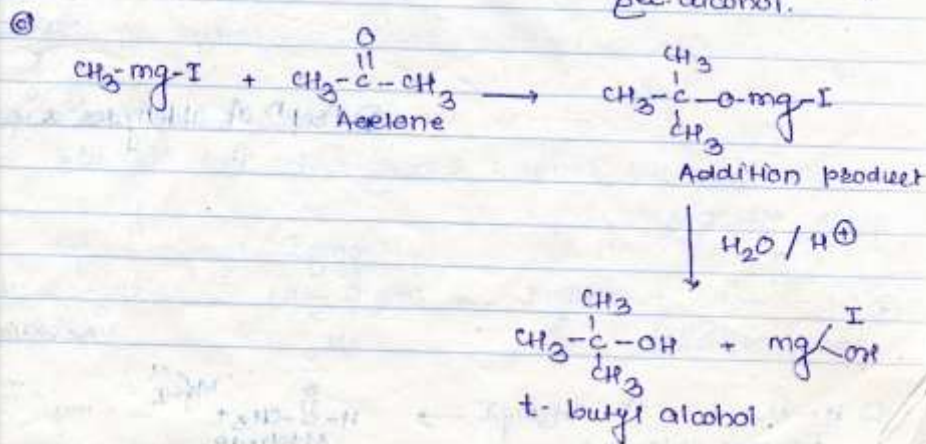
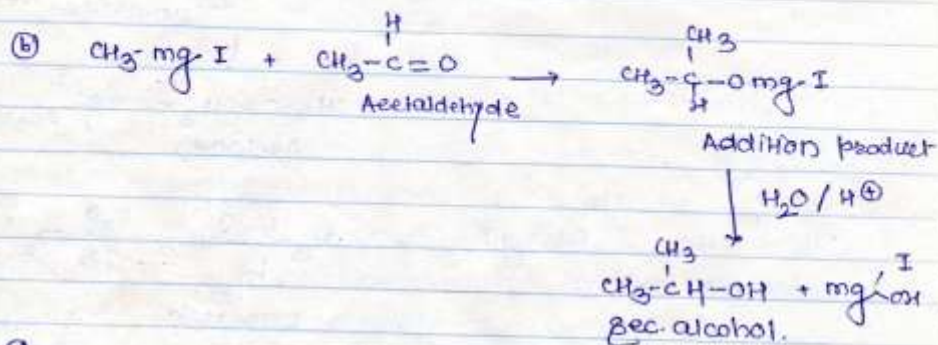
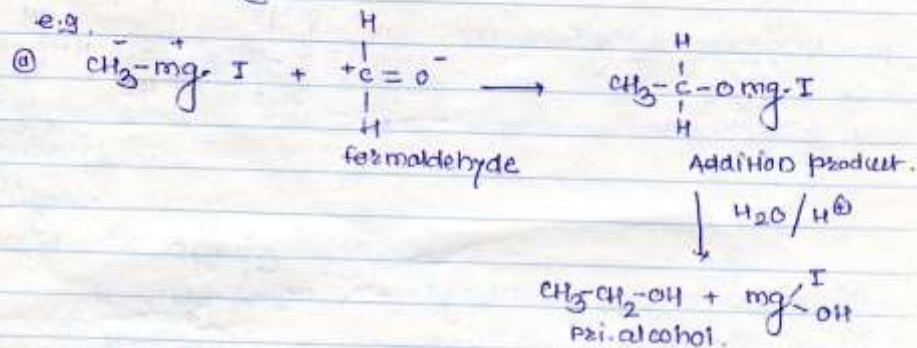
Alkyl magnesium halide is normally present in greater conc. than the dialkyl magnesium. The polarisation of covalent bond in $Rmgx$ as follows



The diethyl ether plays two important role as (a) It provides medium for the reaction (b) It dissolves the $Rmgx$ through the solvolysis (reaction with solvent).

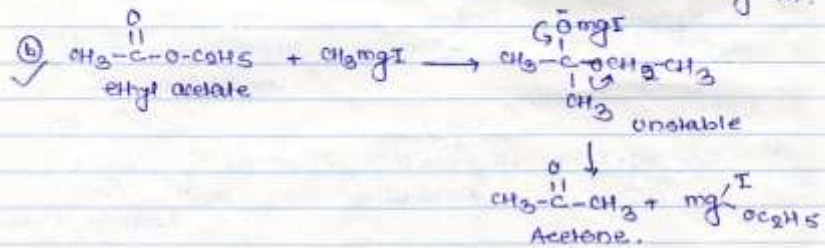
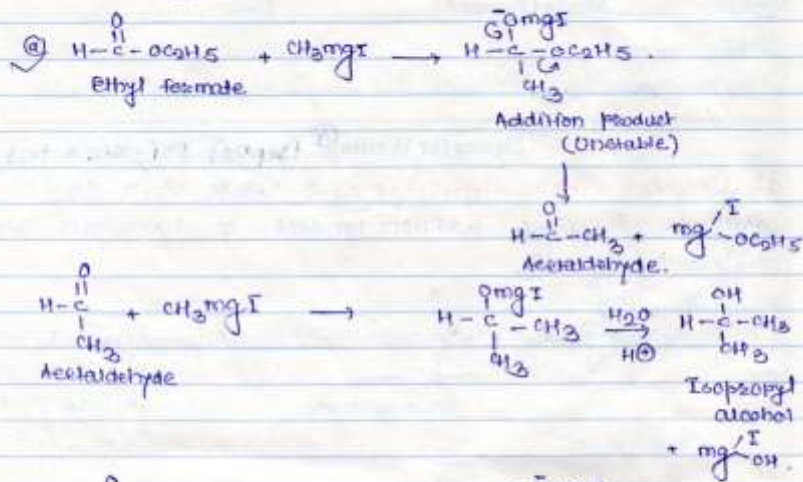
[Space for Writing] ^④ Prepnot Pzi; see a text alcoh.

② Reaction with aldehyde/ketone. G.R reacts with different aldehyde & gives addition product on hydrolysis gives different alcohols.

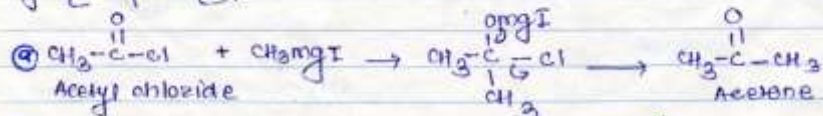


Prepn of alcohol. (Repeat)

(3) **Reaction with esters**:- Grignard reagents reacts with formic esters to form secondary alcohol while other esters yields tertiary alcohols.

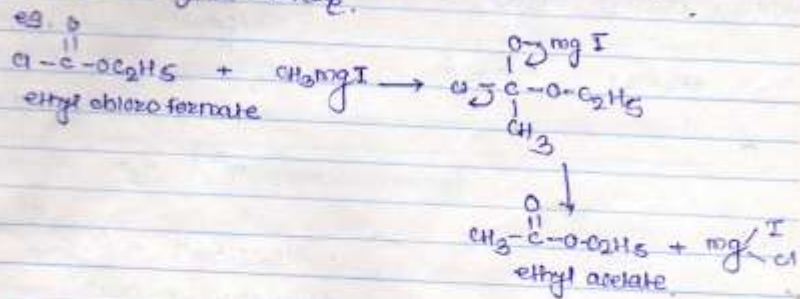


(4) **Reaction with acid chlorides** : (5) **Prepn of aldehydes & ketones**
 Grignard reagent reacts with acid chloride & gives ketones.



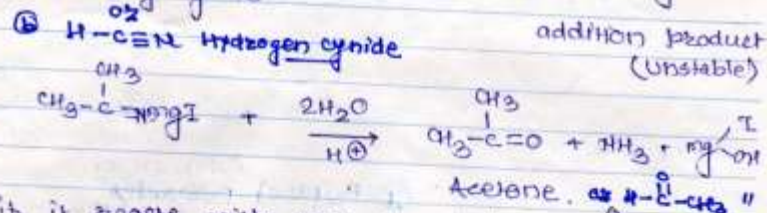
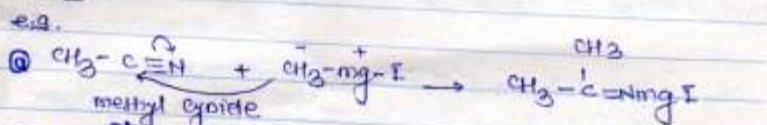
⑤ Reaction with ethyl chloroformate: Preparation of ester.

Grignard reagent reacts with ethyl chloroformate to form higher esters.



⑥ Reaction with cyanides: Preparation of ketones (Repeat)

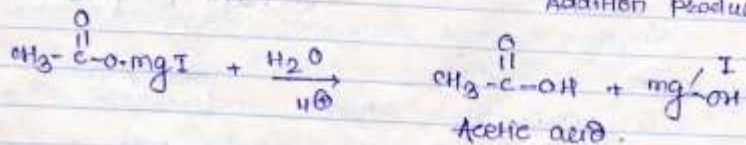
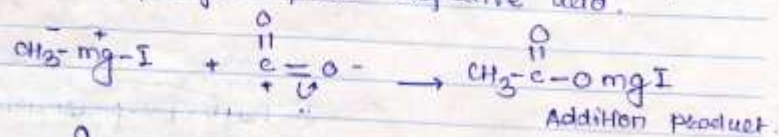
Grignard reagent reacts with cyanides to give addition products which on hydrolysis with dil-HCl yield ketones.



if it reacts with HCN it yields $\text{CH}_3\text{C}(\text{H})\text{CN}$ acetaldehyde

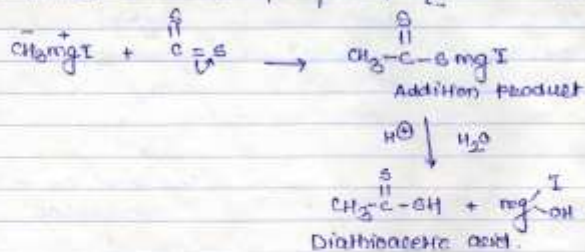
⑦ Reaction with carbon dioxide: Preparation of -COOH acid.

Grignard reagent reacts with CO_2 gives addition product on hydrolysis yields respective acid.



⑧ Reaction with carbon disulphide: ⑧ Prep of thiocacetic acid

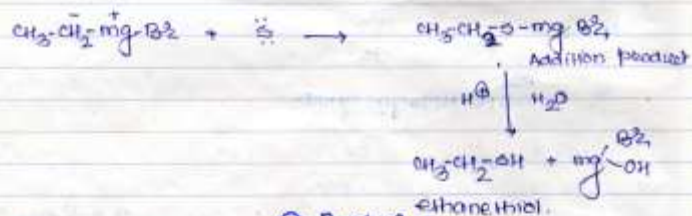
Grignard reagent reacts with CS_2 it gives addition product which on hydrolysis yields dithionic acid.



(continued) reaction with Sulphur

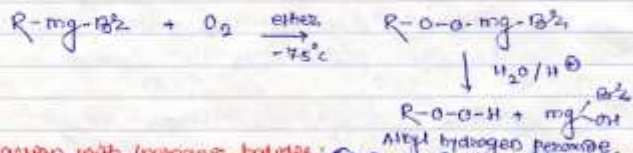
⑨ Reaction with sulphur: ⑨ Prep of thioalcohol.

Sulphur reacts with a G.R. gives the intermediate on hydrolysis gives corresponding thioalcohol.



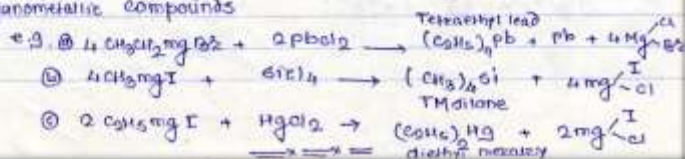
⑩ Reaction with oxygen: ⑩ Prep of Peroxides

G.R. reacts with oxygen at low temp to give a product which on hydrolysis yield peroxides.



⑪ Reaction with inorganic halides: ⑪ Prep of organometallic comp.

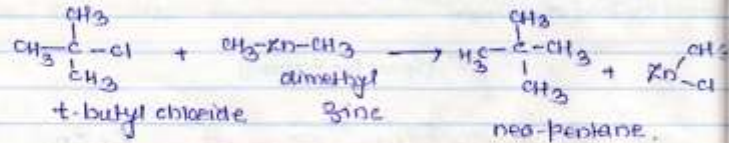
Grignard reagents reacts with inorganic halides to form organometallic compounds



⑧ Chemical properties / synthetic application

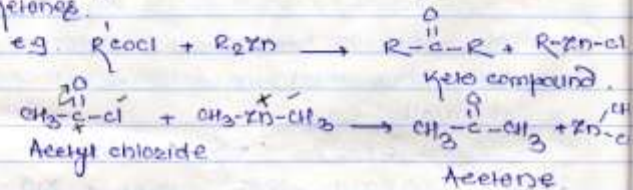
① Preparation of hydrocarbon:-

Dialkyl zinc compounds are used to prepare hydrocarbon containing quaternary carbon atom, e.g. neopentane prepared by the action of dimethyl zinc with t-butyl chloride.



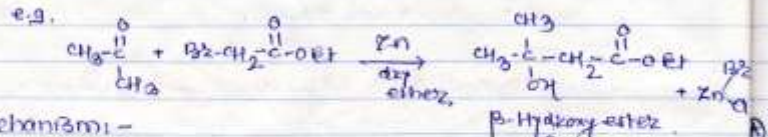
② Preparation of ketone:-

Dialkyl zinc compounds reacts with acid chloride to form ketone.

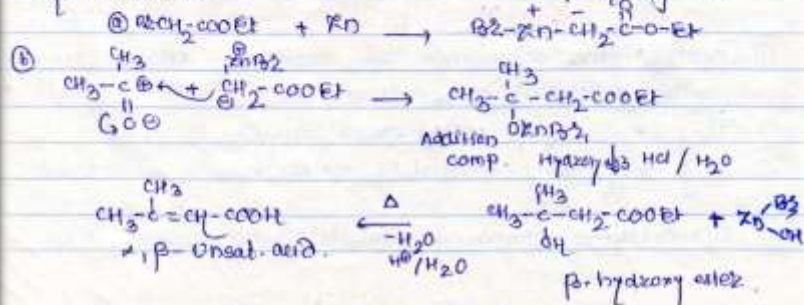


③ Preparation of β -hydroxy ester or Reformatsky reaction.

In this reaction, α -halo ester or ethyl bromoacetate reacts with zinc to form intermediate organo zinc comp. which then adds to carbonyl group of aldehyde or ketone on hydrolysis to yield β -hydroxy ester or α, β -unsaturated ester.



Mechanism:-



① Organolithium compounds Ph-Li

These are some organometallic compounds (alkali) like alkyl sodium, alkyl potassium, alkyl lithium etc. Organolithium compounds like alkyl lithium compounds are somewhat less reactive than others like $R-Na$; $R-K$ etc. But for some synthesis alkyl lithium specially used so they have some synthetic value in organic field.

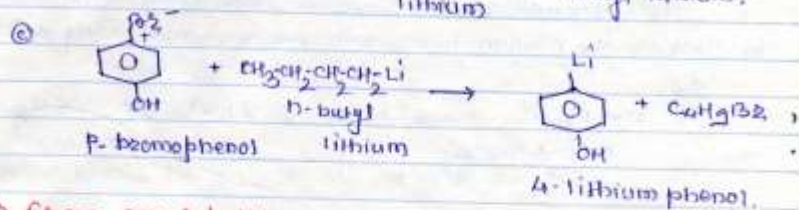
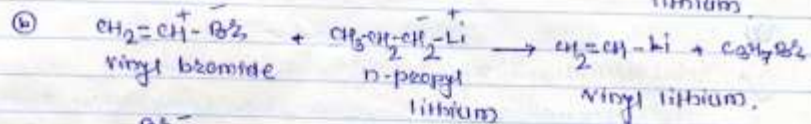
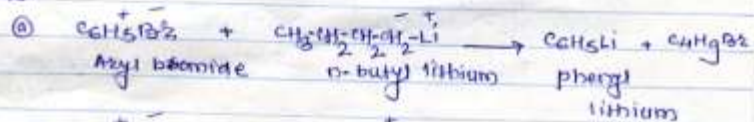
Preparation of Organolithium compound.

It can be prepared by no. of methods some methods given below,

① Metal-halogen exchange method :-

In this method alkyl, aryl or vinyl halocompound treated with any alkyl lithium compound it gives out expected organolithium compound.

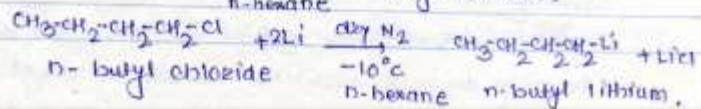
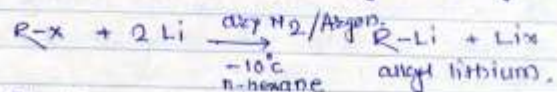
e.g.

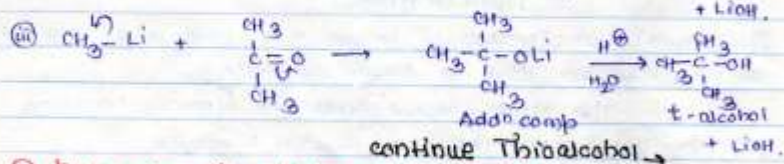
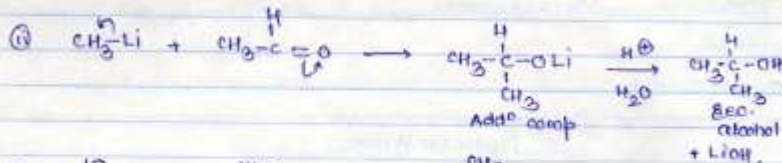
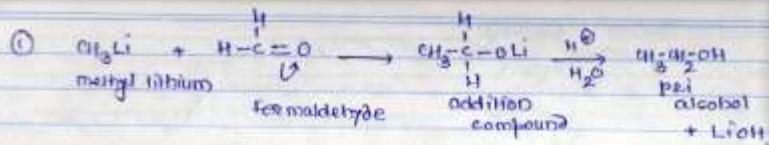


② From alkyl halide & metal :-

Organolithium compound can be prepared by cooling a mixture of organic halide in hexane with metallic lithium at -10°C in presence of dry nitrogen or argon.

e.g.

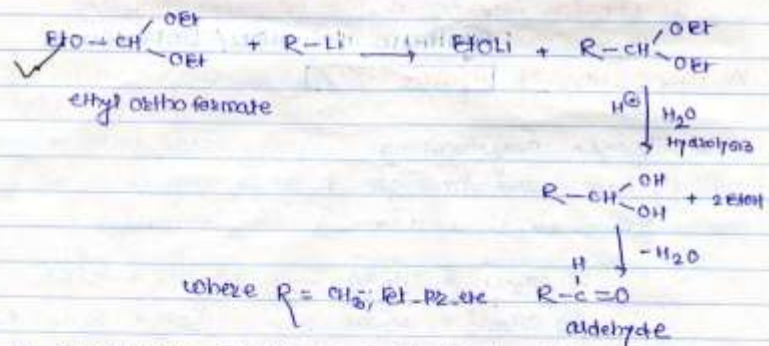




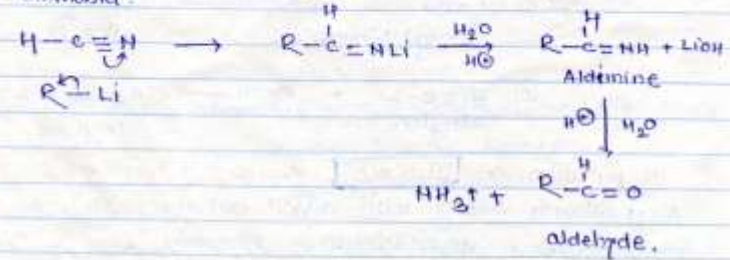
continue Thioalcohol →

© Preparation of aldehydes & ketones:-

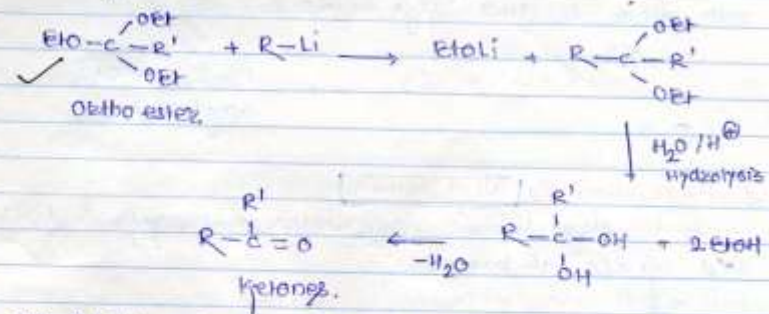
Aldehydes are prepared by the reaction between alkyl-lithium & ethyl orthoformate (orthoformic ester).



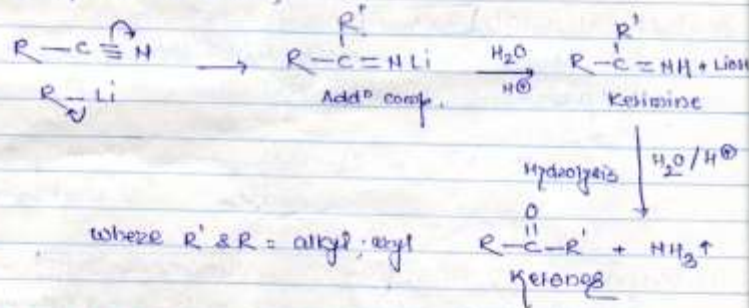
If alkyl lithium & hydrogen cyanide reacts with each gives addition product on hydrolysis in trace of acid gives aldehyde & ammonia.



Ketones can be prepared by reaction between alkyl lithium with any orthoester other than orthoformate ester.



alkyl lithium reacts with sub. cyanide compound gives the addⁿ comp on hydrolysis gives ketimine again hydrolysis gives ketones as follows:



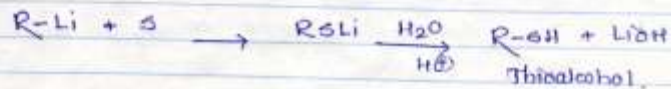
② Preparation of diphenyl :-

Phenyl lithium reacts with fluorobenzene to form diphenyl.



③ Preparation of thioalcohols :-

Alkyl lithium compound reacts with sulphur to form thiolithium which on hydrolysis gives thioalcohol.



(F) Preparation of alkyl halides:-

Alkyl lithium directly reacts with halogen especially with iodine & gives alkyl iodide.

e.g.



(G) Preparation of alkyl cyanides

Alkyl lithium reacts with chlorocyanide & gives alkyl cyanides as product.

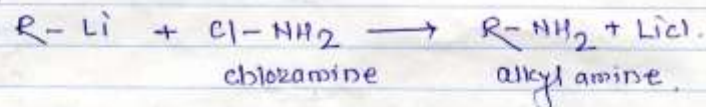
e.g.



(H) Preparation of amines:-

Alkyl lithium reacts with chloramine to form an alkyl amine.

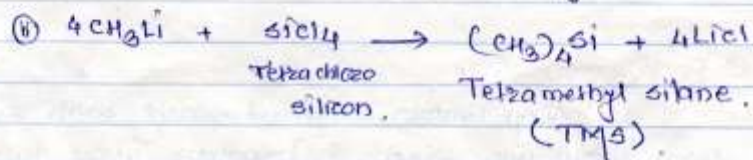
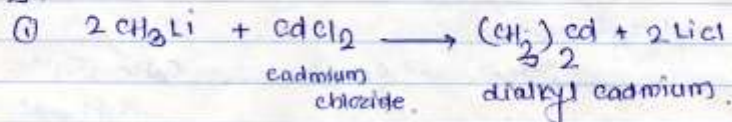
e.g.



(I) Preparation of other organometallic compounds:-

No. of metal halides reacts with alkyl lithium & gives respective organometallic compound as follows

e.g.

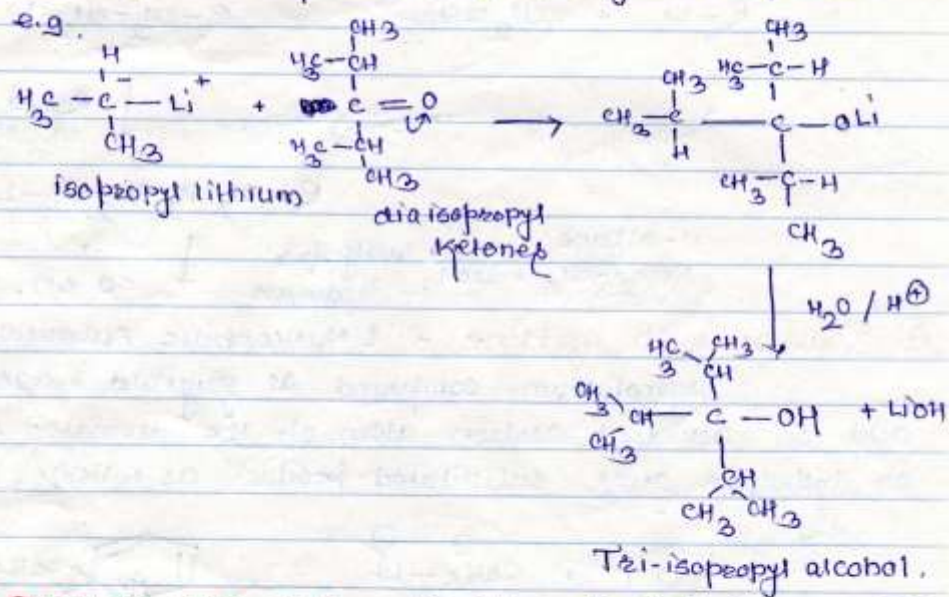


(ii) chemical reaction differ from Grignard reagents :-

(A) Reaction with sterically hindered ketones: Prepⁿ of alcohol.

generally Grignard reagents reacts very slowly & yield very low if starting material sterically hindered in prepⁿ of t-alcohol very low yields.

In organolithium compound containing bulky gr like isopropyl lithium reacts with di-isopropyl ketone (which is sterically hindered) & gives respective alcohol



(B) Reaction with carbon dioxide :- Prepⁿ of keto compound

Grignards reagents reacts with carbon dioxide to form carboxylic acid but organolithium compound reacts with CO₂ to form ketones.

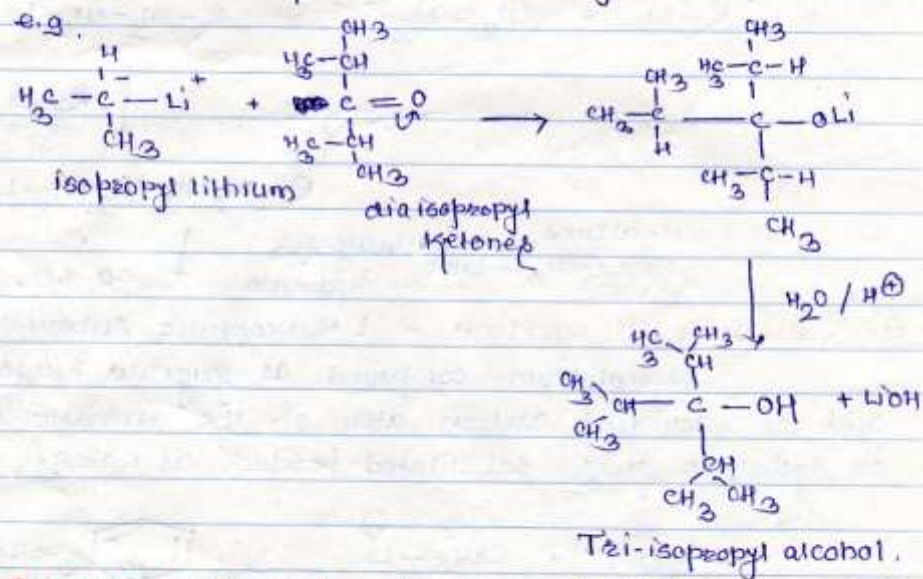
e.g.

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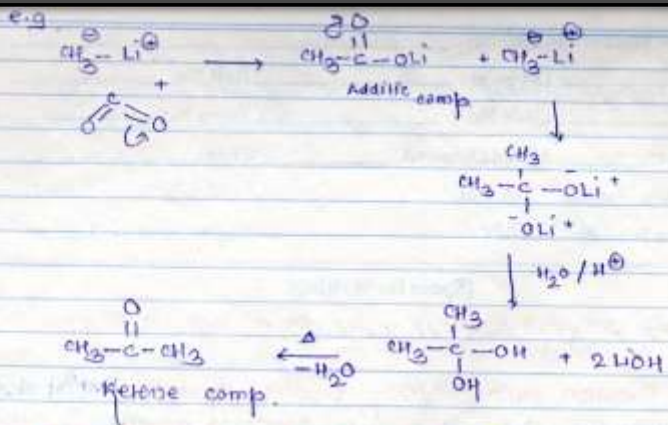
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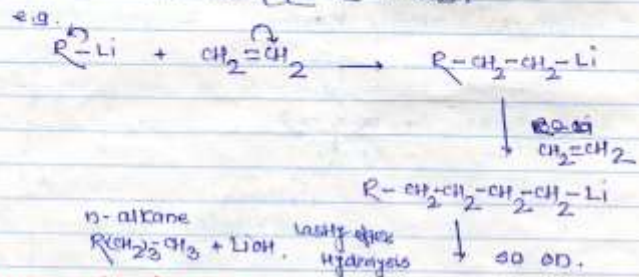
Grignard reagents reacts with carbon dioxide to form carboxylic acid but organolithium compound reacts with CO_2 to form ketones.

e.g.



⊙ Addition to olefinic bond:- Prepⁿ of alkanes.

Organolithium compound add to the olefinic bond & gives addⁿ comp again addition of organolithium compound & chain increases as follows.



⊙ Reaction with pyridine:- (Nucleophilic substitution)

Organolithium compound as Grignard reagents add on activated carbon atom of the aromatic ring on hydrolysis gives substituted product as follows.

