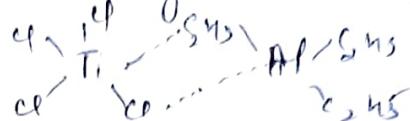
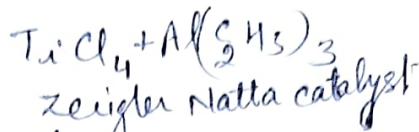
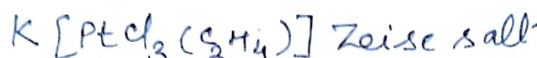


ORGANOMETALLICS

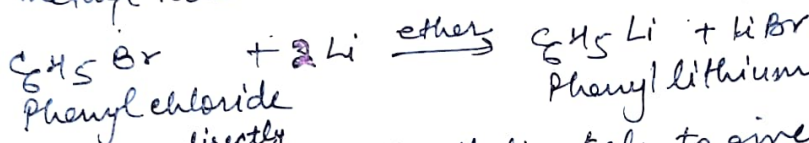
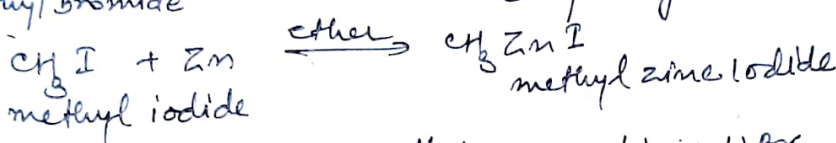
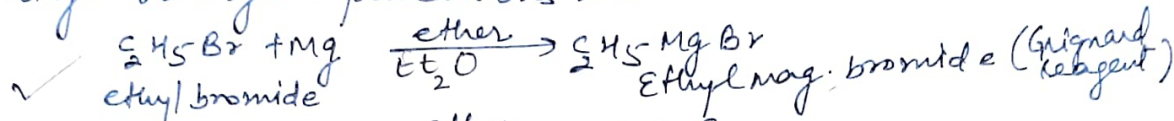
I.

Organometallic compounds are those compounds which contain at least one carbon-metal bond. This carbon atom belongs to any organic group. e.g.



PREPARATION OF ORGANOMETALLICS :-

- (i) Some organometallic compounds are prepared from respective alkyl or aryl hydrocarbons in ether solvent.



- (ii) ~~Some~~ Alkynes ^{directly} react with alkali metals to give organometallic compounds. e.g.
- $$\text{R}-\text{C}\equiv\text{C}-\text{H} + \text{Na} \xrightarrow{370\text{K}} \text{R}-\text{C}\equiv\text{C}-\text{Na} + \frac{1}{2}\text{H}_2$$
- alkyl acetylene sod. alkynide

GRIGNARD'S REAGENT

Of all the organometallic compounds known, organomagnesium (RMgX) or Grignard reagent are the most important. They are so named after Victor Grignard, who discovered and developed their use as synthetic reagents. Almost all classes of organic compounds can be prepared from them.

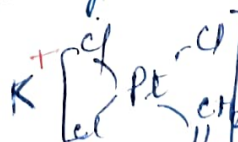
Synthetic applications of Grignard's reagents:-

- (i) Synthesis of alkanes by treating of Grignard's reagent with water, alcohol and amines. For e.g.



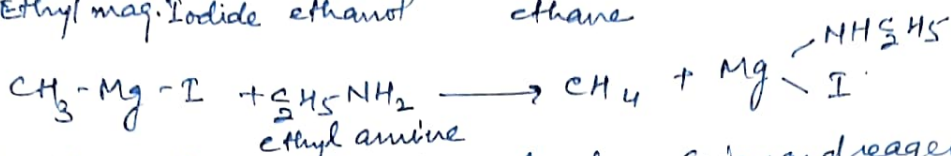
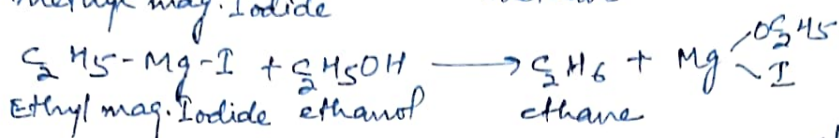
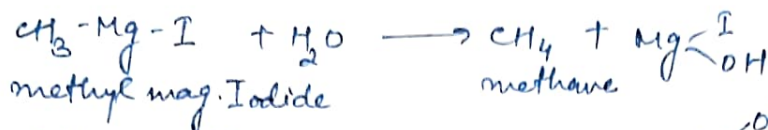
alkyl or aryl
X \rightarrow I, Br, Cl

o. why Et_2O req. for prep
Ans. Et_2O is an esp. good solvent for the formation of G.R. because ethers are non-acidic (aprotic) water & alcohols would destroy the G.R.

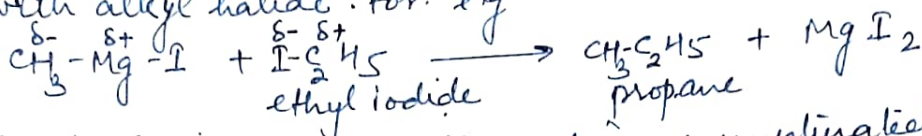


because the Grignard reagent is highly nucleophilic this would form a hydrocarbon.

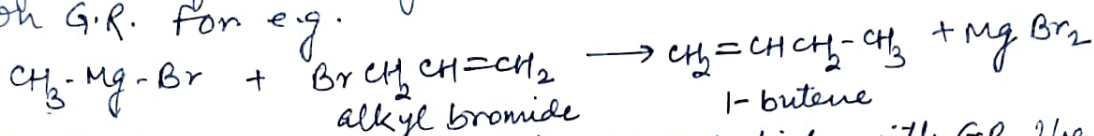
water & alcohols would destroy the G.R.



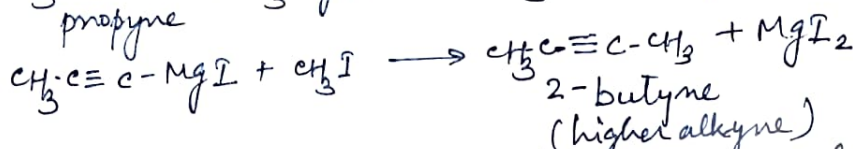
(ii) Higher alkanes are obtained when Grignard reagent is treated with alkyl halide. For e.g.



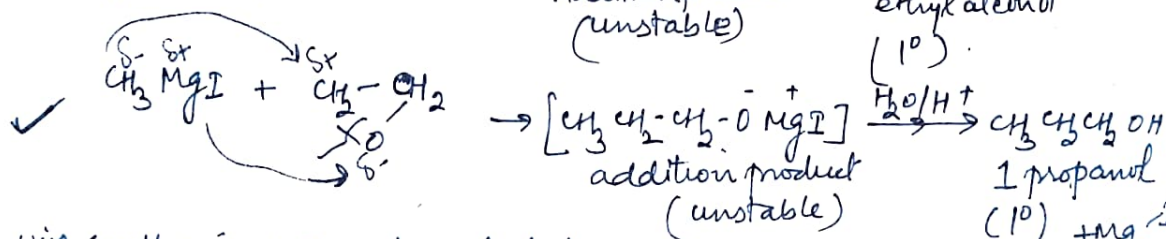
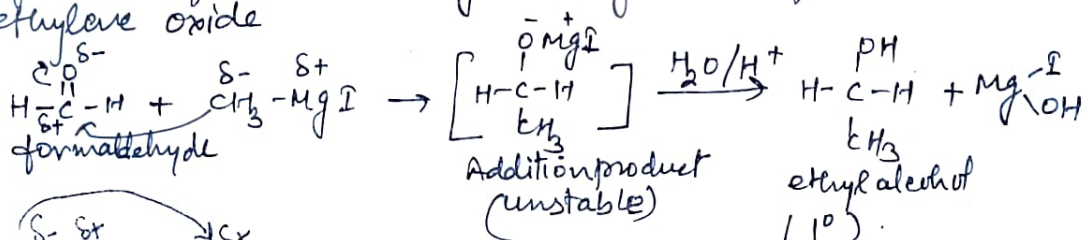
(iii) Synthesis of alkenes by the action of unsaturated halides on G.R. For e.g.



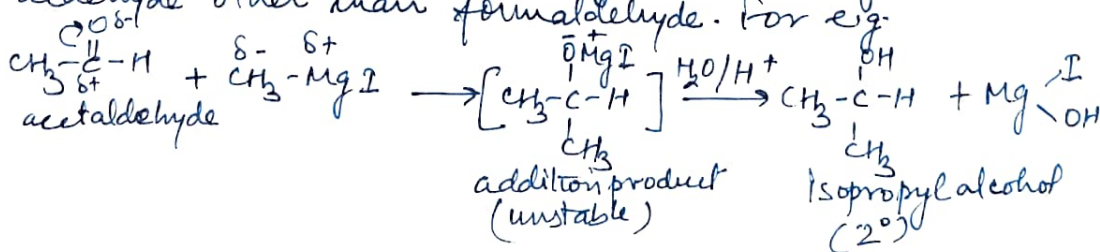
(iv) Synthesis of alkynes by treating alkyl halide with G.R. The product is higher alkyne. For e.g.



(v) Synthesis of 1° alcohols by treating with formaldehyde or ethylene oxide



(vi) Synthesis of secondary alcohols by the action of G.R. on aldehyde other than formaldehyde. For e.g.



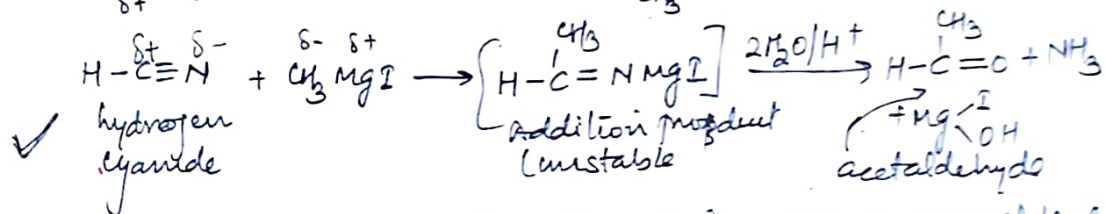
3.

$$\begin{array}{c} \delta^- \quad \delta^+ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{acetone} \end{array} + \text{CH}_3 - \text{Mg} - \text{I} \rightarrow \left[\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{Mg} - \text{I} \right] \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \\ \text{tertiary butyl alcohol} \\ (3^\circ) \end{array} + \text{Mg} - \text{I} - \text{OH}$$

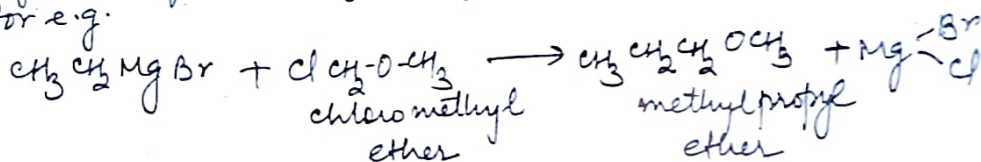
(viii) Synthesis of aldehydes by the action of G.R. with ethyl formate or hydrogen cyanide. For e.g.

$$\text{H}-\overset{\delta+}{\underset{\delta+}{\text{C}}}-\overset{\delta-}{\text{O}}-\overset{\delta-}{\text{C}}-\text{H}_5 \xrightarrow{+} \text{CH}_3-\overset{\delta-}{\text{Mg}}-\overset{\delta+}{\text{I}} \rightarrow \left[\text{H}-\overset{\delta-}{\underset{\text{CH}_3}{\text{C}}}-\overset{\delta+}{\text{O}}-\text{H}_5 \right] \xrightarrow{\text{rearr.}} \text{H}-\overset{\delta-}{\text{C}}-\text{CH}_3 + \text{Mg}-\overset{\delta+}{\text{O}}-\text{C}-\text{H}_5$$

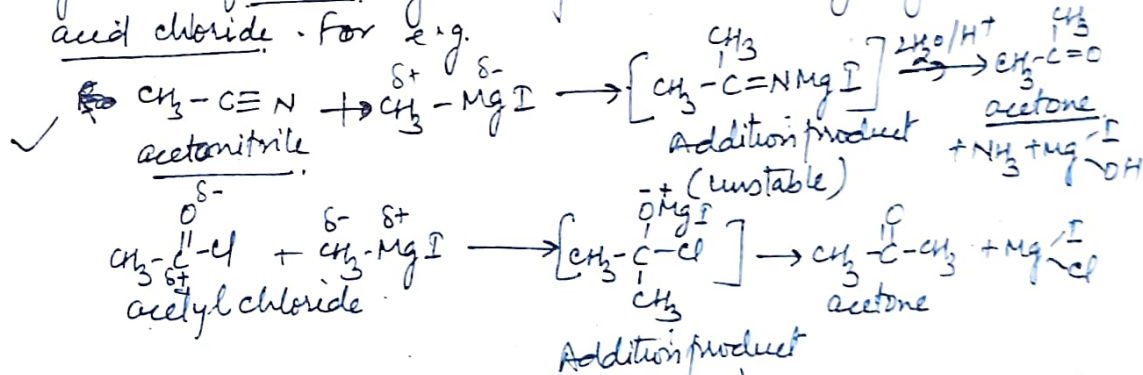
acetaldehyde



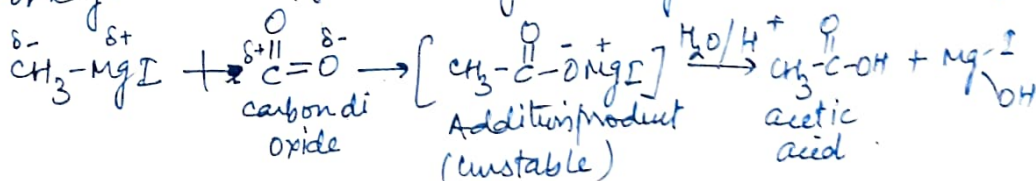
For e.g.



(X) synthesis of ketones by treating G.R. with alkyl cyanide or acid chloride. For e.g.

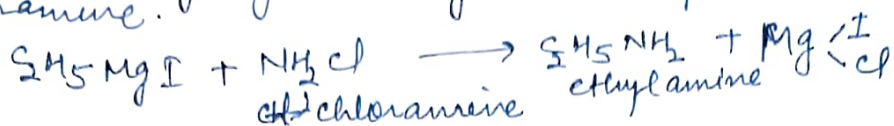


(ii) Synthesis of carboxylic acid by ^(unstable) reacting with solid CO_2 (dry ice).
For e.g.

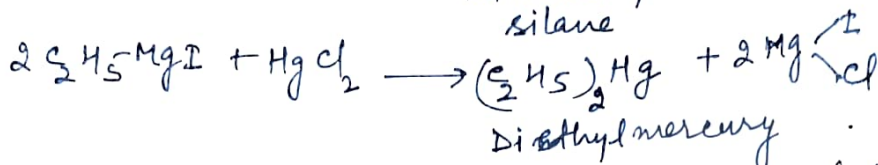
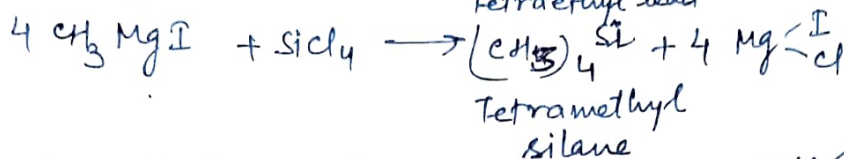
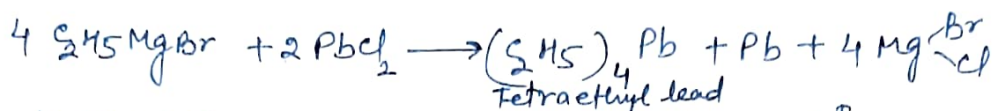




Synthesis of alkyl cyanides by interacting G.R. with chloramine. 4.



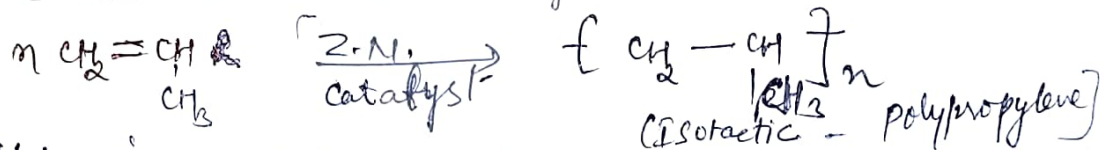
(xiii) Synthesis of other organometallics by reacting with inorganic chlorides.



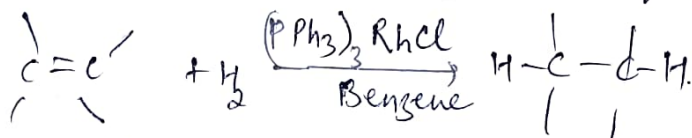
Other

Applications of organometallic compounds

① Z.N. catalyst - $[TiCl_4 + (C_2H_5)_3Al]$ is used for polymerⁿ of ethene and other alkene. (heterogeneous catalyst).



② Wilkinson's catalyst, as homogeneous catalyst is used for selective hydrogenation of $C=C$ (alkenes).



in gasoline & jet fuels

③ TEL, $(C_2H_5)_4Pb$ is used as an anti-knocking agent in petrol.

④ Organometallics like $Ni(CO)_4$, Nickel carbonyl is used in the purification of Nickel by Mond's Process.

Organometallic compounds: CLASSIFICATION

Depending upon the nature of $-C-M$ bond, organometallic compounds are of following types:-

1- IONIC ORGANOMETALLIC COMPOUNDS:- The organometallics in which the organic group (R) is bonded to highly electropositive metals like Na, Ca etc. Such compounds are colourless, salt like solids and are soluble in polar solvents. They are highly reactive and unstable with a short life. The organometallic compounds containing large cations (small polarizing power) and small carbanions (small polarisability) have maximum ionic character.

e.g. $Cs^+CH_3^-$, $Na^+(C_5H_5)^-$, $Na^+(C_6H_5)^-$, etc.

2- COMPOUNDS CONTAINING METAL CARBON SIGMA BOND

(~~COVALENT~~) (COVALENT): Metallic elements of groups 12, 13, 14, 15 and transition metals form σ -bonded organometallics with carbon atoms.

They further can be classified as:-

(a) organomet. compds of group-12 elements \rightarrow
e.g. R_2Hg e.g. $(CH_3)_2Hg$ R_2Zn e.g. $(C_6H_5)_2Zn$ etc.

(b) organomet. compds of group-13 elements \rightarrow
e.g. $(CH_3)_3Ga$, $(CH_3)_3Tl$, $(C_6H_5)_3Ga$ etc.

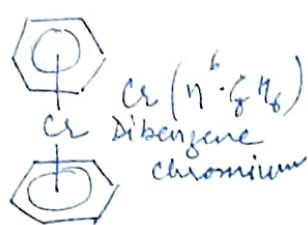
(c) organomet. compds of group-14 elements \rightarrow
e.g. Tetra ethyl lead $(C_2H_5)_4Pb$, $(CH_3)_4Si$ etc.

(d) organomet. compds of group-15 elements \rightarrow
e.g. R_3P trialkyl/aryl phosphine
 R_3As trialkyl/aryl Arsenine etc.

(e) Organomet. compds of Transition metals:-

Very few examples are known in which the oxidation state of metal is very low and it lies near the end of the transition series. e.g. $\text{CH}_5\text{-Rh(NH}_3)_5$, $\text{M-C}\equiv\text{CR}$

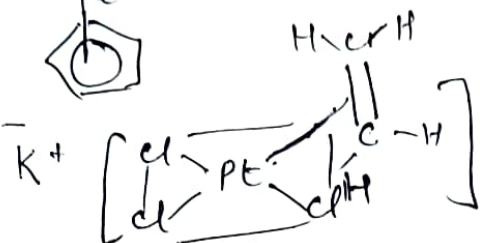
3- ORGANOMETALLICS WITH PI-BONDED LIGANDS:- This category includes organometallics of alkenes, alkynes and some other carbon containing compounds having π in their π -molecular orbital. e.g. ferrocene (bis-cyclopentadienyl) iron



Zeise's salt-



$\text{Fe(C}_5\text{H}_5)_2 \rightarrow$ sandwich comp
or $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$



\rightarrow {Pot. trichloroethene} \rightarrow $\text{K}^+ [\text{PtCl}_3(\eta^2\text{-CH}_2\text{=CH}_2)]^-$
or $\text{K}^+ [\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]^-$
 $\eta \rightarrow$ represents to no. of C-atoms

4- YLIDES:- are organomet. compds in which metal is doubly bonded with the carbon atom of the ligand. e.g. Wittig reagent $\text{PH}_3\text{P}^+\text{=CH}_2^-$

P, S, N etc. +vely charged atom with carbanion (-vely charged carbon)

5- ORGANOMETALLICS WITH MULTICENTRE BONDS:- or non-classically bonded compounds:- Organometallics which are e^- -deficient and occur in polymeric forms fall under this category.

e.g. $(\text{Li}^+\text{CH}_3)_4$, $[\text{Be}(\text{CH}_3)_2]_n$, $[\text{Al}(\text{CH}_3)_3]_2$ etc.

In such compds, bonding can not be explained by the classical concepts of chemical bonding (i.e. by ionic or normal covalent bonding), therefore they are also called as Non-classically bonded organomet.

Q. Why Et_2O (diethyl ether) is required for the prepn of organometallics?
Ans. Et_2O is an ~~app~~ very good solvent for the prepn of G.R. because ethers are non-acidic (aprotic / contain no acidic H), therefore do not have any reaction with the G.R. formed. While solvents like H_2O & alcohols are protic solvents i.e. they contain acidic H, they H protonate the G.R. formed as - & form hydrocarbon.
nucleophilic carbon $\rightarrow \text{R}^-\text{Mg}^+\text{X} + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{Mg}^+\text{OH}^-$
 $\text{C}_2\text{H}_5^-\text{Mg}^+\text{I} + \text{C}_2\text{H}_5\text{OH}^+ \rightarrow \text{C}_2\text{H}_6 + \text{Mg}^+\text{O}^-\text{C}_2\text{H}_5$

Structure $LiAlH_4$



- tetrahedral arrangement of H's around Al^{3+} in $(AlH_4)^-$ ion
- Hybridization of Al is sp^3 hybrid.
- Strong reducing agent.

Synthesis By Lithium hydride & Aluminium hydride reaction

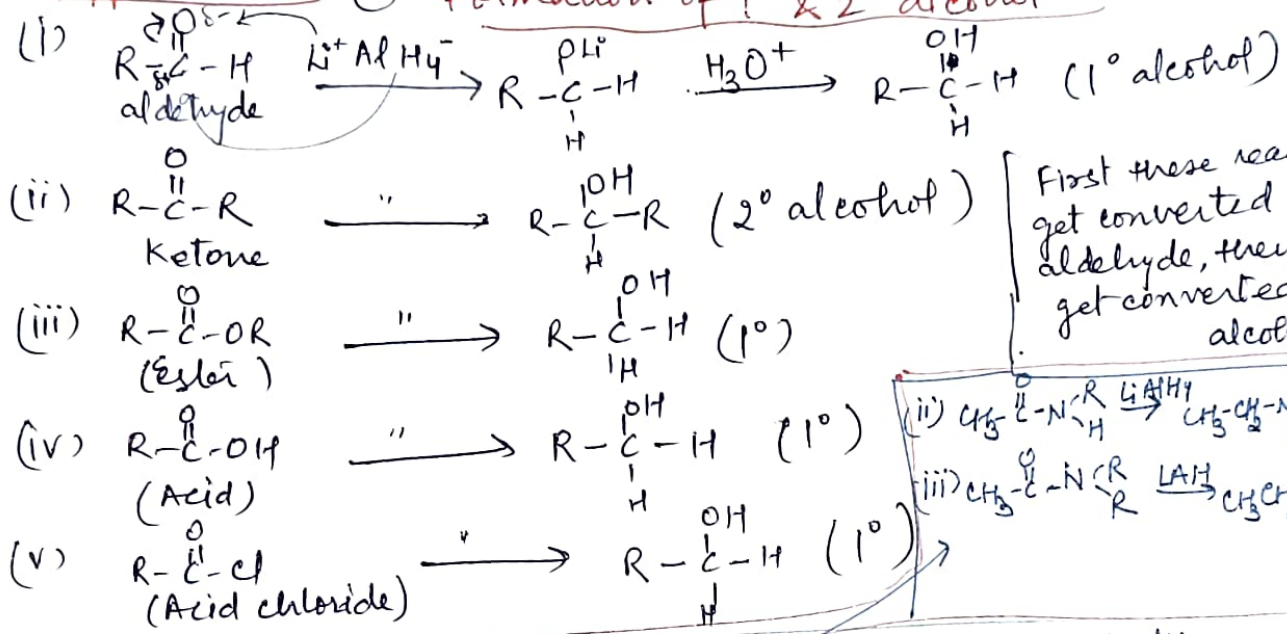


Properties :- White coloured solid
 - should be placed in a dry place, because it violently react with water & release H_2 gas.

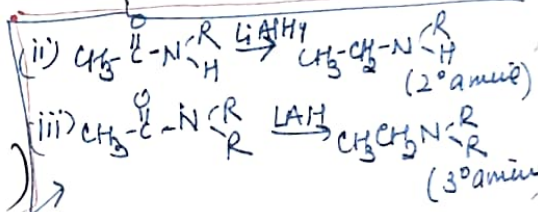


Note :- Reactions must be carried out in dry & inert atm.

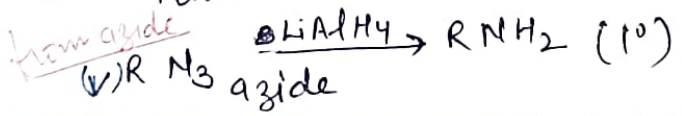
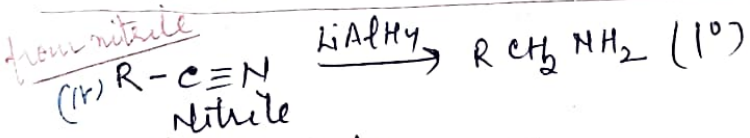
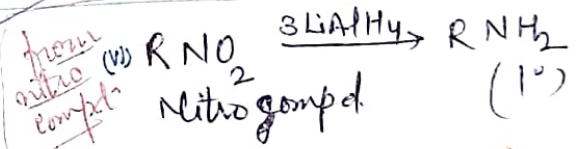
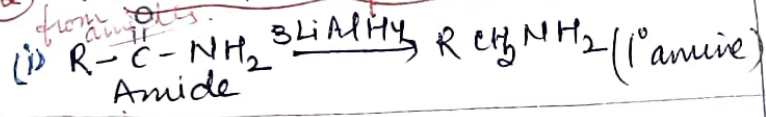
Applications - ① Formation of 1° & 2° alcohol -



First these reactants get converted to aldehyde, then they get converted to alcohols



② Formation of Amines -



③ Formation of Alkanes

