Organometallic Compounds

classmate
Date
Page

Introduction :- Those compound which consist of metal to carbon bonds are called organometallic compounds.

⇒ The general formula of organometallic compounds is R-M where R is the carbon chain.

⇒ Some example of organometallic compounds :-

(i) CH_3Li
methyllithium

(ii) C_6H_5Li
phenyllithium

(iii) R_2CuLi
Lithium dialkyl cuprate

(iv) $(C_2H_5)_2Cd$
Diethyl cadmium

⇒ organolithiums possess the general formula RLi. Because of the small size and high polarization power of lithium, organolithium compounds posses more ionic character than the Grignard reagent.

⇒ organolithium compound can be prepared as,

$$R-X + 2Li \xrightarrow{dry\ Ether} R-Li + LiX$$

⇒ organolithiums is used in making Lithium Diorganocopper compound, R_2CuLi called Gilman reagent

$$3RLi + CuI \xrightarrow{dry\ Ether} R_2CuLi + LiI$$

Lithium dialkyl cuprate

Nature of metal-carbon bond :- Based on the nature of metal to carbon bonds, organometallic compounds are classified into the following types :-

(1.) Ionic organometallic compounds :- They are mainly formed by more electro-positive metals such as Na, K, where metals are present in the form of the cation. In such compounds, the negative charge on the hydrocarbon anion is delocalized over several carbon atoms.

⇒ For e.g :- (i) $K^+C_5H_5^-$
(cyclopentadenyl potassium)

(ii) $Mg^+(C_2H_5)_2^-$
(Bis cyclopentadenyl magnesium)

(2.) Covalent organometallic compounds :- covalent organometallic compounds are mainly formed by less electropositive metals such as Pb, Cd, Zn all etc. In such compounds metal is bonded with carbon atom by a single covalent bond.

⇒ For e.g :- (i) $(C_2H_5)_2Pb$ Diethyl lead

(ii) $(C_6H_5)_2Zn$ Diphenyl zinc

(3) Electron deficient organometallic compounds :- Electron deficient organometallic compounds are mainly formed by Li, Be, mg and Al with bridging alkyl group the formation of such compounds can not be explained based on the formation of usual two electron two-center bonds with carbon and metal atom.

(4) Transition metal organometallic compounds :- Transition metal organometallic compounds are formed by transition metal in which they are bonded with more than one carbon atom of the same organic compounds.

Grignard reagent :- Grignard reagent are the organometallic compounds having the general formula R-mg-x, where R is an organic group, normally alkyl or aryl group and x is a halogen.

⇒ For e.g :-

(i) CH_3MgBr
(methyl magnesium bromide)

(ii) ~~CH_3~~ C_6H_5MgBr
(phenyl magnesium bromide)

Preparation of Grignard Reagent :-

(1.) From alkyl halide :- Aliphatic grignard reagent can be prepared by treating alkyl halide with magnesium in dry ether.

$$R-X + Mg \xrightarrow{\text{dry ether}} R-Mg\,X$$

Alkyl magnesium halide

$$CH_3-Br + Mg \xrightarrow{\text{dry ether}} CH_3-Mg\,Br$$

methyl bromide — methyl magnesium bromide

(2.) From aryl halide :- Aromatic Grignard reagent can be prepared by heating chlorobenzene with magnesium in the presence of tetrahydrofuran (THF) and bromobenzene and iodobenzene with magnesium in the presence of dry ether.

$$C_6H_5Cl + Mg \xrightarrow{THF} C_6H_5Mg\,Cl$$

phenyl magnesium chloride

$$C_6H_5Br + Mg \xrightarrow[\text{ether}]{\text{dry}} C_6H_5Mg\,Br$$

phenyl magnesium bromide

$$C_6H_5I + Mg \xrightarrow[\text{ether}]{\text{dry}} C_6H_5Mg\,I$$

phenyl magnesium iodide

Reaction of Grignard Reagent :-

(1) **Reaction with Water :-** when the Grignard reagent is heated with water, an alkyl group of the reagent combine with active hydrogen at water and forms alkane.

$$R\text{-}MgX + H\text{-}OH \longrightarrow \underset{\text{Alkane}}{R\text{-}H} + Mg(OH)X$$

E.g. :-

$$\underset{\text{Ethyl magnesium bromide}}{CH_3\text{-}CH_2\text{-}MgBr} + H\text{-}OH \longrightarrow \underset{\text{Ethane}}{CH_3\text{-}CH_3} + Mg(OH)Br$$

(2) **Reaction with aldehydes and ketones :-**

(1.) G.R. gives 1° alcohol with methanal.

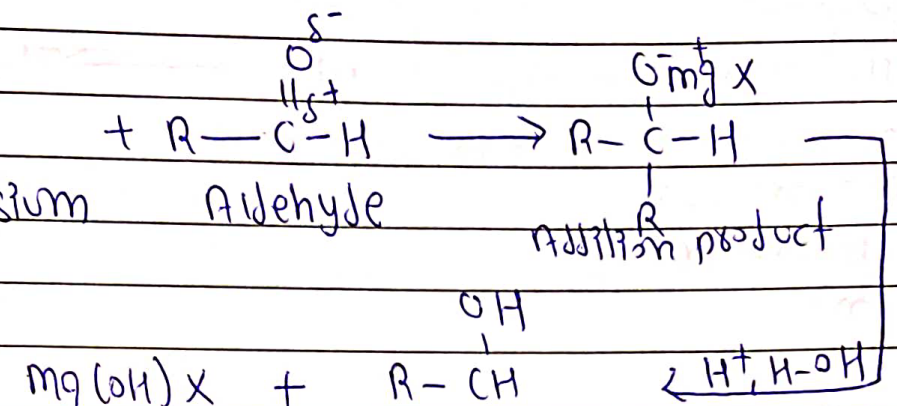
$$\underset{\text{methanal}}{H\text{-}\overset{\overset{O}{\|}}{C}\text{-}H} + R\text{-}MgX \longrightarrow \underset{\text{Addition product}}{H\text{-}\overset{\overset{OMgX}{|}}{C}\text{-}H} \xrightarrow{H^+,\ H\text{-}OH} \underset{\substack{1°\text{ alcohol} \\ + \\ Mg(OH)X}}{R\text{-}CH_2\text{-}OH}$$

E.g. :-

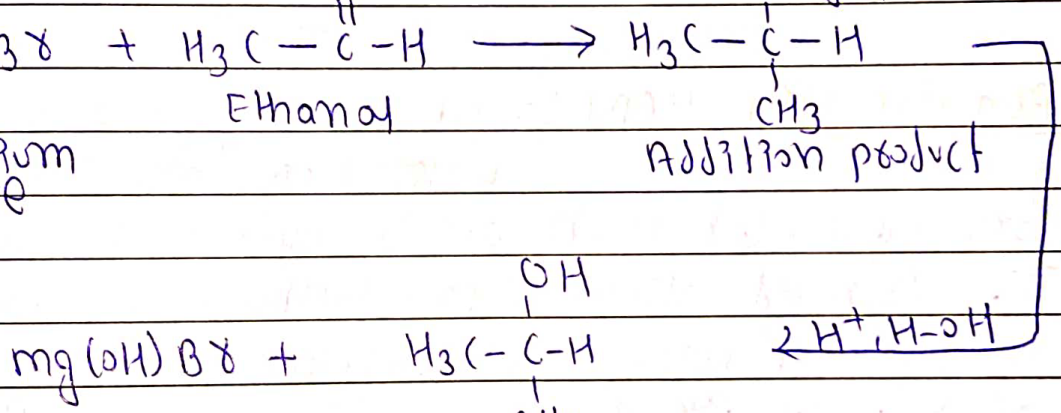
$$\underset{\substack{\text{methyl magnesium bromide} \\ n=1}}{CH_3\text{-}MgBr} + \underset{\text{methanal}}{H\text{-}\overset{\overset{O}{\|}}{C}\text{-}H} \longrightarrow \underset{\text{Addition product}}{H\text{-}\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}H} \xrightarrow{H^+,\ H\text{-}OH} \underset{\substack{\text{Ethanol} \\ n=2 \\ \text{i.e. 2nd} \\ + \\ Mg(OH)Br}}{CH_3\text{-}CH_2\text{-}OH}$$

Note :- methanol cannot be prepared by this method.

(2.) G.R. gives 2° alcohol with aldehydes other than formaldehyde



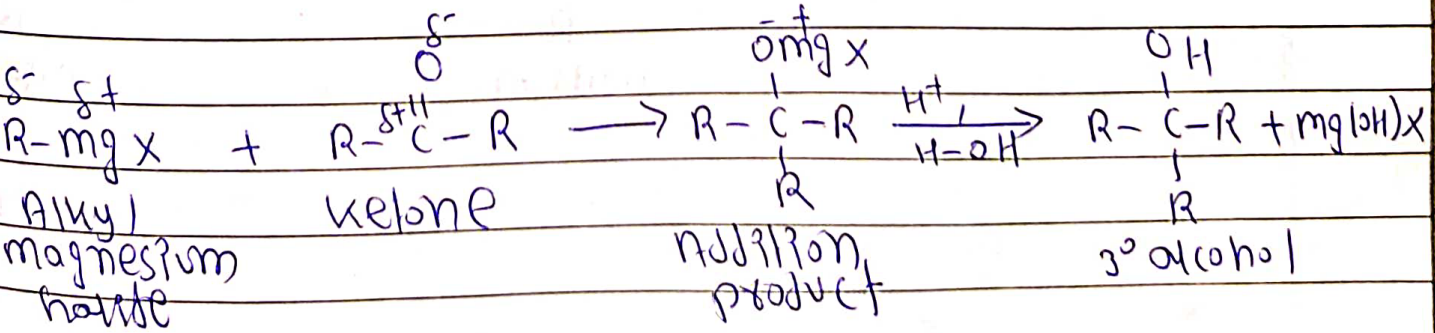
E.g :-



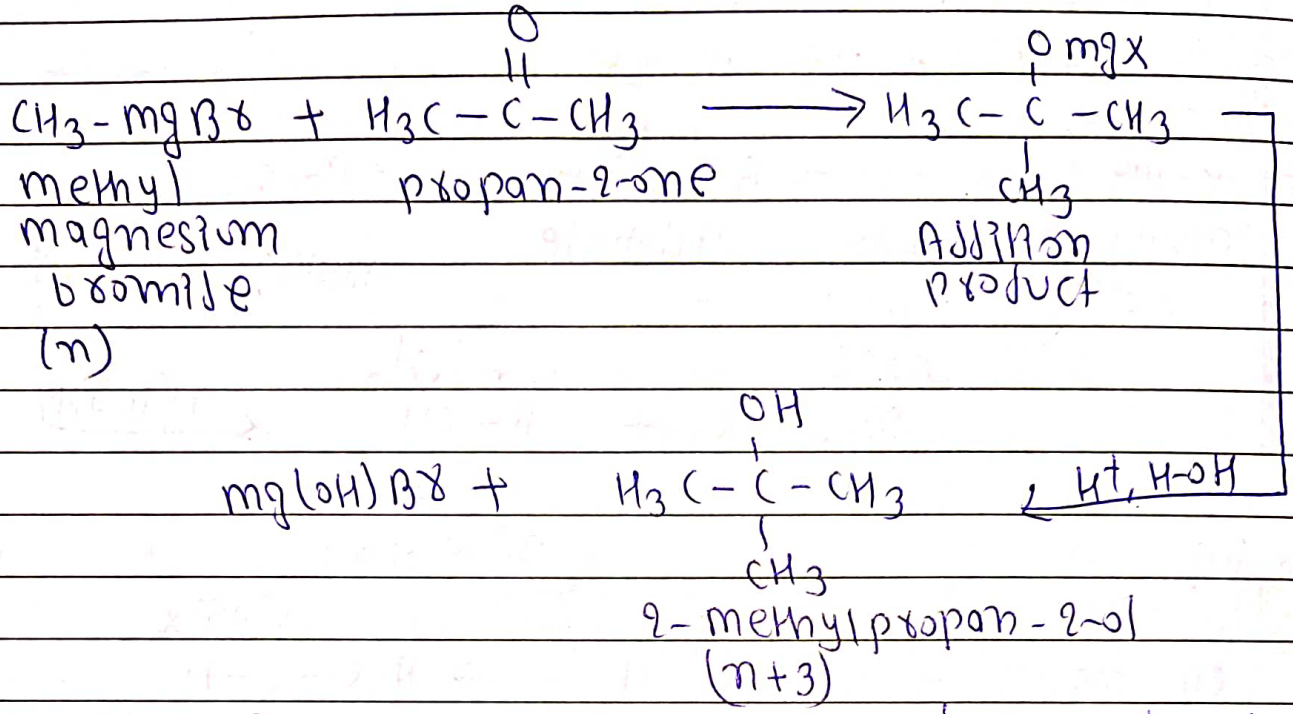
Propan-2-ol

~~n+3~~ (n+2)

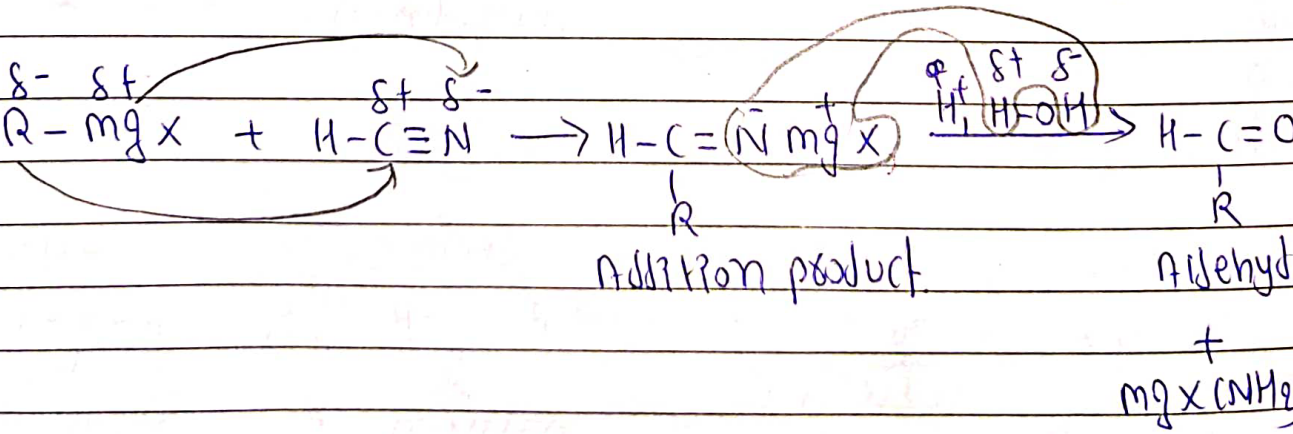
(3.) G.R. gives 3° alcohol with ketone.



E.g :-



(3) Reaction with HCN :- When Grignard reagent is heated with HCN, an addition product is formed which upon acidic hydrolysis gives aldehyde. Thus formed aldehyde can further reacts with another molecule of Grignard reagent to form secondary alcohol. Hence the equimolar amount of HCN and Grignard reagents are used to obtain aldehydes only.



Eg:-

$CH_3-MgBr + H-C\equiv N \longrightarrow H-C(CH_3)=\bar{N}\,Mg^{+}X$

methyl magnesium bromide

Addition product

$MgBr(NH_2) + H-C(CH_3)=O \xleftarrow{H^+,\ H-O-H}$

Ethanal (Acetaldehyde)

(4) **Reaction with RCN :-** When G.R. is heated with RCN, an addition product is formed which upon acid hydrolysis gives ketone.

$R-MgX + R-C^{\delta+}\equiv N^{\delta-} \longrightarrow R-C(R)=\bar{N}\,Mg^{+}X$

G.R. Alkanenitrile Addition product

$MgX(NH_2) + R-\overset{O}{\overset{\|}{C}}-R \xleftarrow{H^+,\ H-O-H}$

ketone

E.g:-

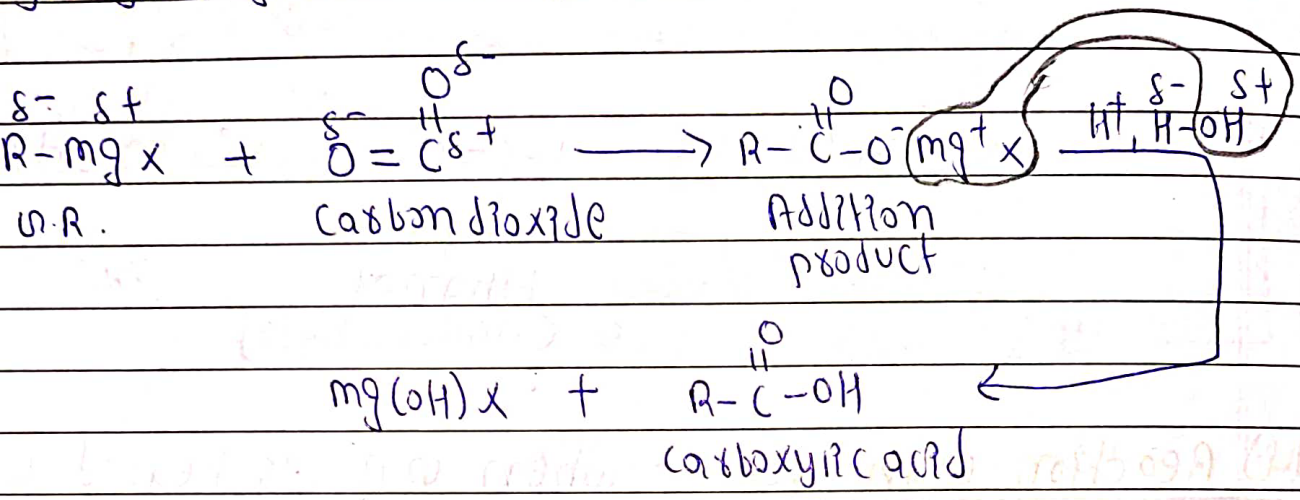
$CH_3-MgBr + CH_3-C\equiv N \longrightarrow CH_3-C(CH_3)=N\,MgBr$

methyl magnesium bromide; Ethanenitrile; Addition product

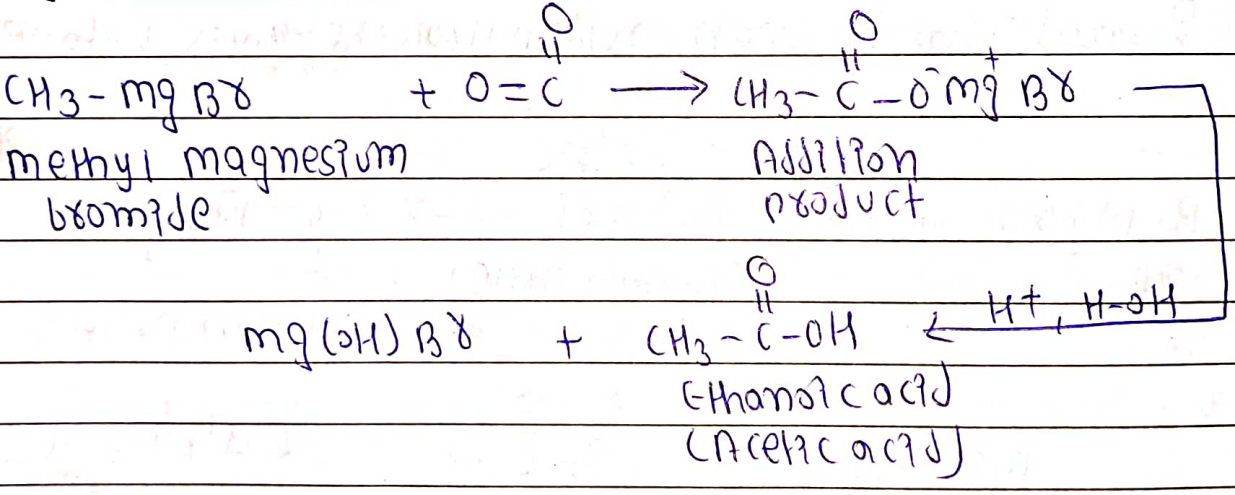
$MgBr(NH_2) + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xleftarrow{H^+,\ H-O-H}$

(Propan-2-one)

(5) Reaction with carbon dioxide :- When the Grignard reagent is treated with carbon dioxide, carboxylate is formed which upon acidic hydrolysis gives carboxylic acid.

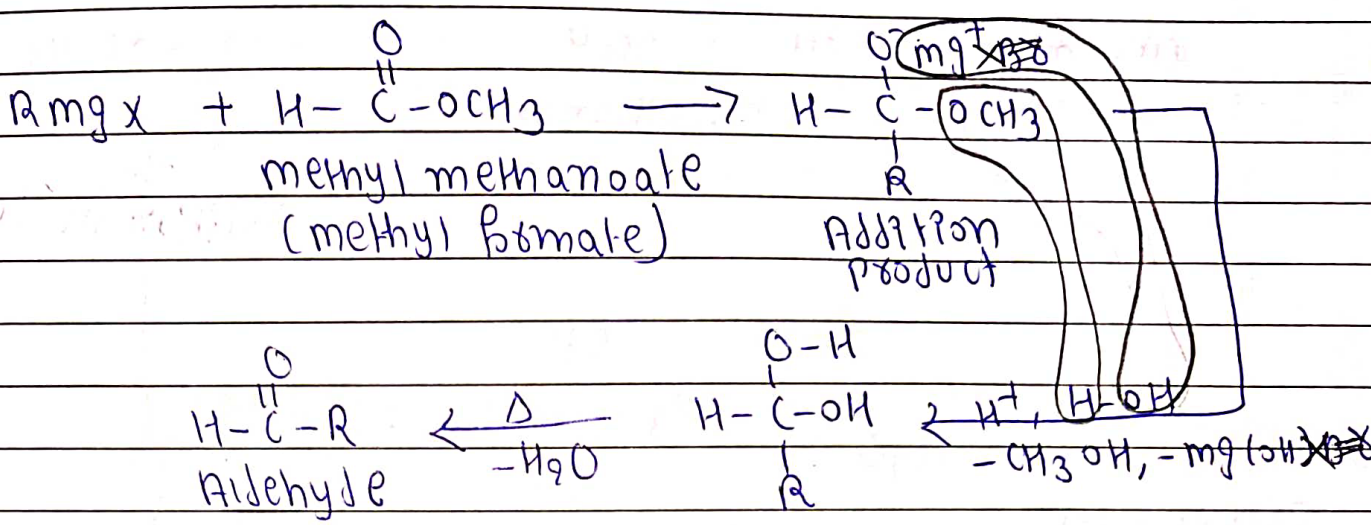


E.g :-

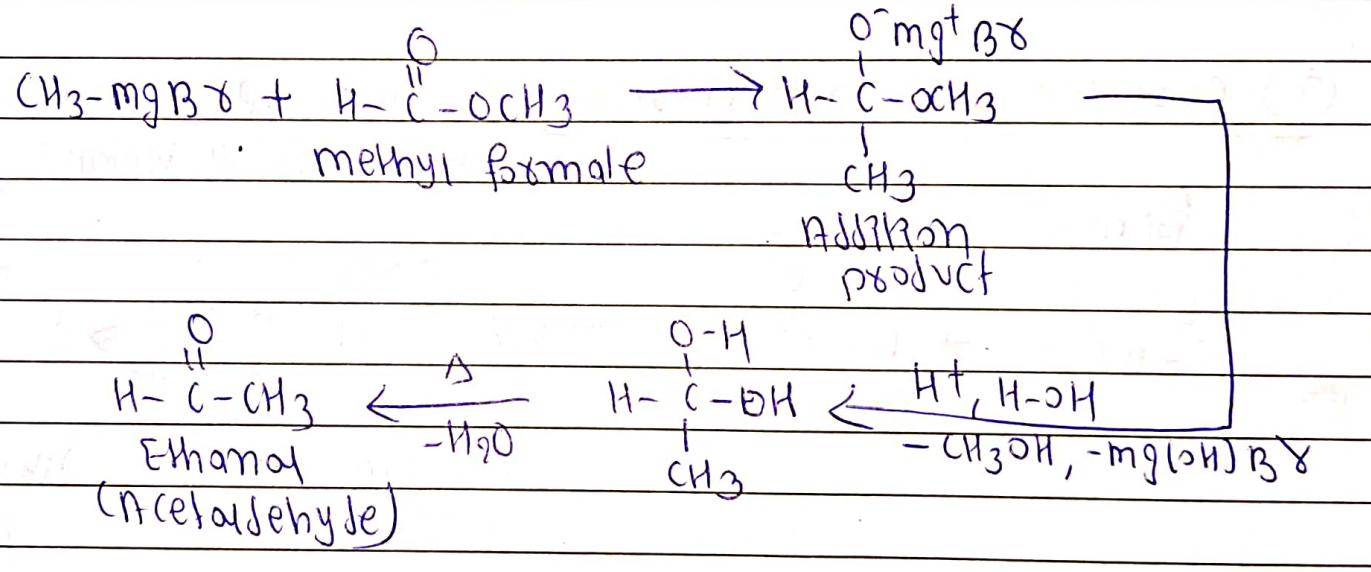


(6) Reaction with ester :- When G.R. is heated with an ester carbonyl compound, aldehyde and ketone are formed.

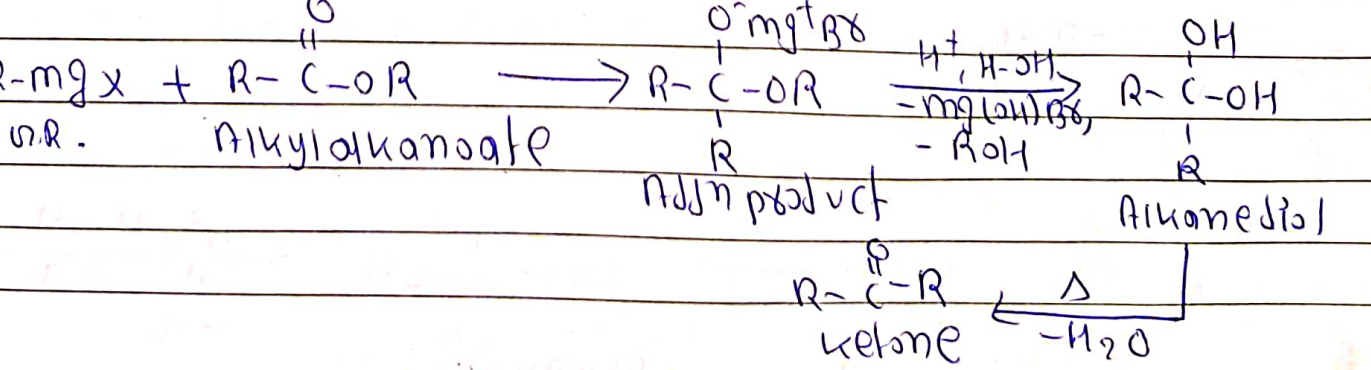
(i.) G.R. gives aldehyde with formic ester.



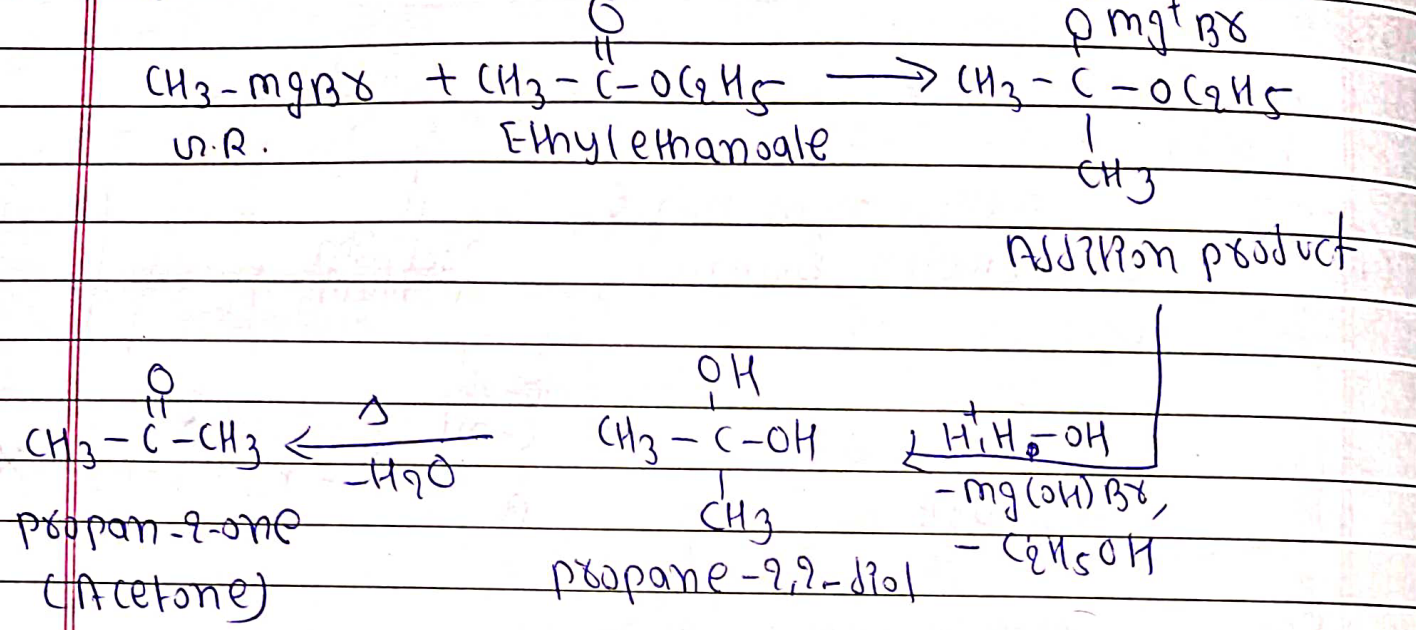
Eg:-



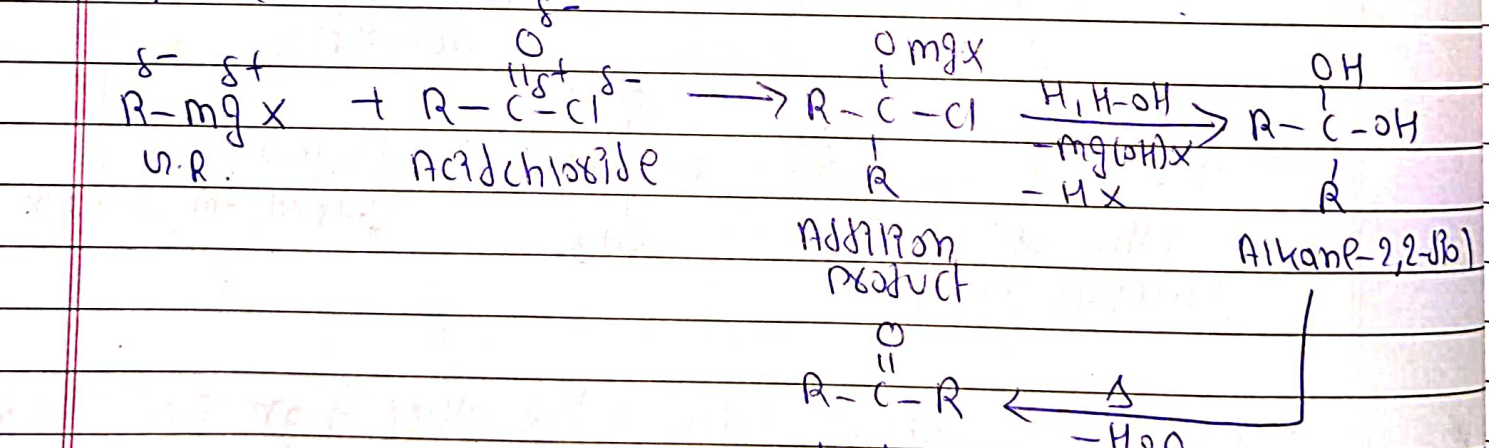
(ii) G.R. gives ketone with ester other than formic ester.



Eg :-



(7.) Reaction with acid chloride :- when G.R. is heated with acid chloride, ketone is formed.



Eg :-

