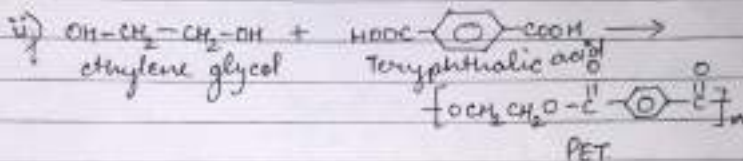
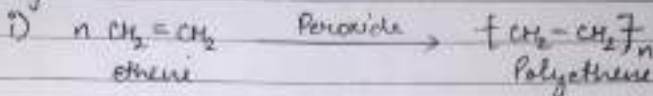


Unit-2

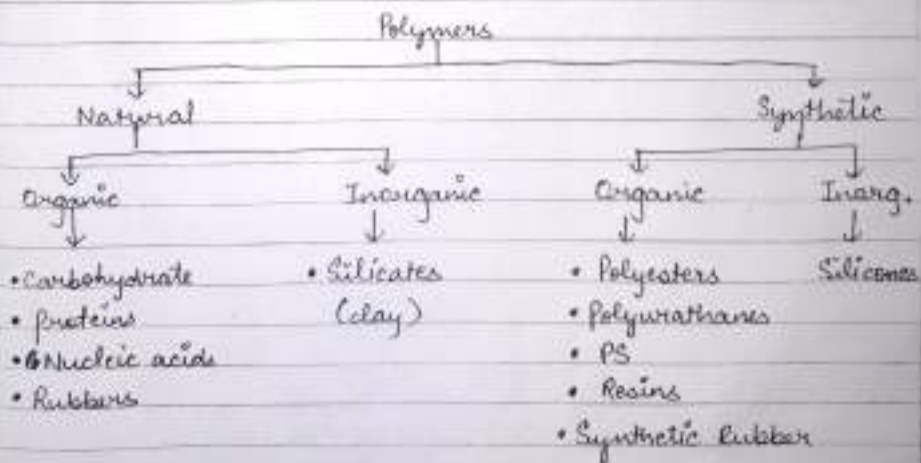
Polymers

Polymer is a macro molecule made up of large no. of repeating units called monomers
E.g.



Classification :

I On the basis of origin :

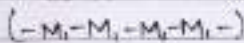


II On the basis of monomers:

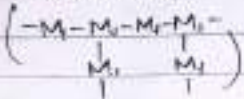
Polymer

Homopolymer

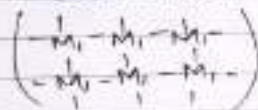
- Linear



- Branched



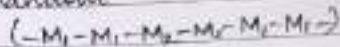
- Cross-linked



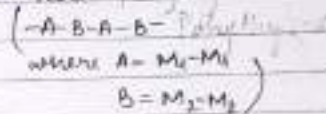
Heteropolymers

- Alternating $(-M_1-M_2-M_1-M_2-)$

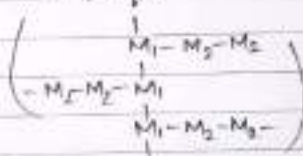
- Random



- Block Polymers



- Graft

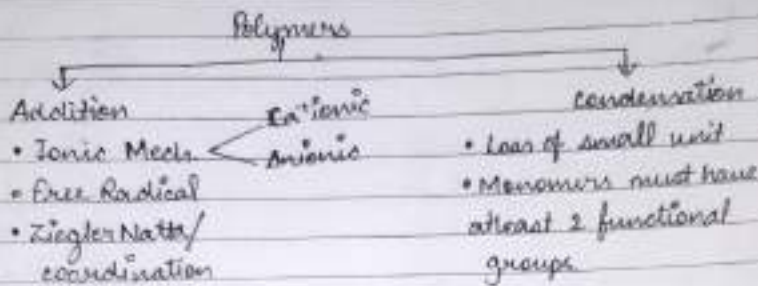


III On the basis of Tacticity:

Tacticity

(next Page) →

IV On the basis of polymerisation technique:



<u>Addition</u>	<u>Condensation</u>
1. Formed by addition reactions.	formed by condensation reactions.
2. Monomers must be unsaturated	Monomers need not be unsaturated but they must be bifunctional.
3. called chain growth polymers	called step-growth polymers
4. Mol. weight of polymer is equal to the total weight of the monomer	Mol. weight of polymer is always less than the total weight of the monomer
5. Loss of no unit during polymerisation.	Small the unit like NH_3 , CO_2 , H_2O , R-OH , etc are lost during polymerisation.
6. Generally, linear or branched polymers are formed	Generally, cross-linked polymers are formed.

7. Generally, thermoplastic polymers are obtained.

Generally, thermosetting polymers are obtained.

8. Polymerisation proceeds in 3 steps:

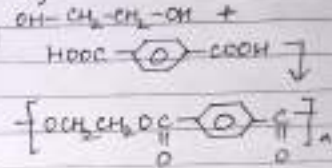
- Initiation
- Polymerization
- Termination

Polymerisation is normally a single step process.

9. Eg. Polyethylene



Eg.



Homopolymer

1. The polymers that are formed by the polymerization of a single monomer are known as homopolymer.

2. There is only one repeating unit and generally form linear structure.

3. Eg. PVC, Polyethylene, polyacrylonitrile, etc.

Copolymer

The polymers that are formed by the polymerization of two different monomers are known as copolymers.

The two monomers can join in any fashion to make a polymer.

Eg. Styrene/ Butadiene co-polymer, Styrene acrylonitrile

Based on hydrogenation reaction.
... of group ...

V On the basis of engineering properties:

various intermolecular forces (van der Waals forces, H-Bonds, dipole-dipole interaction) present b/w polymeric chains, they affect chemical/mechanical properties (tensile strength, elasticity, toughness) which depend on the secondary forces. Magnitude of secondary forces depends on the size of the molecule and no. of functional groups along the polymeric chain.

1. Elastomers
2. Fibres
3. Thermoplastics
4. Thermosetting

Elastomers:

It is a randomly oriented amorphous polymer. Weak van der Waals forces are present between the chains. Such random chains stretch out but there are insufficient van der Waals forces to maintain them in that configuration and position. Therefore when the stretching force is removed, they go back to their random shape. They stretch out to more than 10 times their normal length. Normally, addition polymers obtained from Butadiene and its derivatives are elastomers.

Eg. Natural rubbers, synthetic rubber (Buna-S, Buna-N)

Fibres:

They are linear fib polymers where individual chains are held together by H-Bonds or dipole-dipole attraction giving highly ordered polymeric chains, having high tensile strength but minimum or least elasticity, crystalline with high melting point and low solubility.

Eg. M. Terylene, Arlon, Nylons, Cellulose, Silk, wool, Myosins, etc.

Thermoplastics

- They become soft and melt on heating and on cooling they harden. The process is reversible.

- Can be moulded, remoulded and reshaped

- These are addition polymers.

- Generally linear.

- Generally soft, weak and less brittle.

Thermosetting

Because hard on heating the process is irreversible.

can be moulded once only, cannot be reshaped or remoulded.

These are condensation polymers.

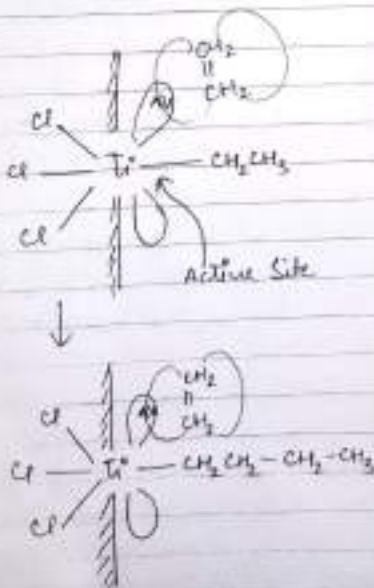
Generally crosslinked

Usually hard, strong and more brittle.

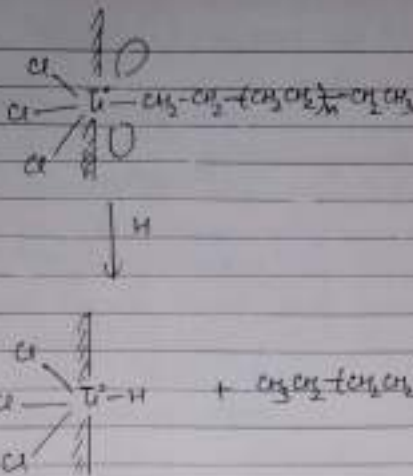
- | | |
|---|--|
| <ul style="list-style-type: none"> • Can be reclaimed from waste. | <ul style="list-style-type: none"> cannot be reclaimed from waste |
| <ul style="list-style-type: none"> • Soluble in some organic solvents. | <ul style="list-style-type: none"> Insoluble in almost all organic solvents |
| <ul style="list-style-type: none"> • Eg. Polyethylene, polypropylene, etc. | <ul style="list-style-type: none"> Eg. Bakelite, Polyesters, etc. |

Mechanism of Polymerisation

1. Coordination Polymerisation / Ziegler-Natta Polymerisation:



↳



Ziegler and Natta had discovered that in the presence of combination of transition metal halide (TiCl_4 , TiCl_3 , TiCl_2 , halides of Co, Ni, etc) with an organo metallic compound, polymer synthesis can be achieved.

Mechanism of polymerisation using ZN catalyst is not fully understood as yet. Monomers, unsaturated monomers in an inert solvent like heptane, in presence of ZN catalyst result in the formation of linear polymers with high order of stereochemistry (isotactic and syndiotactic).

As in ZN polymerisation, highly branched monomers are not preferred as a result they can pack more efficiently giving better mechanical properties to the material. By choosing appropriate reaction condition and catalyst polymer stereo regularity is maintained.

Organo-Metallic Compounds

Organo metallic compounds also known as organo-inorganics, metallo-organics, constitute a class of organic compounds in which carbon is directly linked to a metal atom in such a way that the compound has high degree of ionic character.

A large no. of metals such as Li, Na, Mg, Zn, Hg, Pb, Cd, etc. and transition metals, Lanthanoids, actinoids and semi-metals such as Boron, Si, Arsenic, selenium, etc are considered to form organo-metallics.

Eg. CH_3MgBr , CH_3Li , $(\text{C}_2\text{H}_5)_2\text{Hg}$, $(\text{C}_2\text{H}_5)_4\text{Pb}$, $(\text{CH}_3)_3\text{B}$



Nomenclature:

1. In general, while naming an OMS name of the metal is written after the organic group which may be alkyl, aryl, alkene, alkyne, carbonyl or aromatic. Eg:

CH_3Li - Methyl lithium
 $(\text{C}_2\text{H}_5)_2\text{Hg}$ - Diethyl Mercury
 $(\text{C}_2\text{H}_5)_4\text{Pb}$ - Tetraethyl Lead
 CH_3MgBr - Methyl Magnesium Bromide

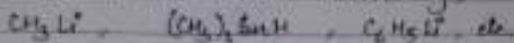
2. Organo metallics of semi-metals are named as derivatives of their hydrides, such as, Boranes, Silanes, etc. Eg:

$(\text{CH}_3)_2\text{B}$ - Dimethyl Borane
 $(\text{C}_2\text{H}_5)_4\text{Si}$ - Tetraethyl Silane
 $(\text{CH}_3)_4\text{Sn}$ - Tetramethyl Stannate
 $(\text{CH}_3)_3\text{SnH}$ - Trimethyl Stannate hydride

Classification:

1. Simple OM:

Organic metallica having hydrocarbon or H bonded to the metal atom. Eg:



2. Mixed OM:

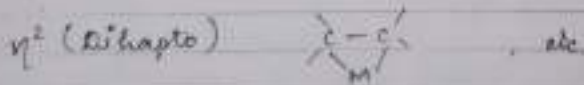
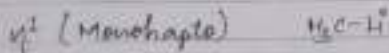
Organic metallica having groups other than H and hydrocarbons also attached to the carbon part of the organic group. Eg,



→ Based on Hapticity:

(η)

Hapticity of a ligand is the no. of C atoms which are within the bonding system of the metal atom.



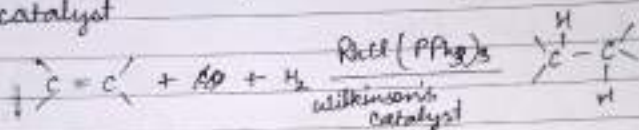
Preparation, & Applications of Organo. Comp.

Applications

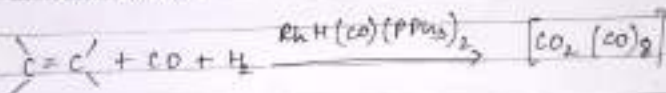
1. Heterogeneous catalysis :- Ziegler Natta catalyst are used for the synthesis of stereo regular polymers. (refer to Ziegler Natta Mechanism)

2. Homogeneous catalysis :-

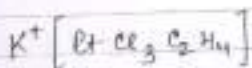
- Hydrogenation of alkenes using Wilkinson's catalyst



Oxonection :-



Zeise Salt :-



3. Metallurgical Processes :-

for purification of nickel (Mond's Process):
[Ni(CO)₄]

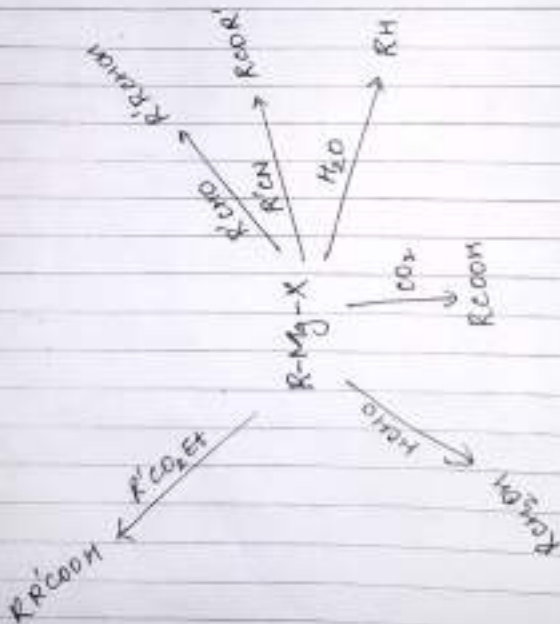
4. It's anti-knock agent for petrol and gasoline

5. organo silicones - (refer to synthetic rubbers)

6. Biological application in agriculture and pharmacy - prevents infection of seeds Eg. R_2HgX
Alkyl Mercury Halide used as fungicide
As antiseptic - trialkyl tin, Mercurochrome

7. Tetra Methyl Silanes (TMS) used as a reference in NMR spectroscopy.

8. Organo - synthesis ;
 RLi , R_2Ca and RMgX



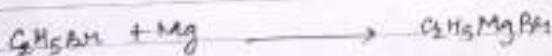
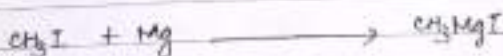
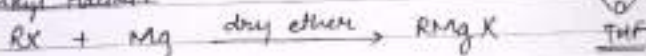
Grignard Reagents

Extremely important reagents, also known as organo magnesium halide, have general formula,
 $RMgX$ or $ArMgX$

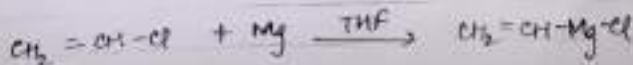
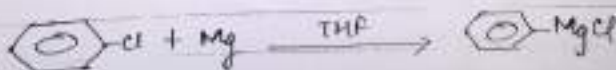
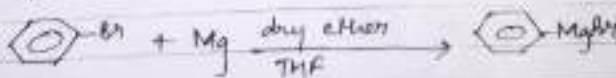
Preparation:

Prepared by the action of alkyl / aryl halide (Bromide / Iodide) on magnesium turnings in dry ether or tetrahydrofuran (THF)

Alkyl Halide:



Aryl Halide:

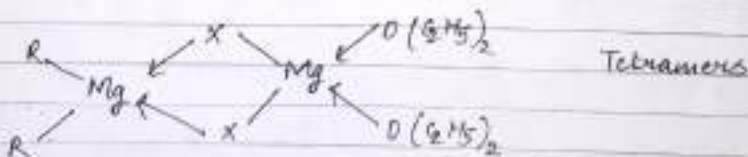
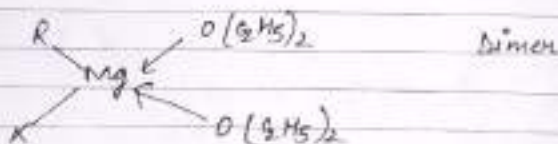


Note:

- for a given alkyl group, ease of formation of Grignard reagent is $I > Br > Cl$
- alkyl or aryl magnesium fluorides are not known because these are unstable.
- for a given halogen atom, $MeX > C_2H_5X > C_3H_7X \dots$
because due to increased C atoms, stability reduces due to steric hindrance.

Structure:

Obtained as white solids having ether of crystallisation in such a way

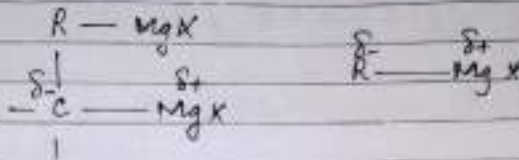


Diethers of G.R.

Basic formula $\rightarrow RMgX$

Reactions of G.R.

Page No. _____



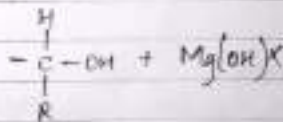
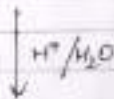
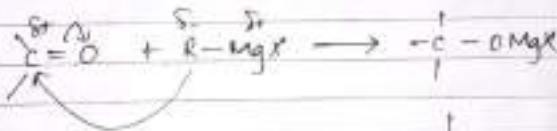
It undergoes:

It undergoes:

- Nucleophilic substitution



- Nucleophilic addition reaction

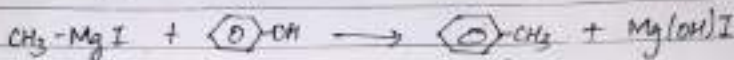


Applications :

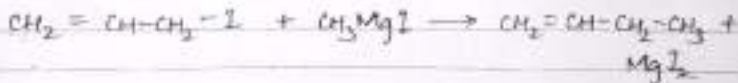
1. Alkanes:



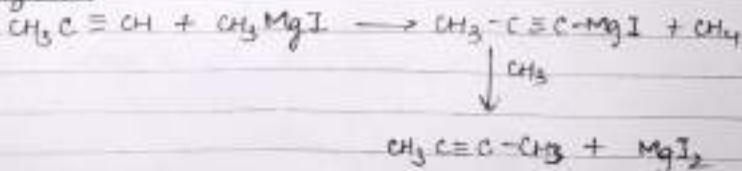
Here, B \rightarrow OH, SH, NH₂, NHR, NR₂, etc.



2. Alkenes:

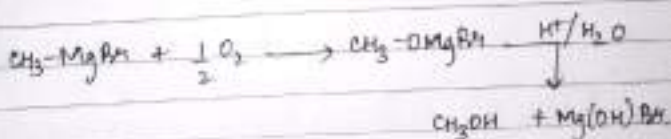
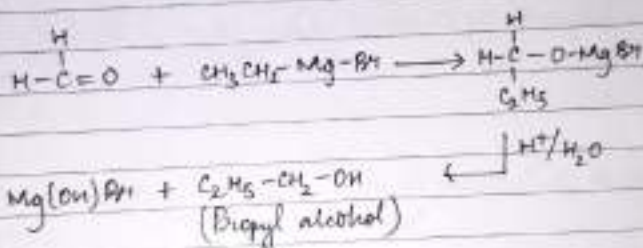
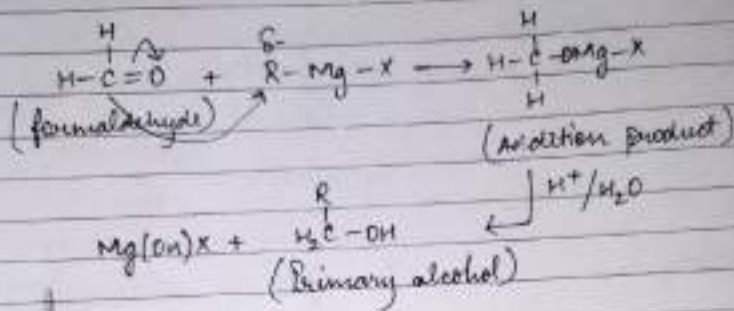


3. Alkynes:

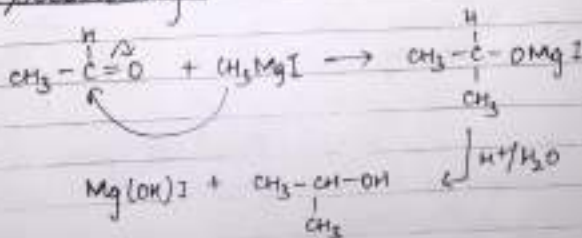


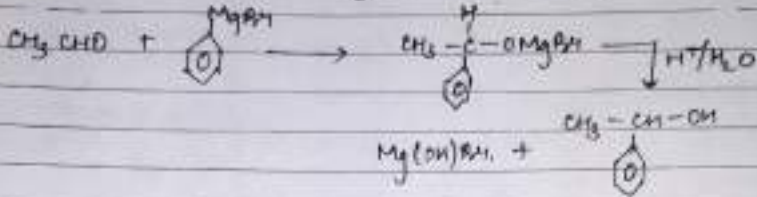
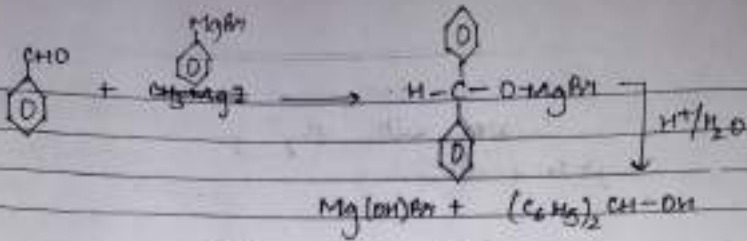
Preparation of Alcohols :

i) Primary :

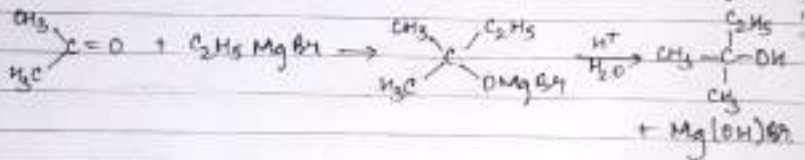
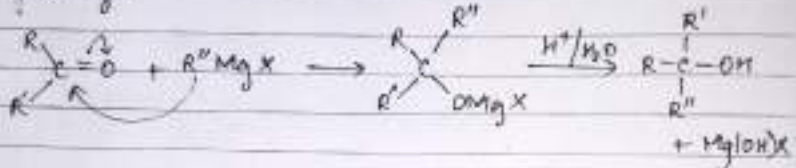


ii) Secondary :





iii) Tertiary :



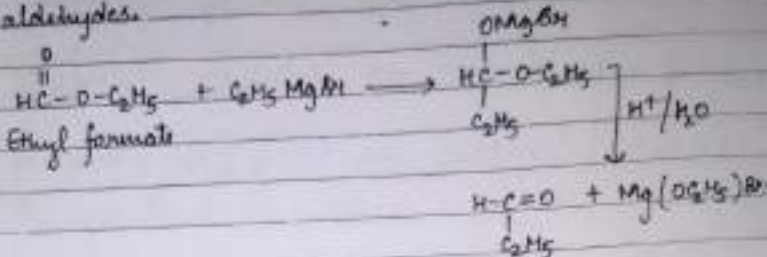
Formation of Ethers :

Gr reacts with lower halogenated ethers to obtain higher ethers.

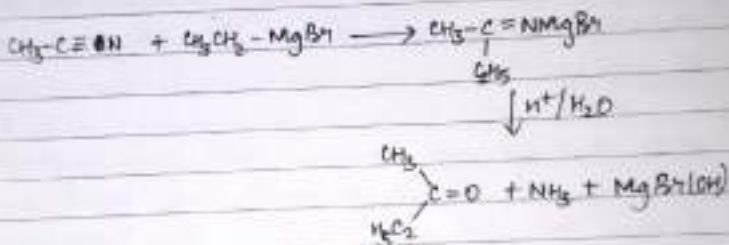


Formation of Aldehydes:

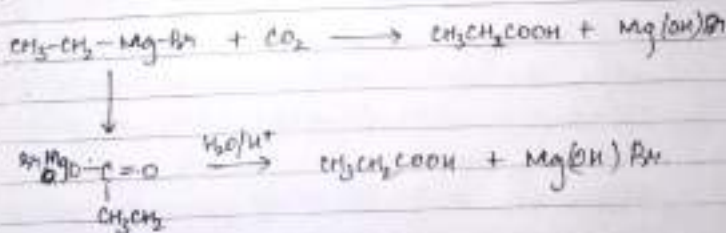
GR are treated with ethyl formates to get aldehydes.



Formation of Ketones:



Formation of -ic acids:



Primary Amine:

