

ORGANOMETALLIC COMPOUNDS

Rijoy Kodiyan Jacob

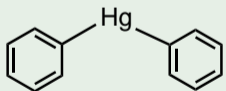
October 1, 2020



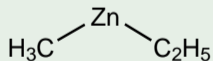
DEFINITION

An organometallic compound is a compound that contains a direct carbon metal bond. The organic moiety is an alkyl, alkenyl, alkynyl or aryl group.

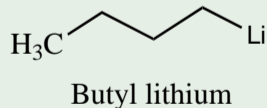
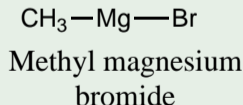
EXAMPLE



Diphenyl mercury



Ethyl methyl Zinc



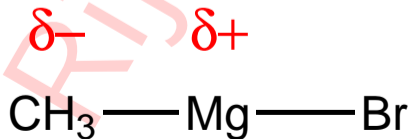
The compounds are polar and carbon bonded to the metal is nucleophilic.



GRIGNARD REAGENT

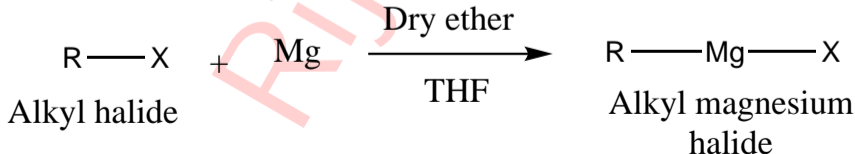
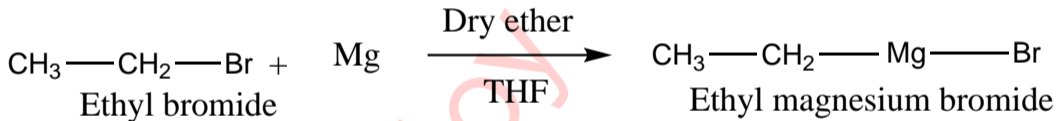
Grignard reagents are organomagnesium halides having the general formula in R-Mg-X. 'R' can be alkyl or aryl, etc. X = Cl, Br, I, etc.

Here the Mg-X bond is essentially ionic and C-Mg bond is highly polarised covalent bond.



PREPARATION

They are generally prepared by the reaction of an organic halide with magnesium in dry ether or tetrahydrofuran solution



- A solution of organic halide R-X where X=Cl or I in dry ether or THF is poured over Magnesium turnings in a flask.
- Reaction takes place vigorously, the solution turns cloudy, then begins to boil and the magnesium metal gradually disappears.
- The resulting solution is Grignard reagent.

For a given 'R' group the reactivities of organic halides are in the order.

Iodide > Bromide > Chloride

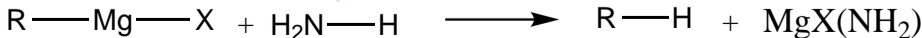
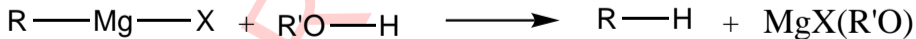
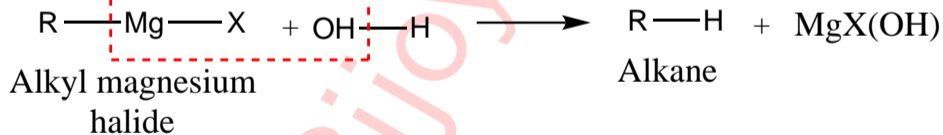
Synthetic utility of Grignard reagent depends upon the nucleophilicity of 'C' atom of alkyl group attached to the metal. It can be used for the synthesis of a wide variety of compounds.



A. NUCLEOPHILIC SUBSTITUTION REACTIONS

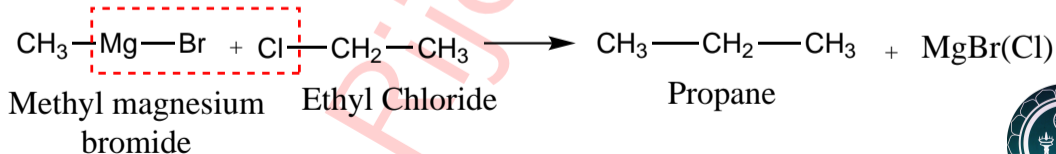
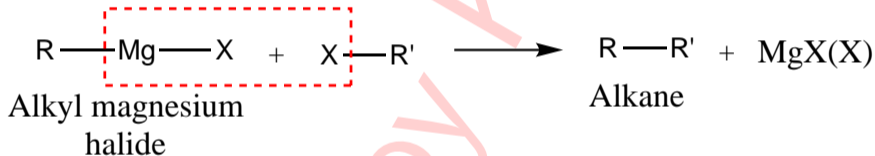
1. PREPARATION OF ALKANES

Grignard reagents yield alkanes when treated with water, alcohols, ammonia, etc.

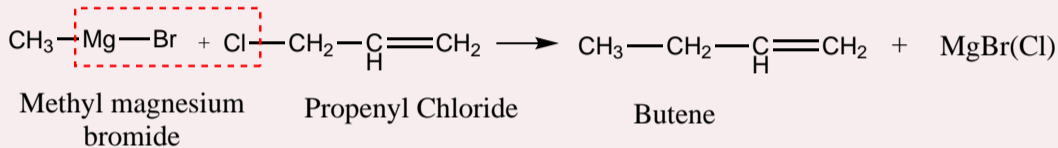


2. PREPARATION OF HIGHER ALKANES

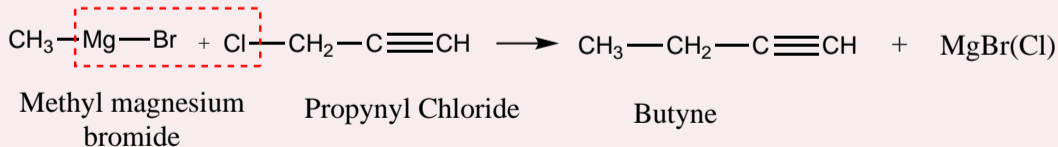
Grignard reagents react with alkyl halides to form higher alkanes.



3. PREPARATION OF ALKENES



3. PREPARATION OF ALKENES



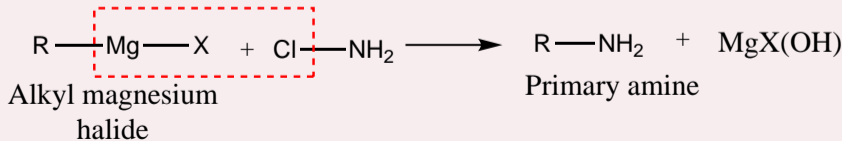
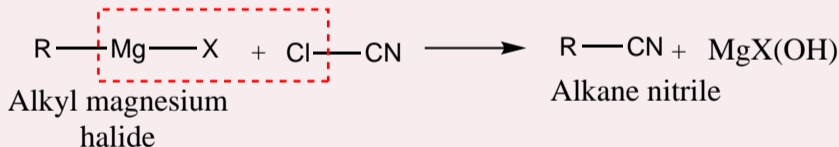
4. ETHERS, NITRILES AND AMINES



Methyl magnesium
bromide

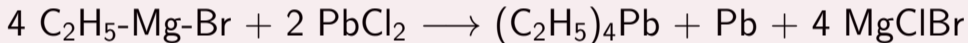
Chlorodimethyl
ether

Ethylmethyl ether

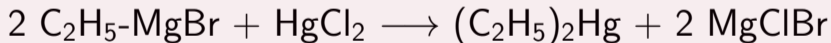


5. ORGANOMETALLIC AND NON-METALLIC COMPOUND PREPARATION

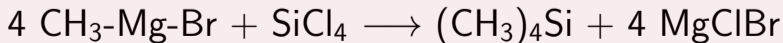
A. PREPARATION OF TEL



B. PREPARATION OF DIETHYL MERCURY



C. PREPARATION OF TMS



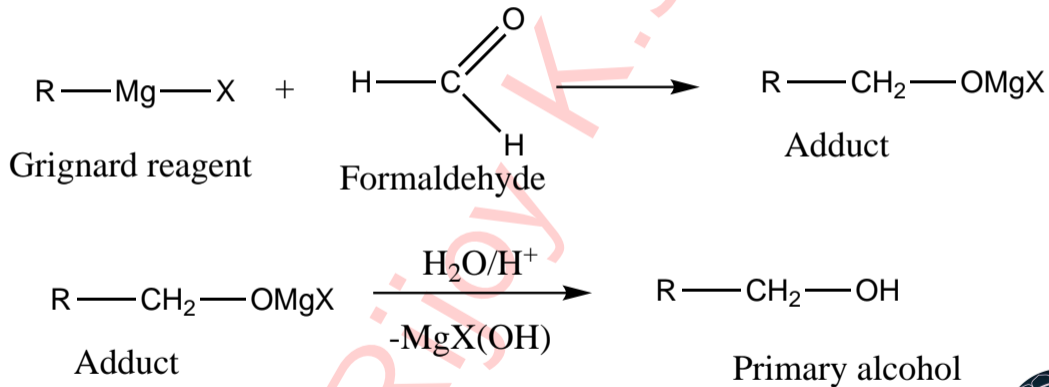
PREPARATION OF ALCOHOLS

Grignard reagents(alkyl magnesium halides) react with aldehydes and ketones to give adducts which on hydrolytic decomposition with dilute acid give alcohols.

FORMATION OF PRIMARY ALCOHOLS

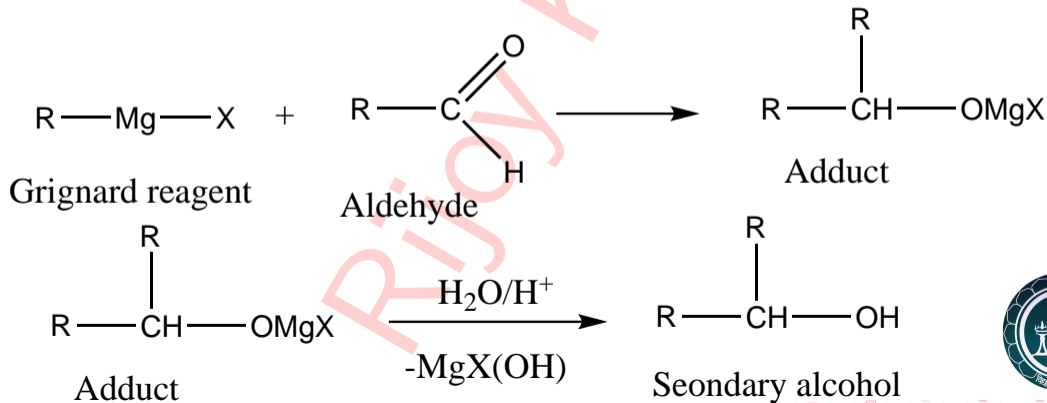
Formaldehyde react with Grignard reagents and followed by hydrolysis of the product formed gives a primary alcohol.





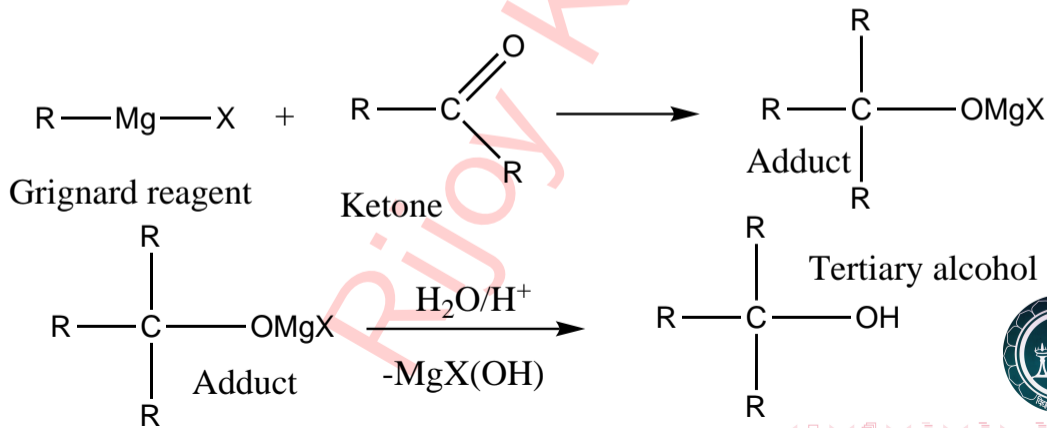
PREPARATION OF SECONDARY ALCOHOL

Aldehydes other than formaldehyde react with Grignard reagent followed by hydrolysis give secondary alcohols.



PREPARATION OF TERTIARY ALCOHOLS

Ketones react with Grignard reagents to give tertiary alcohols

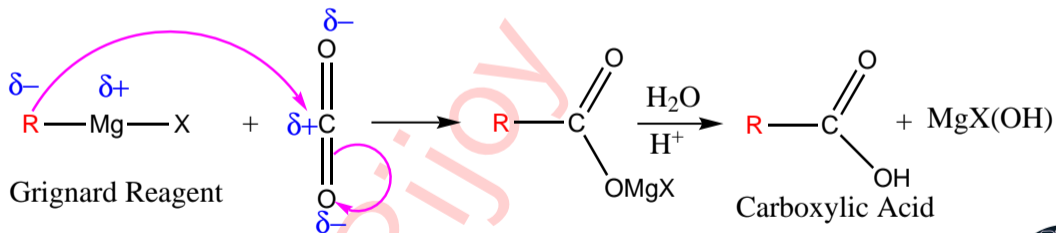


Grignard reagents ($R-Mg-X$) reacts with CO_2 to form addition product that can be hydrolysed to carboxylic acids.

Rijoy

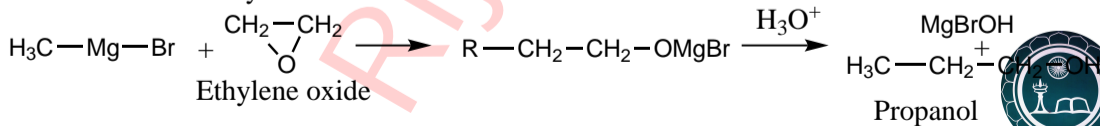
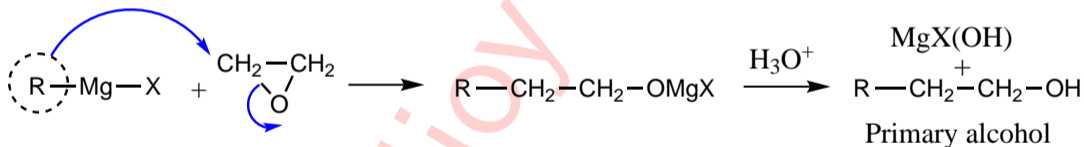


Grignard reagents (R-Mg-X) reacts with CO₂ to form addition product that can be hydrolysed to carboxylic acids.



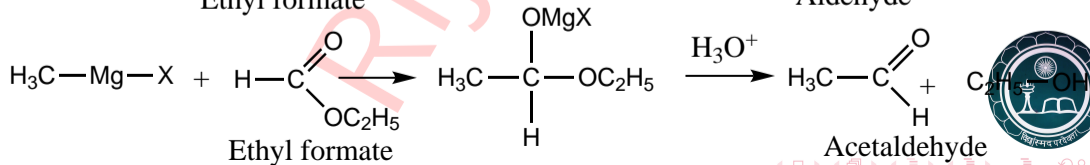
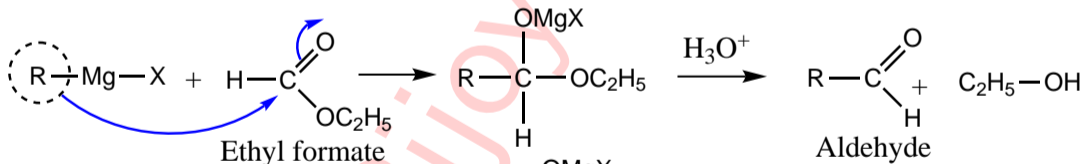
REACTION WITH EPOXIDE

Ethylene oxide reacts with Grignard reagents to form addition products which on acidic hydrolysis give primary alcohols.



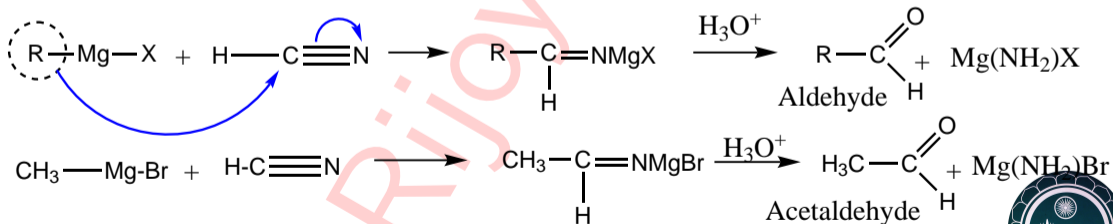
PREPARATION OF ALDEHYDES

Ethyl formate reacts with Grignard reagents in equimolar proportions to form addition products which on acidic hydrolysis give aldehydes.



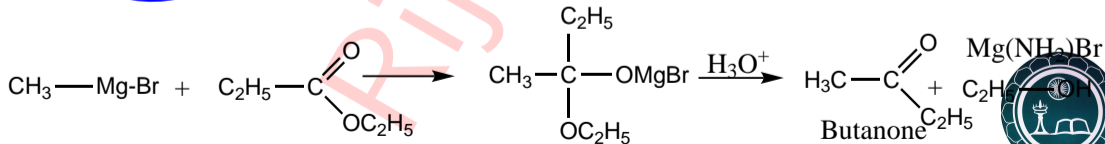
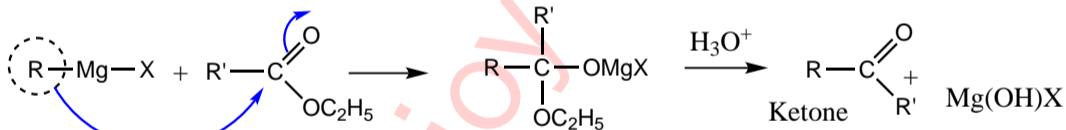
REACTION WITH HCN

Grignard reagents react with HCN to form addition product which on hydrolysis give aldehydes.



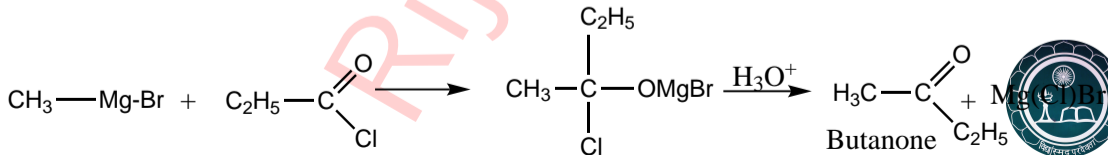
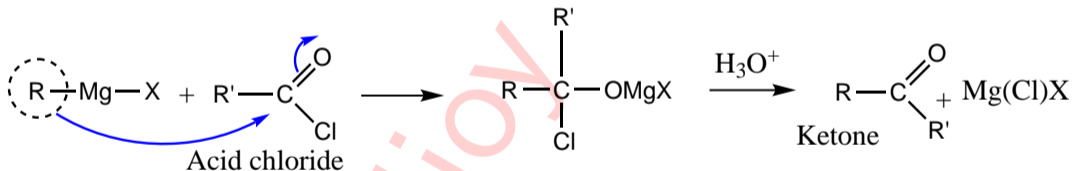
REACTION WITH ESTER

Esters other than ethyl formate react with Grignard reagents followed by acidic hydrolysis give ketones.



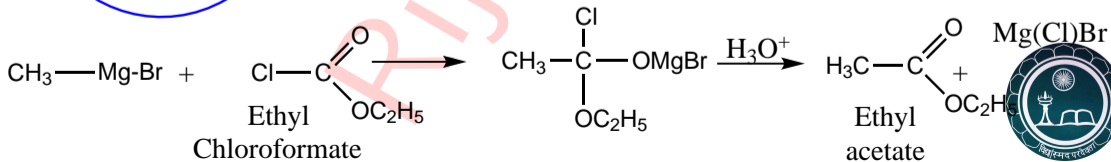
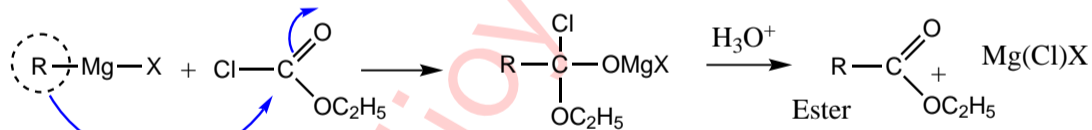
REACTION WITH ACID HALIDES

Grignard reagents react with Acid halides in equi molecular amounts to form addition products which on acidic hydrolysis give ketones.



PREPARATION OF HIGHER ESTERS

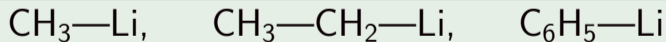
Ethyl chloroformate reacts with Grignard reagent in equimolecular amounts to form addition products which on hydrolysis give higher ethyl esters.



ORGANO LITHIUM COMPOUNDS

Organolithium compounds are organometallic compounds having the general formula 'R-Li'. Where 'R' is generally an alkyl or aralkyl or aryl group, whose 'C' atom is directly linked to the Li atom.

EXAMPLE

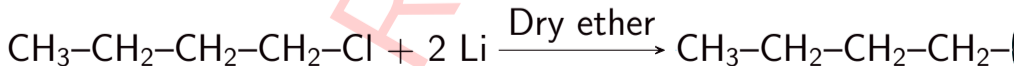


Methyl lithium Ethyl lithium Phenyl lithium

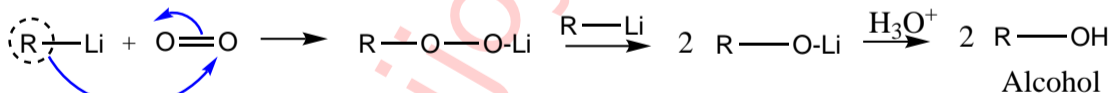


PREPARATION

Organo lithium compounds are generally prepared by the reaction of the suitable organic halides with lithium in dry ether or hexane or benzene solution under inert atmosphere at low temperatures.



Alkyl lithiums react with oxygen to give an intermediate peroxide and followed by hydrolysis of the peroxide gives corresponding alcohols.



- 1 Preparation of alkanes
- 2 Preparation of primary, secondary and tertiary alcohols.
- 3 Reaction with ethylene oxide.
- 4 Reaction with oxygen.
- 5 Preparation of aldehydes
- 6 Preparation of ketones
- 7 Preparation of Carboxylic acid.
- 8 Preparation of higher alkyl lithiums.

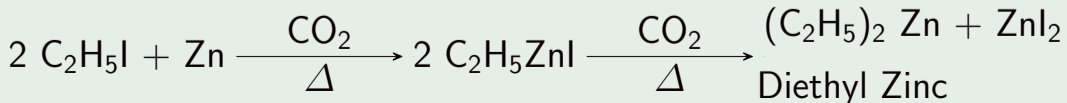


ORGANO ZINC COMPOUNDS-PREPARATION

Compounds where there is a direct bond between Carbon atom of a alkyl or aryl group with Zinc metal are known as so.

Organo Zinc compounds are also known as **Frankland compounds**.

Zinc dialkyls are prepared by heating alkyl halides with Zinc filings in an inert atmosphere of CO_2 or N_2



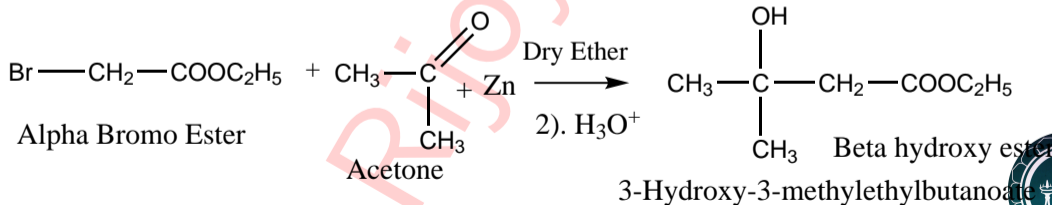
REACTIONS

- Reaction with active hydrogen Compounds.
- Reaction with alkyl halides.
- Reaction with Acid Halides.
- Reaction with aldehydes and ketones
- Reformatsky Reaction.

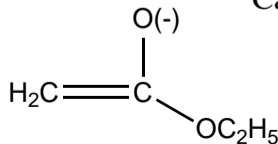
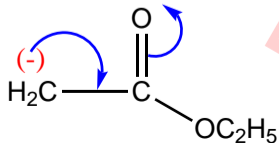
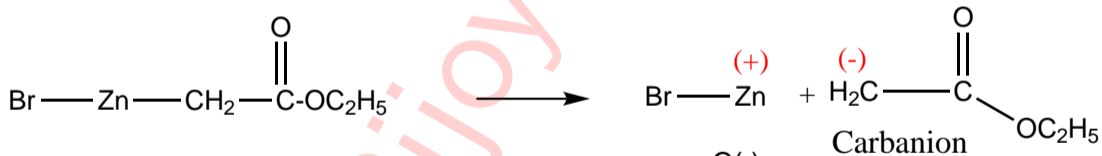
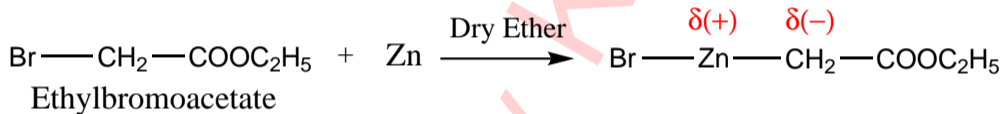


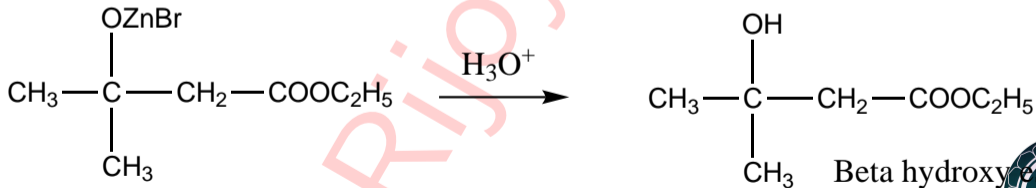
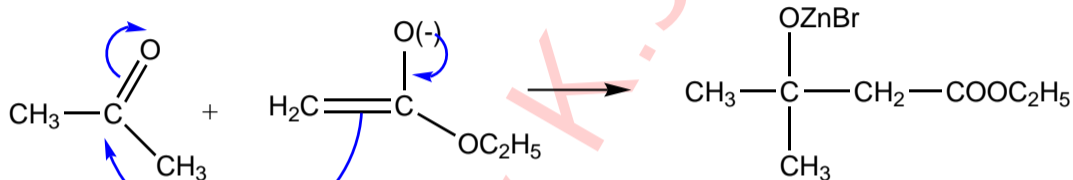
REFORMATSKY REACTION

The reaction of an α -Bromoester with a carbonyl compound in presence of Zinc in ether solution and on subsequent acidic hydrolysis to give a β -hydroxy ester.



MECHANISM





Beta hydroxy ester
3-hydroxy-3-methylethylbutanoate

