

# Organometallic Compounds

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# Organometallic Compounds

- A compound that contains a carbon-metal bond e.g. metal is directly bonded to carbon
- these classes illustrate the usefulness of organometallics in modern synthetic organic chemistry.
- they illustrate how the use of organometallics can bring about transformations that cannot be accomplished in any other way.

- The nature of C-M (carbon metal) bond is ionic in nature.
- That makes a carbon negatively charged means it is nucleophilic in nature so reaction with electrophilic carbons can make carbon-carbon bonds.
- Ionic character order depends on metal used and that is  $\text{Na} > \text{Li} > \text{Mg} > \text{Al} > \text{Zn} > \text{Cd} > \text{Hg}$ .
- Sodium and Potassium alkyls are salts.
- The greater the ionic character, the more reactive is the metal alkyl.

# The First Organometallic Reagents...Grignard Reagents

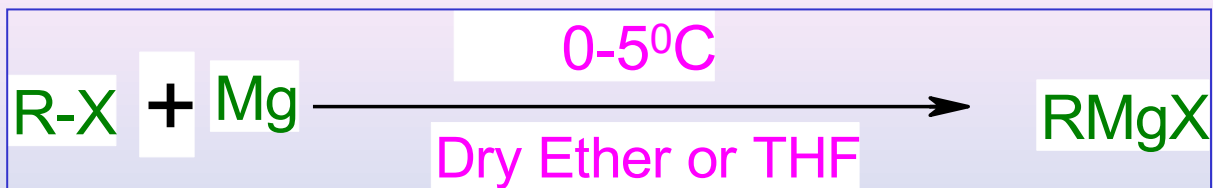


- ❖ Discovered by Victor Grignard in 1900
- ❖ Awarded Nobel Prize in 1912



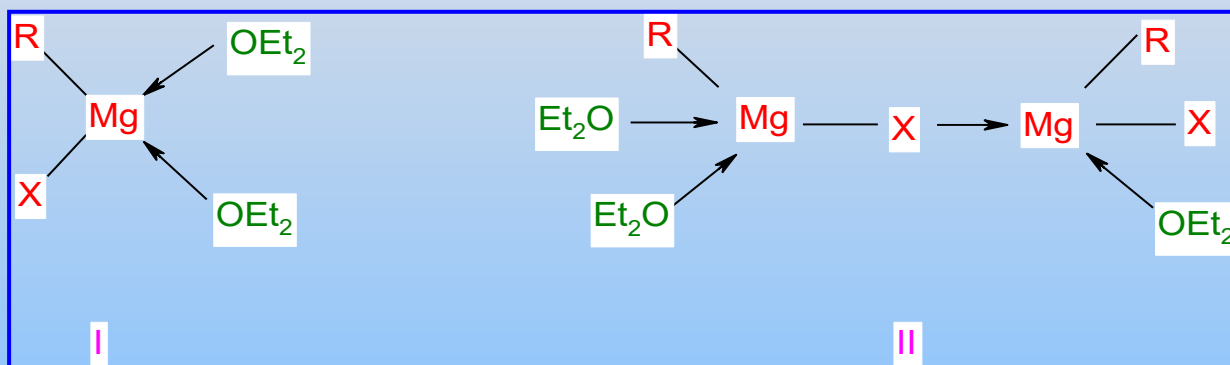
Victor Grignard

**Grignard reagent:** An organo magnesium compound prepared by addition of an alkyl, aryl, or alkenyl (vinylic) halide to Mg metal in diethyl ether or THF



- Dry ether means free from water and alcohol.
- Other solvent may be used e.g. tertiary amines, THF and dimethyl ether of ethylene glycol.
- In synthetic community THF being used as solvent because it increases the reactivity of RX towards Mg and handling of RMgX in THF is easy.
- Order of reactivity of alkyl halide towards Mg  
 $\text{RI} > \text{RBr} > \text{RCl}$ .
- The formation of a GR becomes increasingly difficult as the number of carbon atoms in the alkyl group increases
- Ease of GR formation is  
 $\text{CH}_3\text{X} > \text{C}_2\text{H}_5\text{X} > \text{C}_3\text{H}_7\text{X} \dots$
- Tertiary alkyl chlorides are used instead of tertiary alkyl iodide because t-alkyl iodides readily eliminates hydrogen iodide with the formation of an alkene

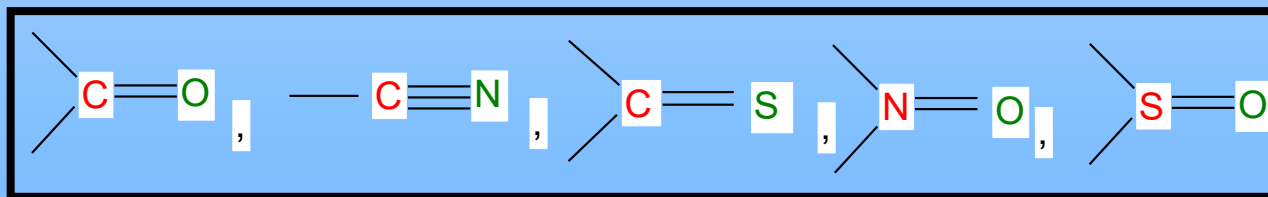
# Structure of Grignard Reagent



Grignard Reagent isolated as Monomer(I) or Dimer(II) which contains ether in its structure, which is called as “Ether of crystallisation”

## Reaction of Grignard Reagent(GR)

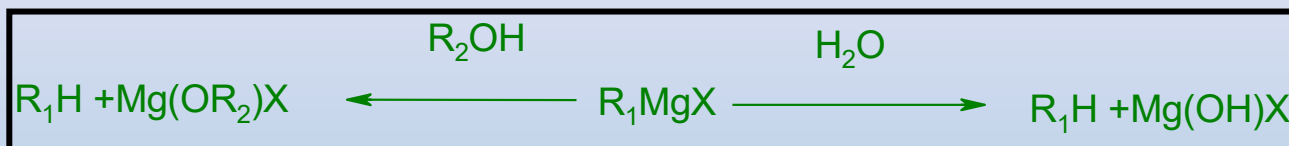
- Grignard reagent is ionic reagent so its reaction is very fast.
- Reaction of GR with other reagent usually takes place in ethereal solution and addition should be very slow.
- Broadly the reaction of GR fall into two groups:
  - (i) Addition of the GR to a compound containing a multiple-bond group in which R groups of RMgX adds to less electronegative atom(red color atoms in given structure below) and MgX group at the more electronegative atom(green color atoms).



- (ii) Double decomposition with compounds containing an active hydrogen atom.

## Active Hydrogen

- An active hydrogen atom is one joined to oxygen, nitrogen and sulphur.
- When hydrogen containing compounds reacts with GR to form alkane.



- Due these reason dry ether (free from water and alcohol) was used in synthesis of GR.
- Reaction of an active hydrogen atom containing compounds with GR results in quantitative yield of hydrocarbon.
- That is valuable for the determination of the number of active hydrogen atoms in a compounds and is known as **Zerewitinoff active hydrogen determination** (1907).
- Methyl magnesium iodide ( $\text{CH}_3\text{MgI}$ ) is used as GR.



- One molecule of methane being equivalent to one active hydrogen atom.
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**Answer the following question:**

- Which one is not organometallic compound :  $\text{RMgX}$ ,  $(\text{CH}_3)_2\text{Zn}$ ,  $\text{CH}_3\text{ONa}$ ,  $\text{BuLi}$ .
- Nature of Metal carbon bond.
- Why dry ether was used.
- Order of reactivity of alkyl halide towards Mg.
- What is “ether of crystallization” and how many ether.
- How many active hydrogen in following compound:  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ ,  $\text{ROH}$ ,  $\text{HOH}$ ,  $\text{RSH}$  and in glucose.
- Which Grignard reagent used in Zerewitinoff active hydrogen determination.

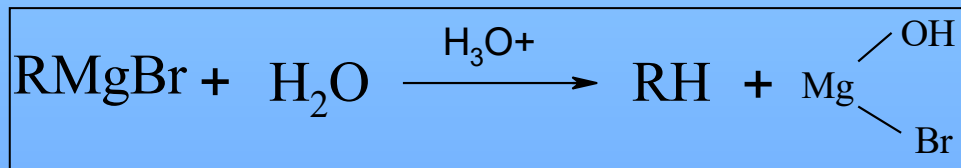
## Order of reactivity of functional group

- Order of reactivity of functional group of a compound containing two or more functional groups toward GR.
- An active hydrogen reacts very much faster than any other group.
- Order of reactivity of the oxo group like  
 $\text{CHO} > >\text{C}=\text{O} > -\text{COCl} > -\text{CO}_2\text{R} > -\text{CH}_2\text{X}$

## Synthetic use of the Grignard Reagent (GR)

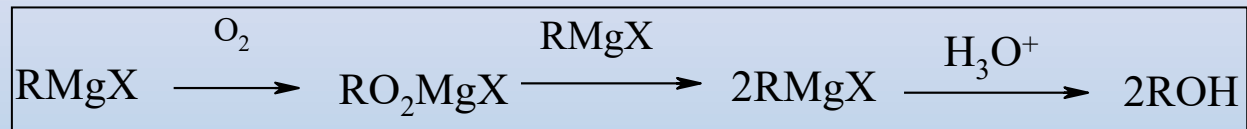
### Synthesis of Hydrocarbons:

When a GR reacts with a active hydrogen containing compound hydrocarbon is formed

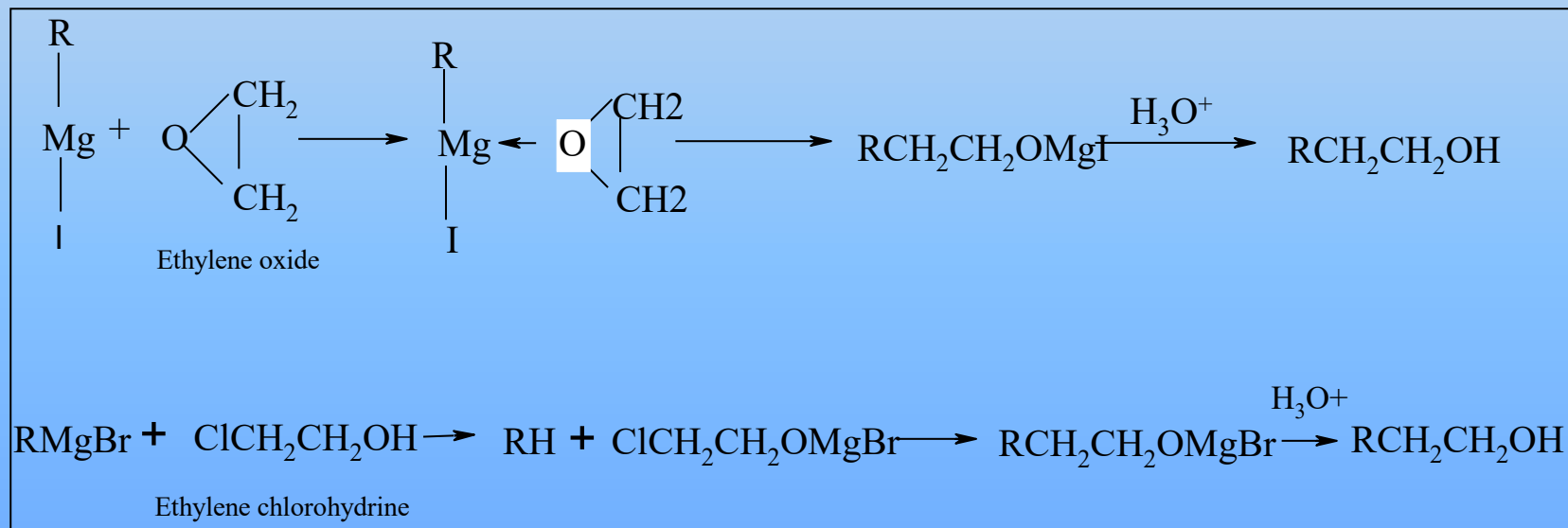


## Synthesis of 1<sup>o</sup>Alcohols

When GR reacts with dry oxygen and then acidified to give 1<sup>o</sup>alcohol



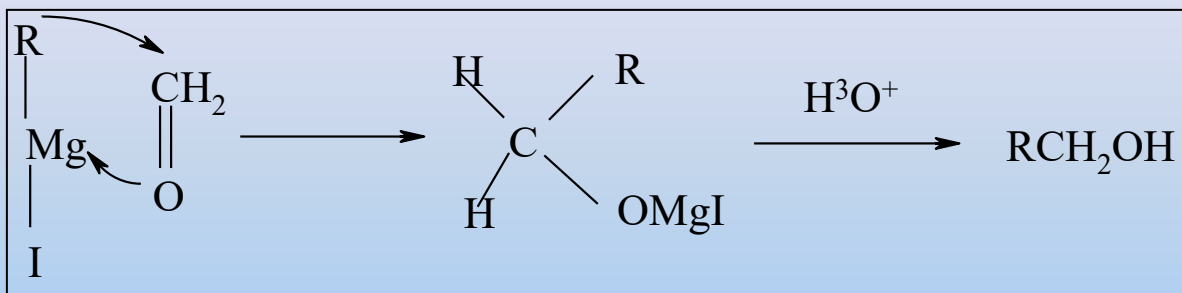
Reaction with ethylene oxide and ethylene chlorohydrine



- In both cases product alcohol contains two more carbon than the Grignard alkyl group.
- With ethylene chlorohydrine two molecules of Grignard reagents are required

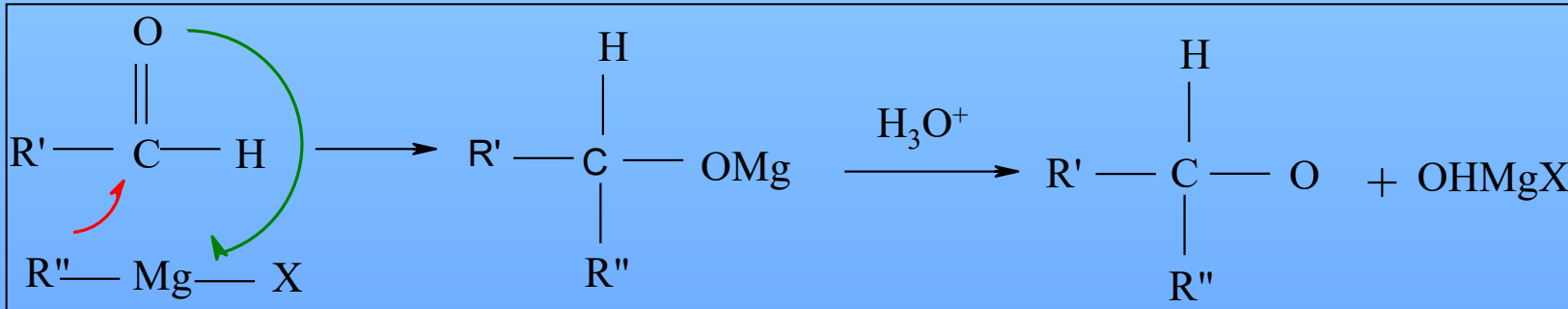
### Reaction with formaldehyde:

GR reacts with formaldehyde formed a complex which on acidification gives primary alcohol.

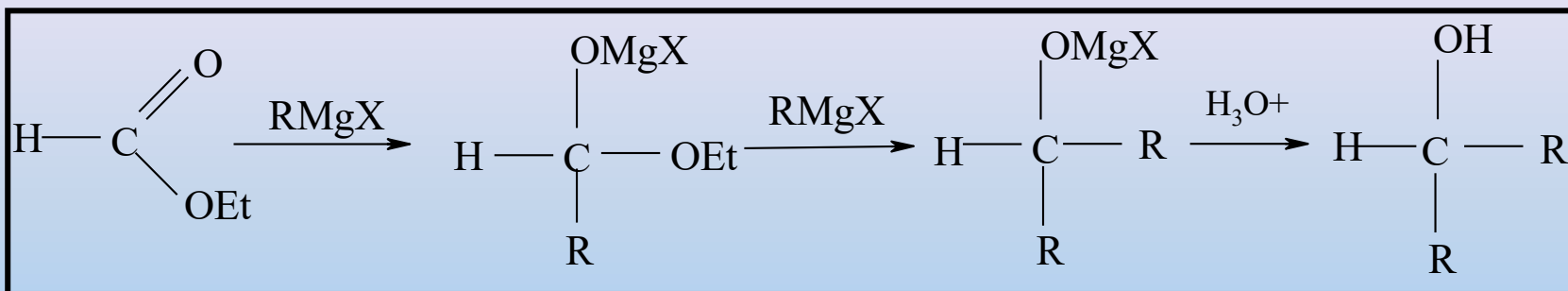


## Synthesis of 2<sup>o</sup> alcohol

Reaction of GR with aldehyde other than formaldehyde gives secondary alcohols

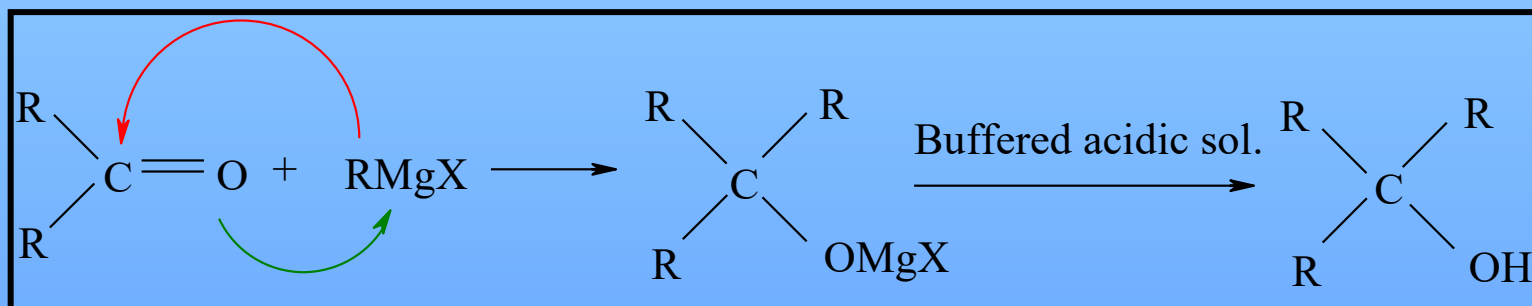


Reaction of GR (2 moles) with ethyl formate (1 mole) also gives secondary alcohol



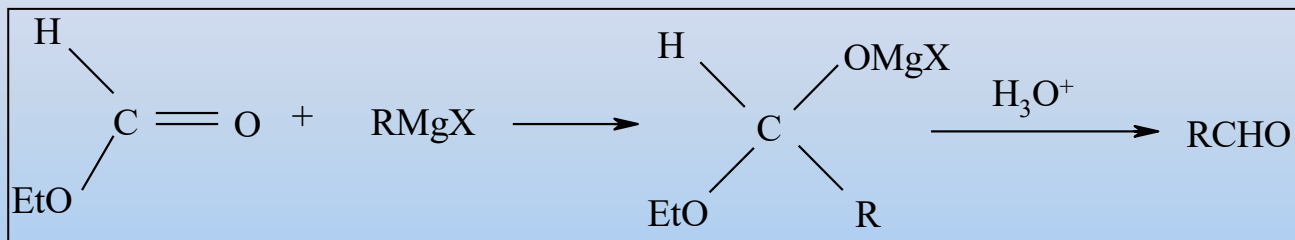
### Synthesis of 3<sup>o</sup> alcohol

Reaction of GR with ketone gives tertiary alcohol



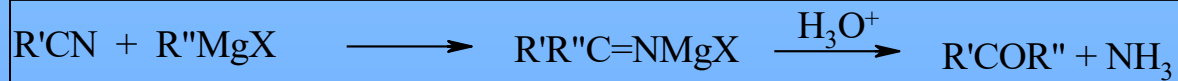
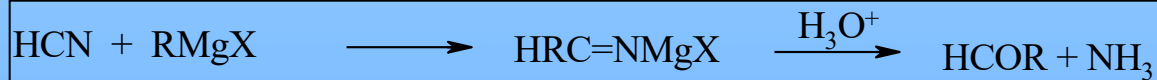
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➤ Aldehydes are prepared by the reaction between a GR (1 mole) and ethyl formate(1mole).



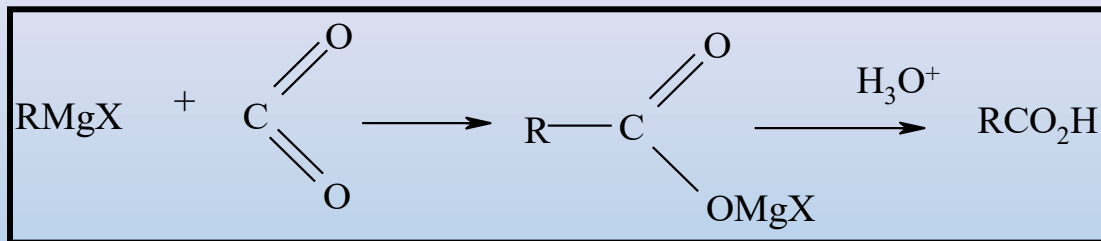
If excess of GR is used in above reaction secondary alcohol will be product.

➤ Reactions of GR with HCN and RCN

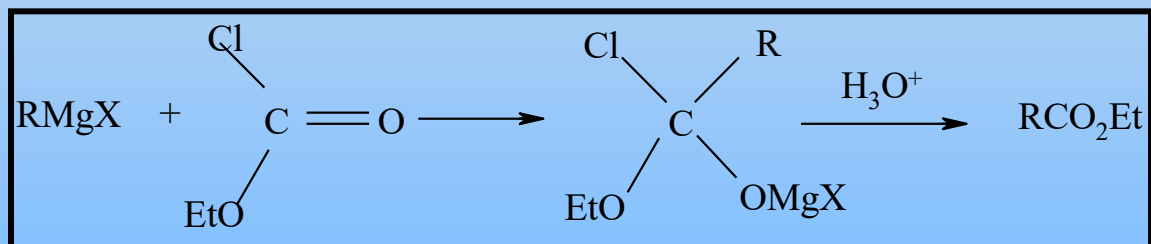


Question : Reaction of GR with acid chloride gives ketone .....how?

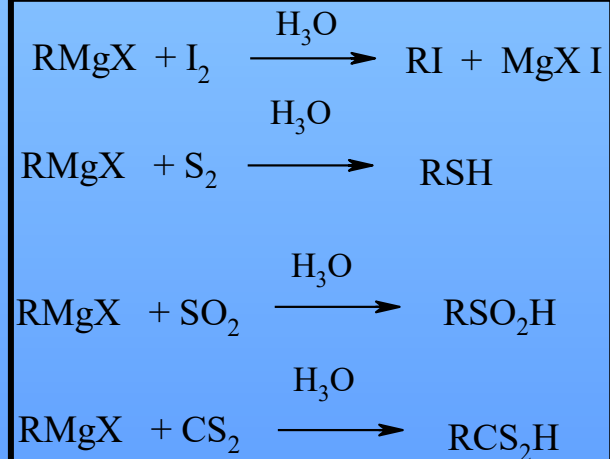
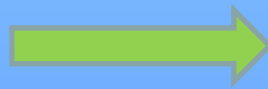
➤ Reaction of GR with solid CO<sub>2</sub> gives carboxylic acid



A GR (1 mole) reacts with ethyl chloroformate (1 mole) an ester is formed.



Preparation of alkyl halide, thioalcohols, sulphinic acids and dithiols



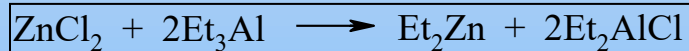
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## Organozinc compounds ( $R_2Zn$ ) or Frankland reagents

- Organozinc compounds were among the first organometallic compounds made.
- Edward Frankland prepared the first organozinc compound in 1848, diethylzinc, by heating ethyl iodide in the presence of zinc metal known as Frankland reaction.



- other method: reaction between zinc chloride and an aluminium alkyl.



- The zinc dialkyls (collinear molecules) are volatile liquids, spontaneously inflammable in air and readily attacked by water.
- Organozinc are less reactive than many other analogous organometallic reagents, such as Grignard and Organolithium reagents because Organozinc compounds do not react with  $CO_2$  and reacts slowly with cyanides, ketones and esters.



## The Reformatsky Reaction

The Refomatsky reaction is the reaction between an  $\alpha$ - bromoacid ester and a carbonyl compound (aldehyde, ketone) in the presence of zinc to form a  $\beta$ -hydroxy-ester.

