

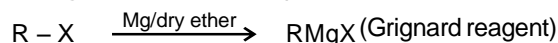
GRIGNARD REAGENT**1.1 Organometallic compounds**

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond. For example

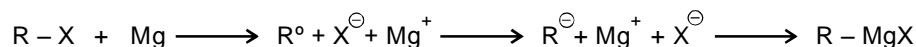


(Where C is a carbon atom of an organic molecule and M is a metal atom)

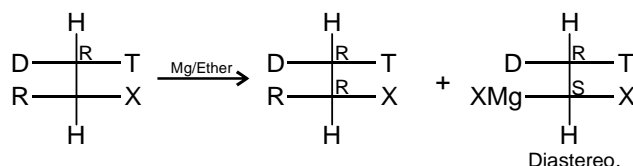
If the metal atom is attached to oxygen, nitrogen, sulphur, etc. then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.



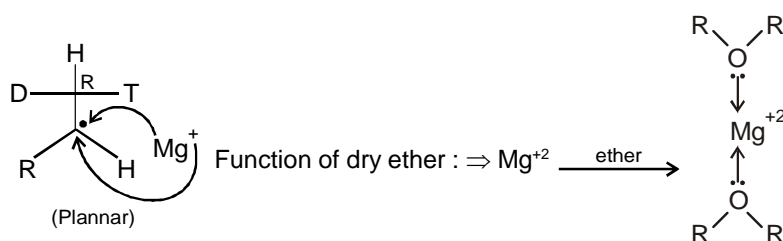
Mechanism



*(RMgX is only Nucleophile)



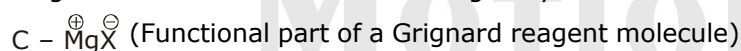
Reason



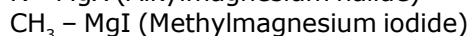
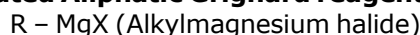
RONa (sodium alkoxide), CH_3COONa (Sodium acetate), CH_3COOAg (Silver acetate), RSK (Potassium mercaptide) RNHL (N-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc.

Note : It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

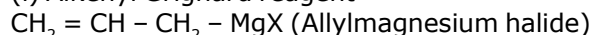
Most important examples of organometallic compounds are Grignard reagents. In Grignard reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.



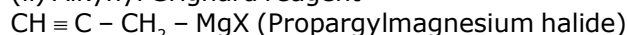
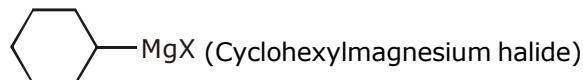
In organometallic compounds, the metal atom can be bonded to carbon of a hydrocarbon radical (Saturated, unsaturated, aliphatic, alicyclic or aromatic) or carbon atom of a heterocyclic radical. Some examples are given below.

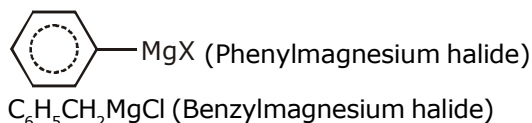
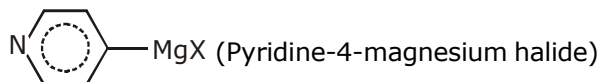
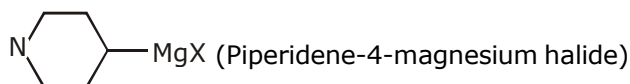
1. Saturated Aliphatic Grignard reagent**2. Unsaturated Aliphatic Grignard reagent**

(i) Alkenyl Grignard reagent



(ii) Alkynyl Grignard reagent

**3. Alicyclic Grignard reagent**

4. Aromatic Grignard reagent**5. Heterocyclic Aromatic Grignard reagent****6. Heterocyclic Nonaromatic Grignard reagent**

In a Grignard reagent, X is generally Cl, Br or I (Halogen). Order of reactivity is as follows:
 $\text{RMgI} > \text{RMgBr} > \text{RMgCl}$

Some specific examples of organometallic compounds of magnesium and other metals are as follows>

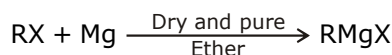
- Q.1** Which of the following is not an organometallic compounds?
 (A) $(\text{CH}_3)_2\text{Zn}$ (B) Tetramethyllead (C) R_2CuLi (D) Tetramethylsilane

Ex. Which of the following formula represents Grignard reagent?
 (A) H_2NMgX (B) $\text{HC} \equiv \text{CMgX}$ (C) R_2Mg (D) $\text{Mg}(\text{OH})\text{Br}$

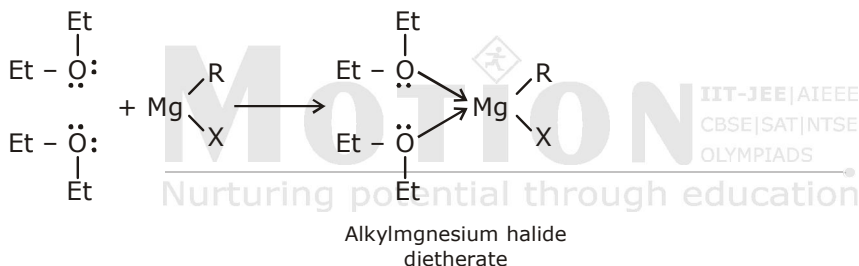
Ans. B

Ex. Which of the following is not a Grignard reagent?
 (A) $(\text{CH}_3)_2\text{CHMgCl}$ (B) CH_3COOMgI (C) $\text{C}_6\text{H}_{11}\text{MgBr}$ (D) $\text{C}_2\text{H}_5\text{MgCl}$

Ans. B

1.2 Preparation

Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard reagent by completing the octet on magnesium atom.



Ex. What is the motive of adding iodine in small amount during preparation of methylmagnesium iodide?

- (A) It acts as a catalyst (B) It converts ether into alkyl iodide
 (C) It decreases the violence of the reaction (D) It acts as an electrophilic

Ans. A

Ex. The reaction of an alkyl halide and magnesium is initially very slow, but later becomes very fast, because

- (A) The reaction is autocatalytic (B) The Grignard reagent formed is ether-soluble
 (C) The reaction is endothermic (D) The reaction is exothermic

Ans. D

- Ex.** A grignard reagent is formed on reacting magnesium with
 (A) Alkyl halide in the presence of dry ether
 (B) Alkyl halide in the presence of phenol
 (C) Alkyl halide in the presence of alcohol
 (D) Alkyl halide in the presence of alcoholic ether

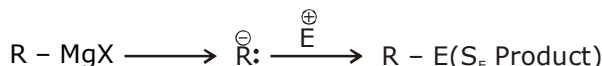
- Q. 2** Grignard reagent gets stabilised in ether medium, because ether.
 (A) Is a high quality solvent
 (B) Restricts ionisation
 (C) Favours free radical mechanism
 (D) It solvates Mg^{+2} ion

1.3 Reactivity of grignard reagents.

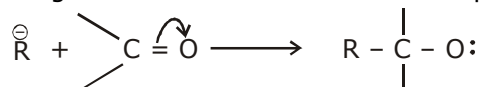
It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of grignard reagent. Therefore, there is a tendency of forming carbonion by heterolysis of this polar coordinate bond as follows.



The carbanion (a nucleophile) formed as shown above, attacks the positively, charged electrophilic centre of other compound. Therefore. It can be said that if a Grignard reagent is regarded as the substrate, then electrophile displaces MgX , i.e, electrophilic substitution (E_S) reaction takes place.



If Grignard reagent is regarded as the attacking reagent, then the nucleophilic carbonion of Grignard reagent will attack on the other compound taken as substrate.



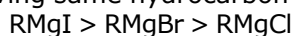
- Ex.** Which of the following types of bond exists between carbon and magnesium in a Grignard reagent?

(A) completely covalent (B) Ionic (C) Coordinate (D) Polar covalent

Ans. D

1.4 Reactions of Grignard reagent

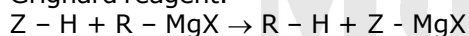
On having same hydrocarbon radical, the order of reactivity of Grignard reagents will be as follows:



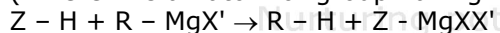
Grignard reagent gives the following two type of reactions.

(i) Substitution Reactions.

compounds having reactive hydrogen or halogen atom give substitution products on reacting with Grignard reagent.



(Where Z is an atom or group having high electron attracting capacity)

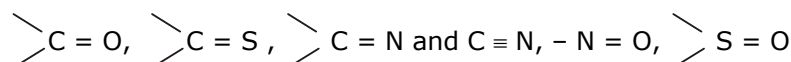


(Where X and X' are halogen atoms)

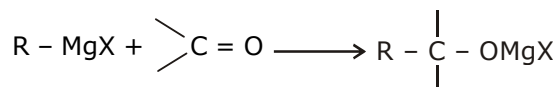
Both the above are examples of nucleophilic substitution reaction of $Z - H$ and $Z - X$ (not of the Grignard reagents).

(ii) Reactions involving addition on polar π -Bond

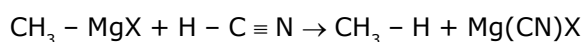
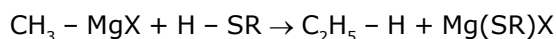
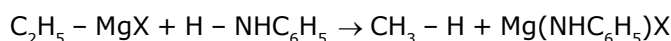
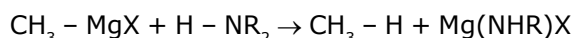
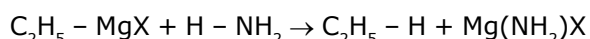
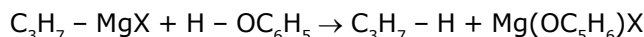
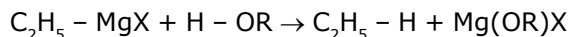
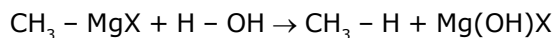
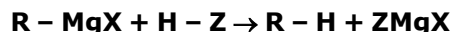
Grignard reagents form adducts by addition on the following types of π -Bonds



Example



Adduct

1.6 Synthetic Importance of Grignard reagents**1. Synthesis of Alkanes****(i) With compounds having reactive hydrogen atom**

Methane gas is released on reacting methylmagnesium iodide with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called **Zerewitinoff method of estimation of reactive hydrogen atoms**.

Ex. Zerewitinoff's method is used for

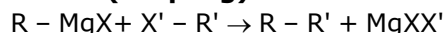
(A) the estimation of reactive hydrogen atom

(B) the estimation of alkoxy group

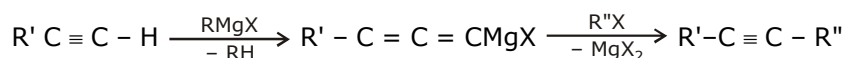
(C) the preparation of a higher ether

(D) the preparation of a Grignard reagent

Ans. A

(ii) with alkyl halide (coupling)**2. Synthesis of alkenes****3. Synthesis of higher alkynes**

(i) Non-terminal alkynes



Ex. Which of the following products is formed on reacting 1-propenylmagnesium chloride with ethyl iodide?

(A) β - Amylene (B) α - Amylene (C) α - Isoamylene (D) β - Isoamylene

Ans. B

Ex. Which of the following is obtained on the reaction of the simplest unsymmetrical alkyne with methylmagnesium iodide?

(A) Simplest branched alkane

(B) Simplest alkane

(C) Higher Alkyne

(D) Isomeric Alkyne

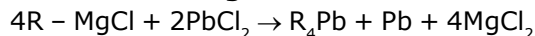
Ans. D

Ex. Which of the following should be reacted with a Grignard reagent for preparing the third member of the terminal alkyne family?

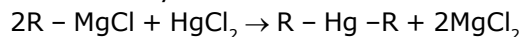
- (A) An alkanal that gives iodoform test (B) Propyne
(C) Propyne followed by methyl chloride (D) Acetylene followed by ethyl chloride

Ans. D

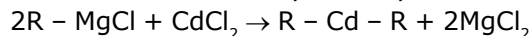
4. Synthesis of other organometallics



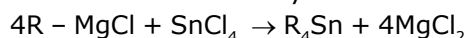
Two important antiknock compounds, tetraethyllead (T. E. L.) and tetramethyllead (T. M.L.) are manufactured by the above reaction.



Dialkylmercury



Dialkylcadmium



Tetraalkyl tin

Ex. Which of the following is the product obtained by the reaction of ethylmagnesium chloride with lead chloride?

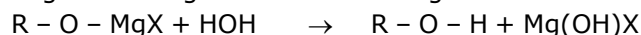
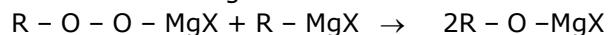
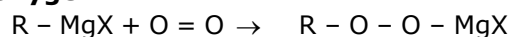
- (A) An antiknock (B) An explosive (C) A white pigment (D) A fuel

Ans. A

5. Synthesis of Alcohols

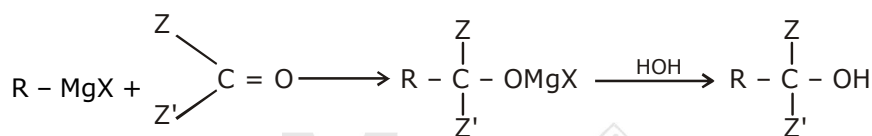
There are following methods to obtain alcohols from Grignard reagent.

(i) From Oxygen



Primary, secondary and tertiary alcohols can be obtained by above reaction.

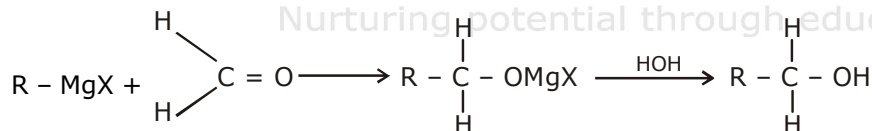
(ii) From Carbonyl compounds



alcohol

(a) Primary or 1° Alcohols

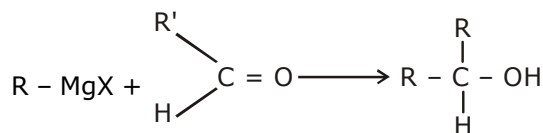
Primary alcohols are formed on taking formaldehyde



1° Alcohol

(b) Secondary or 2° alcohols

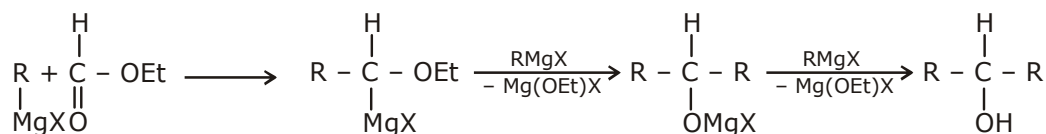
(1) From RCHO Secondary alcohols are formed of any aldehyde other than formaldehyde.



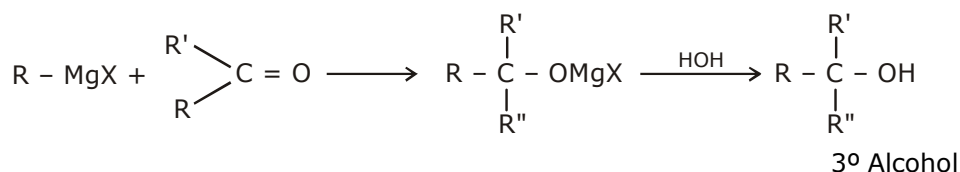
2° Alcohol

(2) From formic ester:

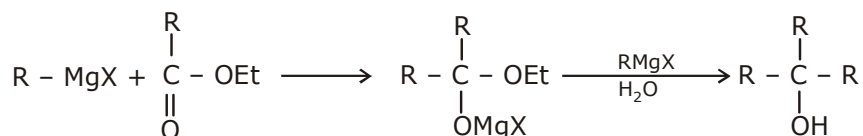
Secondary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and adding formic ester to it.

**(c) Tertiary or 3° alcohols**

(1) Tertiary alcohols are formed by taking any ketone

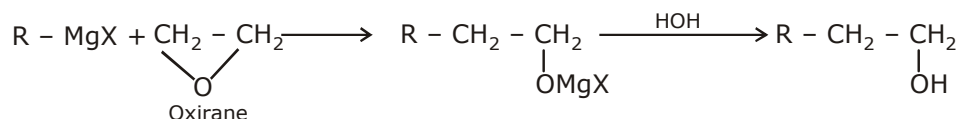


(2) Tertiary alcohols are also obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester of a higher homologue of formic acid.



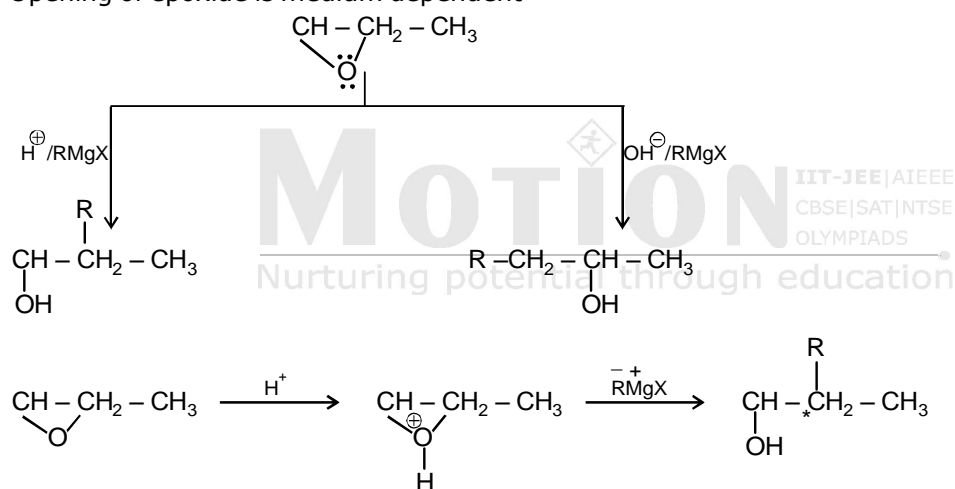
Various alcohols can be prepared by changing R in the above synthesis.

(iii) From Epoxides

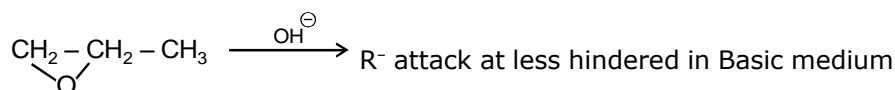


1° Alcohol having two more C

Opening of epoxide is medium dependent



(R⁻ attack at that carbon where ⊕ charge is less in acidic medium)



Ex. Primary alcohol cannot be obtained by the reaction of a Grignard reagent with
 (A) The simplest alkanal (B) Dimethylene oxide
 (C) Ethylene glycol (D) Oxygen

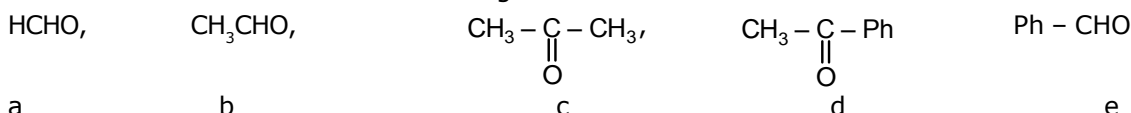
Ans. C

Q. 3 Primary, secondary and tertiary alcohols can be obtained by hydrolysis of the products formed on reaction by a Grignard reagent with

- (A) Isobutyraldehyde (B) Butanone
 (C) Oxygen (D) Oxirane

Ex. Compare the reactivity of following compound with RMgX ?

Ans. NAR So steric hindrance and +ve charge \uparrow

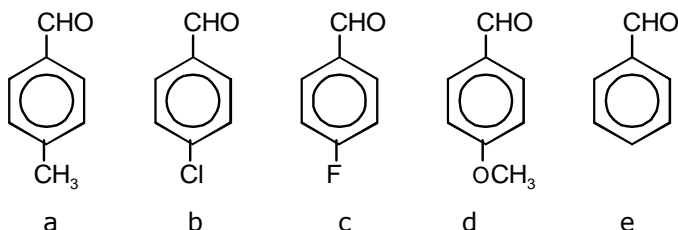


$$a > b > c > e > d$$

* Aliphatic aldehyde is more reactive than aliphatic Ketone

* But aliphatic Ketone more reactive than aromatic aldehyde and ketone both

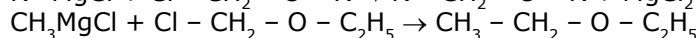
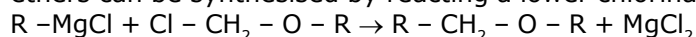
Ex. compare the reactivity with RMgX with following compounds.



Ans. reactivity $b > c > e > a > d$

6. Synthesis of Ethers

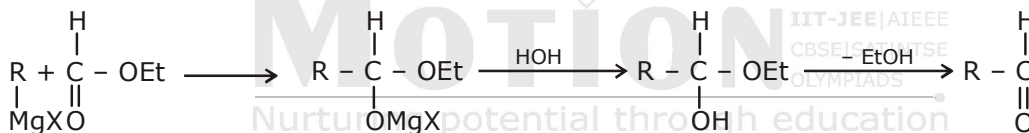
Higher ethers can be synthesised by reacting a lower chlorinated ether with Grignard reagent.



Chloromethyl ethyl ether Diethyl ether

7. Synthesis of Aldehydes

Corresponding aldehyde is obtained on hydrolysis of the product obtained by reacting of formic ester and Grignard reagent in equimolecular ratio.

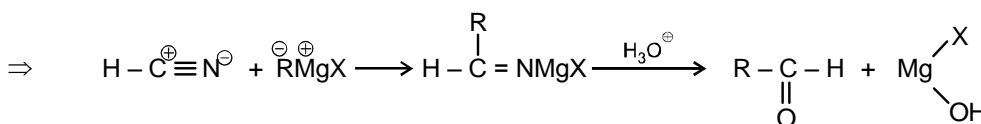
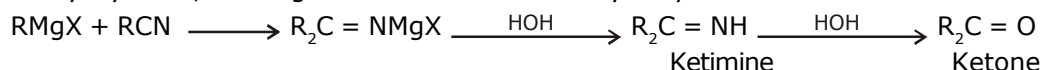


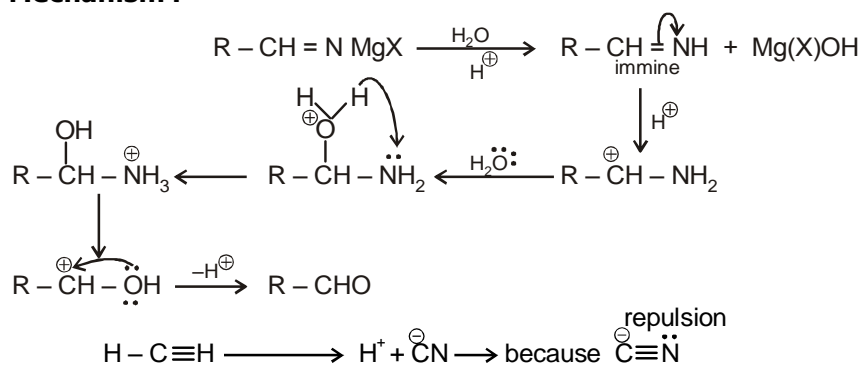
The above conversion can be simplified as follows for convenience.

8. Synthesis of Ketones

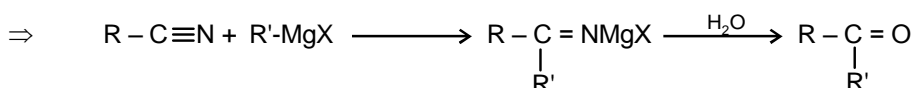
(i) From Alkyl cyanides

A ketimine is formed on hydrolysis of the adduct obtained by the reaction of Grignard reagent and an alkyl cyanide, which gives ketone on further hydrolysis.

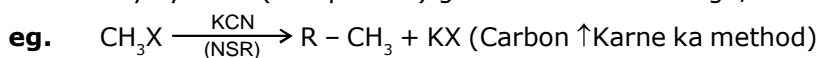


Mechanism :

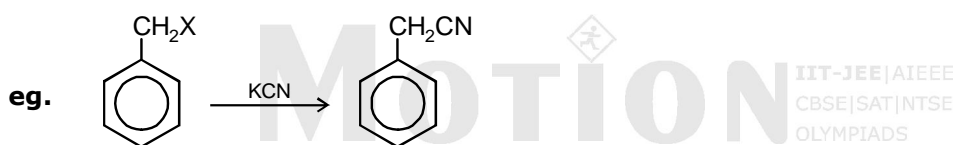
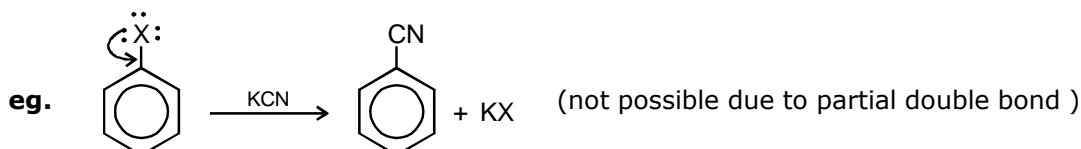
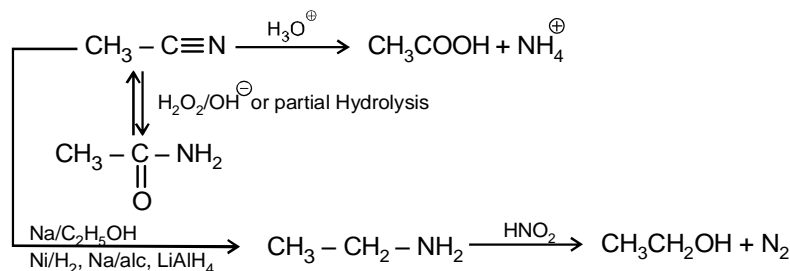
* Only $\text{HC}\equiv\text{N}$ (Weak acid) can give aldehyde with $\text{RMgX}/\text{H}_2\text{O}$.



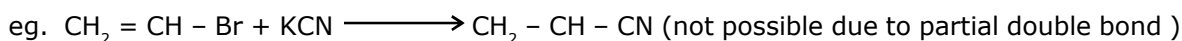
* All alkyl cyanide (except HCN) gives ketone with RMgX/Water .



Ex.

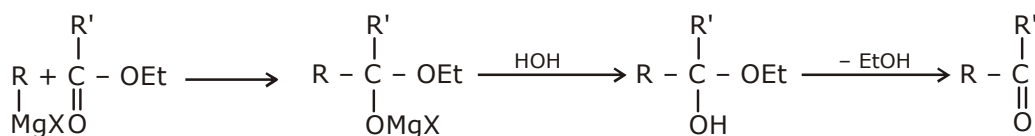


* Benzene gives ESR reaction not FSR

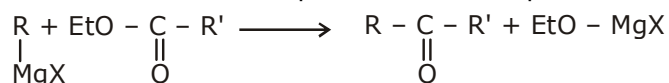


(ii) From carboxylic esters (other than formic ester)

Ketone is formed on taking R' in place of H of formic ester.



The above reaction sequence can be simplified as follows for convenience.



Ex. Which of the following is formed on the reaction of one mole of acetyl chloride with one mole of methylmagnesium chloride?

(A) 2-Butanol

(B) Acetone

(C) Isobutyl alcohol

(D) t-Butyl alcohol

Ans. B

Q.4 Which of the following is formed on the reaction of one mole of acetyl chloride with two mole of methylmagnesium chloride followed by hydrolysis?

(A) 2-Methyl-1-propanol

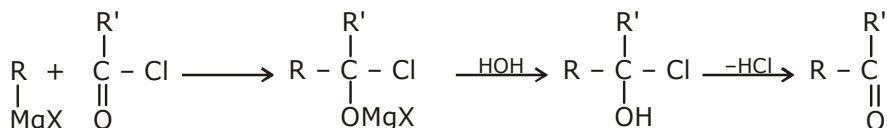
(B) 1-Butanol

(C) tert-Butyl alcohol

(D) Acetone

(iii) From carboxylic acid chlorides

Formyl chloride is unstable. Therefore, acetyl chloride is regarded as the first member of this family.

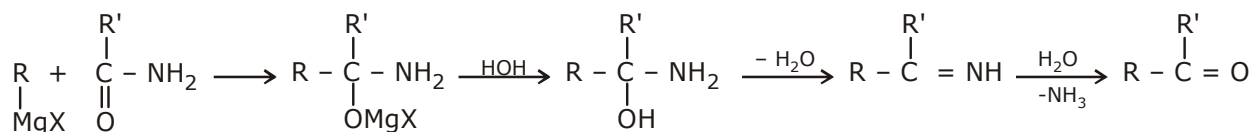


or



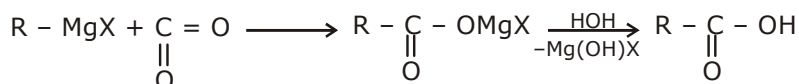
(iv) From carboxylic acid amides

Ketones are formed on reacting acetamide or its higher homologue with Grignard reagent, followed by hydrolysis of the product.



9. Synthesis of carboxylic acids

A carboxylic acid is formed on hydrolysis of the adduct formed by passing carbon dioxide in the ethereal solution of a Grignard reagent.



10. Synthesis of carboxylic acid esters

Higher esters are formed on reacting the chlorinated ester of lower carboxylic acid with grignard reagent.



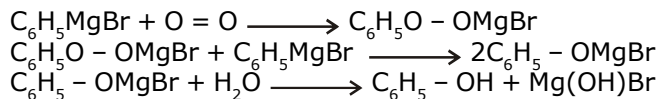
11. Synthesis of mercaptans

Alkanethiols, i.e. mercaptan is formed on hydrolysis of the product obtained by adding sulphur to the ethereal solution of Grignard reagent.



12. Synthesis of phenols

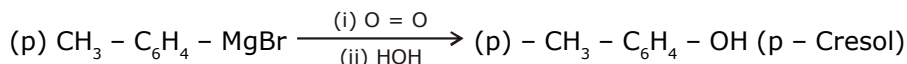
Phenol is obtained on hydrolysis of the product obtained by reaction of arylmagnesium bromide with oxygen.



Other phenols can be prepared by taking any aryl (Ar) group in place of phenyl group.

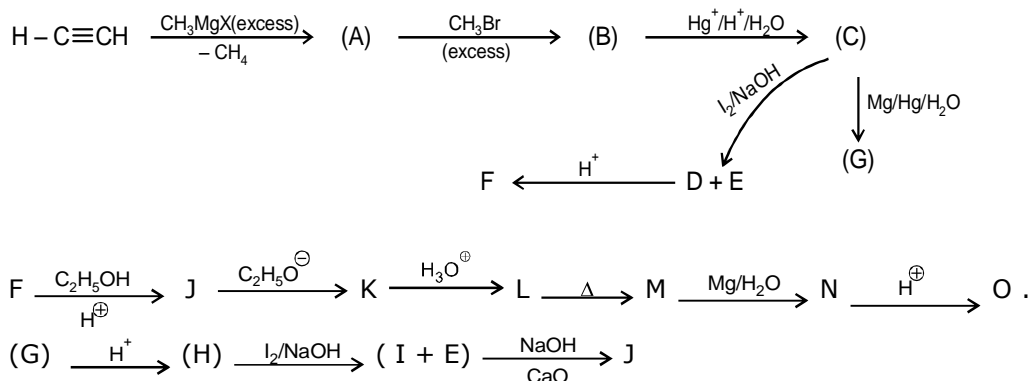


For example, on taking p-toluenemagnesium bromide p-cresol is formed in the end.

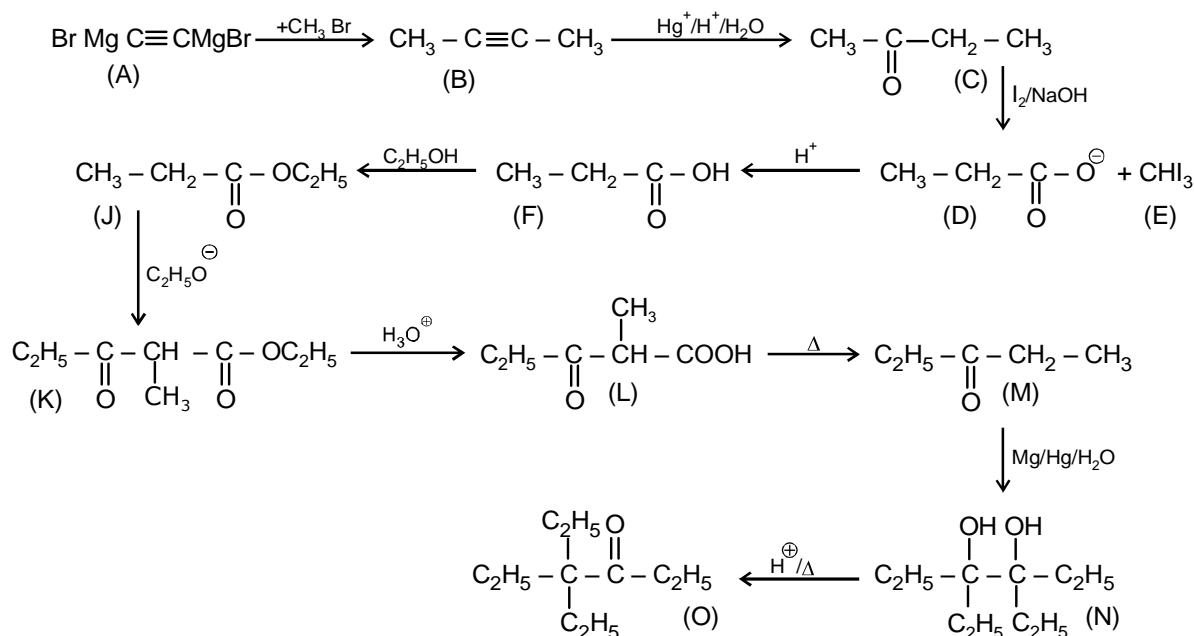


p - Toluenemagnesium bromide

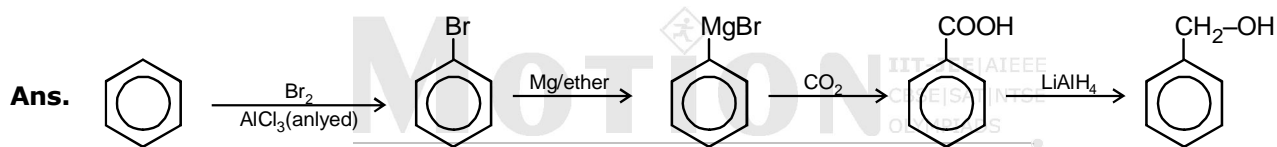
Ex. Road map problem



Ans.

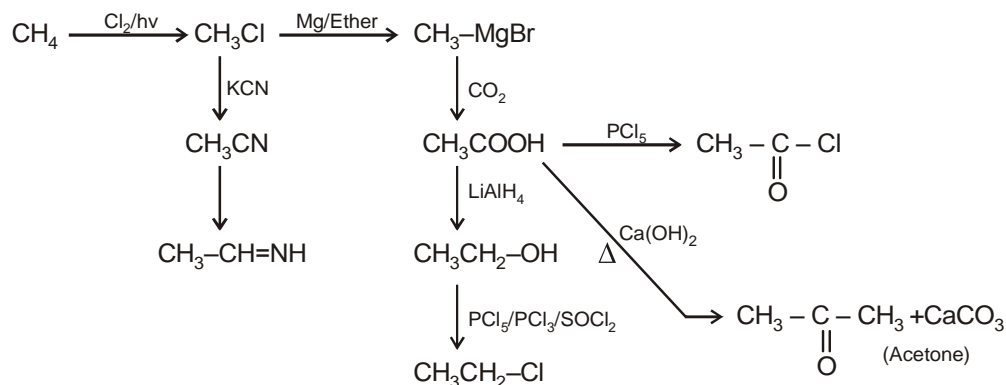


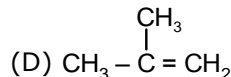
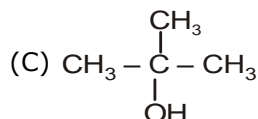
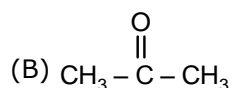
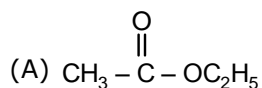
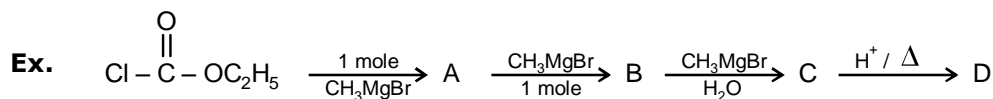
Ex. Prepare benzyl alcohol from benzene ? without using organic compound ?



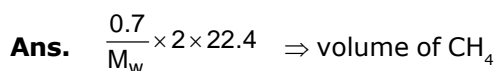
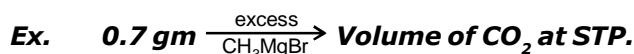
Ex. Prepare acetone from methane without using any organic compound?

Ans.

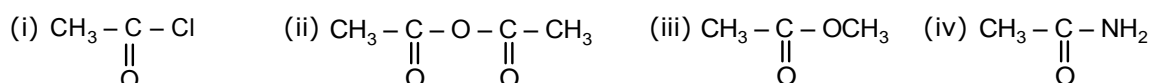




Ans. C

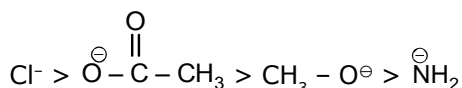


Ex. Compare the reactivity of the above derivative with grignard reagent (Nu^\ominus).

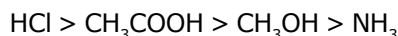


Ans. All acid derivative gives NSR

$a > b > c > d$ Reason extent of the positive charge at $>\text{C}=\text{O}$ or leaving group.



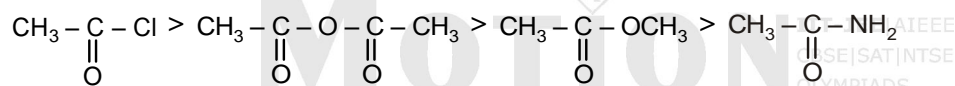
poor Base



most ceridic

weaker the conjugate base bast the leaving group.

Reactivity with Nu^\ominus



MOTION
Nurturing potential through education