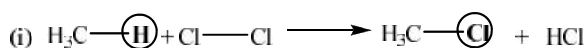


## What is organic reaction?

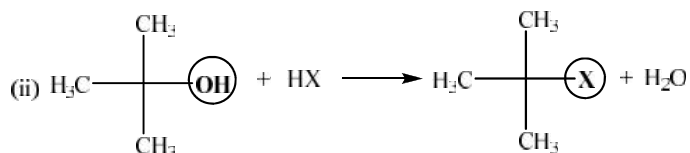
- Organic compounds can be transformed into product and the process is termed as organic reaction. It is represented by **stoichiometric equation**. Most organic reactions belong to one of the five main classes.

### 1) Substitution Reaction

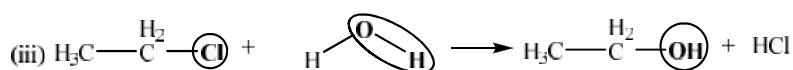
In a substitution reaction, one atom or group of atoms in a molecule is replaced by another.



Hydrogen is substituted by chlorine



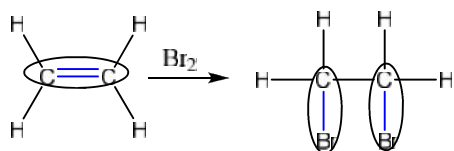
-OH is substituted by halogen



Chlorine is substituted by -OH

### 2) Addition Reaction

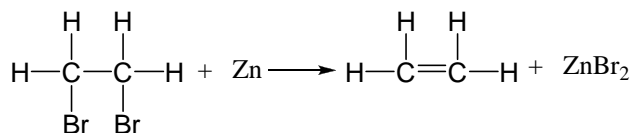
In these reactions, atoms or group of atoms are added to a double bond or triple bond without elimination of any atoms or groups. At least one  $\pi$ -bond is lost while two new  $\sigma$ -bonds are formed.



$\pi$ -Bond is lost while two new  $\sigma$ -bonds are formed

### 3) Elimination Reaction

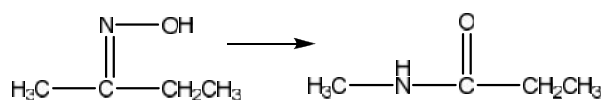
Elimination reactions are those which evolve the removal of atoms or groups from two adjacent atoms in a substrate molecule to form a multiple bond. Here two  $\sigma$ -bonds are lost a new  $\pi$ -bond is formed.



$\sigma$  - Bond is converted into  $\pi$ -bond

### 4) Rearrangement

Rearrangement reactions involve the migration of atom or group of atoms from one site to another site within the same molecule. The product is always the structural isomer of the substrate.



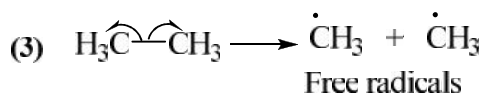
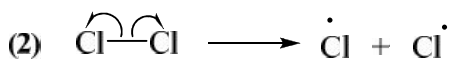
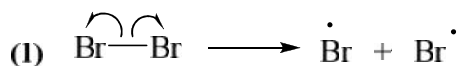
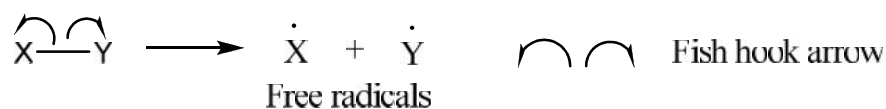
## 5) Redox reactions

### What is Reaction Mechanism?

- A detailed study of the sequence of steps which are involved in the conversion of reactants into products is known as **reaction mechanism**.
- Organic reactions are proceed by rupture of covalent bond and formation of new bonds. The bonds are broken in one of the two ways.
  - 1) By Homolytic bond fission
  - 2) By Heterolytic bond fission
- 3) Electronegativity differences between the bonding atoms
- 4) The presence of low temperature
- 5) The presence of a polar solvent

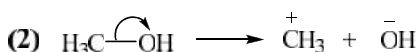
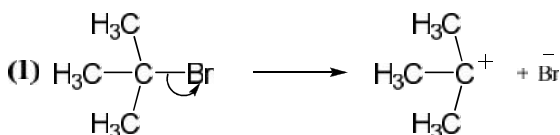
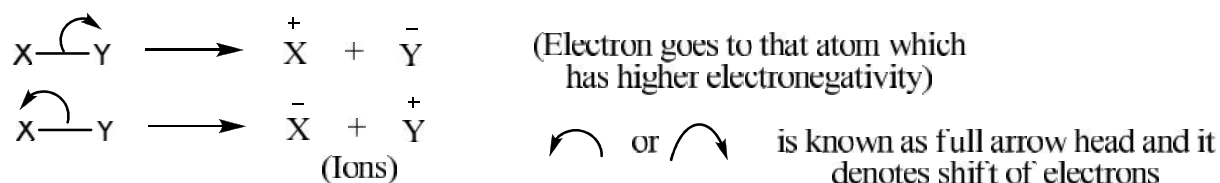
### Homolytic bond fission:

In homolytic fission, the covalent bond is broken symmetrically so that one electron of the bonding pair remains with each of the originally bonded atoms.



### Heterolytic bond fission:

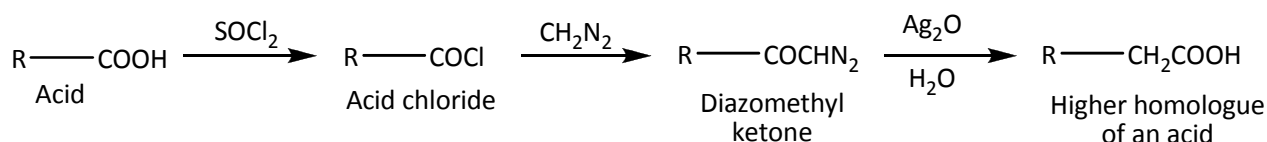
In heterolytic bond fission, the covalent bond is broken in such a way that the shared electron pair remains attached with only one of the two originally bonded atoms. It results in formation of ions.



Electron donating functional groups ( <i>ortho-para</i> directing)	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{O}}\text{CH}_3, -\text{CH}_3, -\ddot{\text{O}}\text{H}, -\ddot{\text{N}}\text{HCOCH}_3$
Electron withdrawing functional groups ( <i>meta</i> directing)	$-\text{COOH}, -\text{COOR}, -\text{NO}_2, \text{CONH}_2, -\text{CN}$

Ardnt Eistert reaction

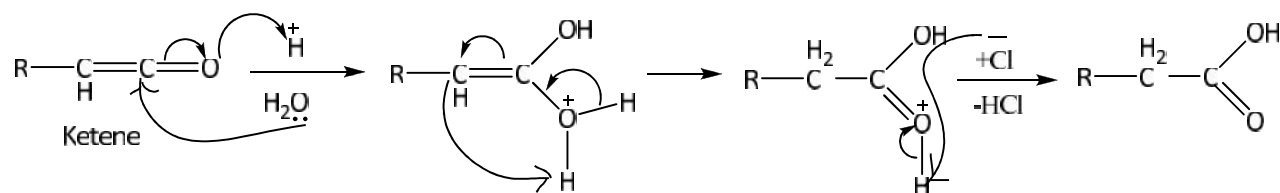
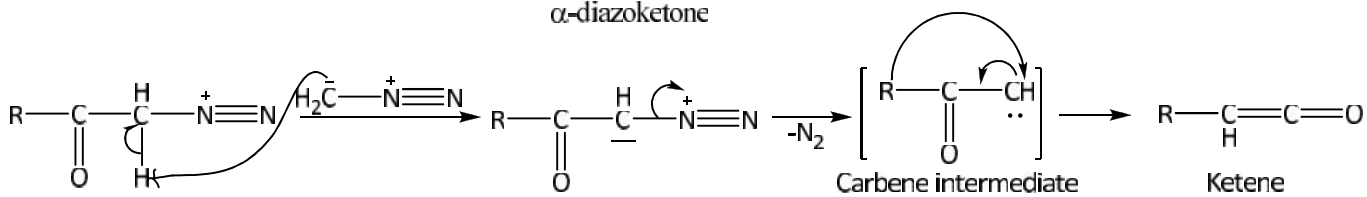
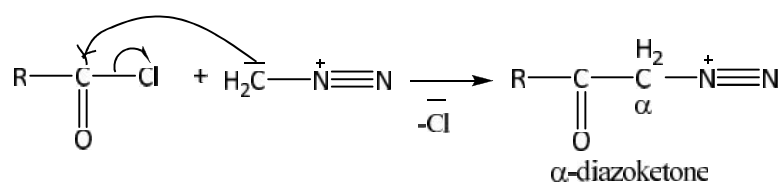
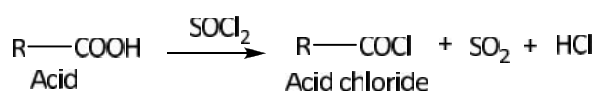
- It is a simple general method for converting an acid into its next higher homologue or to a derivative of the homologous acid, such as amide or ester.
- The various steps involved in reaction are as follows.

Reaction:

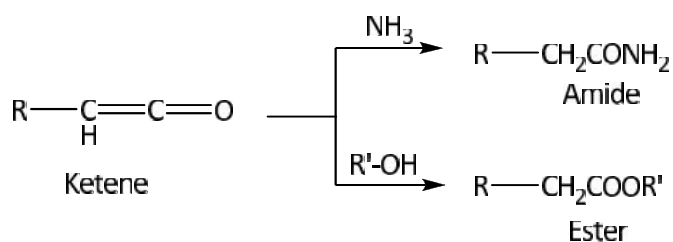
Conversion: Acid  $\longrightarrow$  Next Higher homologue of acid

Mechanism:

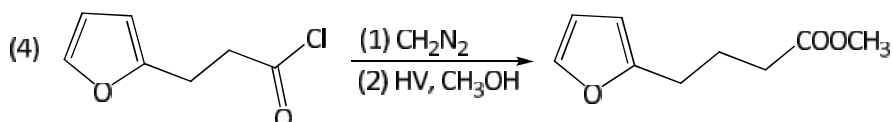
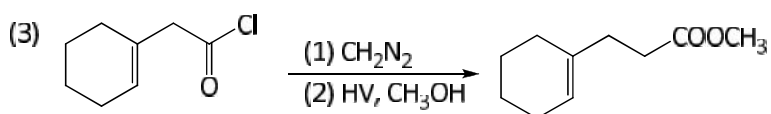
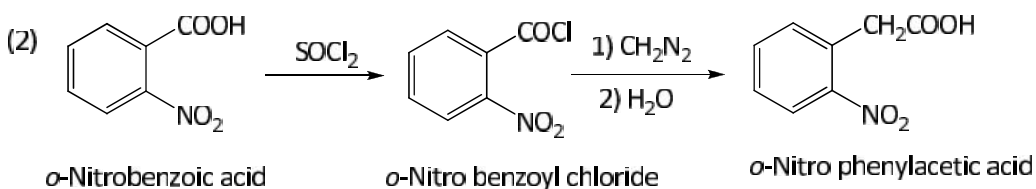
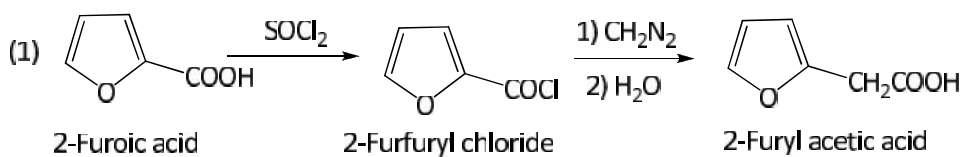
- Carboxylic acid on reaction with thionyl chloride gives acid chlorides.
- Acid chlorides react with diazomethane to give  $\alpha$ -diazoketone. This  $\alpha$ -diazoketone eliminates nitrogen molecule and rearranges to ketene in the presence of solid silver oxide or by irradiation with light.
- It involves formation of **carbene intermediate** which is highly reactive. Formation of this carbene undergoes **intramolecular rearrangement** of alkyl group to give ketene.
- This ketene on acidic hydrolysis gives carboxylic acid with one more carbon atom than the starting carboxylic acid.
- Ketene can be converted into acid, amide or ester on treatment with water, ammonia or alcohol respectively.



### Other possible reactions of Ketene



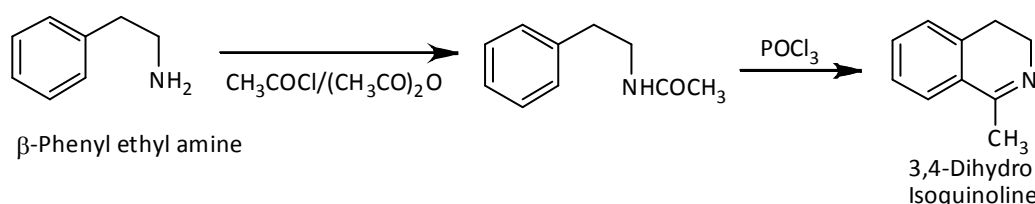
Exercise: Write down mechanisms for the following reactions. (Application part)



### Bischler Napieralski Reaction

- This reaction was first reported by August Bischler and Bernard Napieralski in 1893.
- The Bischler Napieralski Reaction involves cyclization of phenethyl (phenyl ethyl) amides ( $\beta$ -phenyl ethyl amides) in presence of dehydrating agents such as  $P_2O_5$  or  $POCl_3$  to afford 3,4-dihydroisoquinoline derivatives.
- This reaction is one of the most commonly employed and versatile methods for the synthesis of the isoquinoline ring system, which is found in large no. of alkaloid natural products.

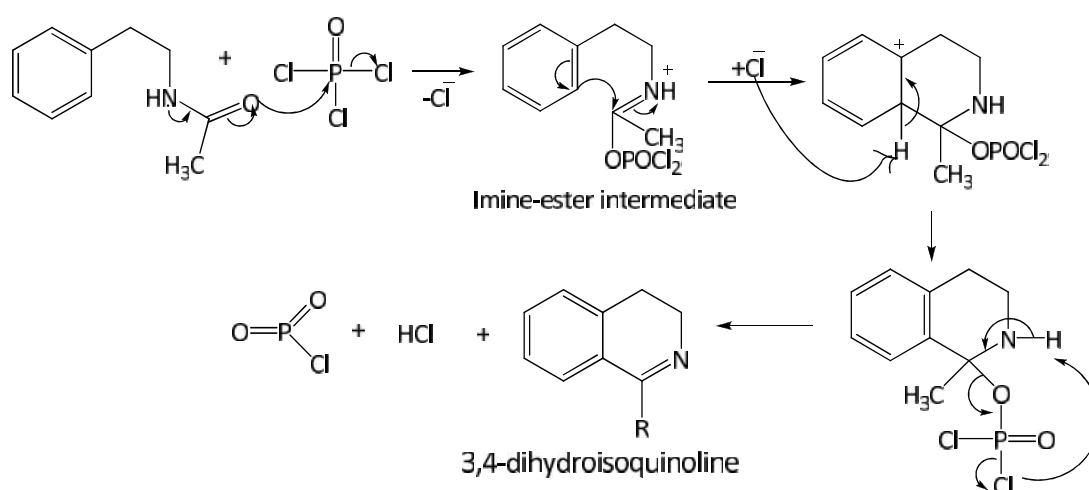
#### Reaction:



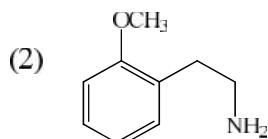
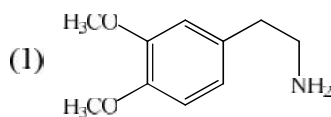
#### Conversion: $\beta$ -Phenyl ethyl amine $\longrightarrow$ 3,4-Dihydro isoquinoline

#### Mechanism:

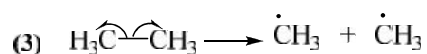
- The reaction is carried out at low temperature.
- Inert solvents like benzene, toluene or nitrobenzene are used.
- It is an example of **intramolecular electrophilic aromatic substitution** reaction that allows cyclization of  $\beta$ -phenylethyl amide.
- **Amides with electron donating functional group on the aromatic ring are readily cyclized while e-withdrawing groups hinder the reaction.**



**Exercise:** Apply mechanism of Bischler Napieralski Reaction to the following starting materials and draw the product of the reaction. (Application part)



(1) The reaction given below is an example of heterolytic fission. TRUE or FALSE?



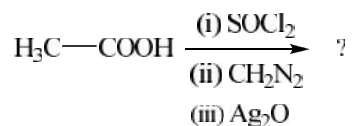
**Ans: False**

(2) Free radicals are generated after homolytic fission. TRUE or FALSE?

**Ans: TRUE**

(3) Give any one example of reaction which involves heterolytic fission.

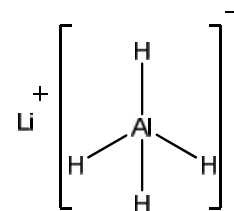
(4) Complete the following reaction.



(6) Isoquinoline ring system can be synthesized using ..... Reaction.

(7) Amide is electron donating functional group. TRUE or FALSE?

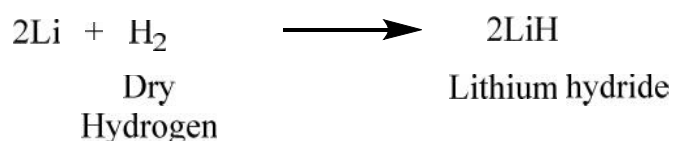
**Ans: False**

**Lithium aluminium hydride (LiAlH<sub>4</sub>)****Structure:**

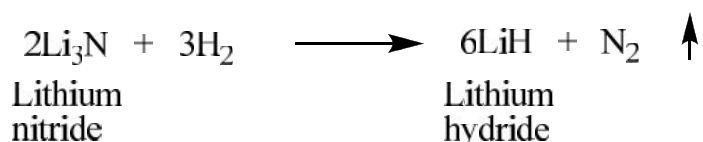
Al is central metal which is attached with four hydrogen atoms. Electronegativity of hydrogen is higher than that of Al and due to this reason hydrogen is removed from LiAlH<sub>4</sub> as Hydride ion.

**Preparation:**

1) Lithium reacts with dry hydrogen at 700°C to give LiH.



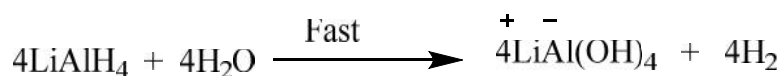
2) Guantz's (name of scientist) synthesized lithium hydride by the reaction of lithium nitride with hydrogen.



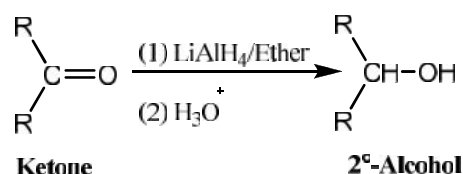
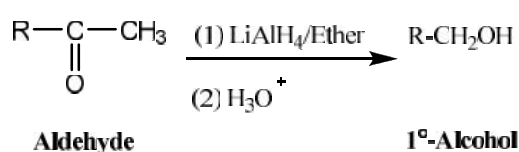
Lithium hydride synthesized by above method reacts with anhydrous aluminium chloride in presence of dry ether to give lithium aluminium hydride.

**Reaction of LiAlH<sub>4</sub> with water**

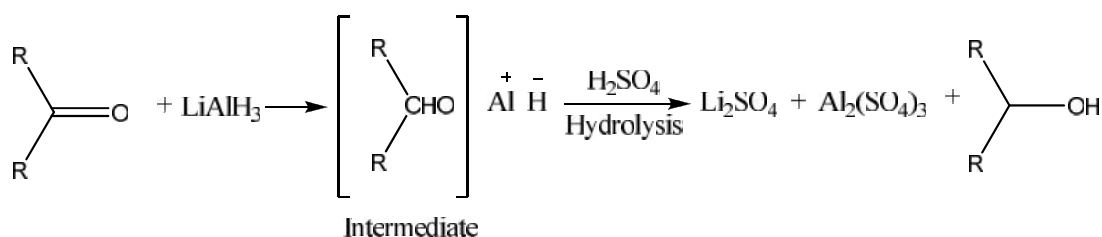
It reacts violently with water or protic solvents resulting in the liberation of hydrogen. The reaction is generally carried out in dry ether, tetrahydrofuran or dioxane.

**Application****(1) Reduction of Carbonyl Compounds**

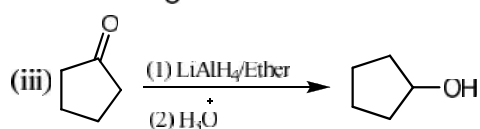
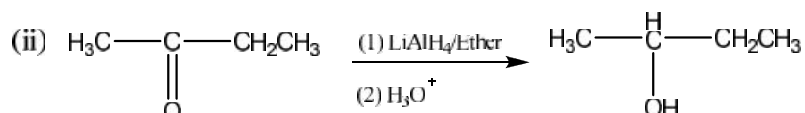
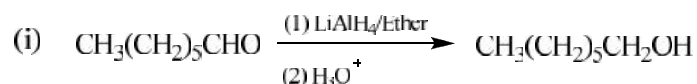
- LiAlH<sub>4</sub> reduces **aldehydes to 1°-alcohols** and **ketones to 2°-alcohols**.
- Reduction of aldehydes is faster than ketones because of less steric hindrance.



Reduction of ketone using LiAlH<sub>4</sub> can be explained by formation of the following intermediate.

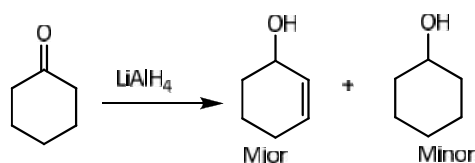
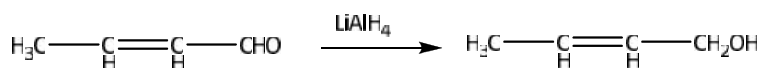


Some examples for application of  $\text{LiAlH}_4$  as reducing agent are given below.



## 2) Reduction of $\alpha,\beta$ -unsaturated carbonyl compounds

Reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds generally give **1,2-reduction product**, i.e. double bond or triple bond is not reduced.



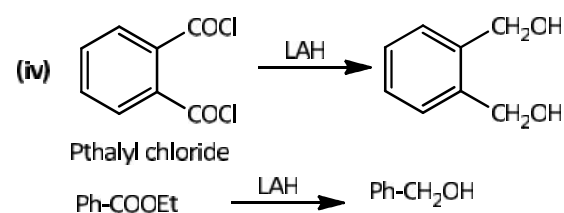
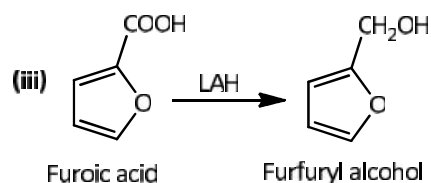
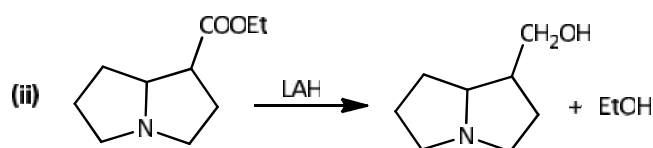
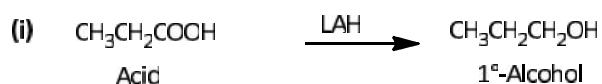
## 3) Reduction of carboxylic acid and its derivatives

Compounds which can be derived from carboxylic acids are termed as derivatives of carboxylic acid.

Carboxylic acid and their derivatives on reduction with  $\text{LiAlH}_4$  gives  $1^\circ$ -alcohol.

The order of reactivity of carboxylic acid and their derivatives towards LAH reduction is

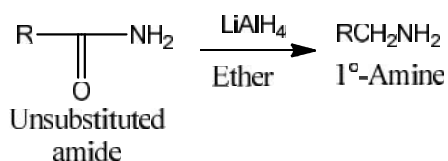
**R-COCl > R-COOR > R-CONR<sub>2</sub> > R-COOH.**



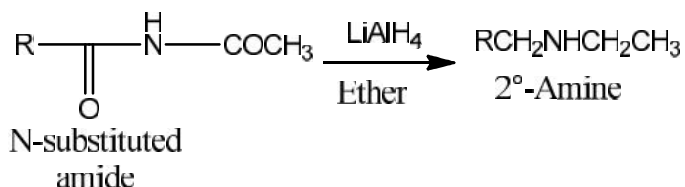


## 4) Reduction of Amides

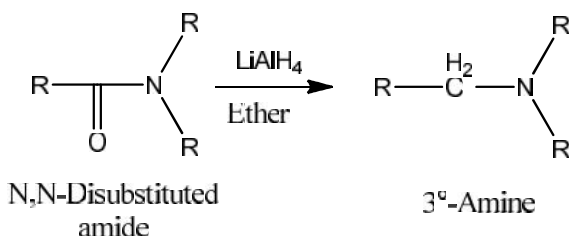
- Unsubstituted amides give 1°-amines on reduction with LiAlH<sub>4</sub>.



- N-substituted amides give 2°-amines on reduction with LiAlH<sub>4</sub>.

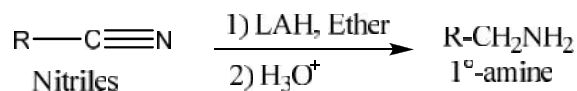


- N,N-disubstituted amides give 3°-amines on reduction with LiAlH<sub>4</sub>.



## 5) Reduction of Nitriles

- Nitriles on reduction with LiAlH<sub>4</sub> gives 1°-amines.



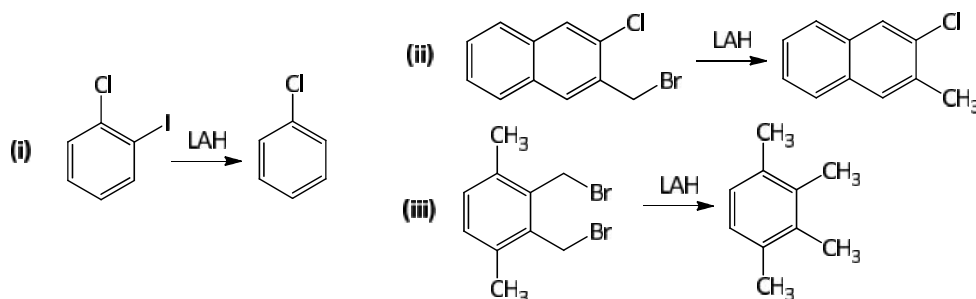
Intermediate formed in above reaction is  $\text{R}-\text{CH}_2-\text{N}(\text{AlH}_3)_2$  Which on acidic hydrolysis gives 1°-amine.  
Two molecules of LAH is used.

## 6) Reduction of alkyl halides and aryl halides

- 1° and 2°-alkyl halides are reduced to alkanes by LAH.



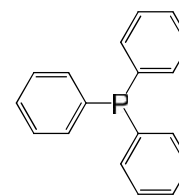
- Aryl halides are resistant to reduction by LAH, but activated halides can be reduced.



## Triphenyl Phosphine

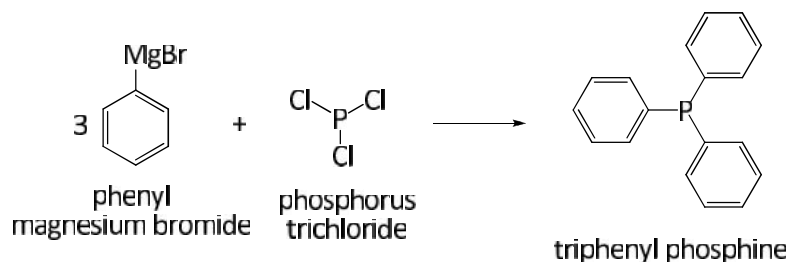
Triphenyl phosphine is a common organophosphorus compound with formula  $P(C_6H_5)_3$ , often abbreviated as  $PPh_3$ .

It is widely used in synthesis of organic and organometallic compounds.

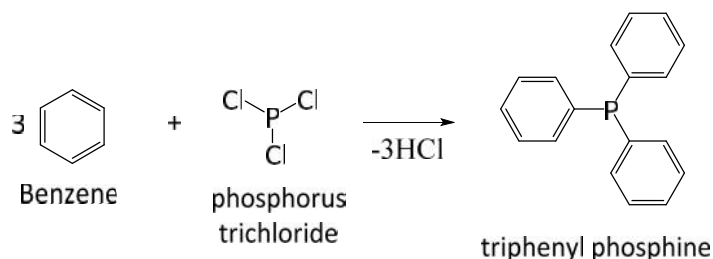


### Preparation:

- 1) Denny et al have synthesized triphenyl phosphine from phenyl magnesium bromide and phosphorus trichloride.



- 2) It can be also synthesized by reaction of 3 moles of benzene with phosphorus trichloride, in absence of air.



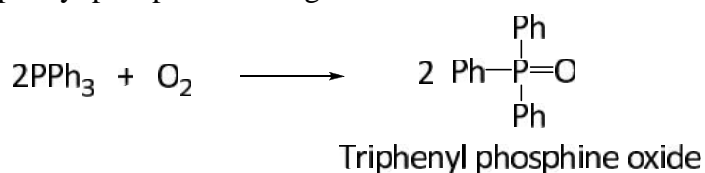
- $PPh_3$  is freely soluble in organic non-polar solvents like benzene, ether, chloroform and soluble in glacial acetic acid.
- It is less soluble in alcohol and partially soluble in water.

### Uses:

- It is used in synthesis of organic and organometallic compounds.
- It is used as polymerization initiator.
- It has wide application in Wittig reaction, Corey-Fuchs reaction and Fukuyama amine synthesis.

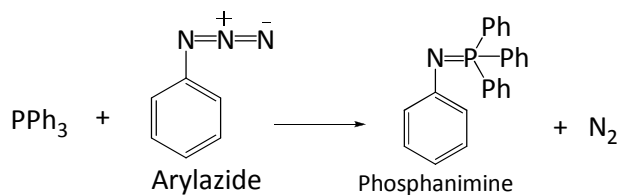
### Reaction with Oxygen:

- Triphenyl phosphine undergoes slow oxidation with air to give triphenyl phosphine oxide.

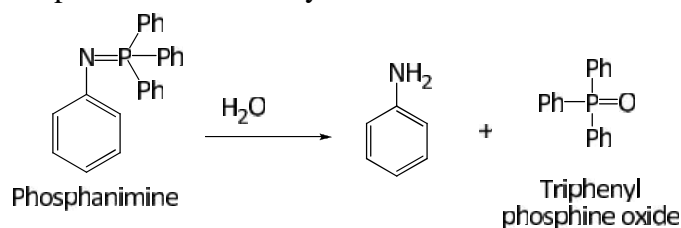


**Applications:**

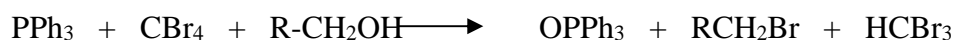
1) It reacts with arylazide to give phosphanimines, which is analogue of triphenyl phosphine oxide



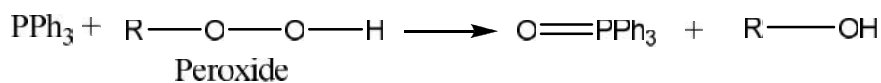
Phosphanimine formed by above reaction is unstable and it can be hydrolyzed to the amine.



2) Triphenyl phosphine reacts with  $\text{CX}_4$  ( $\text{X}=\text{Cl}, \text{Br}$ ) and also to give alkyl halides forming  $\text{OPPh}_3$  as by product and the reaction is termed as Appel reaction.



3) It is used for deoxygenation of organic peroxides.



4) It is also used for preparation of Wittig reagent (organo-metallic compound). Wittig reagent is used for conversion of carbonyl compound to alkenes.

