# HYDROCARBONS

# INTRODUCTION

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### Introduction of 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**

$$C - M \quad \text{or} \quad \overset{\Theta}{C}\ \overset{\oplus}{M}$$

**e.g.** $R - MgX$, $R_2CuLi$, $R_2Zn$

(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.

RONa (Sodium alkoxide). $CH_3COONa$ (Sodium acetate), $CH_3COOAg$ (Silver acetate), RSK (Potassium mercaptide) RNHK (N-Alkyl potassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc.

### (I) Grignard Reagent

#### 1. Saturated Aliphatic Grignard's reagent

$R - MgX$ (Alkyl magnesium halide)

$CH_3 - MgI$ (Methyl magnesium iodide)

#### 2. Unsaturated Aliphatic Grignard's reagent

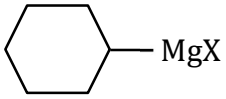
(i) Alkenyl Grignard's reagent

$CH_2 = CH - CH_2 - MgX$ (Allyl magnesium halide)

(ii) Alkynyl Grignard's reagent

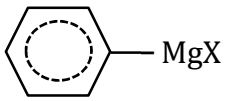
$CH = CH - CH_2 - MgX$ (Propargyl magnesium halide)

#### 3. Alicyclic Grignard's reagent




(Cyclohexyl magnesium halide)

#### 4. Aromatic Grignard's reagent



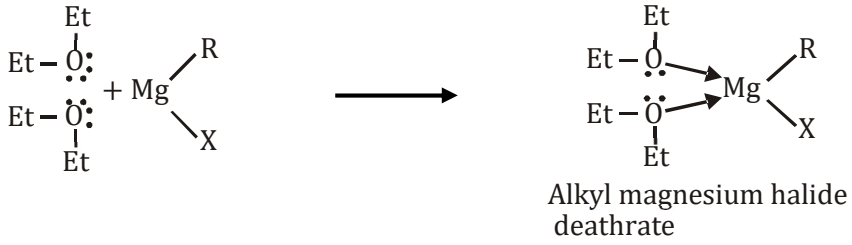

(Phenyl magnesium halide)

$C_6H_5CH_2MgCl$ (Benzyl magnesium halide)

**Preparation**

$$RX + Mg \xrightarrow[\text{Ether}]{\text{Dry and pure}} RMgX$$

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's reagent by completing the octet on magnesium atom.




Alkyl magnesium halide deathrate

**Process**

To an ethereal solution of alkyl halide Mg metal is added at very low temp. (0.5°C). A vigorous reaction takes place, and a solution of G.R. is obtained. It cannot be evaporated to obtain a solid state. The reaction will be explosive. It is **stable only in solution state.**

**Reactivity order with respect to X (For preparation of RMgX)**

R – X:

$$R - I > \underbrace{R - Br}_{\text{Most Commonly used}} > R - Cl > \underbrace{R - F}_{\text{(No G.R. form}}$$

Iodides forms organometallic compounds at the fastest rate.

**Structural stability of G.R.**

If the alkyl part has more stable negative charge, then RMgX is more stable. It will be less reactive

**Ex.**

$CH_3 - CH_2 - MgX$; $CH_2 = CH - MgX$; $CH_3C \equiv C - MgX$

Reactivity order : $1 > 2 > 3$

Stability order : $1 < 2 < 3$

**Reactivity order of Grignard's reagent**

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

$$RMgI > RMgBr > RMgCl$$

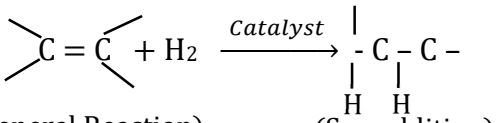
**Reactivity order with respect to active H**

$$\text{Acidic H} > \text{- CHO} > \text{R–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–R} > \text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–X} > \text{R–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O–R'} > \text{R–X}$$

Except X (halogen) all other functional groups must be absent in the alkyl group otherwise. G.R. will be destroyed by internal reactions.
[– NO2, – CN must also be absent]

## (II) REDUCTION

### (a) CATALYTIC HYDROGENATION



(General Reaction) (Syn addition)

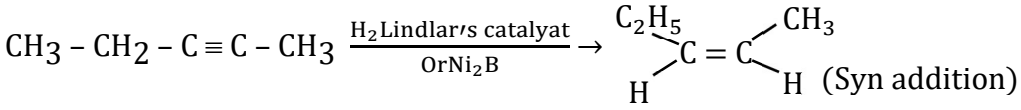
Hydrogenation of an alkene is an **exothermic reaction ($\triangle H^{o} \cong$ -120 KJ mol $^{-1}$)**

$$R - CH = CH - R + H_2 \xrightarrow{Ni} R - CH_2 - CH_2 - R + \text{heat}$$

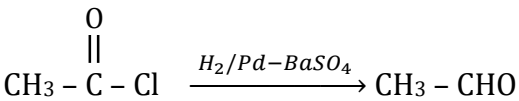
### (b) PARTIAL REDUCTION

**Lindlar's catalyst**

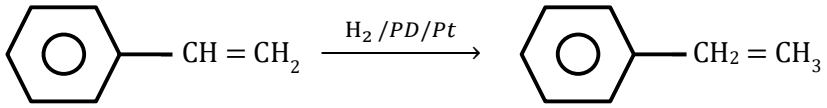
It is a poisoned palladium catalyst (composed of powdered barium sulphate coated with palladium) poisoned with quinoline or sulphur. Nickel boride Ni2B (P-2 catalyst) (made from sodium acetate and sodium borohydride) is an excellent alternative catalyst for the conversion of alkyne into alkene. (Syn addition)
The partial reduction of alkyne to alkene is heterogeneous hydrogenation with Landlar's catalyst.



Acid chloride reduced to aldehyde by using $Pd/BaSO_4$ catalyst is called **Rosamund Reduction.**

(i) 

(ii) $O_2N - CH = CH - CH_2 - CH_3 \xrightarrow{H_2/Pd/Pt} H_2N - CH_2 - CH_2 - CH_2 - CH_3$




**Reduction by Dissolving Metals**

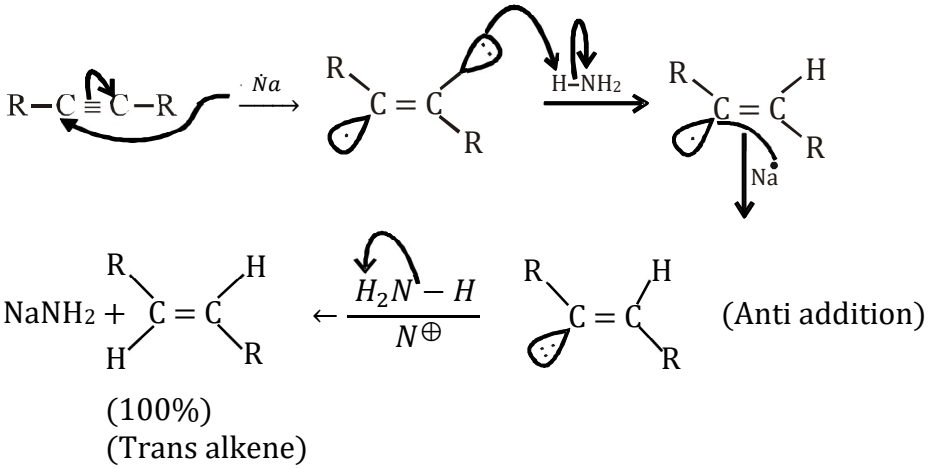
The general mechanism of reduction by dissolving metals is based on the fact that the metal acts as a source of electrons first an electron adds to the substrate causing fission of a single bond into a free radical and an anion or it can add to a double bond forming a resonance-stabilized radical ion.

$$A - B \xrightarrow{\bar{e}} A + \overset{\Theta}{B}: \quad or \quad \overset{\Theta}{A}: + B$$

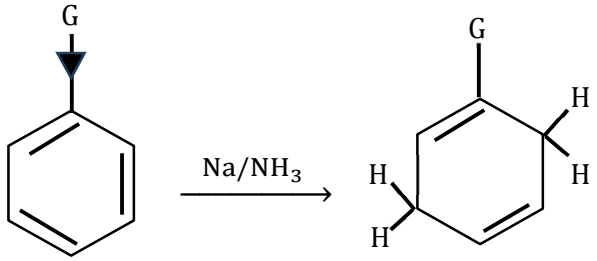
## (c) REDUCTION BY NA OR LI/$NH_3$ (BIRCH REDUCTION)

**Mechanism**

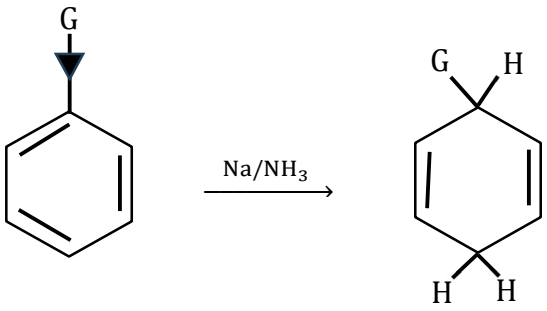
Reagents Na (or Li, K) + liq $NH_3$ → $Na^+$ e– (solvated electron)




Typical example of reduction for aromatic system:
(Electron releasing group – R, – OR, – $NH_2$)




(Electron withdrawing grow – $NO_2$, COOH, -CHO, -CN)




## (d) REDUCTION BY NA/$C_2H_5OH$ [BOUVEALT-BLANC REDUCTION]

(a) $CH_3CHO$ (Acetaldehyde) $\xrightarrow{Na/C_2H_5OH}$ $CH_3CH_2OH$ (Ethanol)

(b) $CH_3 - COCH_3$ (Acetone) $\xrightarrow{Na/C_2H_5OH}$ $(H_3C)_2CHOH$ (Propane–2–ol)

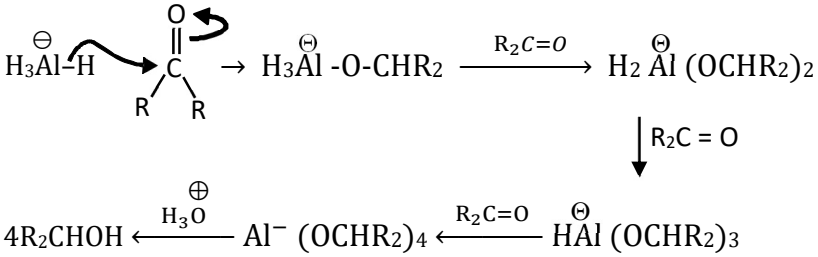
(c) $CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5$ (Ethyl acetate) $\xrightarrow[H_2O]{Na/C_2H_5OH}$ $CH_3CH_2OH$ (Ethanol)

## (e) REDUCTION BY METAL HYDRIDES AND ALKOXIDES

$LiAlH_4$(LAH) Lithium aluminum hydride (strong reducing agent):

NaBH4 Sodium borohydride (Mild reducing agent):

**Mechanism**




## (f) DIBAL-H (DIISOLBUTYL ALUMINIUM HYDRIDE) (ALANE)

Most important Alane is Di isobutyl aluminum hydride. It runs parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

➢ $Ph\text{-}CH{=}CH\text{-}COOC_2H_5 \xrightarrow[H_2O]{LiAlH_4-THE} Ph{-}CH_2{-}CH_2{-}CH_2OH + C_2H_5OH$

$Ph\text{-}CH{=}CH\text{-}COOC_2H_5 \xrightarrow{DIBAL\text{-}H} Ph\text{-}CH{=}CH\text{-}CH_2OH$

By DIBAL at ordinary temperature esters are reduced to alcohols but at low temperature esters are reduced to aldehyde.

➢ $C_6H_5 - \underset{\underset{O}{\|}}{C} - OCH_3 \xrightarrow[toluene\ 25^\circ]{DIBAL} C_6H_5CH_2OH$

$C_6H_5 - \underset{\underset{O}{\|}}{C} - OCH_3 \xrightarrow[toluene\ -\ 78^3C]{DIBAL} C_6H_5CHO$

LAH reduce RCN to amine but DIBAL is found to be reduce it to aldehyde.

➢ $CH_3 - C \equiv N \xrightarrow{LiA1H_4-The} CH_3\text{-}CH_2\text{-}NH_2$

$CH_3 - C \equiv N \xrightarrow[25^\circ C]{DIBAL} CH_3 - CHO$

## (g) MPV REDUCTION (BY ISOPROPYL ALCOHOL AND ALUMINIUM ISOPROPOXIDE)

$$R - \underset{\underset{O}{\|}}{C} - R' + \underset{\underset{OH}{|}}{CH_3 - CH} - CH_3 \overset{Al(OCMe_2)_3}{\rightleftharpoons} R - \underset{\underset{O}{|}}{CH} - R' + CH_3 - \underset{\underset{O}{\|}}{C} - CH_3$$

### Stephen's Reduction

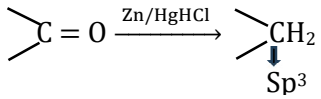
When reduction of compounds is carried out with acidified stannous chloride ($SnCl_2/HCl$) at room temperature, imine hydrochloride is obtained which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called Stephen's reduction.

$$R - C \equiv N \xrightarrow[Complete\ Reduction]{LiAlH_4 or Na/C_2H_5OH} \underset{(1^\circ\ Amine)}{R - CH_2NH_2}$$

$$R - C \equiv N \xrightarrow[(Partial\ Reduction)]{(i)SnCl_2/HCl\ (ii)H_2O} \underset{Aldehyde}{R - CHO}$$

**Clemmensen's Reduction**

Used to get alkane from carbonyl compounds:



Clemmensen reduction is not used for compounds which have **acid sensitive** group.

## (h) WOLFF-KISHNER REDUCTION ($NH_2NH_2$/KOH)

Used to get alkane from carbonyl compounds

Wolff-kishner reduction is not used for compounds which have **base sensitive** groups.

**By Red P & HI**

All the functional groups reduced into corresponding hydrocarbon

(a) $R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{Re\ dP+HI} R-CH_3$

(b) $R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Re\ dP+HI} R-CH_3$

(c) $R-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{Re\ dP+HI} R-CH_3$

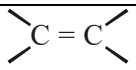
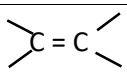
(d) $R-\underset{\underset{O}{\|}}{C}-R \xrightarrow{Re\ dP+HI} R-CH_2-R$

(e) $CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{Re\ dP+HI} CH_3CH_3$

(f) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{Re\ dP+HI} CH_3CH_2CH_3$

**Various functional groups and their products by the use of different reducing agents**

| S. No. | Group | Product | $H_2$ + Catalyst | $LiAlH_4$ in ether | $NaBH_4$ in EtOH | $LiAlH(OBu^t)_3$ in THF |
|---|---|---|---|---|---|---|
| 1 | – CHO | $-CH_2OH$ | + | + | + | + |
| 2 |  |  | + | + | + | + |
| 3 | $-CO_2H$ | $-CH_2OH$ | - | + | - | - |
| 4 | – COOR' | $-CH_2OH$ | - | + | - | - |
| 5 | $-CHNH_2$ | $-CH_2NH_2$ | - | + | - | - |
| 6 | – COCl | $RCH_2OH$ | + | + | + | + |
| 7 | – epoxide | alcohol | + | + | - | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | – CN | $-CH_2NH_2$ | + | + | - | - |
| 9 | $RNO_2$ | $RNH_2$ | + | + | - | - |
| 10 |  |  | + | - | - | - |

**(*)** double bond can be reduced by $LiAlH_4$/THF only in cinnamic system.

**Ex.** Ph – CH = CH – CHO PH – $CH_2$ – $CH_2$ – $CH_2$OH