01 Reduction

Metal hydrides reduction:

Certain complex metal and boron hydrides are important reagents for reduction.

(i) $LiAlH_4$ (LAH) Lithium aluminium hydride [$LiAlH_4$/Ether or THF] :

LAH is most common and versatile reagent. It is sensitive to protic solvent and therefore used in ether.

Reagent	**$LiAlH_4$**	**$LiAlH_4$**	**$LiAlH_4$/ Excess**	**$LiAlH_4$/ Excess**	**$LiAlH_4$**	**$LiAlH_4$**	**$LiAlH_4$**	**$LiAlH_4$**	**$LiAlH_4$**
Reactant	Aldehyde	Ketone	Acid	Acidanhy dride	Acid chloride	Ester	Cyanide	Amide	Nitro
Product	1°alcohol	2°alcohol	1°alcohol	1°alcohol	1°alcohol	1°alcohol	1°amine	1° amine	1° amine

Note :

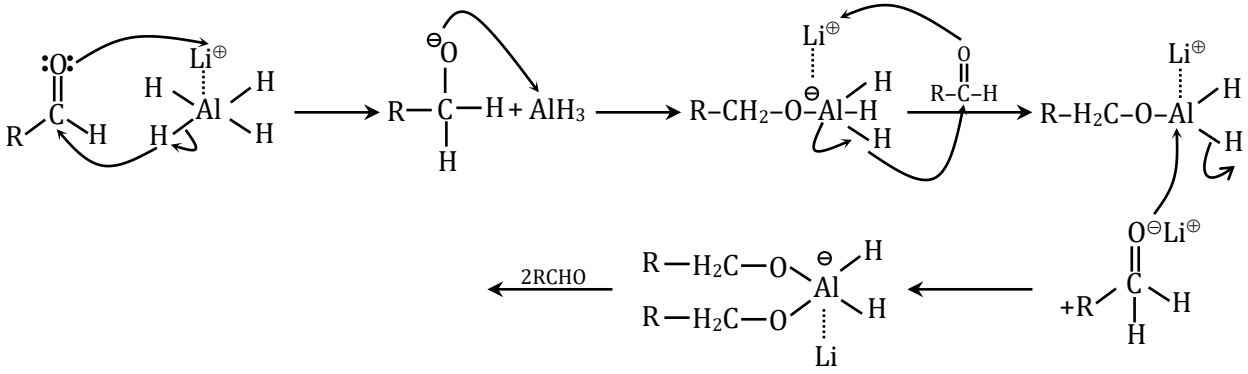
(i) Alkene, alkyne, benzene rings are not reduced by $LiAlH_4$.

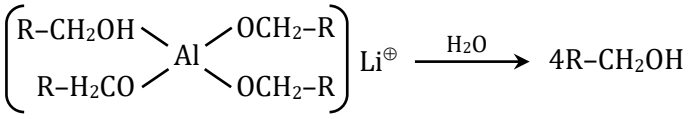
(ii) double bond can be reduced by $LiAlH_4$ / THF in few cases like :

$$Ph{-}CH{=}CH{-}CHO \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4-THF} Ph{-}CH_2{-}CH_2{-}CH_2OH$$

[Cinnamaldehyde]

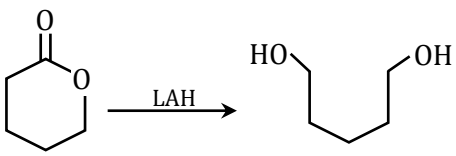
Mechanism of $LiAlH_4$



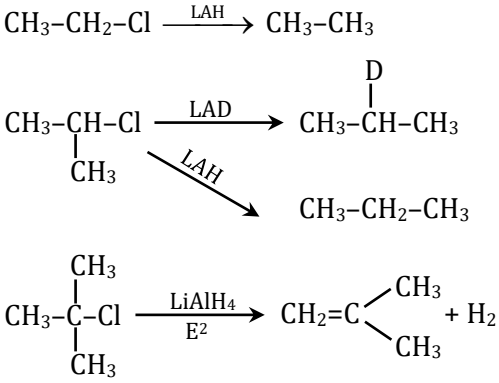


$$4RCHO + LiAlH_4 \longrightarrow 4R{-}CH_2OH + LiOH + Al(OH)_3$$

Illustration 1:



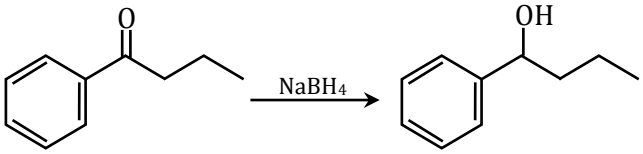
Note : It can reduce 1° and 2° alkyl halide into Alkane but not 3°



(ii) Sodium borohydride [$NaBH_4$ / C_2H_5OH or Ether] :

It is more specific than LAH as a reducing agent. It reduces ketones and aldehydes to the corresponding alcohols without affecting other functional groups, reduces acid chlorides to 1° alcohols. It is effective even in protic solvent like alcohol.

Reagent	$NaBH_4$	$NaBH_4$	$NaBH_4$
Reactant	Aldehyde	Ketone	Acid chloride
Product	1° alcohol	2° alcohol	1° alcohol



Note :

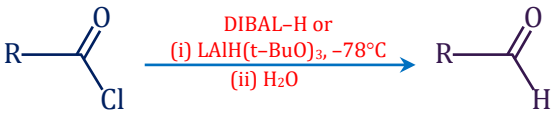
1. $NaBH_4$ can also reduce imine group ($\diagdown C = NH$).

(iii) Diisobutyl Aluminium Hydride [DIBAL-H / Inert solvent] :

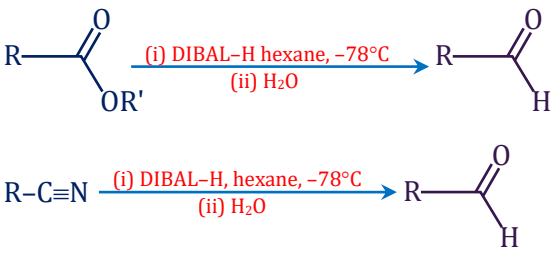
Diisobutyl aluminium hydride is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

Reduction of acyl halides, esters and nitriles :

(a) Acyl chlorides can be reduced to aldehydes by treating them with lithium-tri-tert-butoxyaluminium hydride, $LiAlH[OC(CH_3)_3]_3$ or with DIBAL–H at –78°C.

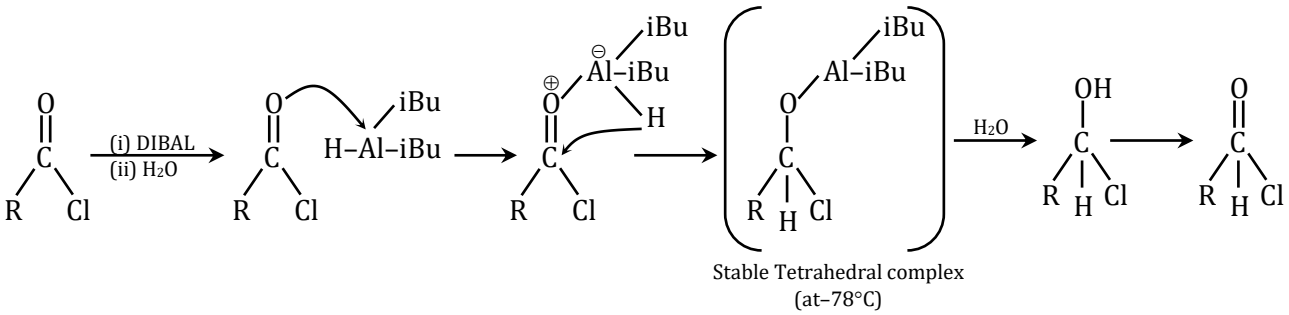


(b) Both esters and nitriles can be reduced to aldehydes by DIBAL–H. Reduction must be carried out at low temperatures. Hydrolysis of the intermediates gives the aldehyde.



Reagent	DiBAL-H/(–78°C)		
Reactant	Ester	Cyanide	Acyl chlorides
Product	Aldehyde	Aldehyde	Aldehyde

Mechanism of DIBAL H



Note :

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

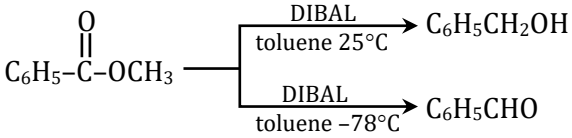


Illustration 2:

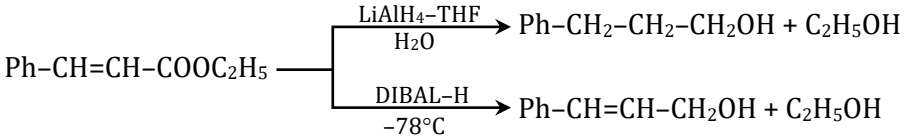
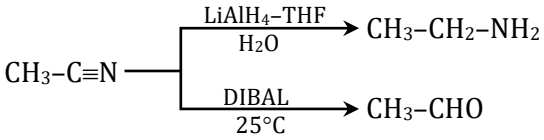


Illustration 3:

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



(iv) B_2H_6 or BH_3/THF

B_2H_6/THF gives BH_3 which is a electrophile(Lewis acid) so B_2H_6 does not reduce electrophilic functional groups.

Note : -

Acyl chloride and esters are relatively electron poor (Cl and OR are very electronegative). Boron will not reduce acyl chloride and reduces esters slowly.

Reactant	Remark	Product
	Not usually Reduced	
$R - NO_2$	Not usually Reduced	
R – X	Not usually Reduced	

>C=N–OH	Not usually Reduced	
O ‖ —C—H	Reduced slowly	$-CH_2OH$
O ‖ —C—	Reduced slowly	OH | —CH—
O ‖ R—C—OR	Reduced slowly	$R - CH_2OH + ROH$
O ‖ —C—OH	Reduced	$-CH_2OH$
O ‖ R—C—NH_2	Reduced	$R-CH_2-NH_2$

Note :

1. B_2H_6 in THF not able to reduce cyclic ester.

Catalytic Hydrogenation :

From alkenes and alkynes (Sabatier and Senderens reaction)

Alkenes and alkynes on catalytic hydrogenation gives alkanes.

$$\underset{\text{Alkene}}{R-C=CH-R} + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Alkane}}{R-CH_2-CH_2-R}$$

$$\underset{\text{Alkyne}}{R-C\equiv C-R} + 2H_2 \xrightarrow{\text{Catalyst}} R-CH_2-CH_2-R$$

Catalyst :

(a) Pd/Pt at ordinary temp. and pressure

(b) Ni, 200–300° C (sabatier)

(c) Raney Nickel at room temp.

(d) Raney nickel is obtained by boiling Ni/Al with NaOH. Al dissolved & Ni obtained in finally divided state.

(e) Methane cannot be prepared by this method (From unsaturated hydrocarbon).

$$-\overset{O}{\overset{\|}{C}}-X > -NO_2 > -C\equiv N > -C\equiv CH > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}- > -C=NH > -CH=CH_2 > R-\overset{O}{\overset{\|}{C}}-OR > R-\overset{O}{\overset{\|}{C}}-NH_2$$

Higher electrophilicity more reactive for hydrogenation.

They do not reduce –COOH .

Alkenes and alkynes on catalytic hydrogenation gives alkanes

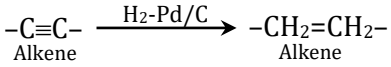
Illustration 4:

$$\underset{\text{Alkene}}{>C=C<} + H_2 \xrightarrow[\Delta]{\text{Ni, Pt or pd}} \underset{\text{Alkene}}{>CH-CH<}$$

$$\underset{\text{Alkene}}{-C\equiv C-} + 2H_2 \xrightarrow[\Delta]{\text{Ni, Pt or pd}} \underset{\text{Alkene}}{-CH_2-CH_2-}$$

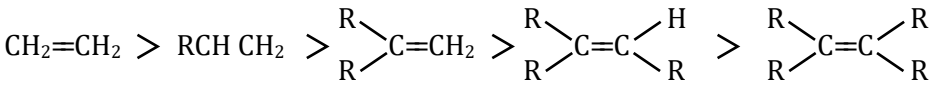
This method is called Sabatier–senderens reaction or hydrogenation of alkenes and alkynes

Selective reduction by H_2–Pd/C



Greater the crowding at double bond carbon more difficult the hydrogenation

Rate of Hydrogenation



Mendius reduction (complete reduction)

Note : -

Alkyl cyanides (nitriles) can be reduced to 1° amine and isocyanides are reduced to 2° amine .

Reagent –H_2 + Na/ROH.

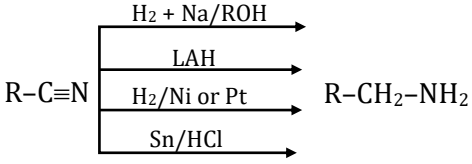
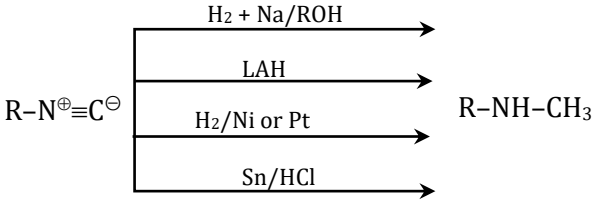


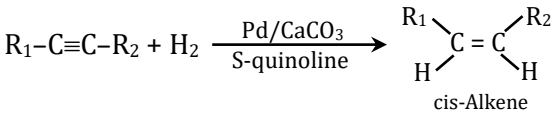
Illustration 5:



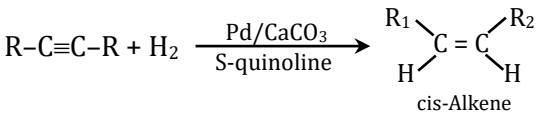
By partial reduction of Alkynes -

By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)

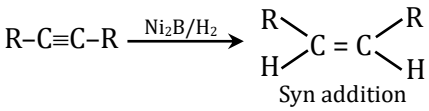
(i) **Lindlar's catalyst ($Pd/CaCO_3$)** : Metallic palladium deposited on calcium carbonate conditioned with lead acetate and quinoline.



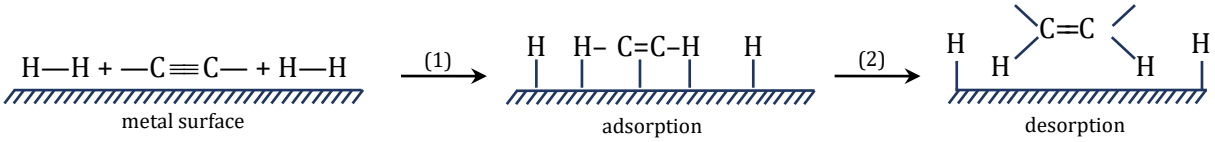
(ii) **Rosenmund catalyst ($Pd/BaSO_4$) :** Metallic palladium deposited on Barium sulfate conditioned with lead acetate and quinoline.



(iii) **P–2 catalyst (Ni_2B nickel boride)**



Mechanism of hydrogenation :



Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atoms from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes **Quinoline** therefore is called catalyst poison and such palladium is called deactivated catalyst or poisoned catalyst.

Note : Rosenmund's reduction :

Quinoline or sulphur act as a poisoned catalyst, controls the further reduction of aldehyde to alcohols.

$$RCOCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} RCHO + HCl$$

This reaction controls further reduction of aldehyde to alcohols.

In case if only Pd is used, formation of alcohol takes place.

$$RCOCl + H_2 \xrightarrow{Pd} RCHO \xrightarrow{H_2/Pd} RCH_2OH$$

Formaldehyde cannot be prepared by this method because HCOCl is highly unstable at room temperature it decompose into CO + HCl.

Example : $C_2H_5COCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} C_2H_5CHO + HCl$
(Propionyl chloride → Propanal)

Illustration 6:

$$CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{Or } H_2/Pd/CaCO_3]{H_2/Ni_2B(P-2)} \underset{\text{(Z)-3-Hexene (cis-3-Hexene) (97\%)}}{\overset{CH_3CH_2}{H}\!\!>\!C{=}C\!<\!\overset{CH_2CH_3}{H}}$$

3–Hexyne; (syn addition)

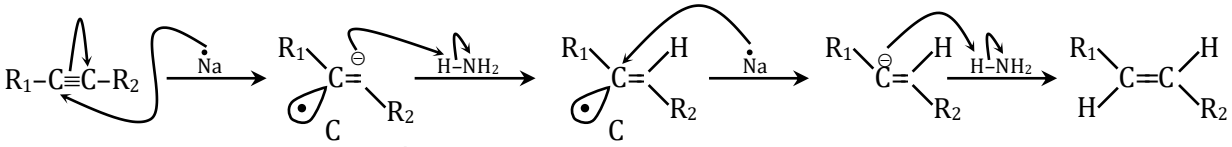
Illustration 7:

$$R{-}C{\equiv}N \xrightarrow[\text{S-quinoline}]{H_2\text{–}Pd/BaSO_4} R{-}CH{=}NH$$

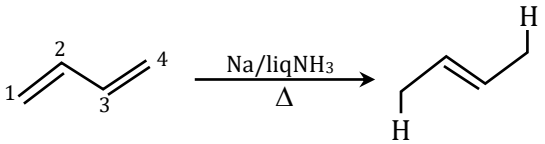
BIRCH REDUCTION:

$$\underset{\text{Alkene}}{R_1{-}C{\equiv}C{-}R_2} \xrightarrow[\Delta]{Na/\text{liq. } NH_3} \underset{\text{cis-Alkene}}{\overset{R_1}{H}\!\!>\!C{=}C\!<\!\overset{R_2}{H}}$$

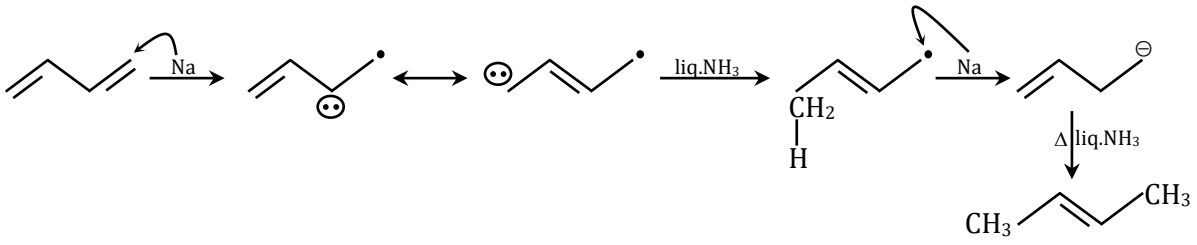
Mechanism



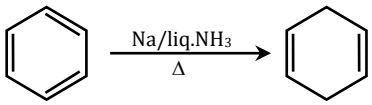
BIRCH REDUCTION IN CONJUGATED DOUBLE BOND



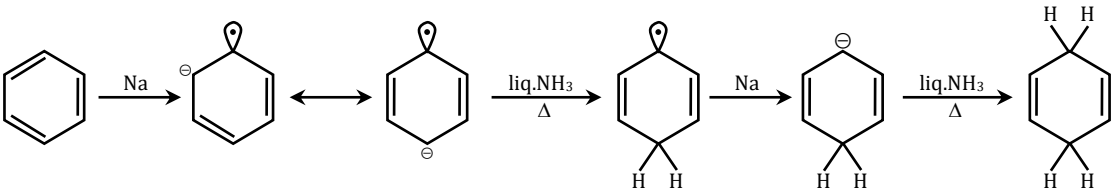
Mechanism:



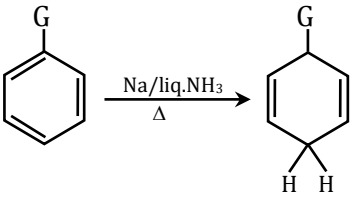
Birch Reduction In Benzene Ring



Mechanism:

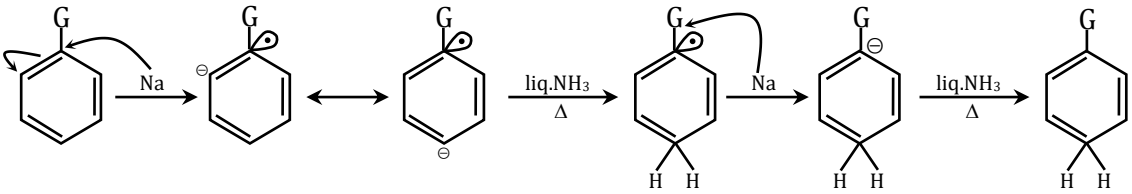


CASE–I ⇒ Presence of electron releasing group (–R, –OR, $–NH_2$ etc.)

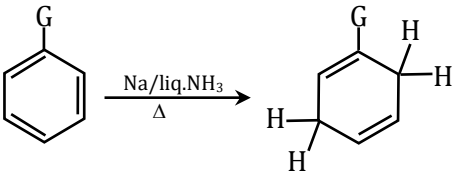


G = E.W.G

Mechanism:



CASE–II ⇒ Presence of electron withdrawing group ($–NO_2$, –COOH, –CHO, –CN etc.)



G = E.D.G

Mechanism:

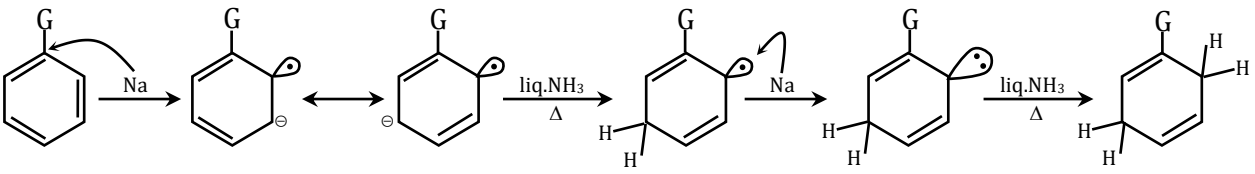


Illustration 8:

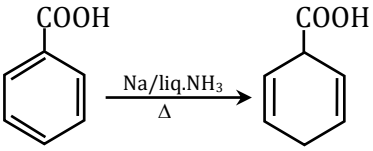
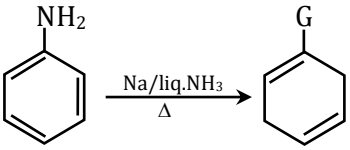
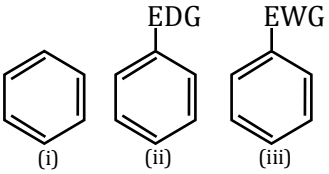


Illustration 9:



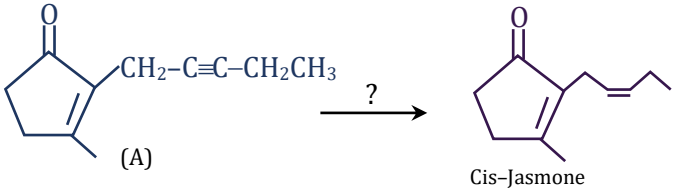
Rate of reaction with Na/liq NH_3



(iii) > (i) > (ii)

Illustration 10:

Identify the reagent for following synthesis



Solution:

H_2/Lindlar's catalyst

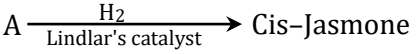
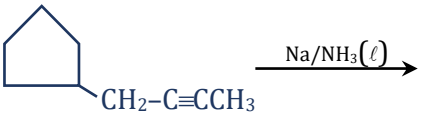
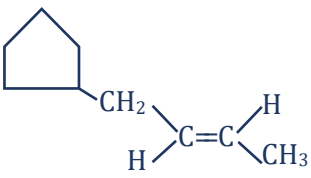


Illustration 11:

Identify the product in the following reaction :

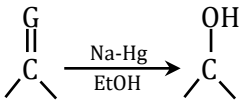


Solution:



Bouveault Blank Reduction (Na-Hg/EtOH) :

Reduces all which are reduced by LAH except -COOH



Mechanism:

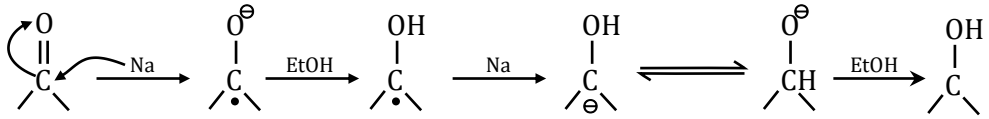
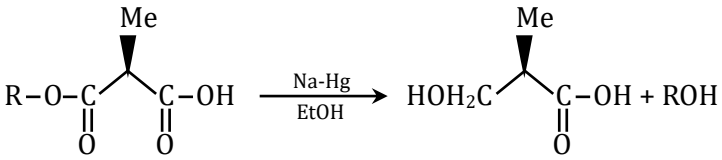
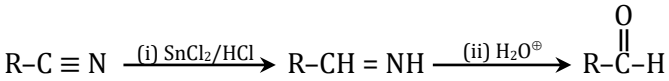


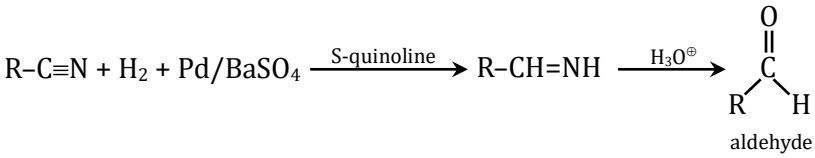
Illustration 12:

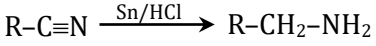


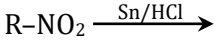
Stephen's Reduction ($SnCl_2$/HCl)

Partial reduction







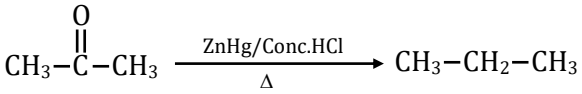


Clemmensen Reduction :

The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction.

Reagent : Zn-Hg/Conc. HCl

Function : Aldehyde/Ketone to Alkane

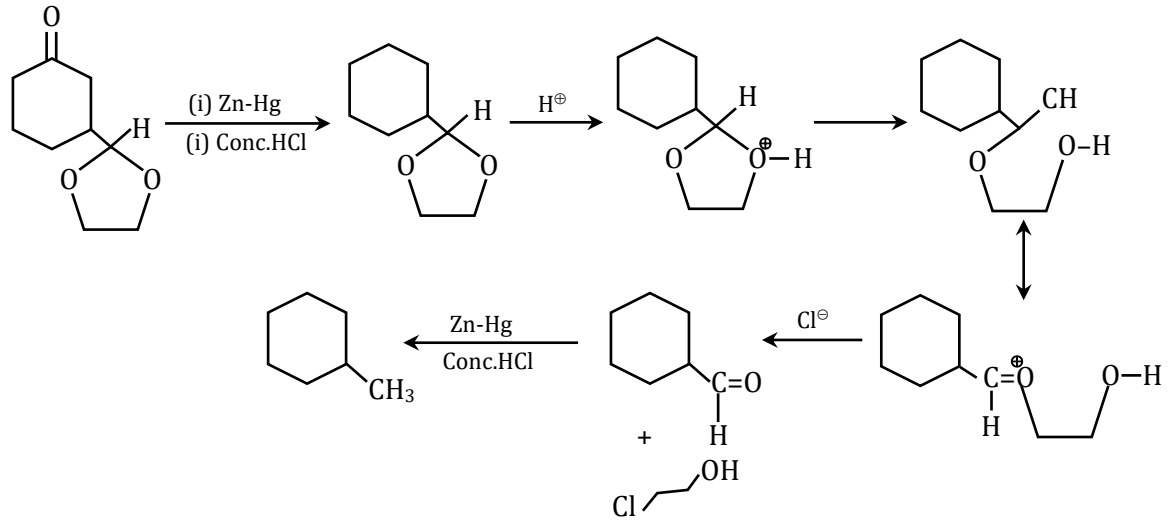


In this reaction  is converted into $-CH_2-$

Note : -

If other acid sensitive group is also attached then $H^{\oplus}$ will react with that group and If we want retain acid-sensitive group in the product then we will not use clemensen Reduction.

Mechanism



The Wolf Kishner reduction :

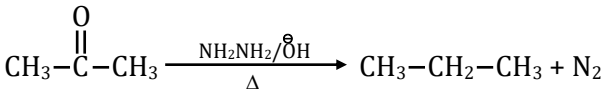
When a ketone or an aldehyde is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group this process is called Deoxygenation because an oxygen is removed from the reactant. The reaction is known as the Wolf-kishner Reduction.

Reagent : $N_2H_4/OH/\Delta$

H_2C—OH

H_2C—OH

Function : Aldehyde/Ketone to Alkane

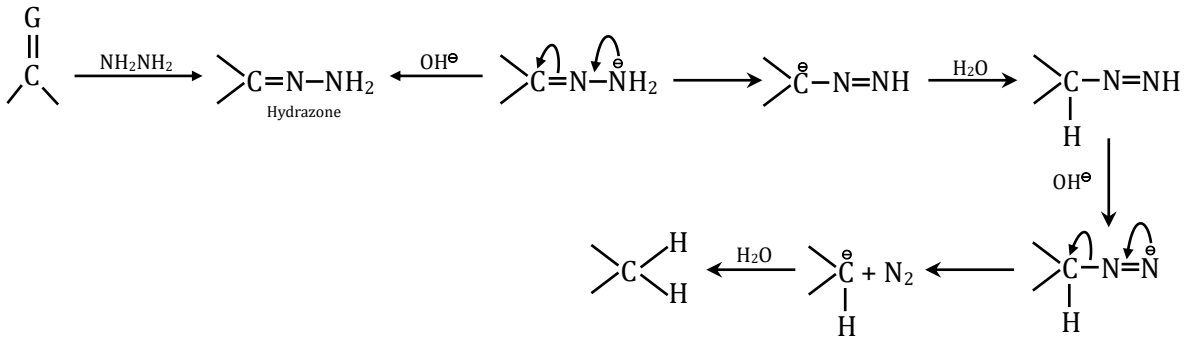


Note

It reduce aldehydes and ketones to alkanes,but does not reduce alkene and alkyne

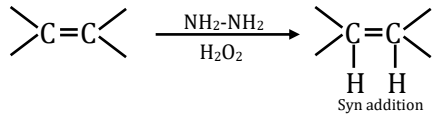
This is a base catalysed reaction ,so simultaneouslydehy drohalogenation of RX also take place

Mechanism :

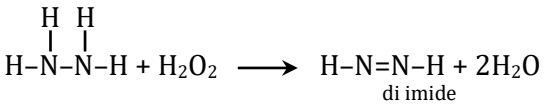


Reduction by transfer hydrogenation:

Reagent N_2H_4/H_2O_2 Or N_2H_2



Mechanism:



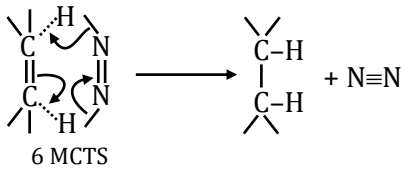


Illustration 13:

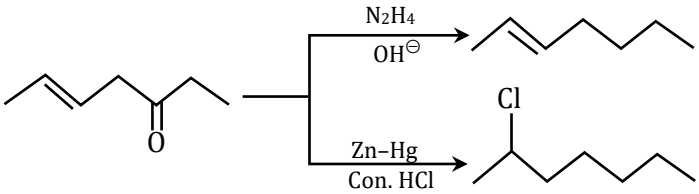
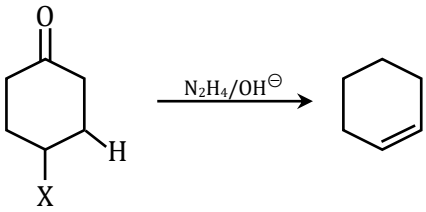
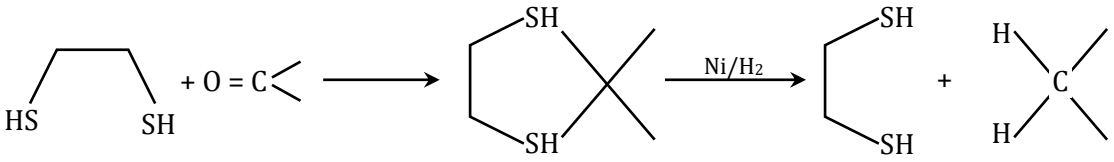


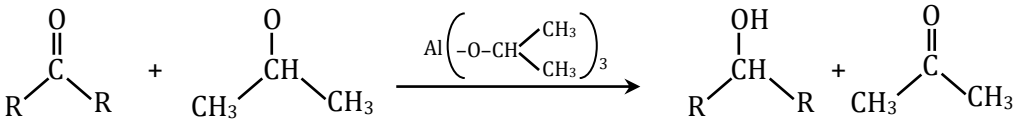
Illustration 14:



Mozingo Reaction :



MPV Reduction :



In this reaction, carbonyl is reduced into corresponding alcohol by aluminium isopropoxide taken in isopropanol.

Wilkinson's catalyst :

Reagent - $[(Ph_3P)_3RhCl] + H_2$

It gives Syn addition.

Reduce only alkene or alkyne.

Reduction by Red P and HI :

$R-I \xrightarrow[\Delta]{\text{Red P + HI}} R-H + I_2$

Mechanism:

$HI \xrightarrow[\Delta]{\text{HI/red P}} H^{\bullet} + I^{\bullet}$

$R-I \xrightarrow[\Delta]{\text{HI/red P}} R^{\bullet} + I^{\bullet}$

$R^{\bullet} + H^{\bullet} \xrightarrow[\Delta]{\text{HI/redP}} R-H$

$H^{\bullet} + I^{\bullet} \xrightarrow[\Delta]{\text{HI/redP}} H-I$

$2I^{\bullet} \longrightarrow I_2$

All organic compound containing O convert into Alkane Containing N Convert into amine

$R-OH \xrightarrow[\Delta]{\text{Red P + HI}} R-H$

$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\Delta]{\text{Red P + HI}} R-CH_3$

$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\Delta]{\text{Red P + HI}} R-CH_3$

$R-\overset{\overset{O}{\|}}{C}-OR \xrightarrow[\Delta]{\text{Red P + HI}} R-CH_3$

$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[\Delta]{\text{Red P + HI}} 2R-CH_3$

$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{\text{Red P + HI}} R-CH_2-CH_3$

$R-CN \xrightarrow[\Delta]{\text{Red P + HI}} R-CH_2-CH_3$

$\text{Glucose} \xrightarrow[\Delta]{\text{Red P + HI}} \text{n-hexane}$

No. of moles of (Red P + HI) required for Reduction of alcohol, aldehyde, ketone, carboxylic acid in presence of Red P and HI

$R-OH + 2HI \xrightarrow[150°C]{\text{Red P}} R-H + H_2O + I_2$

$R-CHO + 4HI \xrightarrow[150°C]{\text{Red P}} RCH_3 + H_2O + 2I_2$

$R-CO-R + 4HI \xrightarrow[150°C]{\text{Red P}} R-CH_2-R + H_2O + 2I_2$

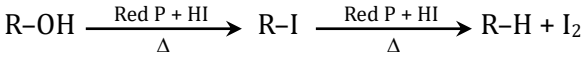
$RCOOH + 6HI \xrightarrow[150°C]{\text{Red P}} R-CH_2-H + H_2O + 3I_2$

In the above reaction I_2 is formed which acts as reducing agent and may reduce alkane and form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.

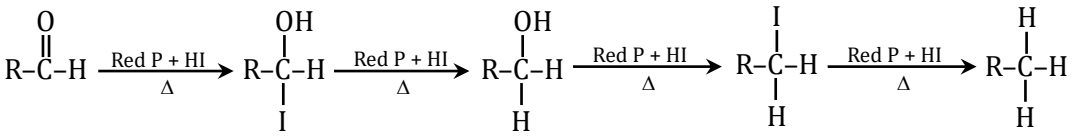
$R-CH_3 + I_2 \rightleftharpoons R-CH_2-I + HI$

$2P + 3I_2 \longrightarrow 2PI_3$

(i) Alcohol

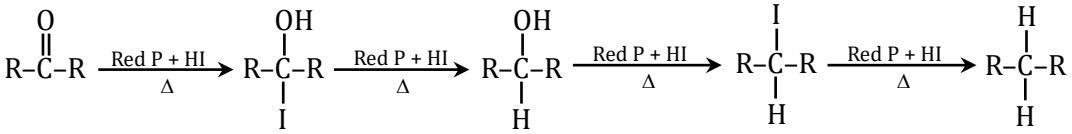


No. of moles of (Red P +HI) required = 2



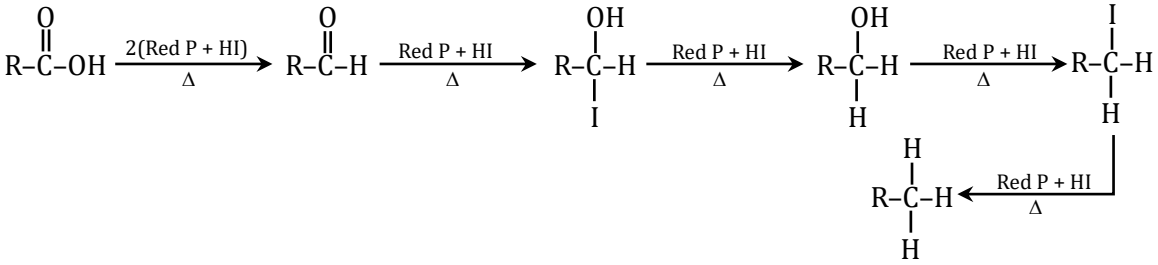
No. of moles of (Red P +HI) required = 4

(ii) Ketone



No. of moles of (Red P +HI) required = 4

(iii) Carboxylic Acid



No. of moles of (Red P +HI) required = 6

Illustration 15:

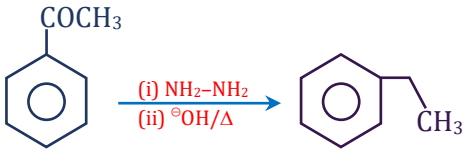


Illustration 16:

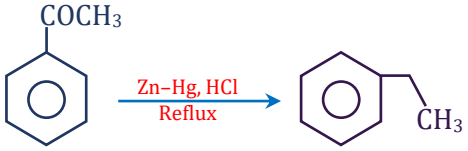


Illustration 17:

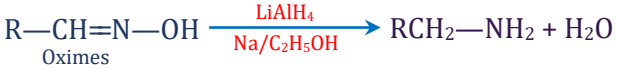


Illustration 18:

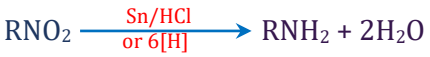
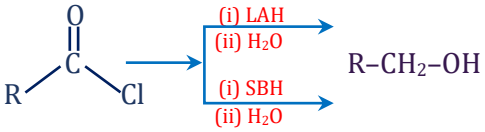


Illustration 19:



Solution:

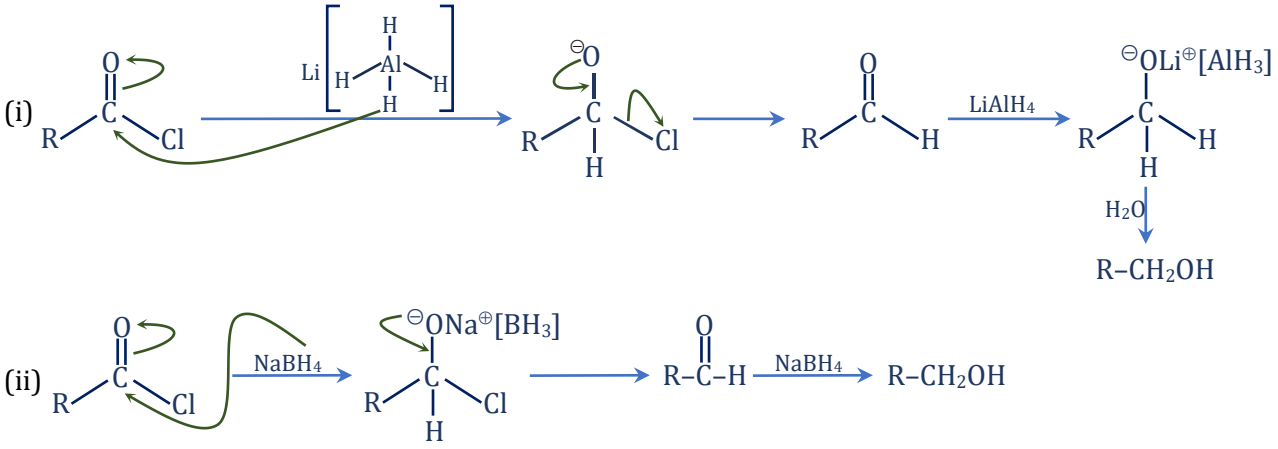
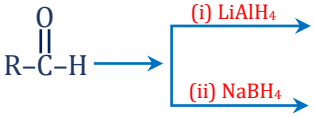


Illustration 20:



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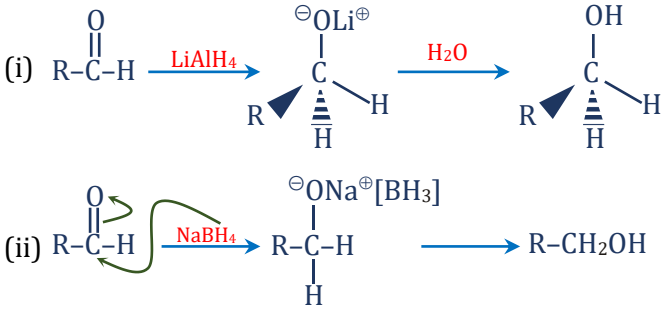

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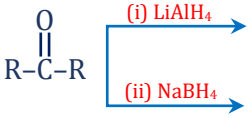

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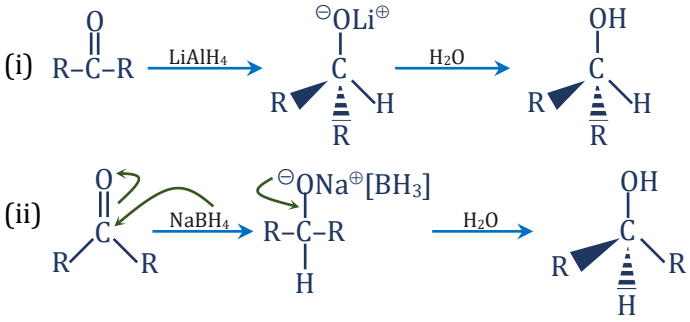
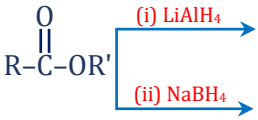


Illustration 22:



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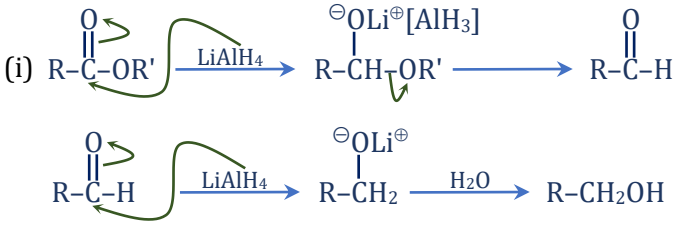
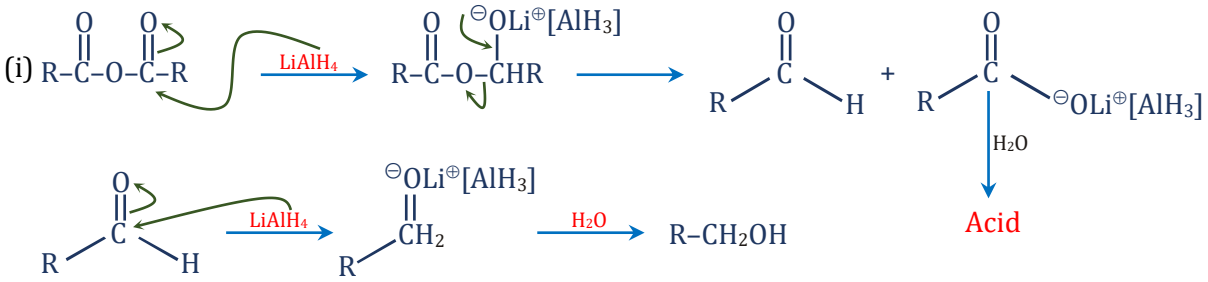


(ii) No reaction

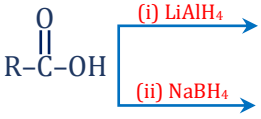
Illustration 23:

Solution:



(ii) No reaction

Illustration 24:



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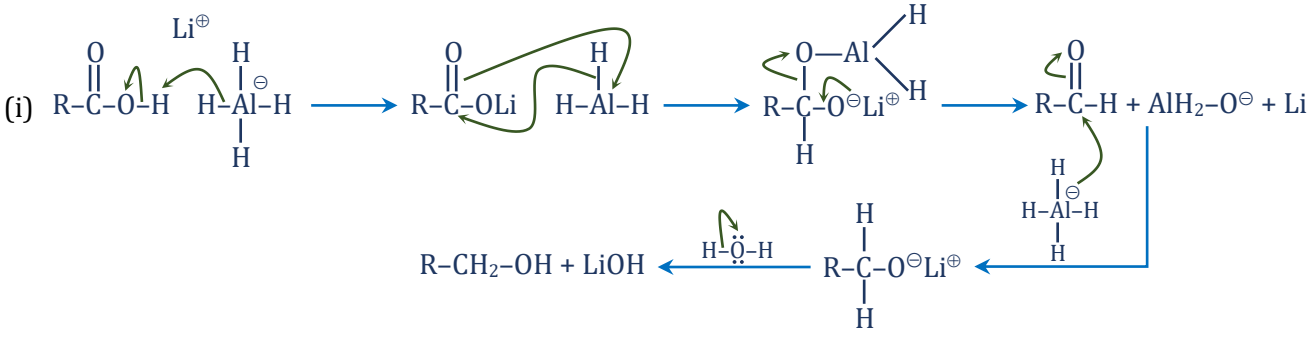
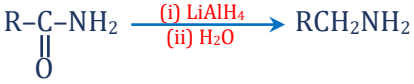


(ii) No reaction

Illustration 25:



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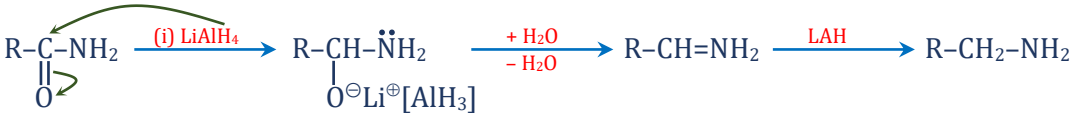


Illustration 26:

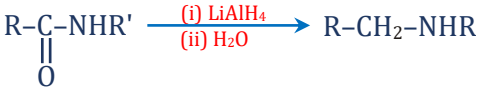


Illustration 27:

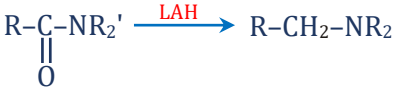
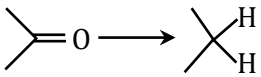
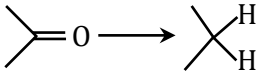
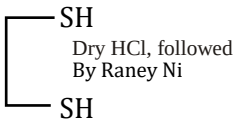
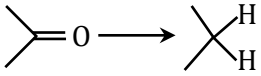
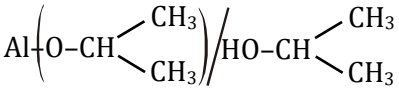
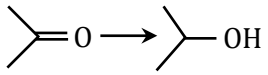
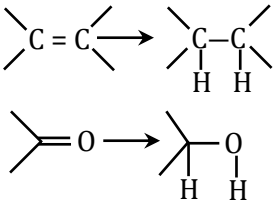
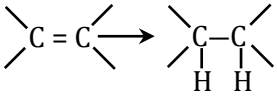
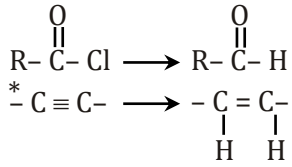
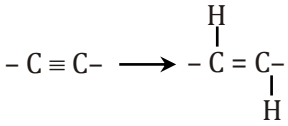
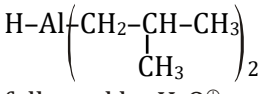
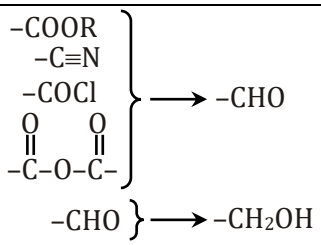


Chart-1

Group	Product	LAH in Ether	$NaBH_4$ in H_2O	B_2H_6 in THF	H_2/Catalyst Δ
–CHO	$-CH_2OH$	+	+	+	+
>C = O	>CH – OH	+	+	+	+
$-CO_2H$	$-CH_2OH$	+	–	+	–
$-CO_2R$	$-CH_2OH$	+	–	+	+
–COCl	$-CH_2OH$	+	+	–	+
$-CONH_2$	$-CH_2NH_2$	+	–	+	+
$(RCO)_2O$	RCH_2OH	+	–	+	+
–CN	$-CH_2NH_2$	+	–	+	+
>C = NOH	$-CH_2NH_2$	+	–	–	+
>C = C<	>CH – CH<	–	–	+	+
–C ≡ C–	–CH = CH–	–	–	+	+
1° RX	RH	+	–	–	+
2° RX	RH	+	+	–	+
3° RX	RH	–	+	–	+

Chart-2

Name	Reagent	Function
Wolf Kishner Reduction	(i) N_2H_4 / (ii) KOH, Δ	
Clemenson Reduction	Zn–Hg / HCl	

Mozingo Reduction		
Stephen's Reduction	$SnCl_2$ / HCl followed by $H_3O^{\oplus}$	$R–C\equiv N \longrightarrow R–CH=O$
MPV Reduction		
Hydroboration Reduction	B_2H_6 / AcOH, H_2O	
Bouvoult Blank Reduction	Na / EtOH	$R–COO–R \longrightarrow RCH_2OH + ROH$
Transfer Hydrogenation	N_2H_4 / H_2O_2	
Rosenmund Reduction	H_2, Pd–$BaSO_4$	
Birch Reduction	Na / Liq. NH_3	
DIBAL-H (–78°C)		
Red phosphorus in presence of HI	Red P + HI	$R–CO_2H \longrightarrow RCH_3$ $R–CH=O \longrightarrow RCH_3$ $R–\underset{\underset{O}{\|}}{C}–R \longrightarrow RCH_2R$ $R–OH \longrightarrow R–H$