Reduction: Addition of hydrogen ⇄ or loss of oxygen.
Also in a reaction, if $\bar{e}$ is added to reactant, then it is said, reactant is reduced.

$RCH=O \longrightarrow RCH_2OH$.

$R-\underset{\underset{O}{\|}}{C}-OH \longrightarrow RCH=O$.

$R-X + \bar{e} \longrightarrow R^{\cdot} + X^-$

$CH_2(Br)-CH_2(Br) \longrightarrow CH_2=CH_2$.

Also loss of X_2 is also called reduction.

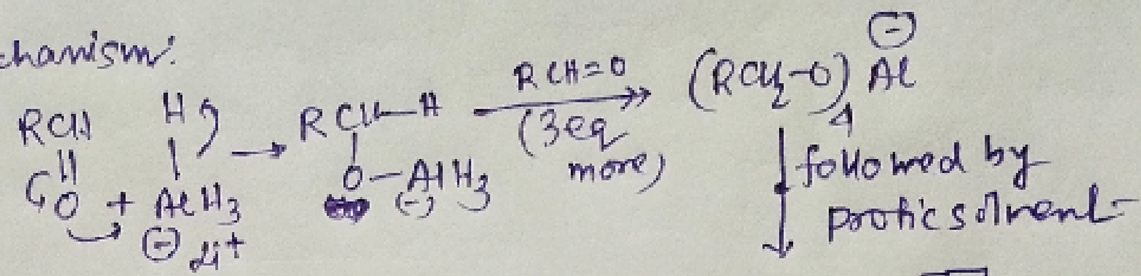
In all the reactions, reactant is reduced.

Acyl cpds.	Reduced part.	$LiAlH_4$	$NaBH_4$
$-CH=O$	$-CH_2OH$	✓	✓
$-\underset{\underset{O}{\|}}{C}-R$	$-\underset{\underset{OH}{|}}{CH}-R$	✓	✓
$-\underset{\underset{O}{\|}}{C}-OH$	$-CH_2OH$	✓	x
$-\underset{\underset{O}{\|}}{C}-Cl$	$-CH_2OH$	✓	✓
$-\underset{\underset{O}{\|}}{C}-OEt$.	$-CH_2OH + EtOH$.	✓	x
$-\underset{\underset{O}{\|}}{C}-NH_2$	$-CH_2-NH_2$	✓	x
$-C\equiv N$	$-CH_2-NH_2$	✓	x
RNO_2	$R-NH_2$	✓	x
$ArNO_2$	$Ar-N=N-Ar$	✓	x
$>C=C<$	x	x	x
$-C\equiv C-$	x	x	x
$R-X$.	$R-H$ [when $R = 1^\circ/2^\circ$]. ✓	✓	[$R = 2^\circ/3^\circ$]. ✓

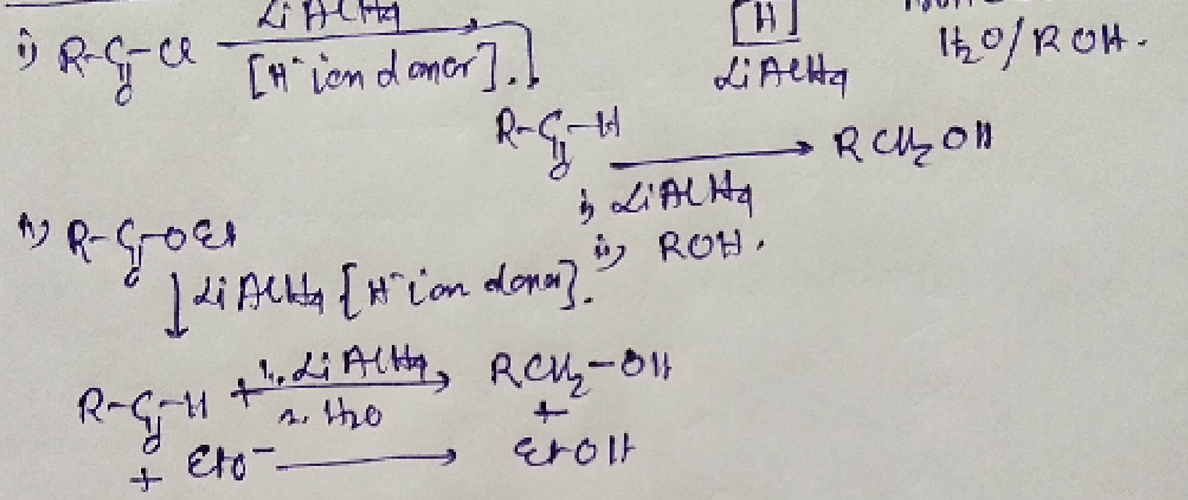
$LiAlH_4$: Source of H^- [very strong reducing agent] it reduce all except $C=C$ & $C\equiv C$.

$NaBH_4$: Source of H^- [very selective reducing agent]. it reduce only $-CH=O$, $-\underset{\underset{O}{\|}}{C}-R$, $-\underset{\underset{O}{\|}}{C}-Cl$.

'Mechanism'



'Question'



iii) $CH_3-CH_2-Cl \xrightarrow{LiAlH_4} CH_3-CH_3$

$CH_3-CH(CH_3)-Cl \xrightarrow{LiAlH_4} CH_3-CH_2-CH_3$

$CH_3-C(CH_3)(CH_3)-Cl \xrightarrow{LiAlH_4} CH_2=C(CH_3)(CH_3)$.

iv) $CH_3-CH=CH_2 \xrightarrow{LiAlH_4}$ no reaction

nucleophile — nucleophile.

v) $CH_3-C\equiv C-CH_3 \xrightarrow{"}{"}$ no reaction

vi) $CH_3-C(=O)-NH_2 \xrightarrow[HO^-]{LiAlH_4} CH_3-C(=O^-)-NH_2$ (Protic solvent)

vii) $CH_3-CH=NH \xleftarrow{-H_2O} CH_3-CH(OH)-NH_2$ (better L.G).

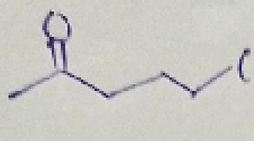
electrophile

$\xrightarrow[ii)\ H_2O]{i)\ LiAlH_4} CH_3-CH(H)-NH-H$ solvent

H AAH

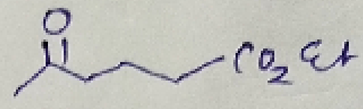
viii) $CH_3-CH(O)-CH_2 \xrightarrow[ROH]{LiAlH_4} CH_3-CH(OH)-CH_3$

ix)

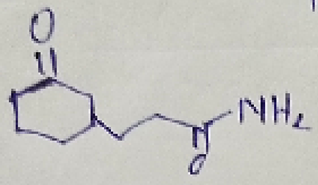


$\xrightarrow{LAH}$ $CH_3OH + EtOH$

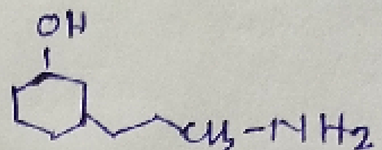
$\xrightarrow{NaBH_4}$



x)

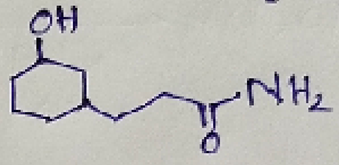


$\xrightarrow{LAH}$



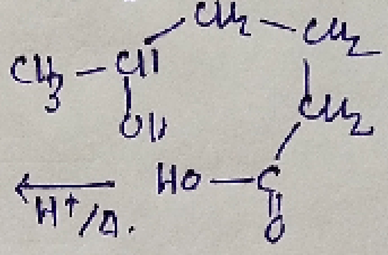
xi)

$\xrightarrow{NaBH_4}$

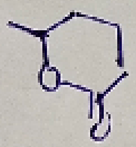


xii) $CH_3-C(=O)-CH_2-CH_2-CH_2-C(=O)-OH$

$\xrightarrow{NaBH_4}$



$\xleftarrow{H^+/\Delta.}$



xiii)

$HO_2C-(CH_2)_4-C(=O)-Cl \xrightarrow{NaBH_4} HO_2C-(CH_2)_4-CH_2OH$

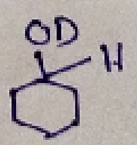
$\xrightarrow{LiAlH_4} HOH_2C-(CH_2)_4-CH_2OH$

xiv) $RCH=NH \xrightarrow{LiAlH_4} RCH_2-NH_2$

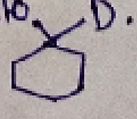
$\xrightarrow{NaBH_4} RCH_2-NH_2$.

xv)

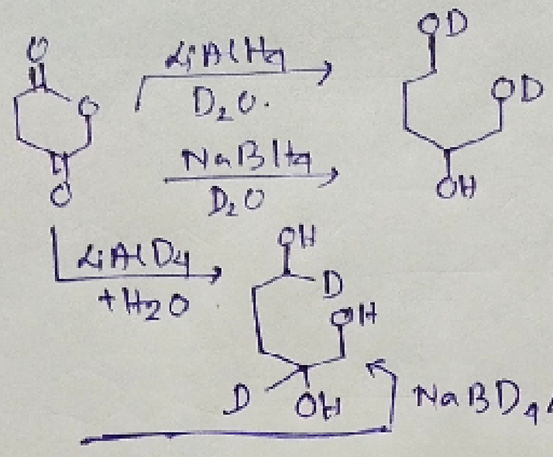
$\xrightarrow[ii)\ D_2O]{i)\ LiAlH_4}$



$\xrightarrow[ii)\ H_2O]{i)\ LiALD_4}$



xvi)



xvii) Compound which gives alcohol on reduction with $LiAlH_4$.

a) $MeCOCl$ b) $MeCONH_2$ c) $Me-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Me$

d) $CH_3-CH-CH_2$ (O) e) $RCHO$ d) $R-\overset{O}{\overset{\|}{C}}-R$. e) RNO_2.

: $LiAlH(OtBu)_3$: source of H^-

very very selective reducing agent.

Source of H^-: $R-CH=O$, $R-\overset{O}{\overset{\|}{C}}-R$ $\xrightarrow{LiAlH(OtBu)_3}$ RCH_2OH, R_2CHOH.

$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-78^\circ C.]{LiAlH(OtBu)_3} RCH=O.$

: B_2H_6 : It is also source of H^-.

3c-2ē bond; H has −ve oxidation state.

It can reduce. i) $RCH=O$ ✓ iii) $RCOR$ ✓ iii) $RCH=CH_2$ ✓ iv) $RC\equiv CR$ ✓

v) $RCONH_2$ ✓ vi) $RC\equiv N$ ✓ vii) RCO_2H ✓

Can't reduce $R-\overset{O}{\overset{\|}{C}}-Cl$; RNO_2;

: $H_2(Ni)$: Can reduce all except RCO_2H.
or other catalyst. [Pt; Pd]

$RCH=O \xrightarrow{H_2(Ni)} RCH_2OH$

$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow{H_2(Ni)} R_2CHOH$

$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{H_2(Ni)} RCH_2OH$

$R-NO_2 \xrightarrow{H_2(Ni)} R-NH_2$

$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{H_2(Ni)} RCH_2-NH_2$

$RC\equiv C-R \xrightarrow[(XS)]{H_2(Ni)} RCH_2-CH_2-R$

$R-CH=CH-R \xrightarrow{H_2(Ni)} RCH_2-CH_2R$

It can not reduce RCO_2H; $R-\underset{\underset{O}{\|}}{C}-OR$.

H_2 (C/Ru) can reduce $RCO_2H \longrightarrow RCH_2OH$.

In IIT [so many times]. question paper.

$RCO_2H \xrightarrow{H_2(Ni)}$ always given no reaction.

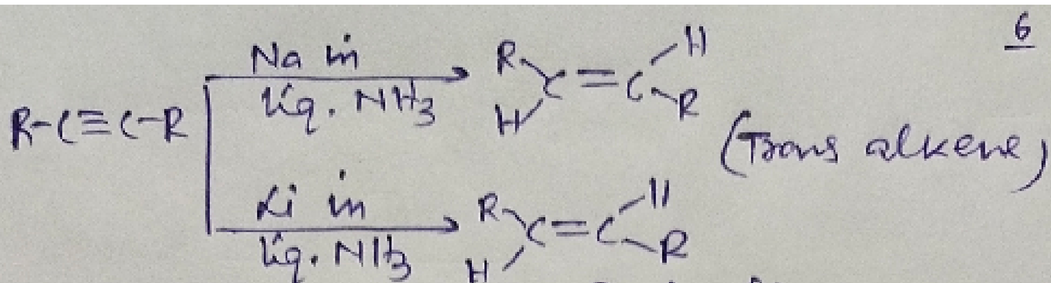
$R-C\equiv C-R$ $\xrightarrow{H_2}$ $\underset{\text{(Lindlar Catalyst)/Quinoline/s}}{Pd-BaSO_4}$ $\xrightarrow{H_2}$ $Pd-CaCO_3$/Quinoline/s.

$\xrightarrow[(Ni_2B)]{H_2}$ P-2-catalyst.

$\underset{H}{\overset{R}{}}\!\!>C=C\!\!<\!\!\underset{H}{\overset{R}{}}$ (cisalkene)

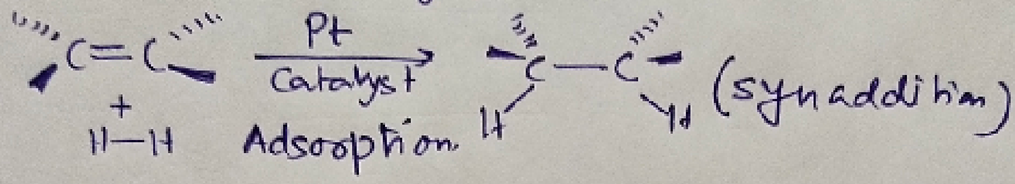
$\underset{H}{\overset{R}{}}\!\!>C=C\!\!<\!\!\underset{R}{\overset{H}{}}$

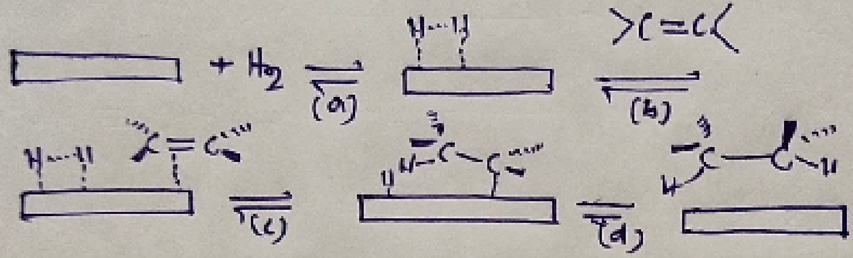
$\underset{H}{\overset{R}{}}\!\!>C=C\!\!<\!\!\underset{H}{\overset{R}{}}$ (cisalkene)



This is called Birch Reduction!

: Mechanism: using H_2(Ni). Catalytic Hydrogenation.

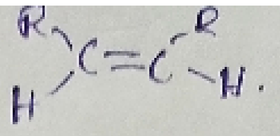


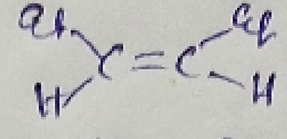


The adsorption of H_2 is essentially a chemical reaction [chemisorption]; unpaired e on the surface of the metal pair with es of H_2 & bind the hydrogen to the surface. The collision of an alkene with surface bearing adsorbed H_2 causes adsorption of alkene as well. A stepwise transfer of H atom takes place, this produces an alkane before organic molecule leaves the catalyst surface. As a consequence both H atoms usually add from the same side of molecule. It is called syn addition.

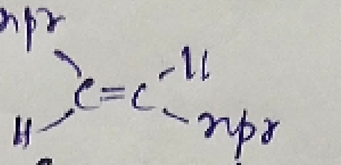
$CH_3-C\equiv C-CH_3 \xrightarrow[(Pt)]{H_2} CH_3CH=CHCH_3 \xrightarrow[(Pt)]{H_2} CH_3CH_2CH_2CH_3$.

$R-C\equiv N \xrightarrow{H_2(Ni)} RCH=NH \xrightarrow[(Ni)]{H_2} RCH_2-NH_2$

a) $R-C\equiv C-R \xrightarrow[\text{Quinoline.}]{H_2 \text{ Pd-CaCO}_3}$ 

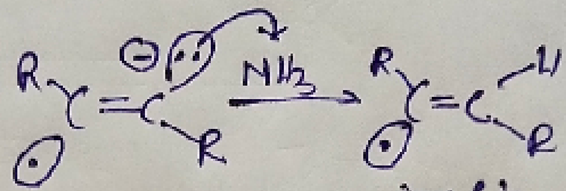
b) 3 Hexyne $\xrightarrow[\text{(P-2 catalyst)}]{H_2/Ni_2B}$ 

z-Hex-3ene.

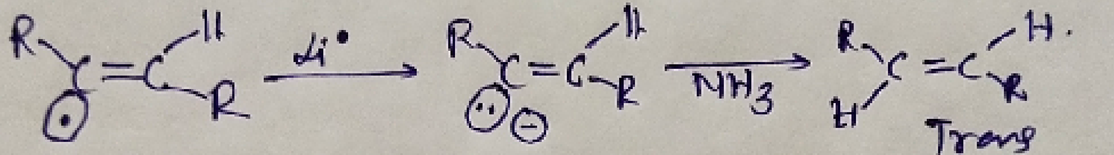
c) 4octyne $\xrightarrow{Li/NH_3}$ 

(E-4-octyne)

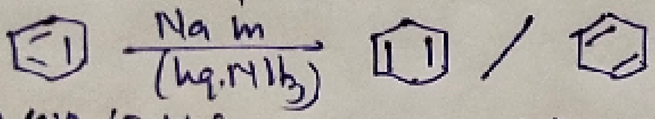
:Mechanism:

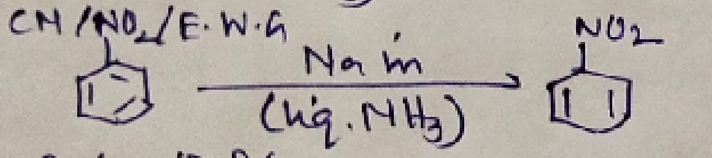
$Li/Na + R-C\equiv C-R \longrightarrow$ 

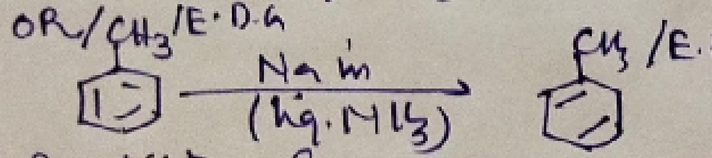
(1ē donor) Radical anion (acts as base) vinylic radical



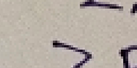
Trans vinylic anion. Trans alkene



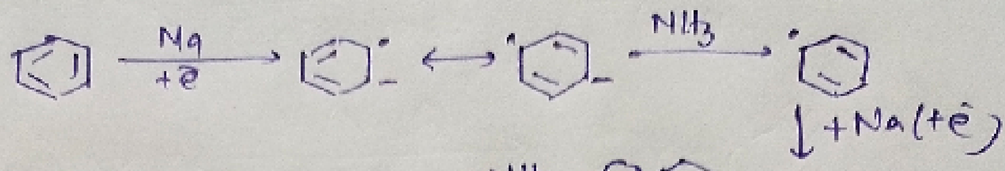


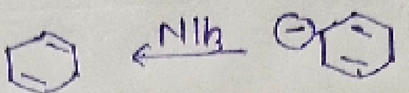


: Reactivity order: [Towards Hydrogenation].

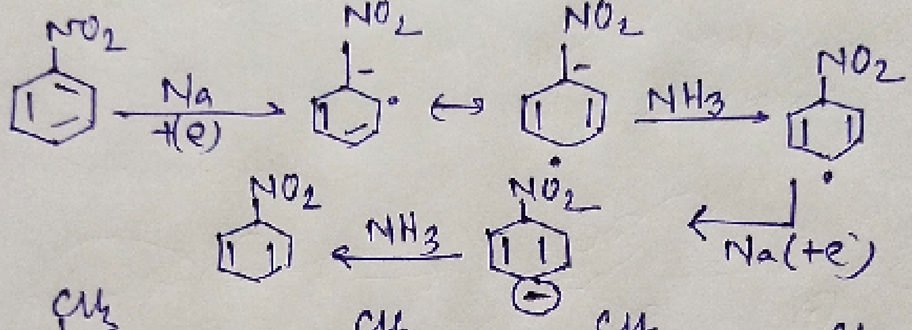
$C\equiv C > CH_2=CH_2 > RCH=CH_2 >$  $> R_2C=CH_2 > R_2C=CHR > R_2C=CR_2$

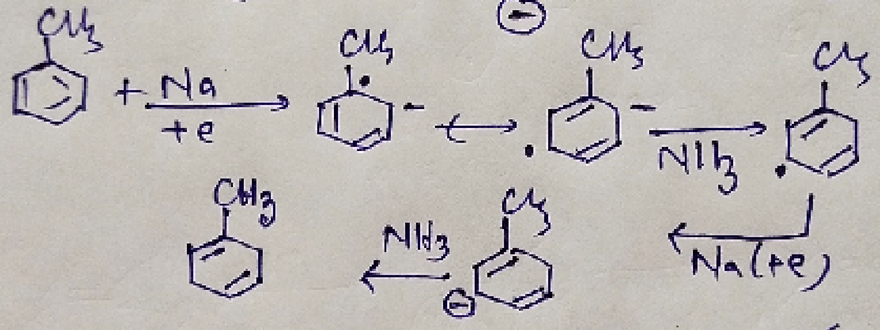
:Mechanism:

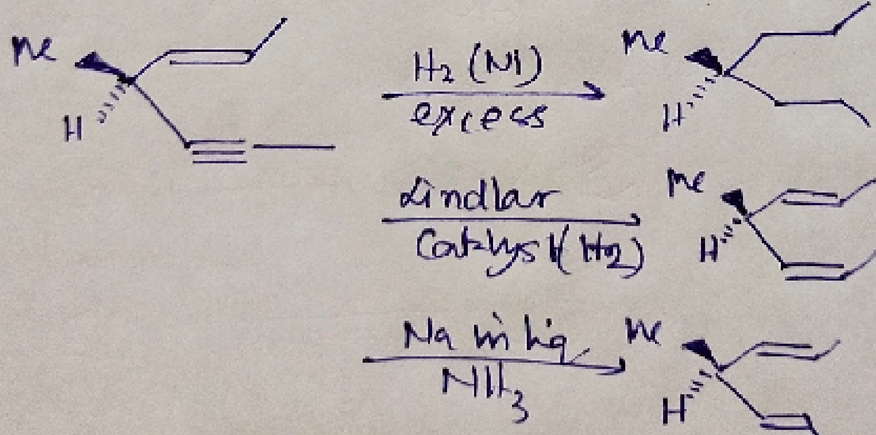


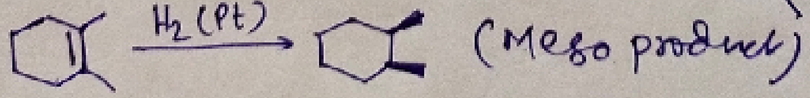
[Aromaticity is lost] 

(very rare example where product is non aromatic & reactant is aromatic)

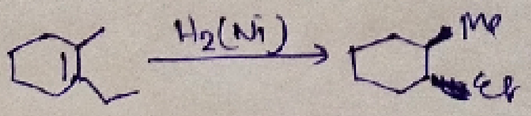






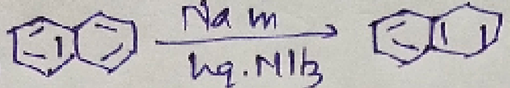


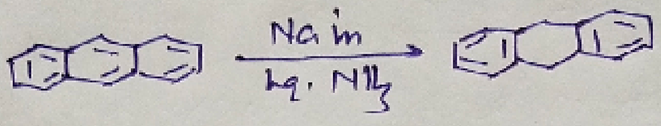
(Meso product)

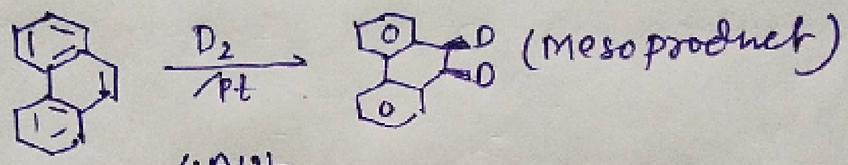


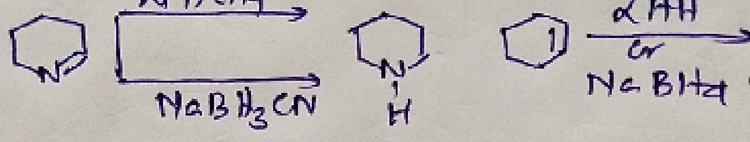
+ Enantiomer.

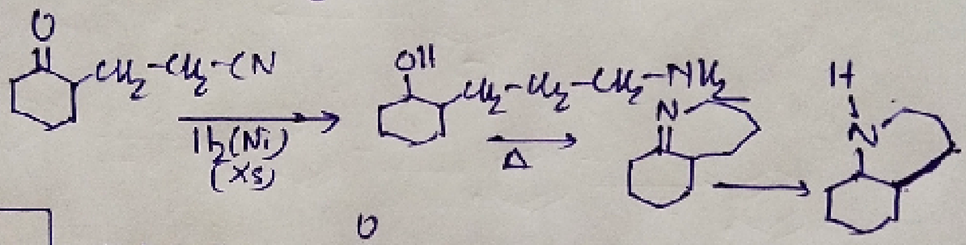
Other questions based on reduction:

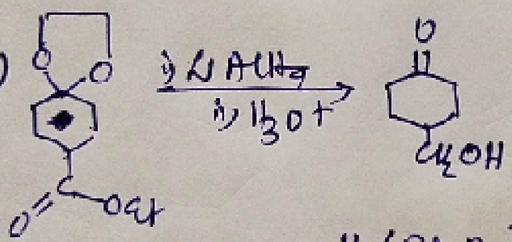
a) 

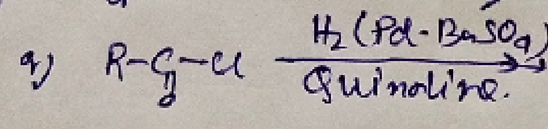
b) 

c) 
(Meso product)

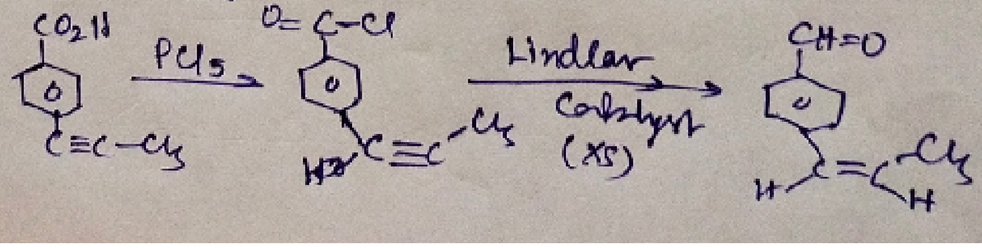
d) 
reaction.

e) 

f) 

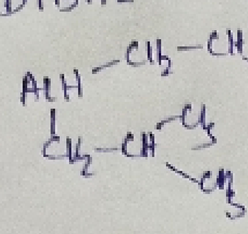
g) 

This reduction is known as Rosenmund Reduction.
So Lindlar Catalyst reduce C≡C & $-\overset{O}{\overset{\|}{C}}-Cl$ to cis alkene & $-CH=O$ respectively. This is example of partial reduction.



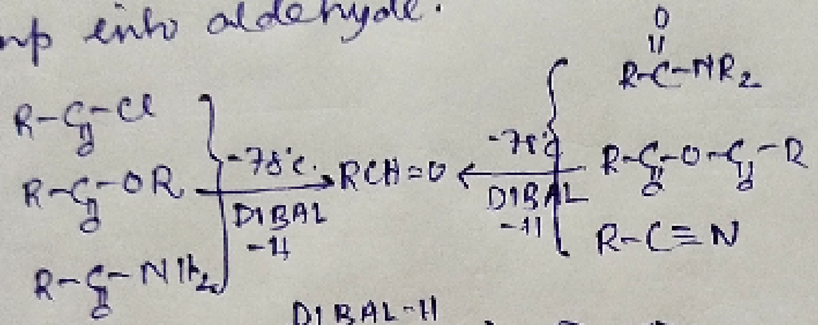
: Other reducing agent:

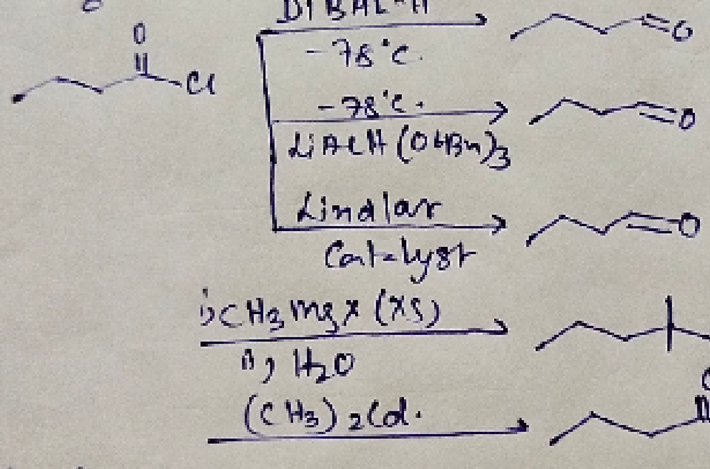
Ⓐ : DIBAL-H : (Diisobutyl aluminium hydride).

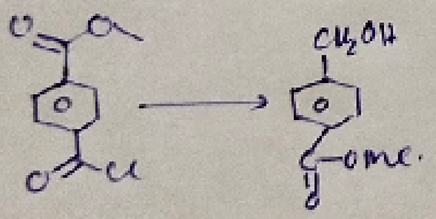


→ H attached with Al has -ve oxidation state. So it can loose H: electrophilic reducing agent.

• Purpose: It reduce acid derivative & cyanide group into aldehyde.





i) 

The conversion is done by.
a) LAH b) SBH.
c) H_2(Pt) d) all of these.

ii) $O_2N-(CH_2)_4-CH=CH_2$

Ans: (i) H_2(Ni) XS
(ii) B_2H_6.
(iii) LAH.