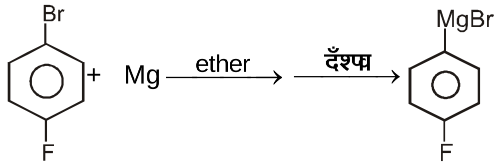
TOPIC : GRIGNARD REAGENT
EXERCISE # 1

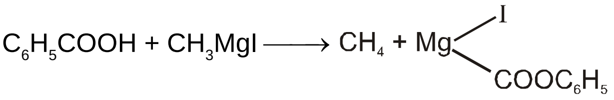
Section (A) :Grignard Reagent

1.



Flourine will not form G.R.

2.

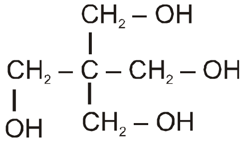


$C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + Mg\begin{matrix} I \\ COOC_6H_5 \end{matrix}$

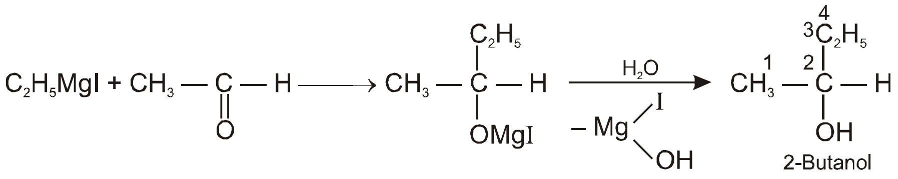
3. $(CH_3)_3\ CMgCl + D_2O \longrightarrow (CH_3)_3CD$

4. $C_5H_{12}O_4 \xrightarrow{CH_3MgBr} 4CH_4\uparrow$.

It means compound (A) contains 4 acidic hydrogen.

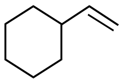


6.

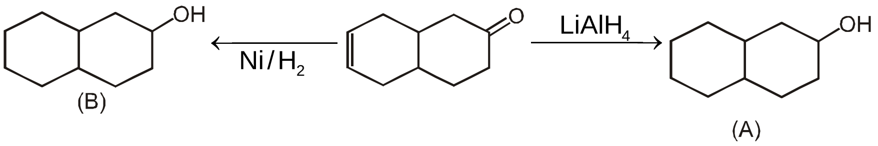


So, option (1) is correct.

Section (B) : Reduction

1.  has maximum heat of hydrogenation and unstabiliity.

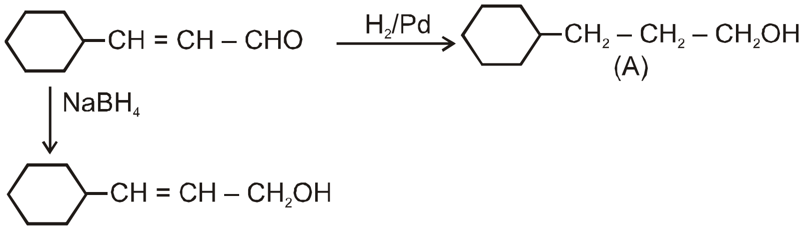
2.



4. $Ph–COOH \xrightarrow[\text{Reduction}]{LiAlH_4} Ph–CH_2OH$

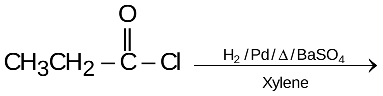
5. (1) $CH_3I \xrightarrow{KCN} CH_3 — CN \xrightarrow{LiAlH_4} CH_3 — CH_2 — NH_2$

6.



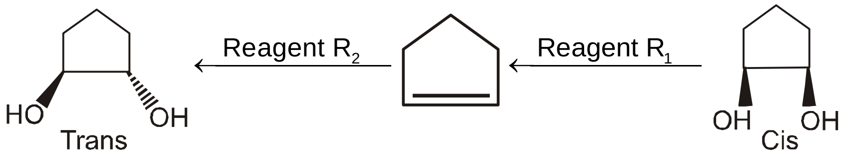
8. $R{-}Cl + AgCN \longrightarrow R-N\equiv C \xrightarrow{\text{Reduction}} R-NH-CH_3$

9. cis-alkene formed by lindlar catalyst and trans - alkene formed by Na/NH_3

10. 
$CH_3CH_2-\overset{\overset{\large O}{\|}}{C}-Cl \xrightarrow[\text{Xylene}]{H_2/Pd/\Delta/BaSO_4} CH_3CH_2-\overset{\overset{\large O}{\|}}{C}-H$ (Rossenmund reaction)

Section (C) :Oxidation

1. Baeyer's reagent is alkaline $KMnO_4$ solution.

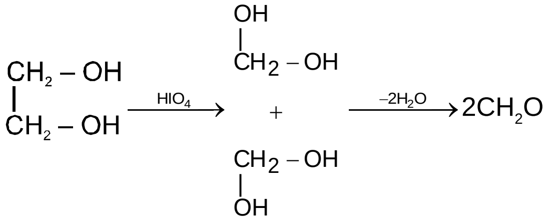
2. 

Syn addition with Baeyer's Reagent, So cis will form meso compound however peroxy acid in anti addition gives enantiomer.

3. Oppenauer's oxidation, oxidised secondary alcohol into ketone and also there is no effect on double bond.

4. $CH_3{-}CH_2{-}C\equiv C{-}H$ + alk. $KMnO_4 \longrightarrow CH_3CH_2{-}COOH + CO_2 + H_2O$

7. When alcohols are passed into Cu tube at 300ºC; primary alcohol → Aldehyde
Secondary alcohol → Ketone
Tertiary alcohol → Alkene

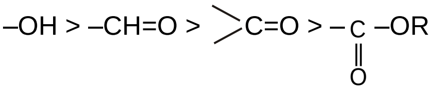
11. 
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} \xrightarrow{HIO_4} \begin{array}{l}OH\\ |\\ CH_2-OH\\ \quad +\\ CH_2-OH\\ |\\ OH\end{array} \xrightarrow{-2H_2O} 2CH_2O$$

12. See mechanism of ozonolysis of alkene and alkyne.

EXERCISE # 2

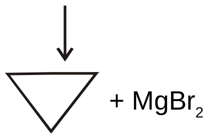
2. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr.

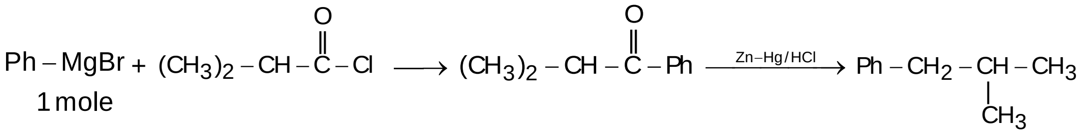
3. Order of Rate of functional group with RMgX :


$-OH > -CH{=}O > \;>C{=}O > -\underset{\underset{\large O}{\|}}{C}-OR$

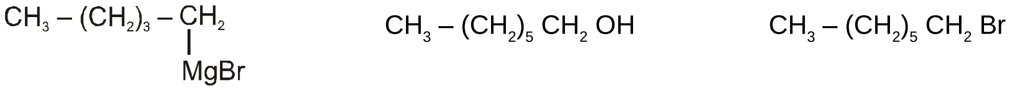
4. $EtMgX + HCHO \xrightarrow{H_2O/H^+} CH_3-CH_2-CH_2-OH$

6. (3) $BrCH_2CH_2CH_2Br + Mg \xrightarrow{Et_2O} Br-CH_2-CH_2-CH_2\,MgBr$



7. 

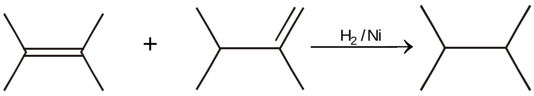
$$\underset{\text{1 mole}}{Ph-MgBr} + (CH_3)_2-CH-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow (CH_3)_2-CH-\overset{\overset{O}{\|}}{C}-Ph \xrightarrow{Zn-Hg/HCl} Ph-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

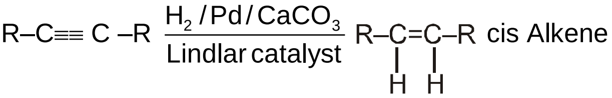
8. 

$$CH_3-(CH_2)_3-\underset{\underset{MgBr}{|}}{CH_2} \qquad CH_3-(CH_2)_5\,CH_2\,OH \qquad CH_3-(CH_2)_5\,CH_2\,Br$$

(A) (B) (C)

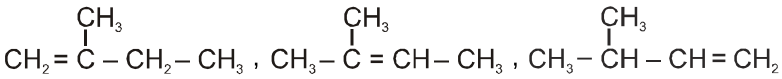
10. Catalytic hydrogenation $\propto \dfrac{1}{\text{Stability of alkenes}}$

11. 

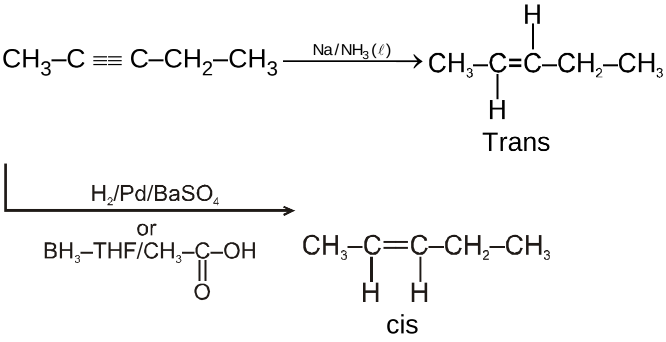
12. 

$$R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2/Pd/CaCO_3} R-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-R \text{ cis Alkene}$$

13. Na/NH$_3$(ℓ) with C_2H_5OH is known as Birch reduction.

14. 

$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3,\ CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3,\ CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2$$

15. 

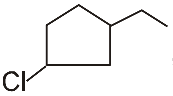
$$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow{Na/NH_3(\ell)} CH_3-\underset{\underset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_2-CH_3$$

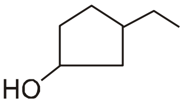
Trans

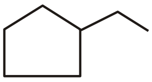
$$\xrightarrow[\text{or } BH_3-THF/CH_3-\underset{\underset{O}{\|}}{C}-OH]{H_2/Pd/BaSO_4} CH_3-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_2-CH_3$$

cis

16. It is birch reduction

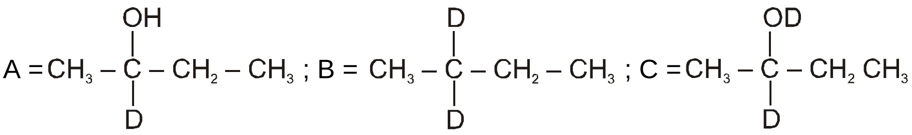
17. M = 

, N = 

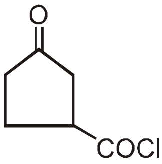
, Y = 

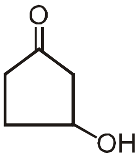
18. Syn additon of D_2 on double bond

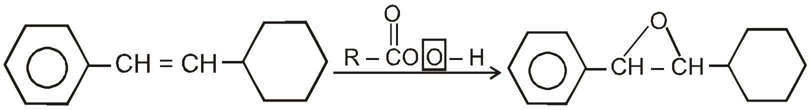
19. esters are not reduced by $NaBH_4$, >C=O (carbonyl) change to – CH(OH)- by use of $NaBH_4$

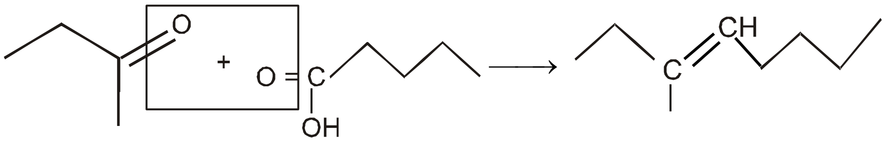
20. 

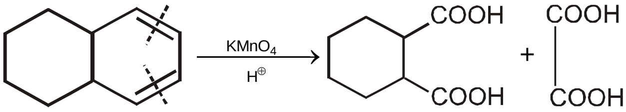
$$A=CH_3-\overset{\overset{OH}{|}}{\underset{\underset{D}{|}}{C}}-CH_2-CH_3\ ;\ B=CH_3-\overset{\overset{D}{|}}{\underset{\underset{D}{|}}{C}}-CH_2-CH_3\ ;\ C=CH_3-\overset{\overset{OD}{|}}{\underset{\underset{D}{|}}{C}}-CH_2\,CH_3$$

22.  due to presence of –COCl group

23.  due to presence of –OH group

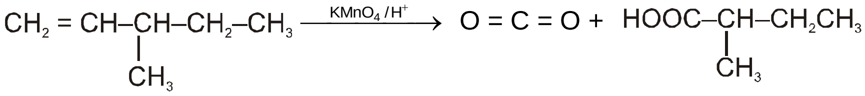
24. 

25. 

26. 

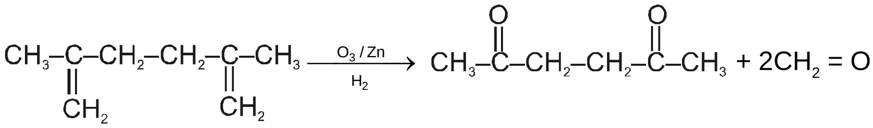
27. $CH_3–CH_2–HC=CH–CH_2–CH_2–CH_2–CH_3 \xrightarrow{[O]} CH_3–CH_2COOH + CH_3(CH_2)_3–COOH$

cis / trans

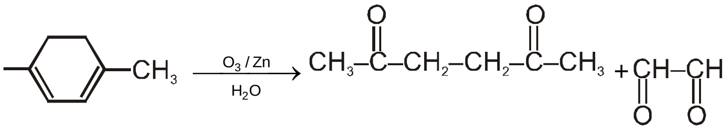
28. 

$$CH_2 = CH–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–CH_3 \xrightarrow{KMnO_4 / H^+} O = C = O + HOOC–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2CH_3$$

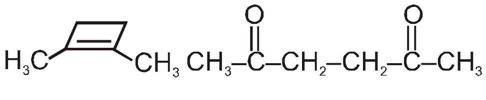
29. $CH_3–CH= O + O = CH–CH_3 \longrightarrow CH_3–CH=CH–CH_3$

30. 

$$CH_3–\underset{\displaystyle CH_2}{\underset{||}{C}}–CH_2–CH_2–\underset{\displaystyle CH_2}{\underset{||}{C}}–CH_3 \xrightarrow[H_2]{O_3 / Zn} CH_3–\overset{\displaystyle O}{\overset{||}{C}}–CH_2–CH_2–\overset{\displaystyle O}{\overset{||}{C}}–CH_3 + 2CH_2 = O$$

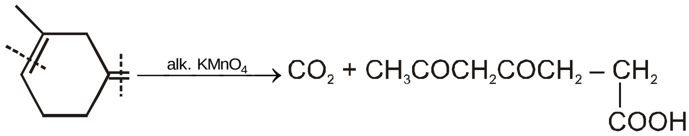


$$\xrightarrow[H_2O]{O_3 / Zn} CH_3–\overset{\displaystyle O}{\overset{||}{C}}–CH_2–CH_2–\overset{\displaystyle O}{\overset{||}{C}}–CH_3 + \underset{\displaystyle O}{\underset{||}{CH}}–\underset{\displaystyle O}{\underset{||}{CH}}$$

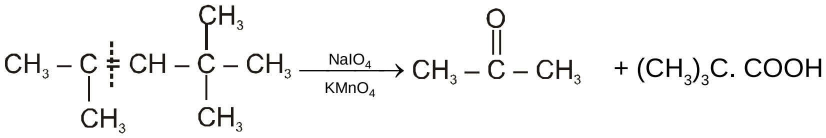


$$CH_3–\overset{\displaystyle O}{\overset{||}{C}}–CH_2–CH_2–\overset{\displaystyle O}{\overset{||}{C}}–CH_3$$

31. Alkene gives epoxide on reaction with per acid, Bayer's reagent give syn addition of –OH group with Alkene.

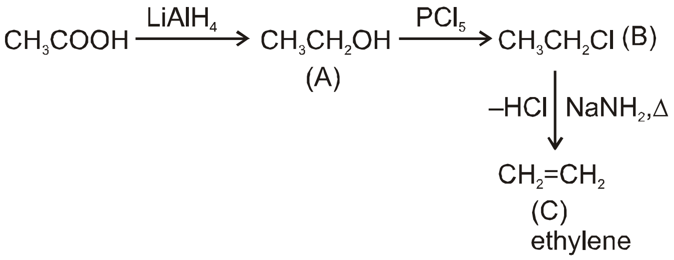
32. 

$$\xrightarrow{alk.\ KMnO_4} CO_2 + CH_3COCH_2COCH_2 – \underset{\displaystyle COOH}{\underset{|}{CH_2}}$$

33. 

$$CH_3-\underset{CH_3}{C}=CH-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[KMnO_4]{NaIO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + (CH_3)_3C.COOH$$

34. $CH_3-CH_2-C\equiv CH \xrightarrow[\substack{KMnO_4\\+\\H^\oplus}]{} CH_3CH_2COOH + CO_2 + H_2O$

36. 

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4"] & \underset{(A)}{CH_3CH_2OH} \arrow[r, "PCl_5"] & CH_3CH_2Cl\ (B) \arrow[d, "-HCl"', "{NaNH_2,\Delta}"] \\ & & \underset{\text{ethylene}}{\underset{(C)}{CH_2=CH_2}} \end{tikzcd}$$

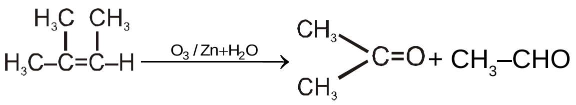
EXERCISE # 3
PART - I

5. Pyridinium chlorochromate (PCC) ($C_5H_5NHCrO_3Cl^-$) is a very good oxidising agent for converting 1° alcohol to aldehydes and 2° alcohols to ketone. It prevents further oxidation of aldehydes to carboxylic acid.

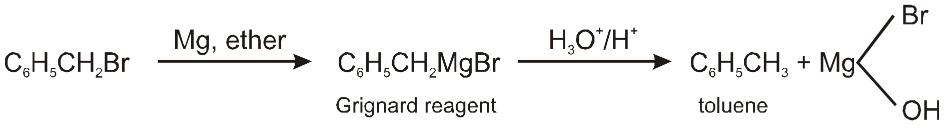
$$\underset{\text{p-alcohol}}{RCH_2OH} \xrightarrow[CH_2Cl_2\ \text{solvent}]{(C_5H_5N)_2CrO_3} \underset{\text{Aldehyde}}{RCHO} + H_2O$$

[PCC is prepared by mixing pyridine (C_5H_5N), CrO_3 and HCl]

$$ROH \xrightarrow[\text{acidified}\ K_2Cr_2O_7]{\text{alkaline}\ KMnO_4} \text{Carboxylic acid}$$

8. 

$$H_3C-\overset{H_3C}{C}=\overset{CH_3}{C}-H \xrightarrow{O_3/Zn+H_2O} (CH_3)_2C=O + CH_3-CHO$$

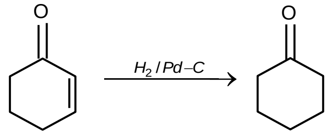
9. 

$$C_6H_5CH_2Br \xrightarrow{\text{Mg, ether}} \underset{\text{Grignard reagent}}{C_6H_5CH_2MgBr} \xrightarrow{H_3O^+/H^+} \underset{\text{toluene}}{C_6H_5CH_3} + Mg\begin{cases}Br\\OH\end{cases}$$

10. Clemmenson reduction is

$$>C=O \xrightarrow{Zn-Hg/HCl} >CH_2$$

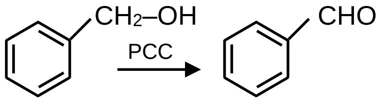
11. Ethalpy of hydrogenation is inversally proportional to stability of alkene.

12. 

During hydrogenation of α,β unsaturated carbonyl compound by pd catalyst selective reduction is observed of double bond.

13. (1) $Hg^{2+}/H^+,H_2O$ → Addition of H_2O at alkene
(2) Na/liquid NH_3 →Birch reduction (Alkyne → trans alkene)
(3) H_2,Pd/C, quinolone → reduce alkyne → Cis alkene
(4) Zn/HCl → Reduce alkyne → alkyl halide

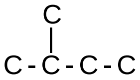
14. PCC is a weak oxidizing agent oxidized 1º alcohol to aldehyde :



all other Reagent oxidized alcohol to —COOH group.

PART - II

4. Since, the compound gives 2-methyl butane,it must contain the following carbon skeleton.

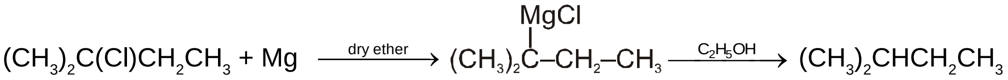


$$\overset{\displaystyle C}{\underset{}{C-C}}-C-C$$

Thus, the structure of alkyl chloride may be

$(CH_3)_2C(Cl)CH_2CH_3$ or $(CH_3)_2CHCH_2CH_2Cl$

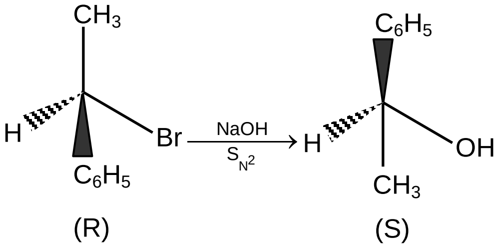
and the reactions are as follows



$$(CH_3)_2C(Cl)CH_2CH_3 + Mg \xrightarrow{\text{dry ether}} (CH_3)_2\overset{MgCl}{C}-CH_2-CH_3 \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_2CH_3$$

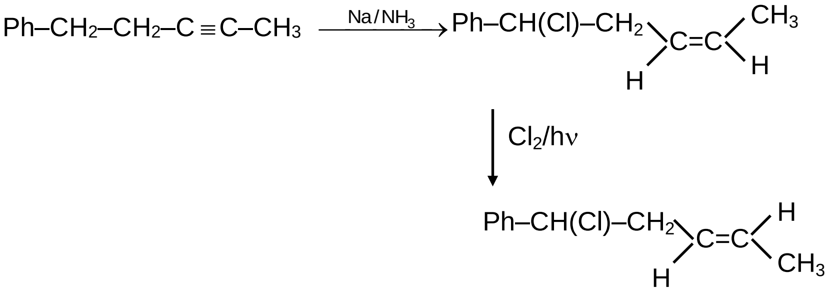
5. Aldehydes, other than formaldehyde, when treated with RMgX give 2º alcohol

10.



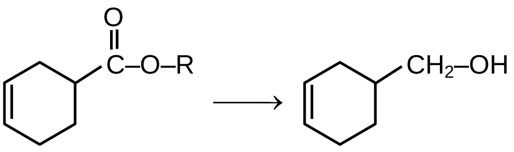
inversion of configuration

11.



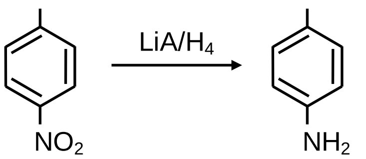
Na/NH_3(l) this is Birch reduction reduce only alkyne into trans alkene and Cl_2/hν is free radical substitution reaction

12.



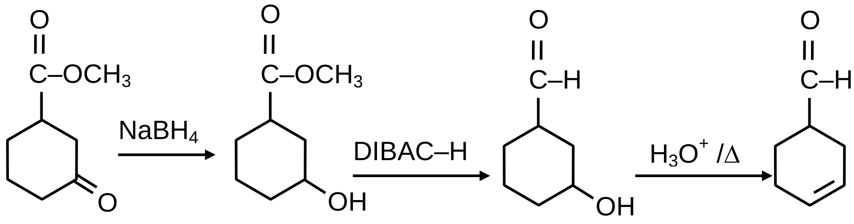
Suitable Reagent for this conversion is $LiAlH_4$.

13.

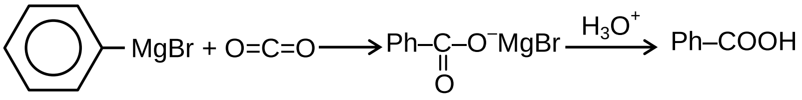


$LiAlH_4$ is strongest Reducing agent. Reduce all functional group except. C=C / C ≡ C and Benzene.

14.



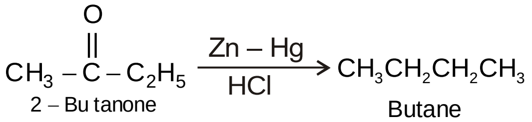
15.



PART - III

1. $\underset{\text{Butene - 1}}{H_3C-CH_2-CH=CH_2} \xrightarrow{Pd/H_2} \underset{\text{Butane}}{H_3C-CH_2-CH_2-CH_3}$

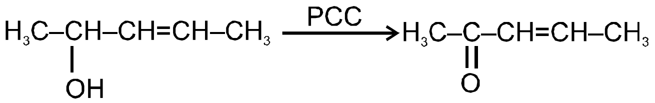
2.



$$\underset{2-\text{Butanone}}{CH_3-\overset{\overset{O}{||}}{C}-C_2H_5} \xrightarrow[HCl]{Zn-Hg} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

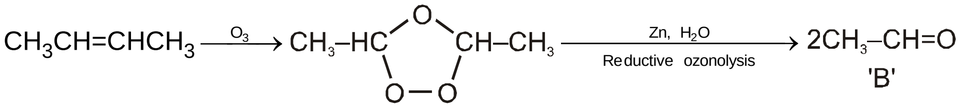
It refers to Clemensen's reduction

3.

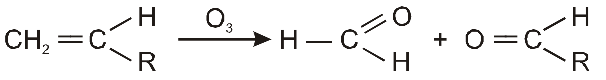


$$H_3C-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_3 \xrightarrow{PCC} H_3C-\underset{\underset{O}{||}}{C}-CH=CH-CH_3$$

4.

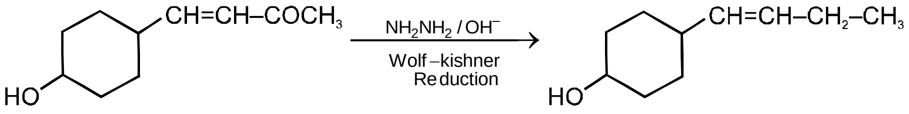


5.



Presence of one vinyl group gives formaldehyde as one of the product in ozonolysis. -

6.

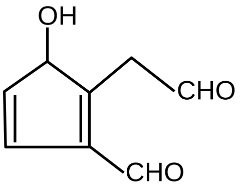


–OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used.

7. $R-CH_2OH \xrightarrow{PCC} R-CH=OH$

Pyridinium chlorochromate is the mild oxidising agent.

8.



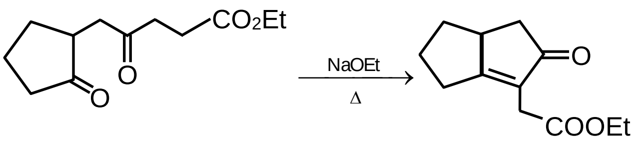
DIBAL–H reduces ester and carboxylic acid both into aldehyde at low temperature.

9. Na in liquid ammonia carryout anti and partial hydrogenation of alkyne to trans alkene.

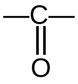
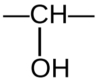
10. $R{-}C{\equiv}N \xrightarrow[(2)H_2O]{(1)AlH(i{-}Bu)_2} R{-}CHO$

11. Ester and alkene are not reduced by $NaBH_4$.

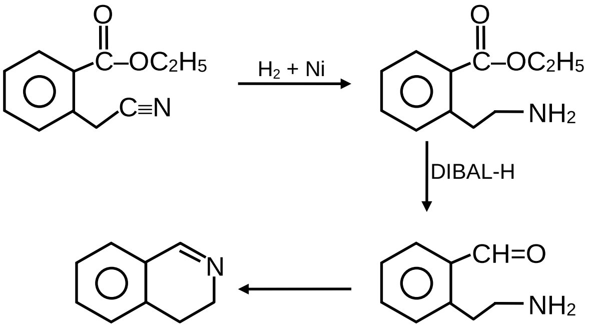
12.



Intramolecular aldol condensation

13. $NaBH_4$ selectively reduce  $-\underset{\underset{O}{\parallel}}{C}-$ group to  $-\underset{\underset{OH}{|}}{CH}-$ and imine group to amine.

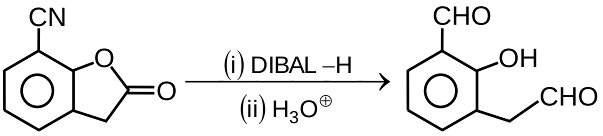
14.



15. $LiAlH_4$ reduces carboxylic acid, ketone, nitro group but it does not reduce alkenes.

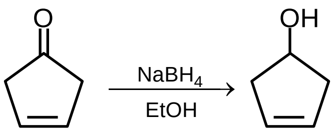
17. HCHO with GR always gives 1° alcohol.

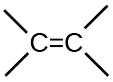
18.



Nitriles are selectively reduced by DIBAL-H to imines followed by hydrolysis to aldehydes similarly, esters are also redecued to aldehyde with DIBAL-H

19.



$NaBH_4$ does not reduce 

20. B and D gives acid-base reaction with Grignard reagent.