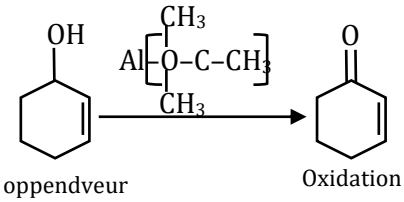
Oxidation

SOLUTIONS

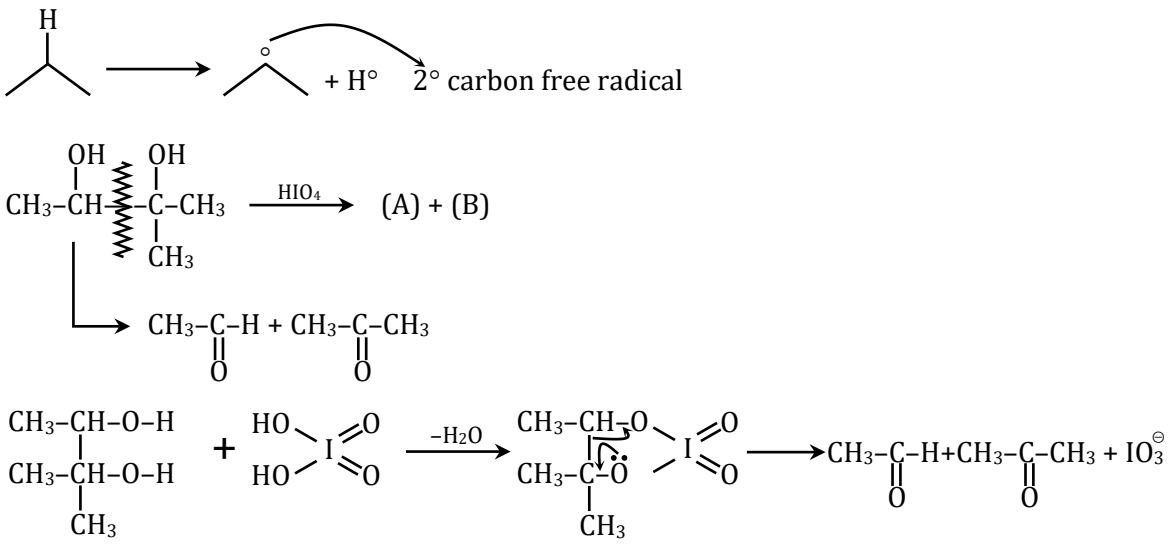
EXERCISE - O

1. Ans. (D)



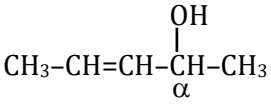
Oxidise 2° Alchol into Ketone.

2. Ans. (B)



3. Ans. (C)

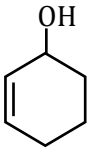
MnO_2 Use for Allylic oxidation



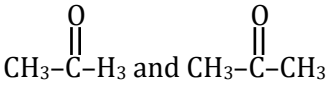
4. Ans. (C)

Only Allylic alcohol

Oxidise by MnO_2



5. Ans. (A)



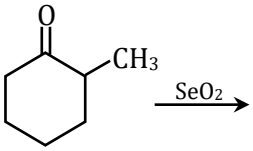
Differentidted Byu Tollen's Reagant test AID give TVE test write ketone Does Not.

$\rightarrow$ LUCAS $\rightarrow$ Only for Alcohol

$\rightarrow$ Iodoform $\rightarrow$ Both Gives

$\rightarrow$ $NaHSO_3$ $\rightarrow$ Both Gives

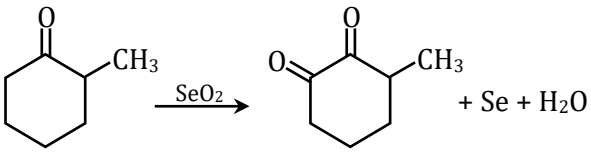
6. Ans. (B)



SeO_2 Use for α-Oxidation of Carbonyl compound.

Most acidic α-carbon oxidise first.

Rate of oxidise $1° > 2° > 3°$.



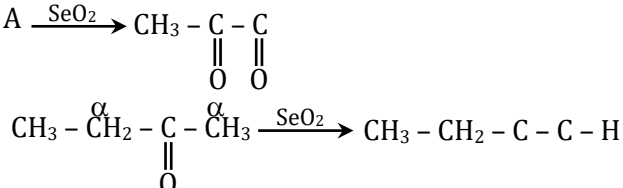
7. Ans. (D)

Silver Mirror Test

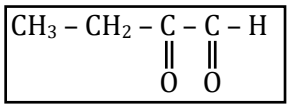
Give By $-\overset{\overset{O}{\|}}{C}-H$

So, $PH-\overset{\overset{O}{\|}}{C}-H$ $H-\overset{\overset{O}{\|}}{C}-OH$ $CH_3-\overset{\overset{O}{\|}}{C}-H$

8. Ans. (C)

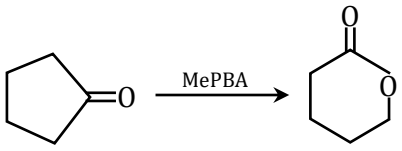


OR

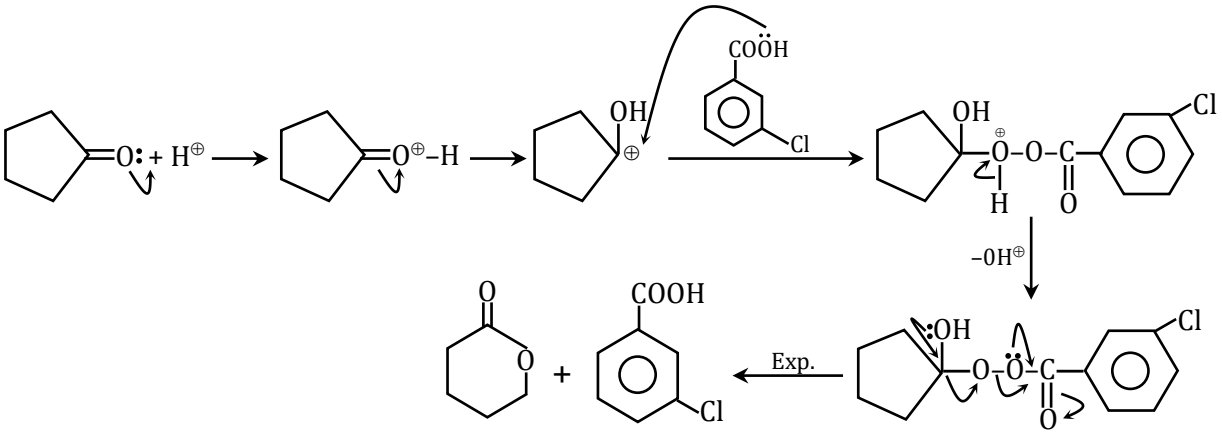


Dimethyl Glycolyl

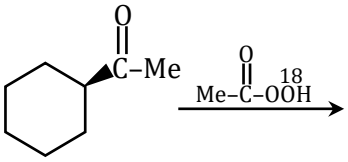
9. Ans. (B)



Bayers villegar oxidation



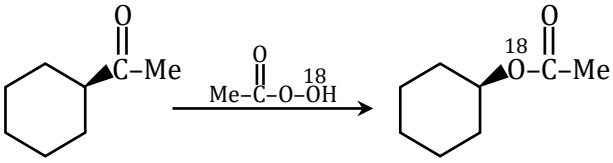
10. Ans. (D)



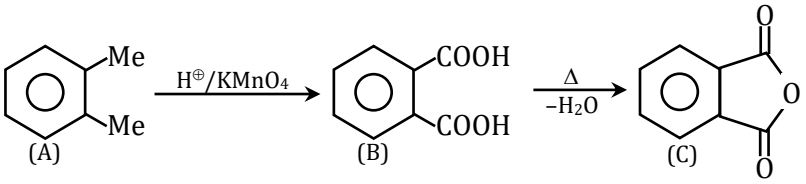
Bayer Villeger Oxidation follow Migrating Attitude.

H° > 3° > 2° > pH° > 1° > Me

* Insert oxygen between best migrating group.



11. Ans. (C)



12. Ans. (A,B.C)

Double and triple bonds are dissociaed in ozonolysis.

13. Ans. (A,B,C)

$KMnO_4$, OsO_4 give syn addition and Per-acid give anti-addition

14. Ans. (A,B)

$$CH_3-CH_2-HC \underset{cis/trans}{=} CH-CH_2-CH_2-CH_2-CH_3 \xrightarrow{[O]}$$

$$CH_3-CH_2COOH + CH_3(CH_2)_3-COOH$$

15. **Ans. (B,C)**

When alcohols are passed inot Cu tube at 300° C ;

Primary alcohol → Aldehyde

Secondary alcohol → Ketone

Tertiary alcohol → Alkene

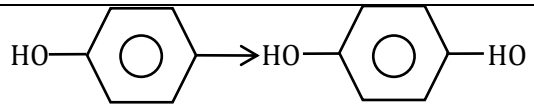
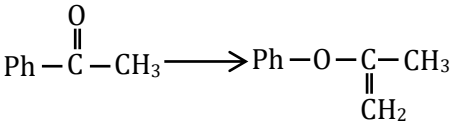
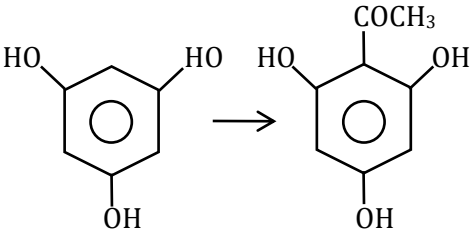
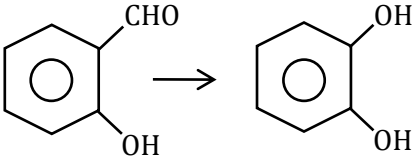
When alcohols are treaed with PCC then ;

Primary alcohol → Aldehyde

Secondary alcohol → Ketone

Tertiary alcohol → No reaction

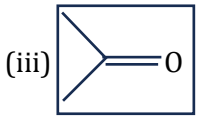
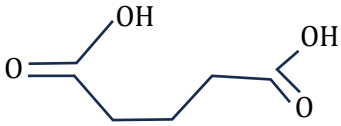
16. **Ans.** (A→ r,i), (B→ s,ii), (C→ q,iii), (D→ p,iv)

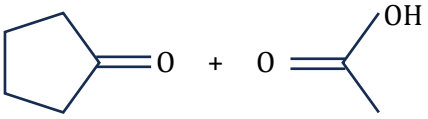
Column I		Column II		Column III	
a.		r.	$K_2S_2O_8$ + NaOH	i.	Elbs persulphate oxidation
b.		s.	Per acid	ii.	Baeyer-Villiger oxidation
c.		q.	$CH_3 - C \equiv N$, $ZnCl_2/HCl$	iii.	Houben-Roesch synthesis
d.		p.	H_2O_2 + NaOH	iv.	Dakin reaction

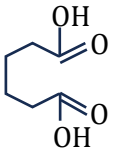
17. **Ans.** (A→ r), (B→ t), (C→ q), (d→ p) (E→S)

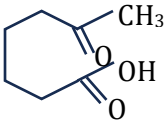
EXERCISE - S

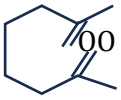
1. **Ans.** (i) $CO_2 + H_2O$ (ii) $O = C = O + H_2O$

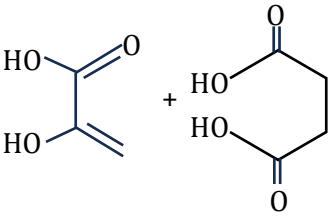
(iii)  ,  , $CO_2 + H_2O$

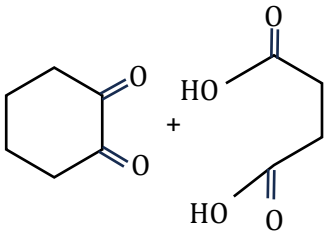
(iv) 

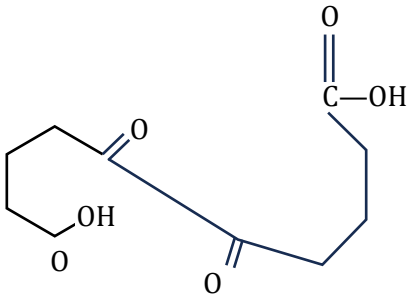
(v) 

(vi) 

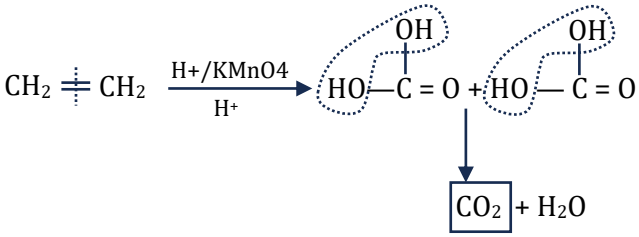
(vii) 

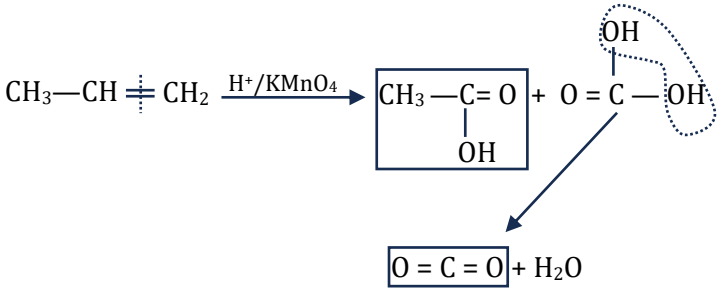
(viii) 

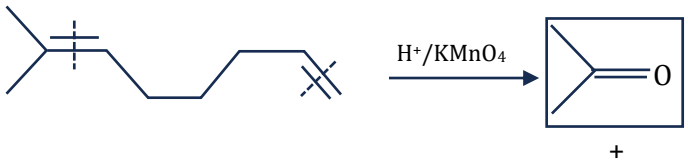
(ix) 

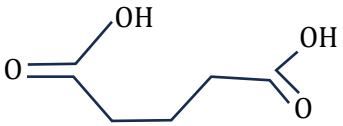
(x) 

[$KMnO_4/H^+$(Acidic Medium) is similar to oxidative Ozonalysis]

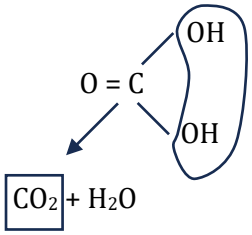
(i) 

(ii) 

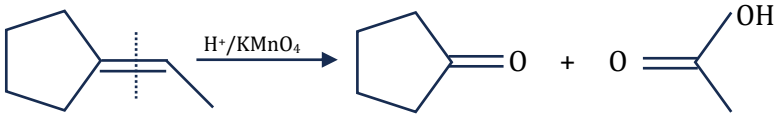




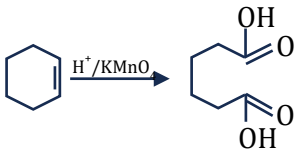
(iii)



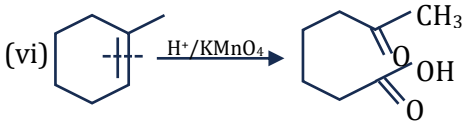
(iv)



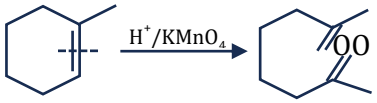
(v)



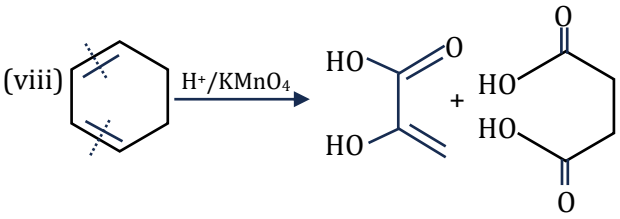
(vi)



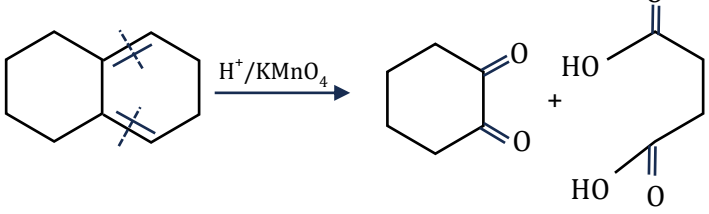
(vii)



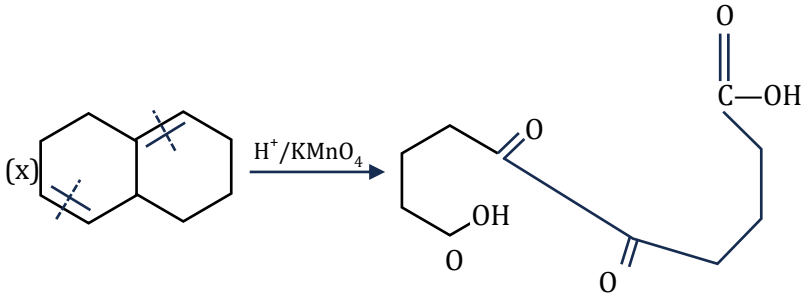
(viii)

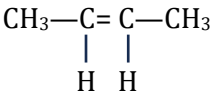


(ix)

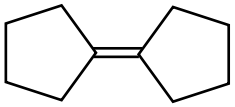


(x)

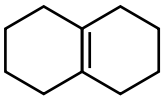


2. **Ans.** (i) 

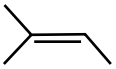
(A)

(ii) 

(B)

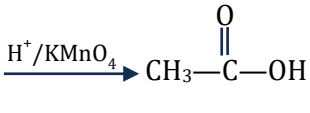
(iii) 

(C)

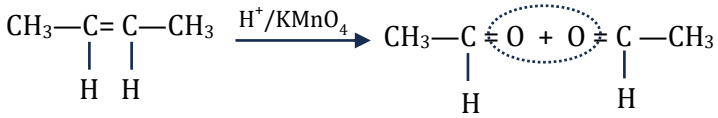
(iv) 

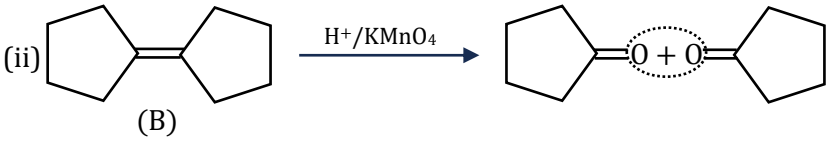
(D)

(Like Reverss Ozenalysis) Hint

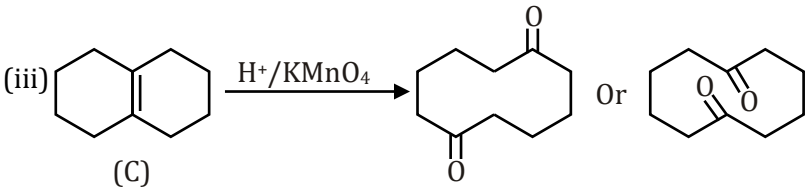
(i) Minimum Possible Carbon Reaction 

Only one Type Product

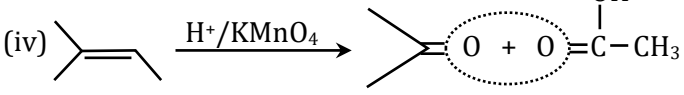


(ii) 

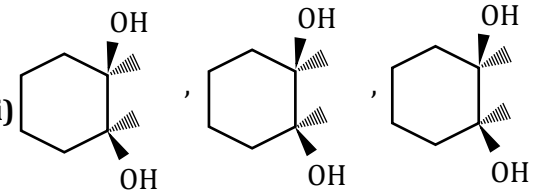
(B)

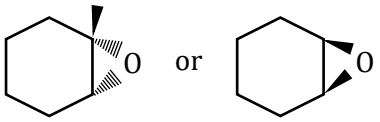
(iii) 

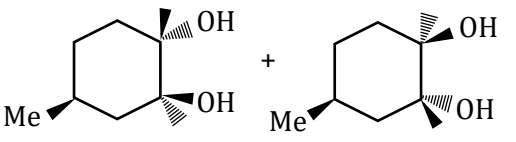
(C) (Like Reverse Ozonolyses) Both Same

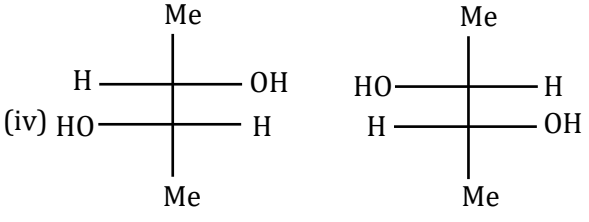
(iv) 

(D) Acetone Ethanoic Acid

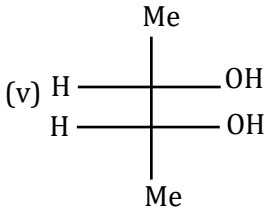
3. **Ans.** **(i)** 

(ii) 

(iii) 

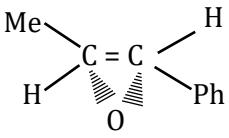
(iv) 

(v)

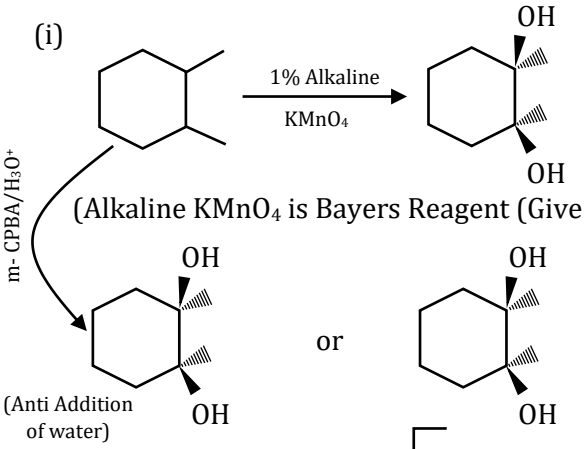


(Erythro)

(vi)

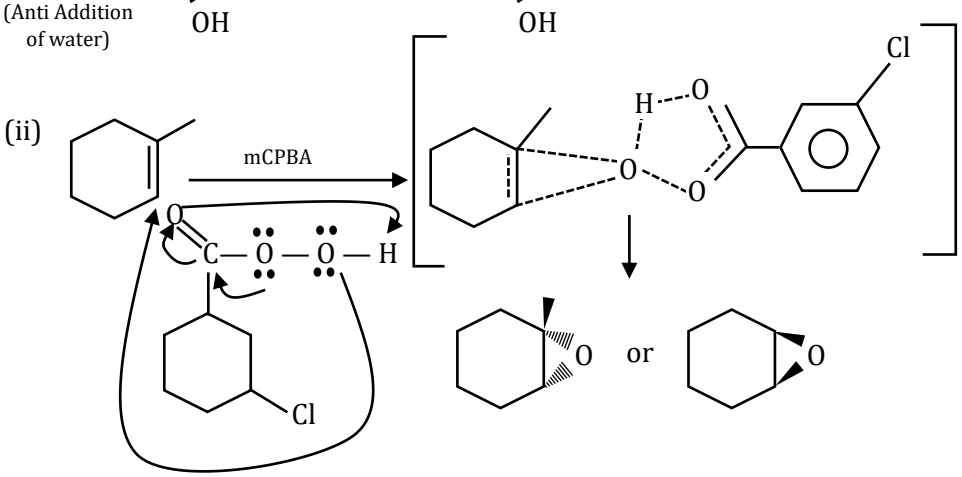


(i)

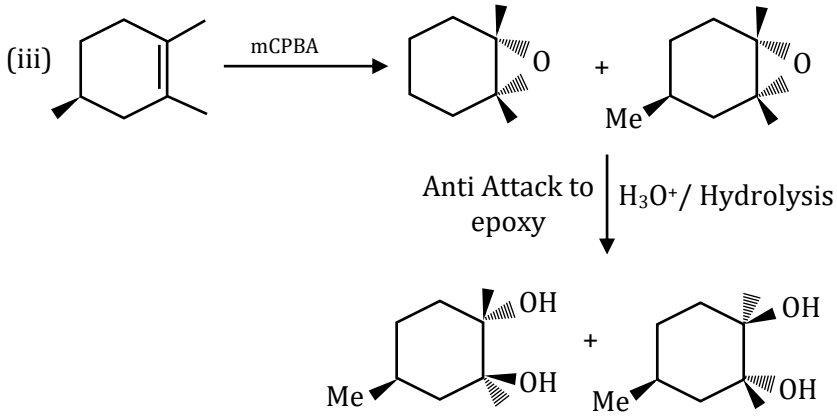


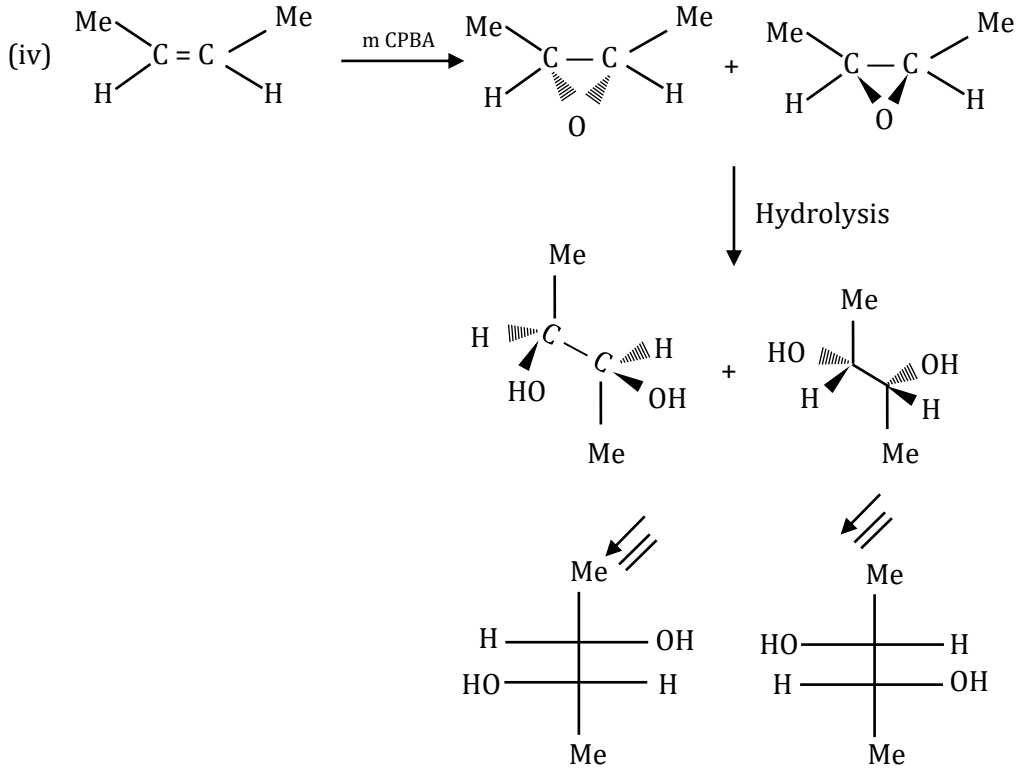
(Alkaline $KMnO_4$ is Bayers Reagent (Give Syn Addition) at Low temp.)

(ii)

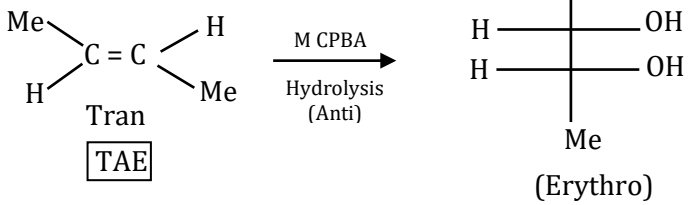


(iii)

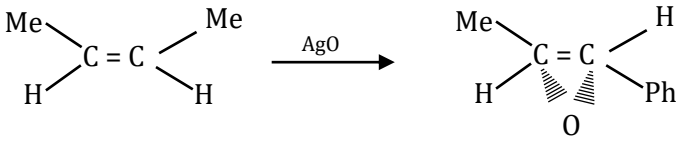


(iv) 

Hint: Cis + Anti + Threo [CAT]

(v) 

(Erythro)

(vi) 

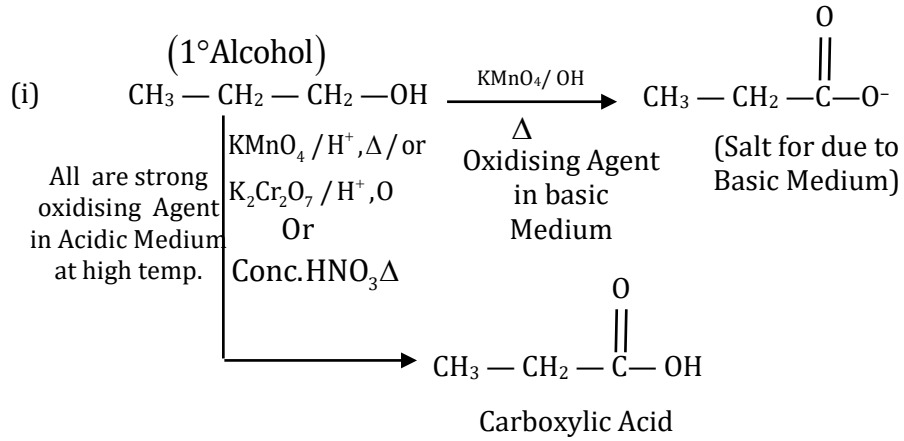
4. **Ans.** **(i)** $CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - O^-$, $CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - OH$

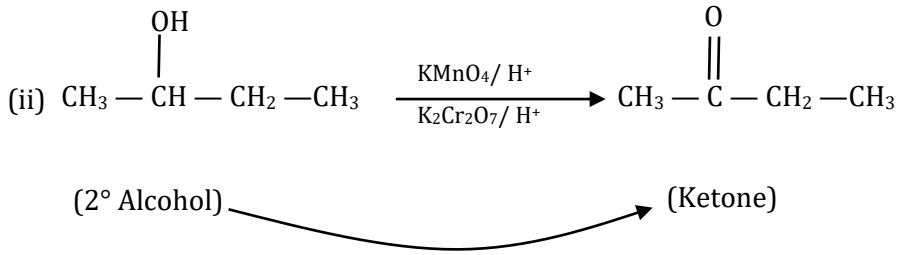
(Salt for due to Basic Medium)

Carboxylic Acid

(ii) $CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_3$

(Ketone)

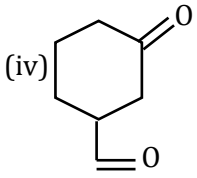




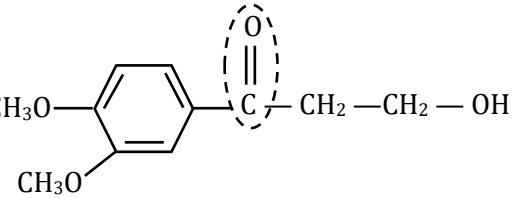
5. **Ans.** (i) $CH_2 = CH—(CH_2)_3—CHO$

(ii) $C_6H_5 — CH = CH — CHO$

(iii) $CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_2—CH=O$

(iv) 

(v) $CH_2 = CH — CHO$

(vi) 

Chromic anhydride in glacial acetic acid and PCC'

↓

Convert 1° alcohol to aldehyde
2° alcohol to ketone
3° alcohol no reaction

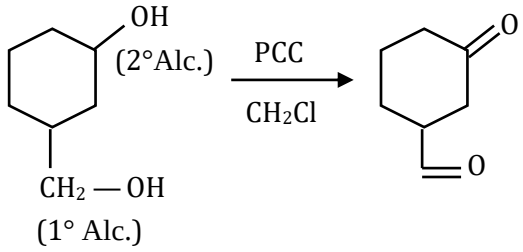
Do not effect C = C , C C

(Mno_2 ocidise allylic / Benzylic. OH to ald / Ketone)

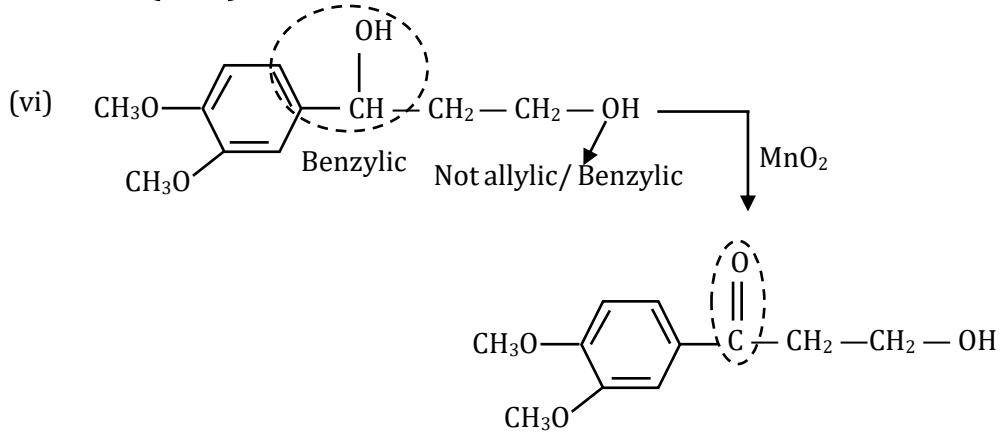
(i) $CH_2 - CH(CH_2)_3 - CH_2-OH$ (1°) $\xrightarrow[\text{Acetic Acid}]{\text{Chronic Anhyd. Glacial}}$ $CH_2 = CH-(CH_2)_3-CHO$

(ii) $C_6H_5 - CH = CH - CH_2-OH$ (1°Alc) $\xrightarrow{\text{Chromic Anhydride}}$ $C_6H_5 - CH = CH - CHO$

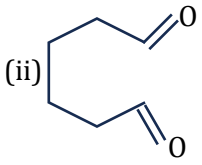
(iii) $C_6H_5 - CH(OH) - CH_2 - CH_2 - CH_2 - OH$ (2°Alc) (1°Alc) $\xrightarrow[CH_2Cl_2]{PCC}$ $CH_3 - C(=O) - CH_2 - CH_2 - CH = O$

(iv) 

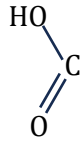
(v) $CH_2 = CH(OH) - CH_2$ (Allylic OH) $\xrightarrow{MnO_2}$ $CH_2 = CH - CHO$

(vi) 

6. **Ans.** (i) $Me—CH=O + O=CH_2$

(ii) 

(iii) $CH_2(OH)—CH_2—C(=O)—H + O=CH_2$

(iv) OCH_2  $O=CH-CH_3$

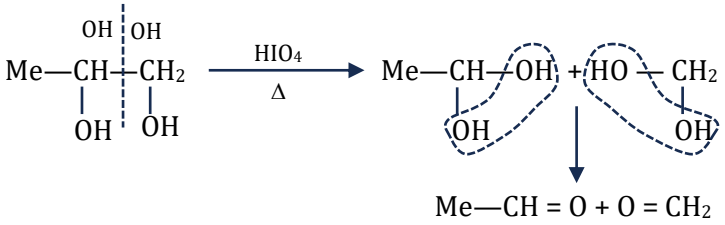
(v) $O=CH_2$, $O=CH(OH)$, $O=CH(OH)$, $O=CH_2$

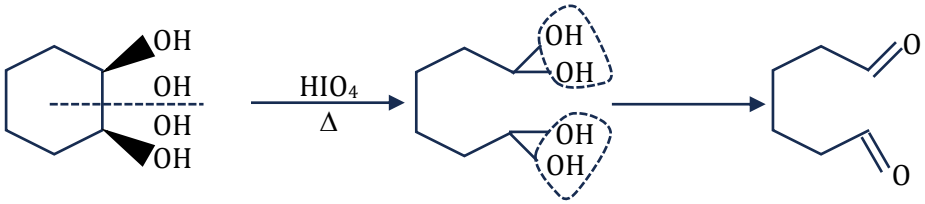
(vi) $Me-C(=O)-OH$, $O=CH-M$

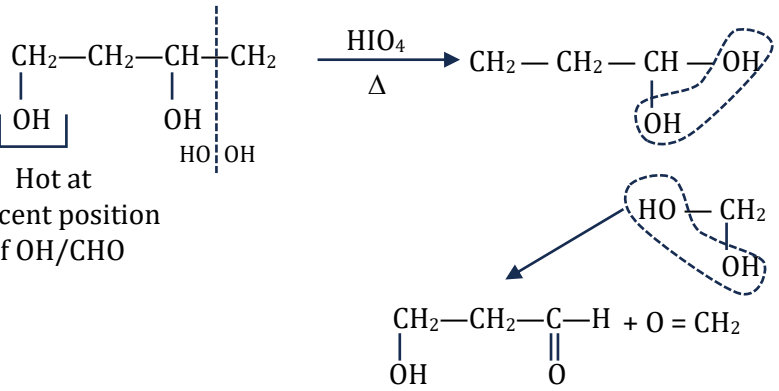
(vii) $Me-C(=O)-OH$, $HO-C(=O)-Me$

HIO_4 Oxidise Vicinal diol / Vincinal alcohol / Aldehyde

It oxidise by breaking C = C bond of vicinal diol.

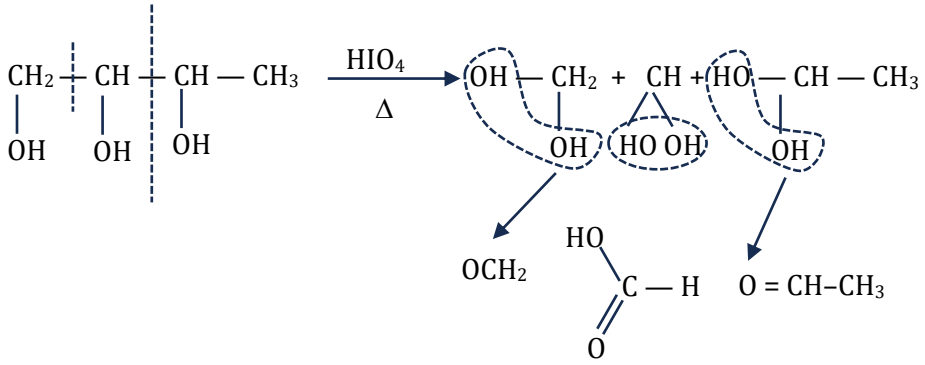
(i) 

(ii) 

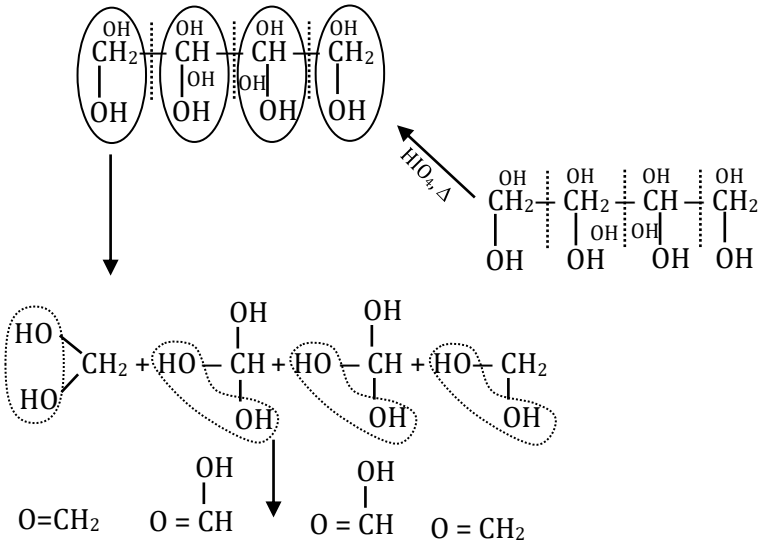
(iii) 

Hot at adjacent position Of OH/CHO

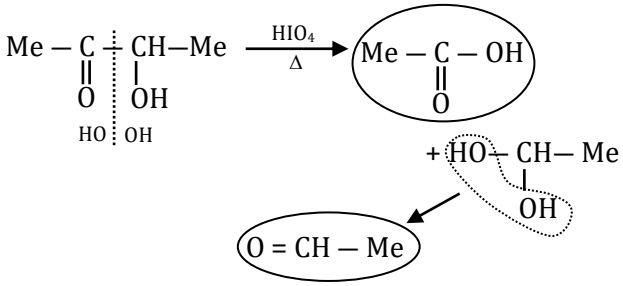
(iv)



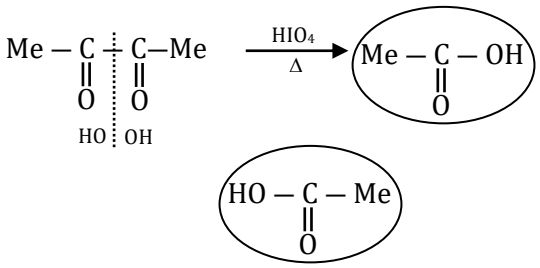
(v)

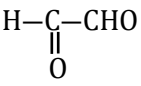
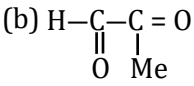
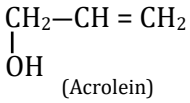


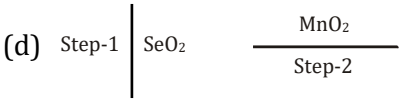
(vi)

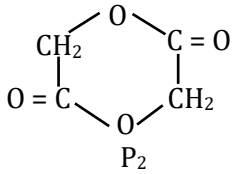


(vii)



7. **Ans.** (a)  (b)  (c) 
(Acrolein)

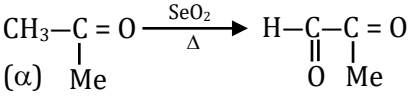
(d) 

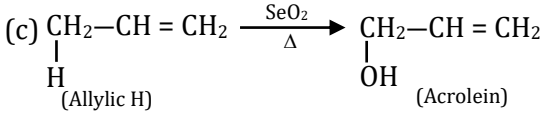
(e) 

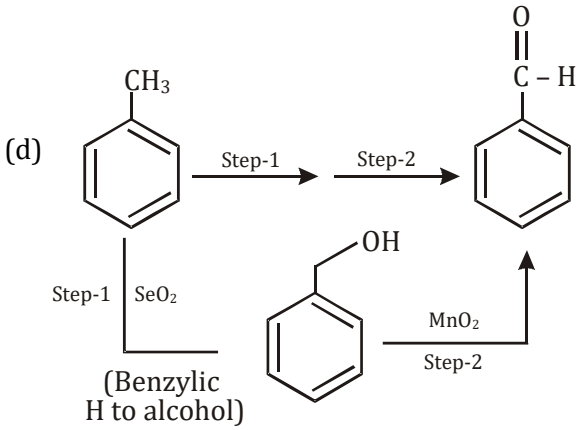
SeO_2 Oxidise a-C of aldehyde / Ketone to C = O

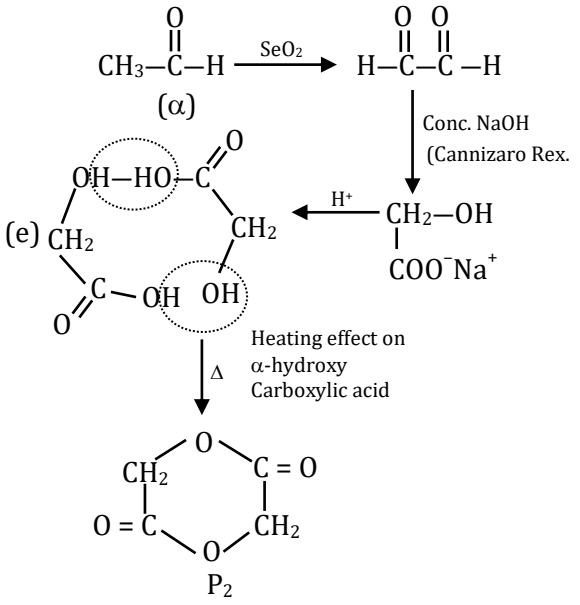
SeO_2 Also oxidise Allylic / Benziylic (H) to alcohol.

(a) 

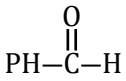
(b) 

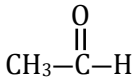
(c) 

(d) 

(e) 

8. **Ans.** (i) +Ve Fehling test –Ve Fehling test
(ii) +Ve Benedict –Ve Benedict
(Benzaldehyde do not give Fehlling / Benedict test)

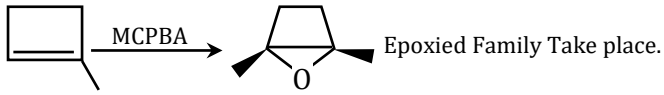
(a)  
(i) +Ve Fehling test –Ve Fehling test
(ii) +Ve Benedict –Ve Benedict

(b)  
–Ve Iodoform test Positive Iodoform test
(Methyl all/Ketone gives +ve Iodoform test.)

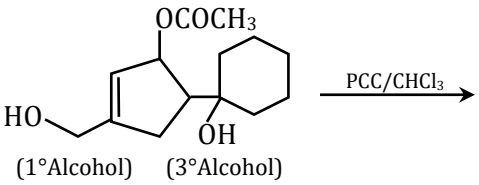
Note: (Oxidation of Alkene in Acidic $KMnO_4$ H^+ / $KMnO_4$ is similar like Oxidative Ozonolysis.)

EXERCISE - JEE (Main) PYQ

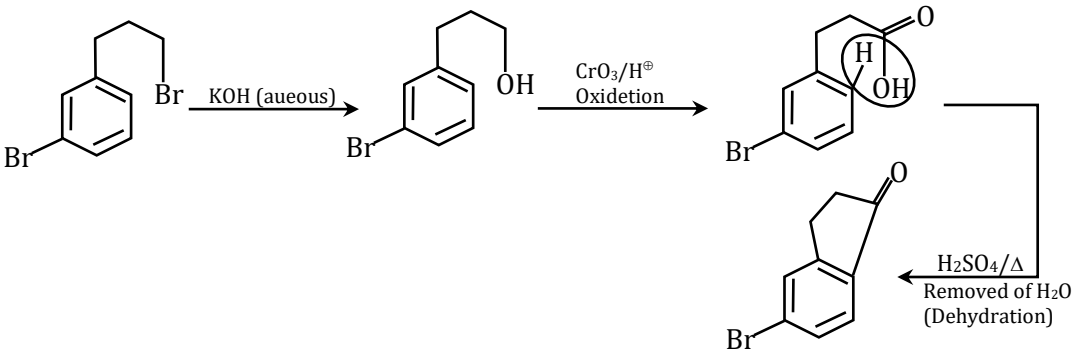
1. **Ans. (1)**
3° Alcohol cannot be oxidised by $H_2Cr_2O_7$ / $H^{\oplus}$. So colour change does not take place (B), (C), (D) all are 3° Alcohol ; only (i) is 1° Alcohol so reaction can take place.

2. **Ans. (3)**


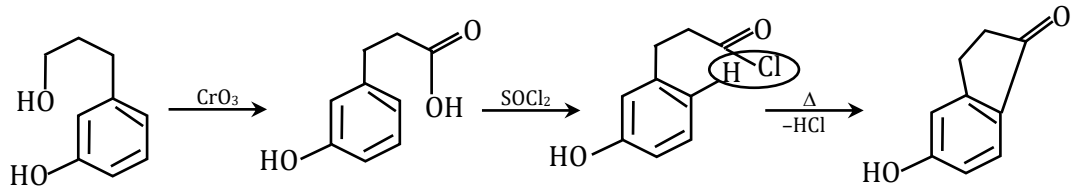
3. **Ans. (2)**
$RCH_2OH \longrightarrow RCH = O$ the Most snitable reagent for oxidisation is pcc.
$KMnO_4$ / $H_2Cr_2O_7$ / CrO_3 / H_2O converts $RCH_2OH \rightarrow RCO_2H$.

4. **Ans. (4)**


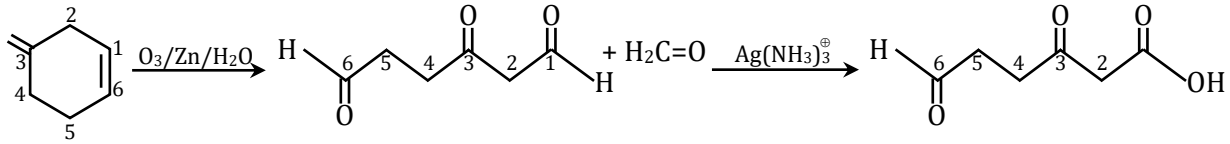
It can oxidise 1° Alcohol but not 3° Alcohol. & 1° alcohol is converts with aldehyde.

5. **Ans. (2)**


6. Ans. (4)



7. Ans. (1)



8. Ans. (3)

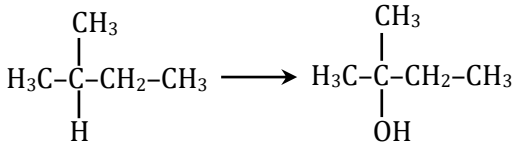
$$CH_3CH_2CH_3 \xrightarrow[\text{(Catalytic Oxidation)}]{\text{Molybdenum oxide}} CH_3CH_2CHO$$

9. Ans. (4)

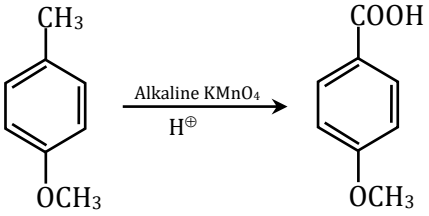
$$CH_3CH_2OH_3 \xrightarrow{CrO_3-H_2SO_4} CH_3-\overset{\overset{O}{\|}}{C}-O-H$$

10. Ans. (3)

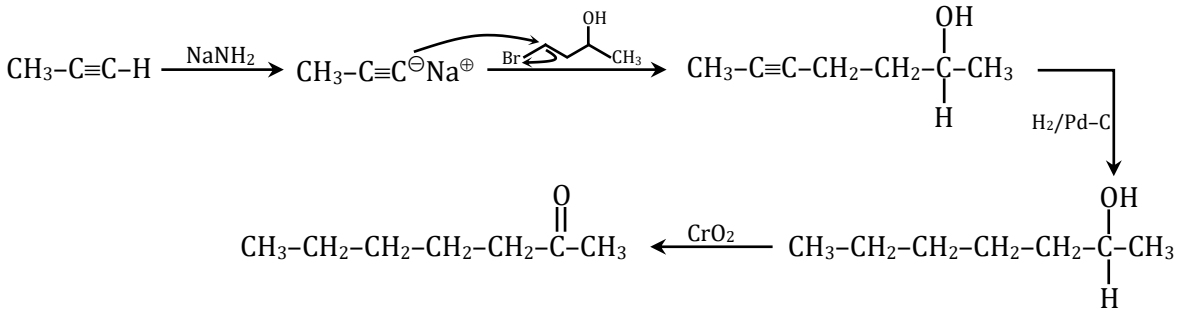
Alkanes resist oxidation but alkanes having tertiary H-atom can be oxidized to corresponding alcohols by $KMnO_4$.



11. Ans. (3)

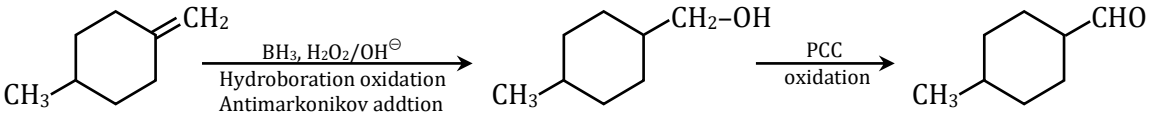


12. Ans. (4)

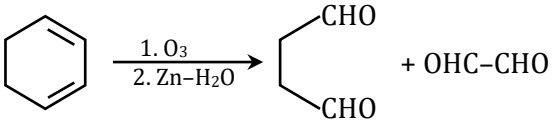


13. Ans. (3)

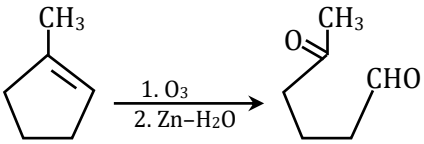
BH_3, $H_2O_2/^{\ominus}OH$ followed by PCC oxidation.



14. Ans. (4)

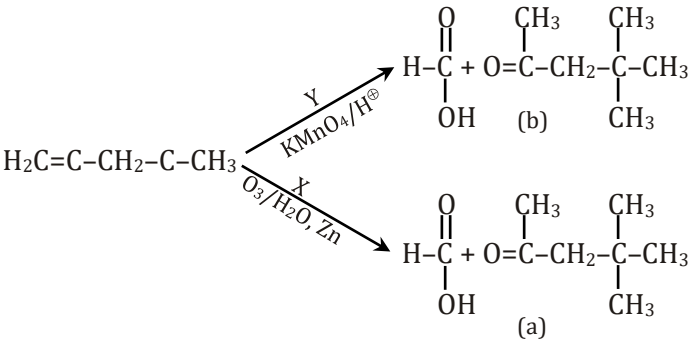


Ethane–1, 2–dicarbaldehyde

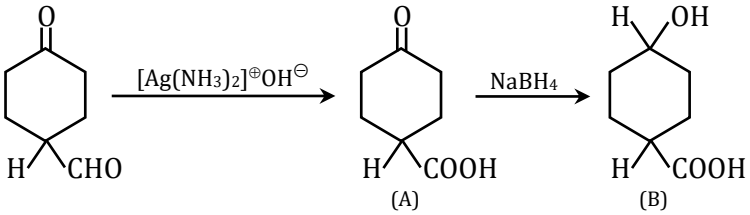


5–oxohexanal

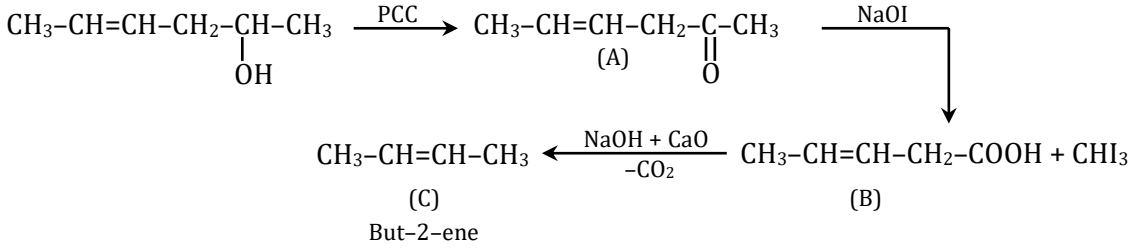
15. Ans. (4)



16. Ans. (3)

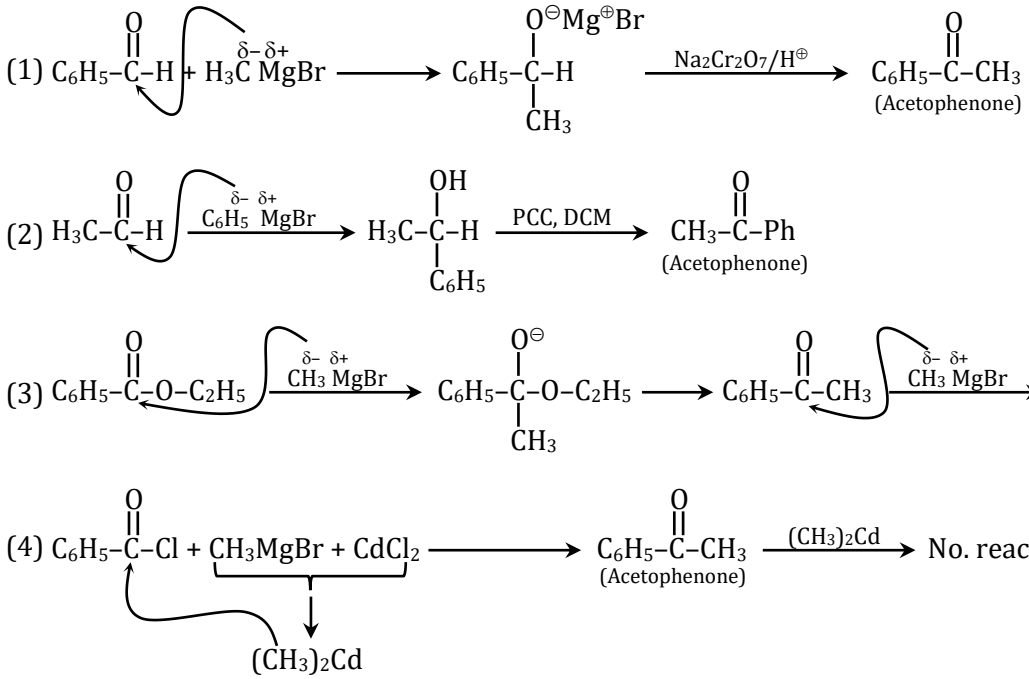


17. Ans. (3)

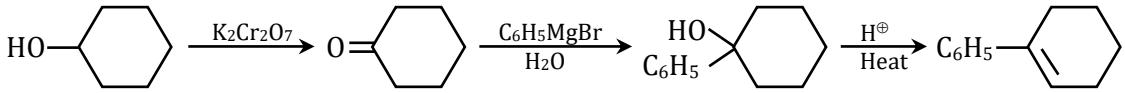


But–2–ene

18. Ans. (3)

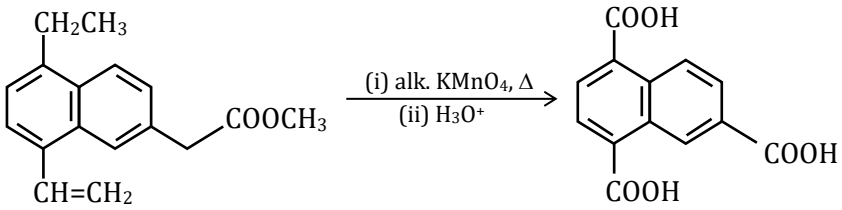


19. Ans. (8)



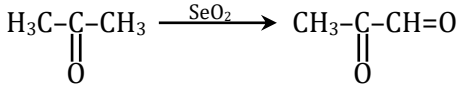
20. Ans. (4)

$KMnO_4$ oxidises benzylic carbon containing atleast one α-hydrogen atom to –COOH.



EXERCISE - JEE (Advanced) PYQ

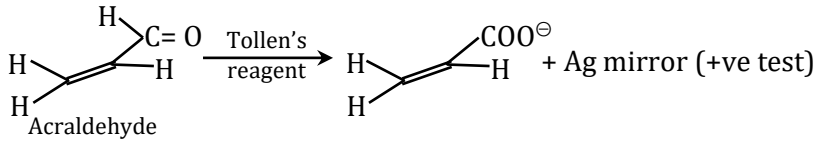
1. Ans. (A)

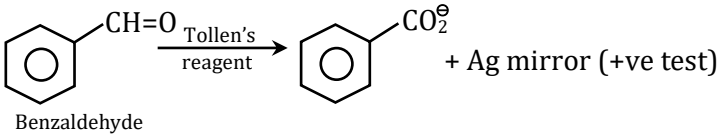


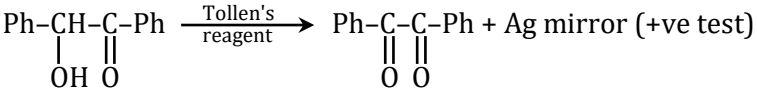
Here $-CH_2$ group adjacent to $-\overset{\overset{O}{\|}}{C}-$ is oxidised to $-\overset{\overset{O}{\|}}{C}-$ group by this conversion monocarbonyl compound is converted into dicarbonyl compound.

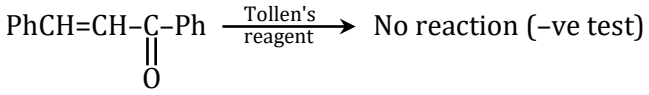
2. Ans. (A,B,C)

Tollens's test is given by compounds having aldehyde group. Also α-hydroxy carbonyl gives positive tollen's test.

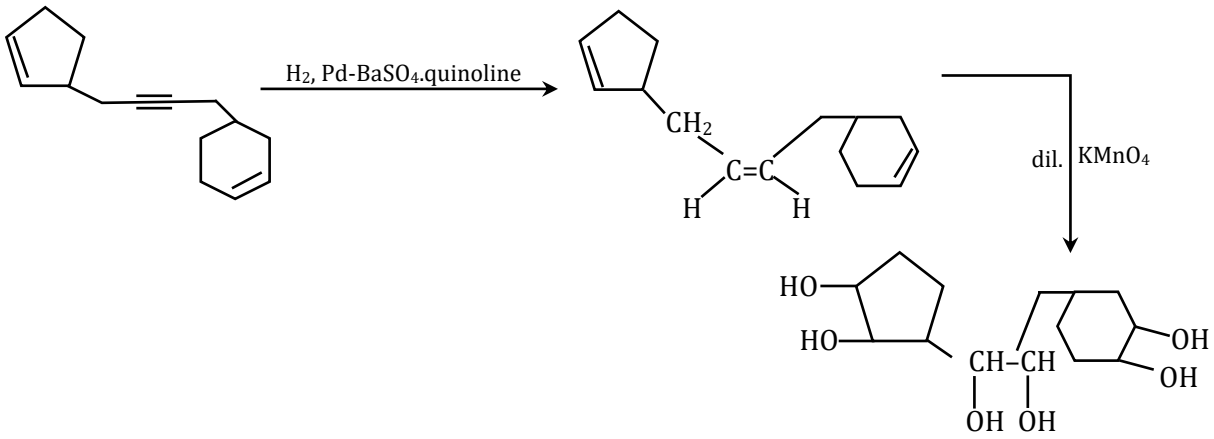
(A) 

(B) 

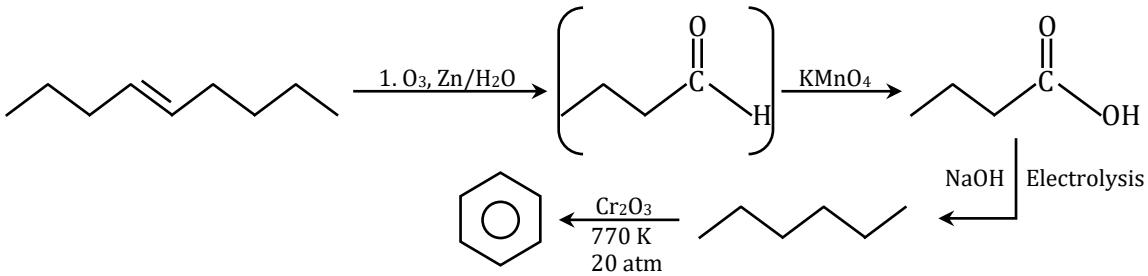
(C) 

(D) 

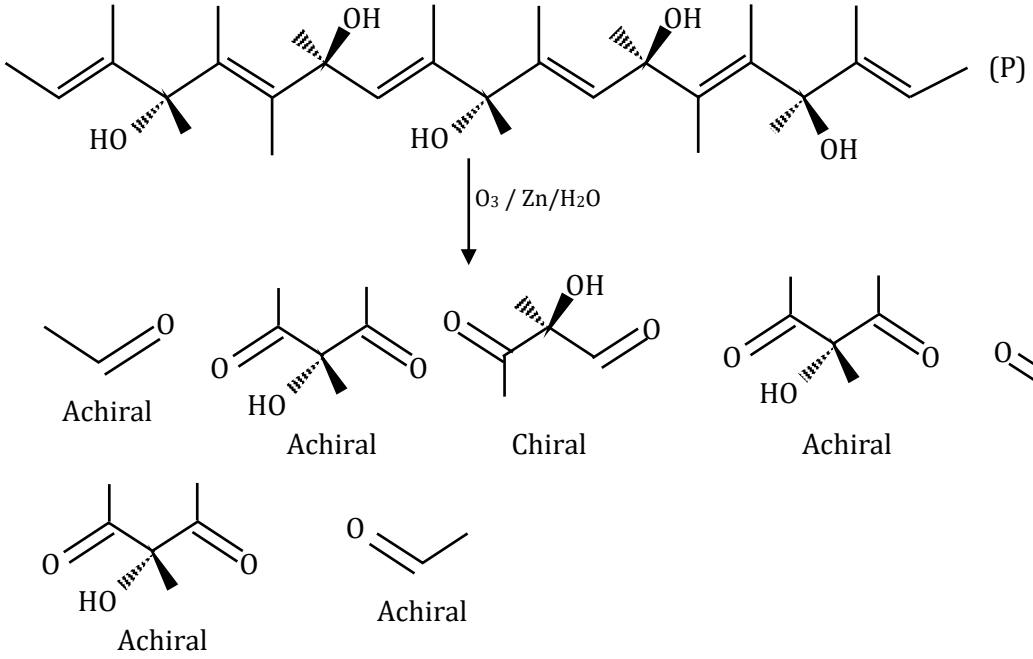
3. Ans. (6.00)



4. Ans. (0)



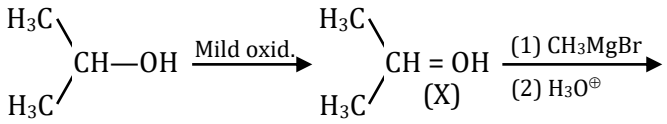
5. **Ans. (2)**



JEE (Main) Practice Paper

SECTION–A

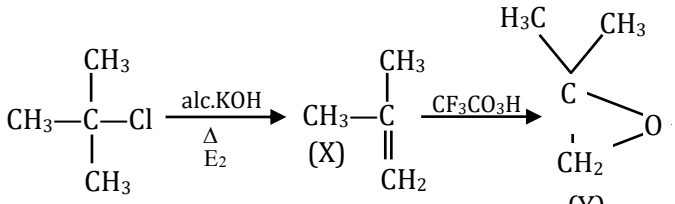
1. **Ans. (2)**



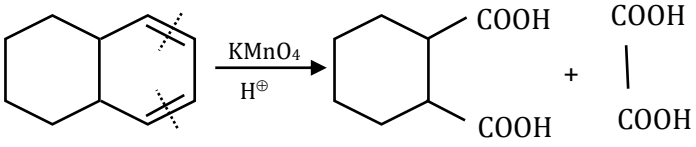
(3° alcohol)

(Y)

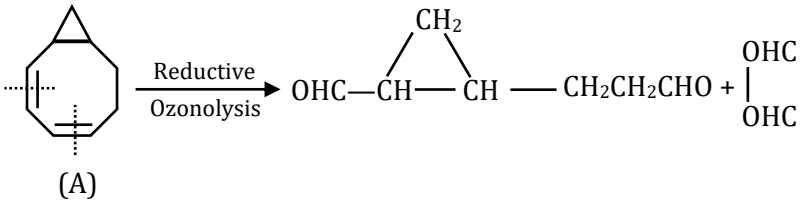
2. **Ans. (2)**



3. **Ans. (4)**

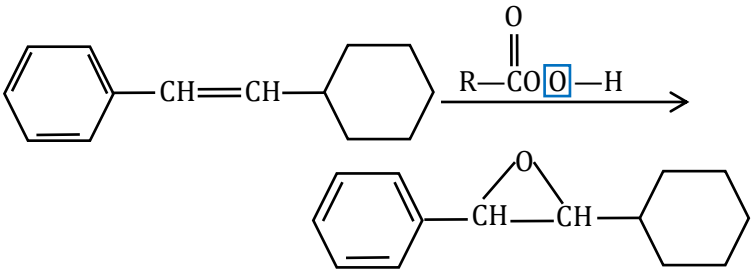


4. **Ans. (2)**



(A)

5. **Ans. (1)**



6. **Ans. (2)**

1° alcohols are converted to acid, 2° alcohols to carbonyl and 3° alcohols are not affected.

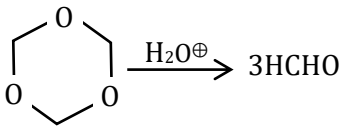
7. **Ans. (4)**

Only primary and secondary alcohols will be able to change the colour as they will be easily oxidised by CrO_3/ aq. H_2SO_4.

8. **Ans. (1)**

Cis $\rightarrow$ syn-addition $\rightarrow$ Erythro

9. **Ans. (2)**



10. **Ans. (2)**

Oppenauer oxidation, oxidised seconary alcohol into ketone and there is no efect on double bond.

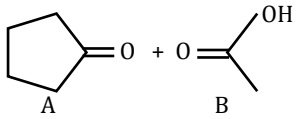
11. **Ans. (1)**

Jones reagent oxidised 1° alcohol in acid

Jones reagent oxidised 2° alcohol in aldehyde or ketone

Jones reagent not oxidised 3° alcohol

12. Ans. (2)



13. Ans. (3)

Five mole of HCOOH formed from one mole of glucose and three mole of HCOOH formed from one mole fructose on treating them with periodic acid.

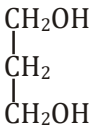
14. Ans. (3)

2° alcohol on oxidation with Cu gives ketone.

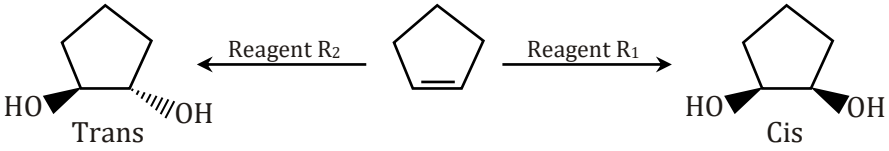
15. Ans. (3)

Acetaldehyde reacts with Tollens, Schiff's and Fehling's solution but acetone does not. But with H_2 / Ni both reacts.

16. Ans. (2)



17. Ans. (2)



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

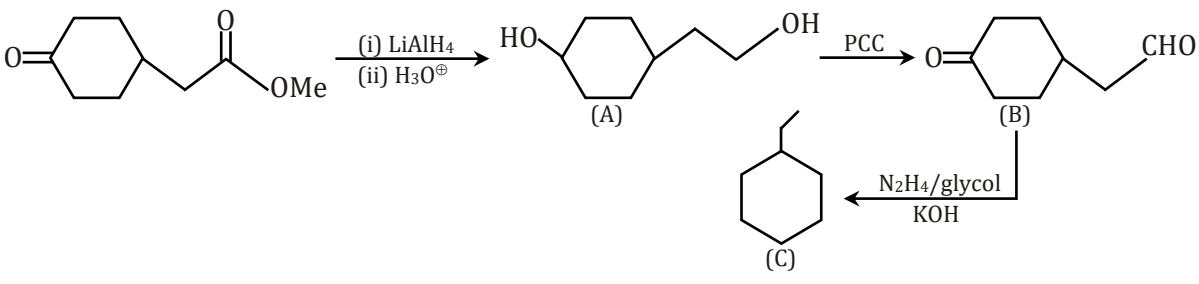
18. Ans. (3)

Acidic $KMnO_4$ breaks the double bond and also oxidises 2° alcohol to ketone, whereas PCC only oxidises 2° alcohol to ketone. So, the answer is (C).

19. Ans. (4)

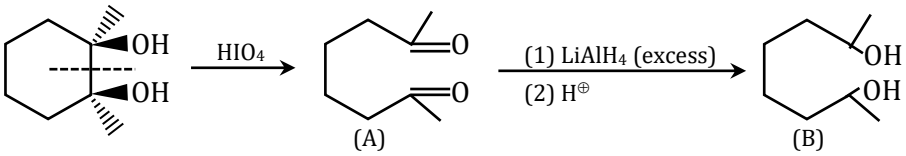
Only primary and secondary alcohols will be able to change the colour as they will be easily oxidised by CrO_3 / aq. H_2SO_4.

20. Ans. (4)

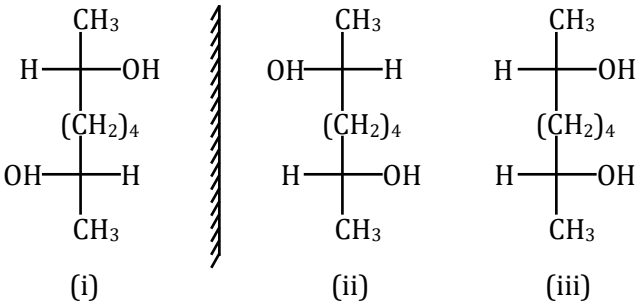


SECTION-B

1. Ans. (3)



Stereoisomers of B

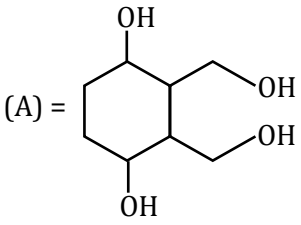


Chiral centers and plane of symmetry is present in compound (III) so the total stereoisomer of product (B) will be 3 (2 stereoisomers are optically active whereas one stereoisomer is optically inactive which is meso form (III).

2. Ans. (2)

(x = 2) HIO_4 will not cleave ether.

3. Ans. (4)

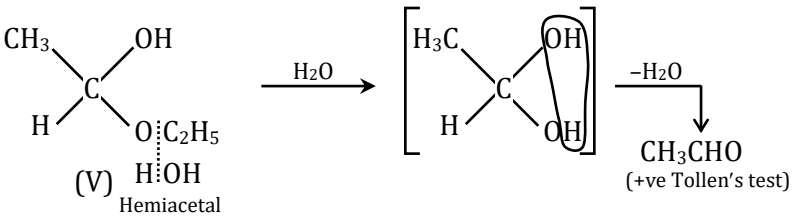


No. of alcohol = No. of moles of Ac_2O consumed. = 4

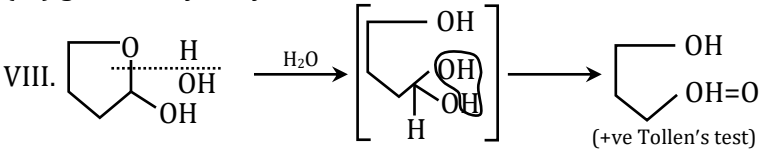
4. Ans. (6)

Six compounds (I, II, III, V, VII and VIII)

Aliphatic and aromatic aldehydes (I, II) and formic acid (III), hemiacetal (V), terminal alkyne (VII) and (VIII) gives this test.



(VI) gives on hydrolysis ketone.

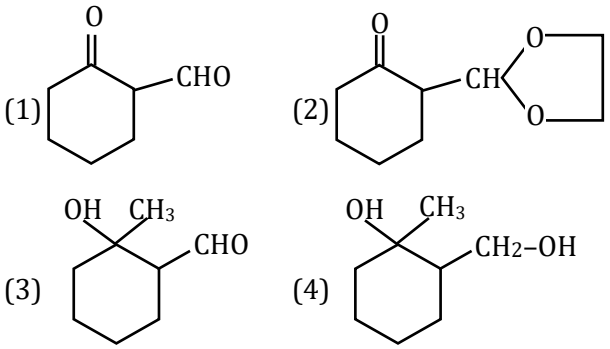


5. **Ans. (7)**
Seven compounds (I, II, VI, VII, VIII, IX and X)
Methyl ketone or aldehyde (I, II, VIII and IX) and 1, 3-dikentone or cyclic 1, 3-didetone (VI and VII) gives iodoform test.

6. **Ans. (4)**
PCC, called Corey's reagent. Oxidises primary alcohols to aldehydes in good yields and does not oxidise aldehydes further. Secondary alcohols are oxidise to ketones. C = C & C ≡ C bond remain unaffected towards oxidation under this condition.

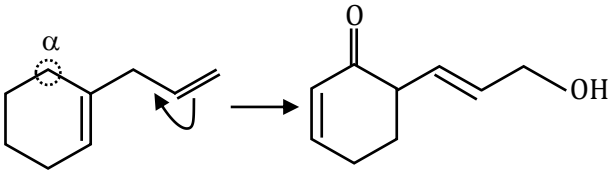
JEE (Advanced) Practice Paper

1. **Ans. (B)**



2. **Ans. (B)**
MnO_2 Selectively oxidises allylic or benzylic hydroxyl group to (C=O) group, whereas jones reagent oxidises 1° and 2° ROH to aldehydes and ketones, respectively. So, the answer is (2).

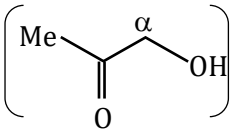
3. **Ans. (C)**
In cycloalkenes (unsubstituted), the ring methylene group at α – position to double bond is oxidised to (C=O) group, and simultaneously the terminal double bond is oxidised to 1° alcoholic group along with allylic migration of the double bond.

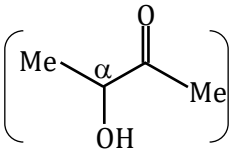


So, the answer is (3)

4. **Ans. (A)**
Symmetrical alkenes on acid-catalysed hydration, oxymercuration-demercuration, and HBO reactions give the same product. So, the answer is (1).

5. **Ans. (A)**
(A) Fehling's solution reacts only with aliphatic aldehyde, not with aromatic aldehyde.

(B) F.S. reacts with MeCHO and also with α–hydroxy ketones 

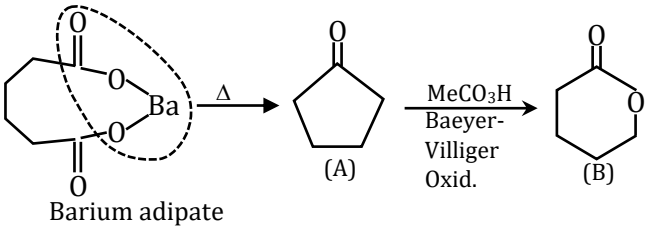
(C) F.S. reacts with both HCHO and with α-hydroxy ketone 

(D) F.S. reacts with both aliphatic aldehydes (MeCHO and HCHO). So, the answer is (1).

6. **Ans. (C)**

It gives phenol.

7. **Ans. (B)**



Barium adipate

8. **Ans. (A,C,D)**

1° Alcohol shows Highest rate of oxidation & Change its colour & oxidation state.

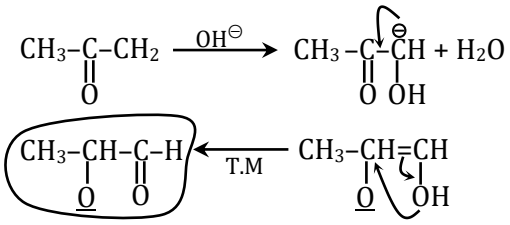
$CH_3-CH_2-OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$

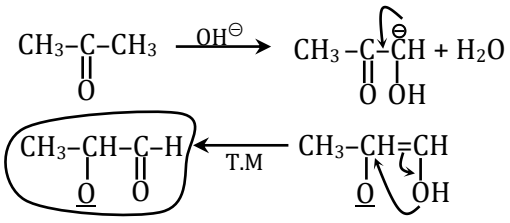
9. **Ans. (B,D)**

Fehling solution gives Red ppt with aliphatic Aldehyde

α-Hydroxy Ketone in Alkaline Medium.

Give





10. **Ans. (A,B,C)**

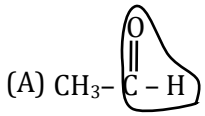
Tollens test given By

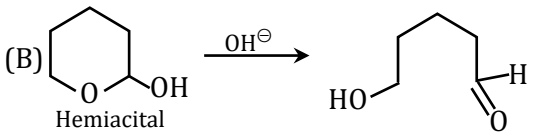
– A;dehyde

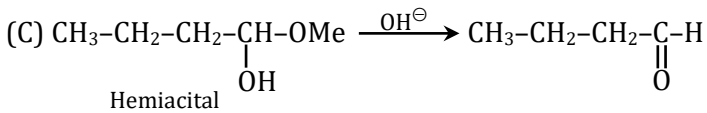
– Hemiacitol

– α-Hydroxy Ketone

– Formic Acid



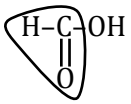




11. **Ans. (A,B)**

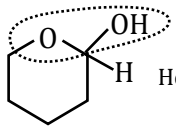
Shiff Reagant Test

Give By $-\underset{\underset{O}{\|}}{C}-H$ Group

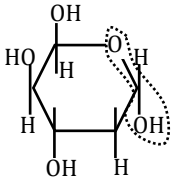
(A) $CH_3-\underset{\underset{O}{\|}}{C}-H$ (B) 

12. **Ans. (A,C,D)**

Aldehyde, Hemiacctal and a-Hydroxy ketone Compound gives positive Tollen Test.

(A)  Hemiactal

(B) $R-\underset{\underset{O}{\|}}{C}-\underset{(\alpha)}{CH_2}$ (OH) α-Hydroxy Ketone

(C)  Hemitactal

13. **Ans. (C,D)**

(A) Substitution

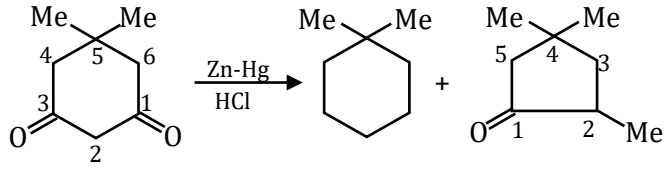
(B) Reduction

(C) Oxidation (Addition of Halogen (More EN atoms)) at alkene

14. **Ans. (A)**

a → iv

Cyclic 1,3–diketones give, under Clemmensen reduction, a fully reduced product along with a mono ketone with ring contraction.



5,5- Dimethyl Cyclohexane-1,3- dione

1,1- Dimethyl Cyclohexane

2,4,4- Trimethyl Cyclohexane

b → i,r

c → ii,p

PARTIAL OXIDATION

Aromatic aldehydes can be prepared by the oxidation o methyl benzene with CrO_3 + $(MeCO)_2$ O (Chromium trioxide in acetic anhydride). The gem-diacetate first formed is isolated and hydrolysed with alkali to yield the corresponding aldehyde. The function of acetic anhydride is to form gem-diacetate which resists the further oxidation of benzaldehyde to benzoic acid, e.g.

$$\underset{\text{Toluene}}{PhCH_3} + CrO_3 + (CH_3CO)_2O \xrightarrow{273-283K} \underset{\text{Benzylidene acetate}}{C_6H_5CH(OCOCH_3)_2} \xrightarrow{\ominus OH/H_2O} PhCHO + 2CH_3COOH$$

It can also be oxidised to aldehydes with a solution of chromyl chloride (CrO_2Cl_2) in CCl_4 or CS_2. The brown complex thus precipitated is separated and decomposed with H_2O to give the aldehyde. For example :

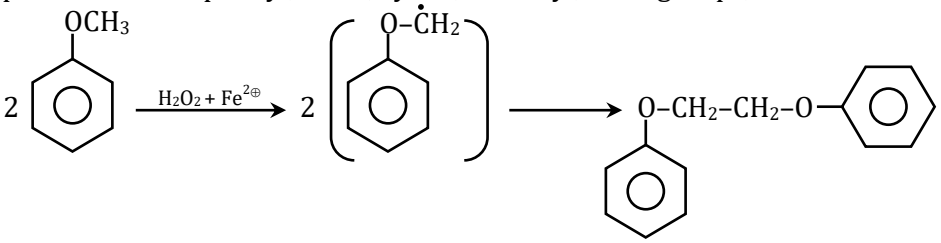
$$\underset{\text{Toluene}}{PhCH_3} + 2CrO_2Cl_2 + CCl_4 \longrightarrow \underset{\substack{\text{Brown complex}\\ \text{Or}\\ \text{Chromium complex}}}{\left(PhCH(OCrCl_2OH)_2\right)} \xrightarrow{H_2O} PhCHO$$

The above reaction is called Etard reaction. Side chains bigger than CH_3 are oxidised by CrO_2Cl_2 at the last C atome.

$PhCH_2CH_3 \xrightarrow[(ii)H_2O]{(i)CrO_2Cl_2/CCl_4} \underset{\text{Phenylacetaldehyde}}{PhCH_2CHO}$

d → iii,s

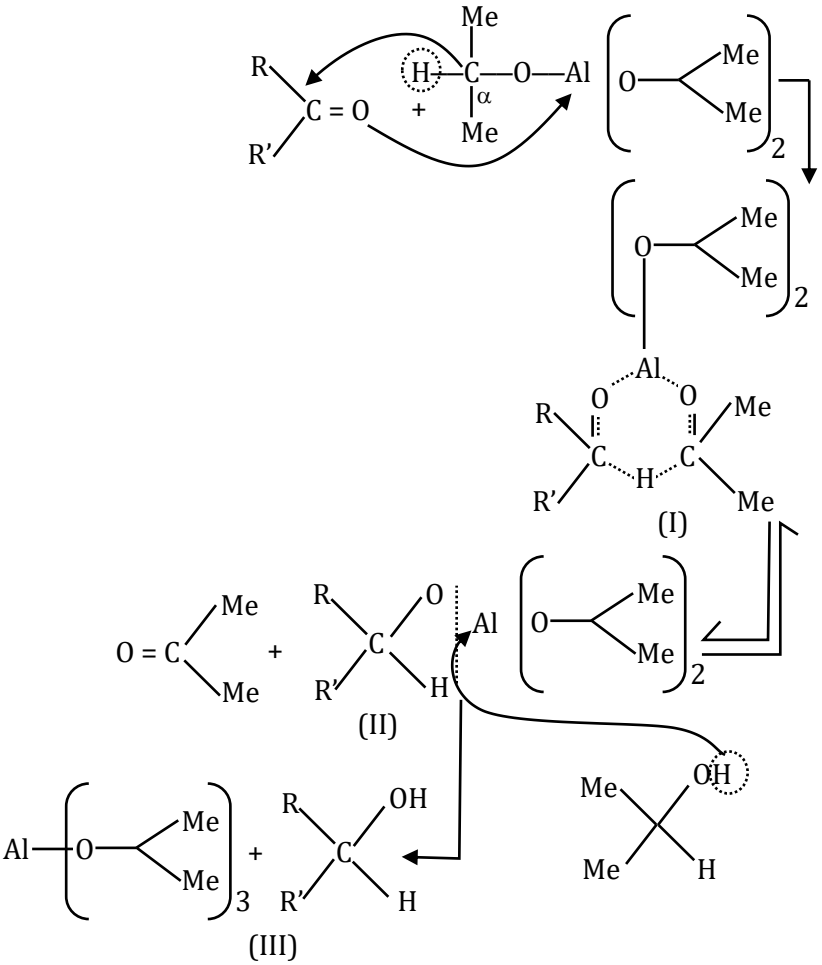
Coupling : The $\dot{O}H$ radical may abstract a hydrogen from the susceptible position of the substrate producing radicals which couple. The susceptible reactive positions are supposed to be the α-positions to the phenyl, ether, cyano, carboxyl, ester groups, et



15. Ans. (B)

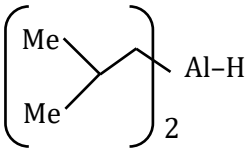
MECHANISM

The reaction probably involves a cyclic transition state (I) in which a hydride ion ($H^{\ominus}$) from the α - CH bond of the alkoxide migrates to the carbonyl carbon of the ketone to yield the mixed alkoxide (II).

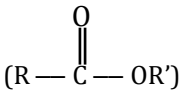


b → I,q

REDUCTION WITH DIBAL-H (DI- ISOBUTYL ALUMINIUM HYDRIDE)

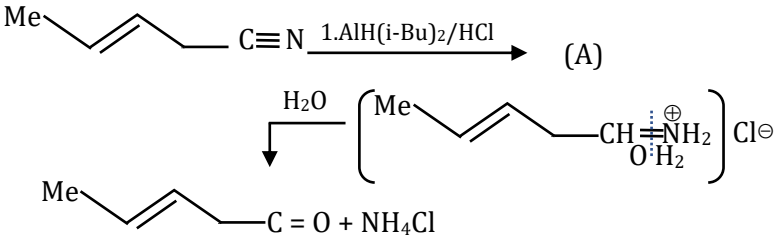


is written as $AlH(i\text{-}Bu)_2$. It reduces R –C ≡ N to R–CHO and also ester

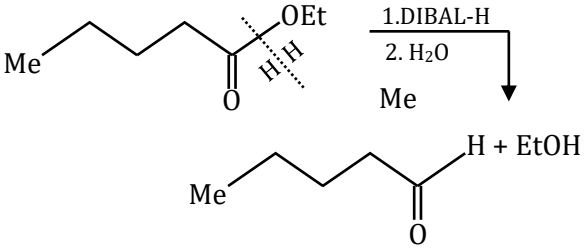


to RCH = O and alcohol. It does not reduce (C = C) or (C ≡ C) bond.

Nitriles are selectively reduced by DIBAL-H to imine hydrochlorides followed by hydrolysis to aldehydes.



Similarly, esters are also reduced to aldehydes with DIBAL -H.



c → II,p

TOLLENS, FEHLING'S BENEDICT'S AND SCHIFF'S REAGENTS

Aldehydes are easily oxidised to acids containing the same number of C atoms. Hence, they are oxidised not only by strong O.A. such as MNO_4 and $K_2Cr_2O_7$ but also by weak O.A. such as Br_2 water, $Ag^{\oplus}$, $Cu^{2\oplus}$ions, etc, as a result, aldehydes act as strong reducing agents. They reduce (i) Tollens reagent to metallic silver (silver mirror), and (ii) Fehling's or Benedict's solution (F.S. or B.S.) to a red precipitate of cuprous oxide (Cu_2O).

a. Reduction of Tollens reagent : T.R. is an ammoniacal solution of $AgNO_3$. When an aldehyde is heated with T.R., the latter is reduced to metallic Ag and aldehydes are oxidised to acids. Thus. T.R. is called an oxidising agent.

$$AgNO_3 + NH_4OH \longrightarrow \underset{\text{Grey ppt.}}{AgOH} + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{Tollens reagent}}{[Ag(NH_3)_2]^{\oplus}\,\overset{\ominus}{O}H} + 2H_2O$$

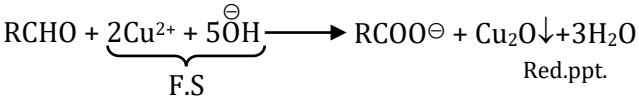
$$RCHO + 2[Ag(NH_3)_2]^{\oplus} + 3\overset{\ominus}{O}H \longrightarrow RCO\overset{\ominus}{O} + 2Ag\downarrow + 4NH_3 + 2H2O$$

Silver mirror

The silver, thus deposited, shines like a mirror. Hence, this test is known as silver mirror test T.R. does not attack olefinic bond. For example

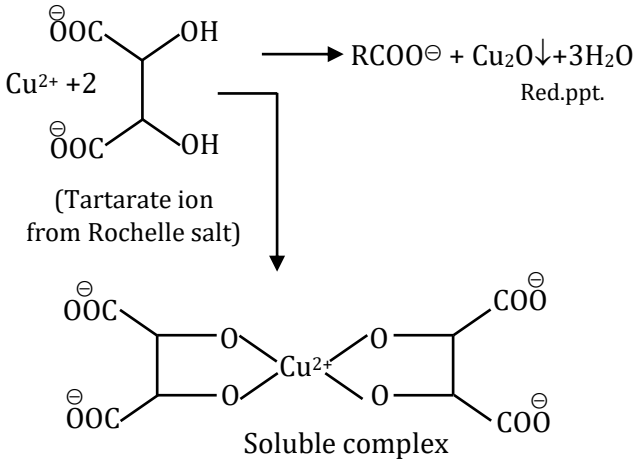
$$RCH{=}CH{-}CHO \xrightarrow{T.R.} RCH{=}CH{-}COOH$$

b. Reduction of Fehling's solution : It is an alkaline solution of $CuSO_4$ containing some Rochelle salt, i.e. sodium potassium tartarate (NaOOC–CH (OH) –CH (OH) –COOK). When an aldehyde is heated with F.S., the latter is reduced to give a red precipitate of cuprous oxide.



F.S.' 'A' contains aqueous solution of $CUSO_4$, while F.S. 'B' contains ammoniacal solution of Rochelle salt. For testing aldehydes. F.S. A and B are mixed in equal amounts.

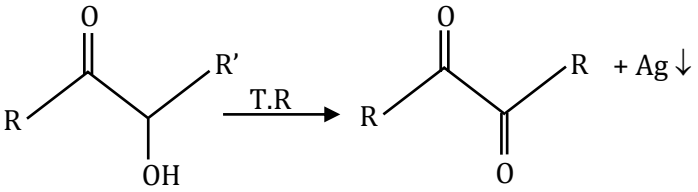
c. Function of Rochelle salt in Fehling's Cu^{2+} ions get precipitated in alkaline medium as $Cu(OH)_2$. So, Rochelle salt is added to keep Cu^{2+} in alkaline solution. The insoluble $Cu(OH)_2$ first formed goes into the solution due to the formation of a soluble complex between Cu^{2+} ions and tartarate ion as shown below



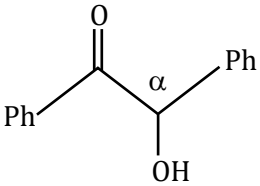
Note:

(i) Aromatic aldehyde are not oxidized by F.S. and B.S.

(ii) T.R. test is also given by a - hydroxy ketone.



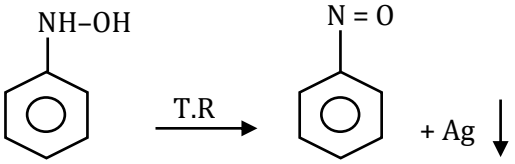
It is due to rearrangement in aldehydes via enediol intermediate (however this need a terminal a - carbon.



This compound, although a- hydroxy ketone but does not have a- C, does not give positive Tollen's test.

(iii) All of them do not oxidise olefinic bond.

(iv) T.R. test is also given by alkyl or aryl hydroxyl amine.



d. Reduction of Bendict's solution ; it is an alkaline solution of $CuSO_4$ containing some sodium citrate. ($NaOOC - CH_2-C(OH)(COONa)-CH_2COONa$). It reacts in the same way as Fehling's solution.

e. Reduction of Schff's reagent : It is a dilute solution of rosanaline hydrochloride in H_2O, whose red (magenta) colour has been discharged by passing SO_2. When this reagent is added to aldehyde, magenta colour is restored.

Note : Formic acid reduces Tollens reagent and Fehling's and Fehling's solution. This is because formic acid can be considered to contain both an aldehyde (–CH = O) and a carboxyl (–COOH) group. Therefore, formic acid behaves as a reducing agent. Therefore, T.R. and F.S. can distinguish between HCOOH and CH_3COOH, e.g.

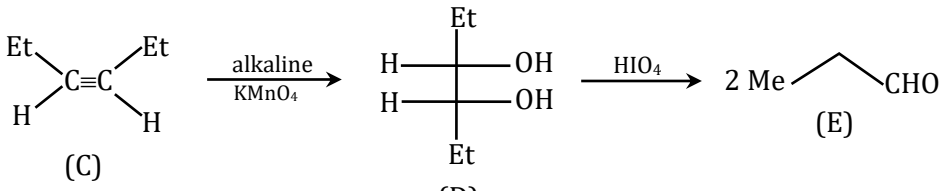
(i) $HCOOH + [Ag(NH_3)_2]^{\oplus} + 2\overset{\ominus}{O}H \rightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$

(ii) $CH_3COOH \xrightarrow{\text{T.R.}}$ No silver mirror

(iii) $HCOOH + \underbrace{2Cu^{2\oplus} + 4O^{\ominus}H}_{\text{F.S}} \rightarrow \underset{\text{Red.ppt}}{Cu_2O\downarrow} + CO_2\uparrow + 3H_2O$

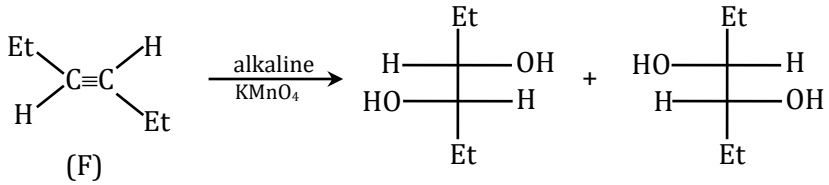
(iv) $CH_3COOH \xrightarrow{\text{F.S.}}$ No red ppt. of Cu_2O

16. Ans. (A)



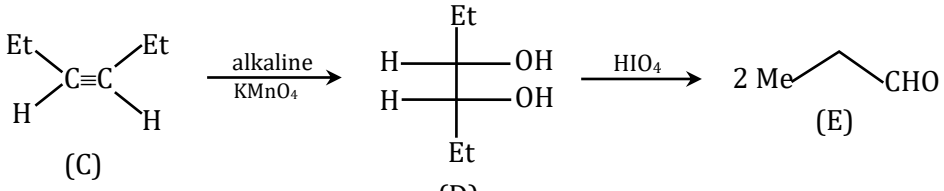
(C) (D) (E)

17. Ans. (D)



(F) (G)

18. Ans. (A)



(C) (D) (E)

19. Ans. (3)

Correct reaction are (i), (ii), (iv)

(iii) Benzylic hydrogen is absent

(v) Racemic mixture is formed

20. Ans. (3)

(i) $2H-\underset{\underset{O}{\|}}{C}-H + CO_2 + 3HCOOH$

(ii) $H-\underset{\underset{O}{\|}}{C}-H + 5HCOOH$