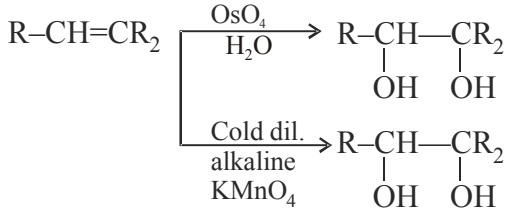
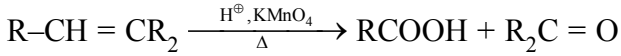
OXIDATION

(I) OXIDATION OF ALKENES



* Cold dil. alkaline $KMnO_4$ is called as Bayer's reagent, use as a test of unsaturation.
* Overall syn addition
* Given by alkenes & alkynes
* Benzene & Cyclopropane can not give this reaction.

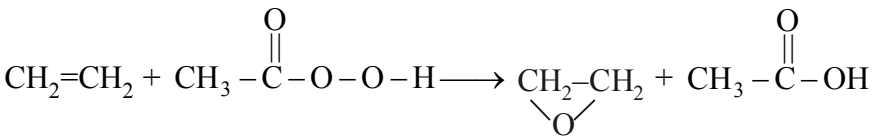
If we use acidic $KMnO_4$ or warm $KMnO_4$ or concentrated $KMnO_4$ the oxidative cleavage of Glycol occurs resulting in mixture of Carboxylic acids & Ketones.



Hot acidic $KMnO_4$, Hot acidic $K_2Cr_2O_7$ & hot acidic $NaIO_4$ gives same result with alkene. The effect is similar to that of oxidative ozonolysis on alkenes.

Preilschaive reaction :

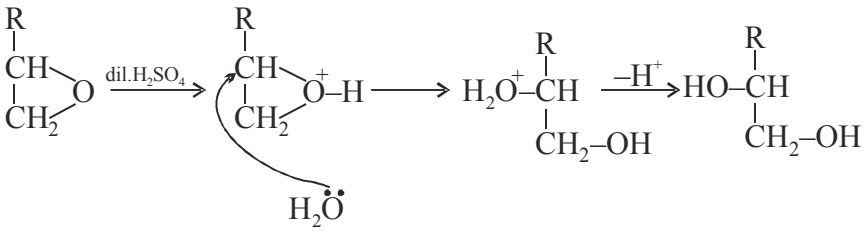
Epoxidation of alkenes is reaction of alkenes with peroxyacids.

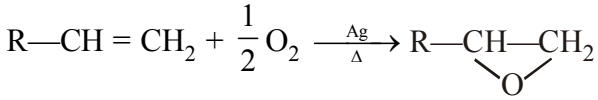


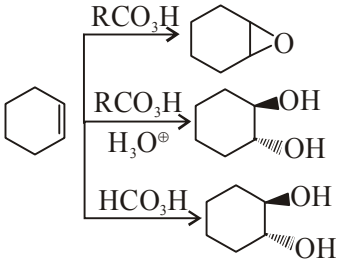
→ Rate α nucleophicity of alkene.

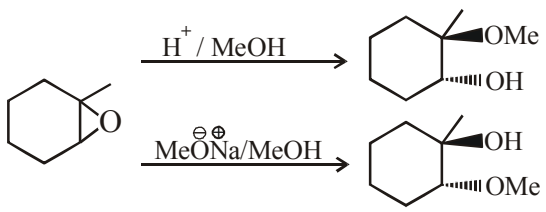
→ With the increase in e^- withdrawing substituents in leaving group, rate increases.

→ Hydrolysis of epoxides form anti diols.



→ 





OXO PROCESS :

Hydroformylation/rolyen synthesis :

$$CH_2 = CH_2 \xrightarrow[\text{Lewis acid high T / P}]{CO+H_2} CH_3–CH_2–CHO$$

Carbonylation / Koch's reaction :

$$CH_2 = CH_2 \xrightarrow[\text{Lewis acid high T / P}]{CO+H_2O} CH_3–CH_2–COOH$$

$$CH_2 = CH_2 \xrightarrow[\text{Lewis acid high T / P}]{CO+ROH} CH_3–CH_2–\overset{O}{\overset{\|}{C}}–OR$$

$$HC \equiv CH \xrightarrow[\text{Lewis acid high T / P}]{CO+H_2O} \underset{\text{Acrylic acid}}{CH_2=CH–COOH}$$

$$HC \equiv CH \xrightarrow[\text{Lewis acid high T / P}]{CO+MeOH} \underset{\text{Methyl acrylate}}{CH_2=CH–\overset{O}{\overset{\|}{C}}–OMe} \xrightarrow{\text{Polymerisation}} \underset{\text{PMA}}{\left(CH_2—\overset{COOMe}{\overset{|}{CH}}\right)_n}$$

(II) <u>OXIDATION OF ALCOHOLS</u>

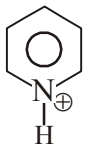
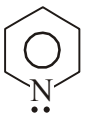
<u>Oxidising agents</u>

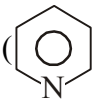
(1) $H^{\oplus}/K_2Cr_2O_7, \Delta$ (Strong oxidising agent)

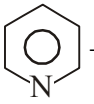
(2) $H^{\oplus}/KMnO_4, \Delta$ (Strong oxidising agent)

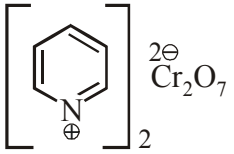
(3) **Jones reagent :** CrO_3 / H_2SO_4 treated with alcohol usually taken in acetone (strong oxidising agent)

(4) Cu / 300°C (or Red hot Cu tube)

(5) PCC (Pyridinium chloro chromate)  or 

(6) Collin's reagent ( (2 mol) + CrO_3 + CH_2Cl_2)

(7) Sarett reagent (i.e. PCC in CH_2Cl_2)  + CrO_3 + HCl + CH_2Cl_2

(8) $\underset{\text{(Pyridinium dichromate)}}{\text{PDC}}$ 

(9) $TsCl + DMSO + NaHCO_3$

$$RCH_2OH \xrightarrow{Ts–Cl} RCH_2OTs \xrightarrow[NaHCO_3]{DMSO} RCHO$$

$$R_2CHOH \xrightarrow{Ts–Cl} R_2CH–OTs \xrightarrow[NaHCO_3]{DMSO} R_2CO$$

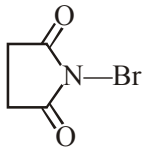
$$R_3COH \xrightarrow{Ts–Cl} R_3C–OTs \xrightarrow[NaHCO_3]{DMSO} \times$$

(10) MnO_2-Oxidises only allylic or benzylic– OH. 1° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Aldehyde

2° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Ketone

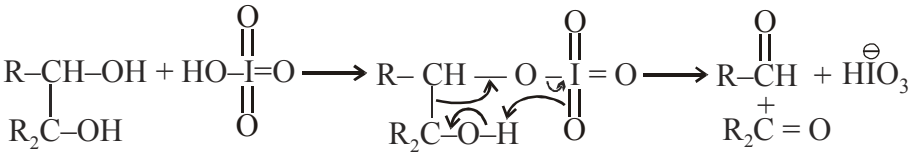
No effect on 3° ROH and on Carbon-Carbon multiple bond.

(11) NBS (N-Bromosuccinamide)



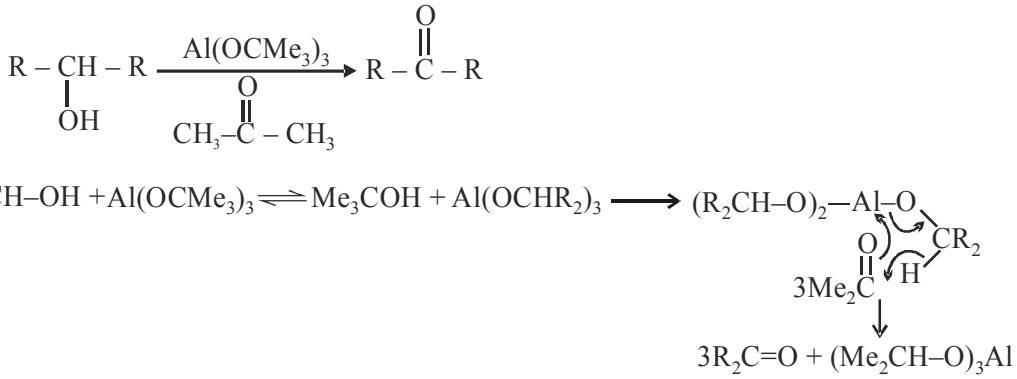
(12) **Periodic cleavage**

A similar oxidation is obtained in case of HIO_4 known as periodic cleavage.



Reaction is observed for Vic-diols.

(13) **Openaur oxidation**



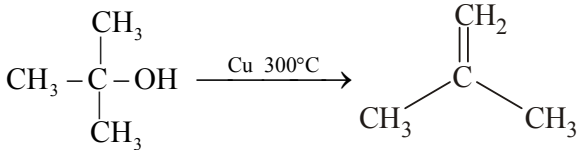
Oxidation of alcohol with aluminium tertiary butoxide is Openaur oxidation.

Ex. Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.

e.g. (I) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{1,2,3,} R-\underset{\underset{O}{\|}}{C}-OH$

(II) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{4,5,6,7,8,9,10,11} R-\underset{\underset{O}{\|}}{C}-H\ (\text{Aldehyde})$

(III) $\underset{2°\text{ Alcohol}}{R-\underset{\underset{OH}{|}}{CH}-R'} \xrightarrow{1,2,3,4,5,6,7,8,8,9,10,11} R-\underset{\underset{O}{\|}}{C}-R'\ (\text{Ketone})$

(IV)  Dehydration takes place.

(V) Double bond or Tripple bond is not affected by 4,5,6,7,8,9,10

(VI) No effect on 3° alcohol by 1,2,3,5,6,7,8,9,10,12,13

(III) OXIDATION OF CARBONYL COMPOUNDS

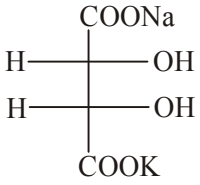
1. Tollen's Test (Silver mirror test)

$RCHO + [Ag(NH_3)_2]OH$ (Tollen's Reagent) $\xrightarrow{\Delta}$ $RCOOH + NH_3 + Ag \downarrow$ (Silver mirror)

Aldehyde acts as reducing agent, they can reduce mild oxidizing agents like Tollen's Reagent.

Tollen's test gentle Heating for 20 to 25 mins.

2. **Fehling's Solutions**



Fehling's A	Fehling's B
aq. $CuSO_4$	Alkaline solution of Roschelye salt (sodium potassium tartrate)

It act's a carrier for Cu^{2+} as it make reversible complex with Cu^{2+}

This test is also used is Blood and Urine test.

$$RCHO + Cu^{2+} \xrightarrow[\Delta]{H_2O} \underset{\downarrow}{RCOOH} + \underset{\downarrow}{Cu^{\oplus}}$$
$$\underset{\downarrow}{RCOO^-} \quad \underset{\downarrow}{Cu_2O}\,(\text{red ppt.})$$

Note : Aromatic aldehyde shows negative test with fehling reagent.

3. **Benedict's solution**

Sodium Citrate + NaOH + $NaHCO_3$ + $CuSO_4$

$$RCHO + Cu^{2+} \xrightarrow[\Delta]{H_2O} \underset{\downarrow}{RCOOH} + \underset{\downarrow}{Cu^{\oplus}}$$
$$\underset{\downarrow}{RCOO^-} \quad \underset{\downarrow}{Cu_2O}\,(\text{red ppt.})$$

It is similar to Fehling test

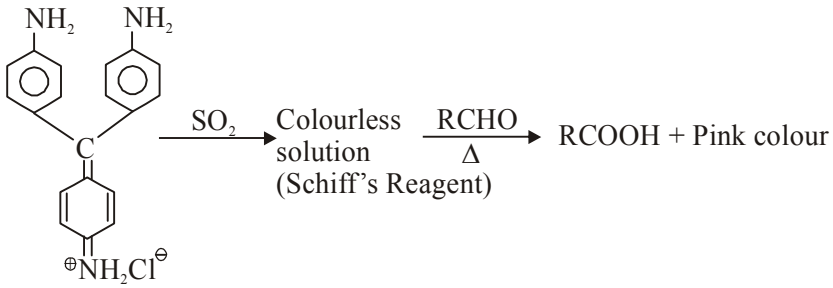
4. $RCHO + HgCl_2 + H_2O \xrightarrow[\Delta]{} RCOOH + 2HCl + Hg_2Cl_2$ (white)

$RCHO + Hg_2Cl_2 + H_2O \xrightarrow[\Delta]{} RCOOH + 2HCl + 2Hg \downarrow$ greyish black

5. **Schiff's Reagent**

Schiff's Reagent is aq. solution of following base decolourised by passing SO_2.

Aldehyde restore pink colour of Schiff's reagent.



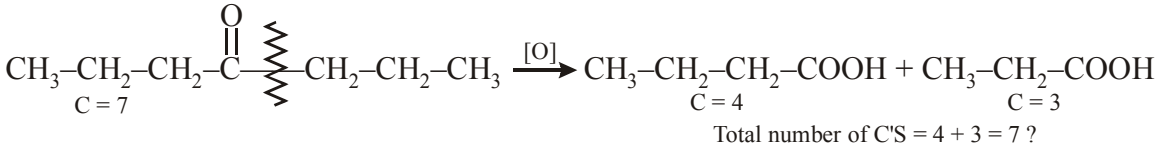
p-Rosaniline Hydrochloride
Magenta colour (Fuschin)

Ketons are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2,4 DNP test

Oxidation of ketones : Ketones undergo oxidation only in drastic conditions.

During the oxidation of ketones there is breaking of carbon-carbon bond between α-carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

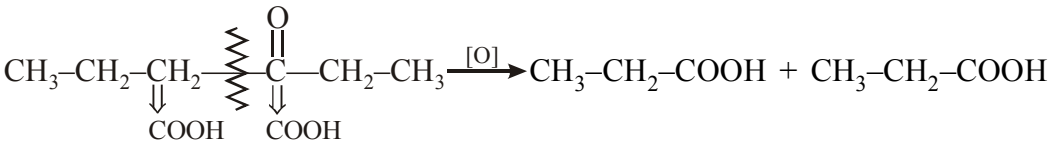
Case - I : Oxidation of Symmetrical ketones :



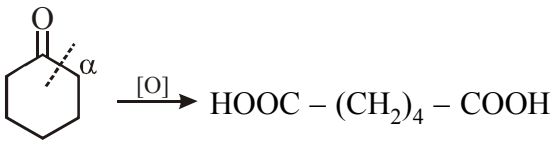
Total number of C'S = 4 + 3 = 7 ?

Thus number of carbons in any product is less than the number of carbons in ketone.

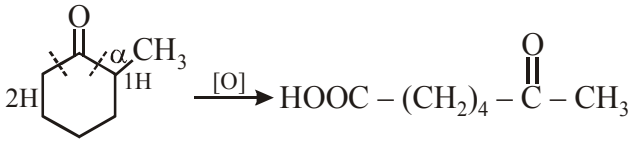
Case - II : Oxidation of unsymmetrical ketones : In case of unsymmetrical ketones, those —C(=O)—R bond break in which alkyl group has more number of carbons. This rule is known as **Poff's rule.**



Case - III : Oxidation of cyclic ketones : Formation of dibasic acid takes place from cyclic ketones. In this case number of carbons in ketone and dibasic carboxylic acid is always same.

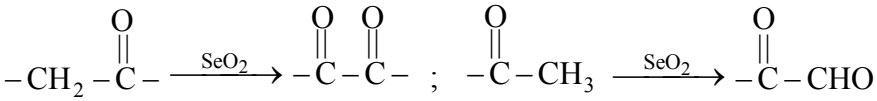


Note : If both α-carbons are not identical then ;

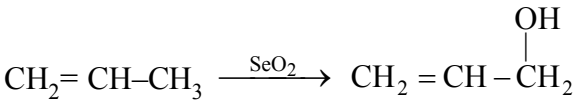


Allylic oxidation

SeO_2 is a selective oxidizing agent with converts $-CH_2-$ group adjacent to carbonyl group into carbonyl group.The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.

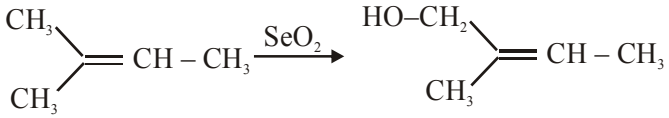


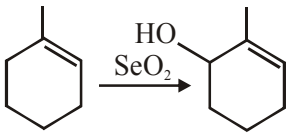
Double bonds, triple bonds and aromatic rings may also activate the methylene group.The methylene or methyl group α to the most highly substitued end of the double bond is hydroxylated according to the order of preference of oxidation $CH_2 > CH_3 > CH$ groups.



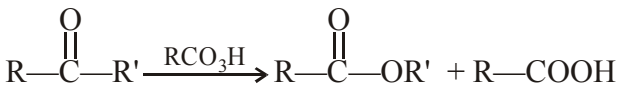
$2° C-H > 1° C-H > 3° C-H$

Rate of reactivity order





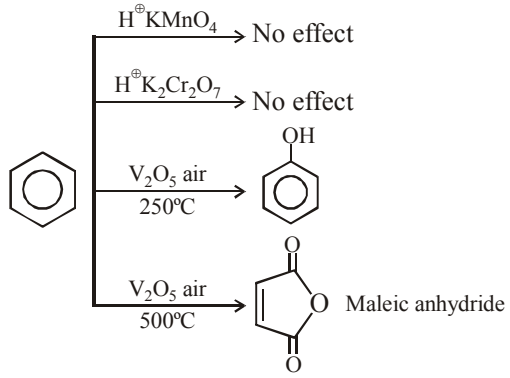
Baeyer villiger oxidation

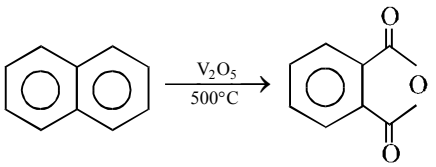


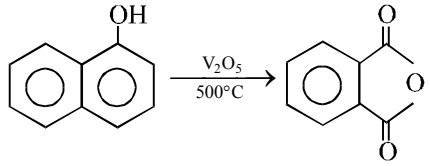
Migratory order for above reaction

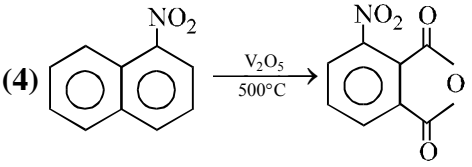
–H > 3º > 2º > –Ph > 1º > –Me

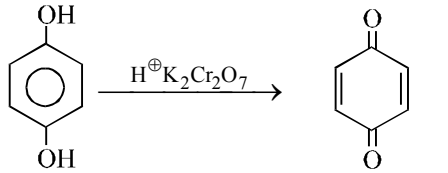
Oxidation of Aromatic Compounds.

(1) 

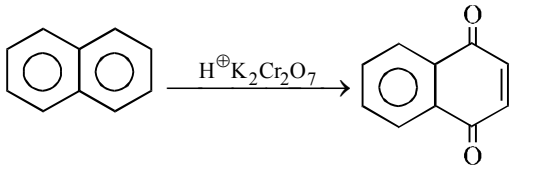
(2) 

(3) 

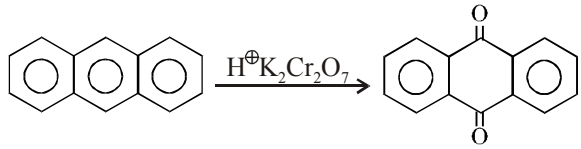
(4) 

(5) 

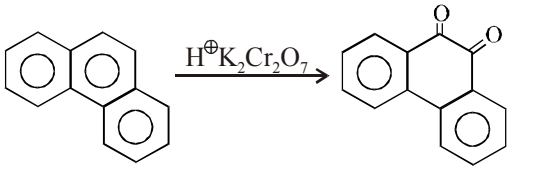
Benzoquinone

(6) 

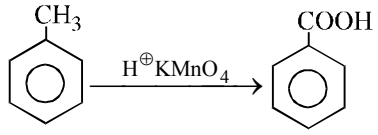
Naphthoquinone

(7) 

Anthraquinone

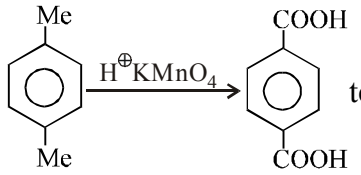
(8) 

Phenanthroquinone

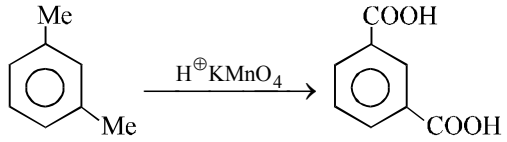
(9) 

(10) $Ph\text{-}(CH_2)_n CH_3$, $PhCHMe_2$, $Ph–CH_2OH$, $Ph–CH_2Br$, $PhCHCl_2$, PhCHO, Ph-  & all the compounds having at least one α H give PhCOOH.

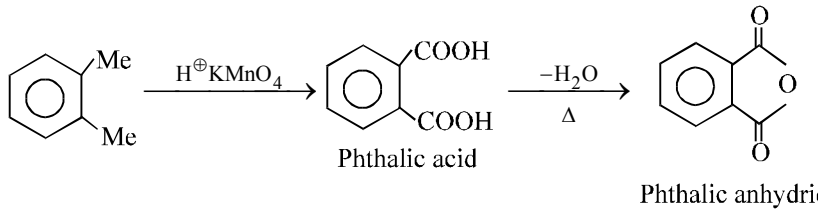
(11) $Ph–CMe_3 \xrightarrow[\Delta]{H^{\oplus}KMnO_4} Me_3C–COOH$

(12) 

terephthalic acid

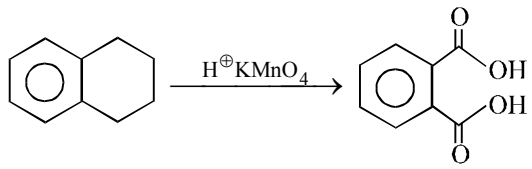
(13) 

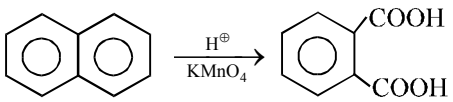
isophthalic acid

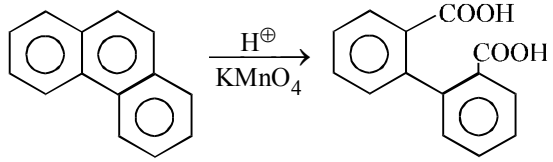
(14) 

Phthalic acid

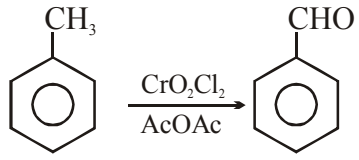
Phthalic anhydride

(15) 

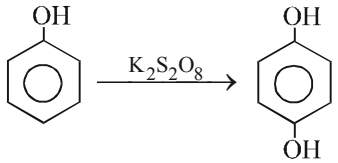
(16) 

(17) 

Etard oxidation

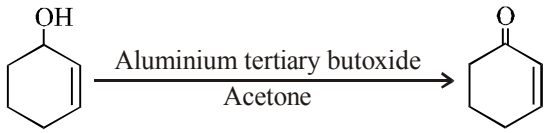
(18) 

Elb's persulphate oxidation:

(19) 

EXERCISE # O-I

1. The given reaction

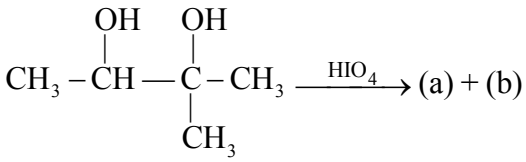


is knows as :

(A) Kolbe reaction (B) Tischenko reaction (C) MPV reaction (D) Oppeneur oxidation

OX0001

2. In the given reaction :



(a) and (b) respectively be :

(A) CH_3CHO and CH_3CHO (B) CH_3COCH_3 and CH_3CHO

(C) CH_3COCH_3 and CH_3COCH_3 (D) CH_3COOH and CH_3COCH_3

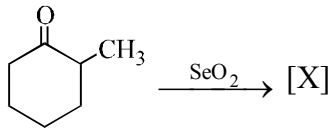
OX0002

3.  and is differentiated by

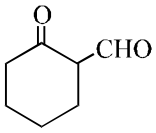
(A) Tollen's reagent (B) Lucas test (C) Iodoform test (D) $NaHSO_3$ test

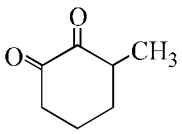
OX0003

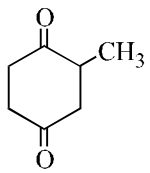
4. In the given reaction

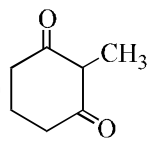


[X] will be:

(A) 

(B) 

(C) 

(D) 

OX0004

5. Which will give silver mirror test with Tollens reagent :

(A) C_6H_5CHO (B) CH_3–CHO (C) HCOOH (D) All of these

OX0005

6. Which one of the following compounds will give dimethyl glyoxal with SeO_2:

(A) Acetone (B) Acetophenone

(C) Ethyl methyl ketone (D) Propanaldehyde

OX0006

7. Which one of the following alcohols can be oxidised by K_2CrO_4?

(A) Ethanol (B) Tert butyl alcohol

(C) Isopropyl alcohol (D) Allyl alcohol

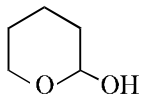
OX0007

8. Fehling solution gives red precipitate with:

(A) Aromatic aldehyde (B) Aliphatic aldehyde (C) Ketones (D) $CH_2(OH)-C(=O)-CH_3$

OX0008

9. Which of the following compound will give positive Tollens test

(A) CH_3CHO (B) 

(C) $CH_3CH_2CH_2CH_2CH(OH)-OCH_3$ (D) $CH_3-CH(OCH_3)_2$

OX0009

10. Schiff's reagent gives pink colour with :

(A) Acetaldehyde (B) Formic acid (C) Acetic acid (D) Methyl acetate

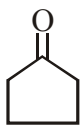
OX0010

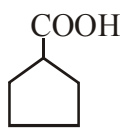
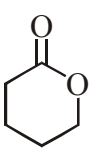
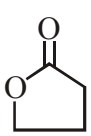
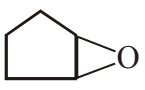
11. Which one of the following alcohols are oxidised by MnO_2?

(A) $C_6H_5-CH_2-CH_2-OH$ (B) $CH_2=CH-CH_2-CH(OH)-CH_3$

(C) $CH_3-CH=CH-CH(OH)-CH_3$ (D) $CH_3-CH_2-CH_2-OH$

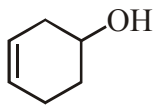
OX0011

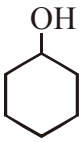
12.  $\xrightarrow{MCPBA}$ Major product is :

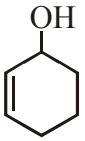
(A)  (B)  (C)  (D) 

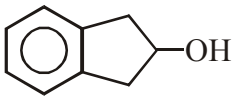
OX0012

13. Which of the following can be oxidised by MnO_2:

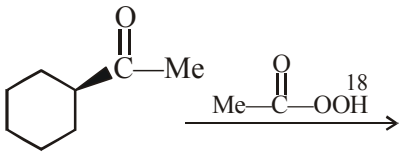
(A) 

(B) 

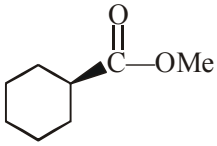
(C) 

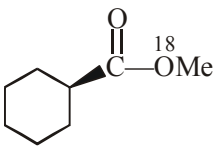
(D) 

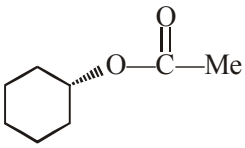
OX0013

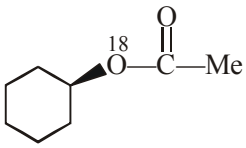
14. 

Major product is :

(A) 

(B) 

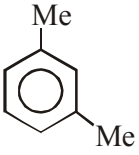
(C) 

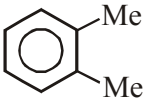
(D) 

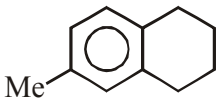
OX0014

15. A $\xrightarrow{H^+ / KMnO_4}$ B $\xrightarrow{\Delta}$ Phthalic Anhydride ; A is :

(A) 

(B) 

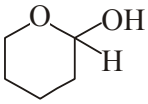
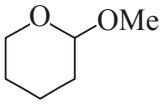
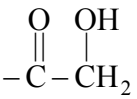
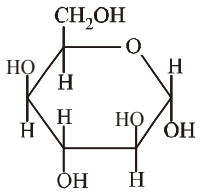
(C) 

(D) 

OX0015

EXERCISE # O-II

1. Which will give the Tollen test.

(A)  (B)  (C)  (D) 

OX0016

2. Which of the following is an example of oxidation reaction :

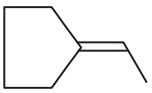
(A) $CH_3 - CH_2 - OH \xrightarrow{PCl_3}$ (B) $CH_3 - CH = CH_2 \xrightarrow{Ni/H_2}$ (C) $CH_3 - CH = CH_2 \xrightarrow[CCl_4]{Br_2}$

OX0017

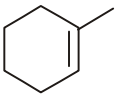
3. (i) $CH_2 = CH_2 \xrightarrow{H^\oplus / KMnO_4}$ **OX0018**

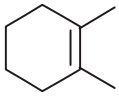
(ii) $CH_3–CH= CH_2 \xrightarrow{H^\oplus / KMnO_4}$ **OX0019**

(iii)  **OX0020**

(iv)  **OX0020**

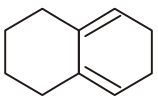
(v)  **OX0021**

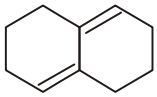
(vi)  **OX0021**

(vii)  **OX0022**

(viii)  **OX0022**

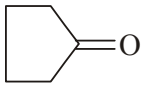
(ix)  **OX0023**

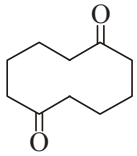
(x)  **OX0023**

(xi)  **OX0023**

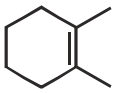
4. A to F alkenes with minimum possible carbon.

(i) $A \xrightarrow[\Delta]{H^{\oplus}/KMnO_4} MeCOOH$ as the only product **OX0024**

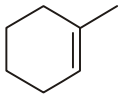
(ii) $B \xrightarrow[\Delta]{H^{\oplus}/KMnO_4}$  as the only product **OX0024**

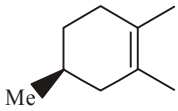
(iii) $D \xrightarrow[\Delta]{H^{\oplus}/KMnO_4}$  **OX0025**

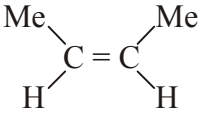
(iv) $F \xrightarrow[\Delta]{H^{\oplus}/KMnO_4}$ Acetone + Ethanoic acid **OX0025**

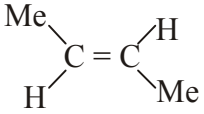
5. (i)  $\xrightarrow[KMnO_4]{1\%\text{ alkaline}}$ A

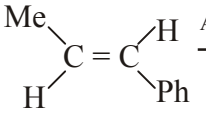
$\xrightarrow{m\text{-CPBA} / H_3O^+}$ B **OX0026**

(ii)  $\xrightarrow{mCPBA}$ **OX0026**

(iii)  $\xrightarrow[\text{hydrolysis}]{mCPBA}$ **OX0027**

(iv)  $\xrightarrow[\text{hydrolysis}]{mCPBA}$ **OX0027**

(v)  $\xrightarrow[\text{hydrolysis}]{mCPBA}$ **OX0028**

(vi)  $\xrightarrow[\Delta]{Ag_2O \text{ or } 2Ag + \frac{1}{2}O_2}$ **OX0028**

6. (i) $CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4/OH^-,\Delta} ?$

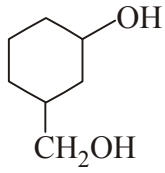
$\xrightarrow[\text{or conc. } HNO_3, \Delta \text{ or } KMnO_4/H^+, \Delta]{K_2Cr_2O_7/H^+, \Delta}$

(ii) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[\text{or } K_2Cr_2O_7, H^{\oplus}]{KMnO_4, H^{\oplus}} ?$ **OX0029**

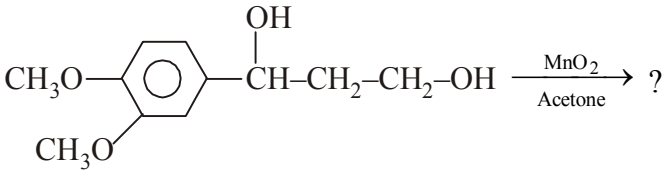
7. (i) $CH_2=CH-(CH_2)_3-CH_2-OH \xrightarrow[\text{in glacial acetic acid}]{\text{Chromic anhydride}}$ **OX0030**

(ii) $C_6H_5-CH=CH-CH_2-OH \xrightarrow[\text{in glacial acetic acid}]{\text{Chromic anhydride}}$ **OX0030**

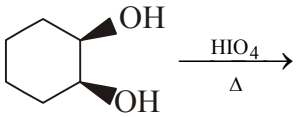
(iii) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-CH_2-OH \xrightarrow[CH_2Cl_2]{PCC}$ (A) **OX0030**

(iv)  **OX0031**

(v) $CH_2 = CH - CH_2 - OH \xrightarrow{MnO_2} ?$ **OX0031**

(vi)  **OX0031**

8. (i) $Me - \underset{\underset{OH}{|}}{CH} - CH_2 - OH \xrightarrow[\Delta]{HIO_4}$ **OX0032**

(ii)  **OX0032**

(iii) $HO - CH_2 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - OH \xrightarrow[\Delta]{HIO_4}$ **OX0032**

(iv) $\underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow[\Delta]{HIO_4}$ **OX0032**

(v) $\underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH_2} \xrightarrow[\Delta]{HIO_4}$ **OX0033**

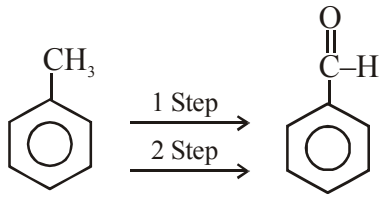
(vi) $Me - \underset{\underset{O}{||}}{C} - \underset{\underset{OH}{|}}{CH} - Me \xrightarrow[\Delta]{HIO_4}$ **OX0033**

(vii) $Me - \underset{\underset{O}{||}}{C} - \underset{\underset{O}{||}}{C} - Me \xrightarrow[\Delta]{HIO_4}$ **OX0033**

9. (a) $CH_3 - CHO \xrightarrow[\Delta]{SeO_2}$ **OX0034**

(b) $Me_2CO \xrightarrow[\Delta]{SeO_2}$ **OX0034**

(c) $CH_3 - CH = CH_2 \xrightarrow{?}$ Acrolein **OX0034**

(d) 

OX0035

(e) $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{SeO_2} P_1 \xrightarrow{\text{Conc. NaOH}} \underset{\underset{COO^-Na^+}{|}}{CH_2OH} \xrightarrow{H^+/\Delta} P_2$

OX0036

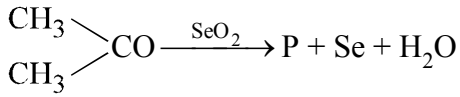
10. (a) How will you differentiate HCHO and PhCHO ?

(b) How will you differentiate HCHO and MeCHO ?

OX0037

EXERCISE # (MAIN & ADVANCED)

1. In the reaction, P is **[IIT 1995]**



(A) CH_3COCHO (B) CH_3COOCH_3 (C) CH_3COCH_2OH (D) None

OX0038

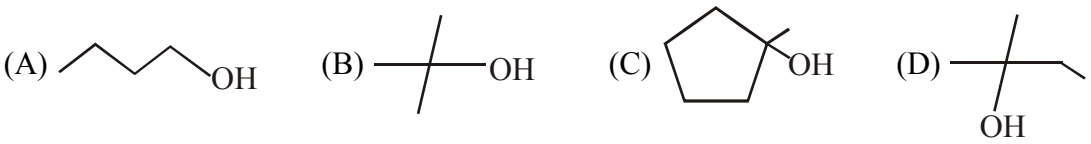
2. The best reagent to convert pent–3–en–2–ol into pent –3–en –2–one is - **[AIEEE-2005]**

(A) Acidic dichromate (B) Acidic permanganate
(C) Pyridinium chloro-chromate (D) Chromic anhydride in glacial acetic acid

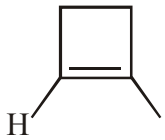
OX0039

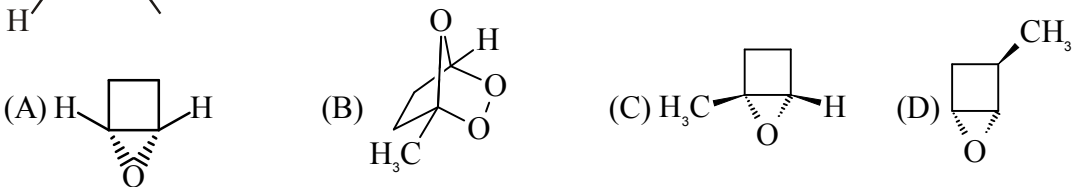
3. Which of the following will change the colour of acidic dichromate solution.

[JEE-MAINS 2013]

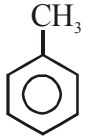


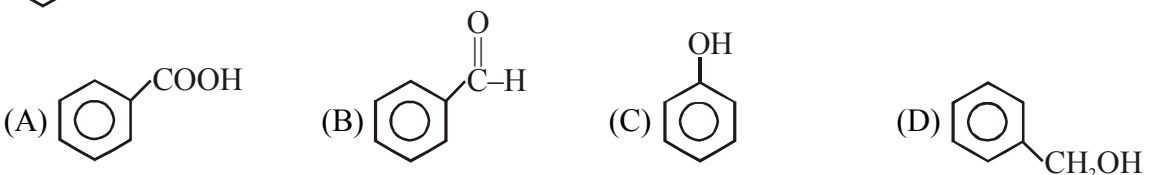
OX0040

4.  Product **[JEE-MAINS 2013]**



OX0041

5.  Major product of reaction is? **[JEE-MAINS 2013]**



OX0042

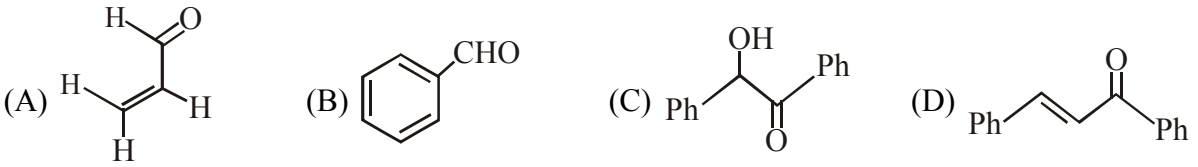
6. The most suitable reagent for the conversion of $R–CH_2–OH \rightarrow R–CHO$ is :-

[JEE-MAINS 2014]

(A) CrO_3 (B) PCC (Pyridinium chlorochromate)
(C) $KMNO_4$ (D) $K_2Cr_2O_7$

OX0043

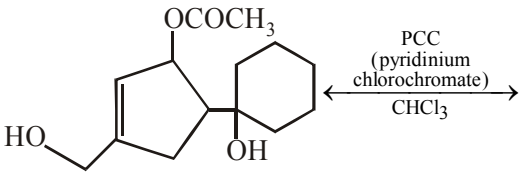
7. Positive Tollen's test is observed for **[JEE-Advance 2016]**

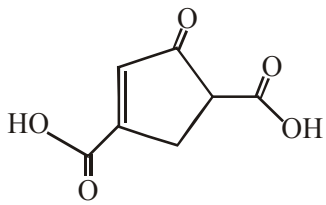


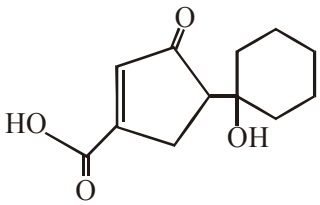
OX0044

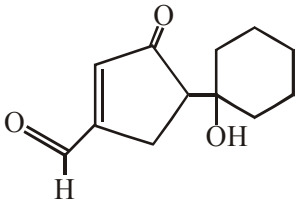
8. The major product formed in the following reaction is :-

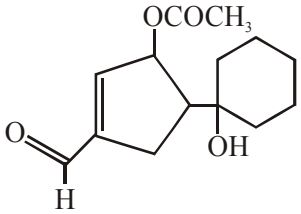
[Jee Main - Onl_line Evening 2018]



(A) 

(B) 

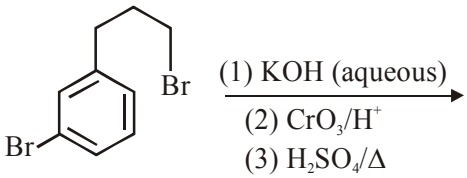
(C) 

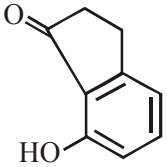
(D) 

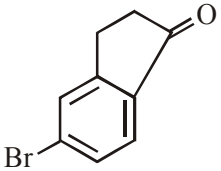
OX0045

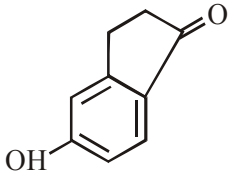
9. The major product of the following reaction is:

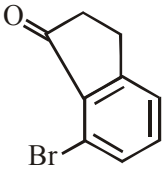
[JEE-MAIN-On-line-(Jan)-2019]



(1) 

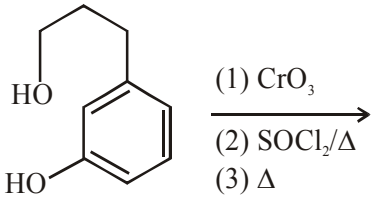
(2) 

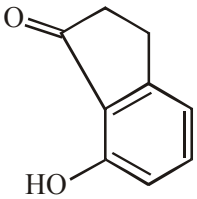
(3) 

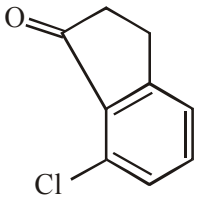
(4) 

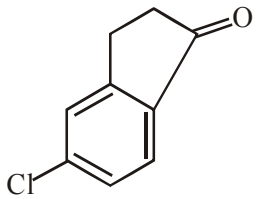
OX0046

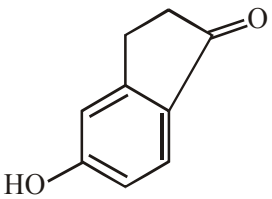
10. The major product of the following reaction **[JEE-MAIN-On-line-(April)-2019]**



(1) 

(2) 

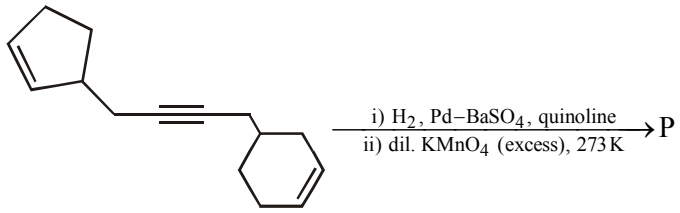
(3) 

(4) 

OX0047

11. Total number of hydroxyl groups present in a molecule of the major product P is ___

[JEE-Advance 2019]



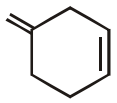
OX0048

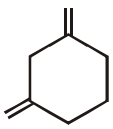
12. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenattion, and also gives following reaction : **[JEE-MAIN-On-line-(Jan)-2020]**

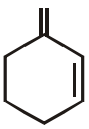
$$X \xrightarrow[Zn/H_2O]{O_3} A \xrightarrow{[Ag(NH_3)_2]^+}$$

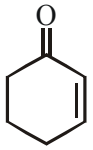
B(3 - oxo - hexanedicarboxylic acid)

X will be :-

(1) 

(2) 

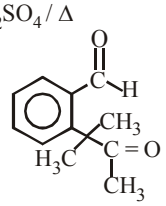
(3) 

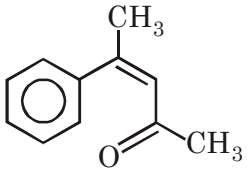
(4) 

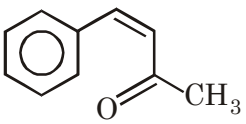
OX0049

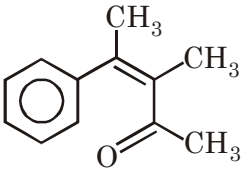
13. Identify (A) in the following reaction sequence : **[JEE-MAIN-On-line-(Jan)-2020]**

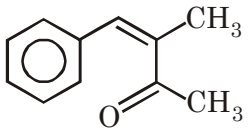
(A) Gives positive iodoform test $\xrightarrow[\text{(ii) } H^+, H_2O]{\text{(i) } CH_3MgBr} (B) \xrightarrow[\text{(iii) Conc. } H_2SO_4 / \Delta]{O_3 / Zn, H_2O}$



(1) 

(2) 

(3) 

(4) 

OX0050

ANSWER KEY

EXERCISE # O-I

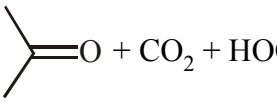
1.	**Ans. (D)**	**2.**	**Ans. (B)**	**3.**	**Ans. (A)**	**4.**	**Ans. (B)**
5.	**Ans. (D)**	**6.**	**Ans. (C)**	**7.**	**Ans. (A,C,D)**	**8.**	**Ans. (B,D)**
9.	**Ans. (A,B,C)**	**10.**	**Ans. (A,B)**	**11.**	**Ans. (C)**	**12.**	**Ans. (B)**
13.	**Ans. (C)**	**14.**	**Ans. (D)**	**15.**	**Ans. (C)**		

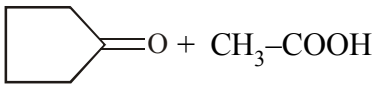
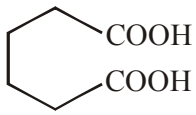
EXERCISE # O-II

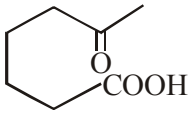
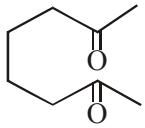
1. **Ans. (A,C,D)** **2.** **Ans. (C)**

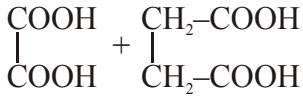
3. **Ans.**

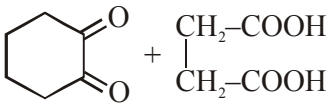
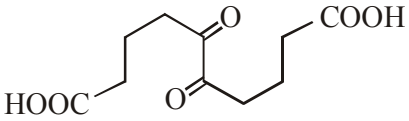
(i) CO_2 (ii) $CH_3–COOH + CO_2$

(iii)  $+ CO_2 + HOOC–C–C–C–COOH$

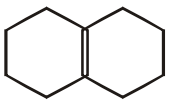
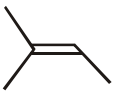
(iv)  (v) 

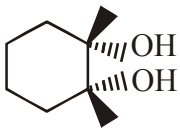
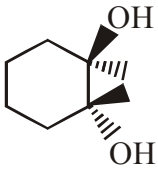
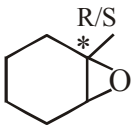
(vi)  (vii) 

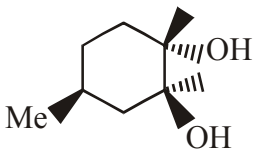
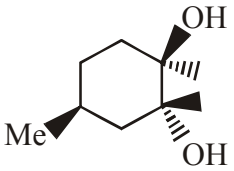
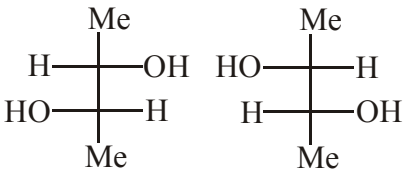
(viii) $2CH_3–COOH$ (ix) 

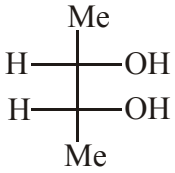
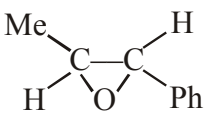
(x)  (xi) 

4. **Ans.**

(i) $Me–CH=CH–CH_3$ (ii)  (iii)  (iv) 

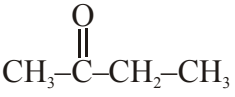
5. **Ans.** (i) (A)  (B)  (ii) 

(iii)   (iv) 

(v)  (vi) 

6. Ans.

(i) $CH_3–CH_2–COO^-$, $CH_3–CH_2–COOH$

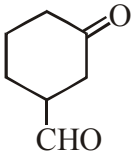
(ii) 

7.

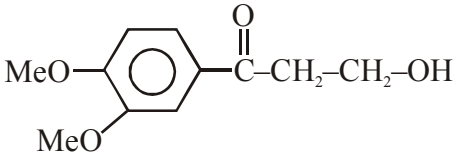
Ans. (i) $CH_2=CH–(CH_2)_3–CHO$

(ii) Ph–CH=CH–CHO

(iii) (A) 

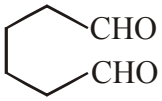
(iv) 

(v) $H_2C=CH–CHO$

(vi) 

8. Ans.

(i) Me–CHO + HCHO

(ii) 

(iii) $HO–CH_2–CH_2–CHO + HCHO$

(iv) $HCHO + HCOOH + CH_3–CHO$

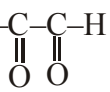
(v) 2HCHO + 2HCOOH

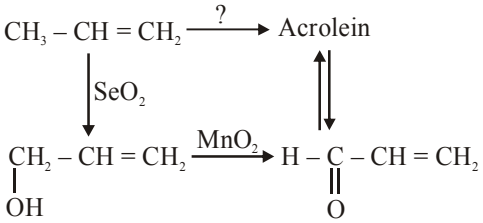
(vi) Me–COOH + Me–CHO

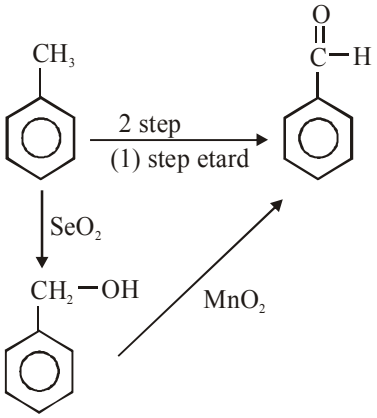
(vii) 2Me–COOH

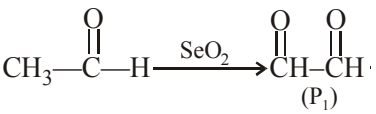
9. Ans.

(a) 

(b) 

(c) 

(d) 

(e) 

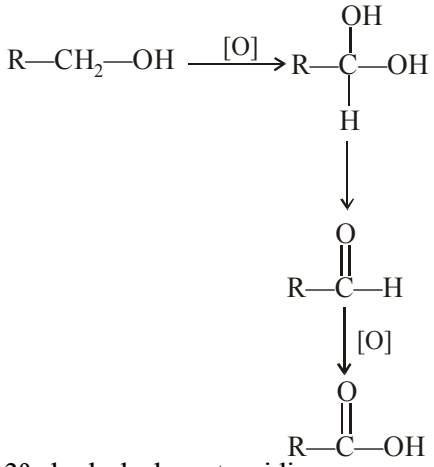
10. (a) Ans. F and B test

(b) Ans. Iodoform test

EXERCISE # (MAIN & ADVANCED)

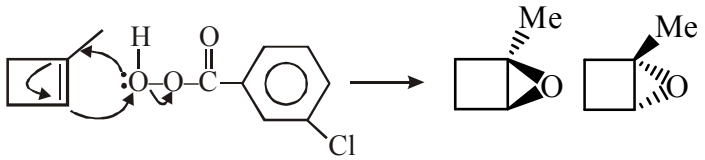
1. **Ans. (A)** **2.** **Ans. (D)**

3. **Ans. (A)**



3º alcohols do not oxidize
they undergo dehydration

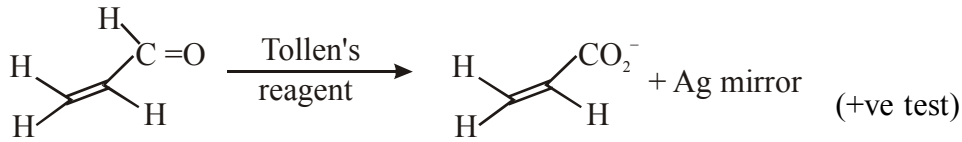
4. **Ans. (C)**



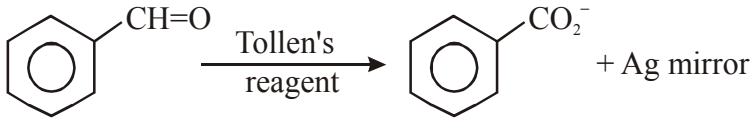
5. **Ans. (A)** **6.** **Ans. (B)**

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

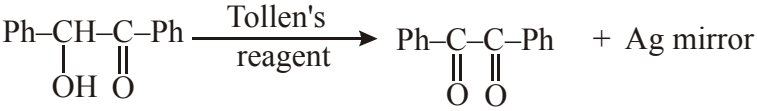
Sol. Tollens's test is given by compounds having aldehyde group. Also α-hydroxy carbonyl gives positive tollen's test.

(A)  (+ve test)

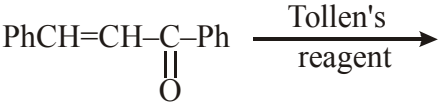
Acraldehyde

(B)  (+ve test)

Benzaldehyde

(C)  (+ve test)

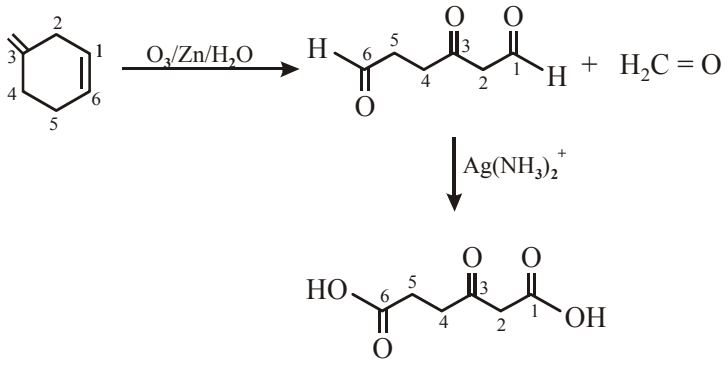
Benzoin

(D) 

8. **Ans. (D)** **9.** **Ans. (2)** **10.** **Ans. (4)** **11.** **Ans. (6.00)**

12. Ans. (1)

Sol.



13. Ans. (4)

Sol.