OXIDATION

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1. Oxidation of alkane:

(a) Complete oxidation or combustion: Burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.

$$C_n H_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \rightarrow nCO_2 + (n+1)H_2O + Q: (\Delta H = -\text{ve})$$

(b) Incomplete oxidation : In limited supply of air gives carbon black and CO.

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \rightarrow C + 2H_2O$$
C-black (used in printing)

(c) Catalytic oxidation:

(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

$$2CH_{4} + O_{2}$$
 Red hot Cu F Fe tube $\rightarrow High P and T$ $2CH_{3}OHCH_{4} + O_{2} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,100 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{2}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000 \ atm} HCHO + H_{3}OHCH_{4} + O_{3} \rightarrow \frac{Mo_{3}O_{3}}{230^{\circ}C,1000$

(ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

$$CH_3(CH_2)_nCH_3 \rightarrow {}_{highTemp}{}^{(CH_3COO)_2Mn}CH_3(CH_2)_nCOOH$$

(iii) Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_{A}$.

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{[O]} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

Illustration 1:

How many litre of Oxygen required for complete combustion of 6.0 g ethane at NTP?

Solution:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O_3$$

60 g ethane required O_2 (at NTP) = 7 × 22.4 litre

1 g ethane required O_2 (at NTP) = $\frac{7 \times 22.4}{2 \times 30}$ litre

6 g ethane required O_2 (at NTP) = $\frac{7 \times 22.4}{2 \times 30} \times 6 = 15.68$ litre

2. Oxidation of alkenes:

Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

(a) alkene on combustion gives CO_2 and H_2O

$$C_n H_{2n} + \frac{3n}{2} O_2 \rightarrow nCO_2 + nH_2O$$

One mole of alkene requires $\frac{3n}{2}$ moles of O_2 for complete combustion.

Illustration 2:

90 mL of oxygen is required for complete combustion of unsaturated 20 mL gaseous hydrocarbon, hydrocarbon is? **Solution:**

Following two formula can be used for solution of the above asked question.

$$\frac{\textit{Volume of Hydrocarbon}}{\textit{Volume of O}_2} = \frac{2}{3n}$$
 (for Alkene)

$$\frac{Volume \ of \ Hydrocarbon}{Volume \ of \ O_2} = \frac{2}{3n-1}$$
 (for Alkyne)

By putting the values in above formula, we can find the hydrocarbon for which n is natural number.

$$\frac{20}{90} = \frac{2}{3n} n = 3$$
 So hydrocarbon is Propene $\left[C_3 H_6\right]$

Illustration 3:

How many mole of oxygen is required for complete combustion of 1 mole of Alkene.

Solution:

$$2C_nH_{2n} + 3nO_2 \rightarrow 2nCO_2 + 2nH_2O$$

keeping in mind, the above equation.

- \because for 2 mole of Alkene, 3n mole of O_2 is required for combustion.
- \therefore for 1 mole of Alkene, $\frac{3n}{2}$ mole of O_2 is required for combustion.
- = 1.5n mole of O_2

Illustration 4:

30 mL mixture of ethylene and Butylene is burnt in presence of oxygen then 150 mL of oxygen is required, what is the volume of Ethylene & Butylene in mixture.

Solution:

Let the volume of $C_2H_4 = xmL$

So volume of Butylene = (30 - x)mL

For
$$C_2H_4$$
, $C_2H_4 + 30_2 \rightarrow 2CO_2 + 2H_2O$

from equation

- \because for 1 volume C_2H_4 , 3 volume of O_2 is required.
- \because for x ml vol. of C_2H_4 , 3xml volume of O_2 is required.

For
$$C_4 H_8$$
, $C_4 H_8 + 60_2 \rightarrow 4C0_2 + 4H_20$

- \because for 1 volume C_4H_8 , 6 volume of O_2 is required.
- : for (30 x)ml volume C_4H_8 ", 6(30 x)ml of O_2 is required.

Total volume of $O_2 = 3x + 6(30 - x)ml = 150ml$ (Given)

$$x = 10$$

- \because Volume of C_2H_4 in mixture is 10 ml
- : Volume of C_2H_4 in mixture is 20 ml

(b) Hydroxylation: Oxidation of carbon-carbon double bond to OHOH is is mown as hydroxylation.

(i) Oxidation by Baeyer's reagent (A test for unsaturation): Alkenes on passing through dilute alkaline 1% cold $KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $KMnO_4$ and gives brown ppt MnO_2 and glycol.

(ii) By OsO_4 :

(iii) By peracid:

(c) Epoxidation:

(i) Alkenes reacts with oxygen in the presence of Ag catalyst at $250^{\circ} - 400^{\circ}C$ to form epoxide.

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag} CH_2 - CH_2 \xrightarrow{H_2O} CH_2 - CH_2$$

$$\downarrow OH$$

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag} CH_2 - CH_2 \xrightarrow{(anti addition)} CH_2 - CH_2$$

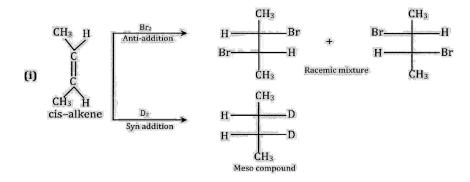
(ii) When an alkene is treated with perbezoic acid an epoxide is formed.

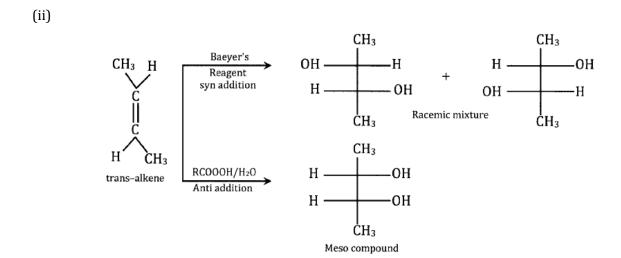
RCH=CH₂ + C₆H₅COOOH
$$\longrightarrow$$
 R—CH \longrightarrow CH₂ O + C₆H₅COOH \longrightarrow Expoxide

Emmons have found that perbenzoic oxy trifluoroacetic acid (CF_3COOH) is a very good reagent for epoxidation and hydroxylation.

Syn addition on alkene $\rightarrow H_2O_2$, Baeyer's reagent, OsO_4/H_2O Anti addition on alkene $\rightarrow X_2$, HOX, $RCOOH/H_2O$, Ag_2O/H_2O

Example:





(d) Oxidation by strong oxidising agent (Oxidative cleavage): The alkenes themselves are readily oxidised to acid or ketone by means of acid permanganate or acid dichromate. If HCOOH is formed, it further oxidized to CO_2 and H_2O . Keep it in mind that no further oxidation of ketones will takes place.

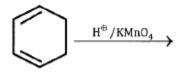
$$\begin{split} CH_{2} &= CH_{2} + 4[O] {\longrightarrow} 2HCOOH {\rightarrow}^{2[0]} 2CO_{2} + H_{2}O \\ CH_{3}CH &= CH_{2} {\rightarrow}^{5[0]} CH_{3}COOH + CO_{2} + H_{2}O \\ CH_{3}CH &= CHCH_{3} {\rightarrow}^{4[0]} 2CH_{3}COOH \end{split}$$

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}$$
 $C=CH_2 \xrightarrow{4[0]} \begin{array}{c} CH_3 \\ CH_3 \end{array}$ $C=0+CO_2+H_2O$

(e) Oxidation with retention of Carbon-Carbon bond - (Waker process) :

$$CH_2 = CH_2 + H_2O_2 \xrightarrow{PdCl_2} CH_3CHO$$

Illustration 5:



Solution:

$$\begin{array}{ccc} \text{COOH} & \text{CH}_2\text{--COOH} \\ \mid & + \mid \\ \text{COOH} & \text{CH}_2\text{--COOH} \end{array}$$

Illustration 6:

(i)
$$\begin{array}{c}
1\% \text{ alkaline} \\
KMnO_a
\end{array}$$

$$\xrightarrow{\text{m-CPBA/H}_3O^{\oplus}} B$$

(iv)
$$H$$
 $C = C \underbrace{\begin{array}{c} Me \\ mCPBA \\ hydrolysis \end{array}}$

(v)
$$H$$
 $C = C$ H $\frac{\text{mCPBA}}{\text{hydrolysis}}$

(vi)
$$H$$
 $C = C \xrightarrow{H} \frac{Ag_2O \text{ or } 2Ag + \frac{1}{2}O_2}{\Delta}$

Solution:

Illustration 7:



(A) H (B)
$$H_3$$
 (C) H_3 (D) H_4 (D)

Ans. (C)

Solution:

3. Ozonolysis: (A test for unsaturation in molecule):

- (i) The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.
- (ii) When ozone is passed through an alkene in an inert solvent, it adds across the double bond to form an ozonide. Ozonides are explosive compound they are not isolated.
- (iii) On warming with Zn and H_2O , ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.

Example:

$$\begin{array}{cccc} CH_3-C=CH-CH_3 & \xrightarrow{Ozonolysis} & CH_3-C=O+CH_3CHO \\ & & & & & \\ CH_3 & & & & CH_3 \end{array}$$

(iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.

Example:

It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond. In an reduction of ozonide by $LiAlH_A$ or $NaBH_A$ gives corresponding alcohols.

$$R'$$
— CH CH — R'' — CH_2OH CH_2O

4. Oxidation of Alkyne:

(a) Combustion:

$$C_n H_{2n-2} + \left(\frac{3n-1}{2}\right) O_2 \longrightarrow nCO_2 + (n-1)H_2O + \text{Heat}$$

 $2HC \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312 \text{ K. ccal}$

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp $(3000^{\circ}C)$ is produced.

(b) Oxidation with alkaline $KMnO_4$: Oxidation with alkaline $KMnO_4$ gives carboxylic acids.

$$\begin{array}{c} \text{CH} & \xrightarrow{\text{alk.KMnO}_4} & \text{COOH} \\ \parallel & +4[0] & \xrightarrow{\text{alk.KMnO}_4} & \mid \\ \text{COOH} \\ \text{Acetylene} & \text{Oxalic acid} \\ \\ \textit{CH}_3 - \textit{C} \equiv \textit{CH} + 4[\textit{O}] \rightarrow & \text{alk.KMnO}_4 \textit{CH}_3 - \textit{COOH} + \textit{HCOOH} \end{array}$$

(c) Oxidation with acidic $KMnO_4$ or $K_2Cr_2O_7$: In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$. Alkynes are oxidised to monocarboxylic acids.

$$R-C \equiv C-R' + 2[O] \longrightarrow R-C-C-R' \xrightarrow{H_2O+[O]} RCOOH + R'COOH$$

$$CH \\ \parallel + 2[O] \longrightarrow CHO \\ CHO \longrightarrow CHO$$

glyoxal
$$CH_3-C \equiv CH + 2[0] \longrightarrow CH_3 - C = 0 \xrightarrow{H_2O+[0]} CH_3COOH + HCOOH$$

$$CHO$$

Illustration 8:

An alkyne on oxidation with acidic KMnO_4 , only acetic acid is obtained what is given alkynes ?

Solution:

In Oxidation of alkynes two moles of mono carboxylic acids are obtained.

$$CH_3 - C - OH + HO - C - CH_3 \longrightarrow CH_3 - C \equiv C - CH_3$$

$$0 \qquad \qquad 2-Butyne$$

(d) Oxidation with selenium dioxide: Selenium dioxide oxidises alkynes to the dicarbonyl compounds.

$$\begin{array}{c} \text{CH} & \underset{\text{SeO}_2}{2[0]} & \underset{\text{CHO}}{\text{CHO}} \\ \text{CHO} & \underset{\text{Glyoxal}}{\text{Glyoxal}} \end{array}$$

$$\begin{array}{c} \text{CH}_3 - \text{C} \\ \text{CH}_3 - \text{C} \\ \text{CH}_3 - \text{C} \end{array} \qquad \begin{array}{c} \underset{\text{SeO}_2}{2[0]} & \underset{\text{CH}_3}{\text{CH}_3 - \text{CO}} \\ \text{CH}_3 - \text{CO} \end{array}$$

$$\begin{array}{c} \text{CH}_3 - \text{CO} \\ \text{CH}_3 - \text{CO} \\ \text{CH}_3 - \text{CO} \end{array}$$

$$\begin{array}{c} \text{CH}_3 - \text{CO} \\ \text{CH}_3 - \text{CO} \\ \text{CH}_3 - \text{CO} \end{array}$$

(e) Oxidation with ozone ((O_3) : In the ozonolysis both sp-C-atoms are converted into -C-C - group.

$$R-C = C-R+O_3 \longrightarrow R-C-C-R \longrightarrow R-C-C-R+H_2O_2 \longrightarrow R-C-OH+R-C-OH$$

$$0 \longrightarrow 0 \longrightarrow 0$$
Ozonide
(Addition of ozone)
$$R-C-C-R$$

$$0 \longrightarrow 0 \longrightarrow 0$$

$$0 \longrightarrow$$

In this reaction H_2O_2 is oxidant which oxidize $\begin{array}{ccc} R-C-C-R & & & \\ II & II & \\ O & O & \\ & & \text{nto acids.} \end{array}$

But if we use some amount of Zn as reductant with H_2O then it reduce H_2O_2 so oxidation does not take place $H_2O_2 + Zn \rightarrow ZnO + H_2O$

Example:

$$CH_{3}-C=CH \xrightarrow{(i) \ O_{3}} CH_{3}-C-C-H+H_{2}O_{2} \xrightarrow{C} CH_{3}-C-OH+HCOOH$$

$$O \quad O \quad O$$

$$(i) \ O_{3}$$

$$(ii) \ H_{2}O/Zn \xrightarrow{C} CH_{3}-C-C-H+ZnO$$

$$O \quad O \quad O$$

5. Oxidation of alcohols:

(a) Oxidation of alcohol by $KMnO_4$:

- 1. $KMnO_4$ is a very strong oxidising agent.
- 2. It never depends upon the type of medium used.
 - i. Primary alcohol

$$RCH_2OH \rightarrow {}^{KMnO_4}RCOOH$$

ii. Secondary alcohol

$$\begin{array}{ccc} R_1 - CH - OH & \xrightarrow{KMnO_4} & R_1 - C - R_2 \\ \downarrow & & \downarrow \\ R_2 & & O \end{array}$$

iii. Tertiary alcohol

$$\begin{array}{c} R_3 \\ I \\ R_1 - C - OH & \xrightarrow{KMnO_4} & No \ reaction \\ I \\ R_2 \end{array}$$

(b) Oxidation of alcohol by $(CrO_3 + H_2SO_4)$:

3.
$$(CrO_3 + H_2SO_4)$$
 is called of Jones reagent.

It is strong oxidising agent.

i. Primary alcohol

$$RCH_2OH \rightarrow {}^{KMnO_4}RCOOH$$

4.

ii. Secondary alcohol

$$\begin{array}{ccc} R_1 - CH - OH & \xrightarrow{KMnO_4} & R_1 - C - R_2 \\ & & & | & & | \\ & & R_2 & & & O \end{array}$$

iii. Tertiary alcohol

$$R_1$$
 R_1
 R_2
 R_3
 R_4
 R_5
 R_6
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8

(c) Oxidation of alcohol by PCC (Pyridinium chloro chromate):

- 1. It is milder oxidising agent.
- 2. It is efficient reagent to produce aldehydes/ketones from primary/secondary alcohols.

i. Primary alcohol

$$\begin{array}{c} RCH_2OH \xrightarrow{PCC} & R-C-H \\ & || \\ O \end{array}$$

ii. Secondary alcohol

$$\begin{array}{ccc} R_1 - CH - OH & \xrightarrow{PCC} & R_1 - C - R_2 \\ \downarrow & & \downarrow \\ R_2 & & O \end{array}$$

iii. Tertiary alcohol

$$R_{1}$$
 R_{1}
 R_{1}
 R_{2}
 R_{1}
 R_{2}
 R_{1}
 R_{2}
 R_{2}

(d) Oppenaur oxidation

The reaction involves the oxidation of secondary alcohols with a ketone and a base to the corresponding ketone of the alcohol.

$$R \xrightarrow{\text{CH}} \text{OH} \xrightarrow{\text{CH}_3 = \text{CO} = \text{CH}_3} \text{R} \xrightarrow{\text{CO}} \text{R} + \text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$$

$$R_2\text{CH} - \text{OH} + \text{Al}(\text{OCMe}_3)_3 \Longrightarrow \text{Me}_3\text{COH} + \text{Al}(\text{OCHR}_2)_3 \Longrightarrow \text{(R}_2\text{CH} - \text{O)}_2 - \text{Al}_2 - \text{O}_2 - \text{Al}_3 - \text{O}_3 - \text{$$

Oxidation of alcohol with aluminium tertiary butoxide is Openaur oxidation

Two structural requirements for the oxidation to carbonyl products are

- i. The carbon atom bonded to oxygen must also bear a hydrogen atom. Tertiary alcohols $(R_3C OH)$ cannot be oxidized in this fashion.
- ii. The oxygen atom must be bonded to a hydrogen atom so that a chromate ester intermediate (or other suitable

leaving group) may be formed. Ethers (R - O - R) cannot be oxidized in this fashion.

(e) Oxidation by $HIO_{_{4}}$ [per iodic acid] :

When diols reacts with HIO_4 [Periodic acid]. Those diols/ Polyols in which -OH group attached to vicinal C-atom after reaction with HIO_4 forms aldehyde and ketone.

This reaction is also used in identification of no. of OH group in polyol. Reaction is observed for Vic-diols

(f) By dehydrogenation of $(1^{\circ}82^{\circ})$ alcohols:

Dehydrogenation means removal of hydrogen and reagent used is heated copper or silver. The alcohol vapours are passed over heavy metal catalyst to yield the following products.

Condition for oxidation by HIO_4 :

At least 2 — OH or 2
$$C=0$$
 or 1—OH and 1 $C=0$ should be at adjacent carbons.

	SUMMARY	
S. No.	Oxidising agents	Type
1.	$H^{\oplus}/K_{2}Cr_{2}O_{7}$, Δ	Strong
2	$H^{\oplus}/K_{2}Cr_{2}O_{7}$, Δ (Strong oxidising agent)	Strong
3.	Jones reagent: CrO_3/H_2SO_4 treated with alcohol usually taken in acetone	Strong
4.	PCC (Pyridinium chloro chromate) \bigcirc	Milder

5.	Collin's reagent (\bigcirc (2 mol) + CrO ₃ + CH ₂ Cl ₂)	Milder
6.	Sarett reagent (i.e. PCC in CH_2Cl_2) + $CrO_3 + HCl + CH_2Cl_2$	Milder
7.	(Pyridinium dichromate) (Pyr	Milder
8.	$TsCl + DMSO + NaHCO_{3} RCH_{2}OH \rightarrow {}^{Ts-Cl}RCH_{2}OTs \rightarrow {}^{DMSO}_{NaHCO_{3}}RCHO R_{2}CHOH \rightarrow {}^{Ts-Cl}R_{2}CHOH \rightarrow {}^{Ts-Cl}R$	Milder
9.	NBS (N-Bromosuccinamide) N-Br	Milder

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

e.g.

(I) R-CH₂-OH
$$\xrightarrow{1,2,3}$$
 R-C-OH

(II) R-CH₂-OH $\xrightarrow{4,5,6,7,8,9,11}$ R-C-OH

(III) R-CH-R' $\xrightarrow{1,2,3,4,5,6,7,8,9,11}$ R-C-R' (Ketone)

- (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

6. Oxidation of Carbonyl compounds:

1. Tollen's Test (Silver mirror test)

$$RCHO + \left[Ag(NH_3)_2\right]OH \text{ (Tollen's Reagent)} \rightarrow^{\Delta} RCOOH + NH_3 + Ag \downarrow \text{ (Silver mirror)}$$

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 aq.
$$CuSO_4$$

Fehling's B

Alkaline solution of Roschelye

salt (sodium potassium tartrate)

It act's a carrier for $Cu^{2\oplus}$ as it make reversible complex with $Cu^{2\oplus}$. This test is also used is Blood and Urine test.

RCHO +
$$Cu^{2\oplus}$$
 $\xrightarrow{H_2O}$ RCOOH + Cu^{\oplus} \downarrow \downarrow RCOO \ominus Cu_2O (red ppt.)

Note: Aromatic aldehyde shows negative test with fehling reagent.

S.No.	Reactant	Fehling solution	Tollen's Reagent
1.	Glucose, Fructose	+	+
2.	α-hydroxy aldehyde	+	+
3.	α-hydroxy ketone	+	+
4.	Formic acid	+	+
5.	Succinaldehyde	+CHO	+
	CH ₂ —CHO CH ₂ —CHO		
6.	Pyruvaldehyde <i>CH</i> ₃ <i>COCHO</i>	+	+
7.	Glyoxal	-	+
8.	Benzaldehyde and other aromatic aldehyde	-	+
9.	Glyoxylic acid	-	+
	СНО СООН		

3. Benedict's solution

 ${\rm Sodium\ Citrate} + {\it NaOH} + {\it NaHCO}_{3} + {\it CuSO}_{4}$

$$\begin{array}{ccc} RCHO + Cu^{2\oplus} & \xrightarrow{H_2O} & RCOOH + Cu^{\oplus} \\ & \downarrow & \downarrow \\ & & \downarrow & \downarrow \\ & & RCOO^{\ominus} & Cu_2O \text{ (red ppt.)} \end{array}$$

It is similar to Fehling test

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

$$RCHO + Hg_2Cl_2 + H_2O \rightarrow_{\Delta} RCOOH + 2HCl + 2Hg \downarrow \text{greyish black}$$

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.

$$NH_2$$
 NH_2 SO_2 SO_2 SO_3 SO_3 SO_3 SO_3 SO_3 SO_3 SO_4 SO_4 SO_4 SO_5 SO_5

Ketones 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 break in which alkyl group has more number of carbons. This rule is known as Poff's rule.

$$CH_3-CH_2-CH_2 \xrightarrow{Q} C - CH_2-CH_3 \xrightarrow{[0]} CH_3-CH_2-COOH + CH_3-CH_2-COOH$$

$$COOH COOH$$

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.

$$\begin{array}{c}
0\\
 & \xrightarrow{[O]} & \text{HOOC-(CH}_2)_4\text{-COOH}
\end{array}$$

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

$$2H \xrightarrow{O} CH_3 \xrightarrow{[O]} HOOC-(CH_2)_4-C-CH_3$$

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 substituted end of the double bond is hydroxylated according to the order of preference of oxidation $CH_2 > CH_3 > CH$ groups.

$$CH_2=CH-CH_3 \xrightarrow{SeO_2} CH_2=CH-CH_2$$

$$2^{\circ}C - H > 1^{\circ}C - H > 3^{\circ}C - H$$

Rate of reactivity order

$$CH_3-CH=CH-CH_2-CH_3$$
 $\xrightarrow{SeO_2}$ $CH_3-CH=CH-CH_2-CH_3$ \downarrow OH

$$CH_3$$
 CH
 CH_3
 CH
 CH_3
 CH_3
 CH
 CH_3
 CH
 CH_3

$$\begin{array}{c}
 & \text{HO} \\
 & \text{SeO}_2
\end{array}$$

Baeyer villager oxidation

$$\begin{array}{ccc}
0 & 0 \\
\parallel & \parallel \\
R-C-R' & \xrightarrow{RCO_3H} & R-C-OR' + R-COOH
\end{array}$$

Migratory order for above reaction

$$-H > 3^{\circ} > 2^{\circ} > -Ph > 1^{\circ} > -Me$$

7. Oxidation of Aromatic Compounds:

$$\begin{array}{c}
\text{CH}_{3} & \text{COOH} \\
\hline
& & \\
& & \\
\hline
& & \\
& & \\
\end{array}$$

Alkyl group having no a-H atom will not be oxidized to - COOH . Any alkyl group containing at least one a-H atom will be oxidized to -COOH . The product of oxidation will be benzoic acid.

$$CH_2-CH_2-CH_3$$
 COOH

 $KMnO_4/H^{\oplus}$ C(CH₃)₃
 $KMnO_4/H^{\oplus}$ (CH₃)₃-COOH

The order of benzoic acid formation by oxidation of alkyl benzene.

Methyl benzene $> 1^{\circ}$ alkyl benzene $> 2^{\circ}$ alkyl benzene

Phenanthroquinone

(10) $Ph(CH_2)CH_3$, PhCHMe2, $Ph - CH_2OH$, $Ph - CH_2Br$, $PhCHCl_2$, PhCHO, having at least one αH give PhCOOH.

$$(11) Ph - CMe_{3} H^{\oplus} KMnO_{4} \rightarrow Me_{3} C - COOH$$

$$(12) \begin{picture}(12){ll} \hline Me \\ \hline Me \\$$

(14)
$$Me$$
 $H^{\oplus}KMnO_4$
 $COOH$
 $-H_2O$
 Δ
Phthalic anhydride

Etard oxidation

$$(18) \bigcirc \xrightarrow{\text{CrO}_2\text{Cl}_2} \xrightarrow{\text{CHO}}$$

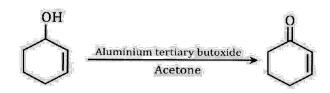
Elb's persulphate oxidatin

$$(19) \bigcirc \longrightarrow \bigcirc \longrightarrow \bigcirc \longrightarrow \bigcirc \longrightarrow \bigcirc$$

SINGLE CORRECT TYPE QUESTIONS

Oxidation of Alcohol

1. The given reaction



is knows as:

- (A) Kolbe reaction
- (C) MPV reaction

- (B) Tischenko reaction
- (D) Oppeneur oxidation

2. In the given reaction:

OH OH
$$\begin{array}{c|c}
CH_3-CH-C-CH_3 & \xrightarrow{HIO_4} & (a) + (b) \\
CH_3 & & \end{array}$$

- (a) and (b) respectively be:
- (A) CH₃CHO and CH₃CHO

(B) CH_3COCH_3 and CH_3CHO

(C) CH_3COCH_3 and CH_3COCH_3

- (D) CH_3COOH and CH_3COCH_3
- 3. Which one of the following alcohols are oxidised by MnO_2 ?

(A)
$$C_6 H_5 - CH_2 - CH_2 - OH$$

(B)

(C)

(D)
$$CH_3 - CH_2 - CH_2 - OH$$

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

Oxidation of Aldehyde and ketone

5.

O O
$$\parallel$$
 \parallel \parallel CH_3-C-CH_3 and CH_3-C-CH_3

is differentiated by

(A) Tollen's reagent

(B) Lucas test

(C) Iodoform test

(D) $NaHSO_3$ test

$$CH_3 \xrightarrow{SeO_2} [X]$$

6. In the given reaction

[X]will be:

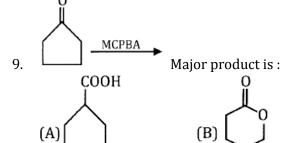
7. Which will give silver mirror test with Tollens reagent:

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

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

- (A) Acetone
- (B) Acetophenone
- (C) Ethyl methyl ketone
- (D) Propanaldehyde

Miscellaneous Oxidising agent







10.

$$C-Me$$
 $Me-C-OOH$
 $Major product is:$
 $C-OMe$
 $C-OMe$

11. $A \ H^{\oplus}/KMnO_4 \rightarrow B \ \Delta \rightarrow Phthalic Anhydride ; A is :$

MULTIPLE CORRECT TYPE QUESTIONS

Oxidation of Alkene

12. An organic compound on reaction with O_3 followed by Zn and H_2O gives $CH_3COCH_2CH_2COCH_3$. The structure(s) is/are

(A)
$$CH_3 - C - CH_2 - CH_2 - C - CH_3$$
 (B) $H_3C - CH_3$ (C) CH_3 (D) CH_3

13. Which of the following give syn addition?

$$(A) \qquad \begin{array}{c} \text{Et} \qquad \text{Et} \qquad \begin{array}{c} \text{(i) KMnO}_4 \\ \text{(ii) H}_2\text{O/OH} \end{array} \end{array} \qquad \begin{array}{c} \text{(B)} \qquad \begin{array}{c} \text{Me} \qquad \begin{array}{c} \text{(i) OsO}_4 \\ \text{(ii) Na}_2\text{SO}_3 \end{array} \end{array}$$

$$(C) \qquad \begin{array}{c} \text{Me} \qquad \begin{array}{c} \text{(i) RCOOH} \\ \text{(ii) H}_2\text{O} \end{array} \end{array} \qquad \begin{array}{c} \text{(b)} \qquad \begin{array}{c} \text{(ii) RCOOH} \\ \text{(iii) H}_2\text{O} \end{array} \end{array} \qquad \begin{array}{c} \text{(c)} \qquad \begin{array}{c} \text{(iii) H}_2\text{O} \end{array} \end{array}$$

14. On oxidation, an unknown alkane C_8H_{16} gives a mixture of propanoic acid and pentanoic acid. The unknown alkene can be

(A) cis-3-octene

(B) trans-3-octene

(C) cis-4-octene

(D) trans-4-octene

Oxidation of Alcohol

- 15. Propan-1-ol and Propan-2-ol can be best distinguished by
 - (A) oxidation with alkaline $KMnO_4$ followed by reaction with H_2O
 - (B) oxidation with PCC followed by reaction with Tollen's reagent
 - (C) oxidation by heating with copper followed by reaction with iodoform test
 - (D) reaction with cone. H_2SO_4 followed by reaction with Fehling solution.

MATRIX MATCH TYPE QUESTION

Oxidation of Alcohol

16. Match the items given in column I with those in column II.

Col	lumn I	Column II			Column III				
a.	HO————————————————————————————————————	p.	$H_2O_2 + NaOH$	i.	Elbs persulphate oxidation				
b.	$ \begin{array}{c} O \\ H \\ Ph - C - CH_3 \end{array} \longrightarrow Ph - O - C - CH_3 $ $ CH_2 $	q.	$CH_3 - C \equiv N,$ $ZnCl_2/HCl$	ii.	BaeyerVilliger oxidation				
c.	HO OH OH OH OH	r.	$K_2 S_2 O_8 + NaOH$	iii.	HoubenRoesch synthesis				
d.	$\overset{\mathrm{OH}}{\longrightarrow}\overset{\mathrm{OH}}{\bigcirc}^{\mathrm{OH}}$	S.	Per acid	iv.	Dakin reaction				

17. Match the items given in column I with those in column II.

(olumn I		Column II
á	$\stackrel{\text{OH}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow}$	p.	MnO_{2}

b	$Ph \xrightarrow{Ph} Ph \xrightarrow{O \qquad O} Ph$	q.	$FeSO_4$ and H_2O_2 (fenton's reagent)
c	$0 \longrightarrow 0$	r.	Jones reagent $(H_2CrO_4$ in aq. acetone)
d	Ph OH OH OH OH OH	s.	CrCO ₃ in glacial acetic acid
e	CH₃COOH + HOOC COOH	t.	SeO ₂ /MeCOOH

EXERCISE - S

Oxidation of Alkene

1.

(i)
$$CH_2 = CH_2 \xrightarrow{H^{\oplus}/KMnO_4}$$

(iii) $\xrightarrow{H^{\oplus}/KMnO_4}$

(vi) $\xrightarrow{H^{\oplus}/KMnO_4}$

(ix) $\xrightarrow{H^{\oplus}/KMnO_4}$

(ii) CH₃-CH= CH₂
$$\xrightarrow{H^{\oplus}/KMnO_4}$$

(iv)
$$\longrightarrow$$
 $\xrightarrow{H^{\oplus}/KMnO_4}$

$$(vi) \overbrace{ \qquad \qquad \stackrel{H^{\oplus}/KMnO_{6}}{\longrightarrow} }$$

(viii)
$$-\frac{H^{\oplus}/KMnO_4}{}$$

$$(x) \xrightarrow{H^{9}/KMnO_{4}}$$

2. A to D alkenes with minimum possible carbon.

(i) A
$$\xrightarrow{H^{\oplus}/KMnO_{\epsilon}}$$
 MeCOOH as the only product

(ii) B
$$\xrightarrow{H^{\oplus}/KMnO_4}$$
 O as the only product

(iii)
$$C \xrightarrow{H^{\oplus}/KMnO_4} A$$

(iv) D
$$\xrightarrow{H^{\oplus}/\text{KMnO}_4}$$
 Acetone + Ethanoic acid

3.

(i)

$$1\% \text{ alkaline} \atop \text{KMnO}_4$$

A

 $m\text{-CPBA/H}_3O^* \rightarrow B$

(iii)

 Me
 $m\text{-CPBA} \rightarrow \text{hydrolysis}$

(v)

 Me
 $C = C$
 Me
 Me

(iv)
$$Me$$
 $C = C$ Me m -CPBA m -hydrolysis m

(vi)
$$\stackrel{\text{Me}}{\longrightarrow} C = C \stackrel{\text{H}}{\longrightarrow} \stackrel{\text{Ag}_2\text{O or } 2\text{Ag}\frac{1}{2}\text{O}_2}{\longrightarrow}$$

Oxidation of Alcohol

4.

(i)
$$CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4/OH^-,\Delta}$$
?
$$\begin{array}{c} K_2Cr_2O_7 / H^+, \Delta \\ \hline or conc. HNO_3, \Delta \end{array} \rightarrow \\ or KMnO_4 / H^+, \Delta \end{array}$$

$$(ii) CH-CH-CH_2-CH_3 \xrightarrow{KMnO_4,H^{\oplus}} ?$$

(iii)
$$CH_3-CH-CH_2-CH_2-CH_2-OH \xrightarrow{PCC \ CH_2Cl_2}$$
 (A)

(iv)
$$OH \xrightarrow{PCC CH_2CI_2}$$

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

(vi)
$$CH_3O$$
 $CH_2CH_2-CH_2-OH$ MnO_2 ?

6.

(i) Me-CH-CH₂-OH
$$\xrightarrow{\text{HIO}_4}$$
 > OH

(iii)
$$HO-CH_2-CH_2-CH-CH_2-OH \xrightarrow{HIO_4}$$

(v)
$$\begin{matrix} CH_2-CH-CH-CH_2 & \xrightarrow{HIO_4} \\ I & I & I \\ OH & OH & OH \end{matrix}$$

(vii) Me-C-C-Me
$$\xrightarrow{\text{HIO}_4}$$
 $\xrightarrow{\Delta}$

(ii)
$$OH \xrightarrow{HIO_4} OH$$

(vi) Me–C–CH–Me
$$\xrightarrow{\text{HIO}_4}$$
 $\xrightarrow{\Delta}$ O OH

Oxidation of Aldehyde and ketone

(a)
$$CH_3 - CHO \frac{SeO_2}{\Delta}$$

(b)
$$Me_2CO \frac{SeO_2}{\Delta}$$

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

(d)
$$CH_3$$

$$1 \text{ Step}$$

$$2 \text{ Step}$$

(e)
$$CH_3$$
— C — H $\xrightarrow{SeO_2}$ P_1 $\xrightarrow{Conc. NaOH}$ \rightarrow CH_2OH $\xrightarrow{H^*/\Delta}$ \rightarrow P_2

- (a) How will you differentiate HCHO and PhCHO?
 - (b) How will you differentiate HCHO and MeCHO?

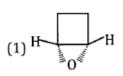
EXERCISE - JEE (Main) PYQ

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

[JEE (Main) 2013]

(1)

2. [JEE (Main) 2013]





3. The most suitable reagent for the conversion of $R - CH_2 - OH \rightarrow R - CHO$ is :-[JEE (Main) 2014]

(1) CrO₃

(2) PCC (Pyridinium chlorochromate)

 $(3) KMNO_{A}$

- $(4) K_{2}Cr_{2}O_{7}$
- The major product formed in the following reaction is:-

[JEE (Main) 2018]

5. The major product of the following reaction is:

$$(2)CrO_3/H^{\oplus}$$
 $(3)H_2SO_4/\Delta$

(2)
 $(3)H_2SO_4/\Delta$

(2)
 $(3)H_2SO_4/\Delta$

(3)
 $(4)H_2SO_4/\Delta$

6. The major product of the following reaction

$$\begin{array}{c}
\text{HO} & \begin{array}{c}
\text{(1) CrO}_3 \\
\text{(2) SOCl}_2
\end{array} \\
\text{(3)} & \begin{array}{c}
\text{(3)} \\
\text{(3)} \\
\text{(4)} \\
\text{(4)}
\end{array}$$

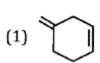
An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenattion, and also gives following reaction : [JEE (Main) 2020]

$$X \quad O_3 \rightarrow_{Zn/H_2O} A \left[Ag(NH_3)_2 \right]^{\bigoplus} \rightarrow$$

7.

B (3-oxo-hexanedicarboxylic acid)

X will be:-









Which of the following reagent is used for the following reaction?

[JEE (Main) 2021]

$$CH_3CH_2CH_3 \rightarrow CH_3CH_2CHO$$

8.

(1) Manganese acetate

(2) Copper at high temperature and pressure

(3) Molybdenum oxide

- (4) Potassium permanganate
- 9. Which one of the following reactions will not form acetaldehyde?

[JEE (Main) 2021]

(1)
$$CH_3CH_2OH \rightarrow Cu_{573 K}$$

2)
$$CH_3CN \rightarrow (ij)H_3C$$

$$(4)$$

$$CH_3CH_2OH \rightarrow CrO_3-H_2SO_4$$

10. Given below are two statements:

(3) $CH_2CN(i)pd[ii]/Cu(ii) \rightarrow_{(ii)H_2O}$

[JEE (Main) 2021]

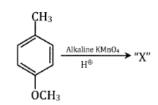
Statement-I : 2-methylbutane on oxidation with $KMnO_A$ gives 2-methylbutan-2-ol.

Statement-II: n-alkanes can be easily oxidised to corresponding alcohols with $KMnO_{A}$.

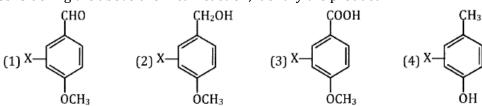
Choose the correct option:

- (1) Both statement I and statement II are correct
- (2) Both statement I and statement II are incorrect
- (3) Statement I is correct but Statement II is incorrect
- (4) Statement I is incorrect but Statement II is correct

11. [JEE (Main) 2021]



Considering the above chemical reaction, identify the product " X " :



12. In the following sequence of reactions, the final product D is :

[JEE (Main) 2021]

(1)

$$CH_3-C=C-H+NaNH_2\rightarrow A \longrightarrow B \xrightarrow{H_2/Pd-C} C \xrightarrow{CrO_3} D$$

(2)
$$CH_3 - CH = CH - CH_2 - CH_2 - CH_2 - COOH$$

$$(3) H_3 C - CH = CH - CH(OH) - CH_2 - CH_2 - CH_3$$

(4)

13. Which of the following reagents/reactions will convert 'A' to 'B'?

[JEE (Main) 2022]

$$CH_3$$
 CH_3
 CH_3

- (1) PCC oxidation
- (2) Ozonolysis
- (3) BH_3 , H_2O_2 / OH followed by PCC oxidation
- (4) HBr , hydrolysis followed by oxidation by $K_2Cr_2O_7$
- 14. 'A' and 'B' respectively are:

[JEE (Main) 2022]

A and B respectively are:
$$A \quad (i)O_3 \quad \rightarrow \quad \text{Ethane-1,2-dicarbaldehyde + Glyoxal/Oxaldehyde}$$

$$B \quad (i)O_3 \quad \rightarrow \quad \text{5-oxohexanal}$$

B
$$(i)O_3 \rightarrow (2)Zn-H_2O$$
 5-oxohexanal

- (1) 1-methylcyclohex-1, 3-diene & cyclopentene
- (2) Cyclohex-1, 3-diene & cyclopentene
- (3) 1-methylcyclohex-1,4-diene & 1-methylcyclopent-1-ene
- (4) Cyclohex-1,3-diene & 1-methylcyclopent-1-ene
- 15. A compound 'A' on reaction with 'X' and 'Y produces the same major product but different by product 'a' and 'b'. Oxidation of 'a' gives a substance produced by ants. [JEE (Main) 2022]

$$CH_{3} CH_{3} CH_{3}$$

$$H_{2}C = C - CH_{2} - C - CH_{3}$$

$$CH_{3} CH_{3}$$

'X' and 'Y' respectively are:

(1) $KMnO_4/H^{\oplus}$ and dil. $KMnO_4$, 273 K

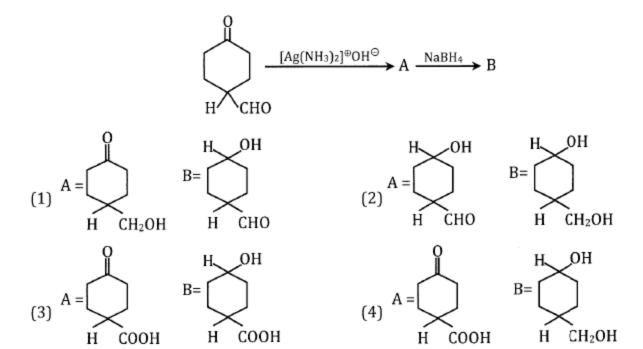
(2) $KMnO_4$,(dilute), 273 K and $KMnO_4/H^{\oplus}$

(3) $KMnO_4/H^{\oplus}$ and O_3 , H_2O/Zn

(4) O_3 , H_2O/Zn and $KMnO_4/H^{\oplus}$

16. The products formed in the following reaction, *A* and *B* are

[Jee (main)2022)]



- 17. Hex-4-ene-2-ol on treatment with PCC gives 'A'. 'A' on reaction with sodium hypoiodite gives 'B', which on further heating with soda lime gives 'C'. The compound 'C' is [JEE (Main) 2022] (1) 2-pentene (2) proponaldehyde (3) 2-butene (4) 4-methylpent-2-ene
- 18. Which of the following conditions or reaction sequence will NOT give acetophenone as the major product?

 [JEE (Main) 2022]

(b) Na₂Cr₂O₇, H[⊕]

(2) (a)
$$H_3C$$
 $+C_6H_5MgBr$

(b) PCC, DCM

19. In the given reaction

HO
$$\longrightarrow$$
 $(i)K_2Cr_2O_7, H^{\oplus}$ (X'')
 $(ii)C_6H_5MgBr$ \longrightarrow Major product
 $(iv) H^{\oplus}, heat$

the number of sp^2 hybridised carbon (s) in compound ' X ' is _____ .

20. The major product ' P ' formed in the given reaction is

$$CH_2CH_3$$

$$COOCH_3 \xrightarrow{\text{(i) alk. KMnO}_4, \Delta} P$$

$$CH=CH_2$$

$$COOCH_3 \xrightarrow{\text{(ii) H}_3O^+} Major product$$

EXERCISE - JEE (Advanced) PYQ

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

$$CH_3$$
 $CO \xrightarrow{SeO_2} P+Se+H_2O$

(A) CH₃COCHO

(B) CH_3COOCH_3

(C) *CH*₃*COCH*₂*OH*

(D) None

2. Positive Tollen's test is observed for

[Jee(Advanced)2016)]

(A)
$$H H H$$

3. Total number of hydroxyl groups present in a molecule of the major product *P* is [JEE (Advanced) 2019]

4. The number of $-CH_2$ - (methylene) groups in the product formed from the following reaction sequence is ______ . [JEE (Advanced) 2022]

5. The total number of chiral molecules formed from one molecule of P on complete ozonolysis $\left(O_3, Zn/H_2O\right)$ is ______ . [JEE (Advanced) 2022]

JEE (Main) Practice Paper

(This paper is for yourself practice and assessment the discussion of this paper is optional though you can) see PDF solutions or video solutions or solutions in hardcopy whichever is provided.

SECTION-A

- This section contains TWENTY questions.
- Each question has FOUR options (1), (2), (3) and (4). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories

Full Marks: + 4, if only the bubble corresponding to the correct option is darkened.

Zero Marks: 0, if none of the bubbles is darkened.

Negative Marks: -1 in all other cases

- 1. $(CH_3)CHOH$ Mild oxid $\rightarrow X$ (1) $CH_3Mgr \rightarrow (2)H_3O^{(1)}$ Y. Here Y is
 - (1) Isobutyl alcohol

(2) tert-Buiyl alcohol

(3) Isobutylene

(4) sec-Butyl alcohol

2. CH_3 CCl alc. $KOH \rightarrow \Delta X CF_3 CO_3 H \rightarrow Y$ The product 'Y' is

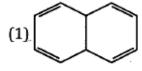
$$(1) CH_2 = CH - CH_2OH$$

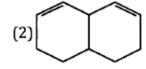
(2)

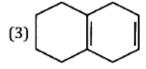
(3)
$$CH_3COCH_2CH_3$$

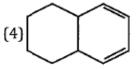
$$(4) \left(CH_3\right)_2 CHCH_2 OH$$

3. An unknown compound decolorizes bromine in carbon tetrachloride, and it undergoes catalytic reduction to give decalin. When treated with warm, conc. Potassium permanganate, this compound give cis-cyclohexane-1, 2-dicarboxylic acid and oxalic acid. A possible structure for the unknown compound is

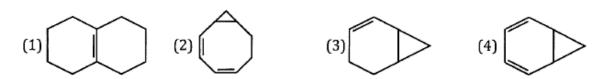








4.



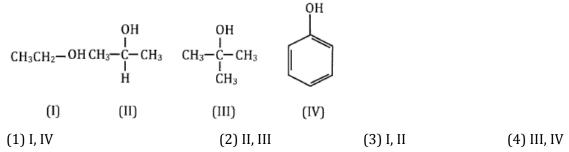
$$(3) \begin{array}{c} O \\ CH - CH \\ O \end{array}$$

6.

OH

OH $KMnO_4/H^+$ (P), product (P) is

7. Which of the following sets of compounds cannot turn clear orange solution of CrO_3/aq . H_2SO_4 to greenish opaque solution?



The given reaction,

is an example of

- (1) Stereospecific reaction
- (3) Both (1) and (2)

- (2) Stereoselective reaction
- (4) Ordinary reaction

9.

$$\begin{array}{c}
0 \\
0
\end{array}$$

$$\xrightarrow{\text{H}_2O\oplus} \text{product}$$

Product obtained in the above reaction is

(1) $3CH_{3}CHO$

(2) 3 HCHO

(3) 3 HCOOH (4) $3CH_3OH$

10. The reaction,

$$Ph - CH_2 - CH = CH - CH_3 \xrightarrow{Al(\iota BuO)_3} Ph CH_2CH = CH - C-CH_3$$

$$Ketone (excess)/\Delta$$

is known as

- (1) Wolff-Kishner reduction
- (3) Meerwein-Ponndorf reaction

- (2) Oppenauer oxidation
- (4) Clemmensen reduction
- 11. Which of the following can be oxidised to aldehyde or ketone by Jones reagent.

(2)
$$CH_3$$
 $C = C$ CH_3

- 13. Glucose as well as fructose are oxidized by periodic acid. The number of moles of HCOOH formed from each mole of glucose and fructose are
 - (1) 5 and 5
- (2) 5 and 4

- (3) 5 and 3
- (4) 4 and 3

- 14. Secondary alcohols on heating with copper at 300°C give
 - (1) Alkenes
- (2) Aldehydes
- (3) Ketones
- (4) tert-alcohols
- 15. The reagent, with which both acetaldehyde and acetone react easily is:
 - (1) Tollens reagent
- (2) Schiff's reagent
- (3) H_2/Ni
- (4) Fehling's solution
- 16. . Which of the following compounds is resistant to periodic acid oxidation?

17.

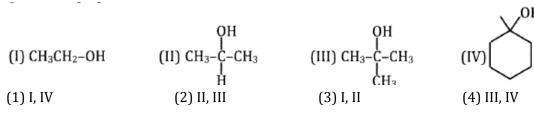
HO Reagent
$$R_2$$
 Reagent R_1 HO OH R_1 and R_2 are

- (1) Cold alkaline KMnO_4 , $\mathit{OsO}_4/\mathit{H}_2\mathit{O}_2$
- (2) Cold alkaline $KMnO_4$, $HCO_3H \& H_3O^+$
- (3) Cold alkaline $KMnO_4$, $C_6H_5CO_3H$
- $(4) C_6 H_5 CO_3 H, HCO_3 H$
- 18. Identify (P) and (Q) respectively in the given reaction:

$$(P) \xrightarrow{\text{Acidic}} OH \xrightarrow{\text{PCC, CH}_2\text{Cl}_2} (Q)$$

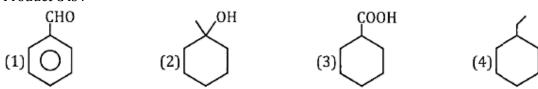
$$(1) \qquad 0 \qquad (2) \qquad COOH \qquad COOH$$

19. Which of the following sets of compounds cannot turn clear orange solution of CrO_3/aq . H_2SO_4 to greenish opaque solution



20.

Product C is:



SECTION-B

- This section will have SIX questions. Candidate can choose to attempt any 5 questions out of these 10 questions. In case if candidate attempts more than 5 questions, first 5 attempted questions will be considered for marking.
- The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value (Answer should be rounded off to the nearest integer).
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : + 4, if only correct answer is given.

Zero Marks: 0, if no answer is given.

Negative Marks: -1, for incorrect answer

1.

$$\begin{array}{ccc}
& OH \\
& OH
\end{array}$$

$$\begin{array}{ccc}
& HIO_4 \\
& OH
\end{array}$$

$$\begin{array}{ccc}
& (A) & (1) \text{ LiAlH}_4 \text{ (excess)} \\
& (2) \text{ H}^{\oplus}
\end{array}$$

$$\begin{array}{cccc}
& (B) \\
&$$

Total number of stereoisomers of product (B) will be:

2.

What is the maximum value of (x)?

3.

Maximum number of moles of Ac_2O consumed by reactant (A) is :

4. Out of the following compounds given below, the number of compounds which given positive test with Tollen's reagent are :

I. *CH*₃*CHO*

II. PhCHO

III. HCOOH

IV. CH₃COOH

VI.

 $V. CH_3CH(OH)OC_2H_5$

$$H_3C$$
 OC_2H_5
 OC_2H_5

 $\text{VII.} \ CH_{_3}C \ \equiv \ CH$

VIII

IX. CH_3COCH_3

5. Out of the following compounds given below, the number of compounds which given positive iodoform test are

. I. *СН₃СНО*

 ${\rm II.}\, {\it CH}_{3}{\it COCH}_{3}$

II. $C_2H_5COC_2H_5$

IV. $PhCOC_2H_5$

V.

VI. PhCOCH₂COPh²

VII.

VIII. PhCOCH₃

IX. $CH_3COC_2H_5$

X.

6. How many of the following can be oxidised to aldehyde or ketone by jones reagent or PCC.

a. H₆C₆—CH₂OH

c. C₆H₆

$$H_3C$$
 H_3C
OH

f.
$$H_3C$$
 $C=C$
 CH_3
 CH_3

SECTION-I

- This section contains SEVEN questions.
- Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories:

Full Marks :+ 3, if only the bubble corresponding to the correct option is darkened.

Zero Marks: 0, if none of the bubbles is darkened.

Negative Marks : -1 , in all other cases

1.

OH OH

$$PCC \rightarrow (A) \xrightarrow{OH OH} (B) \xrightarrow{(1)MeMgBr H_3O^{\oplus}} (C) \xrightarrow{NaBH_4, EtOH} (D)$$

Product (D) in above reaction is:

$$(A) OH OH$$

$$(B) OH OH$$

$$(C) OH OH$$

$$(D) OH OH$$

2.

$$OH \xrightarrow{MnO_2} (B) \xrightarrow{H_2CrO_4^{\oplus}} (C)$$

$$OH$$

$$OH$$

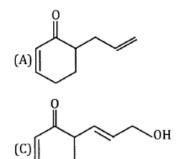
The compounds (B) and (C), respectively, are:

$$(A) \longrightarrow 0 \qquad (B) \longrightarrow 0 \qquad (C) \longrightarrow 0 \qquad (D) \text{ Both } \bigcirc 0 \qquad (D) \text{ Both }$$

3.

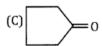
$$\underbrace{\text{SeO}_2/\text{MeCOOH}}_{\text{SeO}_2/\text{MeCOOH}} (A)$$

The compound (A) is



- 4. Acid-catalysed hydration, oxymercuration- demercuration, and hydroboration oxidation reaction will give the same product with
 - (A) But-2-ene

(B) But-l-ene



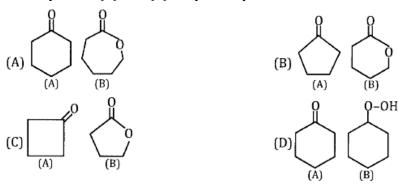
- (D) M6
- 5. Fehling's solution can make distinction between:
 - (A) MeCHO and PhCHO
 - (B)

(C)

- (D) MeCHO and HCHO
- 6. Fenton's reagent $\left(Fe^{2\oplus} + H_2O_2\right)$ with benzene gives
 - (A) No reaction
 - (B)

- (C)
- (D) 3(HOOC COOH)
- 7. Barium adipate $Dry \ distillation \rightarrow (A) \ MeCO_3 H \rightarrow (B)$

The compounds (A) and (B), respectively, are;



SECTION-II

- This section contains SIX questions.
- Each question has FOUR options for correct answer(s). ONE OR MORE THAN ONE of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : + 4, if only (all) the correct option(s) is (are) chosen.

Partial Marks : + 3, if all the four options are correct but ONLY three options are chosen.

Partial Marks: + 2, if three or more options are correct but ONLY two options are chosen, both of which are correct options.

Partial Marks: + 1, if two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks: 0, if none of the options is chosen (i.e. the question is unanswered).

Negative Marks: -2 in all other cases.

- 8. 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
- 9. Fehling solution gives red precipitate with:
 - (A) Aromatic aldehyde

(B) Aliphatic aldehyde

- (C) Ketones
- (D)

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

(A)
$$CH_3CHO$$
 (B) OH (C) $CH_3CH_2CH_2CH_2CH_3CH_3$ (D) $CH_3-CH < OCH_3$ OCH₃

- 11. Schiff's reagent gives pink colour with:
 - (A) Acetaldehyde
- (B) Formic acid
- (C) Acetic acid
- (D) Methyl acetate

12. Which will give the Tollen test.

$$(B)$$
 O O O O O O O

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

(A)
$$CH_3 - CH_2 - OH \rightarrow^{PCl_3}$$

(B)
$$CH_3 - CH = CH_2 \rightarrow^{Ni/N_2}$$

(C)
$$CH_3 - CH = CH_2 \rightarrow CCl_4$$

(D)
$$CH_2 = CH_2 \rightarrow^{H^{\oplus}}_{KMnO_4}$$

SECTION-III

• This section contains TWO question.

• Each question has matching lists. The codes for the lists have choices (A), (B), (C) and (D) out of which ONLY ONE is correct

• For each question, marks will be awarded in one of the following categories :

Full Marks: + 3, if only the bubble corresponding to the correct option is darkened.

Zero Marks: 0, if none of the bubbles is darkened.

Negative Marks: -1, in all other cases

14. Match the items given in column I with that in column II and III.

			D t -		Ola a sa a tani ati a a
\vdash	_		Regents		Characteristics
a	O Reagent O	i	Birch reduction	p	Formed via brown complex
b	Reagent	ii	Etard reaction	q	Formed via a diradical with subsequent intramolecular (C-C) bond formation
c	Reagent	iii	Fenton's reagent	r	Formed via a stable intermediate redical anion
d	OCH ₃ Reagent	iv	Clemenson's reduction	S	Formed by radical formation

(A) (
$$a \rightarrow iv, q; b \rightarrow i, r; c \rightarrow ii, p; d \rightarrow iii, s$$
)

(B) (a
$$\rightarrow$$
 ii, q; b \rightarrow i, r; c \rightarrow ii, p; d \rightarrow iii, s)

(C)
$$(a \rightarrow iv, q; b \rightarrow i, r; c \rightarrow i, p; d \rightarrow iii, s)$$

(D)
$$(a \rightarrow iii, q; b \rightarrow i, r; c \rightarrow ii, p; d \rightarrow iii, s)$$

15. Match the items given in column I with that in column II and III.

	Reactions		Regents		Characteristics
a.	0=\bigcap_NO2 \bigcap_Reagent \bigcap_OH \bigcap_NO2	i	DIBAL-H	p	Silver mirror

b	C≡N CHO	ii	Tollen's reagent	q	Involves a imine salt
	OEt CHO				
c.	NHOH N = 0	iii	MPV reduction	r	Forms solvent complex
d.	CHO CHO CHO CHO	iv	Fehling's reagent	S	Involves a cycle transition state with $H \ominus$ ion migration

(A)
$$(a \rightarrow iv, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iv, r)$$
 (B) $(a \rightarrow iii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iv, r)$ (C) $(a \rightarrow ii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iv, r)$ (D) $(a \rightarrow iii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iii, r)$

(B) (a
$$\rightarrow$$
 iii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iv, r)

(C) (a
$$\rightarrow$$
 ii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iv, r)

(D)
$$(a \rightarrow iii, s; b \rightarrow I, q; c \rightarrow ii, p; d \rightarrow iii, r)$$

SECTION-IV

- This section contains ONE paragraph.
- Based on each paragraph, there are THREE questions.
- Each question has FOUR options (A), (B), (C) and (D) ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories:

Full Marks: + 3, if only the bubble corresponding to the correct answer is darkened.

Zero Marks: 0, in all other cases.

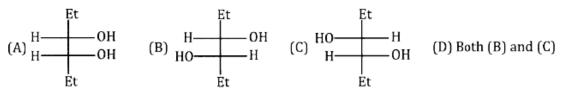
Paragraphs for Q. 16 to 18

Me
$$C \equiv C - Et \xrightarrow{H_2 + Pd - BaSO_4} (C) \xrightarrow{\text{alkaline} \atop \text{KMnO}_4} (D) \xrightarrow{\text{HIO}_4} (E)$$

$$\xrightarrow{\text{Na + liq. NH}_3} (F) \xrightarrow{\text{alkaline} \atop \text{KMnO}_4} (G)$$

16. The compound (D) is:

17. The compound (G) is:



18. The compound (E) is:

(A) Two moles of Me CHO.

(B) Two moles of Me COOH.

(C) One mole of (A) and one mole of (B)

(D) No reaction.

SECTION-V

• This section contains TWO question.

• The answer to each question is a NUMERICAL VALUE.

• For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the second decimal place; e.g. 6. 25, 7. 00, — 0. 33, —. 30, 30. 27, — 127. 30, if answer is 11. 36777.... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

For Example : If answer is -77.25, 5. 2 then fill the bubbles as follows:

• Answer to each question will be evaluated according to the following marking scheme:

Full Marks: + 3 if ONLY the correct numerical value is entered as answer.

Zero Marks: 0 in all other cases.

19. How many reactions are correct?

20.

Sum of moles of formaldehyde obtained in the reaction (i) and reaction (ii)?

ANSWER KEY

EXERCISE - 0

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	В	С	С	A	В	D	С	В	D
Que.	11	12	13	14	15					
Ans.	С	ABC	ABC	AB	ВС					
Que.	16	17								
Ans.	$(A \rightarrow r, i), (B \rightarrow s, ii), (C \rightarrow q, iii), (D$	$(A \rightarrow r), (B \rightarrow t), (C \rightarrow q), (d \rightarrow p)$								

EXERCISE-S

(ii) $O = C = O + H_2O$

1. (i)
$$CO_2 + H_2O$$

(iii) OH OH
$$CO_2 + H_2O$$

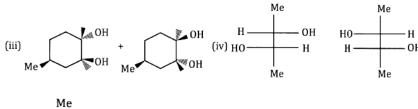
(iv)
$$0 + 0$$

$$(v)$$
 $OH O OH O$

$$(x) \underbrace{ \begin{array}{c} 0 \\ 0 \\ OH \\ 0 \end{array} }$$

2.

3.



$$(vi) \stackrel{Me}{\underset{O}{\longleftarrow}} C = C \stackrel{H}{\underset{Ph}{\longleftarrow}}$$

(Erythro)

4.

(i)
$$CH_3 - CH_2 - C - O$$
-
(Salt for due to Basic Medium)

(Salt for CH₃ - CH₂ - C - OH)

(CH₃ - CH₂ - C - OH)

(CH₃ - CH₂ - C - OH)

$$(ii) CH_3 - C - CH_2 - CH_3$$
(Ketone)

5.

(i)
$$CH_2 = CH - (CH_2)_3 - CHO$$

(ii)
$$C_6H_5$$
 — $CH = CH$ — CHO

(vi)
$$CH_3O$$

$$CH_3O$$

$$CH_3O$$

$$CH_3O$$

$$CH_3O$$

6.

(i)
$$Me-CH = O + O = CH_2$$

(iv)
$$OCH_2$$
 HO $C - H$ $O = CH - CH_2$

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

7.

$$(c)$$
 (c) (c) (c) (c) (c) (c) (c) (c) (c) (c)

$$CH_2 \qquad C = C$$

$$C = C$$

$$CH_2 \qquad CH_2$$

$$CH_2 \qquad CH_2$$

(ii) + V Benedict

-Ve Fehling test-Ve Benedict

EXERCISE - JEE (Main) PYQ

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	1	3	2	4	2	4	1	3	4	3
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	3	4	3	4	4	3	3	3	8	4

EXERCISE - JEE (Advanced) PYQ

Que	1	2	3	4	5	
Ans	A	ABC	6	0	2	

JEE (Main) Practice Paper

	Q.	1	2	3	4	5	6	7	8	9	10
Section-A	A.	2	2	4	2	1	2	4	1	2	2
	Q.	11	12	13	14	15	16	17	18	19	20

	A.	1	2	3	3	3	2	2	3	4	4
	Q.	1	2	3	4	5	6				
Section-B	A.	3	2	4	6	7	4				

JEE (Advanced) Practice Paper

	Q.	1	2	3	4	5	6	7	
Section-I	A.	В	В	С	A	A	С	В	
	Q.	8	9	10	11	12	13		
Section-II	A.	ACD	BD	ABC	AB	ACD	CD		
Section-III	Q.	14	15						
	A.	A	В						
Section-IV	Q.	16	17	18					
	A.	A	D	A					
Section-V	Q.	19	20						
	A.	3	3						