02 Oxidation

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.

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

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

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

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

C–black (used in printing)

(c) Catalytic oxidation :

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

$$2CH_4 + O_2 \xrightarrow[\text{High P and T}]{\text{Red hot Cu or Fe tube}} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[230^0\,C,100atm]{Mo_2O_3} HCHO + H_2O$$

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

$$CH_3(CH_2)_nCH_3 \xrightarrow[\text{high Temp}]{(CH_3COO)_2\,Mn} CH_3(CH_2)_nCOOH$$

(iii) Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.

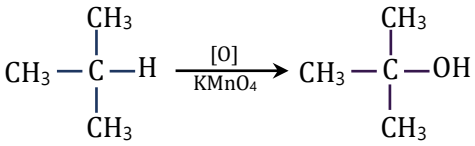


Illustration 1 :

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

Solution:

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$$

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

1 g ethane required O_2 (at NTP) = $\frac{7\times22.4}{2\times30}$ litre

6 g ethane required O_2 (at NTP) = $\frac{7\times22.4}{2\times30}\times6=15.68$ 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

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

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.

$$\frac{\text{Volume of Hydrocarbon}}{\text{Volume of } O_2} = \frac{2}{3n} \qquad \text{(for Alkene)}$$

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

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 [C_3H_6].

Illustration 3 :

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

Solution:

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

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 = x mL

So volume of Butylene = (30–x) mL

For C_2H_4, $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

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, 3x ml volume of O_2 is required.

For C_4H_8 , $C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$

$\because$ 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 = 150 ml (Given)
x = 10
∵ 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 —C(OH)—C(OH)— is known 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.

$$>C=C< + H_2O + [O] \xrightarrow[KMnO_4]{OH^{\ominus}} >C(OH)-C(OH)<$$ Glycol (cis–addition)

(ii) By OsO_4 :

$$R-CH=CH-R + OsO_4 \longrightarrow \underset{\text{cis–addition}}{R-CH(OH)-CH(OH)-R} + H_2OSO_4$$

(iii) By peracid :

$$>C=C< + H-C(=O)-O-O-H \xrightarrow{-HCOOH} >C(-O-)-C(-O-)< \xrightarrow{-H_2O} >C(OH)-C(OH)<$$

Trans glycol

(c) Epoxidation :

(i) Alkenes reacts with oxygen in the presence of Ag catalyst at 250°–400° C to form epoxide.

$$CH_2=CH_2 + \tfrac{1}{2}O_2 \xrightarrow[\Delta]{Ag} \underset{\text{Epoxide}}{CH_2-O-CH_2} \xrightarrow{H_2O} \underset{\text{(anti addition)}}{CH_2(OH)-CH_2(OH)}$$

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

$$RCH=CH_2 + C_6H_5COOOH \longrightarrow \underset{\text{Expoxide}}{R-CH(-O-)-CH_2} + C_6H_5COOH$$

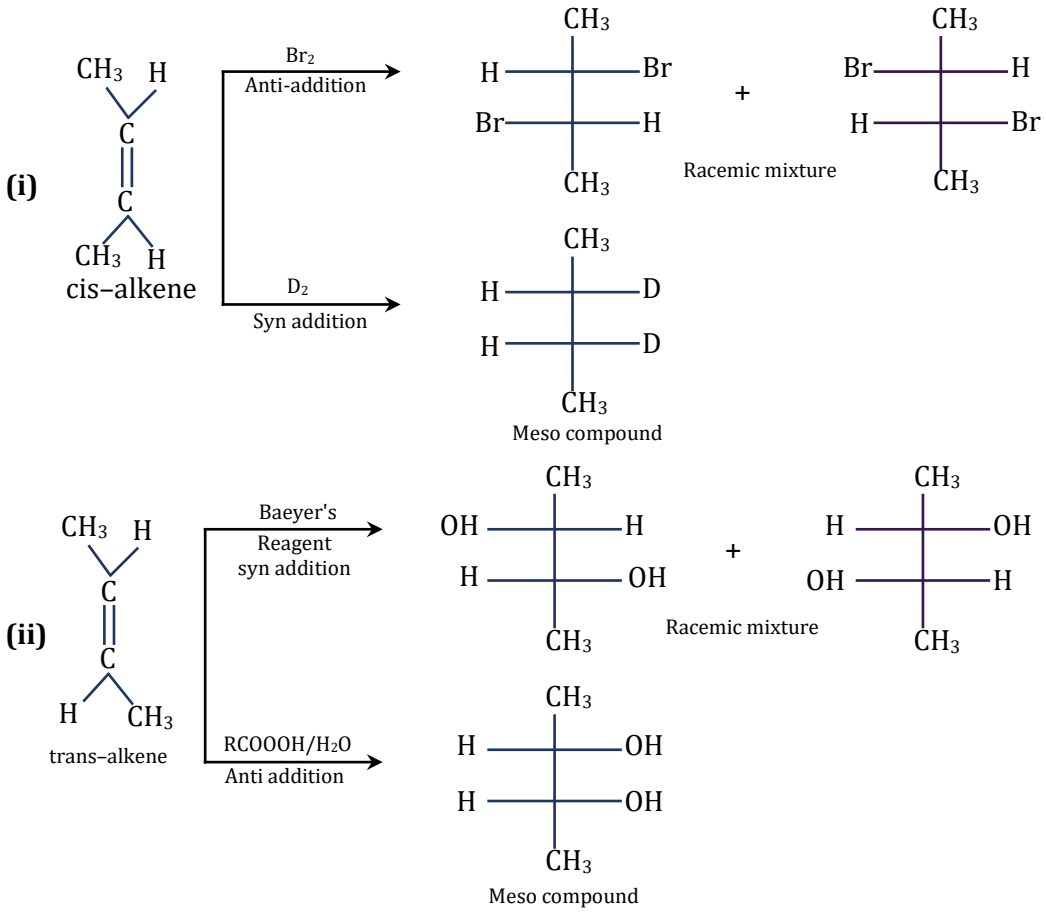
Emmons have found that perbenzoic oxy trifluoroacetic acid (CF_3COOH) is a very good reagent for epoxidation and hydroxylation.

cis alkene —(Syn addition)→ Meso compound
cis alkene —(Anti addition)→ Racemic mixture

trans alkene —(Syn addition)→ Racemic mixture
trans alkene —(Anti addition)→ Meso compound

Syn addition on alkene $\longrightarrow H_2O_2$, Baeyer's reagent, OsO_4 / H_2O
Anti addition on alkene $\longrightarrow X_2$, 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.

$CH_2{=}CH_2 + 4[O] \longrightarrow 2HCOOH \xrightarrow{2[O]} 2CO_2 + H_2O$

$CH_3CH{=}CH_2 \xrightarrow{5[O]} CH_3COOH + CO_2 + H_2O$

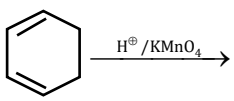
$CH_3CH{=}CHCH_3 \xrightarrow{4[O]} 2CH_3COOH$

$(CH_3)_2C{=}CH_2 \xrightarrow{4[O]} (CH_3)_2C{=}O + CO_2 + H_2O$

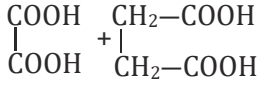
(e) Oxidation with retention of Carbon-Carbon bond - (Waker process) :

$CH_2{=}CH_2 + H_2O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$

Illustration 5 :



Solution:



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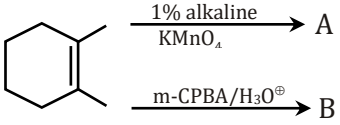
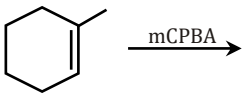
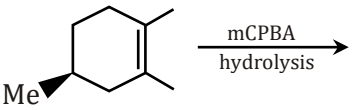
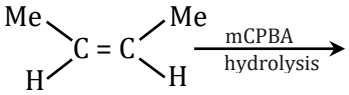
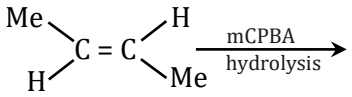
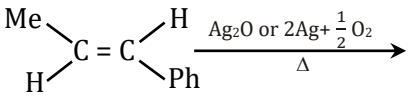
(i) 

(ii) 

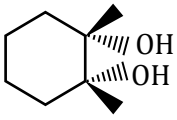
(iii) 

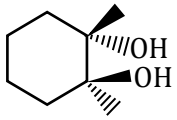
(iv) 

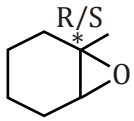
(v) 

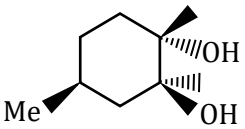
(vi) 

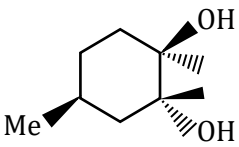
Solution:

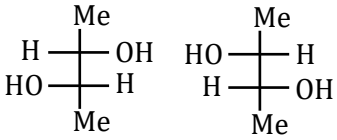
(i) (A) 

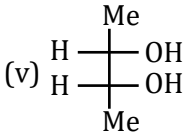
(B) 

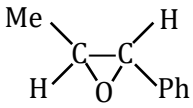
(ii) 

(iii) 



(iv) 

(v) 

(vi) 

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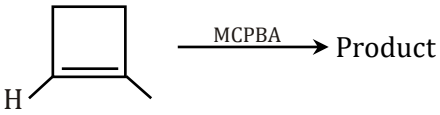
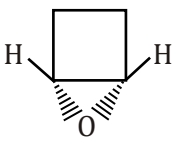
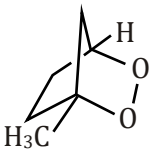
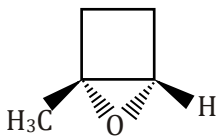
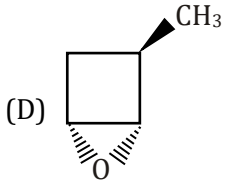


(A) 

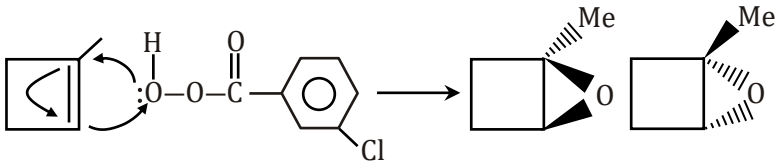
(B) 

(C) 

(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 : $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3 \xrightarrow{\text{Ozonolysis}} CH_3-\underset{\underset{CH_3}{|}}{C}=O + CH_3CHO$

(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 : $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3} \xrightarrow{\text{Ozonolysis}} CH_3-\underset{\underset{H}{|}}{C}=O + O=\underset{\underset{H}{|}}{C}-CH_3$

But–2–ene

Ethanal

Example : $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_3} \xrightarrow{\text{Ozonolysis}} H-\underset{\underset{H}{|}}{C}=O + O=\underset{\underset{H}{|}}{C}-CH_2-CH_3$

But–1–ene

Methanal Propanal

Example : $CH_3-\underset{\underset{H_3C}{|}}{\overset{\overset{CH_3}{|}}{C}}=C-CH_3 \xrightarrow{\text{Ozonolysis}} CH_3-\underset{\underset{CH_3}{|}}{C}=O + O=\underset{\underset{CH_3}{|}}{C}-CH_3$

2,3–Dimethyl but–2–ene

Propanone

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 $LiAlH_4$ or $NaBH_4$ gives corresponding alcohols.

$$R'-\underset{\underset{O-O}{|\quad|}}{\overset{O}{\diagup\diagdown}}CH-CH-R'' \xrightarrow{LiAlH_4} R'CH_2OH + R''CH_2OH$$

(Alcohols)

4. Oxidation of Alkyne :

(a) Combustion :

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

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

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000°C) is produced.

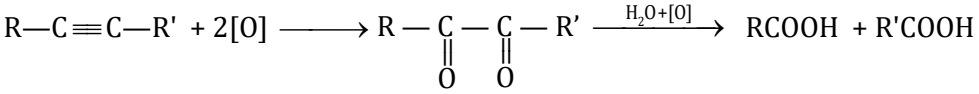
(b) Oxidation with alkaline $KMnO_4$: Oxidation with alkaline $KMnO_4$ gives carboxylic acids.

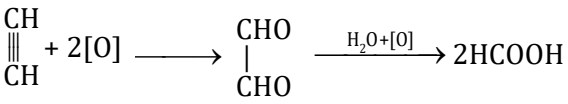
$$\underset{\underset{CH}{\|}}{\overset{CH}{}} + 4[O] \xrightarrow{\text{alk.}KMnO_4} \underset{\underset{COOH}{|}}{\overset{COOH}{}}$$

Acetylene Oxalic acid

$$CH_3-C\equiv CH + 4[O] \xrightarrow{\text{alk.}KMnO_4} CH_3-COOH + HCOOH$$

(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.





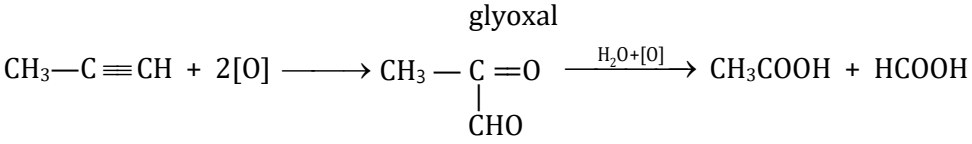
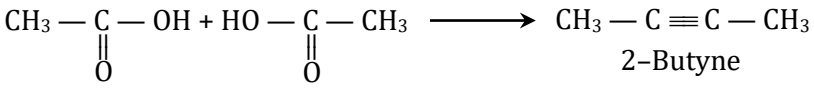


Illustration 8 :

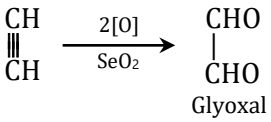
An alkyne on oxidation with acidic $KMnO_4$, only acetic acid is obtained what is given alkynes ?

Solution:

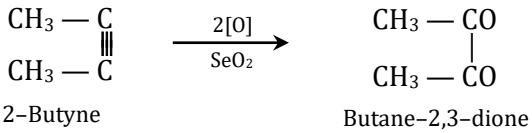
In Oxidation of alkynes two moles of mono carboxylic acids are obtained.



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



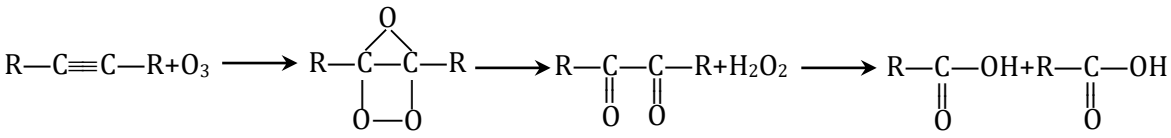
Glyoxal



2–Butyne

Butane–2,3–dione

(e) Oxidation with ozone (O_3) : In the ozonolysis both sp-C-atoms are converted into $-\underset{O}{\overset{||}{C}}-\underset{O}{\overset{||}{C}}-$ group.



Ozonide
(Addition of ozone)

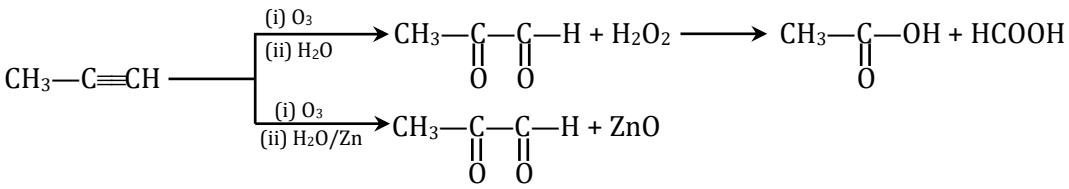
(Acids)

In this reaction H_2O_2 is oxidant which oxidise $R-\underset{O}{\overset{||}{C}}-\underset{O}{\overset{||}{C}}-R$ nto acids.

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

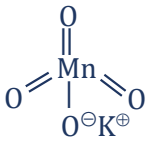
$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

Example :



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

$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

ii. Secondary alcohol

$$R_1-\underset{\displaystyle R_2}{\underset{|}{CH}}-OH \xrightarrow{KMnO_4} R_1-\underset{\displaystyle O}{\underset{||}{C}}-R_2$$

iii. Tertiary alcohol

$$R_1-\underset{\displaystyle R_2}{\overset{\displaystyle R_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{KMnO_4} \text{No reaction}$$

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

1. (CrO_3 + H_2SO_4) is called of Jones reagent.
2. It is strong oxidising agent.

i. Primary alcohol

$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

ii. Secondary alcohol

$$R_1-\underset{\displaystyle R_2}{\underset{|}{CH}}-OH \xrightarrow{KMnO_4} R_1-\underset{\displaystyle O}{\underset{||}{C}}-R_2$$

iii. Tertiary alcohol

$$R_1-\underset{\displaystyle R_2}{\overset{\displaystyle R_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{KMnO_4} \text{No reaction}$$

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

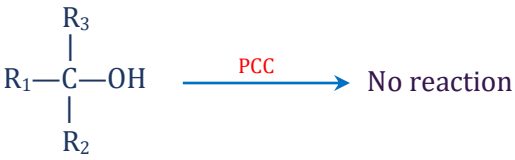
1. It is milder oxidising agent.
2. It is efficient reagent to produce aldehydes/ketones from primary/secondary alcohols.

i. Primary alcohol

$$RCH_2OH \xrightarrow{PCC} R-\underset{\displaystyle O}{\underset{||}{C}}-H$$

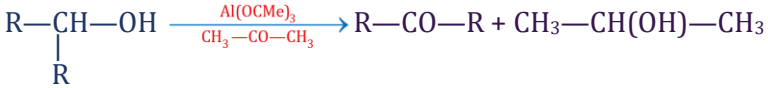
ii. Secondary alcohol

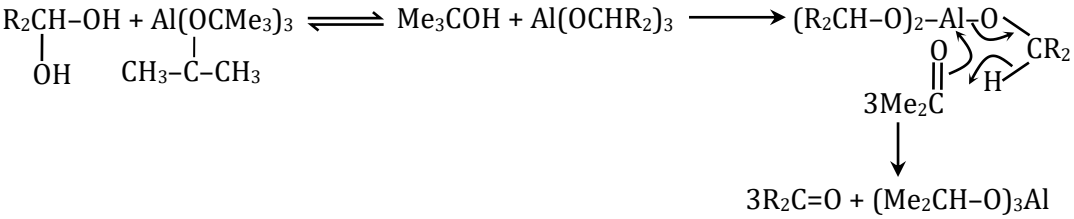
iii. Tertiary alcohol



(d) Oppenaur oxidation

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





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.

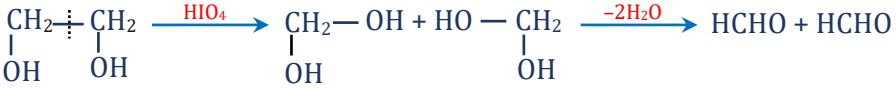
ii. The oxygen atom must be bonded to a hydrogen atom so that a chromate ester intermediate (or other suitable leaving group) may be formed. Ethers (R—O—R) cannot be oxidized in this fashion.

(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.

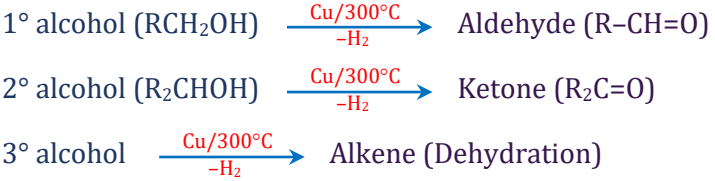
This reaction is also used in identification of no. of OH group in polyol.

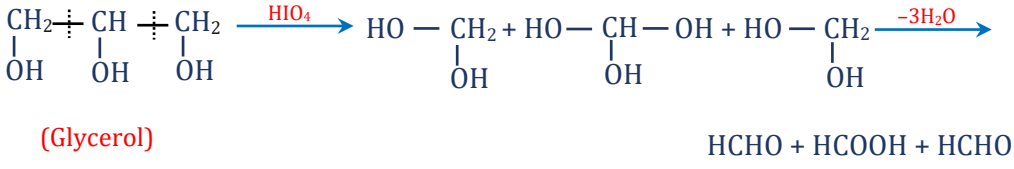
Reaction is observed for Vic-diols



(f) By dehydrogenation of (1° & 2°) 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.

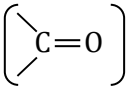
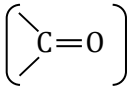


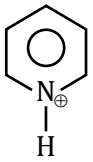
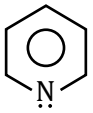
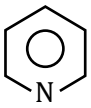
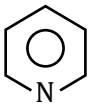
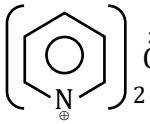
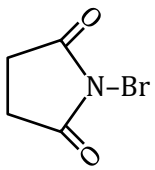


(Glycerol)

$HCHO + HCOOH + HCHO$

Condition for oxidation by HIO_4 :

At least 2 —OH or 2  or 1—OH and 1  should be at adjacent carbons.

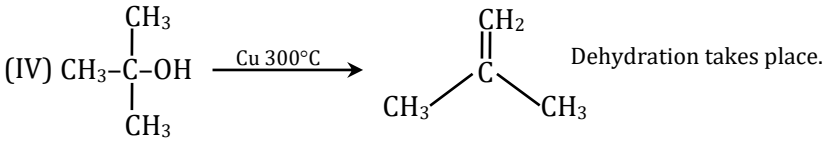
SUMMARY		
S. No.	**Oxidising agents**	**Type**
1.	$H^{\oplus}/K_2Cr_2O_7, \Delta$	Strong
2	$H^{\oplus}/K_2Cr_2O_7, \Delta$ (Strong oxidising agent)	Strong
3.	**Jones reagent :** CrO_3 / H_2SO_4 treated with alcohol usually taken in acetone	Strong
4.	PCC (Pyridinium chloro chromate)  $CrO_3Cl^{\ominus}$ or  CrO_3 + HCl	Milder
5.	Collin's reagent ( (2 mol) + CrO_3 + CH_2Cl_2)	Milder
6.	Sarett reagent (i.e. PCC in CH_2Cl_2)  + CrO_3 + HCl + CH_2Cl_2	Milder
7.	PDC (Pyridinium dichromate) 	Milder
8.	TsCl + DMSO + $NaHCO_3$ $RCH_2OH \xrightarrow{Ts-Cl} RCH_2OTs \xrightarrow[NaHCO_3]{DMSO} RCHO$ $R_2CHOH \xrightarrow{Ts-Cl} R_2CH-OTs \xrightarrow[NaHCO_3]{DMSO} R_2CO$ $R_3COH \xrightarrow{Ts-Cl} R_3C-OTs \xrightarrow[NaHCO_3]{DMSO} \times$	Milder
9.	NBS (N-Bromosuccinamide) 	Milder

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

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

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

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



(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

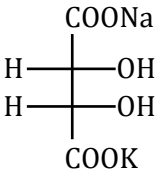
6. Oxidation of Carbonyl compounds:

1. Tollen's Test (Silver mirror test)

$RCHO + [Ag(NH_3)_2]OH$ (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 $Cu^{2\oplus}$ as it make reversible complex with $Cu^{2\oplus}$

This test is also used is Blood and Urine test.

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

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 $CH_2(CHO)-CH_2(CHO)$	+	+
6.	Pyruvaldehyde CH_3COCHO	+	+
7.	Glyoxal	–	+
8.	Benzaldehyde and other aromatic aldehyde	–	+
9.	Glyoxylic acid $CH(CHO)-COOH$	–	+

3. Benedict's solution

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

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

It is similar to Fehling test

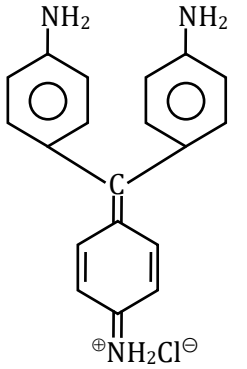
4. $RCHO + HgCl_2 + H_2O \xrightarrow[\Delta]{} RCOOH + 2HCl + Hg_2Cl_2$ (white)

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



$\xrightarrow{SO_2}$ Colourless solution (Schiff's reagent) $\xrightarrow[\Delta]{RCHO}$ RCOOH + Pink colour

p–Rosaniline Hydorchloride
Megenta colour (Fuschin)

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 :

$$\underset{C=7}{CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3} \xrightarrow{[O]} \underset{C=4}{CH_3-CH_2-CH_2-COOH} + \underset{C=3}{CH_3-CH_2-COOH}$$

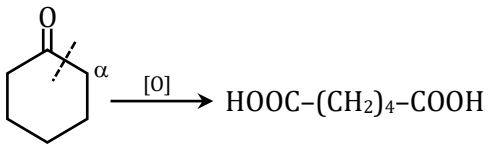
Total number of C'S = 4+3 = 7 ?

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

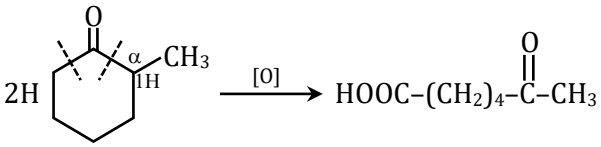
Case - II : Oxidation of unsymmetrical ketones : In case of unsymmetrical ketones, those $-\overset{\overset{O}{\|}}{C}-R$ bond break in which alkyl group has more number of carbons. This rule is known as **Poff's rule.**

$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow{[O]} CH_3-CH_2-COOH + CH_3-CH_2-COOH$$
$$\Downarrow \qquad \Downarrow$$
$$COOH \quad COOH$$

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.

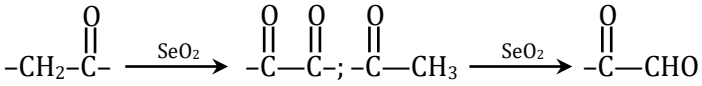


Note : If both α-carbons are not identical then ;

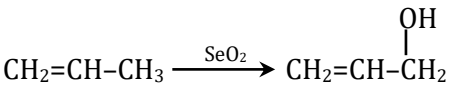


Allylic oxidation

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.

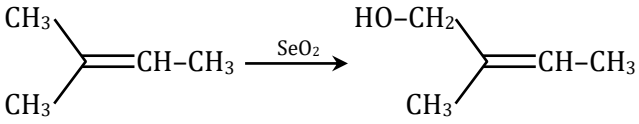


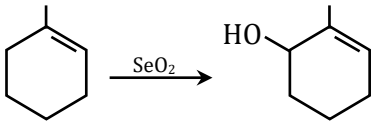
Double bonds, triple bonds and aromatic rings may also activate the methylene group. The methylene or methyl group α to the most highly substituted end of the double bond is hydroxylated according to the order of preference of oxidation $CH_2 > CH_3 > CH$ groups.



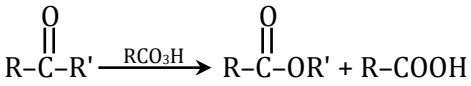
$2° C-H > 1° C-H > 3° C-H$

Rate of reactivity order





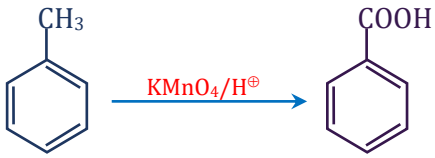
Baeyer villager oxidation



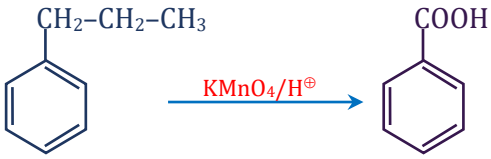
Migratory order for above reaction

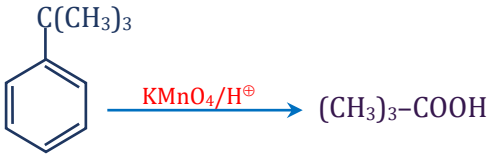
$-H > 3° > 2° > -Ph > 1° > -Me$

7. Oxidation of Aromatic Compounds :

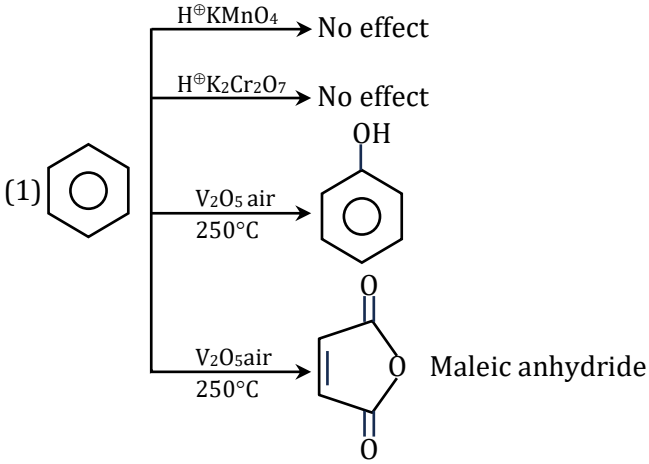


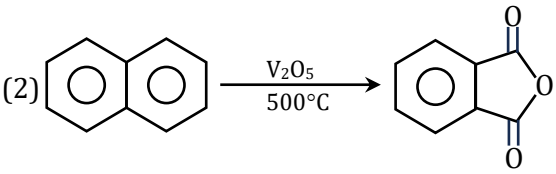
Alkyl group having no a-H atom will not be oxidized to –COOH. Any alkyl group containing at least one a-H atom will be oxidized to –COOH. The product of oxidation will be benzoic acid.

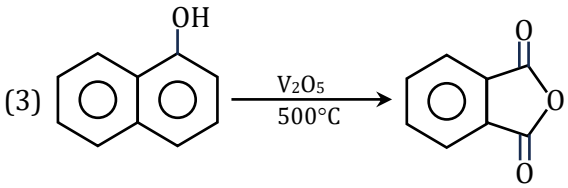


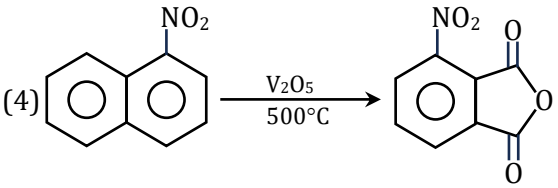


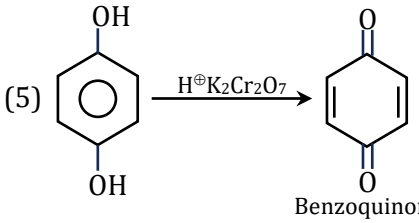
The order of benzoic acid formation by oxidation of alkyl benzene.
Methyl benzene >1° alkyl benzene >2° alkyl benzene

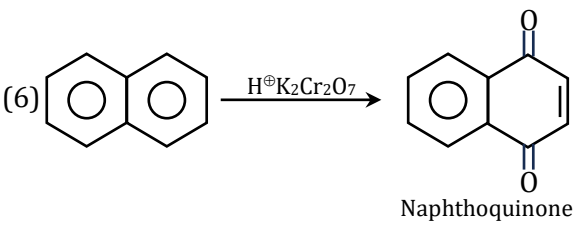


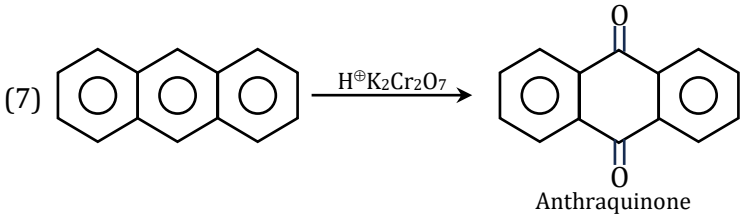


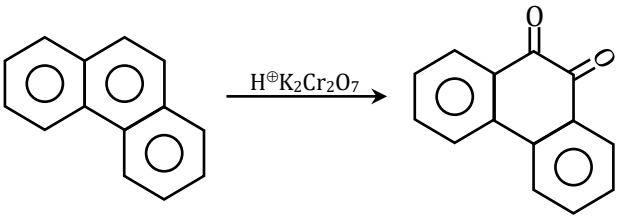




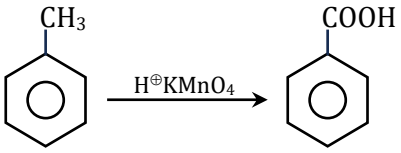






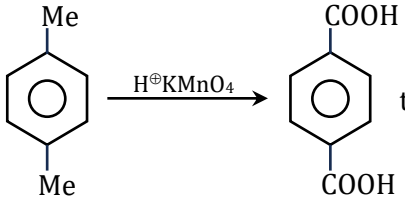
(8) 

Phenanthroquinone

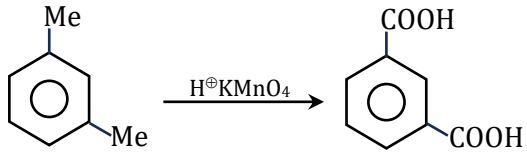
(9) 

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

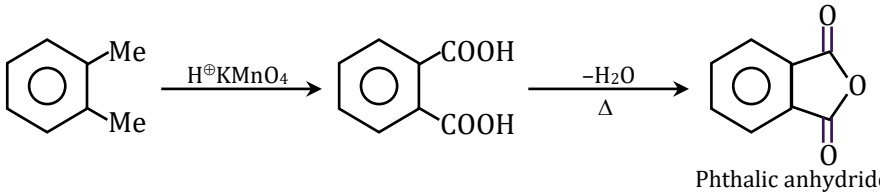
(11) $Ph-CMe_3 \xrightarrow[\Delta]{H^{\oplus}KMnO_4} Me_3C-COOH$

(12) 

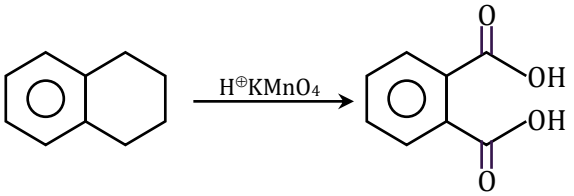
terephthalic

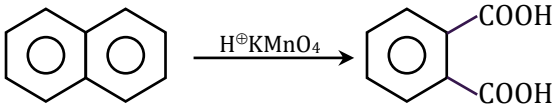
(13) 

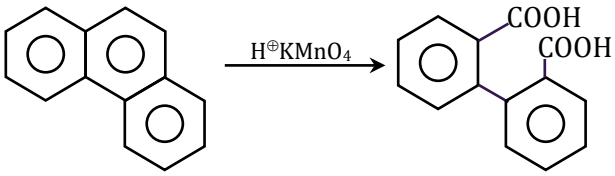
Isophthalic acid

(14) 

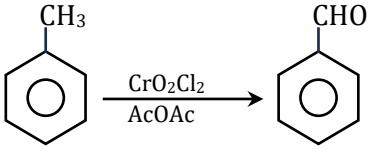
Phthalic anhydride

(15) 

(16) 

(17) 

Etard oxidation

(18) 

EIb's persulphate oxidatin

(19)