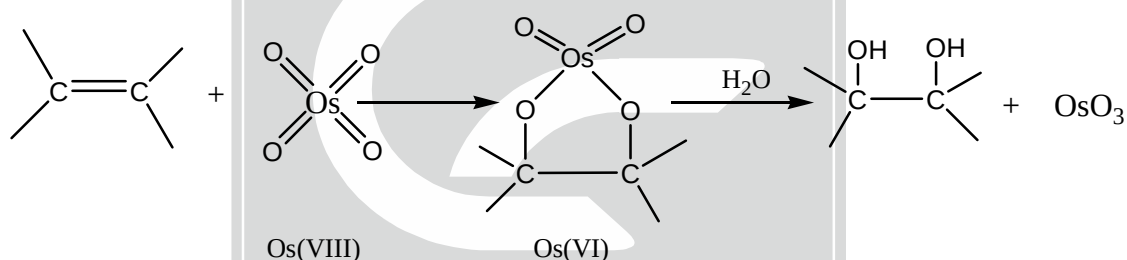


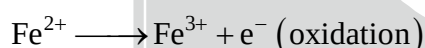
OXIDATION

3.1. Introduction:

A convenient definition of oxidation for an organic compound is the addition or gain of oxygen or removal of hydrogen. Whether a particular organic reaction is a oxidation reaction is that the reagent used in the reaction is reduced. For example in the conversion of an olefin to glycol, Osmium (VIII) is converted to Osmium (VI).



Oxidation is that an oxidation reaction involves loss of electrons or increases in the oxidation state.



Thus, the conversion of a functional group in a molecule, from a lower oxidation state to a higher one will be termed as oxidation, while the opposite of it would be reduction.

The oxidation potential represent the ability of a metal atom be ionized to an ion $(\text{M} \xrightarrow{-\text{e}^-} \text{M}^+)$ with loss of an electron. The product obtained in an oxidation reaction depends on the nature of substrate, the reagent and condition (temperature, pressure, solvent).

3.2. COMPOUNDS TRANSFORMATIONS

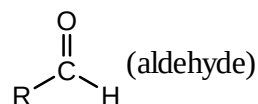
Transformation of one compound to another compound by using reagents. One compound convert into different compounds using different reagents respectively.

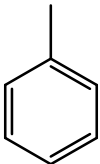
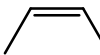
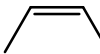
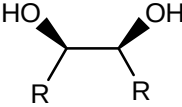
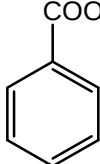
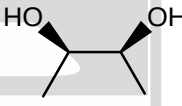
OXIDATION

FUNCTIONAL GROUPS

OXIDIZED PRODUCTS

1. $\text{R}-\text{CH}_2-\text{OH}$ (1° alcohol)



2. R_2CH-OH (2° alcohol)
3. $R-\overset{\overset{O}{\parallel}}{C}-H$ (aldehyde)
4. $R-CH_2-OH$ (1° alcohol)
5.  (Aromatic hydrocarbon)
6. $R_2C=CR_2$ (Alkene)
7. $R_2C=CR_2$ (Alkene)
8. $\text{---}\equiv\text{---}$ (Alkyne)
9.  (Alkene)
10.  (Alkene)
11.  (Diol)
12. $R-\overset{\overset{O}{\parallel}}{C}-R$ (Ketone)
- $R-\overset{\overset{O}{\parallel}}{C}-R$ (ketone)
- $R-\overset{\overset{O}{\parallel}}{C}-OH$ (carboxylic acid)
- $R-\overset{\overset{O}{\parallel}}{C}-OH$ (carboxylic acid)
-  (carboxylic acid)
- $R-\overset{\overset{O}{\parallel}}{C}-H + R-\overset{\overset{O}{\parallel}}{C}-R$
Aldehyde Ketone
- $R'-\overset{\overset{O}{\parallel}}{C}-OH + R-\overset{\overset{O}{\parallel}}{C}-R$
Carboxylic acid Ketone
- $R-\overset{\overset{O}{\parallel}}{C}-OH + R-\overset{\overset{O}{\parallel}}{C}-OH$
Carboxylic acid
-  (Diol)
-  (Epoxide)
- $R-\overset{\overset{O}{\parallel}}{C}-H$ (Aldehyde)
- $R-\overset{\overset{O}{\parallel}}{C}-OR$ (Ester)

3.3. OXIDATIONS (CORRELATION TABLES)

OXIDATION OF HYDROCARBON

ALKANES

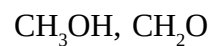
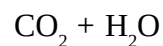


REAGENTS

Chromic acid

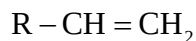
O_2/Cu , O_2/MoO_4 , $400^\circ C$

PRODUCTS



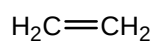
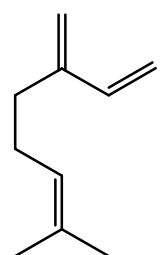
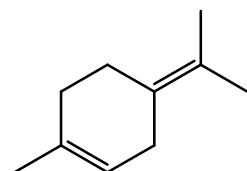
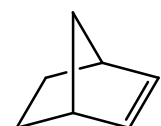
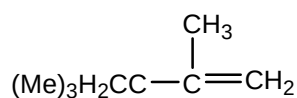
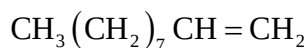
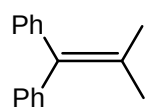
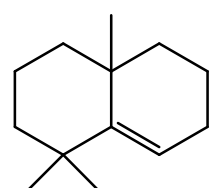
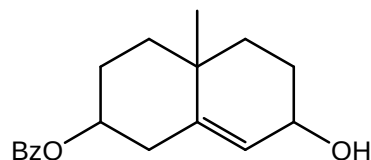
OXIDATION OF ALKENES

ALKENES



Cyclooctene

Norbornene

 α -Pinene

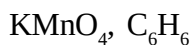
REAGENTS



cetyltrimethyl amm. chloride

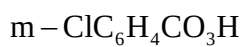
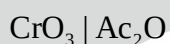
Cyclooctane diol (cis)

cis diol (dialdehyde)

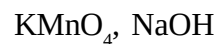
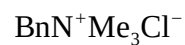
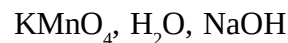
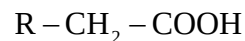


Pyridinium chlorochromate

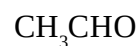
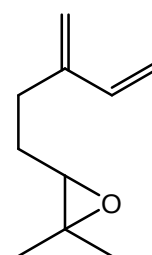
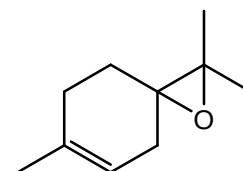
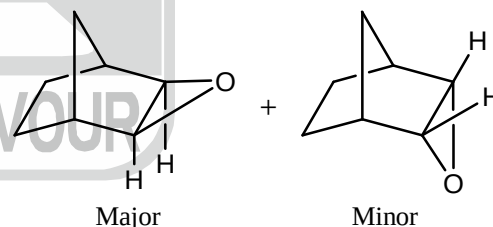
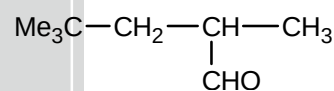
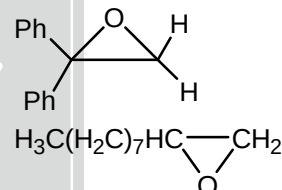
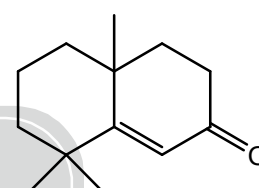
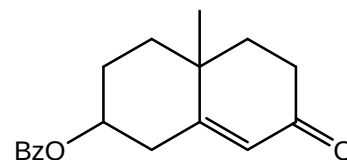
(PCC)

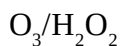
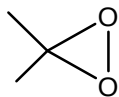
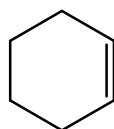
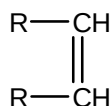
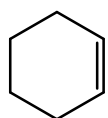
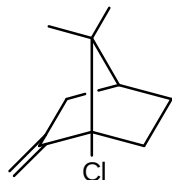
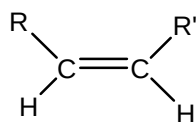
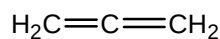


PRODUCTS

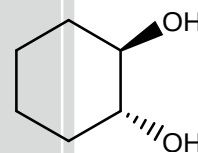
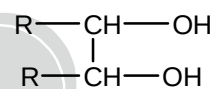
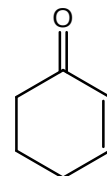
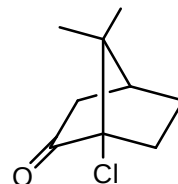
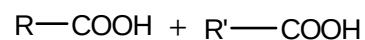
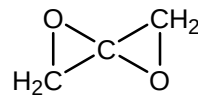


Pinonic acid



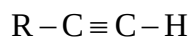
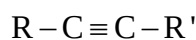
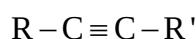
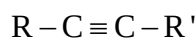


(i) I_2 /silver acetate
(ii) Saponification

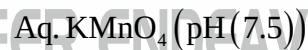


OXIDATION OF ALKYNES

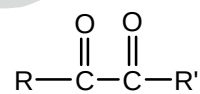
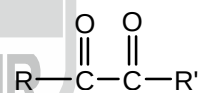
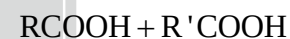
ALKYNES



REAGENTS

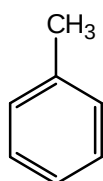


PRODUCTS

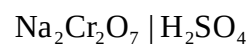
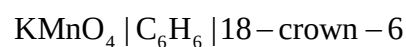


OXIDATION OF AROMATIC HYDROCARBON

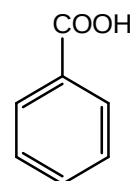
AROMATIC

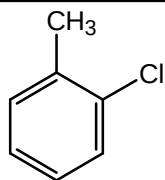
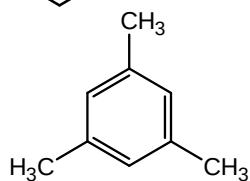
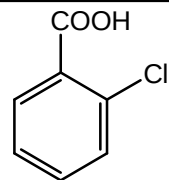
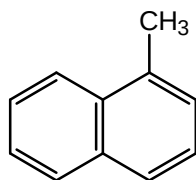
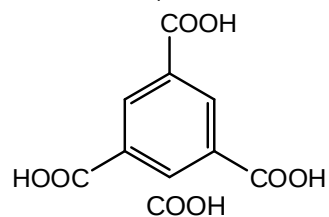
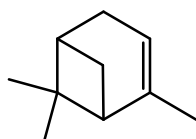
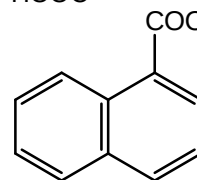


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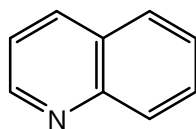
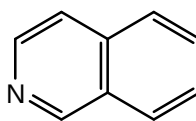
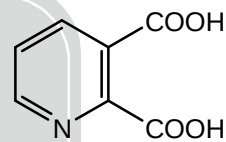
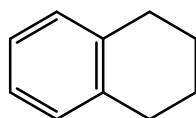
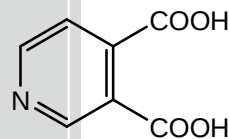
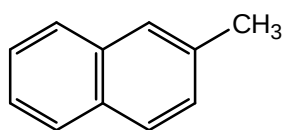
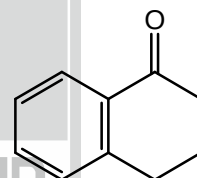
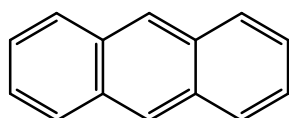
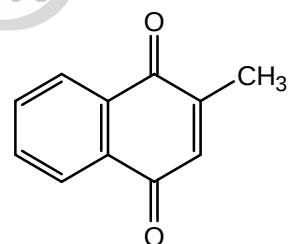
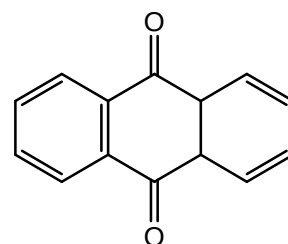


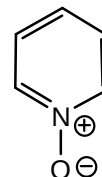
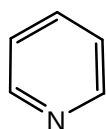
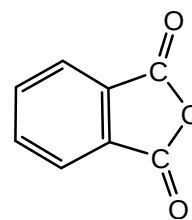
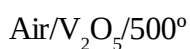
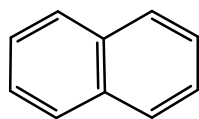
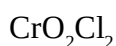
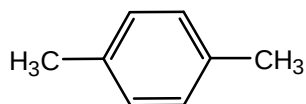
PRODUCTS



KMnO₄KMnO₄KMnO₄KMnO₄, C₆H₆
Dicyclo-18-crown-16

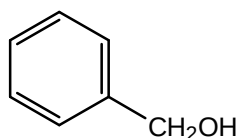
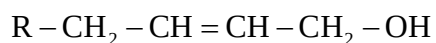
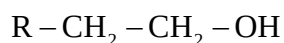
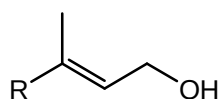
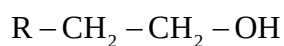
Cis-Pinonic acid

KMnO₄KMnO₄CrO₃/CH₃COOHCrO₃/CH₃COOHCrO₃/CH₃COOH



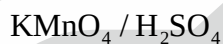
OXIDATION OF PRIMARY ALCOHOL

ALCOHOLS



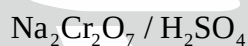
Geraniol

REAGENTS

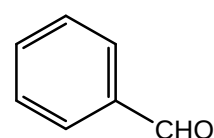
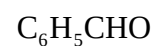
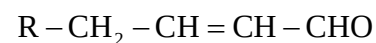
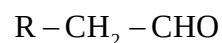
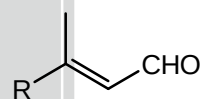
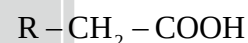


Jones reagent

Enzymatic oxidation

Jones reagent (0°C)PDC, PCC, Ag / Air / 250° Pd(OAc)₂ Py, Fetizon's reagentP-TsCl / DCC / DMSO
(COCl)₂ / DMSO / Et₃NMnO₂ / AcetonePDC + RuCl₂ · P(Ph₃)₂SeO₂MnO₂/etherAgCO₃ or Celite

PRODUCTS



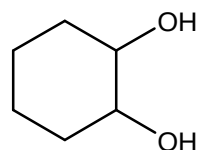
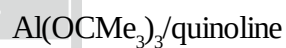
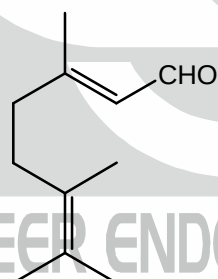
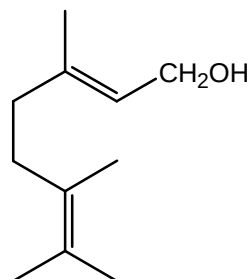
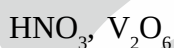
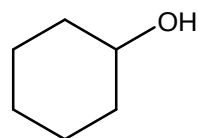
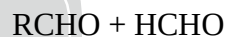
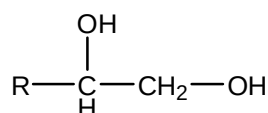
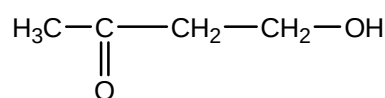
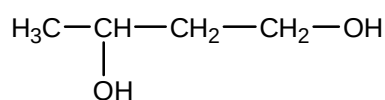
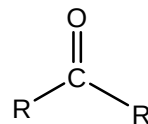
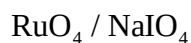
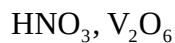
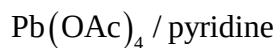
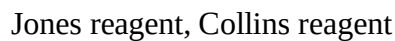
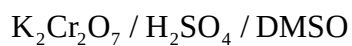
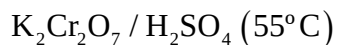
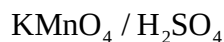
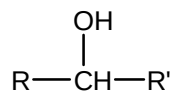
Geranial

OXIDATION OF SECONDARY ALCOHOL

ALCOHOLS

REAGENTS

PRODUCTS

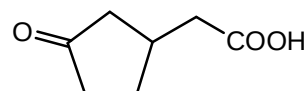
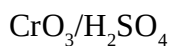
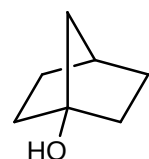


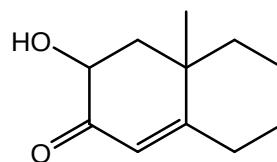
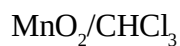
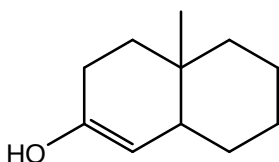
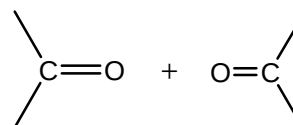
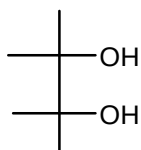
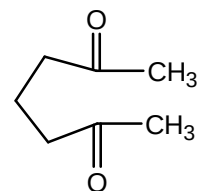
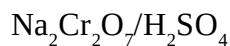
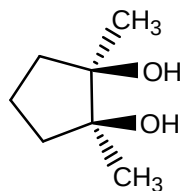
OXIDATION OF TERTIARY ALCOHOL

ALCOHOLS

REAGENTS

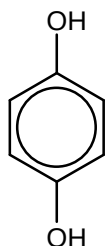
PRODUCTS



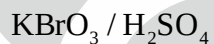
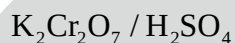


OXIDATION OF PHENOLS

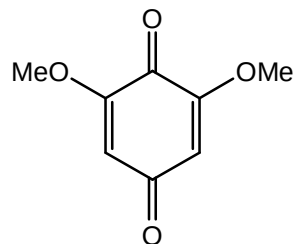
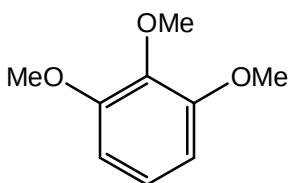
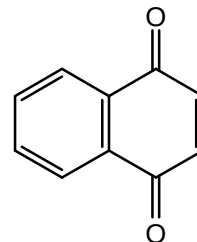
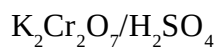
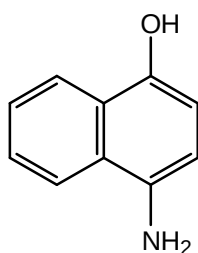
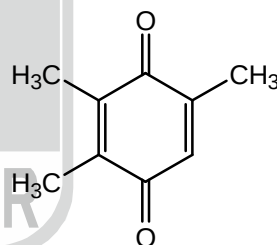
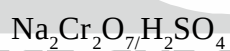
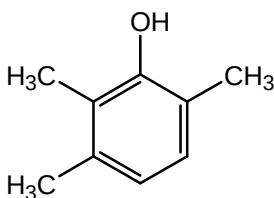
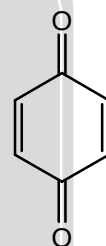
PHENOLS



REAGENTS



PRODUCTS

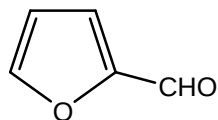


OXIDATION OF ALDEHYDE

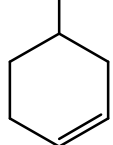
ALDEHYDE

ArCHO

n-Hexanal

 $\text{H}_3\text{C}-\text{CHO}$

CHO



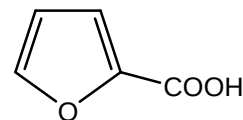
REAGENTS

Alk. KMnO_4
Acidic KMnO_4 $\text{O}_2/\text{Air}/\text{Ag}_2\text{O}/\text{OH}^-$ SeO_2 Ag_2O , NaCN

PRODUCTS

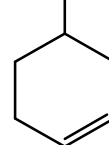
ArCOOH

n-Hexanoic acid



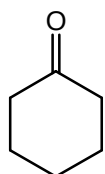
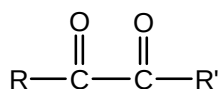
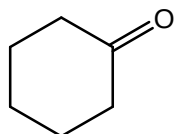
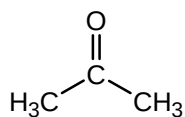
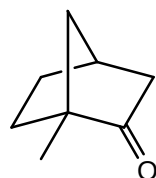
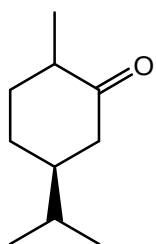
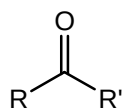
OHC-CHO

COOH



OXIDATION OF KETONE

KETONES

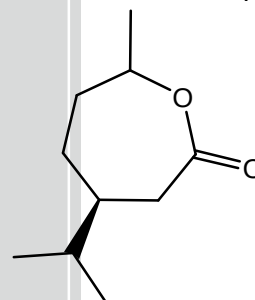
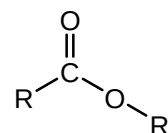


REAGENTS

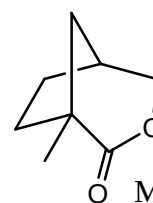
 $\text{C}_6\text{H}_5\text{COOOH}$
 CF_3COOOH
 RCOOOH CF_3COOOH CF_3COOOH SeO_2 SeO_2 HIO_4

Enzymatic oxidation

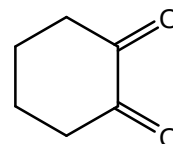
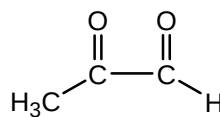
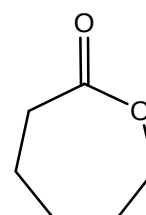
PRODUCTS



Major



Minor

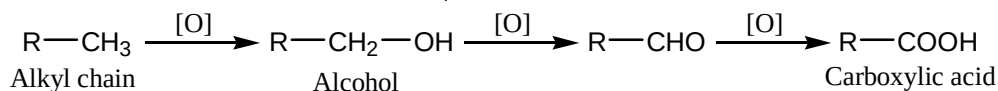
 $\text{RCOOH} + \text{R}'\text{COOH}$ 

3.4. Manganese (VII) Oxidants: (Potassium permanganate):

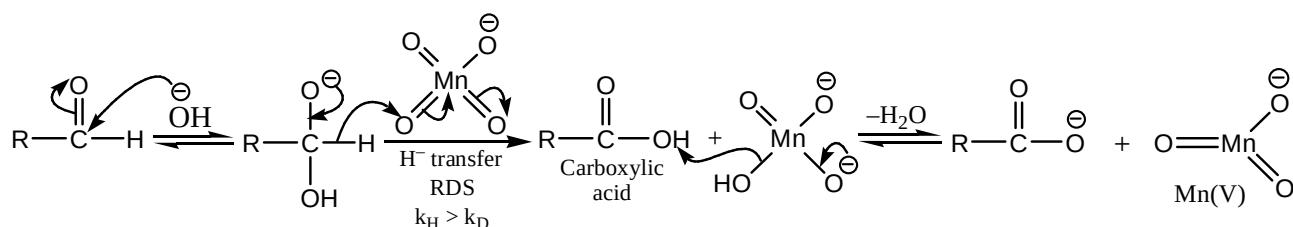
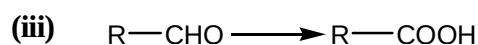
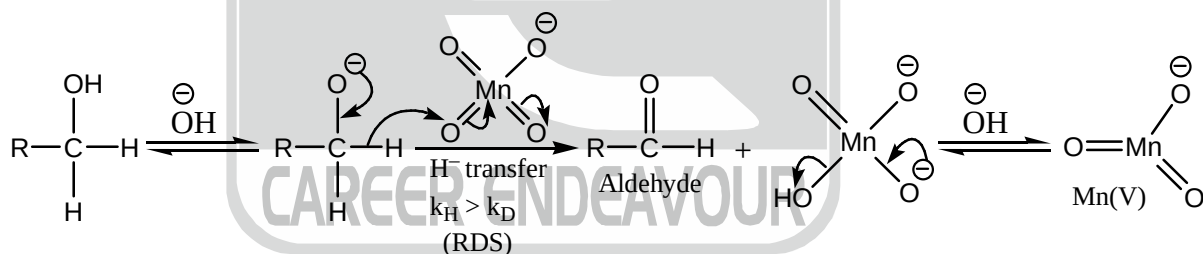
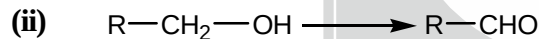
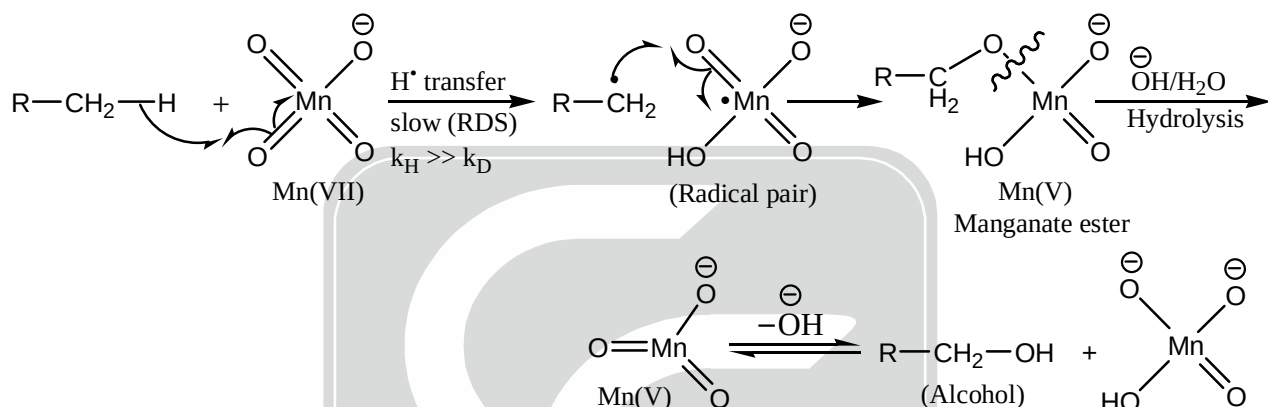
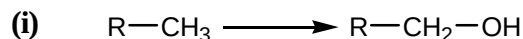
Potassium permanganate, a derivative of hypervalent manganese is a very powerful oxidising agent. Its reactivity depends on whether it is used in acid, neutral or basic condition. In acid solution, Mn(VII) is reduced to divalent manganese (II) with a net transfer of five electrons $\text{Mn(VII)} \rightarrow \text{Mn(II)}$. However, in neutral or basic medium manganese dioxide is usually formed, corresponding to a three-electron change $\text{Mn(VII)} \rightarrow \text{Mn(IV)}$.

It is now well known that the yield in potassium permanganate oxidation are considerably improved by the use of phase transfer catalyst (PTC).

Possible mechanistic pathways with KMnO_4 .

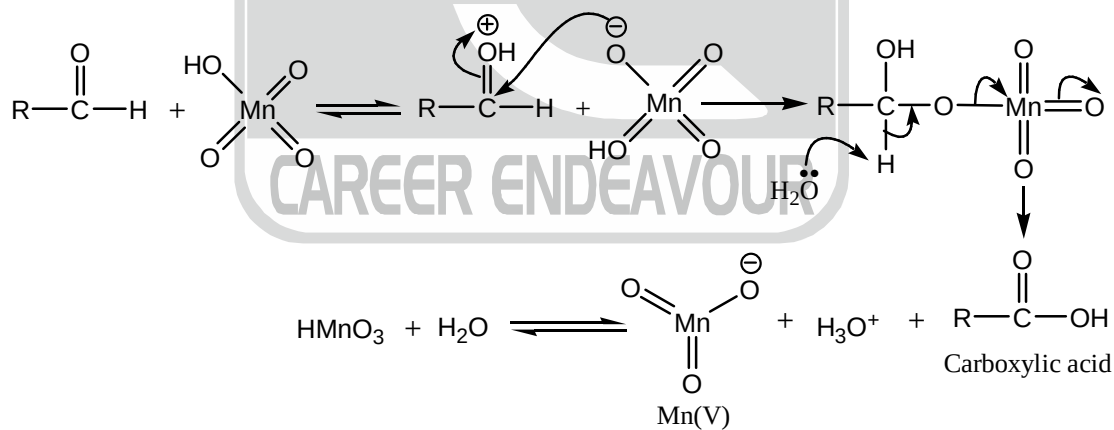
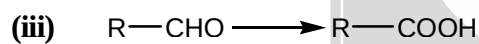
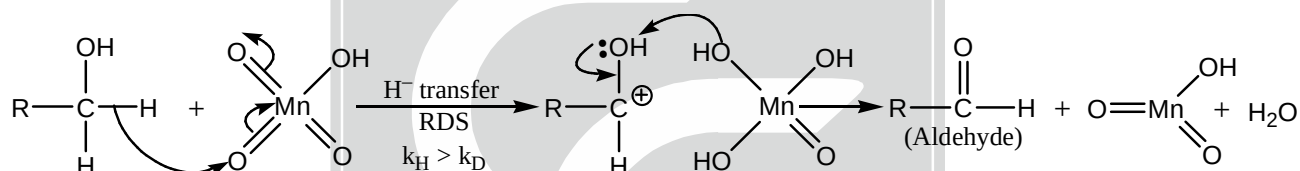
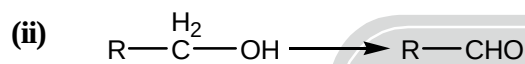
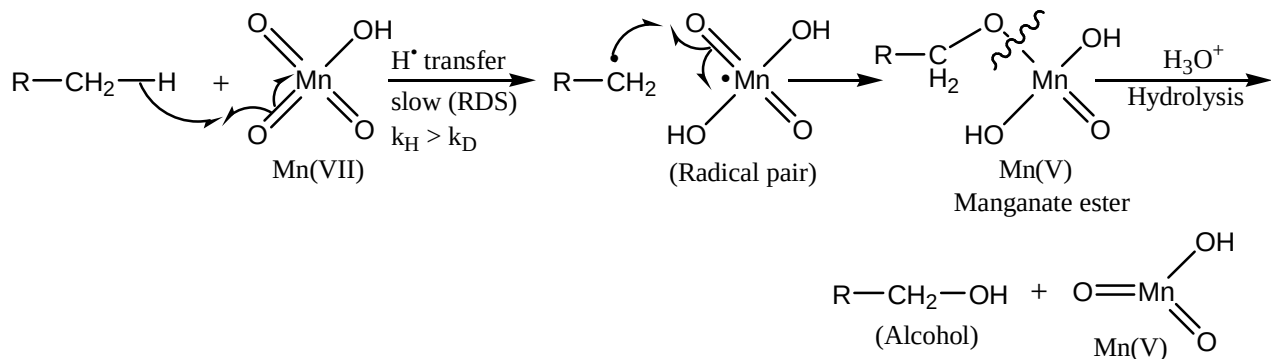
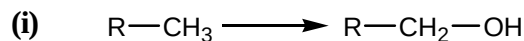
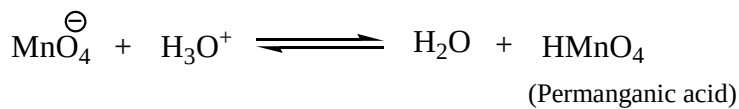


Alkaline medium:



Note: The final fate of MnO_4^{2-} will be MnO_2 via disproportionation of MnO_3^-



Acidic medium: (H₂SO₄)

Note: Disproportionation in acidic medium $[\text{Mn(V)} \longrightarrow \text{Mn(II)}]$

