Hydrocarbon Oxidation:

Hydroxylation $RCH=CHR \xrightarrow{\text{reagents.}} RCH(OH)-CH(OH)R$ vicinal diol.

The reagents used can be

a) Cold dilute (1%) alkaline $KMnO_4$ or Baeyer's Reagent.

b) OsO_4, $NaHSO_3$ / alkaline hydrolysis

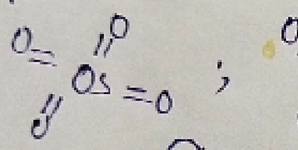
c) H_2CrO_4

d) $RCO_3H + H_2O$

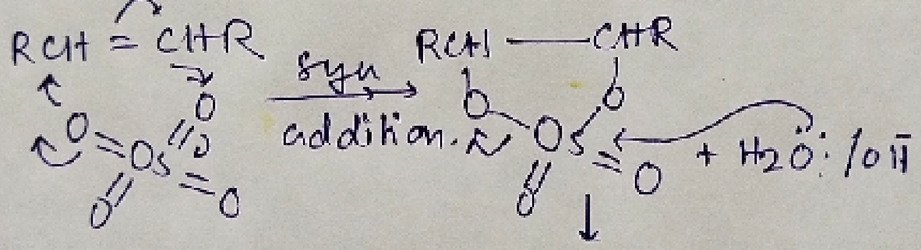
e) moist Ag_2O

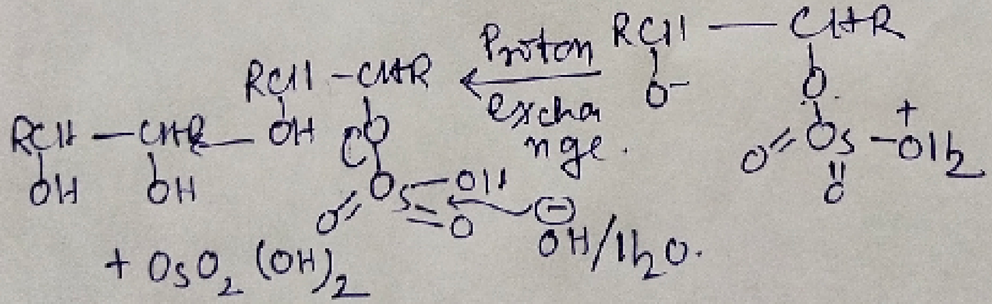
a, b, c are example of syn addition; d, e are example of antiaddition

∴ Mechanism: (syn addition)



[Tetrahedral d^3s].





$+ OsO_2(OH)_2$

vicinal diol.

⇒ syn addition takes place.

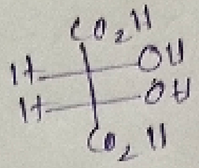
⇒ $Os(VIII)$ converted with $Os(VI)$.

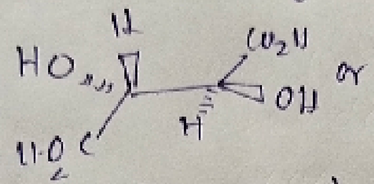
⇒ Using $KMnO_4$, MnO_2 or $Mn(OH)_2$ (brown ppt) is formed. So this reaction is used to identify unsaturation.

Stereochemistry.

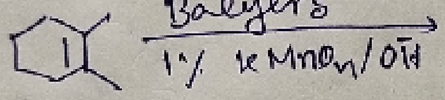
=> CSM. (Cis cpd + Syn addition → Meso pdt)
Symmetrical alkene.

Example: a) Maleic acid $HO_2C-CH=CH-CO_2H$ $\xrightarrow[\text{or Baeyer's reagent.}]{OsO_4, OH^-}$





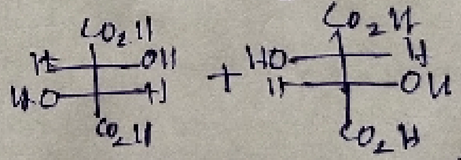
b) Cis but 2 ene
c) Cis hex-3 ene. } all 3 gives meso pdt provided product have 2 chiral centre. Symmetrical alkene
d) PhCH = CHPh (Cis Stilbene)

e) 

=> TSR. (Trans cpd + Syn addition → Racemic mixture)
Symmetrical alkene.

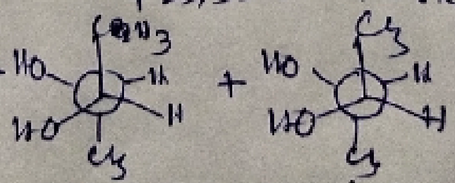
a) fumaric Acid.
b) Trans but ene.
c) Trans hex 3 ene.
d) PhCH = CHPh.

$HO_2C-CH=CH-CO_2H$ $\xrightarrow[KOH]{KMnO_4 \text{ (cold) } 1\%}$



2R,3R tartaric acid + 2S,3S tartaric acid.

$\xrightarrow[+NaHSO_3]{OsO_4}$

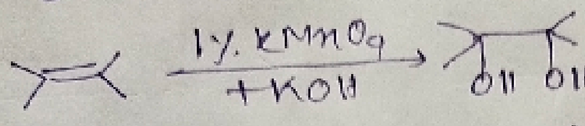


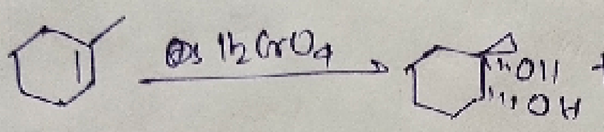
racemic mixture.

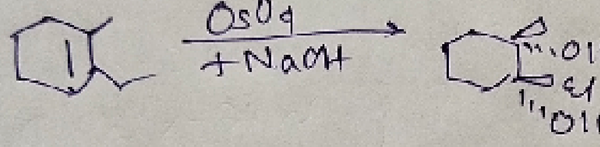
Meso is optically inactive (Internal compensation)
Racemic mixture is optically inactive (External ").

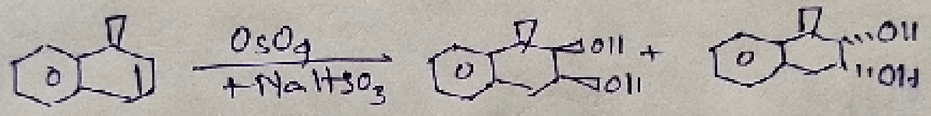
Other examples:

a) $CH_3-CH=CH_2 \xrightarrow[+NaHSO_3]{OsO_4} CH_3-CH(OH)-CH_2OH$ (±) racemic mixture

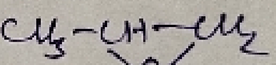
b)  only 1 product neither it is meso / nor it is racemic mixture

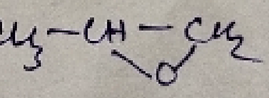
c)  + ENT. } Racemic mixture.

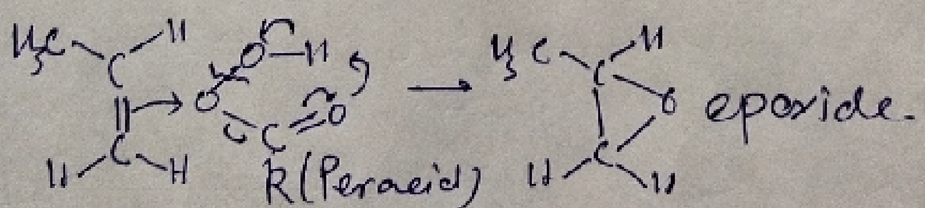
d)  + ENT. } Racemic mixture.

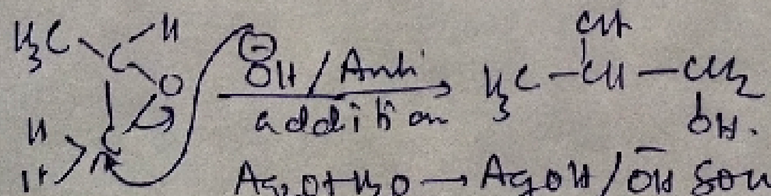
e)  Diastereomeric pair

Mechanism: (Anti addition)

$CH_3-CH=CH_2 + Ag_2O \longrightarrow$  (oxidising reagent)/unstable.

$CH_3-CH=CH_2 + RCO_3H \longrightarrow$  (oxidising reagent)





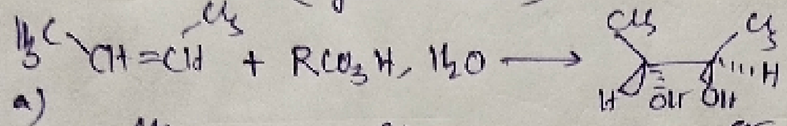
$Ag_2O + H_2O \rightarrow AgOH/\bar{O}H$ source.

Points to be noted:

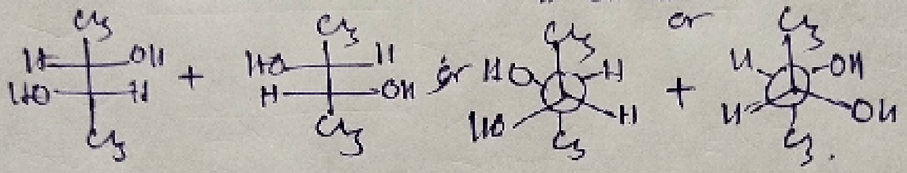
⇒ PNPBA; MCPBA; $C_6H_5CO_3H$; $PhCO_3H$ all can be used. Ag_2O is source of nascent oxygen also

⇒ ~~P~~ ~~H2O~~ ~~OH~~ TAM ⇒ CAR

Cis cpd + Anti addition ⟶ Racemic mixture. (symmetrical)



a)



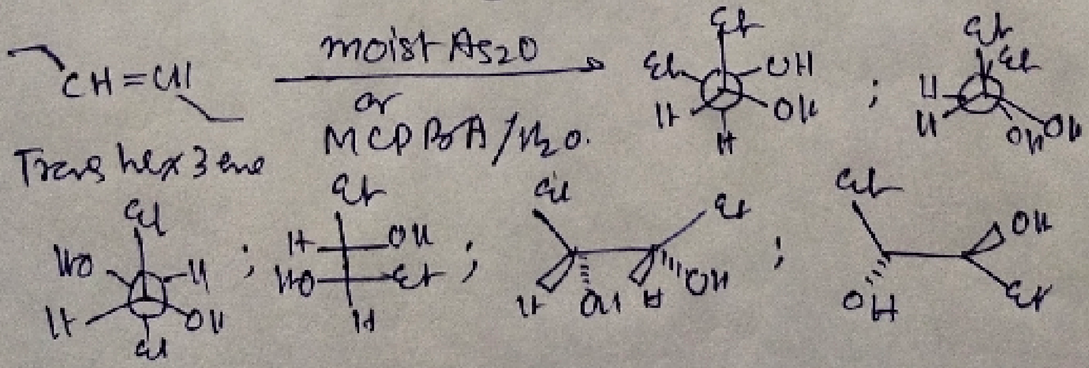
b) Maleic Acid.
c) Cis Stilbene.
d) Cis hex-3-ene.

} product have 2 chiral centre. Cpds are cis / symmetrial alkene.

⇒ TAM Trans cpd + Anti addition ⟶ Meso product (symmetrical alkene).

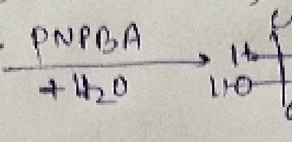
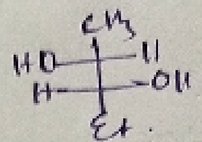
a) Trans but 2 ene
b) Trans hex 3 ene
c) Trans stilbene.
d) fumaric acid

} Product have 2 chiral centre; cpds are trans / symmetrial alkene

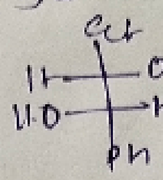


Miscellaneous Questions:

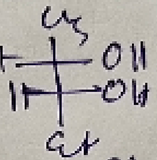
for nonsymmetrical alkene CAR → CAT
(provided product has 2 chiral centre). TAM → TAE

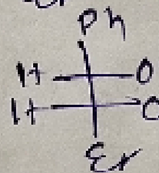
i) $CH_3-CH=CH-Et$ (cis) $\xrightarrow[+H_2O]{PNPBA}$  + 

Threo mixture

ii) $Et-CH=CH-Ph$ (cis) $\xrightarrow{R-CO_3H}$  + ENT.

Threo mixture

iii) $CH_3-CH=CH-Et$ $\xrightarrow[+H_2O]{PhCO_3H}$  + ENT.

iv) $Ph-CH=CH-Et$ $\xrightarrow{\text{moist } Ag_2O}$  + ENT

$\Rightarrow$ {erythro mixture}

Erythro / Threo mixture are examples racemic mixture also.

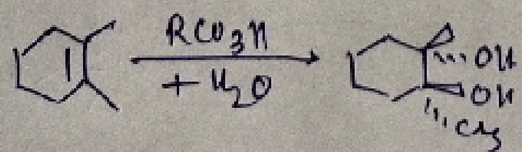
v) $PhCH=CH_2$ (Styrene) $\xrightarrow[H_2O]{RCO_3H}$ $Ph-CH(OH)-CH_2OH$

(single chiral centre)

± racemic mixture

vi) $CH_2=CH_2$ $\xrightarrow[Ag_2O.]{\text{moist}}$ $CH_2(OH)-CH_2(OH)$

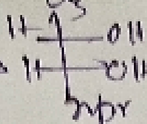
no chiral centre.
optically inactive

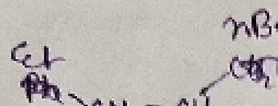
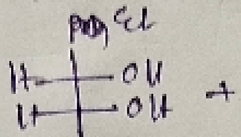
vii) 

viii) for nonsymmetrical alkene

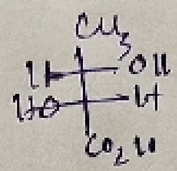
CsM → CsE

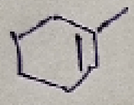
TSR → TST.

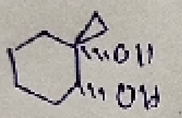
a) $CH_3-CH=CH$ (npr) $\xrightarrow{H_2CrO_4}$  + ENT.

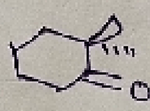
b)  $\xrightarrow{\text{Baeyer's reagent}}$  + ENT.

} erythro pair

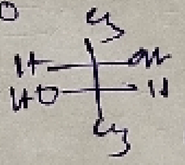
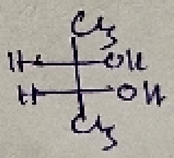
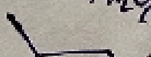
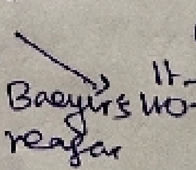
c) $H_3C-CH=CH-CO_2H$ $\xrightarrow[NaHCO_3]{cat.\ OsO_4}$  + ENT.

d)  $\xrightarrow[+NaHSO_3]{OsO_4}$ A $\xrightarrow{H_2CrO_4}$ B

A =  + ENT.

B = 

e) $H_3C-C\equiv C-CH_3$

- H_2/Lindlar or P_2 catalyst →  $\xrightarrow{m\text{-}CPBA}$  + ENT. (CAR)
- $OsO_4 + H_2O$ →  (CSM)
- Li in liq. NH_3 or Na in liq. NH_3 →  $\xrightarrow[+H_2O]{RCO_3H}$ TAM
- Baeyer's reagent →  + EWT. (TSR)

f) Fumaric Acid A → 2R, 3R tartaric acid + 2S, 3S tartaric acid.

Fumaric Acid B → 2R, 3S tartaric Acid

Maleic Acid C → 2R, 3R tartaric acid + 2S, 3S tartaric acid.

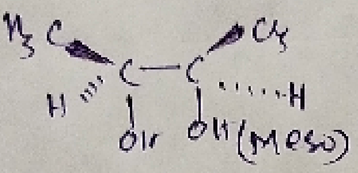
Maleic Acid D → 2R, 3R tartaric acid + 2S, 3S tartaric acid.

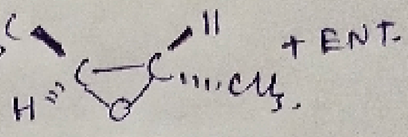
What are A, B, C, D?

Q. Trans but-2-ene $\xrightarrow{RCO_3H}$ P_1 [Pdt is optically inactive due to external compensation]

$\xrightarrow[+H_2O]{RCO_3H}$ P_2 [Pdt is optically inactive due to internal compensation]

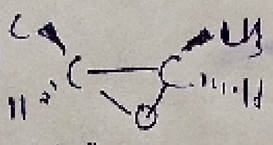
What are P_1 & P_2?

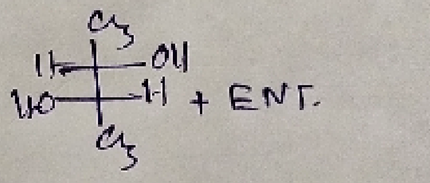
P_2 ⇒ 

P_1 ⇒ 

Q. Cis but-2-ene $\xrightarrow{RCO_3H}$ P_3 [opposite stereochemistry is observed]

$\xrightarrow[+H_2O]{RCO_3H}$ P_4

P_3 ⇒ 

P_4 ⇒ 

: Example of Syn addition:

⇒ H_2/Ni ; Lindlar Cat. ; $N_2H_4 + H_2O_2$

⇒ OsO_4, OH ; $KMnO_4$, KOH ; H_2CrO_4.

⇒ HBO. B_2H_6 (THF) + H_2O_2 + OH.

Example of Anti addition.

⇒ Br_2/CCl_4

⇒ MCPBA + H_2O ; PNPBA + H_2O.

⇒ moist Ag_2O.

⇒ ⊙

To detect unsaturation

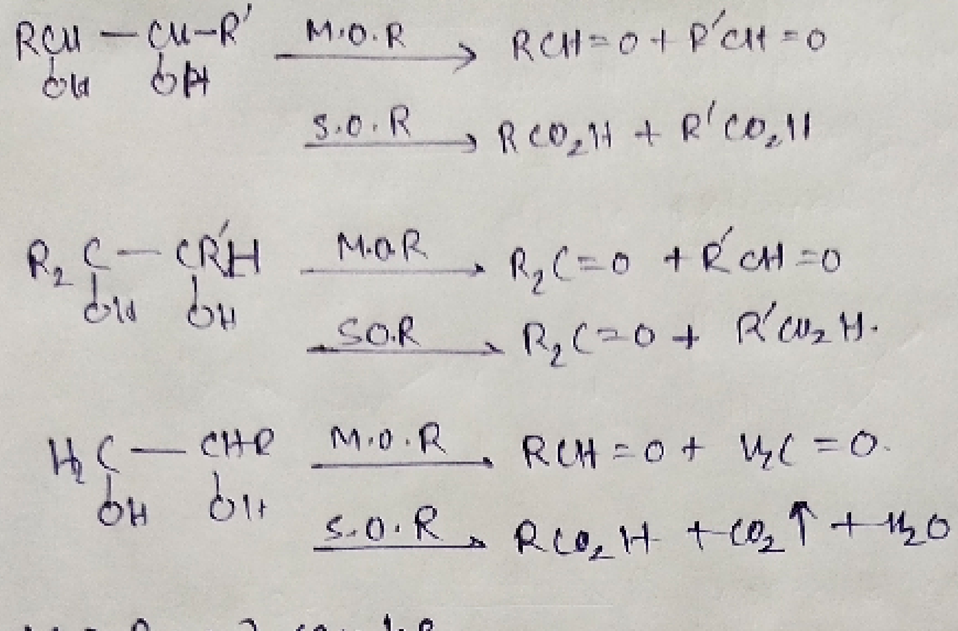
i) Br_2/CCl_4 can be used

Reddish brown → Colorless

ii) Baeyer's can be used

Pink/Purple → Reddish brown ppt

: Oxidative cleavage of diol:



M.O.R used can be

a) HIO_4. (Periodic acid) [I^{+7} can act as oxidant].

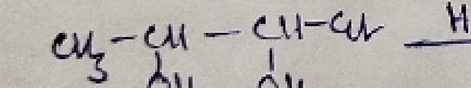
b) $Pb(CH_3CO_2)_4$ (Lead tetra acetate) [Pb^{+4} can act as oxidant].

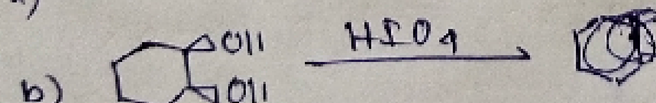
S.O.R used can be.

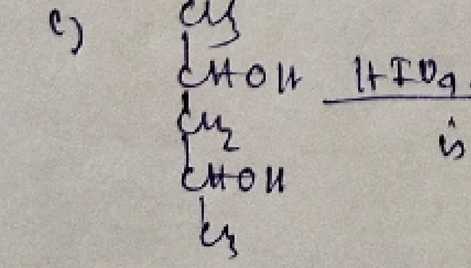
a) Hot $KMnO_4$ / $KMnO_4$, H^+

b) $K_2Cr_2O_7$, H^+

: Examples:

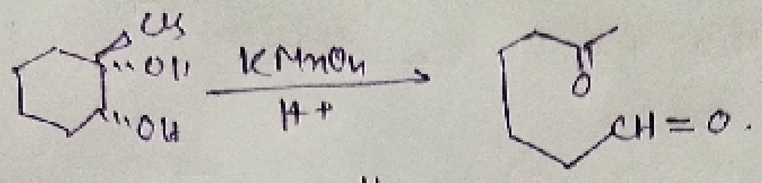
a) 

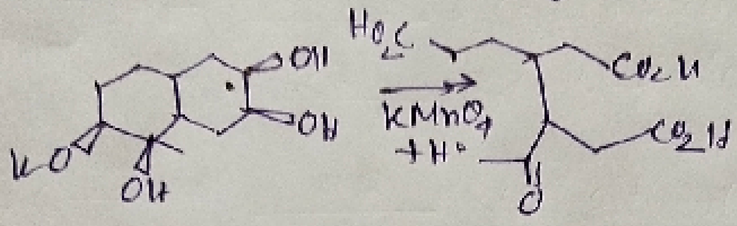
b) 

c) 

$CH_3-CH(OH)-CH_2(OH) \xrightarrow{KMnO_4/H^+} CH_3CO_2H + CO_2\uparrow + H_2O$

a)

b) 

c) 

: Points to be noted:

for alcohol oxidation $KMnO_4/KOH$ or $KMnO_4/H^+$ there is no big difference in ~~product~~ formation.

$$RCH_2OH \xrightarrow[KOH]{KMnO_4} RCO_2K + MnO_2\downarrow \quad \text{---(1)}$$

$$RCH_2OH \xrightarrow{KMnO_4/H^+} RCO_2H + Mn^{2+} \quad \text{---(2)}$$

Observation: Purple/Pink → Brown ppt ---(1)

Purple/Pink → Colorless ---(2)

$R_2CHOH \xrightarrow[\text{or } KMnO_4, H^+]{KMnO_4, KOH} R_2C{=}O + MnO_2 \text{ or } Mn^{2+}$

$R_3COH \xrightarrow[\text{or } KMnO_4, H^+]{KMnO_4, KOH}$ no reaction at normal temp.

But for Hydrocarbon oxidation, using cold/$KMnO_4$/KOH or | $KMnO_4$/H+, pdt formed are different. (alkene) or hot

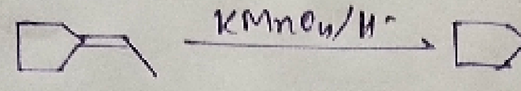
$RCH=CHR \xrightarrow[\text{cold } KMnO_4]{KMnO_4 + KOH\ (1\%)} RCH(OH)-CHR$

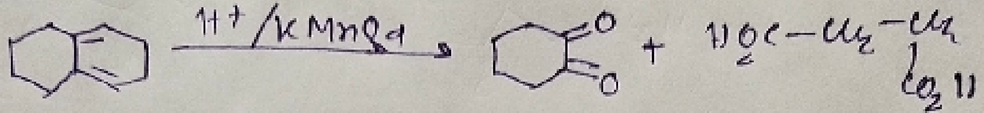
| Baeyer's. vicinal diol is formed as final product

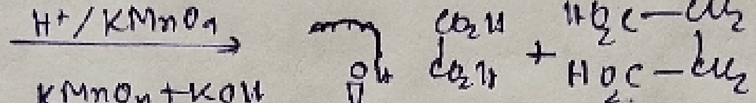
different products are produced.

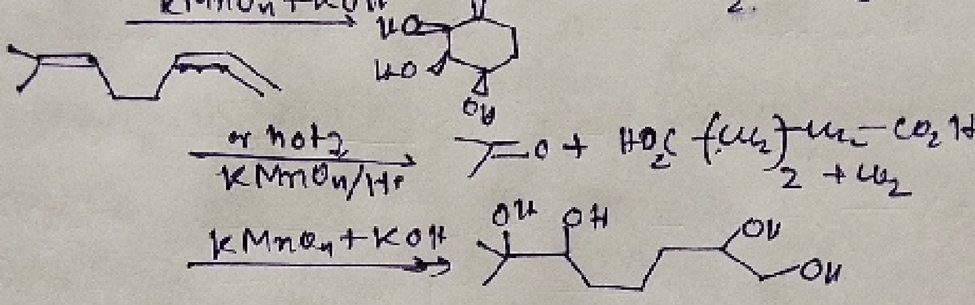
a) $RCH=CHR' \xrightarrow{KMnO_4/H^+} RCO_2H + R'CO_2H$

b) $R_2C=CH_2 \xrightarrow{KMnO_4/\Delta} R_2C=O + CO_2 + H_2O$

c) 

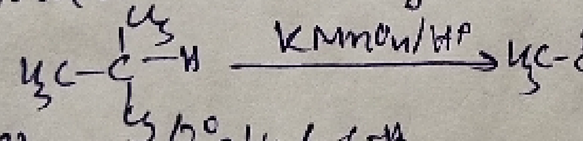
d) 

e) 

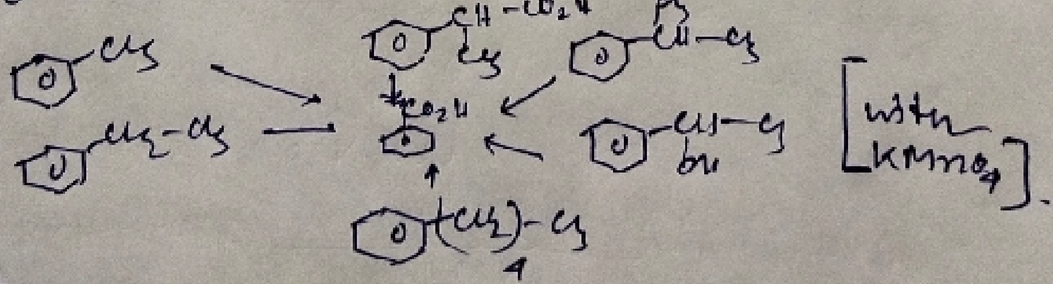
f) 

: Other uses of $KMnO_4$:

Alkane with 3° alkyl C–H is oxidised to C–OH bond.

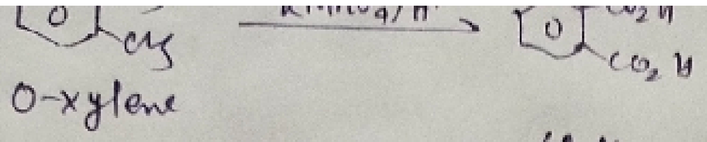
a) 
(3° alkyl C–H bond) benzylic 3° alcohol

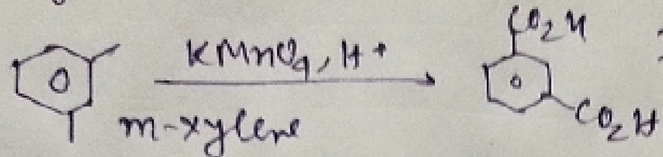
b) Benzene ring with benzylic C–H bond is oxidised to benzoic acid whatever is the side chain.

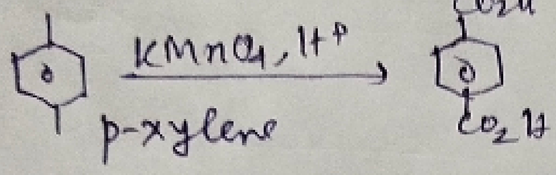


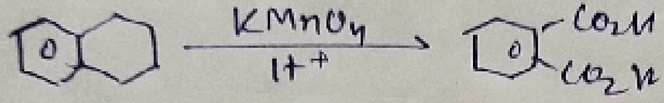
"at least benzylic carbon has one benzylic H."

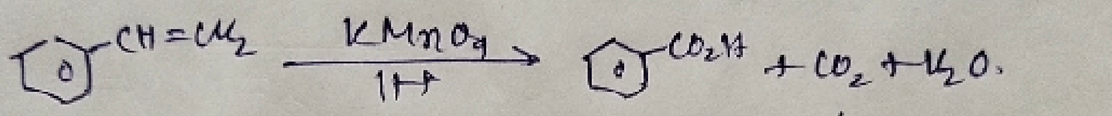
$PhCH_2Cl$, $PhCH=O$. $PhCH_2Br$; $Ph-\triangleleft$ all converted into benzoic acid.

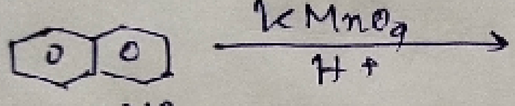
a) 
O-xylene
Phthalic acid
$\xrightarrow{\Delta}$ Phthalic Anhydride.

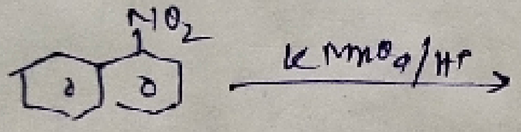
b) 
m-xylene
Isophthalic acid

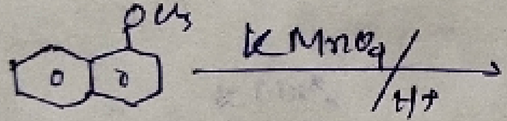
c) 
p-xylene
Terephthalic acid

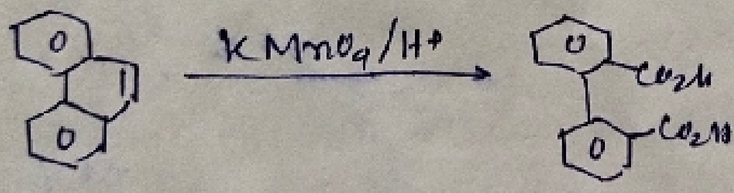
d) 

e) 

f) 

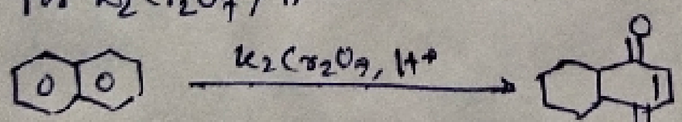
g) 

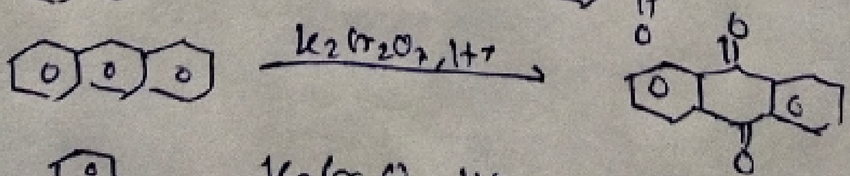
h) 

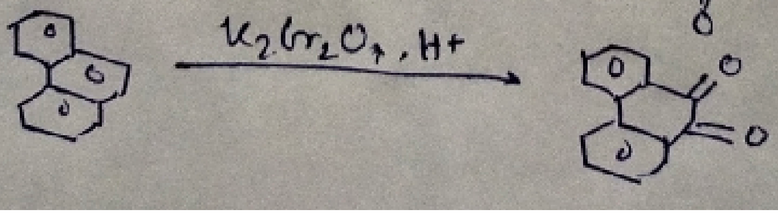
i) 

$KMnO_4$ + KOH same products are formed. in all cases. a to (i) only salt of acid is formed as product.

j) For $K_2Cr_2O_7 / H^+$



k) 

l) 

: Other uses of HIO_4:

It is used to oxidise compounds where adjacent carbon having following group.

i) Bihydroxy compound. $-OH, -OH$

ii) $-CH=O, -OH$

iii) $-CH=O, -CH=O$

iv) $-\underset{|}{C}-, -OH$

v) $-\underset{|}{C}-; -CH=O$.

a) $CH_2OH-CHOH-CH_2OH \xrightarrow[(3eq)]{HIO_4} H_2C=O + HCO_2H + HCH=O$

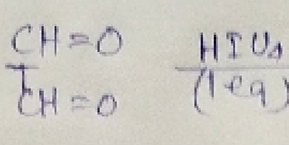
b) $CH_2OH-CH_2-CH_2OH \xrightarrow{HIO_4}$ no reaction. $\xleftarrow{HIO_4} CH=O-CH_2-CH_2OH$

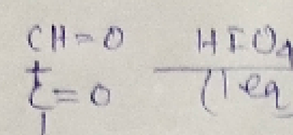
c) $CH=O-(CHOH)_4-CH_2OH \xrightarrow[5eq\ consumed]{HIO_4} 5eq.\ HCO_2H + 1eq.\ HCH=O.$

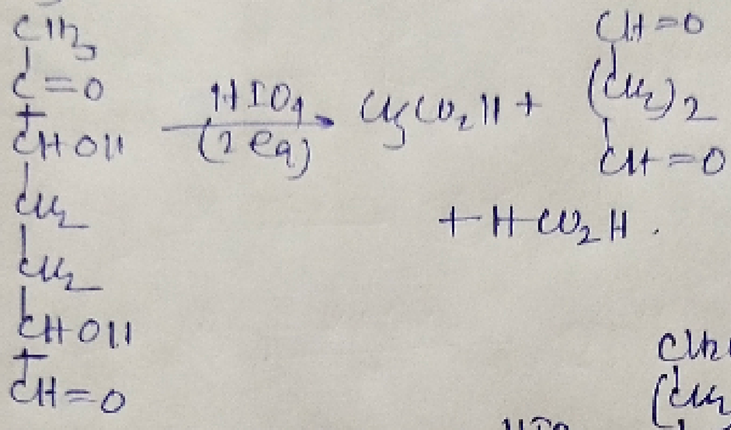
d) $CH_2OH-C(=O)-(CHOH)_3-CH_2OH \xrightarrow[5eq.\ consumed]{HIO_4} 5eq.\ HCO_2H + 1eq.\ HCH=O.$

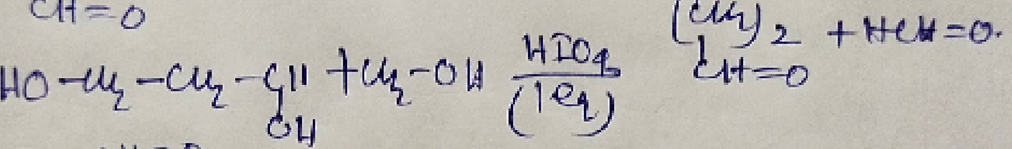
e) $CH_3-CHOH-CHOH-CHOH-CH_3 \xrightarrow{HIO_4}$ No reaction.

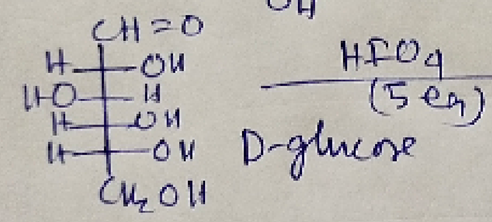
f) $CH=O-CHOH-CH_2-CHOH-C(=O)-CH_2OH \xrightarrow[3eq\ consumed]{HIO_4} HCO_2H + CH=O-CH_2-CH=O + CO_2 + HCHO$

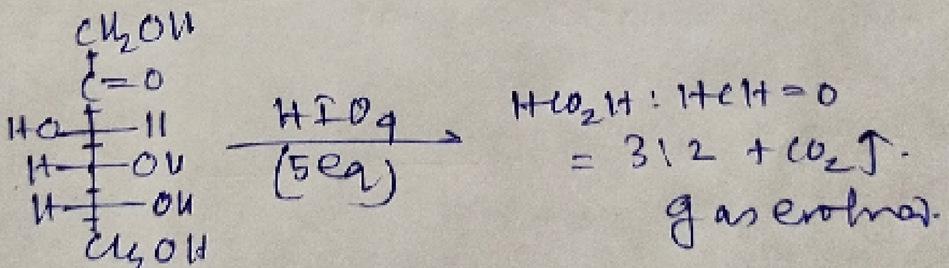
g) 
CH=O
CH=O
HIO4
(1eq)
HCO2H + HCO2H

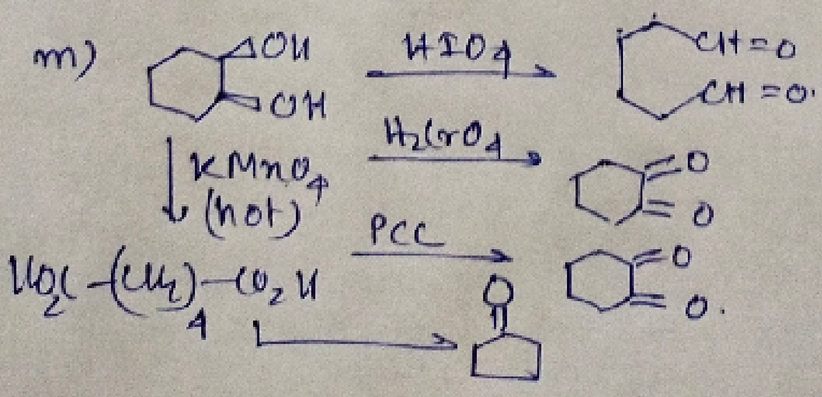
h) 
CH=O
C=O
CH3
HIO4
(1eq)
HCO2H + CH3CO2H.

i) 
CH3
C=O
CHOH
CH2
CH2
CHOH
CH=O
HIO4
(2eq)
CH3CO2H +
CH=O
(CH2)2
CH=O
+ HCO2H.

j) 
HO-CH2-CH2-CH-CH2-OH
OH
HIO4
(1eq)
CH2OH
(CH2)2
CH=O
+ HCH=O.

k) 
CH=O
H-OH
HO-H
H-OH
H-OH
CH2OH
D-glucose
HIO4
(5eq)
HCO2H : HCH=O
= 5 : 1.

l) 
CH2OH
C=O
HO-H
H-OH
H-OH
CH2OH
HIO4
(5eq)
HCO2H : HCH=O
= 3 : 2 + CO2↑.
gaseous.

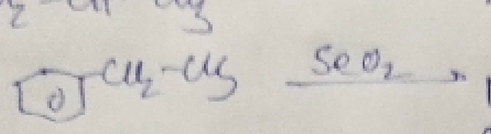
m) 
OH
OH
HIO4
CH=O
CH=O.
H2CrO4
KMnO4
(hot)
O
O
PCC
HO2C-(CH2)4-CO2H
O
O.

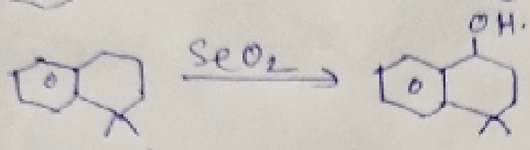
Use of Other oxidising reagents:

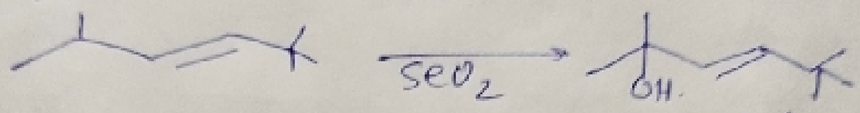
: SeO_2 : (Selenium dioxide)

It is used to substitute allylic hydrogen or benzylic hydrogen by $-OH$ group.

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

b) 

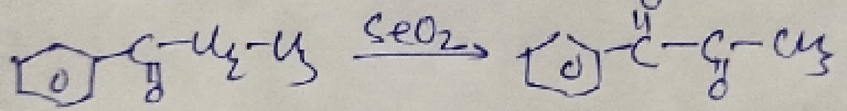
c) 

d) 

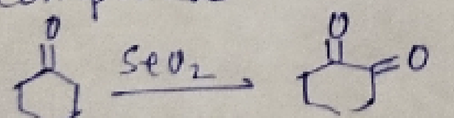
Also it is used to convert $-CH_2-$ group adjacent to $(-\overset{O}{\overset{\|}{C}}-)$ to $-\overset{O}{\overset{\|}{C}}-$.

a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{SeO_2} CH_3-\overset{O}{\overset{\|}{C}}-CH=O$

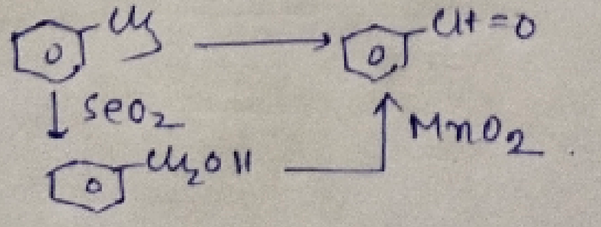
Monocarbonyl compound — Dicarbonyl compound.

b) 

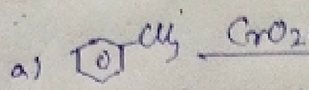
Monocarbonyl compound — Dicarbonyl compound.

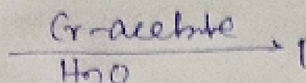
c) 

d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{SeO_2} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

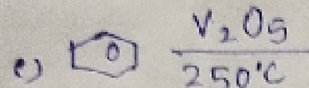
e) 

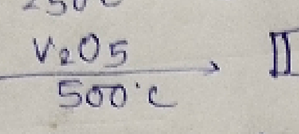
: CrO_2Cl_2 : (Chromyl chloride)

a)  Etard reaction

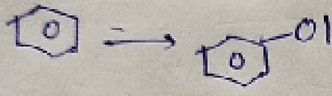
b) 

: V_2O_5 : (Vanadium Pentoxide)

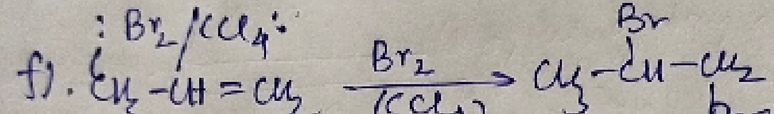
c) 

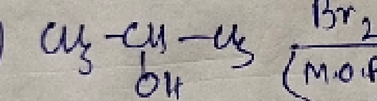
d)  (Maleic anhydride)

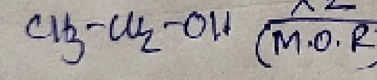
e) $FeSO_4 + H_2O_2$ (fenton's reagent)

e) 

: Br_2/CCl_4 :

f) 

g) 

h) 

: O_2 :

$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$ [complete combustion]

$2CH_4 + O_2 \xrightarrow[100atm]{Cu/523K} 2CH_3OH$ (Methanol)

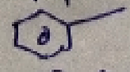
$CH_4 + O_2 \xrightarrow[\Delta]{MO_2O_3} HCHO + H_2O$ (Methanal)

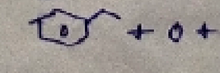
$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$

NCERT P-374.

$\Rightarrow$ controlled Oxidation.

n-hexane $\xrightarrow[\text{or } MO_2O_3]{Cr_2O_3/V_2O_5}$ 

n-heptane $\xrightarrow{\eta}$ 

n-octane $\xrightarrow{\eta}$  + o + m + p xylene.