: Oxidation :

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

reagents	
$OsO_4 + OH^-$	R_1
$MnO_4^- + OH^-$	R_2
H_2CrO_4.	R_3
moist Ag_2O	R_4
mCPBA + H_2O	R_5

Oxidative cleavage of Vicinal diol.

$RCH(OH)-CH(OH)-R' \xrightarrow{HIO_4} RCH=O + R'CH=O$

$RCH(OH)-CH(OH)-R' \rightarrow RCH(OH)-OH + HC(OH)-R'$

$RCH(OH)-OH \rightarrow RCH=O$

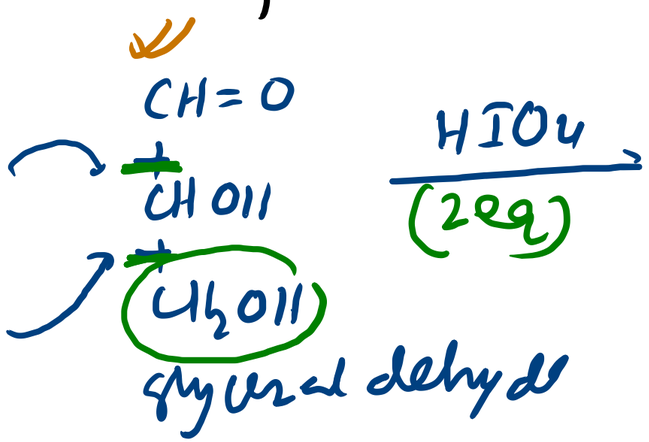
$HC(OH)-R' \rightarrow R'CH=O$.

Polyhydroxy compounds (2-OH groups are at vicinal position.)

[2-OH + $-CH=O$ → $-CH=O + -CH=O$

$-OH + -C(=O)- \rightarrow -C(=O)- + -C(=O)-O$]

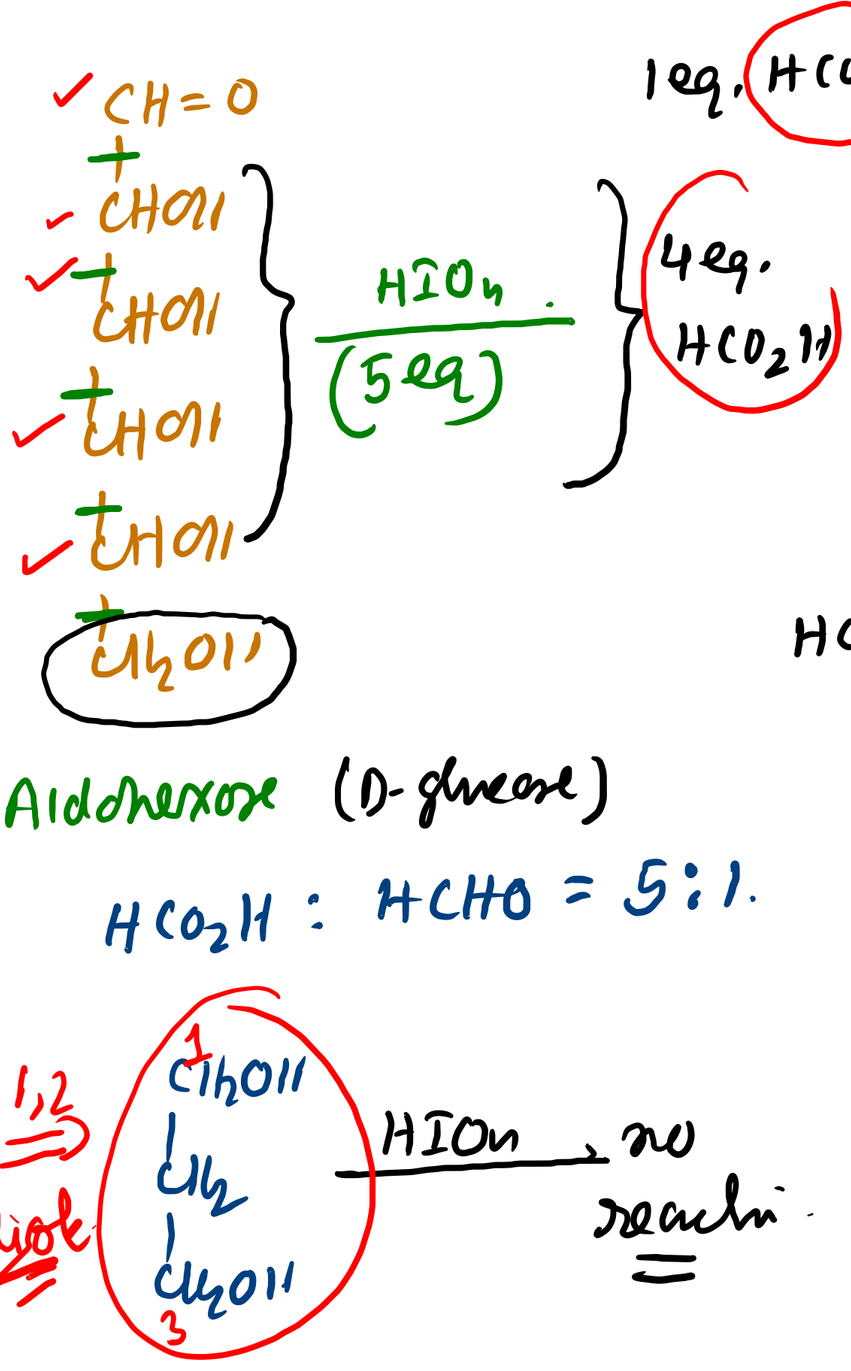
cpd can undergo breakage.

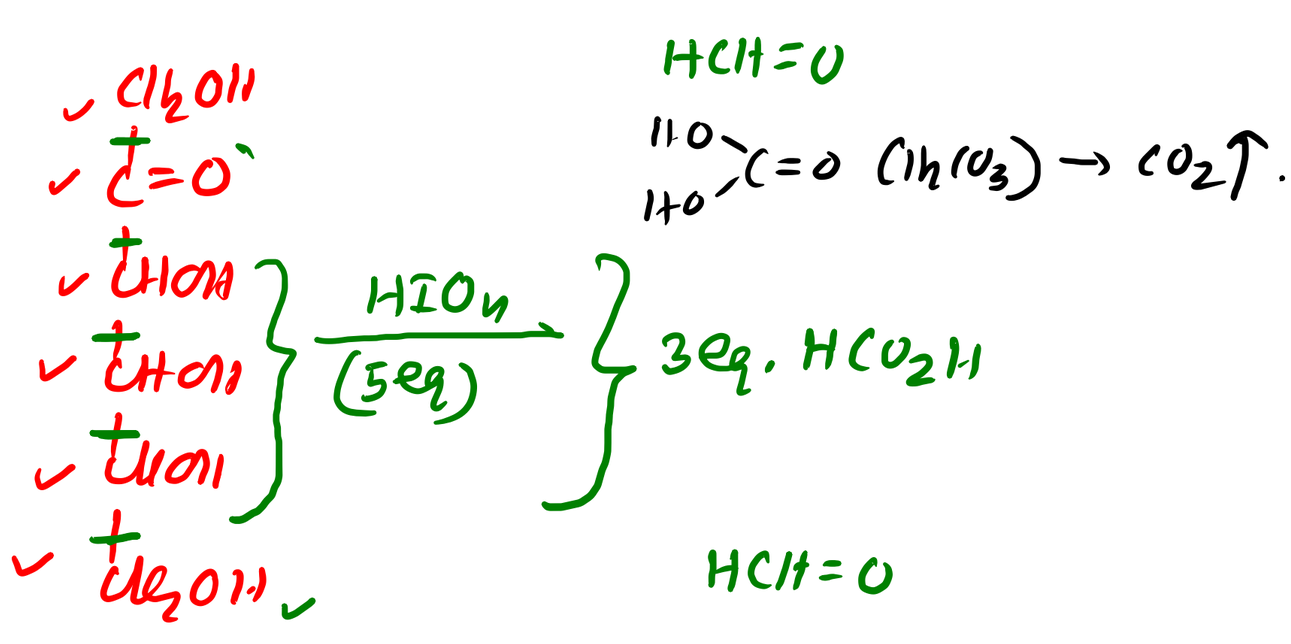


upper-HO : HCO_2H

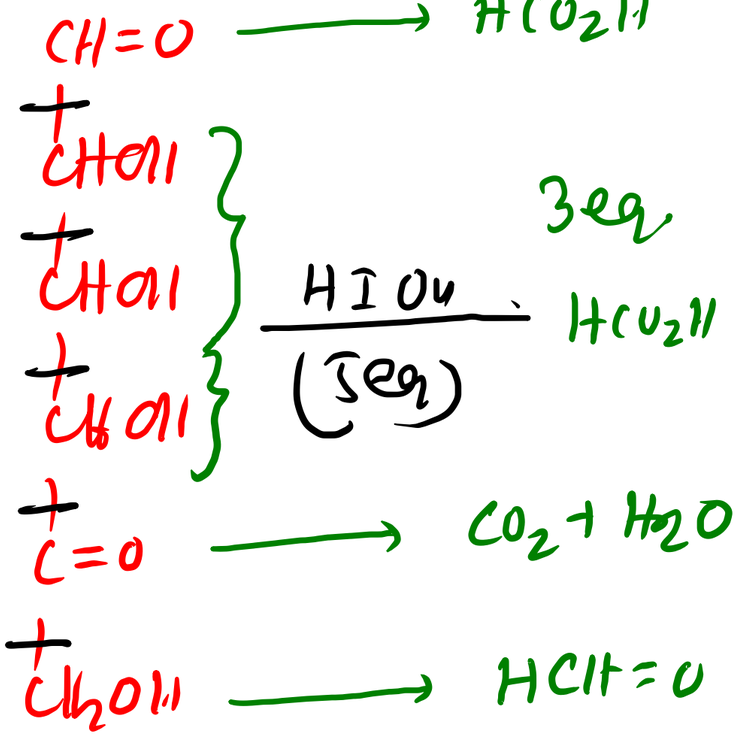
middle alcoholic -OH : HCO_2H

Terminal alcohol $\Rightarrow H_2C=O$.

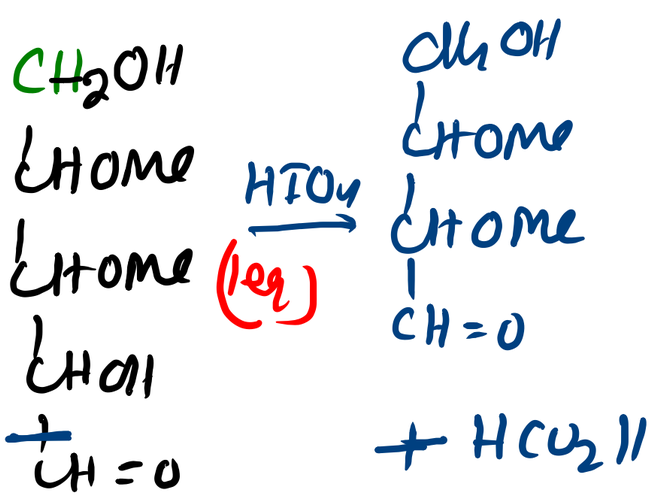

CH=O
CHOH
CHOH
CHOH
CHOH
CH2OH
HIO4
(5eq)
4eq.
HCO2H
1eq. HCO2H
HCH=O
Aldohexose (D-glucose)
HCO2H : HCHO = 5:1.
1,2
diol
1
CH2OH
CH2
CH2OH
3
HIO4
no reaction.

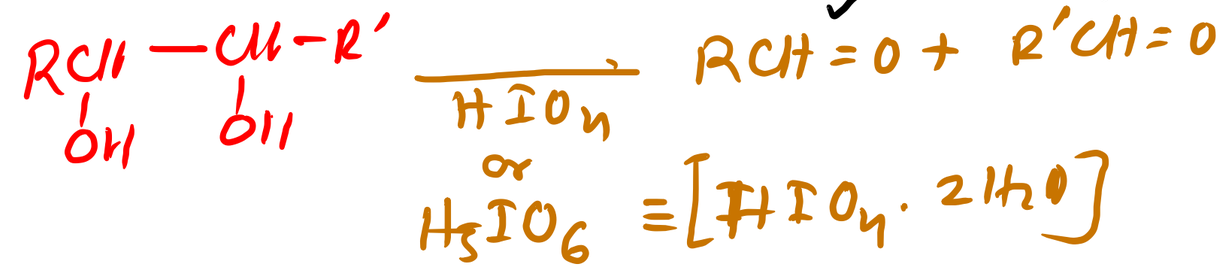

CH2OH
C=O
CHOH
CHOH
CHOH
CH2OH
HIO4
(5eq)
3eq. HCO2H
HCH=O
HCH=O
CO2↑
HCO2H : HCHO = 3:2.
CH=O
CH=O
HIO4
(1eq)
2eq. HCO2H.
keto hexose.
(D-fructose)
CH2OH
CH2
C=O
CHOH
CH2OH
HIO4
(1eq)
CH2OH
CH2
CH=O
+
HCH=O.

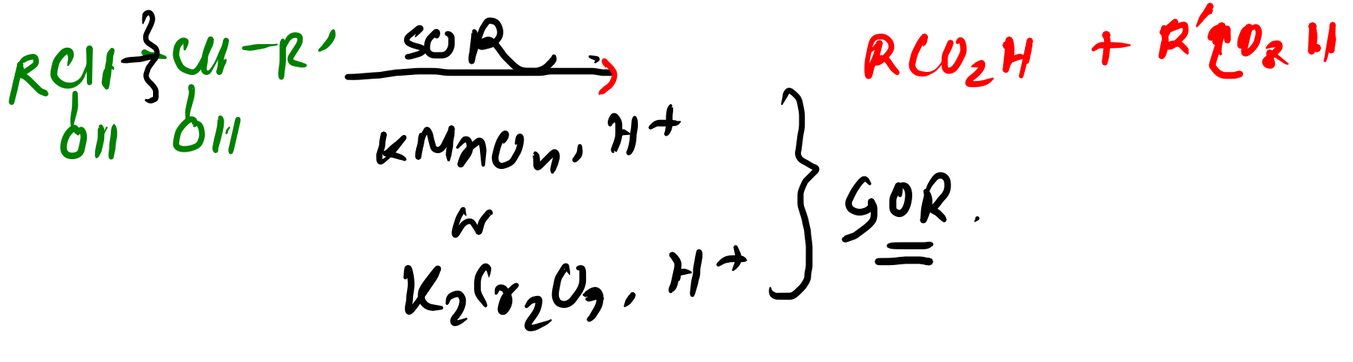
a)

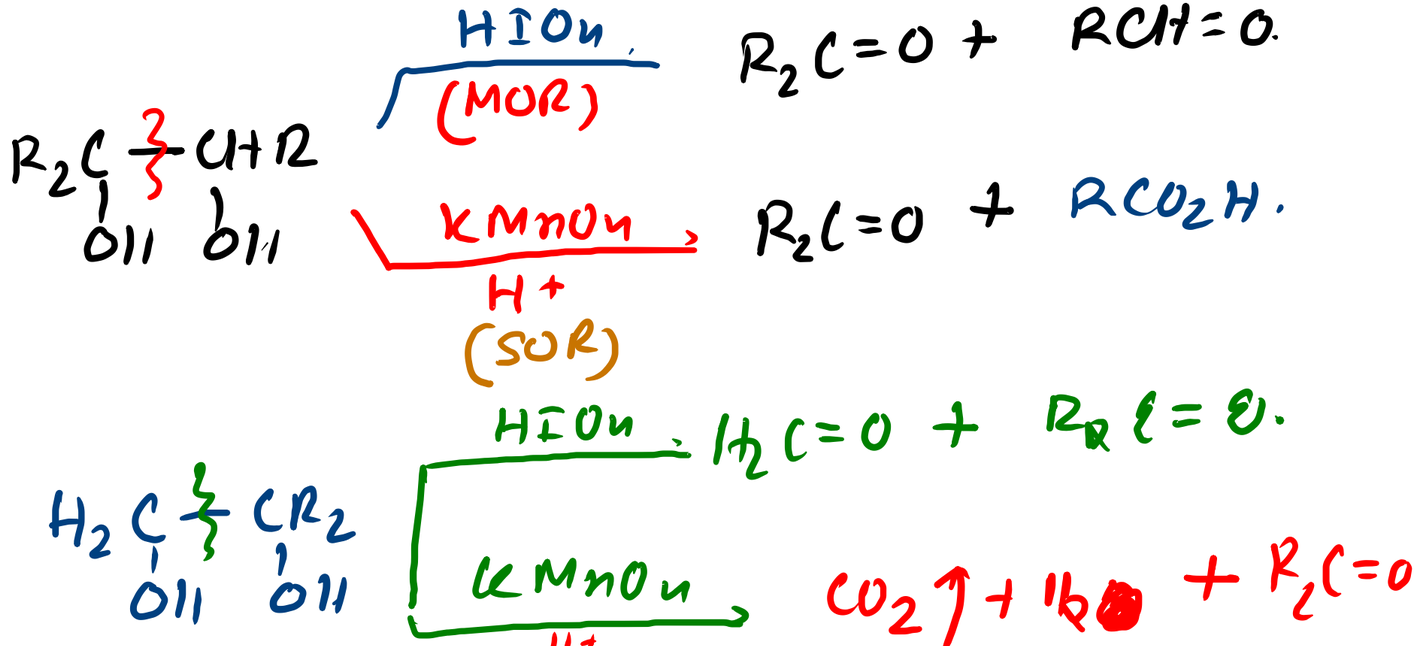

CH=O ⟶ HCO2H
+ CHOH
+ CHOH
+ CHOH
HIO4
(1eq)
3eq.
HCO2H
+ C=O ⟶ CO2 + H2O
+ CH2OH ⟶ HCH=O

b)


CH2OH
CHOH
CHOH
CHOH
CHO
+ CH=O
HIO4
(1eq)
CH2OH
CHOH
CHOH
CH=O
+ HCO2H


RCH — CH — R'
OH OH
HIO4
or
H5IO6 ≡ [HIO4 · 2H2O]
RCH=O + R'CH=O


RCH — CH — R'
OH OH
SOR
KMnO4, H+
or
K2Cr2O7, H+
SOR
RCO2H + R'CO2H


R2C — CHR
OH OH
HIO4
(MOR)
R2C=O + RCH=O
KMnO4
H+
(SOR)
R2C=O + RCO2H
H2C — CR2
OH OH
HIO4
H2C=O + R2C=O
KMnO4
H+
CO2↑ + H2O + R2C=O

(1) $CH_3CH=CH-CH_3$

Alkene

cold, $KMnO_4 + OH^-$ (Basic medium), mild → $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

hot, $KMnO_4$, H^+ (or hot $KMnO_4$, SOR) → $CH_3CO_2H + CO_2H$ CH_3CO_2H.

different PdL depending on medium

(2) $EtCH=C(Et)_2$

Allene.

Baeyer's reagent: $KMnO_4 + OH^-$ → $EtCH(OH)-C(OH)(Et)_2$ (vicinal diol, syn addition.)

$KMnO_4/H^+$ → $EtCO_2H + Et_2C=O$

different PdL depending on medium.

(3) RCH_2OH

$KMnO_4/H^+$ → RCO_2H.

$KMnO_4 + \bar{O}H$ (N_c ↑) → RCO_2^- (N_c^+)

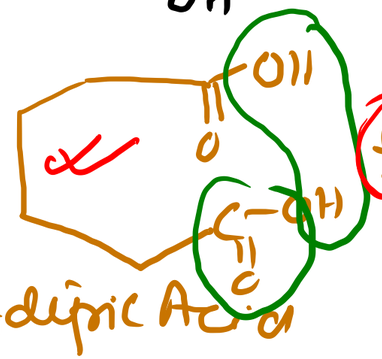
same type of PdL.

i) Syn addn

$KMnO_4$ / cold
$+OH^-$ (0°-5°C)

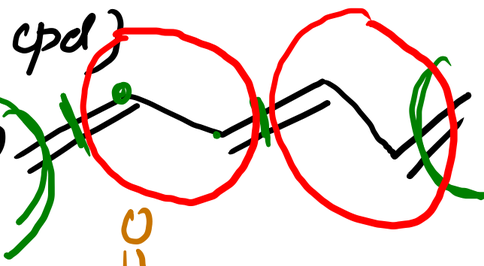
(meso cpd)

$KMnO_4$ Δ
H^+ / hot.



Adipic Acid

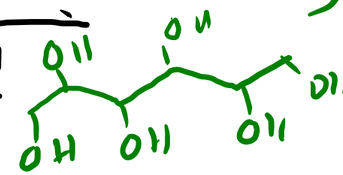
ii)



Δ →  + CO_2 + H_2O

(i). $KMnO_4 + \bar{O}H$ + cold

$KMnO_4$
$+OH^-$



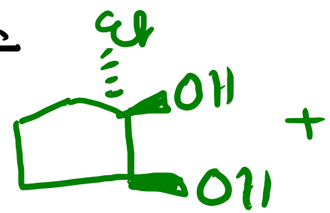
$KMnO_4$
H^+ **

iii)

with temp Δ → $CO + CO_2\uparrow + H_2O$

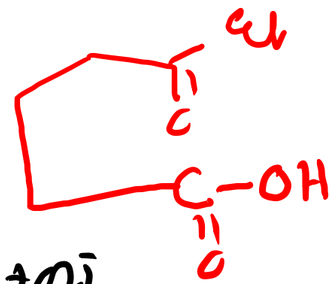
CO_2H (2 eq)
CO_2H
$+ CO_2\uparrow + H_2O$

$KMnO_4$
OH^-

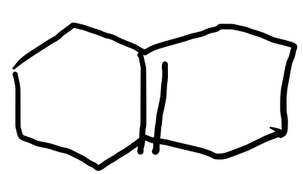


+ ENT.

$KMnO_4$
H^+ / hot.

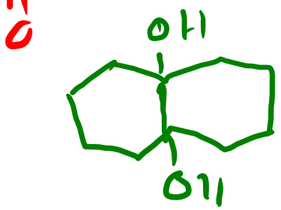


iv)



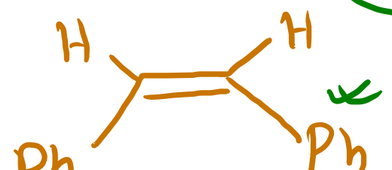
$KMnO_4 + \bar{O}H$

$KMnO_4$, H+



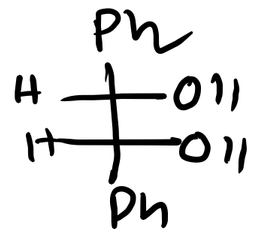
v)

(SM)



cis stilbene.

$KMnO_4$
OH^-
or Baeyer's reagent

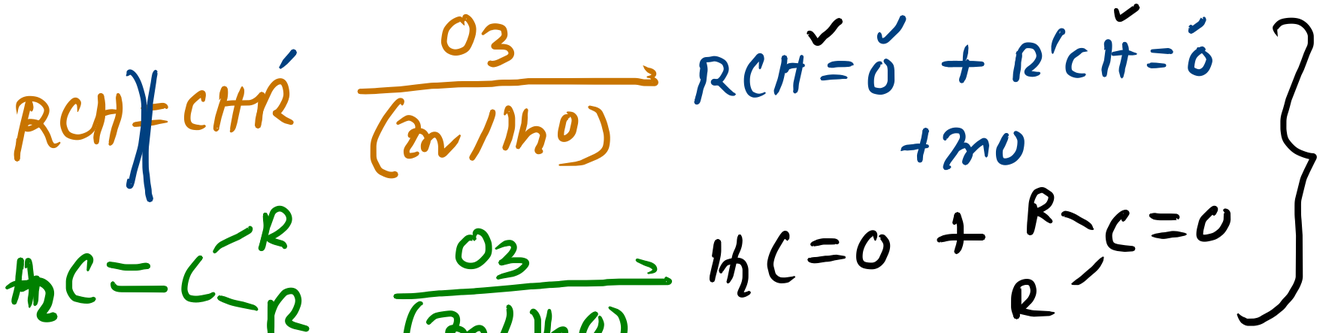


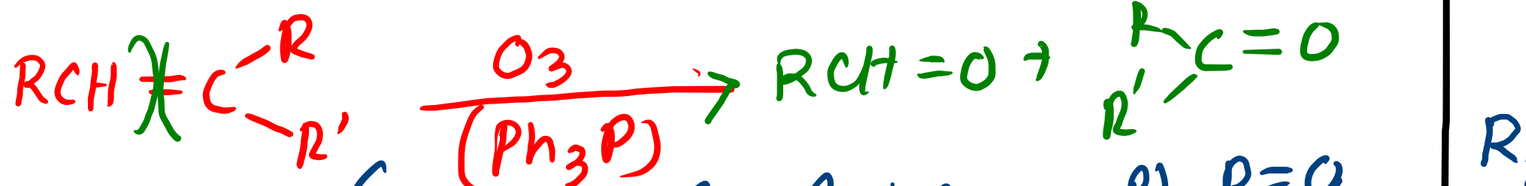
$KMnO_4$
H^+

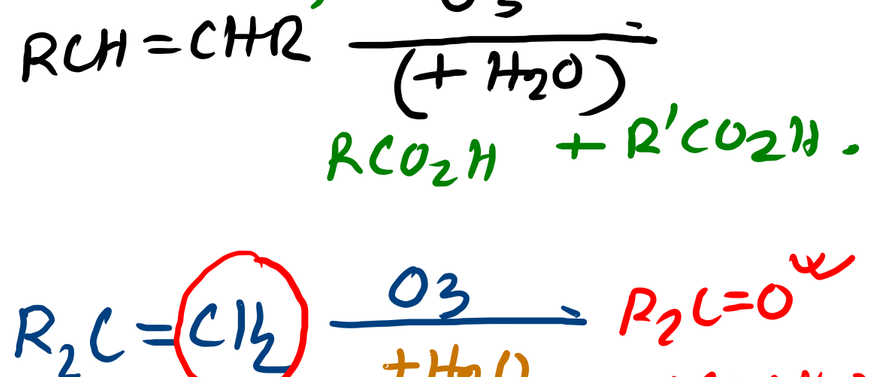
$PhCO_2H$ + $PhCO_2H$

JEE Mains halo + reduct. + Alcohol Ether.
O-I oxidation

: Ozonolysis : (cleavage with the help of O_3 is called ozonolysis)







$RCO_2H + R'CO_2H$ ← oxidative ozonolysis

$O_3 + H_2O_2$ or $O_3 + H_2O$; $O_3 + R(CH_3)_2$

$KMnO_4, H^+/\Delta$ (is equivalent to oxidative ozonolysis)

$RCH \neq CHR'$

open chain alkene.

$R_2C = CH_2$

open chain alkene.

$R_2C=O + CO_2\uparrow + H_2O$ ← oxidative ozonolysis

$KMnO_4 + H^+$

ENT ≡ $KMnO_4 + NaOH$

$KMnO_4 + H^+$ ≡ $O_3 + H_2O$

R_1: OsO_4.

R_2: Baeyers ($KMnO_4 + OH^-$)

R_3: H_2CrO_4

R_4: moist Ag_2O.

R_5: mCPBA / H_2O

$R_1, R_2/R_3/R_4/R_5$

syn addition or Anti addition

$R_1 + HIO_4$; $R_3 \rightarrow HIO_4$; $R_4 + HIO_4$

$R_2 + HIO_4$

$RCH(OH)-CH(OH)-R'$ (vicinal diol)

HIO_4

$RCH=O + R'CH=O$

$O_3 + Zn/H_2O$; $O_3 + (Me_2S)$

simple ozonolysis

$R_1/R_2/R_3/R_4/R_5$

$R_2C(OH)-CH_2(OH)$

simple/reductive Ozonolysis

$R_2C=O + H_2C=O$

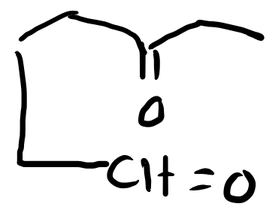
≡ Baeyers + HIO_4

Cycloalkene

Baeyers + HIO_4.

$O_3 + Zn + H_2O$

$O_3 + H_2O$.

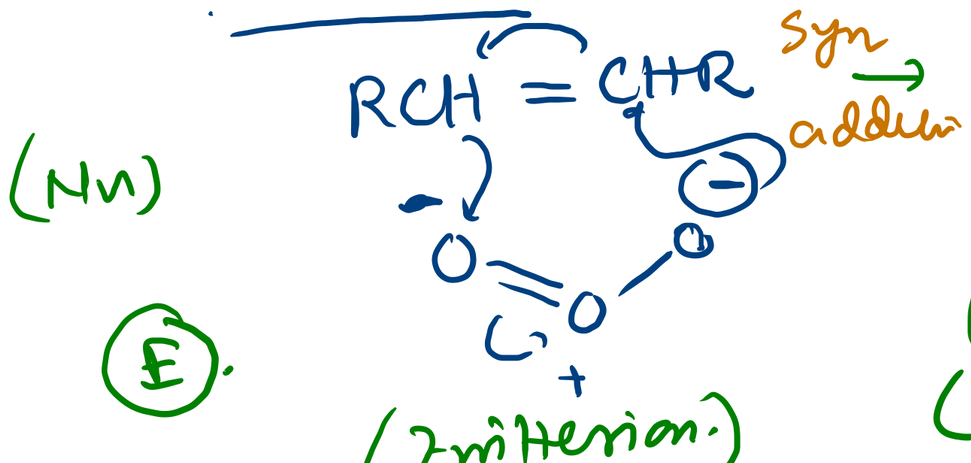


$H_3C-CH_2-C(=O)-CH_2-CH_2-CH_2-CO_2H$.

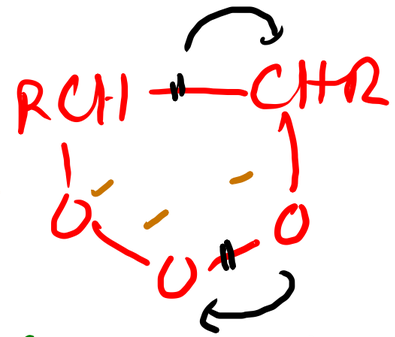
Nucleophile

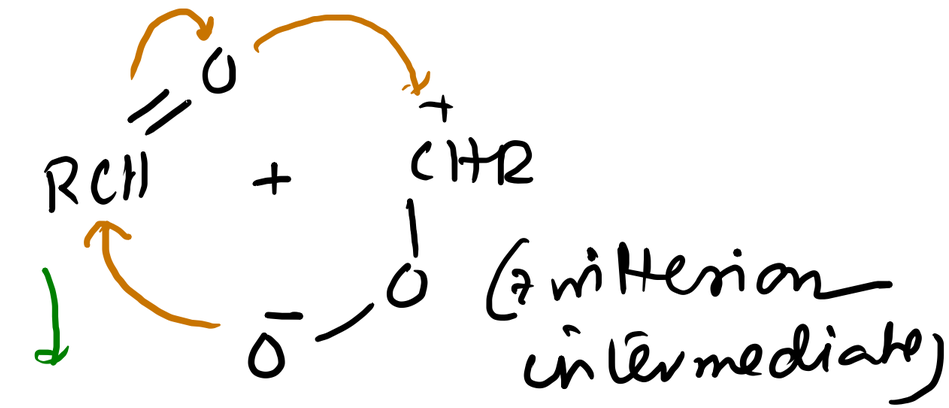
Electrophile $R-C\equiv C-R' \xrightarrow[+H_2O]{O_3} RCO_2H + R'CO_2H$.

• Mechanism:

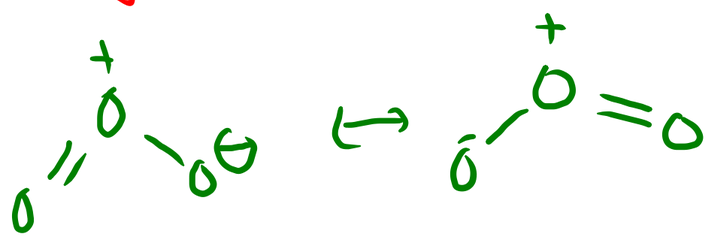


Syn addition





More is the electrophilicity in alkene faster is the reaction

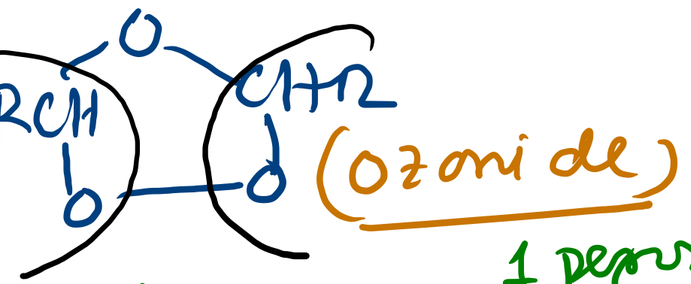


Bond order = 1.5.

simple / reductive ozonolysis.

If zinc is absent

$O_3 + H_2O \rightarrow H_2O_2 \rightarrow [O]$



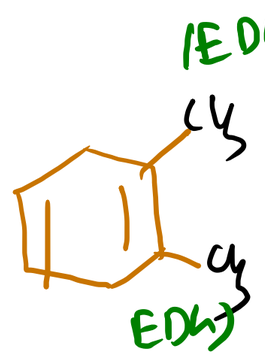
$\downarrow Zn/Me_2S/Ph_3P$

$RCH=O + RCHO + ZnO$.

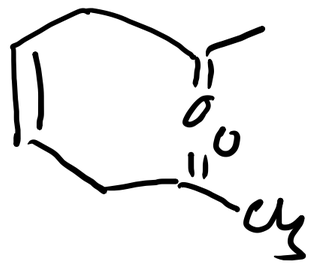
$[O]$ $\quad Me_2S=O$

$RCO_2H + RCO_2H \quad Ph_3P=O$

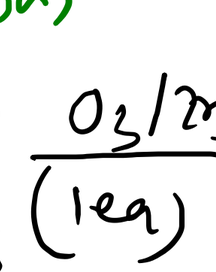
oxidative ozonolysis



$\xrightarrow[(1eq)]{O_3/Zn/H_2O}$

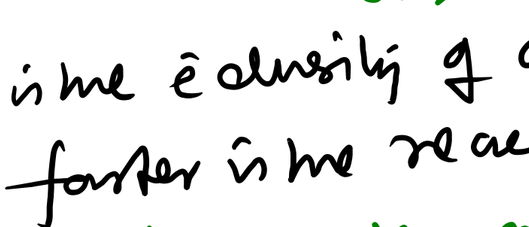


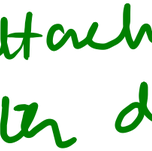
More is the ē density of double bond faster is the reacti. EDG attached with double bond. increases reacti onto; EWG attached with double bond decreases reacti onto.



Birch reduct

$\xrightarrow[liq.NH_3]{Na\ in}$ X $\xrightarrow[(1eq)]{O_3/Zn/H_2O}$ Y.

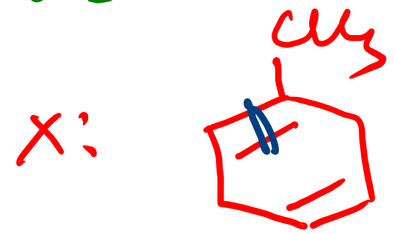




$\xrightarrow[(xs)/Zn]{O_3}$ CH=O, CH=O

H_2O. (3eq)

X:



$\xrightarrow{O_3/Zn/H_2O}$

O_3+H_2O →

CO_2H, CO_2H