Reduction, Oxidation & Hydrolysis Reactions

Section (A) : Reduction-1

Introduction :

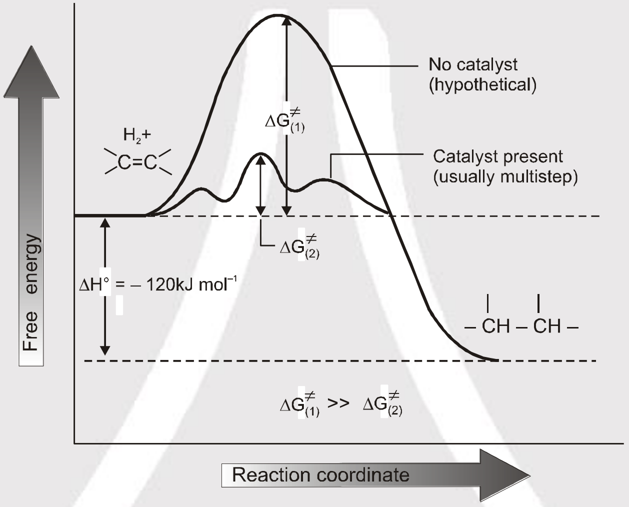
Reduction covers both the addition of hydrogen (or deuterium) to a double bond and the replacement of an atom or group by hydrogen (or deuterium). In other words, reduction means hydrogenation or hydrogenolysis.

Reduction can be carried out in following ways:

(a)	**Catalytic hydrogenation**	**(b)**	**Metal/proton (acid) reduction**
(c)	**Metal hydrides reduction**	**(d)**	**Miscellaneous Reductions**

1.1 Catalytic hydrogenation :

Hydrogenation using H_2(g) on metal surface or other suitable catalyst is called catalytic hydrogenation. A catalyst provides a new pathway for the reaction that involves lower free energy of activation.



Heterogeneous hydrogenation catalysts typically involve finely divided platinum.

The catalysts used can be divided into two broad classes, (a) Heterogeneous catalysts (b) Homogeneous catalysts. Both of which mainly consist of transition metals and their compounds :

(i) Heterogeneous catalysts : (catalysts insoluble in the reaction medium)

In heterogeneous catalytic hydrogenation catalysts are used in powdered form. Raney nickel (Ni), Palladium on charcol (Pd/C), Platinum metal or its oxide are common heterogeneous catalysts.

Facts of catalysis :

(i) Substrate molecules are assumed to undergo homolysis into atoms at the surface of the catalyst.

(ii) The substrate is chemisorbed on the surface of the catalyst and hydrogenation takes place.

(iii) The process is exothermic.

Note : (If H_2 and D_2 mixture is used with a Pt catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H_2 and D_2. (No scrambling occurs in the absence of the catalyst.) The product has both D and H atoms).

Catalytic Reduction of Functional Groups Using H_2/Pd(C) or H_2/Pt or H_2/Ni

$R\text{–}CH{=}CH\text{–}R + H_2 \xrightarrow{Ni\ \ or\ \ Pd} R\text{–}CH_2\text{–}CH_2\text{–}R$ + heat

Substrate	Product
RCOCl	RCH_2OH
RNO_2	RNH_2
$RC{\equiv}CR$	RCH_2CH_2R
RCHO	RCH_2OH
RCH=CHR	RCH_2CH_2R
RCOR	RCHOHR
RCN	RCH_2NH_2

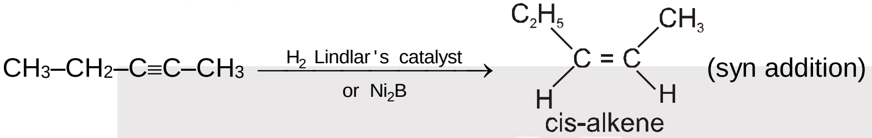
Note : **(i)** Generally RCOOH, RCOOR, $RCONH_2$ groups are **not reduced** by catalytic hydrogenation.
(ii) Stereochemistry of catalytic hydrogenation: The above reaction is syn addition (addition takes place from the same side of alkene or alkyne).

(ii) Homogeneous catalysis :

(catalysts soluble in the reaction medium). It uses reactants and catalyst in the same phase. Both hydrogen atoms **usually** add from the same side of the molecule.
Common example : Use of Wilkinsion catalyst $Rh[(C_6H_5)_3P]_3Cl$.

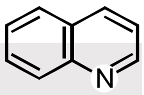
(iii) Lindlar's catalyst : [H_2/Pd, $CaCO_3$, quinoline]

It is a poisoned palladium catalyst. It is composed of powdered calcium carbonate coated with palladium and poisoned with quinoline. It is used to carry out partial reduction of alkyne to alkene and acid chloride to aldehyde.
Stereochemistry : Syn addition.



cis-alkene

(syn addition)



Quinoline

Note : Nickel boride Ni_2B **(P-2 catalyst)** (made from Nickel acetate and sodium borohydride) is an excellent alternative catalyst for the conversion of alkyne into alkene. Stereochemistry : Syn addition.

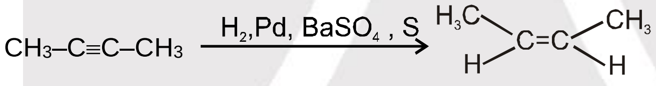
$$Ni(OCOCH_3)_2 \xrightarrow[C_2H_5OH]{NaBH_4} Ni_2B.$$

(iv) Rosenmund catalyst : [H_2/Pd, $BaSO_4$, quinoline]

Hydrogenation in presence of $H_2/Pd/BaSO_4$ is called **Rosenmund Reduction**. It reduces alkyne to alkene and acid halide to aldehyde. It is poisoned palladium catalyst, composed of powdered barium sulphate coated with palladium, poisoned with quinoline or sulphur.

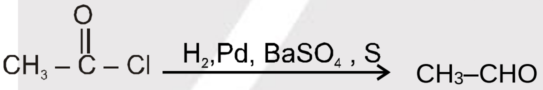
Stereochemistry : Syn addition.

(a)



cis-2-butene

(b)



$$CH_3-\overset{\overset{\large O}{\|}}{C}-Cl \xrightarrow{H_2,Pd,\ BaSO_4\ ,\ S} CH_3{-}CHO$$

1.2 Metal/proton (acid) reduction :

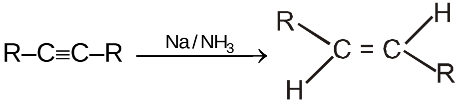
Reduction by dissolving metals is based on the fact that the metal acts as a source of electrons.
Step-1 : Metals give electrons to the electrophilic species and form anion
Step-2 : Proton is abstracted from the acidic source.

$$A{-}B \xrightarrow{\bar{e}} A^{\bullet} + \overset{-}{B}{:} \text{ or } \overset{-}{A}{:} + B^{\bullet} \xrightarrow{H^+} A^{\bullet} + B{-}H$$

$$A{=}B \xrightarrow{\bar{e}} :\overset{\ominus}{A}{-}B^{\bullet} \text{ or } A^{\bullet}-\overset{\ominus}{B}{:}\,A^{\bullet}{-}BH$$

(i) Birch reduction [Na or Li/NH_3(liq.) or (ethyl alcohol)] :

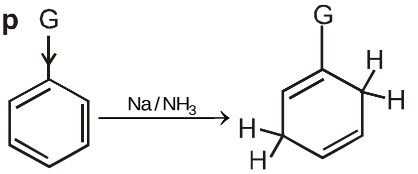
Alkyne and Aromatic Compounds are reduced by Na or Li/NH_3.
Alkynes are reduced to trans alkene. Stereochemistry : anti addition.



(anti addition)

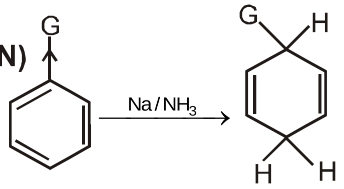
Benzene ring is reduced at 1, 4-position.
Typical example of reduction for aromatic system :
Presence of alkyl, alkoxy, amines reduces the benzene ring at ortho position.

(electron releasing group
– R, – OR, – NH_2)



Presence of nitro, cyano, carboxylic, keto or aldehyded group reduces the benzene ring at ipso position.

(electron withdrawing group
– NO_2, – COOH, – CHO, – CN)



(ii) Bouvealt-Blanc reduction [Na/C_2H_5OH] :

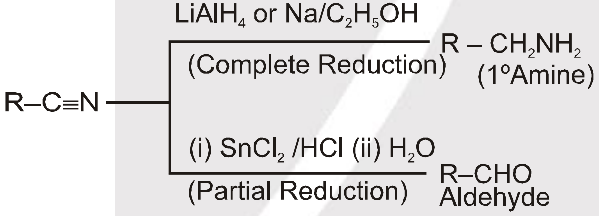
Reduction of aldehydes, ketones, acidhalides, esters or cyanide by means of excess of Na/C_2H_5OH is called Bouvealt-Blanc reduction.
Na + C_2H_5OH is mild reducing agent.

Reagent	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**
Reactant	Aldehyde	Ketone	Cyanide	Ester	acid halide
Product	1° alcohol	2° alcohol	1° amine	1° alchol	1° alchol

$CH_3CHO \xrightarrow{Na/C_2H_5OH} CH_3CH_2OH$
Acetaldehyde Ethanol

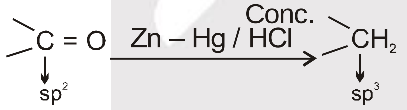
(iii) Stephen's Reductions : [$SnCl_2$/HCl]

When reduction of cyanide is carried out with acidified stannous chloride ($SnCl_2$/HCl) at room temperature, imine hydrochloride is obtained. Which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called stephen's reduction.

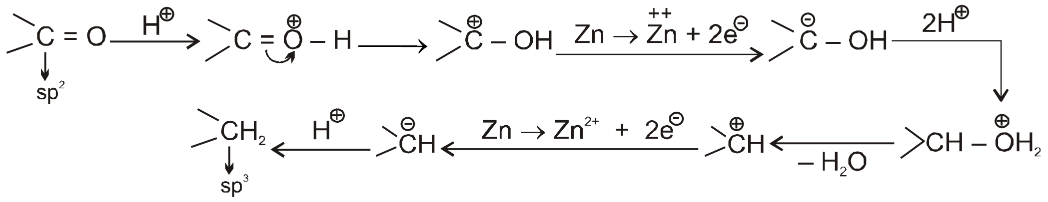


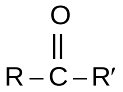
(iv) Clemmensen's Reduction : [Zn-Hg/Conc. HCl]

It is used to prepare alkanes from carbonyl compounds (Aldehyde and ketones in absence of acid sensitive groups).



Mechanism :



(a) $R-CHO \xrightarrow[\Delta]{Zn-Hg/conc.\ HCl} RCH_3 + H_2O$ **(b)** 
$R-\overset{\overset{O}{||}}{C}-R' \xrightarrow[\Delta]{Zn-Hg/conc.\ HCl} RCH_2R' + H_2O$

Note : Clemmensen reduction is avoid to use for compounds which have **acid sensitive** group.
[Like: Alcohol, Alkene, Alkyne, Ether].

Section (B) : Reduction-2

1.3 Metal hydrides reduction

Certain complex metal and boron hydrides, are important reagents for reduction.

(i) $LiAlH_4$ (LAH) Lithium aluminium hydride [$LiAlH_4$ / Ether or THF] :

LAH is most common and versatile reagent. It is sensitive to protic solvent and therefore used in ether.

Reagent	$LiAlH_4$	$LiAlH_4$	$LiAlH_4$/Excess	$LiAlH_4$/Excess	$LiAlH_4$	$LiAlH_4$	$LiAlH_4$	$LiAlH_4$	$LiAlH_4$	$LiAlH_4$
Reactant	Aldehyde	Ketone	Acid	Acidanhydride	Acid chloride	Ester	Cyanide	Amide	Isocyanide	Nitro
Product	1º alcohol	2º alcohol	1º alcohol	1º alcohol	1º alcohol	1º alcohol	1º amine	1º amine	2º amine	1º amine

Note : Alkene, alkyne, benzene rings are not reduced by $LiAlH_4$ in ether but it is reported that (*) double bond can be reduced by $LiAlH_4$ / THF in few cases like :

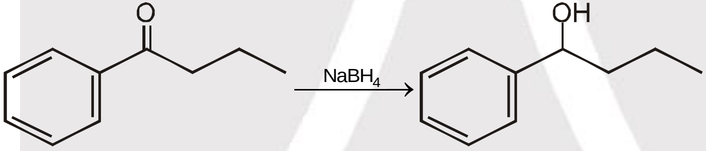
$$\text{Ph–CH=CH–CHO} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4\text{–THF}} \text{Ph–CH}_2\text{–CH}_2\text{–CH}_2\text{OH}$$

[Cinnamaldehyde]

(ii) Sodium borohydride [$NaBH_4$ / C_2H_5OH or Ether] :

It is more specific than LAH as a reducing agent. It reduces ketones and aldehydes to the corresponding alcohols without affecting other functional groups, reduces acid chlorides to 1º alcohols. It does not reduce any other derivative of acid. It is effective even in protic solvent like alcohol.

Reagent	$NaBH_4$	$NaBH_4$	$NaBH_4$
Reactant	Aldehyde	Ketone	Acid chloride
Product	1º alcohol	2º alcohol	1º alcohol



(iii) Diisobutyl Aluminium Hydride [DIBAL-H / Inert solvent] :

Diisobutyl aluminium hydride is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

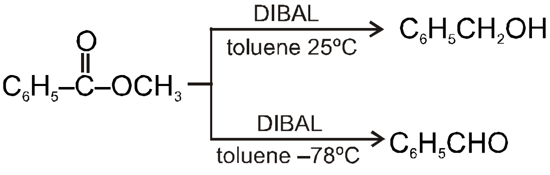
Reagent	DiBAL-H/(–78ºC)	DiBAL-H
Reactant	Ester	Cyanide
Product	Aldehyde	Aldehyde

(a)

$$\text{Ph–CH=CH—COOC}_2\text{H}_5 \xrightarrow[H_2O]{LiAlH_4\text{-THF}} \text{Ph–CH}_2\text{–CH}_2\text{–CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH}$$

$$\text{Ph–CH=CH—COOC}_2\text{H}_5 \xrightarrow[-78^\circ C]{\text{DIBAL-H}} \text{Ph–CH=CH—CHO} + \text{C}_2\text{H}_5\text{OH}$$

(b) By DIBAL at ordinary temperature esters are reduced to alcohols but at low temperature esters are reduced to aldehyde.



$$\text{C}_6\text{H}_5\text{–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–OCH}_3 \xrightarrow[\text{toluene } 25^\circ C]{\text{DIBAL}} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$$

$$\text{C}_6\text{H}_5\text{–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–OCH}_3 \xrightarrow[\text{toluene } -78^\circ C]{\text{DIBAL}} \text{C}_6\text{H}_5\text{CHO}$$

(c) LAH reduce RCN to amine but DIBAL is found to be reduce it to aldehyde.

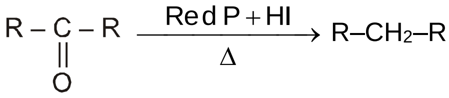
$$\text{CH}_3\text{–C≡N} \xrightarrow[H_2O]{LiAlH_4\text{-THF}} \text{CH}_3\text{–CH}_2\text{–NH}_2$$

$$\text{CH}_3\text{–C≡N} \xrightarrow[25^\circ C]{\text{DIBAL}} \text{CH}_3\text{–CHO}$$

1.4 Miscellaneous reductions :

(i) By Red P & HI :

Used to prepare alkane from carbonyl compounds and alcohols generally.

(a) 

$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[\Delta]{Red\,P+HI} R-CH_2-R$$

(b) $CH_3CH{=}O \xrightarrow[\Delta]{Red\,P+HI} CH_3CH_3$

(c) $R-CH_2OH \xrightarrow[\Delta]{Red\,P+HI} R-CH_3$

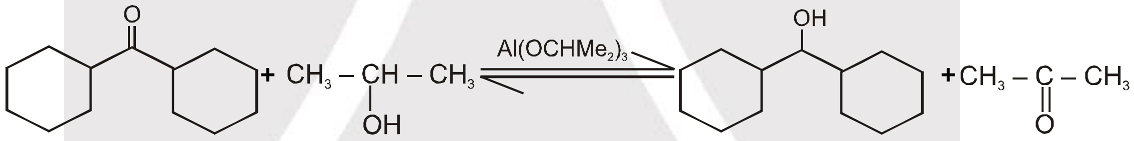
(d) 

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{Red\,P+HI} CH_3CH_2CH_3$$

(ii) Meerwein-Pondorf-Verley reduction (MPV reduction) (Reduction by isopropyl alcohol and aluminium isopropoxide):

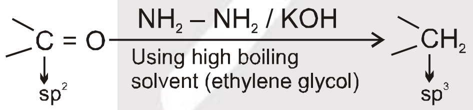
It is selective reduction of ketones to alcohol, even in presence of other functional groups using Aluminium isopropoxide in isopropyl alcohol.

$$R-\underset{\underset{O}{\|}}{C}-R' + CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightleftharpoons{Al(OCHMe_2)_3} R-\underset{\underset{OH}{|}}{CH}-R' + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

eg. 

(iii) Wolff-kishner reduction [NH_2NH_2 / KOH] :

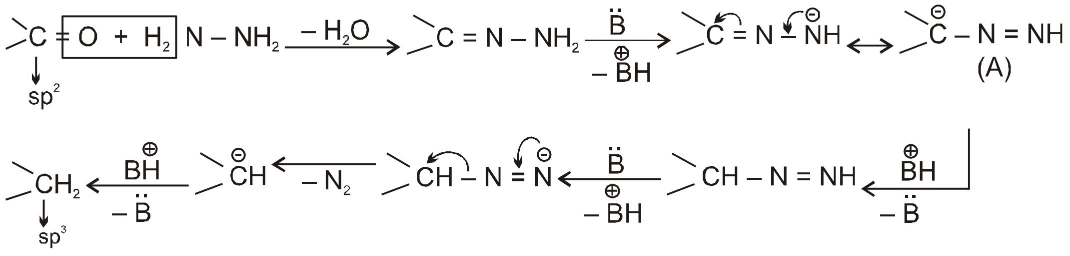
Used to prepane alkane from carbonyl compounds



$$\underset{sp^2}{>C=O} \xrightarrow[\text{Using high boiling solvent (ethylene glycol)}]{NH_2-NH_2\,/\,KOH} \underset{sp^3}{>CH_2}$$

; $RCHO \xrightarrow[\Delta]{NH_2NH_2\ /\ KOH} RCH_3$

Mechanism :



Note : Wolff-kishner reduction is avoid to use for compounds which have **base sensitive** groups. [Like : Halogens, Acid halide, Esters, Anhydride]

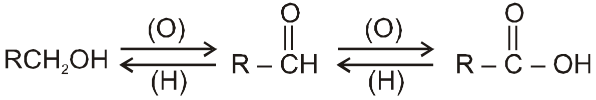
Section (C) : Oxidation-1

Introduction

1. oxidation is defined as the addition of oxygen (electronegative) element to a substance or removal of hydrogen (electropositive) element from a substance.

or

2. Oxidation of an organic molecule usually corresponds to increasing its oxygen content or decreasing its hydrogen content.



$$RCH_2OH \underset{(H)}{\overset{(O)}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}H \underset{(H)}{\overset{(O)}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OH$$

3. Oxidation of an organic compound may be more broadly defined as a reaction that increases its content of any element more electronegative than carbon.

Replacing hydrogen atoms by chlorine atoms is an oxidation

$$Ar{-}CH_3 \underset{(R)}{\overset{(O)}{\rightleftharpoons}} ArCH_2Cl \underset{(R)}{\overset{(O)}{\rightleftharpoons}} ArCHCl_2 \underset{(R)}{\overset{(O)}{\rightleftharpoons}} ArCCl_3$$

When organic compound is oxidised, **oxidising agent** used is reduced. When an organic compound is reduced, the **reducing agent** used must be oxidized.

2.1 Oxidation of alkanes

Different products are formed by the use of different oxidising agents or different reaction conditions.

(i) Chemical oxidation with $KMnO_4$ or $K_2Cr_2O_7$: Alkanes are usually not affected by oxidising agents like $KMnO_4$ or $K_2Cr_2O_7$. However, alkanes having tertiary hydrogen are oxidised by these oxidising agents to an alcohol.

$$\underset{\text{(Isobutane)}}{(CH_3)_3CH} \xrightarrow{KMnO_4} \underset{\text{(Tertiary butyl alcohol)}}{(CH_3)_3COH}$$

Ex. (i) $\underset{9\ :\ 1}{2CH_4 + O_2} \xrightarrow{Cu/523K/1000atm} 2CH_3OH$ (methanol)

(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

(iii) $2CH_3{-}CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO_2)Mn} 2CH_3COOH + 2H_2O$

(iv) $CH_4 + \underset{\text{limited}}{O_2} \xrightarrow{Burn} \underset{\substack{\text{carbon}\\\text{black}}}{C} + 2H_2O$

2.2 Oxidation of alkenes and alkynes

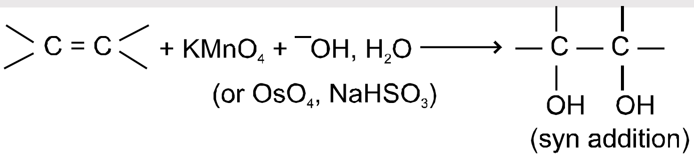
(i) Baeyer reagent [cold diluted to 1% alkaline $KMnO_4$ solution] :

Baeyer Reagent	**Baeyer Reagent**	**Baeyer Reagent**
Reactant	Alkene	Alkyne
Product	Vicinal diol	Diketone

Stereochemistry : syn addition.

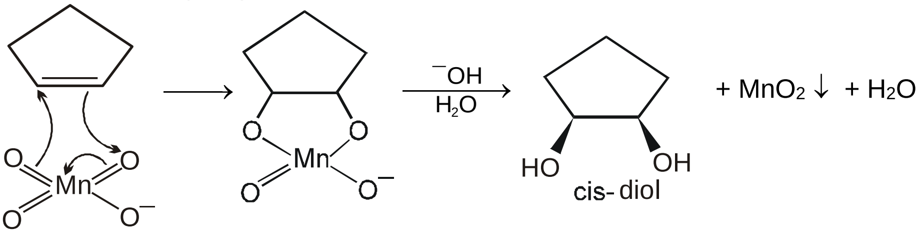
Both-OH groups are add from same stereochemical side.

General Reaction



Stereochemistry : syn addition.

Ex.

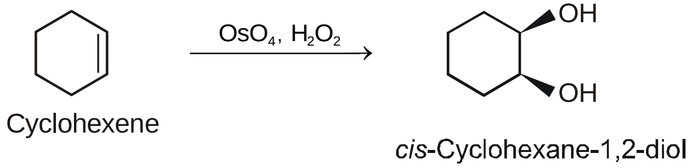


(ii) Osmium tetraoxide in alkaline medium [OsO_4 / $NaHSO_3$] :

Similar to Baeyer's reagent.

OsO_4 /$NaHSO_3$	OsO_4 /$NaHSO_3$	OsO_4 /$NaHSO_3$
Reactant	Alkene	Alkyne
Product	Vicinal diol	Diketone

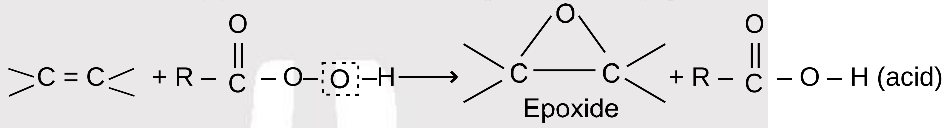
Ex.



(iii) Oxidation with peroxyacids

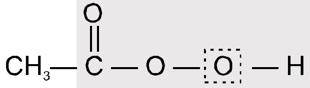
An alkene is converted to an epoxide by a peroxyacid.
[a carboxylic acid that has an extra oxygen atom in a –O–O– (peroxy) linkage].

General Reaction



Some simple peroxyacids (sometimes called peracids) are shown below :

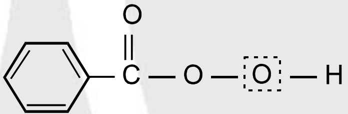
(a)



$CH_3-C(=O)-O-O-H$

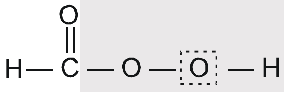
peroxyacetic acid

(b)



Peroxy benzoic acid

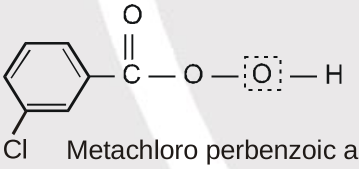
(c)



$H-C(=O)-O-O-H$

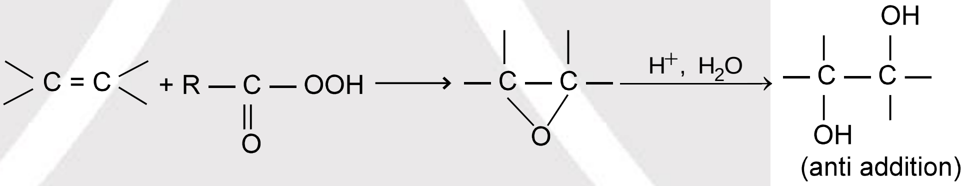
Peroxyformic acid

(d)



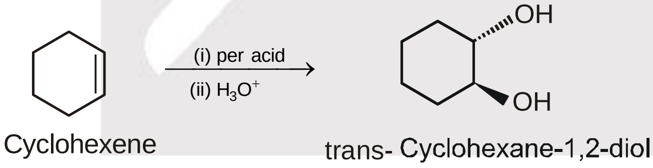
Metachloro perbenzoic acid
(MCPBA)

General Reaction

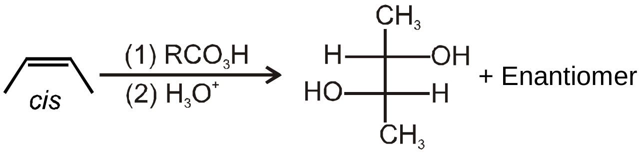


Stereochemistry : anti addition in diol formation.

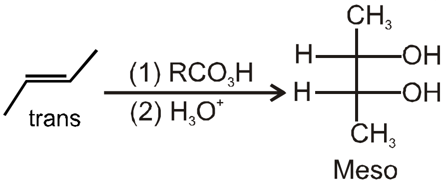
Ex.



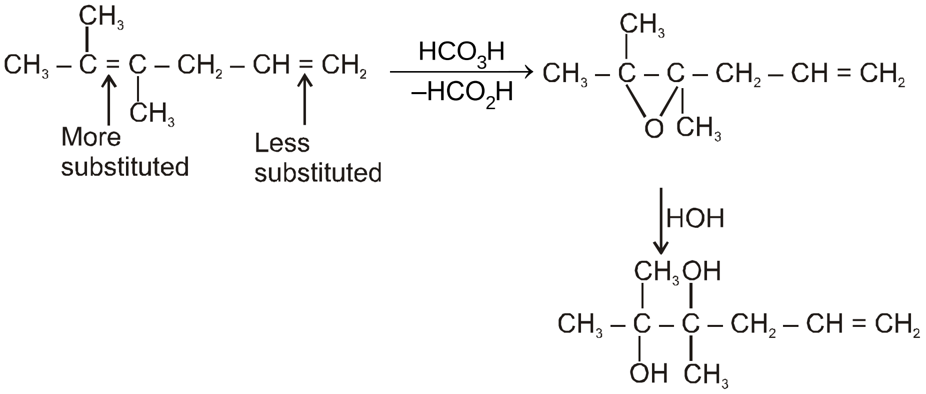
Ex.



Ex.



Note : The more highly substituted olifinic bond is more nucleophilic and therefore reacts faster with the peroxyacid than the less susbstituted double bond.



(iv) Oxidation with acidic KMnO4 [KMnO4/H+] : Stereochemistry : syn addition.

When alkene & alkyne heated with KMnO4 in acidic or in alkaline medium; following changes takes place.

$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$
Reactant	.= CH_2 group	.= CH **R** group	.= CR_1R_2 group	.≡ CH group	.≡ CR group
Product	CO_2	RCOOH	O.= CR_1R_2 group	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

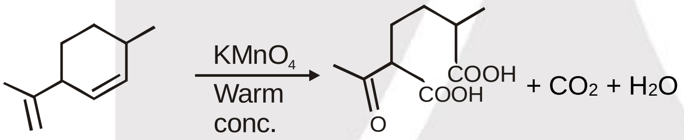
Ex. $RCH=CH_2 \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

Ex. $RC\equiv CH \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

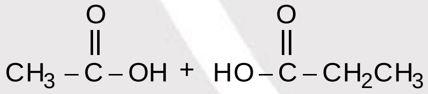
Ex. $RC\equiv C–R \xrightarrow{[O]} 2RCOOH$

w

Ex.

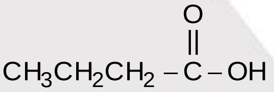


Ex. $CH_3–C\equiv C–CH_2CH_3 \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH,\ \Delta}$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$$

Ex. $CH_3CH_2CH_2–C\equiv CH \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH,\ \Delta}$



$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CO_2\uparrow + H_2O$$

(v). Oxidation with ozone (ozonolysis) :
Alkene & Alkyne

Like permanganate ozone cleaves double at very low temperature (≈ –78ºC) bonds to give Ketones and aldehydes. However, ozonolysis is milder, and both Ketones and aldehydes can be recovered without further oxidation.

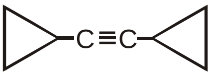
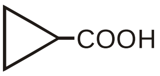
Reductive Ozonolysis Products (O_3/Zn, H_2O)

O_3/Zn, H_2O	O_3/Zn, H_2O	O_3/Zn, H_2O	O_3/Zn, H_2O	O_3/Zn, H_2O	O_3/Zn, H_2O
Reactant	= CH_2 group	= CH R group	= CR_1 R_2 group	≡ CH group	≡ CR group
Product	HCHO	O = CHR group	O = CR_1R_2 group	$-\overset{\overset{\displaystyle O}{\|}}{C}-CHO$	diketone
	Formaldehyde	Aldehyde	Ketone	Keto aldehyde	diketone

Oxidative Ozonolysis Products

O_3/H_2O_2	O_3/H_2O_2	O_3/H_2O_2	O_3/H_2O_2	O_3/H_2O_2	O_3/H_2O_2
Reactant	=CH_2 group	=CH**R** group	= CR_1R_2 group	≡CH group	≡CR group
Product	CO_2	RCOOH	O=CR_1R_2 group	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

Ex. C_8H_{10} (A) $\xrightarrow{O_3,\ H_2O}$ $C_4H_6O_2$ Acid (B). Identify (A) and (B) in the above reaction

Sol. (A)  (B) 

Ex. A certain hydrocarbon has the formula $C_{16}H_{26}$. Ozonolysis followed by hydrolysis gives $CH_3(CH_2)_4CO_2H$ and succinic acid as the only product. What is hydrocarbon

Sol. DU = 4

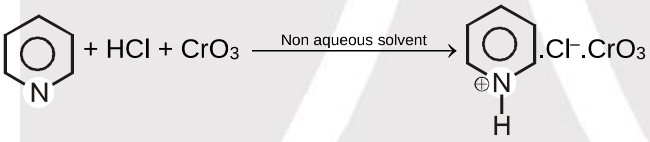
∴ Molecular structure must be: $CH_3(CH_2)_4C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}C(CH_2)_4{-}CH_3$

Section (D) : Oxidation-2

2.3 Oxidation reaction of alcohols :

Oxidation Product of Alcohol-1						
	Weak oxidising agent			**Strong oxidising agent**		
	PCC*	**PDC****	**CrO_3/Inert medium**	**CrO_3 in water or H_2CrO_4**	**$KMnO_4/H^+$**	**$K_2Cr_2O_7/H^+$**
1° alcohol or primary alcohol	Aldehyde			Carboxylic acid		
2° alcohol or secondary alcohol	Ketone			Ketone		
3° alcohol or tertiary alcohol	Not oxidised			Not oxidised		

(a) Pyridinium Chloro Chromate (PCC)



(b) Pyridinium dichromate (PDC) = $(2C_6H_5N.CrO_3)$

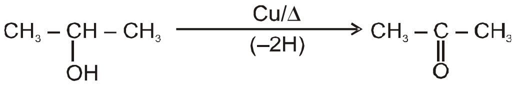
(c) Jones reagent = dilute chromic acid + acetone

(d) Collin's Reagent = CrO_3 + pyridine, CH_2Cl_2

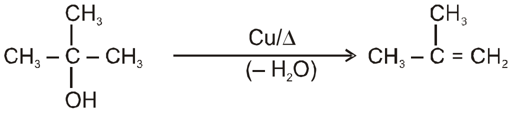
(e) MnO_2 = It is selectively oxidised reagent & oxidised allylic and benzylic alcohol into aldehyde and ketone.

Oxidation Product of Alcohol-2		
	Very-Very Strong oxidising agent $KMnO_4$/H+/Heat	**Copper & heat as oxidising agent**
1° alcohol or Primary alcohol	Carboxylic acid	Aldehyde
2° alcohol or Secondary alcohol	Mixture of Carboxylic acid	Ketone
3° alcohol or tertiary alcohol	Mixture of Carboxylic acid	Dehydrate to alkene

$CH_3-CH_2-CH_2-OH \xrightarrow[(-2H)]{Cu/\Delta} CH_3-CH_2-CH=O$ (dehydrogenation)



$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[(-2H)]{Cu/\Delta} CH_3-\underset{O}{\overset{\|}{C}}-CH_3$ (dehydrogenation)



$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3 \xrightarrow[(-H_2O)]{Cu/\Delta} CH_3-\overset{CH_3}{C}=CH_2$ [dehydration (Reduced Product)]

Oppenaur's oxidation

(i) This reaction involves the oxidation of a secondary alcohol with a ketone and base to the corresponding ketone.

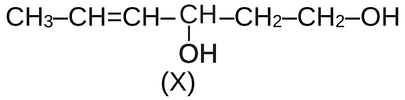
(ii) Commonly used bases are aluminium tert-butoxide.

$$\underset{2^\circ\text{ Alcohol}}{R_2CHOH} + \underset{\text{Acetone}}{(CH_3)_2CO} \xrightleftharpoons{Al(OCMe_3)_3} \underset{\text{Ketone}}{R_2CO} + \underset{2^\circ\text{ Alcohol}}{CH_3CH(OH)CH_3}$$

Rate of Oxidation :

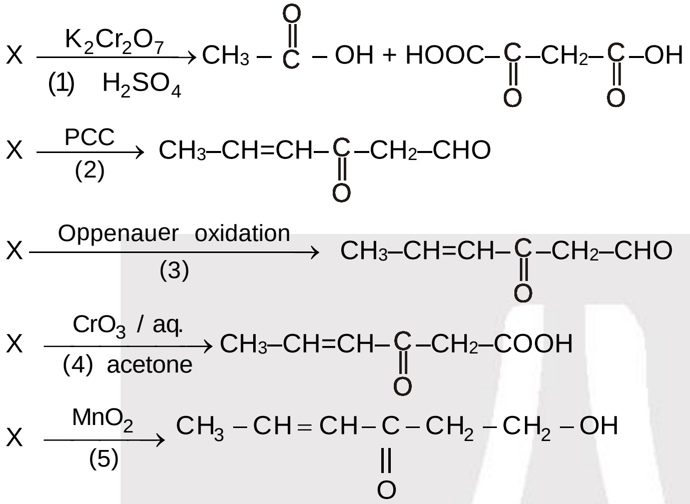
(a) $RCH_2OH > R_2CHOH > R_3C{-}OH$ (inert) (b) $RCHO > RCH_2OH$

Ex. Write the product of following reactions.



$CH_3{-}CH{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}OH$

(X)



$X \xrightarrow[(1)\ H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{||}{C}}-OH + HOOC{-}\underset{O}{\underset{||}{C}}{-}CH_2{-}\underset{O}{\underset{||}{C}}{-}OH$

$X \xrightarrow[(2)]{PCC} CH_3{-}CH{=}CH{-}\underset{O}{\underset{||}{C}}{-}CH_2{-}CHO$

$X \xrightarrow[(3)]{\text{Oppenauer oxidation}} CH_3{-}CH{=}CH{-}\underset{O}{\underset{||}{C}}{-}CH_2{-}CHO$

$X \xrightarrow[(4)\ \text{acetone}]{CrO_3\ /\ aq.} CH_3{-}CH{=}CH{-}\underset{O}{\underset{||}{C}}{-}CH_2{-}COOH$

$X \xrightarrow[(5)]{MnO_2} CH_3-CH=CH-\underset{O}{\underset{||}{C}}-CH_2-CH_2-OH$

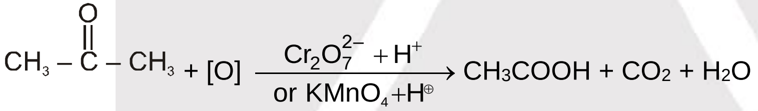
2.4 Oxidation reaction of carbonyl compound

(i) Acidic $KMnO_4$ & $K_2Cr_2O_7$ as oxidising agent :

Aldehydes are oxidised to carboxylic acid having same number of C atoms as aldehyde.

$HCHO + [O] \longrightarrow HCOOH$; $RCHO + [O] \longrightarrow RCOOH$

Ketones are oxidised with difficulty. They are oxidised only on heating with a strong oxidising agent.

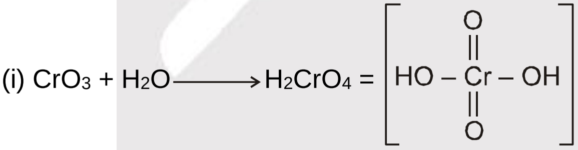


$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + [O] \xrightarrow[\text{or } KMnO_4+H^{\oplus}]{Cr_2O_7^{2-}+H^+} CH_3COOH + CO_2 + H_2O$

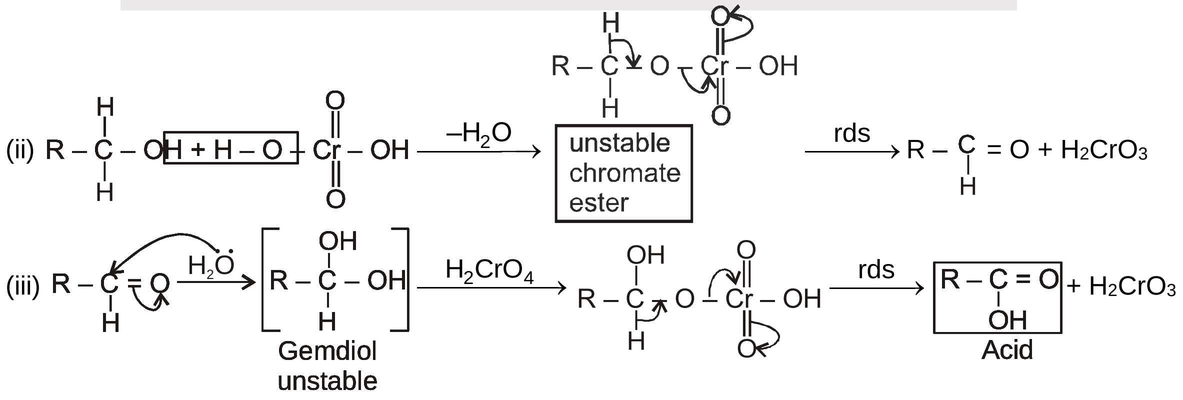
In case of mixed or unsymmetrical ketones the >C = O group remains with the smaller alkyl group. **(Popoff's rule)**

$CH_3COCH_2CH_3 \xrightarrow{[O]} 2CH_3COOH$; $CH_3COCH_2CH_2CH_3 \xrightarrow{[O]} CH_3COOH + CH_3CH_2COOH$

Mechanism (with Cr^{+6} oxidising agents) :



(i) $CrO_3 + H_2O \longrightarrow H_2CrO_4 = \left[HO-\underset{\underset{O}{||}}{\overset{\overset{O}{||}}{Cr}}-OH \right]$



Remarks :

(1) Primary alcohol forms a chromate ester with chromic acid.

(2) The chromate ester decomposes in 2nd slow step with the elimination of α-hydrogen. So the first oxidation product, an aldehyde is obtained.

(3) In **aqueous medium**, aldehyde forms a gemdiol (hydrated aldehyde). It is further oxidised to an acid by similar mechanism.

(4) The following reactivity orders can be explained by this mechanism :

Rate of Oxidation

(a) $R{-}CH_2OH > R{-}CD_2OH$ (Bond Energy : C–H < C–D) (b) $RCHO > RCDO$

(ii) With Tollen's reagent :

RCHO (aldehydes) can be easily oxidised to RCOOH (except HCHO that can be oxidised to CO_2) by weak oxidising agents like ammonical $AgNO_3$ (**Tollen's reagent**) hence they are better reducing agents.

Aldehydes reduce Tollen's reagent to Ag and appears in the form of silver mirror is called **silver-mirror test.** It is given by all aldehydes and reducing sugars.

$$RCHO + 2[Ag(NH_3)_2^+] + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{(Silver mirror)}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

(iii) With Fehling solution :

Aldehydes (except benzaldehyde) reduce **Fehling's** solution (Cu^{2+} reduced to Cu^+) which is an alkaline solution of cupric (Cu^{2+}) ion complexed with tartrate ion.

$$RCHO + 2Cu^{2+} + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{red ppt.}}{Cu_2O\downarrow} + 2H_2O$$

Aldehydes also reduce Benedict's solution (Cu^{2+} complexed with citrate ion) to Cu^+

(iv) With Benedict's solution

Sodium citrate + NaOH + $NaHCO_3$ + $CuSO_4$

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

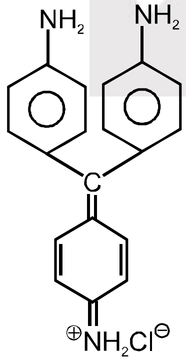
$$RCHO + HgCl_2 + H_2O \xrightarrow[\Delta]{} RCOOH + 2HCl + Hg_2Cl_2$$

$$RCHO + Hg_2Cl_2 + H_2O \rightarrow RCOOH + 2HCl + 2Hg\downarrow \text{ grey ppt.}$$

(v) With 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.



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

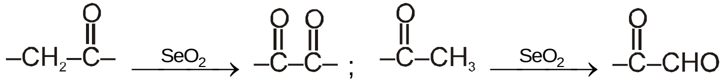
p-Rosaniline Hydrochloride

Magenta colour (Fuschin)

Ketons 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.

(vi) Oxidation by using SeO_2

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.

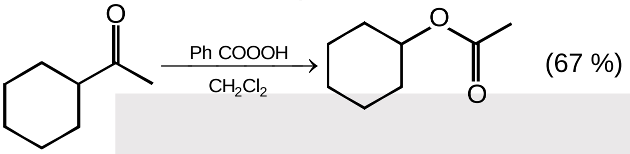


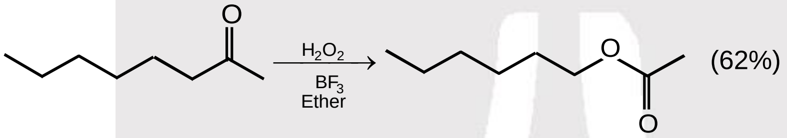
$$-CH_2-\overset{O}{\overset{\|}{C}}- \xrightarrow{SeO_2} -\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}- \;;\; -\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{SeO_2} -\overset{O}{\overset{\|}{C}}-CHO$$

(vii) Baeyer-villiger oxidation

Baeyer-villiger oxidation is the oxidative cleavage of a carbon-carbon bond adjacent to a carbonyl which converts ketones to esters and cyclic ketones to lactones.

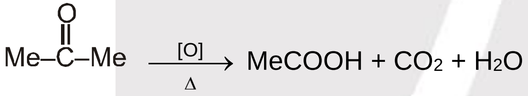
It can be carried out with peracids such as MCBPA, or with hydrogen peroxide and a lewis acid.





KETONES ARE DIFFICULT TO OXIDIZE :

Ketones can be oxidized from their enolic form at high temperature with very strong oxidizing agent. Oxidation of ketones is sometimes governed by Popoff's rule. According to this rule carbonyl group remains with the smaller alkyl group. More electron rich alkene will be easy to oxidized.

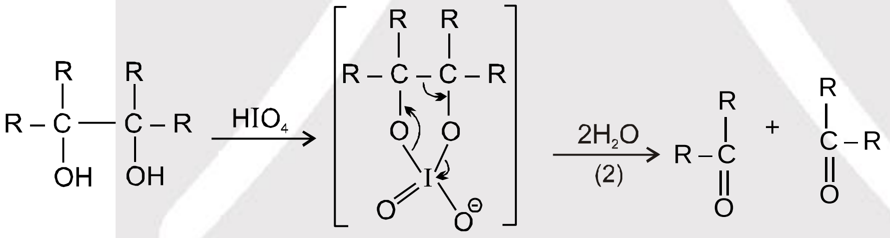


$$Me-\overset{O}{\overset{\|}{C}}-Me \xrightarrow[\Delta]{[O]} MeCOOH + CO_2 + H_2O$$

2.5 Oxidation reaction of diols

(i) HIO_4 oxidation : (Oxidation by lead acetate is similar to HIO_4 oxidation)

Mechanism :



cyclic periodate ester

Remarks

(1) HIO_4 (periodic acid) oxidises vicinal diols (1, 2-diols).

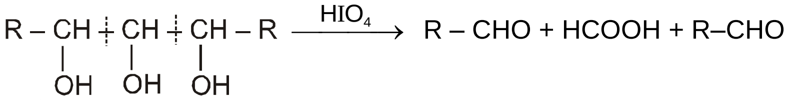
(2) It brings about oxidative cleavage of vicinal diol.

(3) It can also oxidise α-hydroxy carbonyl compound and α-dicarbonyl compound.

(4) HIO_4 forms a cyclic periodate ester as an intermediate. So the two –OH groups should have syn-conformation.

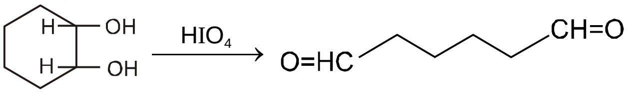
(5) In cyclic diols only cis-vicinal diols are oxidised. Trans isomers are not oxidised.

Ex. **General reaction**



$$R-\underset{OH}{\underset{|}{CH}}\vdots\underset{OH}{\underset{|}{CH}}\vdots\underset{OH}{\underset{|}{CH}}-R \xrightarrow{HIO_4} R-CHO + HCOOH + R-CHO$$

Ex.



Section (E) : Hydrolysis

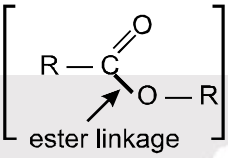
Introduction :

Hydrolysis is a chemical reaction or process in which a **molecule splits into two parts** by reacting with a molecule of water, (H_2O). One of the parts gets OH^- from the water molecule and the other part gets H^+ from the water. Such reactions are endothermic.

This is distinct from a hydration reaction, in which water molecules are added to a substance, but no fragmentation of molecule/species occurs. Such a process is exothermic.

(i) Hydrolysis of an ester :

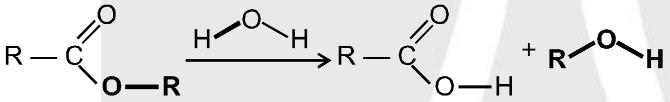
Hydrolysis of an ester involves breaking off an ester link. It can takes place in



(a) Mild acidic medium : Dilute H_2SO_4, dilute HCl.

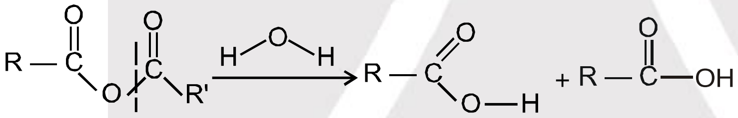
(b) **Strong alkaline medium :** Aqueous NaOH or KOH and heat.

One hydrolysis product contains a hydroxyl functional group, while the other contains a carboxylic acid functional group.



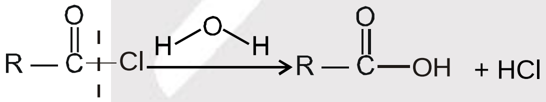
(ii) Hydrolysis of an anhydride :

The hydrolysis of acid anhydride produces two carboxylic acids.



(iii) Hydrolysis of acid halide :

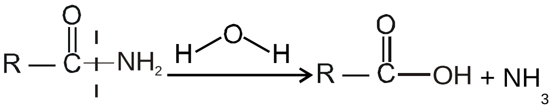
Hydrolysis of an acid halide results into a carboxylic acid and hydrogenhalide. Only the carboxylic acid product has a hydroxyl group derived from the water. Hydrohalic acid product gains the remaining hydrogen ion.



$$R-\overset{O}{\overset{\parallel}{C}}-Cl \xrightarrow{H-O-H} R-\overset{O}{\overset{\parallel}{C}}-OH + HCl$$

(iv) Hydrolysis of acid amide :

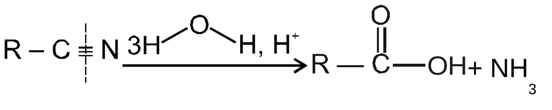
Hydrolysis of an amide results into a carboxylic acid and an amine product or ammonia, only the carboxylic acid product has a hydroxyl group derived from the water. The amine product (or ammonia) gains the remaining hydrogen ion.



$$R-\overset{O}{\overset{\parallel}{C}}-NH_2 \xrightarrow{H-O-H} R-\overset{O}{\overset{\parallel}{C}}-OH + NH_3$$

(v) Hydrolysis of cyanides :

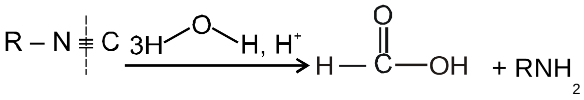
Cyanide on hydrolysis produce ammonia and carboxylc acids. It is carried out in acidic medium generally but hydrolyse in basic medium also.



$$R-C\equiv N \xrightarrow{3H-O-H,\ H^+} R-\overset{O}{\overset{\parallel}{C}}-OH + NH_3$$

(vi) Hydrolysis of isocyanides :

Isocyanides on hydrolysis produce primary amines and formic acids. It is carried out in acidic medium.



$$R-N \equiv C \xrightarrow{3H-O-H,\ H^+} H-\overset{\overset{O}{\|}}{C}-OH + RNH_2$$

Note : Alkylisocyanide does not hydrolyse in basic medium.

(vii) Hydrolysis of imine :

$$R-CH = NH \xrightarrow{H_3O^+} R-CHO + NH_3$$

(viii) Hydrolysis of ethers :

Ethers has R–O–R group. In strong acidic medium (HI or HBr) in hydrolysis to produce 2 equivalent of alcohols.

$$C_2H_5-O-C(CH_3)_3 \xrightarrow{H_3O^+} C_2H_5OH + (CH_3)_3C-OH$$

(ix) Hydrolysis of Vinyl ether :

$$CH_2 = CH - O - R \xrightarrow{H_3O^+} CH_3-CHO + ROH$$

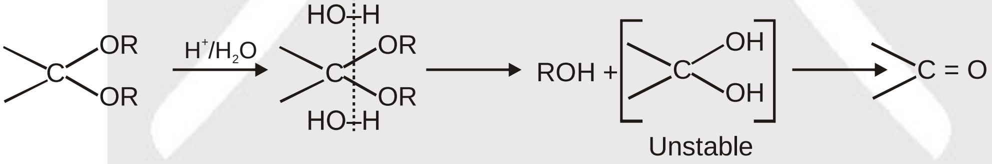
(x) Hydrolysis of phenyl ether :

$$Ph - O - R \xrightarrow{H_3O^+} Ph-OH + ROH$$

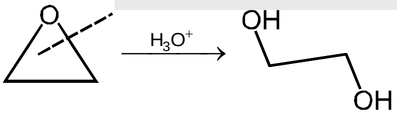
(xi) Hydrolysis of hemiacetals and acetals :

Hemiacetals and Acetals has R–O–R group.

Hemiacetals are unstable and get hydrolysed to aldehyde/ketones even in aq medium. However acetals/Ketals are stable and hydrolyse only in strong acidic medium (HI or HBr) to produce 2 equivalent of alcohols and one equivalent of aldehyde/ketone. Acetals are often used as protecting groups.



(xii) Hydrolysis of epoxide :



Note : Three and four membered expoxides can also be hydrolysed in basic medium.