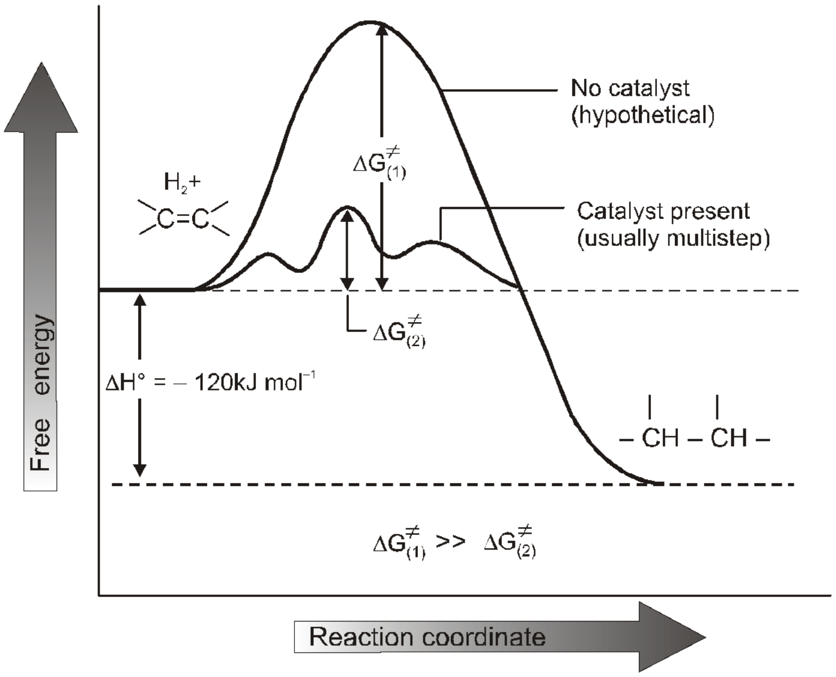
Reduction, Oxidation, Hydrolysis & Decarboxylation reactions

Section (A) : Reduction

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



(a) Catalytic hydrogenation :

Hydrogenation using H_2(gas) 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

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

Substrate	Product
RCOCl	RCH_2OH
RNO_2	RNH_2
RC≡CR	RCH_2CH_2R
RCHO	RCH_2OH
RCH=CHR	RCH_2CH_2R
RCOR	RCHOHR
RCN	RCH_2NH_2

Note : **(i)** Generally RCOOH, RCOOR, $RCONH_2$ and anhydride 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).

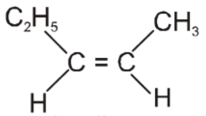
(ii) Homogeneous catalysts : (catalysts soluble in the reaction medium). It uses reactants and catalyst in the same phase. Both hydrogen atoms **usually** add from the same side of the molecule.
Common example : Use of Wilkinsion catalyst $Rh[(C_6H_5)_3P]_3Cl$.

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

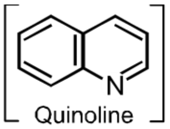
It is a poisoned palladium catalyst. It is composed of powdered calcium carbonate coated with palladium and poisoned with quinoline. It is used to carry out partial reduction of alkyne to alkene.

Stereochemistry : Syn addition.

$CH_3-CH_2-C\equiv C-CH_3 \xrightarrow[\text{or } Ni_2B]{H_2\ \text{Lindlar's catalyst}}$



cis-alkene

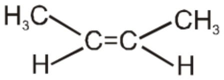


Quinoline

(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.

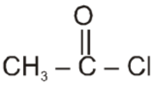
Stereochemistry : Syn addition.

(a) $CH_3-C\equiv C-CH_3 \xrightarrow{H_2,Pd,BaSO_4,S}$



cis-2-butene

(b)



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

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

Stereochemistry : Syn addition.

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

(b) 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.

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

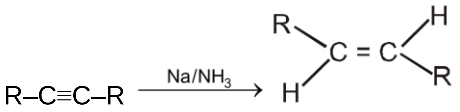
$$A = B \xrightarrow{\bar{e}} :\overset{\ominus}{A}-B^{\bullet} \text{ or } A^{\bullet}-\overset{\ominus}{B}: \xrightarrow{H^{-}} A^{\bullet}-BH$$

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

Alkyne and aromatic compounds are reduced by Na or Li/NH_3.

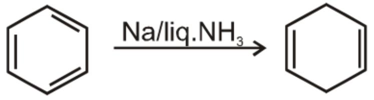
Stereochemistry : anti addition.

Alkynes are reduced to trans alkene.



(anti addition)

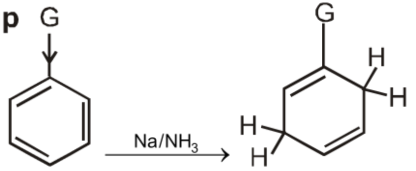
Benzene ring is reduced at 1, 4-position.



Typical example of reduction for aromatic system :

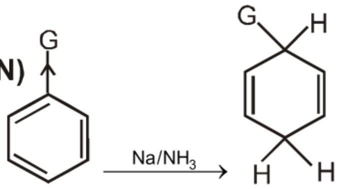
Presence of alkyl, alkoxy, amines reduces the benzene ring at ortho position.

(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)

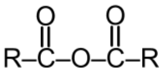


(ii) Bouvealt-Blanc reduction [Na/C_2H_5OH] :

Reduction of aldehydes, ketones, esters or cyanide by means of excess of Na/C_2H_5OH or n-butanol is called Bouvealt-Blanc reduction reduction.

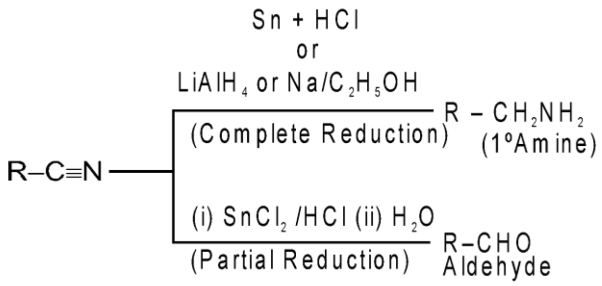
Reagent	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**	**Na/C_2H_5OH**
Reactant	Aldehyde	Ketone	Cyanide	Ester	acid halide
Product	1° alcohol	2° alcohol	1° amine	1º alchol	1º alchol

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

Note- 
$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$, $RCONH_2$, RCOOH, RNO_2 groups are not reduced by Bouvealt-Blanc reduction.

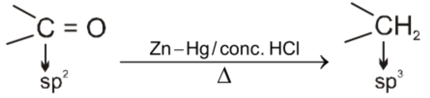
(iii) Stephen's reductions : [$SnCl_2$/HCl] :

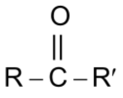
When reduction of cyanide is carried out with acidified stannous chloride ($SnCl_2$/HCl) at room temperature, imine hydrochloride is obtained. Which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called Stephen's reduction.



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

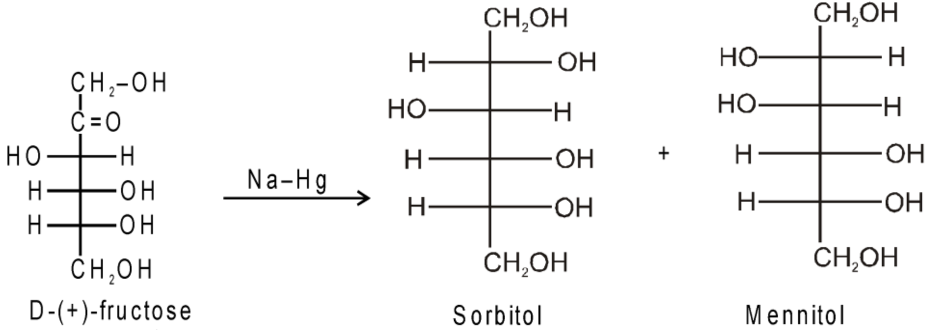
It is used to prepare alkanes from carbonyl compounds (Aldehyde and ketones in absence of acid sensitive groups).

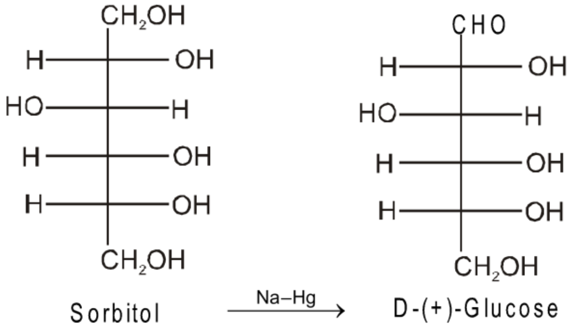


(a) R – CHO $\xrightarrow[\Delta]{Zn-Hg/conc.\ HCl}$ $RCH_3 + H_2O$ **(b)** 
$R-\overset{\overset{O}{||}}{C}-R'$ $\xrightarrow[\Delta]{Zn-Hg/conc.\ HCl}$ $RCH_2R' + H_2O$

Note : Clemmensen reduction is not preferred for compounds which have **acid sensitive** group.
[Like Alcohol, Alkene, Alkyne, Ether].

(v) Na–Hg Reduction :





(vi) Reduction of alkyl halides :

By Zn/HCl

$R-X + Zn/HCl \longrightarrow RH + X^{\Theta}$

Reaction is proceed as

$Zn \longrightarrow Zn^{2+} + 2e^-$

$R-X \longrightarrow R^+ + X^{\Theta}$

$R^+ + 2e^- \longrightarrow R^{\Theta}$

$R^{\Theta} + HCl \longrightarrow RH + Cl^{\Theta}$

Purest form of methane can be obtained as :

$$CH_3I \xrightarrow[\text{Ethanol}]{\text{Zn–Cu(couple)}} CH_4$$

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$CH_3I \longrightarrow CH_3^+ + I^-$$

$$CH_3^+ + 2e^- \longrightarrow \overset{\ominus}{C}H_3$$

$$\overset{\ominus}{C}H_3 + C_2H_5OH \longrightarrow CH_4 + C_2H_5O^{\ominus}$$

(c) 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	1° alcohol	2° alcohol	1° alcohol	1° alcohol	1° alcohol	1° alcohol	1° amine	1° amine	2° amine	1° amine

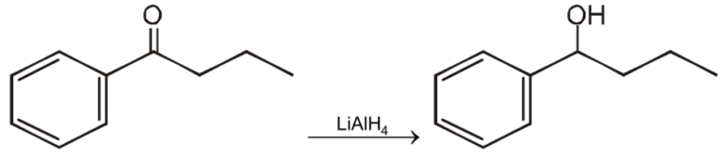
Note : Alkene, alkyne, benzene rings are not reduced by $LiAlH_4$ in ether but it is reported that (*) double bond can be reduced by $LiAlH_4$ / THF in few cases like :

$$\underset{\text{[Cinnamaldehyde]}}{Ph–CH{=}CH—CHO} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4-THF} Ph–CH_2–CH_2–CH_2OH$$

(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 1° 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	1° alcohol	2° alcohol	1° alcohol



(iii) Diisobutyl aluminium hydride [DIBAL-H / Inert solvent] :

Diisobutyl aluminium hydride $(i\text{-}Bu_2AlH)_2$ is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

Reagent	**DIBAL-H/Cold**	**DIBAL-H/Hydrolysis**
Reactant	Ester	Cyanide
Product	Aldehyde	Aldehyde

(a) $$Ph–CH{=}CH—COOC_2H_5 \xrightarrow[H_2O]{LiAlH_4-THF} Ph–CH_2–CH_2–CH_2OH + C_2H_5OH$$

$$\Big\downarrow \text{DIBAL-H}$$

Ph–CH=CH—CH_2OH

(b) DIBAL-H reacts slowly with electron poor compounds and more quickly with electron rich compounds.

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

$$CH_3\text{–}C\equiv N \xrightarrow[H_2O]{LiAlH_4-THF} CH_3\text{–}CH_2\text{–}NH_2$$

$$\Big\downarrow \text{DIBAL-H, } 25^\circ C$$

CH_3–CHO

(d) Miscellaneous reductions :

(i) By Red P & HI :

Used to prepare alkane from acid, acid derivatives and carbonyl compounds.

Red P & HI	**Red P & HI**	**Red P & HI**	**Red P & HI**	**Red P & HI**	**Red P & HI**	**Red P & HI**
Reactant	Aldehyde	Ketone	Acid chloride	Acidanhydride	Ester	Ether
Product	Alkane	Alkane	Alkane	Alkane	Alkane	Alkane

(a) $R-\underset{\underset{O}{\|}}{C}\,OH \xrightarrow[\Delta]{Red\ P + HI} R-CH_3$

(b) $R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\Delta]{Red\ P + HI} R-CH_3$

(c) $R-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow[\Delta]{Red\ P + HI} R-CH_3$

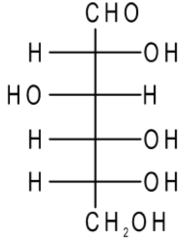
(d) $R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[\Delta]{Red\ P + HI} R-CH_2-R$

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

(f) $CH_3CH_2 \xrightarrow[\Delta]{Red\ P + HI} CH_3$

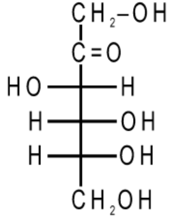
(g) $R\text{–}CONH_2 \xrightarrow[\Delta]{Red\ P + HI} R\text{–}CH_2\text{–}NH_2$

(h) $R\text{–}NO_2 \xrightarrow[\Delta]{Red\ P + HI} R\text{–}NH_2$



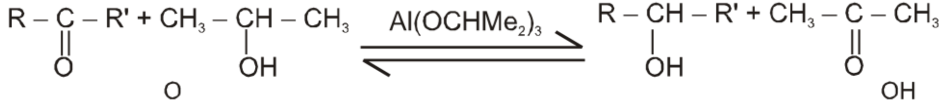
(i) D(+)-glucose $\xrightarrow{Red\ P + HI}$ n-Hexane

On prolonged heating with HI glucose forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



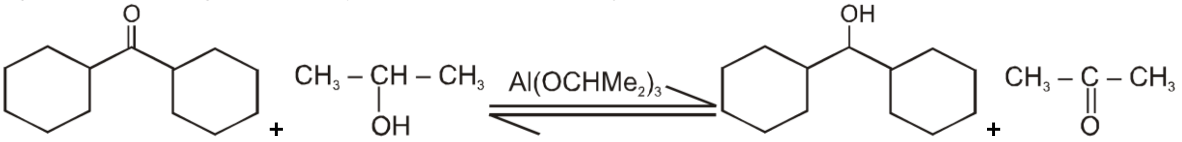
(j) D-(+)-fructose $\xrightarrow{Red\ P + HI}$ n-Hexane + 2-Iodohexane

(ii) Meerwein-Pondorf-Verley 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.

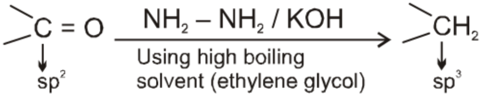


$$R-\underset{\underset{O}{\|}}{C}-R' + CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightleftharpoons{Al(OCHMe_2)_3} R-\underset{\underset{OH}{|}}{CH}-R' + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

eg.



(iii) Wolff-kishner reduction [NH_2NH_2 / KOH] :
Used to prepane alkane from carbonyl compounds



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

sp^2 sp^3

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

Note : Wolff-kishner reduction is not preferred used for compounds which have **base sensitive** groups. [Halogens, Acid halide, Esters, Anhydride]

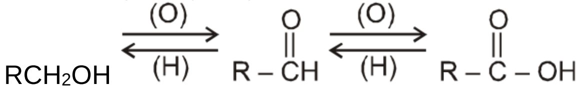
Section (B) : Oxidation

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.



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

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

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

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

(a) Oxidation of alkanes

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

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.

$$(CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3COH$$

(Isobutane) (Tertiary butyl alcohol)

Ex-1. (i) $2CH_4 + O_2\,\text{(Limited amt.)} \xrightarrow{Cu/523K/1000atm} 2CH_3OH$ (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) $\underset{\text{limited}}{CH_4 + O_2} \xrightarrow{\text{Burn}} \underset{\text{carbon black}}{C} + 2H_2O$

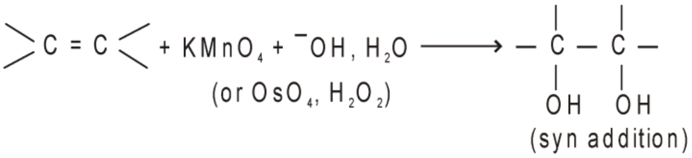
(b) Oxidation of alkenes and alkynes

(i) Baeyer reagent [cold dilute alkaline $KMnO_4$ solution] :

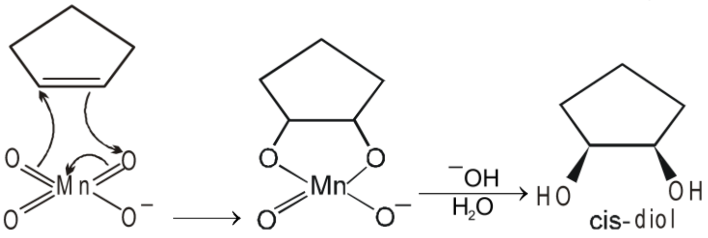
Baeyer Reagent	Baeyer Reagent	Baeyer Reagent
Reactant	Alkene	Alkyne
Product	Vicinal diol	Diketone

Stereochemistry : syn addition (Both-OH groups add from same stereochemical side)

General Reaction



Ex-2.



$+ MnO_2 \downarrow + H_2O$

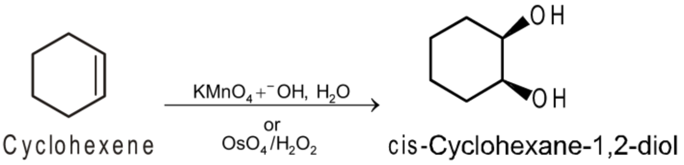
(ii) Osmium tetraoxide in alkaline medium [OsO_4 / H_2O_2 or $NaHSO_3$] :

Similar to Baeyer's reagent.

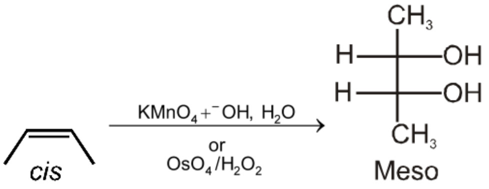
OsO_4 /H_2O_2	OsO_4 /H_2O_2	OsO_4 /H_2O_2
Reactant	Alkene	Alkyne
Product	Vicinal diol	Diketone

Note : **Double bond of Aromatic ring cannot react with Baeyer's reagent and Osmium tetraoxide in alkaline medium.**

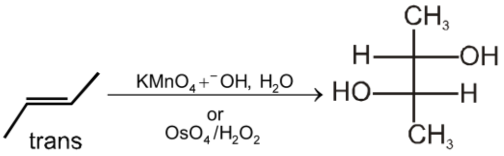
Ex-3.



Ex-4.



Ex-5.

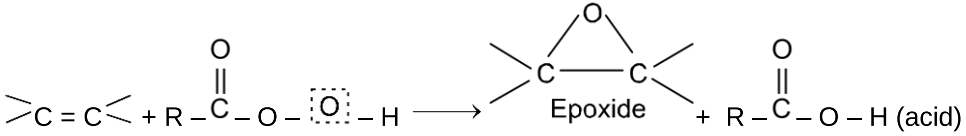


\+ Enantiomer

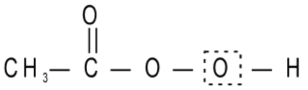
(iii) Oxidation with peroxyacids

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].

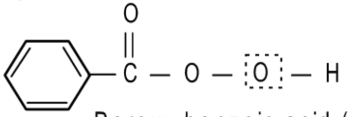
General Reaction



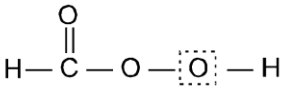
Some simple peroxyacids (sometimes called peracids) are shown below :



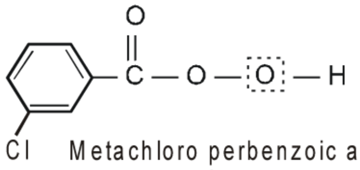
(a) peroxyacetic acid (PAA)



(b) Peroxy benzoic acid (PBA)

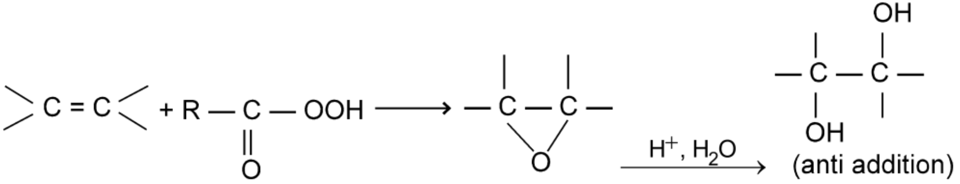


(c) Peroxyformic acid (PFA)



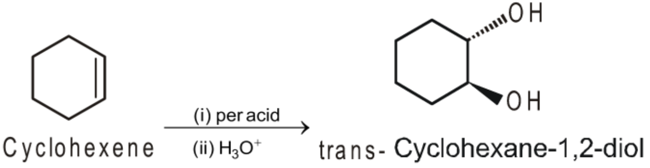
(d) Metachloro perbenzoic acid (MCPBA)

Note :- Double bond of Aromatic ring cannot react with these reagent.

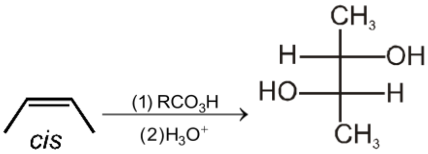


General Reaction :
Stereochemistry : anti addition in diol formation.

Ex-6.

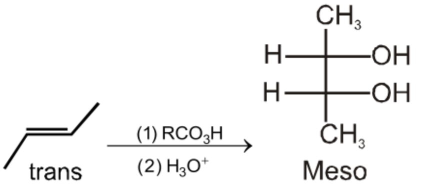


Ex-7.

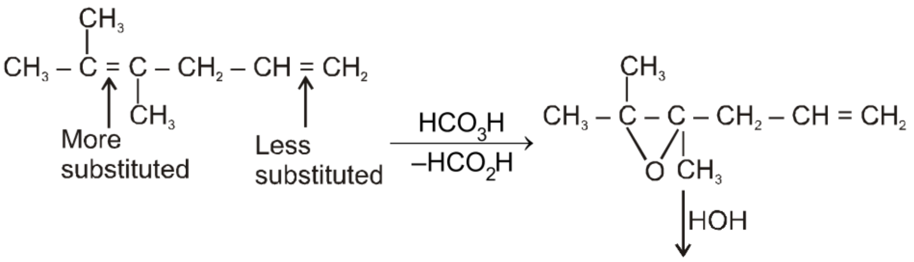


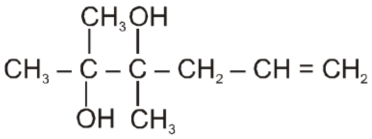
+ Enantiomer

Ex-8.



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



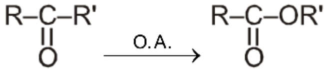


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH=CH_2$$

(iv) Baeyer–Villiger oxidation

General reactions :

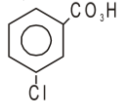
$RCHO \xrightarrow{O.A.} RCOOH$



$$R-\underset{O}{\underset{\|}{C}}-R' \xrightarrow{O.A.} R-\underset{O}{\underset{\|}{C}}-OR'$$

Priority of shift (O accepting aptitude) : **R or R' = H > Ph > 3° > 2° > 1° >Me**

Proxy acids as an oxidising agent may be one of these

(a)  = m-CPBA (Metachloro perbenzoic acid)

(b) CH_3CO_3H = PAA (Peracetic acid)

(c) CF_3 COOOH (TFPAA) Trifluoro peracetic acid

(d) HCO_3H (PAA) Performic acid

(v) Oxidation with acidic $KMnO_4$ [$KMnO_4/H^+$]

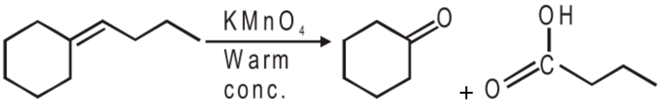
When alkene or alkyne heated with $KMnO_4$ in acidic or in alkaline medium; following changes take place.

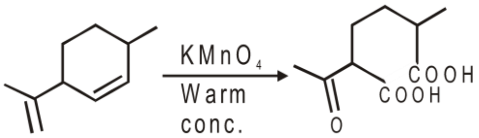
$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$	$KMnO_4/H^+$
Reactant	$=CH_2$ group	=CH-**R** group	$=CR_1R_2$ group	≡CH group	≡CR group
Product	CO_2	RCOOH	$O=CR_1R_2$	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

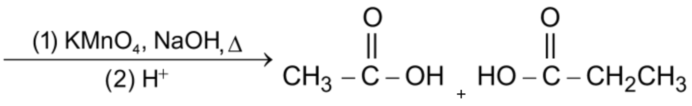
Ex-9. $RCH=CH_2 \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

Ex-10. $RC\equiv CH \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

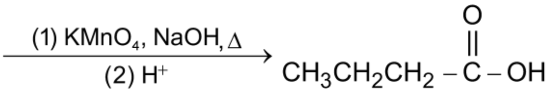
Ex-11. $RC\equiv C-R \xrightarrow{[O]} 2RCOOH$

Ex-12. 

Ex-13.  + CO_2 + H_2O

Ex-14. $CH_3–C\equiv C–CH_2CH_3$ 

$$\xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH,\ \Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

Ex-15. $CH_3CH_2CH_2–C\equiv CH$  + CO_2↑ + H_2O

$$\xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH,\ \Delta} CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$$

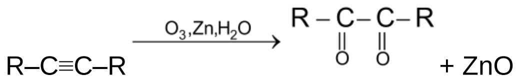
(vi). Oxidation with ozone (ozonolysis) :

Alkene & Alkyne

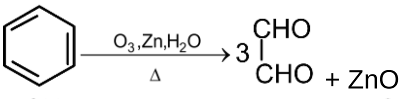
Like permanganate ozone cleaves double bonds to give Ketones and aldehydes. However, ozonolysis is milder, and both Ketones and aldehydes can be recovered without further oxidation.

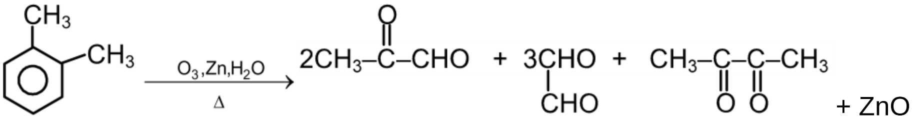
Reductive Ozonolysis Products (O_3/ Zn, H_2O)					
O_3/ Zn, H_2O	**O_3/ Zn, H_2O**	**O_3/ Zn, H_2O**	**O_3/ Zn, H_2O**	**O_3/ Zn, H_2O**	**O_3/ Zn, H_2O**
Reactant	$=CH_2$ group	=CH-**R** group	$=CR_1R_2$ group	R–C≡CH group	RC≡CR group
Product	HCHO	O=CH-**R**	$O=CR_1R_2$	α-keto aldehyde	diketone

Ex-16. $R{-}CH{=}CH{-}R \xrightarrow{O_3,Zn,H_2O} 2RCHO + ZnO$

Ex-17. 

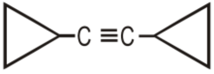
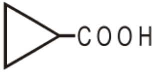
$R{-}C{\equiv}C{-}R \xrightarrow{O_3,Zn,H_2O} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R + ZnO$

Ex-18. 

Ex-19. 

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	$O=CR_1R_2$	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

Ex-20. 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-21. 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

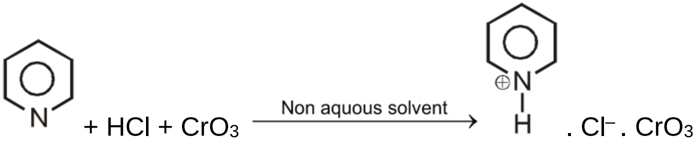
∴ Molecular structure must be :

$CH_3(CH_2)_4C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}C(CH_2)_4{-}CH_3$

(c) Oxidation reaction of alcohols :

	Oxidation Product of Alcohol-1						
	Strong oxidising agent			**Weak oxidising agent**			
	CrO_3 in water or H_2CrO_4	**$KMnO_4/H^+$**	**$K_2Cr_2O_7/H^+$**	**PCC***	**PDC****	**CrO_3/Inert medium**	**Copper & heat as oxidising agent**
1° alcohol or Primary alcohol	Carboxylic acid			Aldehyde			Aldehyde
2° alcohol or Secondary alcohol	Ketone			Ketone			Ketone
3° alcohol or tertiary alcohol	Not oxidised			Not oxidised			Dehydrate to alkene

(1) Pyridinium Chloro Chromate (PCC)



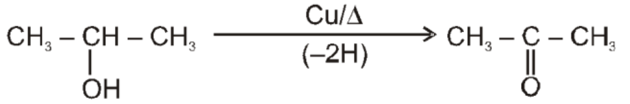
(2) Pyridinium dichromate (PDC) = ($2C_6H_5N.CrO_3$)

(3) Jones Reagent = dilute chromic acid + acetone

(4) Collin's reagent = CrO_3 + pyridine + CH_2Cl_2

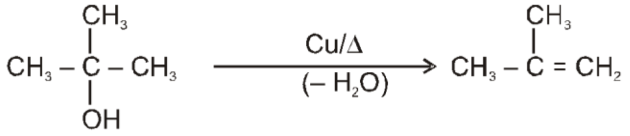
(5) MnO_2 = It is selective oxidising reagent, oxidised only allylic & benzylic alcohol into aldehyde & ketone.

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



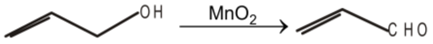
$$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[(-2H)]{Cu/\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$ (dehydrogenation)

Ex-22.

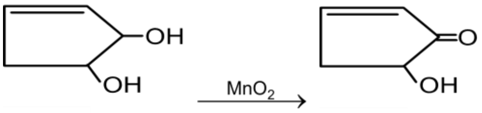


$$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3 \xrightarrow[(-H_2O)]{Cu/\Delta} CH_3-\overset{CH_3}{C}=CH_2$$ [dehydration (Reduced Product)]

Ex-23.

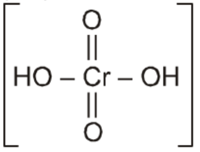


Ex-24.

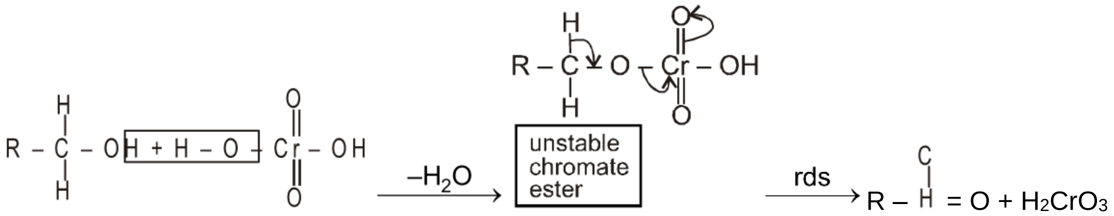


Mechanism (with Cr^{+6} oxidising agents) :

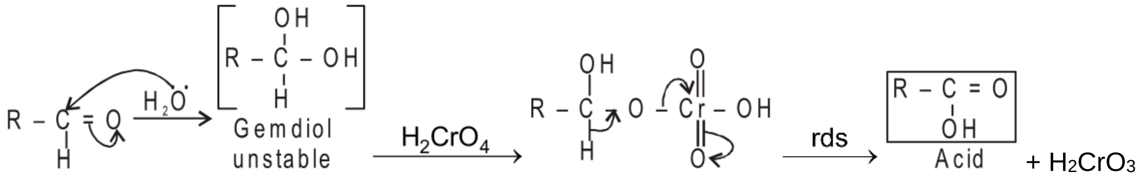
(i) $CrO_3 + H_2O \longrightarrow H_2CrO_4 =$



(ii)



(iii)



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) $RCHO > RCDO$

(i) Oppenaur's oxidation of alcohols

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

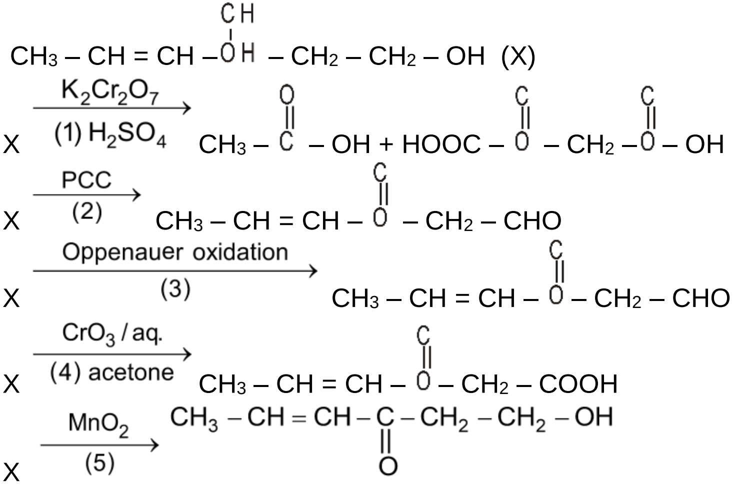
(b) Commonly used bases are aluminium tert-butoxide.

$$\underset{2^0\text{Alcohol}}{R_2CHOH} + \underset{\text{Acetone}}{(CH_3)_2CO} \xrightleftharpoons{Al(OCMe_3)_3} \underset{\text{Ketone}}{R_2CO} + \underset{2^0\text{Alcohol}}{CH_3CH(OH)CH_3}$$

Rate of Oxidation

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

Ex-25. Write the product of following reactions.



$CH_3-CH=CH-\overset{CH}{\overset{|}{OH}}-CH_2-CH_2-OH$ (X)

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

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

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

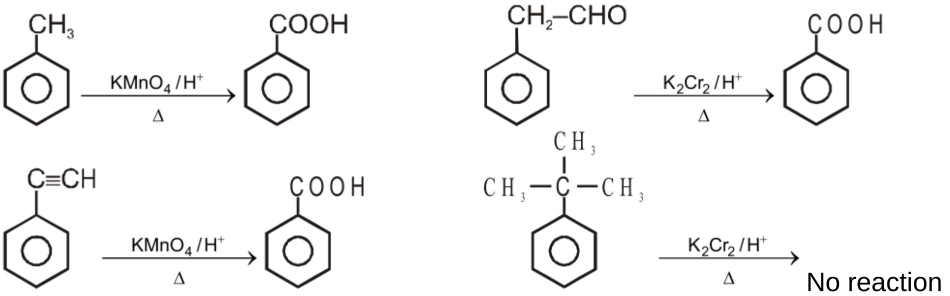
$X \xrightarrow[(4)\ \text{acetone}]{CrO_3\ /\ aq.} CH_3-CH=CH-\overset{C}{\overset{\|}{O}}-CH_2-COOH$

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

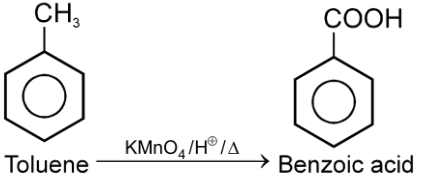
(d) Aromatic side chain oxidation

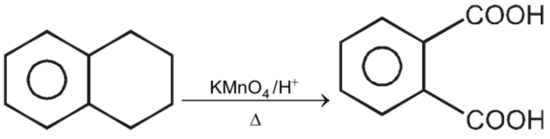
Strong oxidising agents like $KMnO_4/H^{\oplus}/\Delta$ or $K_2Cr_2O_7/H^{\oplus}/\Delta$, oxidises benzylic carbon to – COOH group if benzylic hydrogen or unsaturation is present.

General Reaction



Note :- Tertiary butyl $(CH_3)_3C-$ will not oxidise by oxidising reagent

Ex-26. 

Ex-27. 

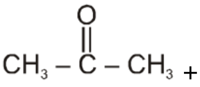
(e) Oxidation of aldehydes & ketones

(i) With Acidic $KMnO_4$ or $K_2Cr_2O_7$:

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

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

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



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

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

$$CH_3COCH_2CH_3 \xrightarrow{[O]} 2\ CH_3COOH \ ; \ CH_3COCH_2CH_2CH_3 \xrightarrow{[O]} CH_3\ COOH + CH_3\ CH_2\ COOH$$

(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.

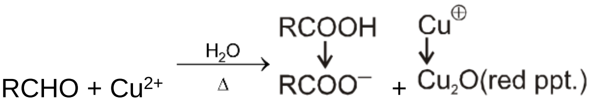
$$RCHO + 2Cu^{2+} + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{red ppt.}}{Cu_2O\downarrow} + 2H_2O$$

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

Note - Benzaldehyde does not reduce Benedict's solution.

(iv) With Benedict's solution

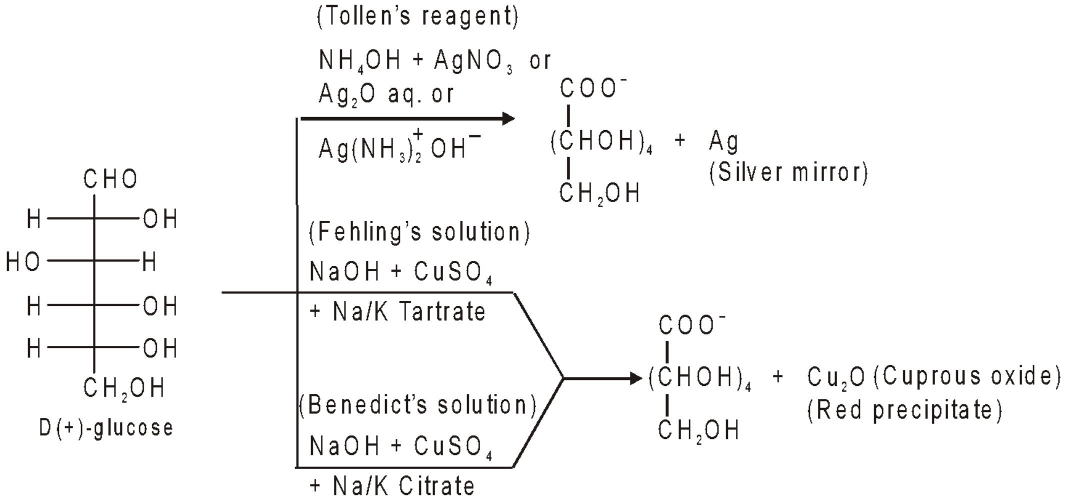
Sodium citrate + NaOH + $NaHCO_3$ + $CuSO_4$

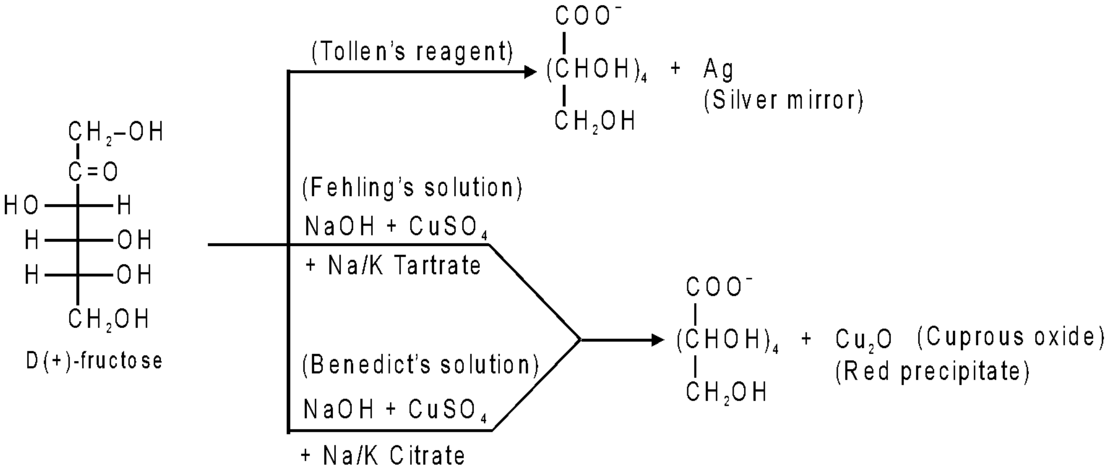


$$RCHO + Cu^{2+} \xrightarrow[\Delta]{H_2O} \overset{RCOOH}{\overset{\downarrow}{RCOO^-}} + \overset{Cu^{\oplus}}{\overset{\downarrow}{Cu_2O\text{(red ppt.)}}}$$

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

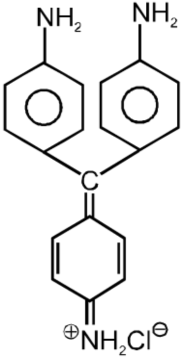
$$RCHO + Hg_2Cl_2 + H_2O \rightarrow RCOOH + 2HCl + 2Hg\downarrow \text{ grey ppt.}$$





(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.



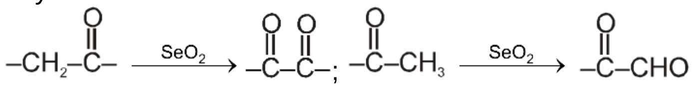
$\xrightarrow{SO_2}$ Colourless solution (Schiff's Reagent) $\xrightarrow[\Delta]{RCHO}$ RCOOH + Pink colour

p-Rosaniline Hydrochloride (Magenta colour)

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

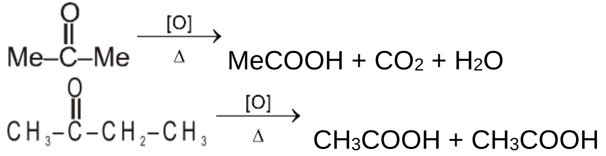
SeO_2 is a selective oxidizing agent with converts $–CH_2–$ group adjacent to carbonyl group into carbonyl group.
The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.



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

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.



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

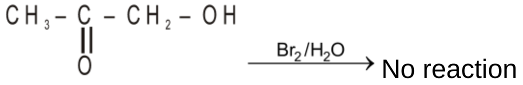
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[\Delta]{[O]} CH_3COOH + CH_3COOH$$

(vii) Oxidation by $Br_2 + H_2O$

It is a mild oxidising agent. It oxidises aldehyde into acid.

Ex-28. $CH_3–CH_2–CHO \xrightarrow{Br_2/H_2O} CH_3–CH_2–COOH$

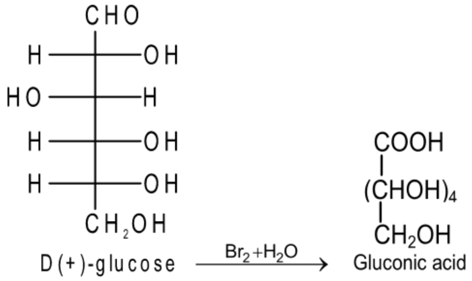
Ex-29.



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-OH \xrightarrow{Br_2/H_2O}$ No reaction

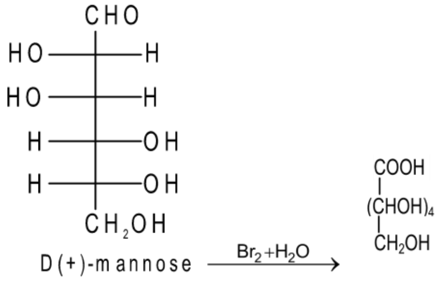
Note : Br_2/ H_2O does not oxidise alcohol.

(a)

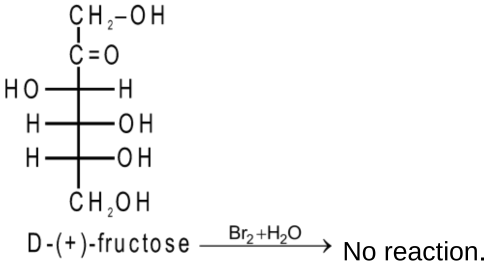


Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

(b)



(c)

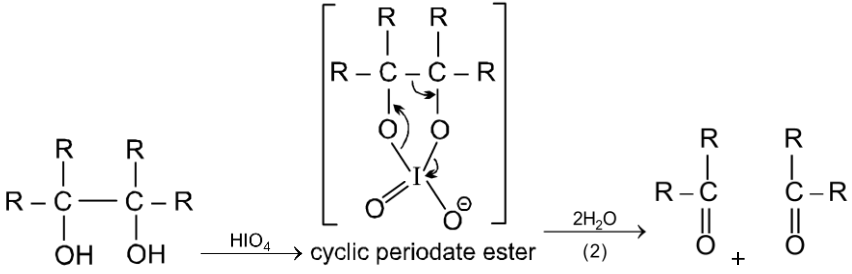


(f) Oxidation reaction of diols/polyols

(i) HIO_4 oxidation :

(Oxidation by lead acetate is similar to HIO_4 oxidation)

Mechanism :



Remarks

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

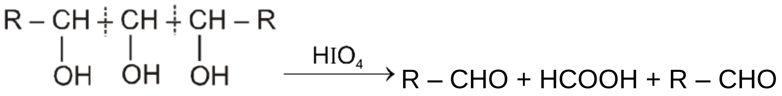
(2) It brings about oxidative cleavage of vicinal diol.

(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.

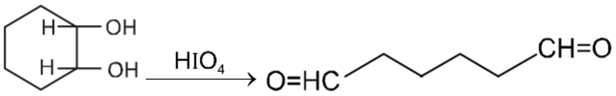
(5) In cyclic diols only cis-vicinal diols are oxidised. Trans isomers are not oxidised.

Ex-30. General reaction

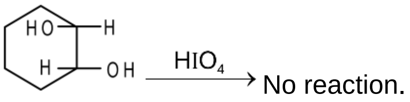


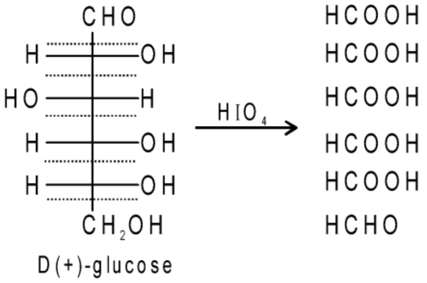
$\underset{OH}{\underset{|}{R-CH}} \vdots \underset{OH}{\underset{|}{CH}} \vdots \underset{OH}{\underset{|}{CH}}-R \xrightarrow{HIO_4} R-CHO + HCOOH + R-CHO$

Ex-31. (1)



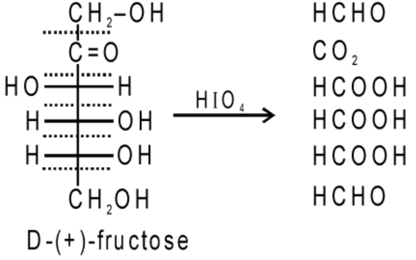
(2)



(3) 

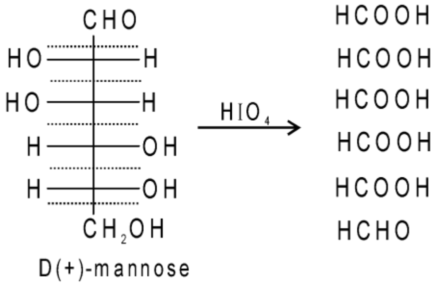
The presence of several pairs of vicinal diols oxidation with periodic acid can lead to the formation of complex product mixture. Glucose is degraded during oxidative cleavage with periodic acid into formic acid, formaldehyde.

Glucose get oxidised by HIO_4 gives 1 mole of HCHO and 5 mole of HCOOH it shows that glucose contains terminal CHO group and terminal 1º alchohol group.

(4) 

Fructose is degraded during oxidative cleavage with periodic acid into formic acid, formaldehyde and CO_2.

Fructose get oxidised by HIO_4 and gives 2 moles formaldehyde, 3 moles formic acid and CO_2 it shows that fructose contains two terminal 1º alcohol groups and 1 ketone group.

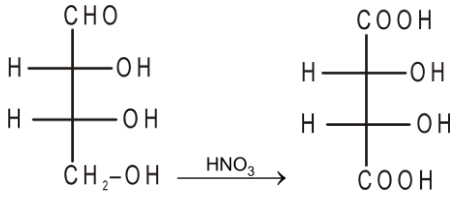
(5) 

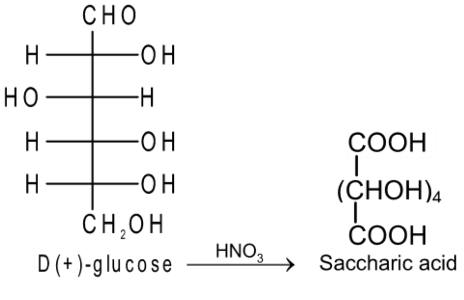
Mannose is degraded during oxidative cleavage with periodic acid into formic acid, formaldehyde.

(ii) Oxidation by conc. HNO_3

It oxidises 1° alcohol and aldehyde into acid.

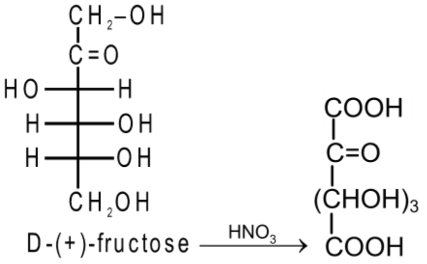
Ex-32. $CH_3–CH_2–CH_2–OH \xrightarrow{HNO_3} CH_3–CH_2–COOH$ **Ex-33.**



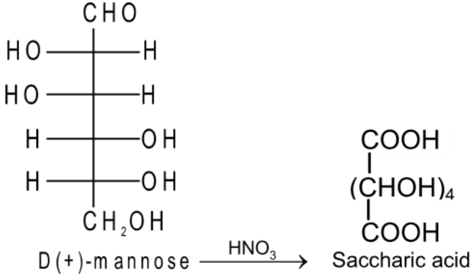
(a) 

On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.

(b)



(c)

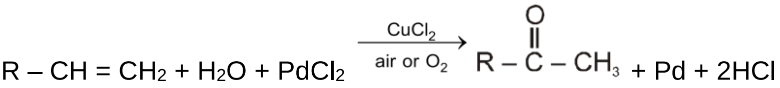


(g) Miscellaneous oxidation reactions

(i) Wacker process

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in presence of air or O_2 . Except ethene any higher alkene will give ketone.

$$CH_2 = CH_2 + H_2O + PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} CH_3 - CH = O + Pd + 2HCl$$



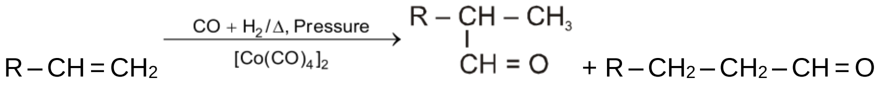
$$R - CH = CH_2 + H_2O + PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 + Pd + 2HCl$$

Note : During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to Cu(I)

(ii) Oxo-process

It is also called as carbonylation here terminal alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

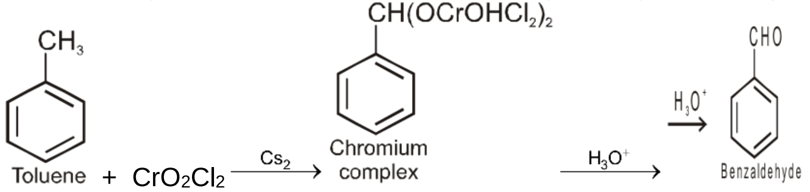
Wilkinson catalyst $[RhH(CO)(Ph_3P)_3]$ can also be used in promoting the oxo-process.



$$R-CH=CH_2 \xrightarrow[{[Co(CO)_4]_2}]{CO + H_2/\Delta,\ \text{Pressure}} \underset{\displaystyle CH = O}{R - \underset{|}{C}H - CH_3} + R-CH_2-CH_2-CH=O$$

(iii) Etard reaction

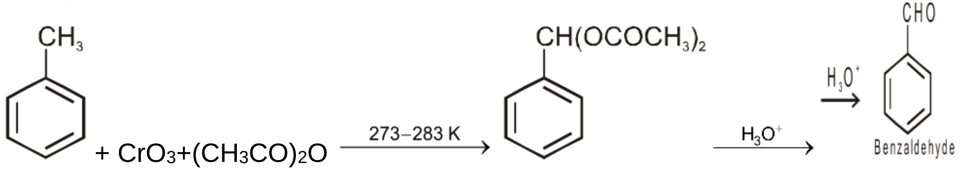
By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2)



This reaction is called **Etard reaction.**

$$Ph-CH_3 \xrightarrow[500°C]{MnO/Air} Ph-CHO$$

(iv) Oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride



(v) Combustion

(a) Combustion of Alkane

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2} H_2O + \Delta\ ; \qquad C_3H_8 + \left(3 + \frac{8}{4}\right) O_2 \longrightarrow 3\,CO_2 + \frac{8}{2} H_2O$$

Hydrocarbon + sufficient supply of $O_2 \Rightarrow CO_2 + H_2O + \Delta$
Hydrocarbon + insufficient supply of $O_2 \Rightarrow CO + H_2O$ or C (black)

Ex-34. How many atoms of oxygen are needed for complete combustion of 2.2 g of propane ?

Ans. $C_3H_8 + 5O_2 \longrightarrow 3\,CO_2 + 4H_2O$

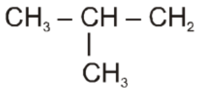
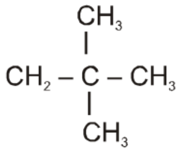
44 gm of C_3H_8 needs = 5 moles of Oxygen = 5 × N_A molecule of Oxygen = 5 × 2 × N_A atom

2.2 gm of C_3H_8 needs = $\frac{5 \times 2 \times 2.2 \times N_A}{44}$ = 0.5 × N_A atoms of Oxygen

Note : 1. Heat of combustion α higher homologues

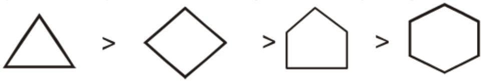
Ex-35. $C_3H_8 > C_2H_6 > CH_4$ $\propto \frac{1}{\text{Branching of alkane (in isomers)}}$

2. Heat of combustion

Ex-36. $CH_3 - CH_2 - CH_2 - CH_2 - CH_3 >$ 
$\underset{\displaystyle CH_3}{CH_3 - \underset{|}{C}H - CH_2}$
$- CH_3 > CH_3 -$ 
$CH_2 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}} - CH_3$

3. Heat of combustion $\propto \frac{1}{\text{size of ring (cycloalkane)}}$

On increasing the size of ring from three to six stability of ring increases and hence heat of combustion (its value) decreases per CH_2 group.

Ex-37. 

(b) Combustion of alkene

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

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

(c) Combustion of alkyne

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

$C_2H_2 + \frac{5}{2} O_2 \longrightarrow 2CO_2 + H_2O$

(d) Combustion of benzene :

When heated in air, benzene burns with sooty flame producing CO_2 and H_2O

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

General combustion reaction for any hydrocarbon may be given by the following chemical equation:

$$C_xH_y + (x + \frac{y}{4})O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Section (C) :Hydrolysis

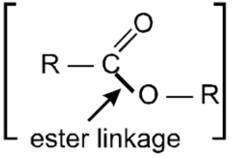
Introduction :

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.

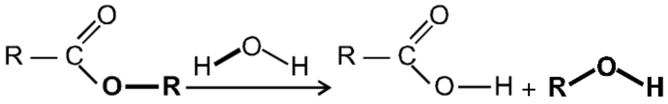
This is distinct from a hydration reaction, in which water molecules are added to a substance, but no fragmentation of molecule/species occurs.Such a process is exothermic.

(i) Hydrolysis of an ester :

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

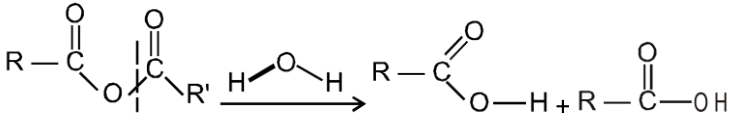


(a) Mild acidic medium : Dilute H_2SO_4, dilute HCl.
(b) Strong alkaline medium : Aqueous NaOH or KOH and heat.
one hydrolysis product contains a hydroxyl functional group, while the other contains a carboxylic acid functional group.



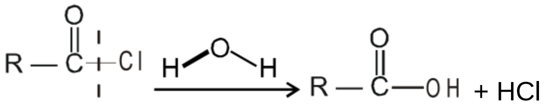
(ii) Hydrolysis of an anhydride :

The hydrolysis of acid anhydride produces two carboxylic acids.



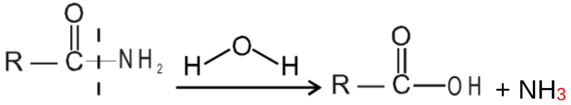
(iii) Hydrolysis of acid halide :

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.



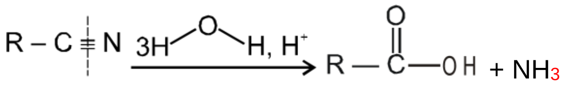
(iv) Hydrolysis of acid amide :

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.



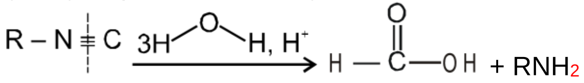
(v) Hydrolysis of cyanides :

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



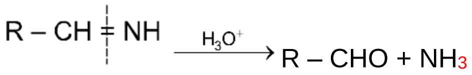
(vi) Hydrolysis of isocyanides :

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



Note : Alkylisocyanide does not hydrolyse in basic medium.

(vii) Hydrolysis of imine :



(viii) 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.

Note : (i) Acetal is formed to protect aldehyde for a long time.
(ii) Acetal has functional groups ether.
(iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
(iv) On treating with ethyleneglycol we get cyclic acetal or ketal.

(ix) Hydrolysis of metal carbide :

(a) Methanides : These give CH_4 on reaction with H_2O.

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$;

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

These carbides contain C^{4-} ions in their constitution.

(b) Acetylides : These give C_2H_2 on reaction with H_2O.

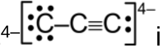
$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$Al_2 (C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C2H_2$

$SrC_2 + 2H_2O \longrightarrow Sr(OH)_2 + C_2H_2$

(c) Allylides : These give 1-propyne on reaction with H_2O.

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3–C≡CH$

Such compounds contain C_3^{4-}  ions.

Section (D) : Decarboxylation and heating effects

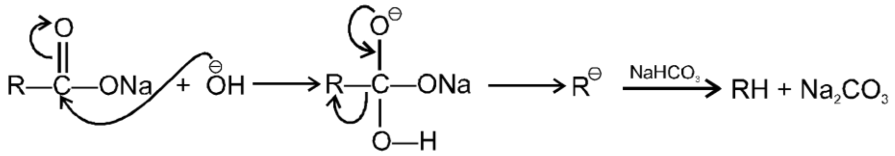
(i) Decarboxylation of sodium salt of acid

(a) Synthesis of alkane :

It is removal of CO_2. This reaction is used to desend the series and proceeds via carbanion intermediate.

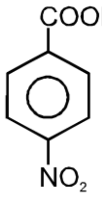
Reagent → Sodalime [mixture of NaOH + CaO]

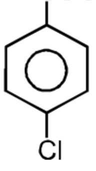
$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

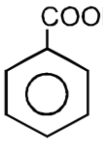


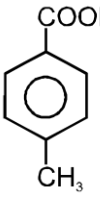
Note - In this reaction carbanion intermediate is formed.
Rate of reaction depends upon the stability of carbanion intermediate.
Electron withdrawing group at R–COOH will increases the rate of decarboxylation.

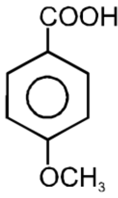
Ex-38.


I


II

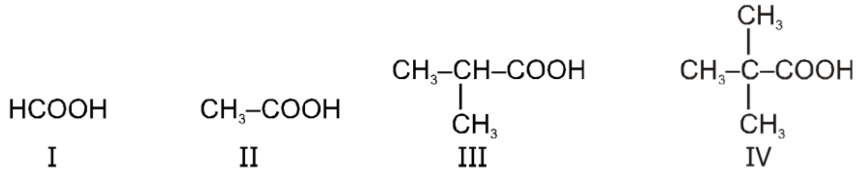

III


IV


IV

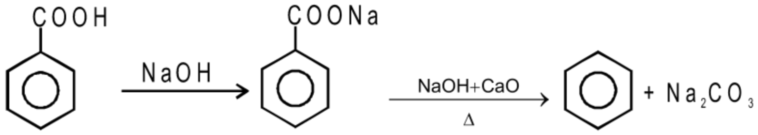
Rate of decarboxylation. I > II > III > IV > V

Ex-39.

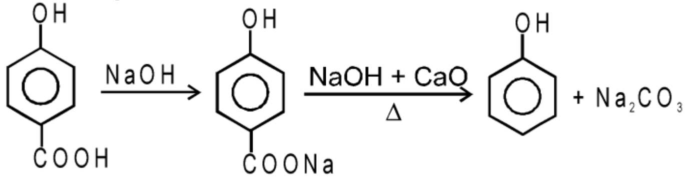

$HCOOH$ (I), CH_3-COOH (II), $CH_3-CH(CH_3)-COOH$ (III), $CH_3-C(CH_3)_2-COOH$ (IV)

Rate of decarboxylation. I > II > III > IV

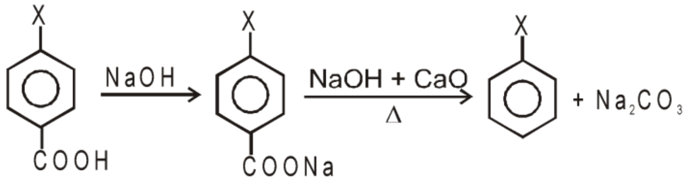
(b) Synthesis of benzene



(c) Synthesis of phenol

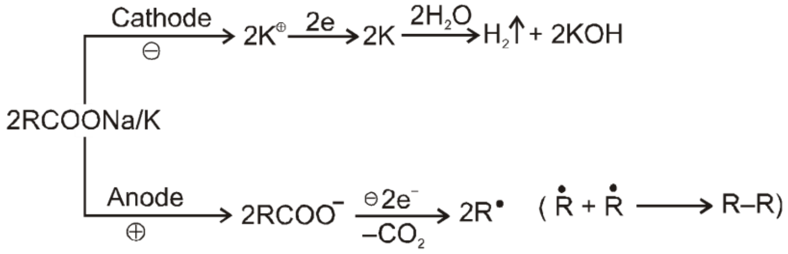


(d) Synthesis of halo benzene



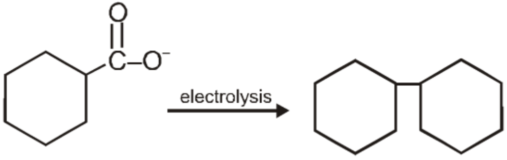
(ii) Kolbe's electrolytic method

(a) Synthesis of alkane : In this method two moles of Na/K - salt of fatty acids is used. During the electrolysis hydrogen gas is liberated at cathode because disharge potential of hydrogen is less than of that metal, while alkane is liberated at anode and this alkane will be dimer of alkyl part of acid.



Note : 1. This method is used for the preparation of alkane having even number of carbon atoms. It is not used for methane as well as alkanes having odd number of carbon atom.

Ex-40.



+ 2 CO_2

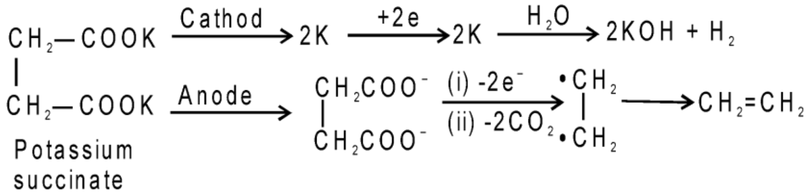
2. During kolbe's electrolysis pH of electrolyte increases progressively due to increases in concentration of alkali.

3. On using two type of Na/K-salt of fatty acids . We get the mixture of three alkanes. Because two type of salt of fatty acids gives us two types of free radicals which may combine to each other as well as itself.

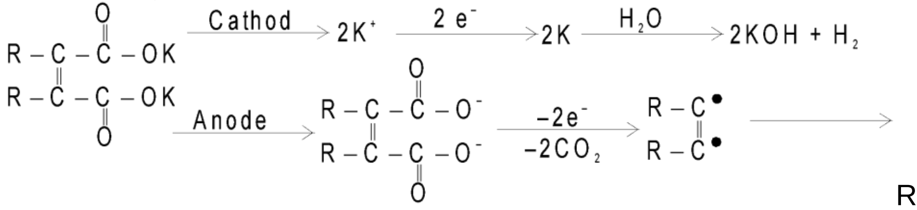
Ex-41. $2CH_3-COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_3 + 2CO_2 + H_2 + 2KOH$.

(b) Synthesis of alkene

This reaction gives ethylene as follows



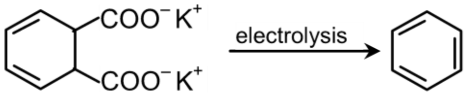
(c) Synthesis of alkyne



R–C≡C–R

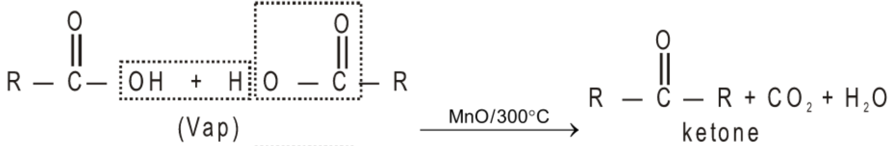
If R = H, product will be CH ≡ CH ; If R = CH_3, product will be $CH_3 – C ≡ C – CH_3$.

(d) Synthesis of benzene :

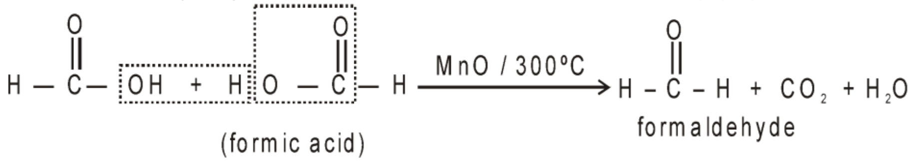


+ $2CO_2 + H_2\uparrow + 2KOH$.

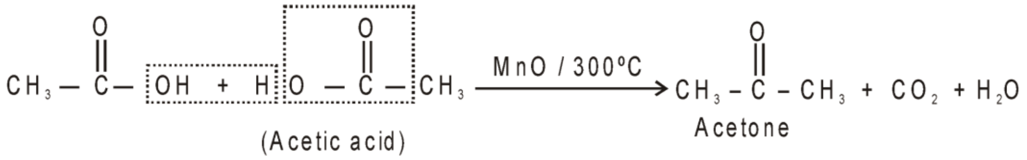
(iii) On passing vapours of fatty acids over Mangnous oxide at 300ºC



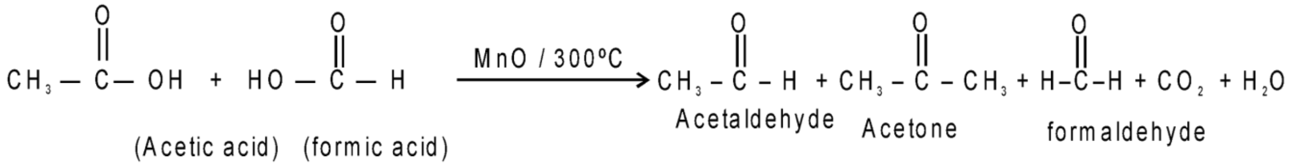
$$\underset{(Vap)}{R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R} \xrightarrow{MnO/300^{\circ}C} \underset{ketone}{R-\overset{O}{\overset{\|}{C}}-R} + CO_2 + H_2O$$



$$\underset{(formic\ acid)}{H-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{MnO / 300^{\circ}C} \underset{formaldehyde}{H-\overset{O}{\overset{\|}{C}}-H} + CO_2 + H_2O$$



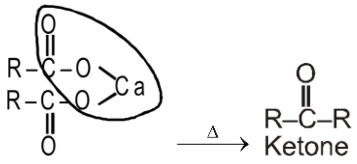
$$\underset{(Acetic\ acid)}{CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{MnO / 300^{\circ}C} \underset{Acetone}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CO_2 + H_2O$$



$$\underset{(Acetic\ acid)}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{(formic\ acid)}{HO-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{MnO / 300^{\circ}C} \underset{Acetaldehyde}{CH_3-\overset{O}{\overset{\|}{C}}-H} + \underset{Acetone}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + \underset{formaldehyde}{H-\overset{O}{\overset{\|}{C}}-H} + CO_2 + H_2O$$

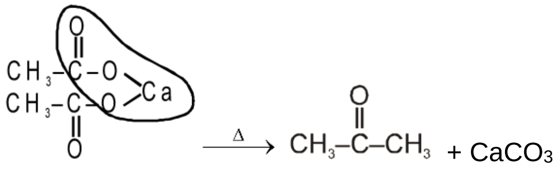
On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

(iv) Dry distillation of calcium salt of acid :



+ $CaCO_3$

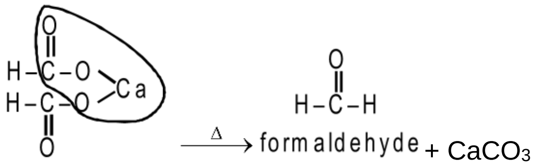
Ex-42.



$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

calcium acetate

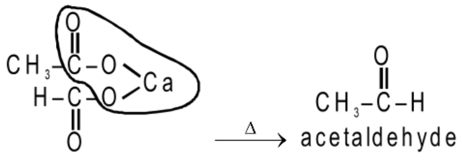
Ex-43.



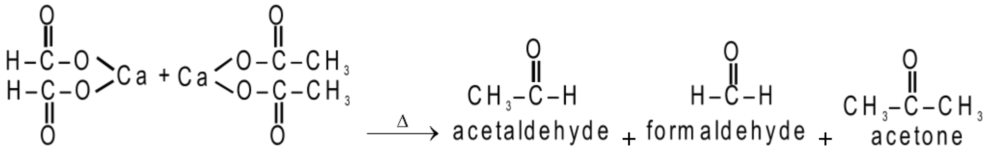
$$(HCOO)_2Ca \xrightarrow{\Delta} H-\overset{O}{\overset{\|}{C}}-H + CaCO_3$$

calcium formate

Ex-44.



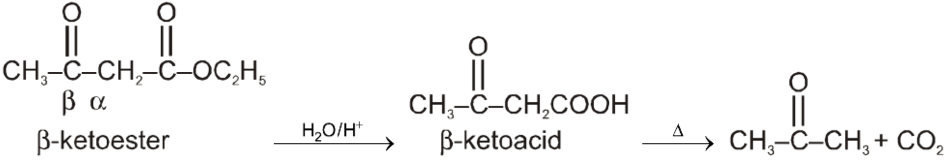
Ex-45.



On dry distillation of calcium salt of acetic acid with calcium salt of formic acid we get a mixture of aldehyde, ketone and formaldehyde.

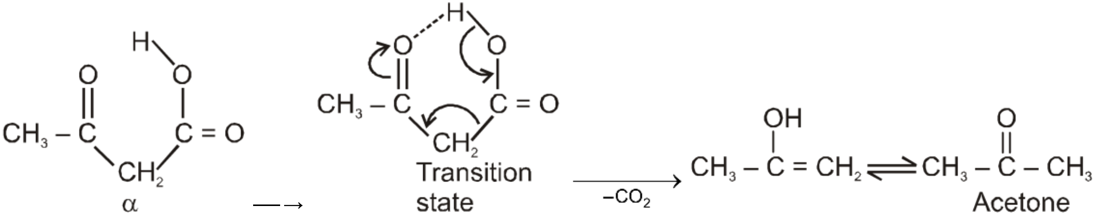
Calcium salt of dibasic acid (1,4 & higher) on distillation) gives cyclic ketones.

(v) Acid hydrolysis followed by heating of β-Ketoester :



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{H_2O/H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOH \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$$

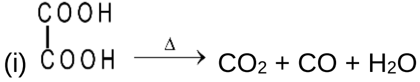
Note : It is β-ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.



(vi) Heating effects :

(a) Heating effect on dicarboxylic acid :

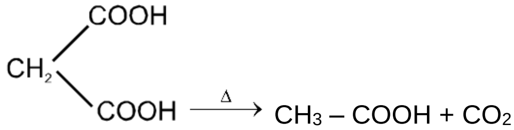
(i)



$$\underset{COOH}{\overset{COOH}{|}} \xrightarrow{\Delta} CO_2 + CO + H_2O$$

Oxalic acid

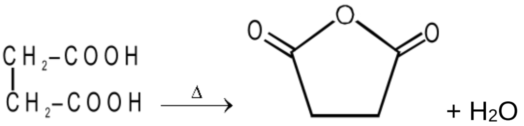
(ii)



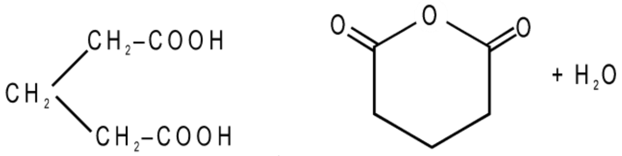
$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3-COOH + CO_2$$

Malonic acid Acetic acid

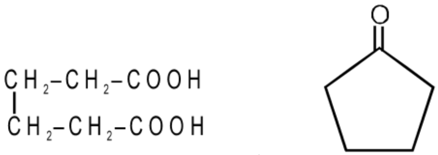
(iii)



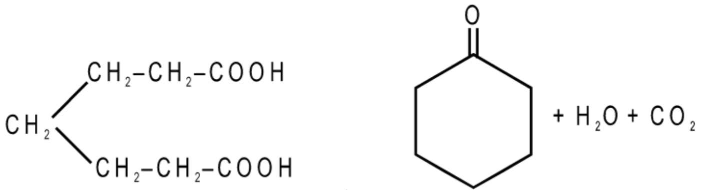
Succinic acid Succinic anhydride (Butan-1, 4-dioic anhydride)



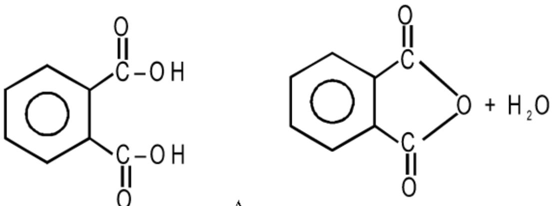
(iv) Glutaric acid $\xrightarrow{\Delta}$ Glutaric anhydride. (Pentan-1, 5-dioic anhydride)



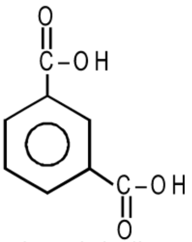
(v) Adipic acid $\xrightarrow{\Delta}$ Cyclopentanone + CO_2 + H_2O



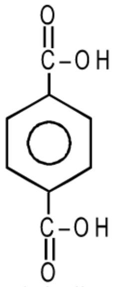
(vi) Pimelic acid $\xrightarrow{\Delta}$ Cyclo hexanone



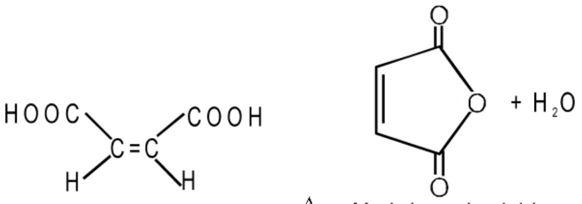
(vii) Phthalic acid $\xrightarrow{\Delta}$ Phthalic anhydride



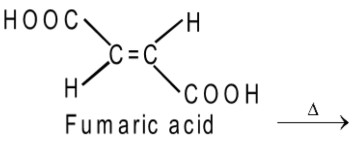
(viii) Iso phthalic acid $\xrightarrow{\Delta}$ No reaction.



(ix) Terphthalic acid $\xrightarrow{\Delta}$ No reaction.



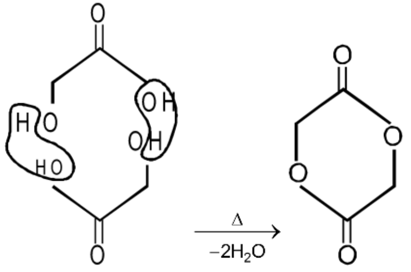
(x) Maleic acid $\xrightarrow{\Delta}$ Maleic anhydride

(xi) 

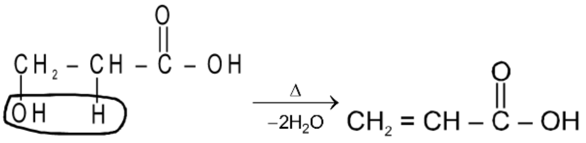
No reaction.

(b) Heating effects on Hydroxy acids :

(1) α–Hydroxy acid

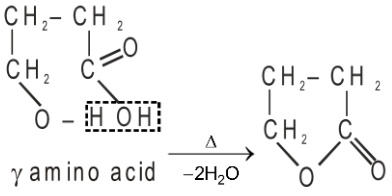


(2) β–Hydroxy acid



$$CH_2-CH-\overset{\overset{O}{||}}{C}-OH \;(\text{with } OH \text{ and } H) \xrightarrow[-2H_2O]{\Delta} CH_2=CH-\overset{\overset{O}{||}}{C}-OH$$

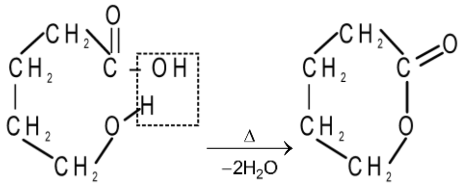
(3) γ–Hydroxy acid



(γ-Lactone)

Since 4 or 8 membered rings are less stable the refore β-Hydroxy acids on heating produce α, β unsaturated carboxylic acid.

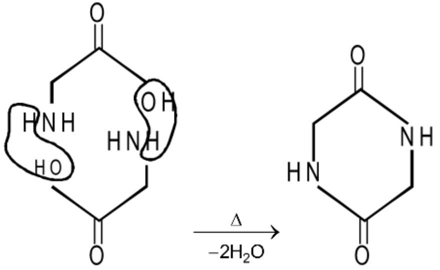
(4) δ–Hydroxy acid



(δ-Lactone)

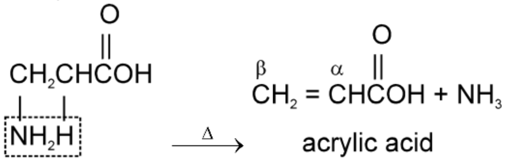
(c) Heating effect on amino acids

α-amino acids undergo intermolecular dehydration on heating at about 200°C to give diketopiperazines.



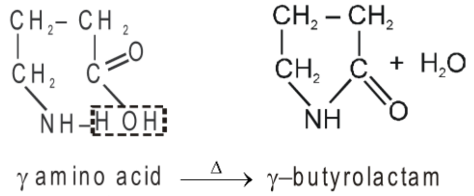
glycine 2,5-diketopiperazine

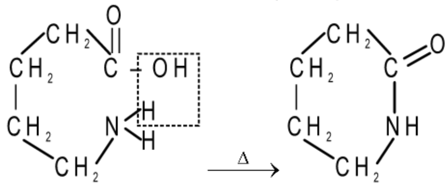
β-amino acids undergo intramolecular deamination on heating to form α, β-unsaturated acids.



$$\underset{NH_2\;\;H}{CH_2CH\overset{\overset{O}{||}}{C}OH} \xrightarrow{\Delta} \overset{\beta}{C}H_2=\overset{\alpha}{C}H\overset{\overset{O}{||}}{C}OH + NH_3$$

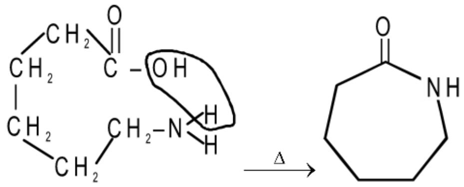
γ-amino acids and δ-amino acid undergo intramolecular dehyderation to form cyclic amides called **lactams.**





+ H_2O

δ-amino acid δ- valerolactam



+ H_2O

ω-amino acid Caprolactam or ω-lactam