REDUCTION, OXIDATION, HYDROLYSIS & DECARBOXYLATION REACTIONS

CONTENTS

JEE (ADVANCED) SYLLABUS

Concepts :

Reduction of alkenes, Alkynes, Alcohols, Aldehydes, Ketones, Acids, Acid halides, Esters, Amides & Anhydrides.

Oxidation of Alkenes, Alkynes, Alcohols, Aldehydes, Ketones, Acids, Acid halides, Esters, Amides & Anhydrides

Hydrolysis reaction of Acid halides, Esters, Amides & Anhydrides, Cyanides, Ethers etc.

JEE (MAIN) SYLLABUS

Reactions of Grignard reagent.

Reduction and oxidation reactions (Alkene, Alkyne, Alcohol, Aldehyde, Ketone & Acid derivatives).

General methods of preparation, properties and reactions.

1. REDUCTION

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 :

(i) Catalytic hydrogenation

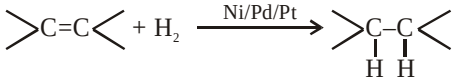
(ii) Metal hydride reduction

(iii) Metal/proton (acid) reduction

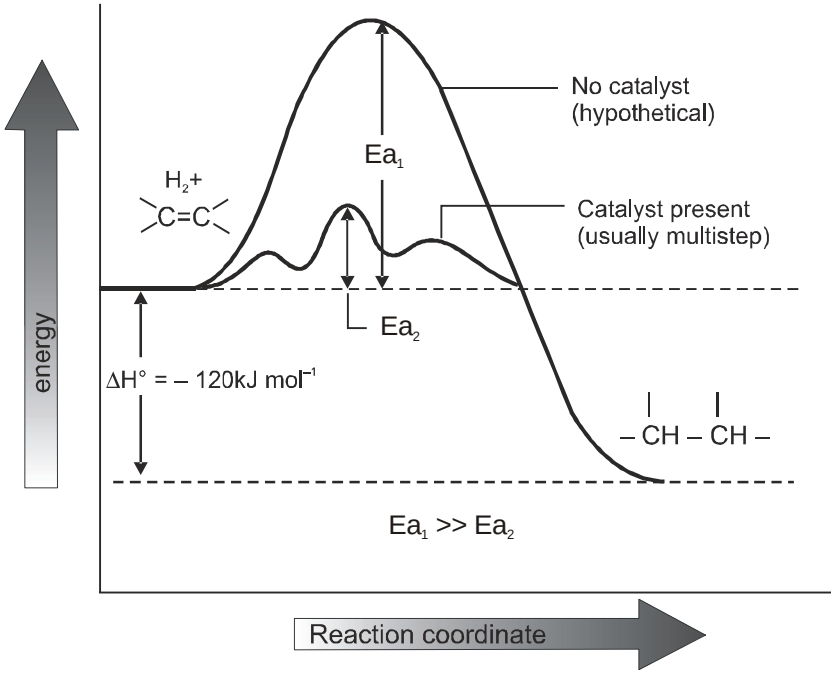
(iv) Miscellaneous reductions

1.1 Catalytic hydrogenation

Hydrogenation of an alkene/alkyne is formally a reduction with H_2 adding across the double bond /triple bond to give an alkane. The process require a catalyst containing Pt, Pd or Ni, at room temperature using hydrogen gas at atmospheric pressure.



A catalyst provides a new pathway for the reaction that involves lower energy of activation .



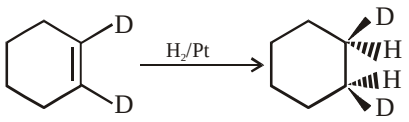
Procedure :

Hydrogenation actually take place at the surface of the metal, where the liquid solution of the alkene comes into contact with hydrogen and the catalyst. Hydrogen gas is adsorbed on to the surface of these metal catalyst, and the catalyst weakens the H–H bond. Hydrogenation is an example of heterogeneous catalyst because the solid catalyst is in a different phase from the reactant solution.

Note : If H_2 and D_2 mixture is used with 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.

Stereochemistry of catalytic hydrogenation

The two hydrogen atoms add from a solid surface they add with syn stereochemistry.



Catalytic reduction of functional groups using H_2/Pd(C) or H_2/Pt or H_2/Ni

	Substrate	Product
1.	R–CH=CH_2	R–CH_2–CH_3
2.	R–C≡CH	R–CH_2–CH_3
3.	R–CHO	R–CH_2–OH
4.	R–CO–R	R–CH(OH)–R

	Substrate	Product
5.	R–C≡N	R–CH_2–NH_2
6.	R–COCl	R–CH_2–OH
7.	R–NO_2	R–NH_2
8.	R–CH=NH	R–CH_2–NH_2

Note : Generally RCOOH, RCOOR, $RCONH_2$ and RCOOCOR groups are **not reduce** by catalytic hydrogenation.

(a) Homogeneous catalyst :

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 $Rh[(C_6H_5)_3P]_3Cl$.

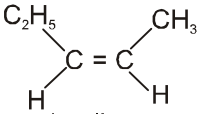
(b) Partial hydrogenation

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

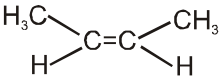
(ii) Rosenmund catalyst : [H_2/Pd, $BaSO_4$, quinoline or sulphur]

(iii) Nickel boride Ni_2B (P-2 catalyst)

Above catalysts convert alkyne into cis alkene (Syn addition)

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

cis-alkene

(ii) $CH_3–C\equiv C–CH_3 \xrightarrow{H_2,Pd,\ BaSO_4\ ,\ S}$ 

cis-2-butene

(c) Rosenmund reaction

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

1.2 Metal hydride reduction

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

(a) $LiAlH_4$ (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.
It reduces following functional groups.

S.No.	Substrate	Product
1	Aldehyde	1º alcohol
2	Ketone	2º alcohol
3	Acid	1º alcohol
4	Acid anhydride	1º alcohol
5	Acid chloride	1º alcohol
6	Ester	1º alcohol

S.No.	Substrate	Product
7	Cyanide	1º amine
8	Amide	1º amine
9	Isocyanide	2º amine
10	Aliphatic nitro	1º amine
11	Imine	1º amine
12	Ethylene oxide	1º alcohol

Note : (1) 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 cinnamaldehyde.

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

(2) $LiAlH_4$ reduce nitrobenzene into azobenzene.

(b) 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 and acid chlorides to 1º alcohols. It does not reduce any other derivative of acid. It is effective even in protic solvents like alcohol.

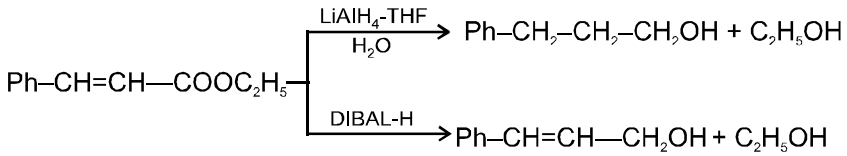
Reagent	**$NaBH_4$**			
Reactant	Aldehyde	Ketone	Acid chloride	RCH=NH
Product	1º alcohol	2º alcohol	1º alcohol	1º amine

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

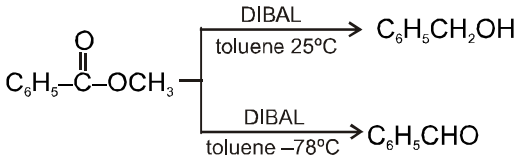
Diisobutyl aluminium hydride $[i\text{-}Bu_2AlH]_2$ is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

Reagent	**DiBAL-H/Cold**	**DiBAL-H/Ordinary Temp.**	**DiBAL-H/Hydrolysis**
Reactant	Ester	Ester	Cyanide
Product	Aldehyde	Alcohol	Aldehyde

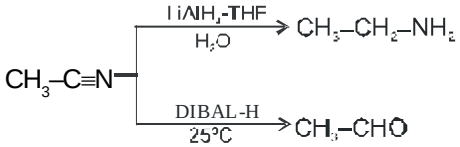
(i)



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

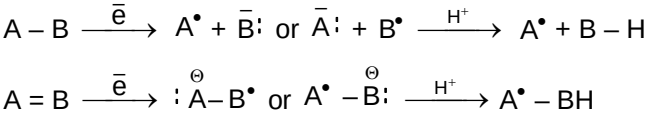


(iii) LAH reduce RCN to amine but DIBAL-H is found to be reduce it to aldehyde.



1.3 Metal/proton (acid) reduction

Reduction by dissolving metals is based on the fact that the metals act 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.

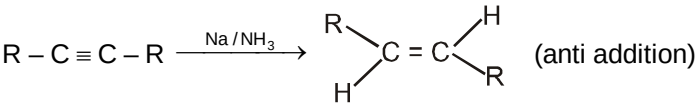


(a) Birch reduction [Na or Li/NH_3(liq.) or (ethyl alcohol)]

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

Alkynes are reduced to trans alkene.

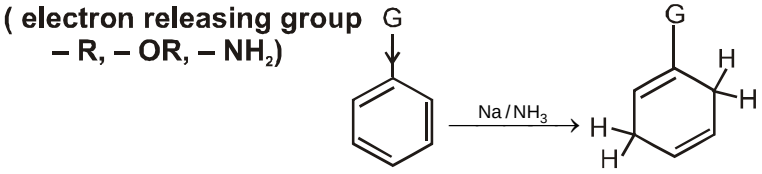
Stereochemistry : Anti addition.



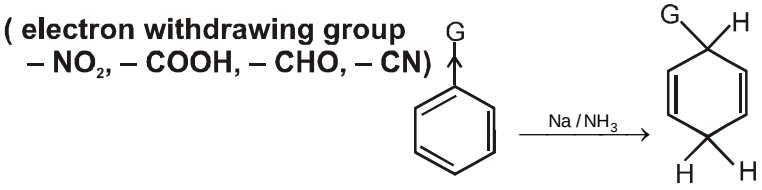
Benzene ring is reduced at 1, 4-position.

Typical example of reduction for aromatic system :

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



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



(b) Bouvealt-Blanc reduction [Na/C_2H_5OH]

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

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

1.4 Miscellaneous reductions

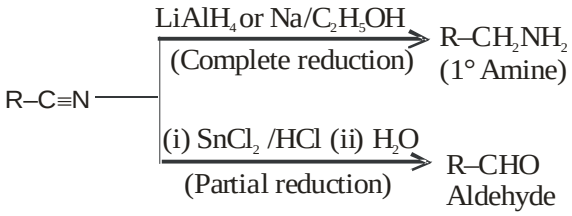
(a) Reduction with Diborane (B_2H_6)

Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or better with diborane. Diborane does not easily reduce fuctional group such as ester, nitro, halo compounds.

$$RCOOH \xrightarrow[(2)\ H_3O^+]{(1)\ B_2H_6} RCH_2OH$$

(b) Stephen's reduction [$SnCl_2$/HCl]

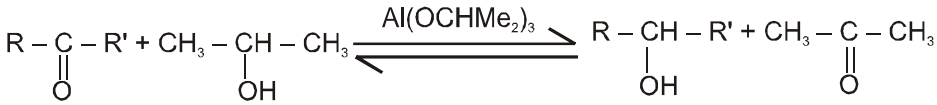
When reduction of alkyl cyanide is carried out with acidified stannous chloride ($SnCl_2$/HCl) at room temperature, imine hydrochloride is obtained, which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called Stephen's reduction.

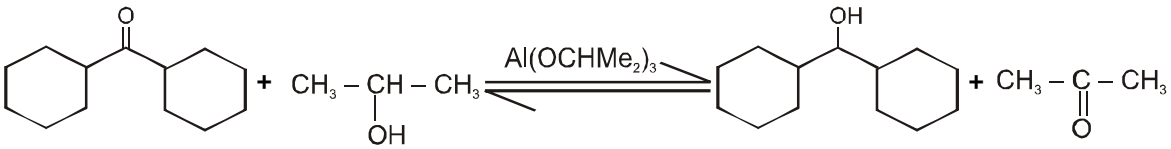


(c) Meerwein-Pondorf-Verley reduction

(Reduction by isopropyl alcohol and aluminium isopropoxide)

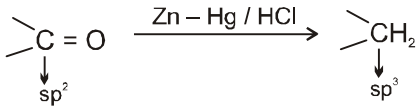
It is selective reduction of ketone to alcohol, even in presence of other functional groups using aluminium isopropoxide in isopropyl alcohol.





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

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



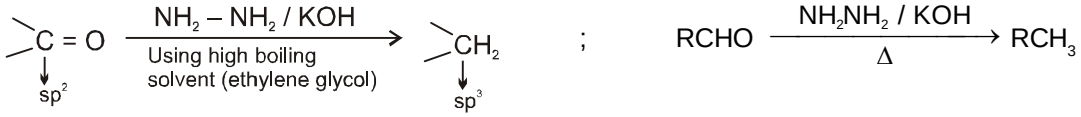
$$R - CHO \xrightarrow[\Delta]{Zn-Hg/conc.\ HCl} RCH_3 + H_2O$$

$$R - \overset{\overset{O}{\|}}{C} - R' \xrightarrow[\Delta]{Zn-Hg/conc.\ HCl} RCH_2R' + H_2O$$

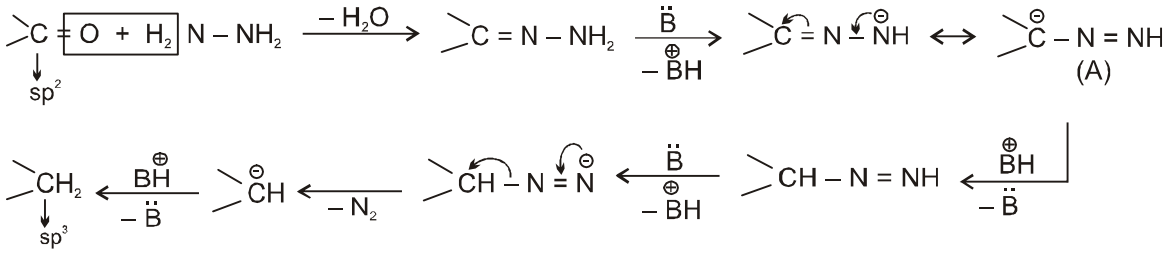
Note : Clemmensen reduction should be avoid to reduce the compounds which have **acid sensitive** group **[Like: Alcohol, Alkene, Alkyne].**

(e) Wolff-kishner reduction [NH_2NH_2 / KOH]

Used to prepare alkane from carbonyl compounds.



Mechanism :



Note : Wolff-kishner reduction should avoid to reduce the compounds which have **base sensitive** groups **[Like : Alkyl halides, Acid halides, Esters, Anhydrides]**

(f) By Red P & HI

Used to prepare alkane from acid derivatives and carbonyl compounds.

Reagent	**Red P & HI**							
Reactant	Aldehyde	Ketone	Acid chloride	Ester	Acid	Alcohol	Anhydride	Ether
Product	Alkane	Alkane	Alkane	Alkane	Alkane	Alkane	Alkane	Alkane

(i) $R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\Delta]{Red\ P + HI} R-CH_3$ **(ii)** $R-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow[\Delta]{Red\ P + HI} R-CH_3 + C_2H_6$

(iii) $R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[\Delta]{Red\ P + HI} R-CH_2-R$ **(iv)** $CH_3CH{=}O \xrightarrow[\Delta]{Red\ P + HI} CH_3CH_3$

(v) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{Red\ P + HI} CH_3CH_2CH_3$ **(vi)** D-Glucose $\xrightarrow[\Delta]{Red\ P + HI}$ n-Hexane

2. OXIDATION

1. Oxidation is defined as the addition of oxygen (electronegative) element to a substance or removal of hydrogen (electropositive element) from a substance.
2. Oxidation of an organic molecule usually corresponds to increase its oxygen content or decrease its hydrogen content.

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

3. Oxidation of an organic compound may be more broadly defined as a reaction that increases its content of any element which is more electronegative than carbon.
   Replacing hydrogen atoms by chlorine atoms is an oxidation reaction.

$$Ar-CH_3 \underset{[R]}{\overset{[O]}{\rightleftharpoons}} ArCH_2Cl \underset{[R]}{\overset{[O]}{\rightleftharpoons}} ArCHCl_2 \underset{[R]}{\overset{[O]}{\rightleftharpoons}} ArCCl_3$$

2.1 Oxidation of alkanes

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

(a) 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 atom are oxidised by these oxidising agents in to an alcohol.

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

(b) Other oxidation of alkanes in presence of catalyst.

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

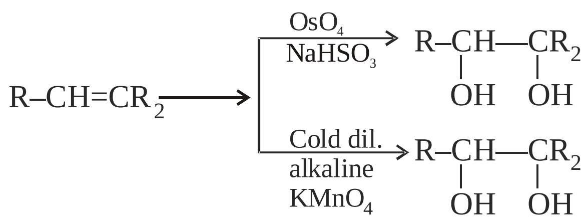
(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

(iii) $2CH_3 - CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$

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

2.2 Oxidation of alkenes and alkynes

(a) By dilute cold $KMnO_4$ or OsO_4



* Cold dil. alkaline $KMnO_4$ is called Bayer's reagent, use as a test of unsaturation.

* Osmium tetraoxide in alkaline medium [OsO_4 / $NaHSO_3$] : same as Bayer's reagent.

* Overall syn addition (Both-OH groups add from same stereochemical side)

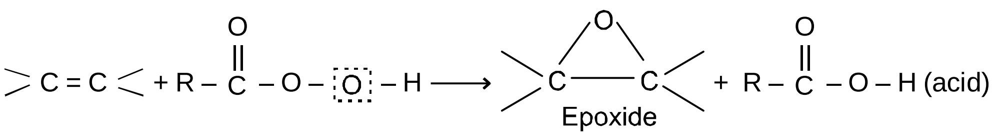
* Given by alkenes & alkynes

* Benzene & cyclopropane can not give this reaction.

(b) Oxidation with peroxyacids

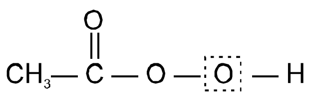
An alkene is converted to an epoxide by a peroxyacid [a carboxylic acid that has an extra oxygen atom in a – O – O – (peroxy) linkage].

General Reaction



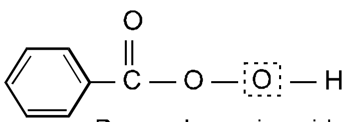
Some simple peroxyacids (sometimes called peracids) are shown below :

(i)

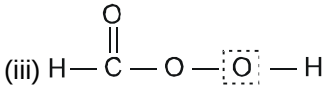


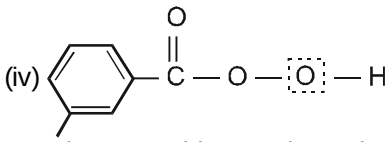
peroxyacetic acid

(ii)



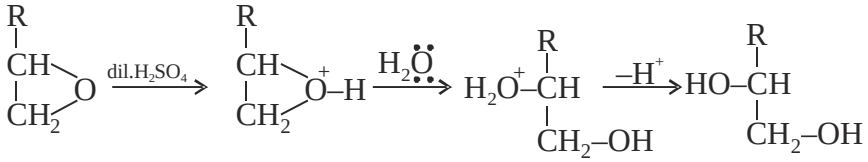
Peroxy benzoic acid

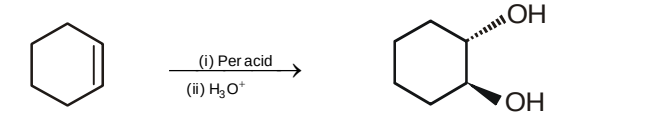
(iii) 
Peroxyformic acid

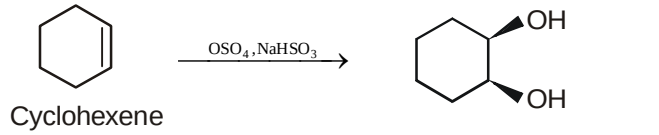
(iv) 
Metachloro perbenzoic acid
(MCPBA)

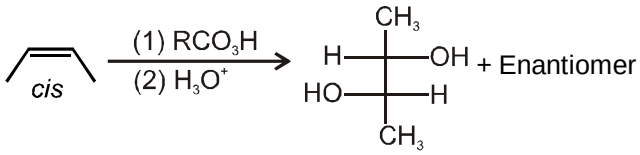
* Rate α nucleophicity of alkene.

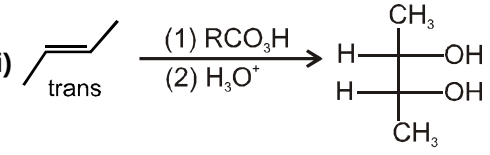
Stereochemistry $\rightarrow$ Hydrolysis of epoxides form anti diols.



(v) 
Cyclohexene
trans- Cyclohexane-1,2-diol

(vi) 
Cyclohexene
cis-Cyclohexane-1,2-diol

(vii) 
+ Enantiomer

(viii) 
Meso

(c) Oxidation with hot acidic $KMnO_4$

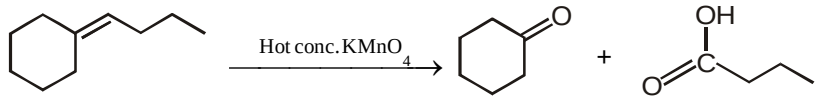
When alkene & alkyne heated with $KMnO_4$ in acidic or in alkaline medium; following changes takes place.

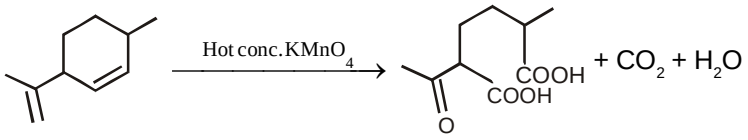
Reagent	**$KMnO_4/H^+$**				
Reactant	$=CH_2$ group	=CHR group	$=CR_1R_2$ group	$\equiv$CH group	$\equiv$CR group
Product	CO_2	RCOOH	$O=CR_1R_2$ group	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

(i) $RCH=CH_2 \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

(ii) $RC\equiv CH \xrightarrow{[O]} CO_2 + H_2O + RCOOH$

(iii) $RC \equiv C - R \xrightarrow{[O]} 2RCOOH$

(iv) 

(v) 

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

(vii) $CH_3CH_2CH_2 - C \equiv CH \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ NaOH,\ \Delta} CH_3CH_2CH_2 - \overset{O}{\overset{\|}{C}} - OH + CO_2\uparrow + H_2O$

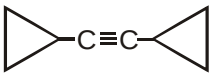
(d) Oxidation of alkenes & alkynes with ozone (ozonolysis)

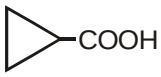
Like permanganate ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

Reagent	**Reductive Ozonolysis (O3/Zn, H2O)**				
Reactant	$=CH_2$ group	=CH R group	$=CR_1R_2$ group	$\equiv$CH group	$\equiv$CR group
Product	HCHO	O=CHR group	$O=CR_1R_2$ group	$-\overset{O}{\overset{\|}{C}}-CHO$	diketone
	Formaldehyde	Aldehyde	Ketone	Keto aldehyde	diketone

Reagent	**Oxidative Ozonolysis O_3/H_2O_2**				
Reactant	$=CH_2$ group	=CHR group	$=CR_1R_2$ group	$\equiv$CH group	$\equiv$CR group
Product	CO_2	RCOOH	$O=CR_1R_2$ group	CO_2	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

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

Ans.. (A) 

(B) 

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

Ans.. DU = 4, $\therefore$ Molecular structure of hydrocarbon must be $CH_3(CH_2)_4C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}C(CH_2)_4{-}CH_3$

2.3 Oxidation of alcohols

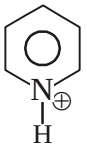
Oxidising agents

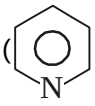
(a) $K_2Cr_2O_7, H^{\oplus}/\Delta$ (Strong oxidising agent)

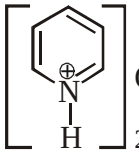
(b) $KMnO_4, H^{\oplus}/\Delta$ (Strong oxidising agent)

(c) Jones reagent : CrO_3 / H_2SO_4 treated with alcohol usually taken in acetone (strong oxidising agent)

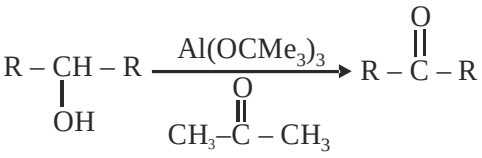
(d) Cu / 300°C (or Red hot Cu tube)

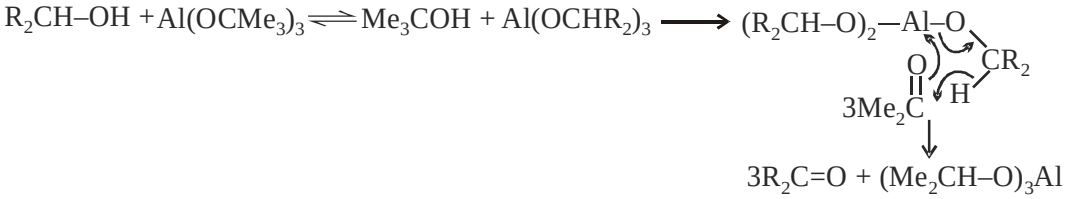
(e) PCC (Pyridinium chloro chromate)  $CrO_3Cl^{\ominus}$ or  CrO_3 + HCl

(f) Collin's reagent ( (2 mol) + CrO_3 + CH_2Cl_2)

(g) Pyridinium dichromate (PDC)  $Cr_2O_7^{\ominus 2}$

(h) Oppenauer oxidation





Oxidation of alcohol with aluminium tertiary butoxide is Oppenaur oxidation.

(i) MnO_2-oxidises only allylic or benzylic– OH.

1° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Aldehyde

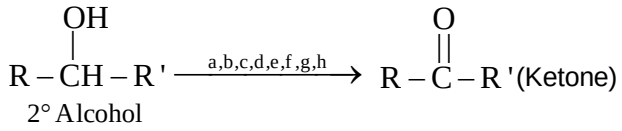
2° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Ketone

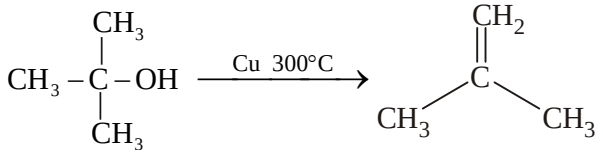
No effect on 3° ROH and on carbon-carbon multiple bonds.

Note : Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.

(i) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{a,b,c,} R-\underset{\underset{O}{\|}}{C}-OH$

(ii) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{d,e,f,g,h} R-\underset{\underset{O}{\|}}{C}-H$ (Aldehyde)

(iii) 

(iv) 

Dehydration takes place.

(v) Double bond & tripple bond are not affected by d,e,f,g,h,i

(vi) No effect on 3° alcohol by a,b,c,e,f,g,h,i (except-d)

2.4 Oxidation of carbonyl compounds

(a) Oxidation of aldehydes

(1) Tollen's test (Silver mirror test)

$RCHO + [Ag(NH_3)_2]OH \text{ (Tollen's reagent)} \xrightarrow{\Delta} RCOOH + NH_3 + Ag\downarrow \text{ (Silver mirror)}$

Aldehyde acts as reducing agent, they can reduce mild oxidizing agents like Tollen's reagent.

(2) Fehling's Solutions

[Fehling's solution A] = aq. $CuSO_4$

[Fehling's solution B] = Alkaline solution of sodium potassium tartrate (Roschelle salt)

$RCHO + Cu^{2+} \xrightarrow[\Delta]{OH^-} RCOO^- + Cu_2O(\text{red ppt})$

Note : This test is also used to detect sugar in blood and urine.

Aromatic aldehyde shows negative test with Fehling & Benedict's reagent.

(3) Benedict's solution

[Benedict's solution A] = aq. $CuSO_4$

[Benedict's solution B] = Alkaline solution of sodium citrate

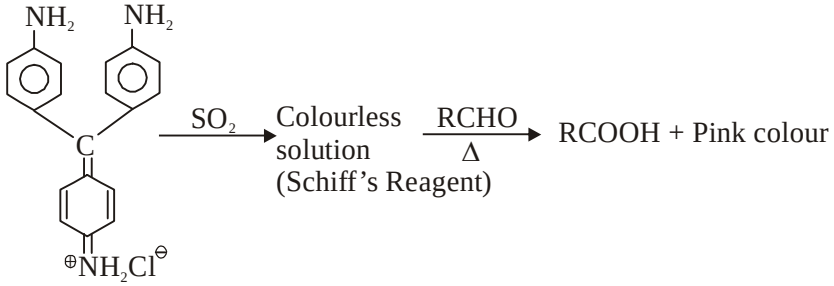
$RCHO + Cu^{2+} \xrightarrow[\Delta]{OH^-} RCOO^- + Cu_2O(\text{red ppt})$

It is similar to Fehling test

(4) 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.



p-Rosaniline Hydrochloride
Magenta colour (Fuschin)

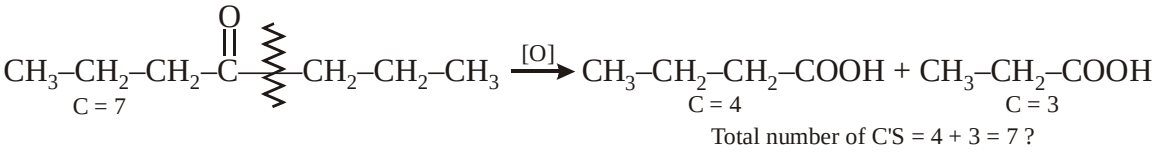
Note : Ketones are not easy to oxidize so they do not give above 4 tests. These four tests can be used to distinguish between aldehydes and ketones. Both aldehyde and ketones give 2,4 DNP test.

(b) Oxidation of ketones :

Ketones undergo oxidation only in drastic conditions.

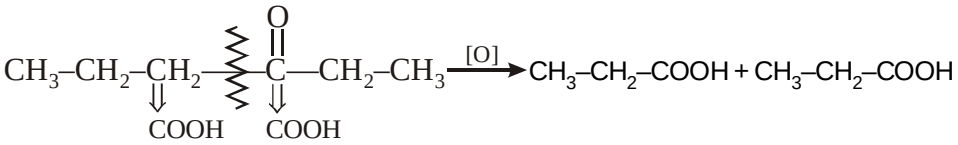
During the oxidation of ketones there is breaking of carbon-carbon bond between α-carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

Case - I : Oxidation of symmetrical ketones :

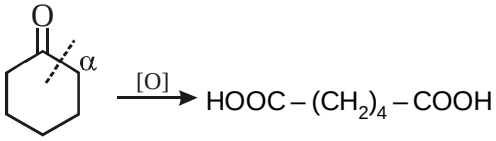


Thus number of carbons in any product is less than the number of carbons in ketone.

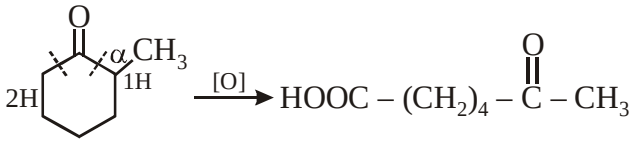
Case - II : Oxidation of unsymmetrical ketones : In case of unsymmetrical ketones, those ⋯C(=O)—R bond break in which alkyl group has more number of carbon atoms. This rule is known as **Popoff's rule.**



Case - III : Oxidation of cyclic ketones : Formation of dibasic acid takes place from cyclic ketones. In this case number of carbon atoms in ketone and dibasic carboxylic acid is always same.

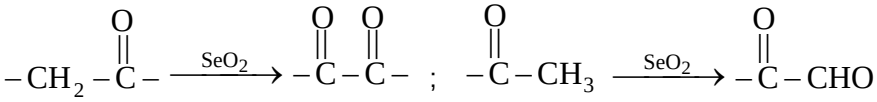


Note : If both α-carbons are not identical then that bond is break where enol form is more stable.



(c) Oxidation with selenium dioxide (SeO_2)

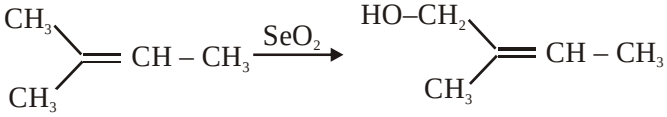
SeO_2 is a selective oxidizing agent which converts $-CH_2-$ group adjacent to carbonyl group into carbonyl group.The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.



Note :- The methylene or methyl group α to the most highly substitued end of the double bond is hydroxylated according to the order of preference of oxidation $CH_2 > CH_3 > CH$ groups.

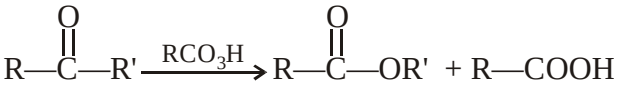
(i) CH_2= CH–CH_3 $\xrightarrow{SeO_2}$ $CH_2=CH-\underset{OH}{\underset{|}{CH_2}}$

(ii) $CH_3-CH=CH-CH_2-CH_3$ $\xrightarrow{SeO_2}$ $CH_3-CH=CH-\underset{OH}{\underset{|}{CH}}-CH_3$

(iii) 

(d) Baeyer villiger oxidation

Ketones oxidise into ester in presence of per acids.

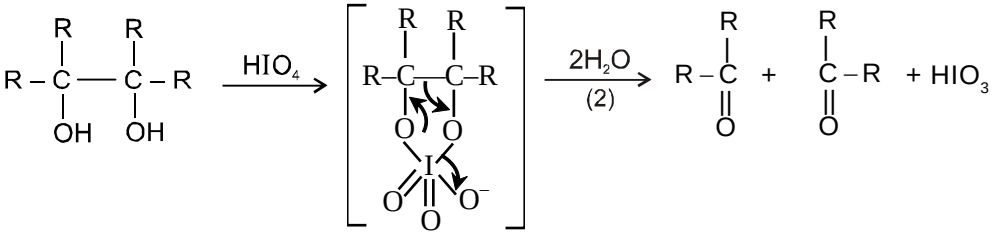


Migratory order for above reaction

3º > 2º > –Phenyl > 1º > –Me

2.5 Periodic oxidation (HIO_4)

Mechanism



Remarks

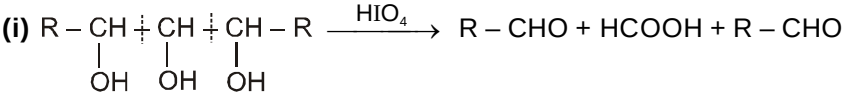
(1) HIO_4 (periodic acid) is used to oxidise vicinal diols (1, 2-diols), α-hydroxy carbonyl compounds, α-dicarbonyl compounds

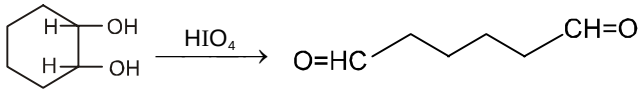
(2) It brings about oxidative cleavage of carbon-carbon bond of above functional groups.

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

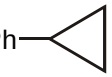
(4) In cyclic diols only cis-vicinal diols are oxidised. Trans isomers are not oxidised.

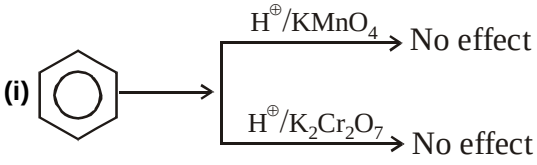
(5) Oxidation by **lead acetate** is similar to HIO_4 oxidation.

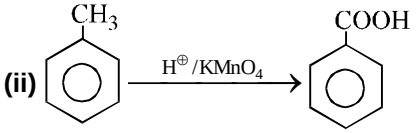
(i) 

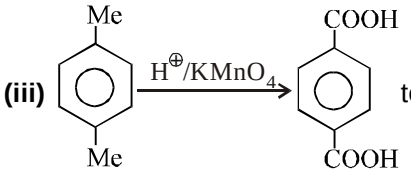
(ii) 

2.6 Oxidation of aromatic compounds

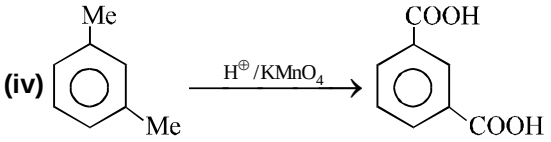
Ph–$(CH_2)_n$–CH_3 , $PhCHMe_2$, Ph–CH_2OH, Ph–CH_2Br, $PhCHCl_2$, PhCHO, Ph–  & all the compounds having at least one α H give PhCOOH on oxidation with strong oxidising agent.

(i) 

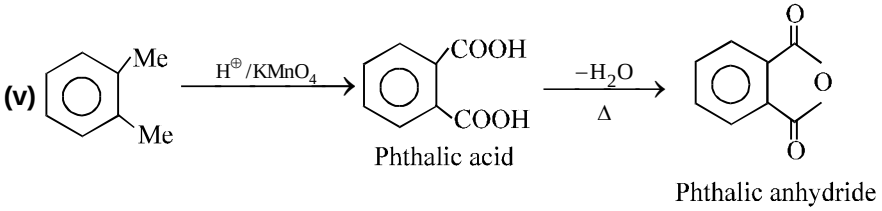
(ii) 

(iii) 

terephthalic acid

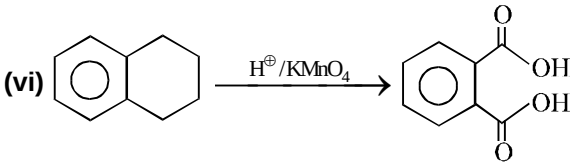
(iv) 

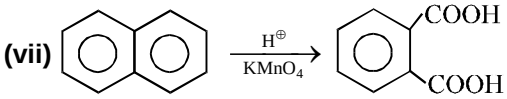
isophthalic acid

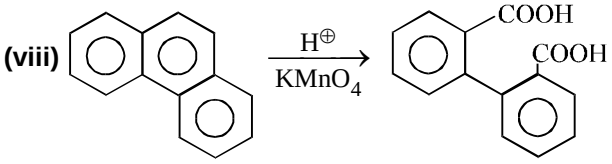
(v) 

Phthalic acid

Phthalic anhydride

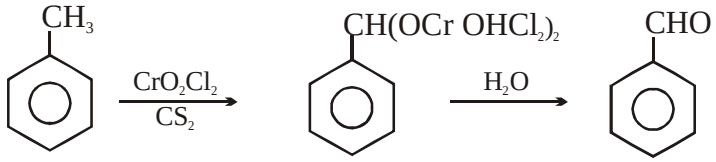
(vi) 

(vii) 

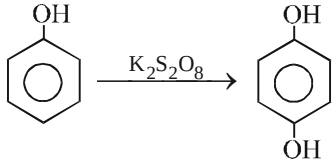
(viii) 

2.7 Miscellaneous oxidations

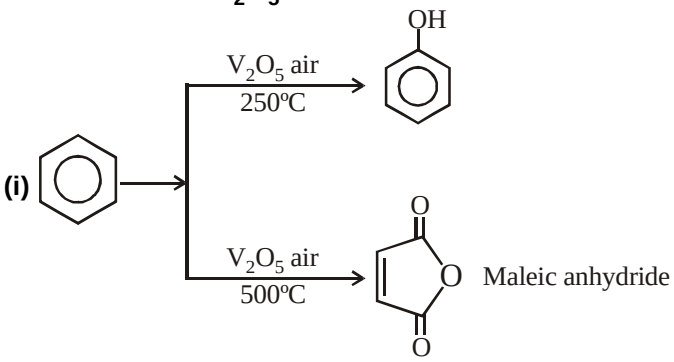
(a) Etard reaction (oxidation of toluene by chromyl chloride)

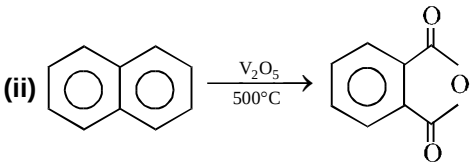


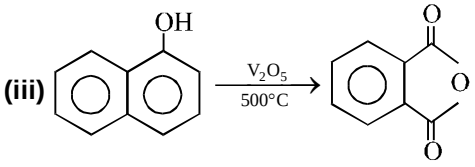
(b) Elb's persulphate oxidation

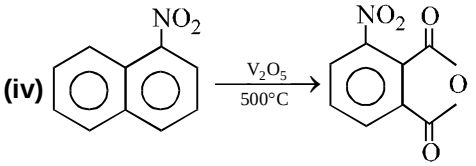


(c) Oxidation with V_2O_5









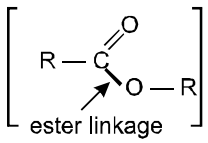
3. HYDROLYSIS

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 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 process is exothermic.

(a) Hydrolysis of an ester

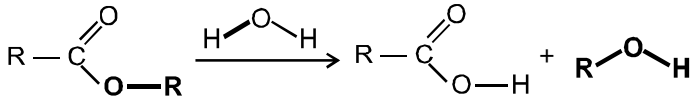
Hydrolysis of an ester involves breaking off an ester link. It can takes place in



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

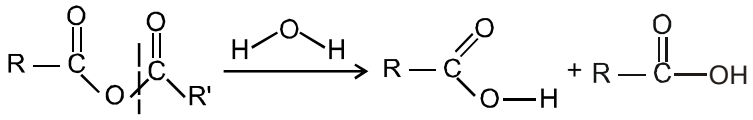
(2) Strong alkaline medium : Aqueous NaOH or KOH and heat.

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



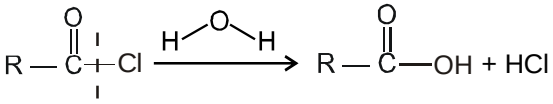
(b) Hydrolysis of an anhydride

The hydrolysis of acid anhydride produces two carboxylic acids.



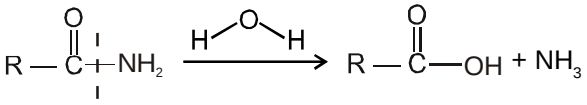
(c) Hydrolysis of acid halide

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.



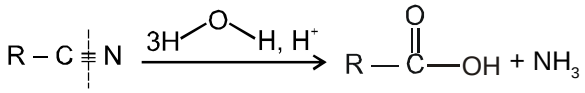
(d) Hydrolysis of acid amide

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.



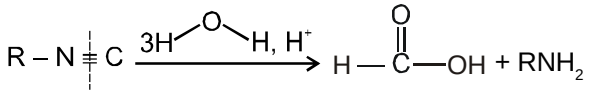
(e) Hydrolysis of alkyl cyanides

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



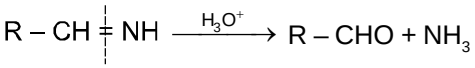
(f) Hydrolysis of isocyanides

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



Note : Alkylisocyanide does not hydrolyse in basic medium.

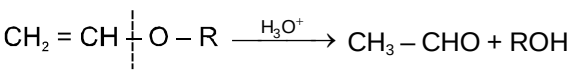
(g) Hydrolysis of imine



(h) Hydrolysis of ethers

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

(i) Hydrolysis of vinyl ether



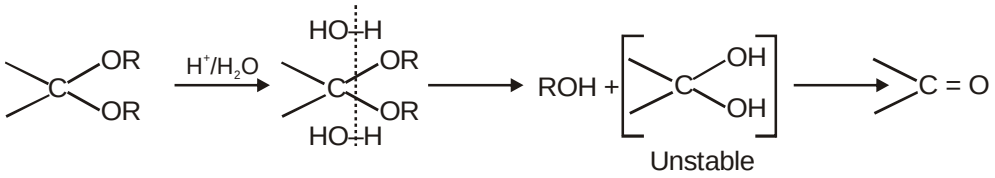
(j) Hydrolysis of phenyl ether

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

(k) 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 to produce 2 equivalent of alcohols. and one equivalent of aldehyde/ketone. Acetals are often used as protecting groups.



(Acetal / ketal)

(l) Hydrolysis of metal carbides

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

$$Mg_2C_3 + 4HOH \longrightarrow CH_3 - C \equiv CH + 2Mg(OH)_2$$

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

4. DECARBOXYLATION AND HEATING EFFECTS

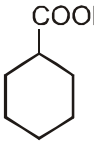
(a) Soda lime decarboxylation of carboxylic acids

$$R - \underset{\underset{O}{\|}}{C} - \overset{\ominus\oplus}{O}Na \xrightarrow[\Delta]{NaOH/CaO} R - H + Na_2CO_3$$

Reaction intermediate is carbanion.(formed in rate determining step)

(i) $CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

(ii) $C_2H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_2H_6 + Na_2CO_3$

(iii) 

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

(b) Decarboxylation of β-keto acids

$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - COOH \xrightarrow{\Delta} CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 + CO_2$$

Decarboxyliation of β-keto acids and similar compounds through 6-membered cyclic transition state via enol formation.

(c) Kolbe's electrolysis

$$2RCOOK + 2HOH \xrightarrow{\text{Electrolysis}} R-R + 2CO_2 + H_2 + 2KOH$$

Mechanism : $R\,CO_2K \rightleftharpoons R\,CO_2^- + K^+$

At Anode: - $R\,CO_2^- \longrightarrow R\,CO_2^{\bullet} + e^-$ (oxidation)

(I)

$R\,CO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2$

(II)

$R^{\bullet} + R^{\bullet} \longrightarrow R-R$

At Cathode : - $2K^+ + 2e^- \longrightarrow 2K \xrightarrow{2H_2O} 2KOH + H_2\uparrow$

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

(d) Dry distillation of calcium salt of carboxylic acid

$$(RCOO)_2Ca \xrightarrow{\Delta} \underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R} + CaCO_3$$

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

calcium acetate

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

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

(e) On passing vapours of fatty acids over Mangnous oxide at 300°C

$$\underset{\text{(Vap)}}{2RCOOH} \xrightarrow{MnO\ /\ 300^{\circ}C} \underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R} + CO_2 + H_2O$$

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

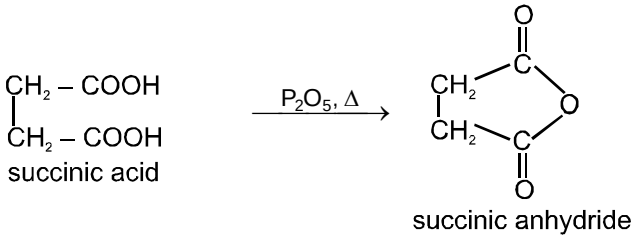
On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

(f) Heating effect on dicarboxylic acid

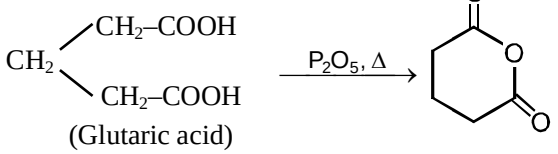
(i) $\underset{\text{(Oxalic acid)}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} \xrightarrow{\Delta} CO_2 + CO + H_2O$

(ii) $CH_2\begin{matrix}\diagup COOH\\\diagdown COOH\end{matrix} \xrightarrow{\Delta} CH_3-COOH + CO_2$

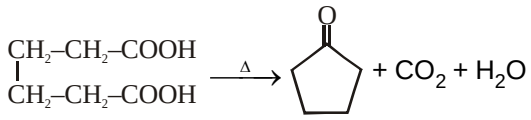
(Malonic acid)

(iii) 

succinic acid → succinic anhydride

(iv) 

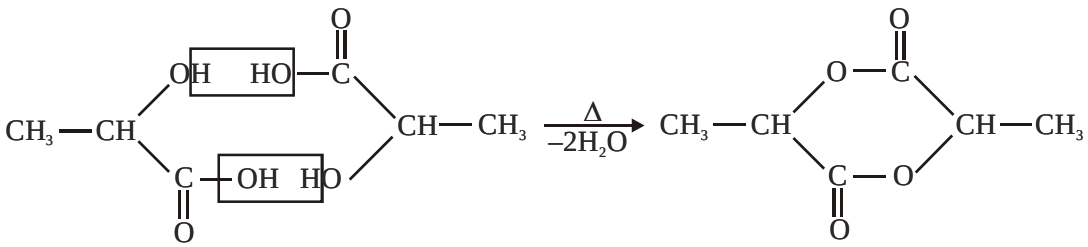
(Glutaric acid)

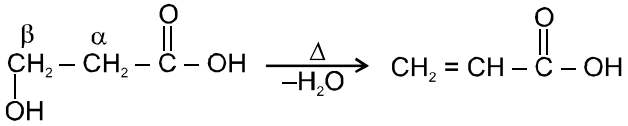
(v) 

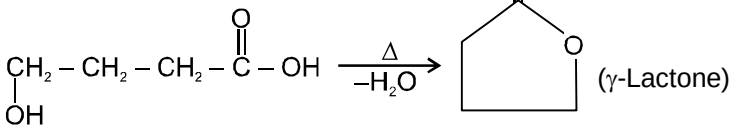
(Adipic acid)

(g) Heating effects on hydroxy acids

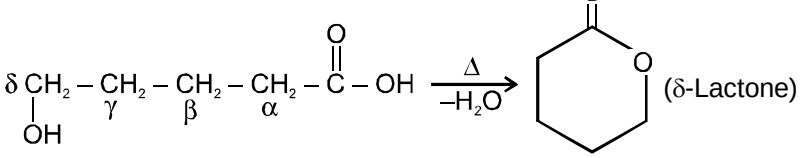
(1) α–Hydroxy acid



(2) β–Hydroxy acid 

(3) γ–Hydroxy acid 

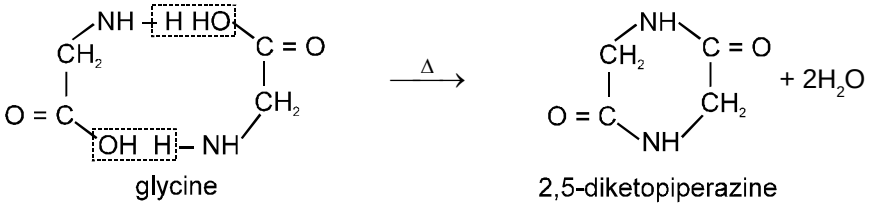
(γ-Lactone)

(4) δ–Hydroxy acid 

(δ-Lactone)

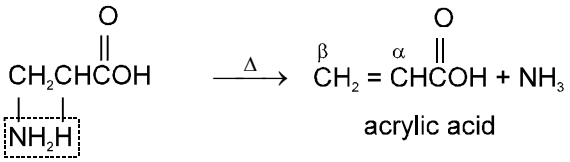
(h) Heating effect of amino carboxylic acid

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



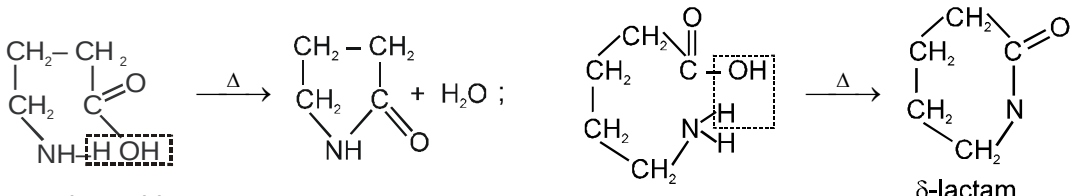
glycine 2,5-diketopiperazine

(**2)** β-amino acids undergo intramolecular deamination on heating to form α, β-unsaturated acids.



acrylic acid

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



γ amino acid γ–butyrolactam δ-amino acid δ-lactam

Exercise-1

Marked Questions may have for Revision Questions.

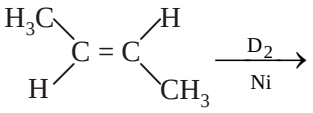
PART - I : SUBJECTIVE QUESTIONS

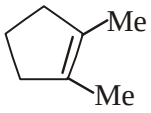
Section (A) : Reduction

A-1 Give the expected major product for each reaction, including stereochemistry where applicable?

(a) $CH_3–CH_2–CH=CH_2 \xrightarrow[Pt]{H_2}$

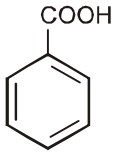
(b)  $\xrightarrow[Pt]{D_2}$

(c) 

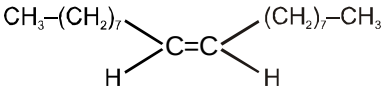
(d) 

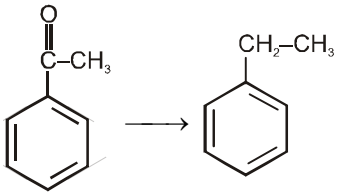
A-2. Complete the following reactions.

(i) $CH_3–CH_2–C\equiv C–CH_2–(CH_2)_6–CH_2OH \xrightarrow[(ii)\ H_2O]{(i)\ Na/NH_3(l)}$

(ii) 

A-3. Give reaction conditions (reagents and/or catalyst) for effecting the following conversions?

(i) $CH_3–(CH_2)_7–C\equiv C–(CH_2)_7–CH_3 \longrightarrow$ 

(ii) 

A-4 Identify the products in the following reactions ?

(i) (P) $\xleftarrow{NaBH_4}$ $Me_2CO \xrightarrow{LiAlH_4}$ (Q)

(ii) (P) $\xleftarrow{NaBH_4}$ $Me–COCl \xrightarrow{LiAlH_4}$ (Q)

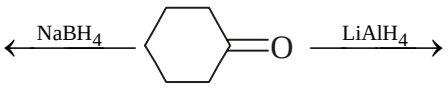
(iii) (P) $\xleftarrow{NaBH_4}$ $Me–COOEt \xrightarrow{LiAlH_4}$ (Q)

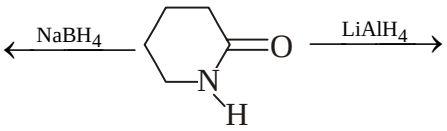
(iv) (P) $\xleftarrow{NaBH_4}$ $Me–COOH \xrightarrow{LiAlH_4}$ (Q)

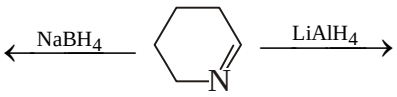
(v) (P) $\xleftarrow{NaBH_4}$ $Me–CONH_2 \xrightarrow{LiAlH_4}$ (Q)

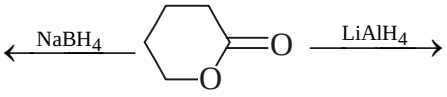
(vi) (P) $\xleftarrow{NaBH_4}$ $CH_3–CH=CH_2 \xrightarrow{LiAlH_4}$ (Q)

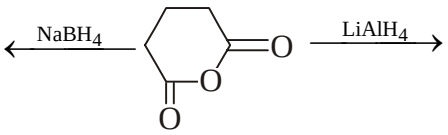
A-5 Give products in following reactions ?

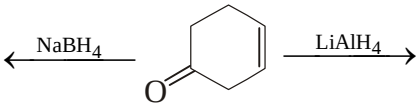
(i) 

(ii) 

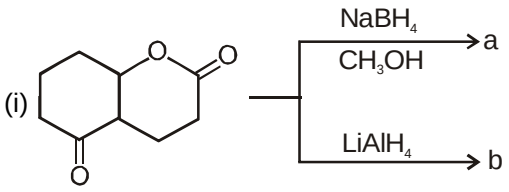
(iii) 

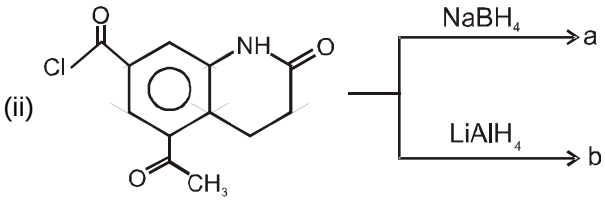
(iv) 

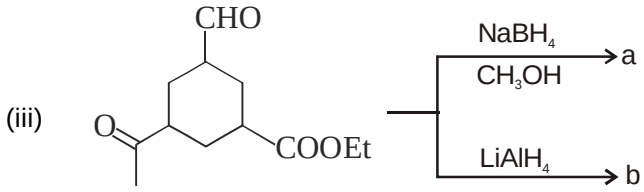
(v) 

(vi) 

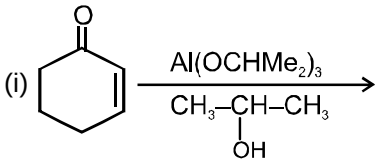
A-6 Identify a and b, in the following reactions ?

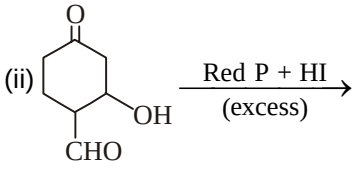
(i) 

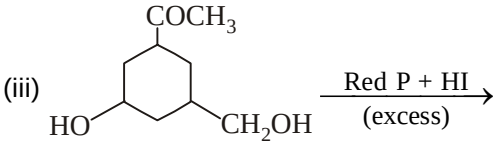
(ii) 

(iii) 

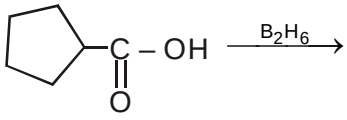
A-7 Complete the following reactions ?

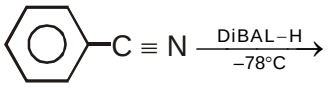
(i) 

(ii) 

(iii) 

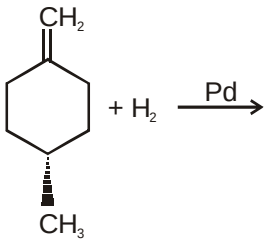
A-8 Give product in the following reactions?

(a) 

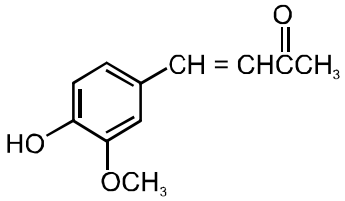
(b) 

(c) $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH_3 \xrightarrow[-78°C]{DiBAL-H}$

A-9 How many stereoisomeric products are formed in following reaction ?



A-10



Zingerone

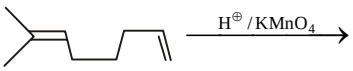
Report your answer as = $\frac{\text{molecular weight of Zingerone.}}{4}$.

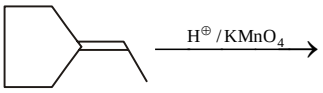
Section (B) : Oxidation

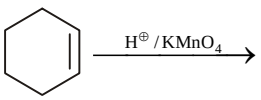
B-1 Write the structural formulas for the products formed when 3-heptyne reacts with $KMnO_4$ under -
(i) neutral condition at room temp. (ii) alkaline or acidic condition at higher temp.

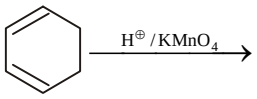
B-2 Complete the following reactions.

(i) $CH_3–CH= CH_2 \xrightarrow{H^\oplus / KMnO_4}$

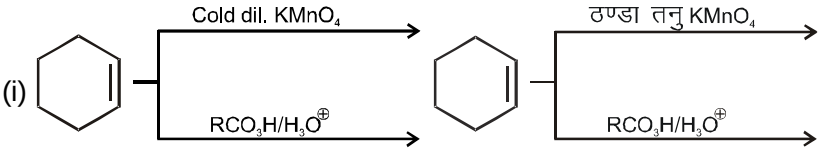
(ii) 

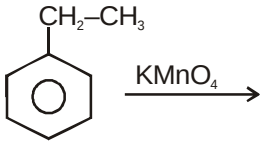
(iii) 

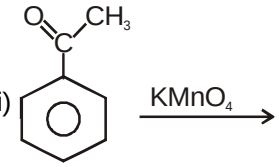
(iv) 

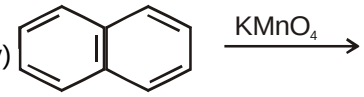
(v) 

B-3 Complete the following reactions.

(i) 

(ii) 

(iii) 

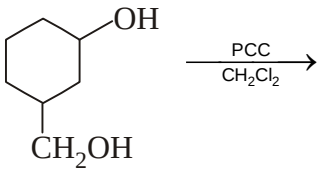
(iv) 

B-4 Give product in the following reaction ?

(i) $CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4/OH^-,\Delta}$

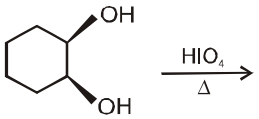
(ii) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[\text{or } K_2Cr_2O_7,H^\oplus]{KMnO_4,H^\oplus}$

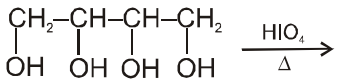
(iii) $C_6H_5-CH=CH-CH_2-OH \xrightarrow[CH_2Cl_2]{PCC}$

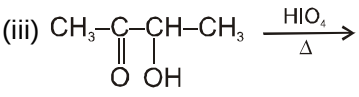
(iv) 

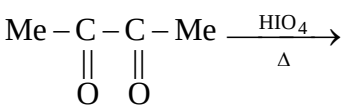
(v) $CH_2=CH-CH_2-OH \xrightarrow{MnO_2} ?$

B-5 Complete the following reactions.

(i) 

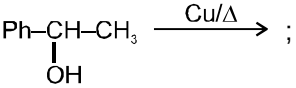
(ii) 

(iii) 

(iv) 

B-6 Complete the following reactions.

(i) $Ph-CH_2-CH_2-OH \xrightarrow{Cu/\Delta}$;

(ii) 

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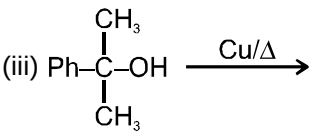
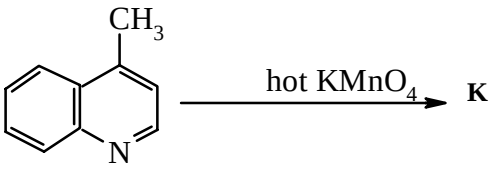
(iii) 

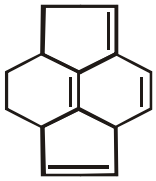
(iv) $CH_3-CHO \xrightarrow[\Delta]{SeO_2}$

B-7 When lepidine **L** (4-methylquinoline) is oxidized, **K** is formed. How many –COOH group are present in K ?



L

B-8 Number of aldehyde functional groups present when the following compound is subjected to reductive ozonolysis.



Section (C) : Hydrolysis

C-1 Write the products of following reactions.

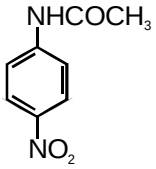
(a) $CH_3–C\equiv N \xrightarrow{H_3O^{\oplus}}$ (b) $CH_3NC \xrightarrow{H_3O^{\oplus}}$

C-2 Reactant $\xrightarrow{H_3O^+}$ $CH_3COOH + HCl$

C-3 $CH_3CONH_2 \xrightarrow{H_3O^+}$ Product is

C-4 The hydrolysis of acid anhydride produces .....

C-5



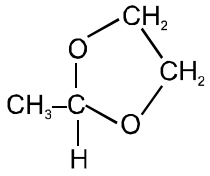
$\xrightarrow{H_3O^+}$ Product is

C-6 Reactant $\xrightarrow{H_3O^+}$ $CH_3CHO + CH_3OH$

C-7 In how many reaction CH_3CHO is obtained as major product ?

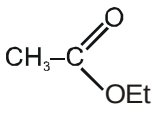
(P) $CH_3–C\equiv N \xrightarrow[2.\ H_3O^+]{1.\ SnCl_2\ /\ dil.\ HCl}$

(Q)



$\xrightarrow{H_3O^+}$

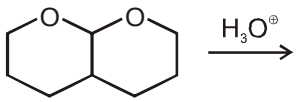
(R)



$\xrightarrow[\text{low temperature}]{\text{DIBAL–H}}$

(S) $CH_3–C\equiv N \xrightarrow[2.\ H_3O^+]{1.\ DIBAL–H}$

C-8 Write the product of following reaction.



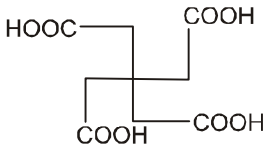
Section (D) : Decarboxylation and Heating effect

D-1. Observe the following reaction sequence

$CH_3–CH_2–CH_2–OH \xrightarrow{PCC} \xrightarrow{KMnO_4} \xrightarrow{Ca(OH)_2/\Delta}$ product is-

D-2. Sodium salt of which acid will be needed for preparation of propane ? Write chemical equation for the reaction.

D-3.



$\xrightarrow[\text{Electrolysis}]{NaOH}$ [X].

D-4. A metallic carbide on treatment with water gives a colourless gas which burns readily in air and gives a precipitate with ammonical silver nitrate solution. The number of carbon atom present in gas is :

D-5. In sodalime decarboxylation sodalime is made of 'x' NaOH and 'y' CaO then ratio of x/y is :

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Reduction

A-1. The relative rates of hydrogenation is in the order of -

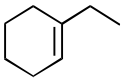
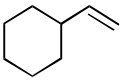
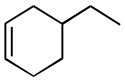
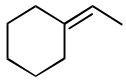
(A) $CH_2 = CH_2 > RCH = CH_2 > RCH = CHR > R_2C = CHR$

(B) $R_2C = CHR > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$

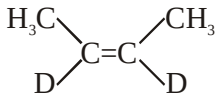
(C) $RCH = CHR > R_2C = CHR > RCH = CH_2 > CH_2 = CH_2$

(D) $R_2C = CHR > CH_2 = CH_2 > RCH = CHR > RCH = CH_2$

A-2. In which case the reaction is most exothermic with H_2 / Ni ?

(A)  (B)  (C)  (D) 

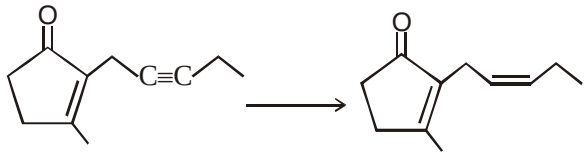
A-3



Product of above reaction will be-

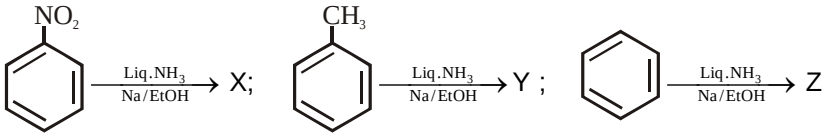
(A) Racemic mixture (B) Diastereomers (C) Meso compound (D) Constitutional isomers

A-4

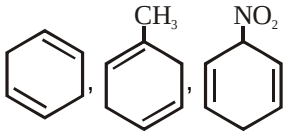


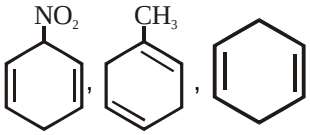
Which reagent will be used for the above conversion ?

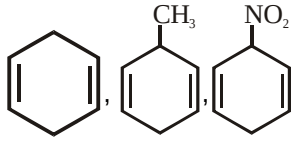
(A) Na/Liq. NH_3 (B) H_2, Pd–$CaCO_3$ (C) Li, Ph–NH_2 (D) H_2, Pt

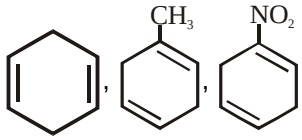
A-5 

The formed products Z, Y, X are respectively :

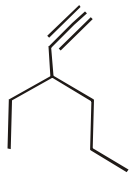
(A) 

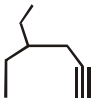
(B) 

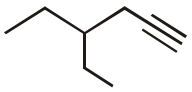
(C) 

(D) 

A-6 Which alkyne gives 3-ethylhexane on catalytic hydrogenation ?

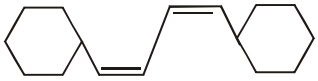
(A) 

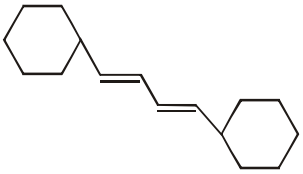
(B) 

(C) 

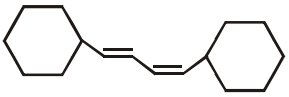
(D) All of these

A-7 

(A) 

(B) 

(C) Both (A) and (B)

(D) 

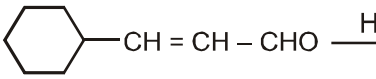
A-8 Which of the following reagents converts both acetaldehyde and acetone to alkanes ?
(A) Ni/H_2 (B) $LiAlH_4$ (C) I_2/NaOH (D) Zn–Hg/conc.HCl

A-9 Stephen reduction ($SnCl_2$ / HCl) converts cyanides to?
(A) Aldehydes (B) Ketones (C) Amines (D) Acids

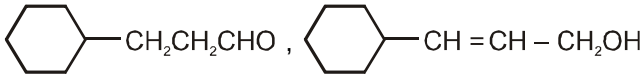
A-10 When benzoic acid is treated with $LiAlH_4$, it forms-
(A) Benzaldehyde (B) Benzyl alcohol (C) Benzene (D) Toluene

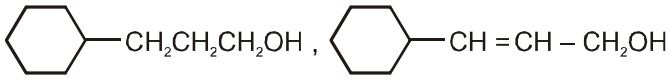
A-11 $R–C\equiv N \xrightarrow[-40^oC]{DIBAL–H,\ H_2O}$ Product

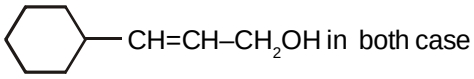
The product formed is :
(A) $R–CO–NH_2$ (B) $R–CH_2–NH_2$ (C) R–CHO (D) $R–CH_2–NO_2$

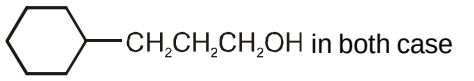
A-12 B $\xleftarrow{NaBH_4}$  $\xrightarrow{H_2/Pd}$ A

A and B are respectively :

(A) 

(B) 

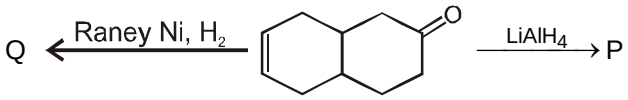
(C) 

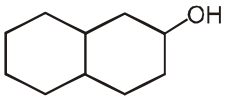
(D) 

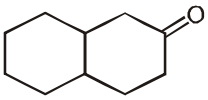
A-13 In the following reaction $C_2H_5OC_2H_5 + 4H \xrightarrow{RedP + HI} 2X + H_2O$, X is

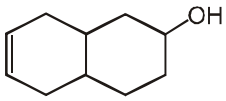
(A) Ethane (B) Ethylene (C) Butane (D) Propane

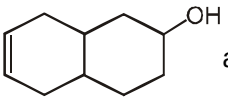
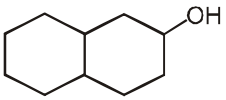
A-14 What are P and Q in the following ?



(A)  in all cases

(B)  in all cases

(C)  in all cases

(D) P =  and Q= 

Section (B) : Oxidation

B-1. Baeyer's reagent decolourises by which of the following ?

(A) Alkane (B) Alkene only

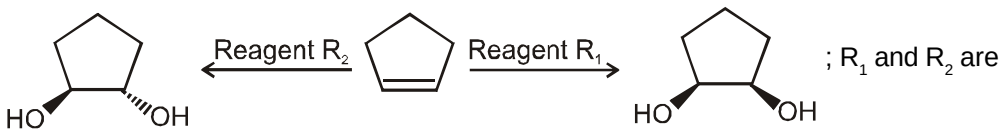
(C) Alkene and alkyne both (D) None of the above

B-2. Ethylene glycol on reaction with alkaline $KMnO_4$ gives:

(A) Ethanal (B) Glyoxal (C) Oxalic acid (D) Acrolein.

B-3. An alkyne C_7H_{12} when reacted with alkaline $KMnO_4$ followed by acidification by HCl, yielded a mixture of $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ & CH_3CH_2COOH. The alkyne is -

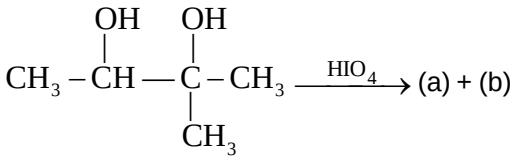
(A) 3-hexyne (B) 4-methyl-2-hexyne (C) 2-methyl-3-hexyne (D) 5-methyl-2-hexyne

B-4.  ; R_1 and R_2 are

(A) Cold alkaline $KMnO_4$, OsO_4/H_2O_2 (B) Cold alkaline $KMnO_4$, HCO_3H & H_3O^+

(C) Cold alkaline $KMnO_4$, $C_6H_5CO_3H$ (D) $C_6H_5CO_3H$, HCO_3H

B-5. In the given reaction -



(a) and (b) are -

(A) CH_3CHO and CH_3CHO (B) CH_3COCH_3 and CH_3CHO

(C) CH_3COCH_3 and CH_3COCH_3 (D) CH_3COOH and CH_3COCH_3

B-6. Secondary alcohols on heating with copper at 300°C give-

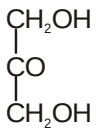
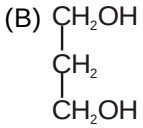
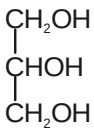
(A) Alkenes (B) Aldehydes (C) Ketones (D) tert-alcohols

B-7. The reagent, with which both acetaldehyde and acetone react easily is -

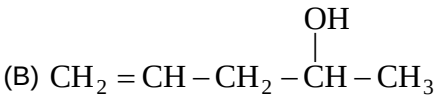
(A) Tollens reagent (B) Schiffs reagent

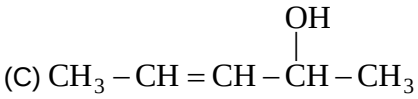
(C) H_2 / Ni (D) Fehling's solution

B-8. Which of the following compounds is resistant to periodic acid oxidation ?

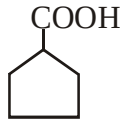
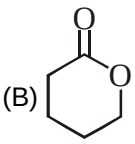
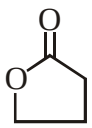
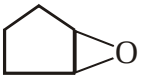
(A)  (B)  (C)  (D) 

B-9. Which one of the following alcohols are oxidised by MnO_2?

(A) $C_6H_5-CH_2-CH_2-OH$ (B) 

(C)  (D) $CH_3-CH_2-CH_2-OH$

B-10.  Major product is

(A)  (B)  (C)  (D) 

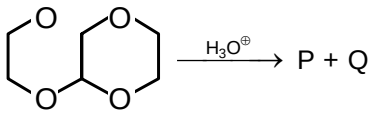
Section (C) : Hydrolysis

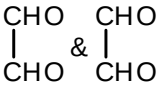
C-1. What product is obtained when benzenecarbonitrile is hydrolysed ?

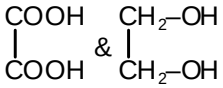
(A) Benzoylchloride (B) Benzenecarboxamide

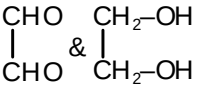
(C) Benzaldehyde (D) Benzoic acid

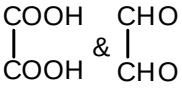
C-2. The acid catalysed hydrolysis products in the following reaction are -

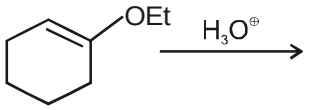


(A) 

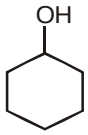
(B) 

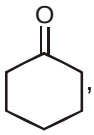
(C) 

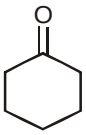
(D) 

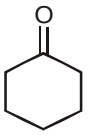
C-3. 

Products obtained in above reaction are :

(A) EtOH, 

(B) 

, CH_3–CHO (C) CH_3COOH, 

(D) EtOH, 

Section (D) : Decarboxylation and heating effect

D-1. On heating calcium propionate, the product formed is-
(A) 3-Pentanone (B) 2-Pentanone
(C) 3-Methyl-2-butanone (D) Propanone

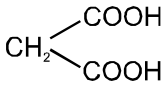
D-2. A mixed salt of calcium acetate formate on dry distillation gives-
(A) ethanal (B) methanal (C) propanone (D) All the three above.

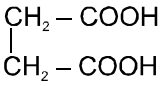
D-3. Acetic acid when heated (300ºC) with MnO gives-
(A) formaldehyde (B) acetaldehyde (C) acetone (D) butaone

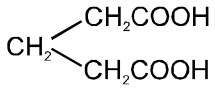
D-4. Acetylene may be prepared by electrolysis of -
(A) potassium oxalate (B) potassium acetate
(C) potassium maleate (D) potassium succinate

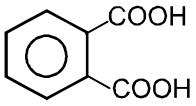
D-5. Which of the following compounds on hydrolysis gives acetylene ?
(A) CaC_2 (B) Mg_2C_3 (C) Al_4C_3 (D) Be_2C

D-6. Which of the following will not yield a cyclic compound on heating ?

(A) 

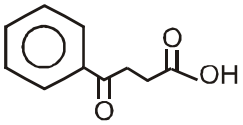
(B) 

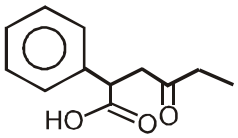
(C) 

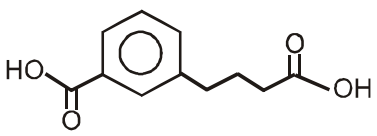
(D) 

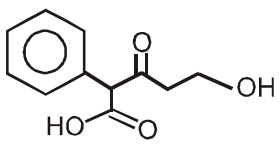
D-7. Which of the following will give cyclopentanone on heating as major product ?
(A) Glutaric acid (B) Succinic acid (C) Adipic acid (D) Malonic acid

D-8. Which of the following undergoes decarboxylation most readily on being heated ?

(A) 

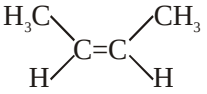
(B) 

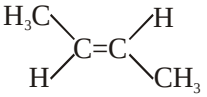
(C) 

(D) 

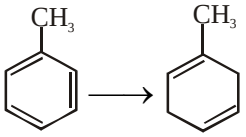
PART - III : MATCH THE COLUMN

1. **Column-I (Conversion)** **Column-II (Required reagent)**

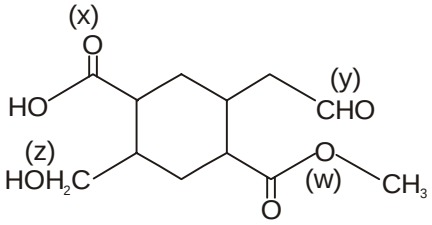
(A) $H_3C–C\equiv C–CH_3 \longrightarrow$  (p) H_2, Pd-$BaSO_4$

(B) $H_3C–C\equiv C–CH_3 \longrightarrow$  (q) Li, Liq.NH_3

(C) $H_3C–CH=CH–CH_3 \longrightarrow H_3C–CH_2–CH_2–CH_3$ (r) H_2/Ni

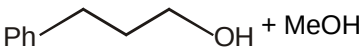
(D)  (s) B_2H_6, CH_3COOH

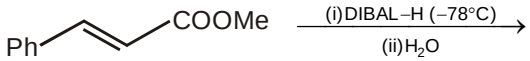
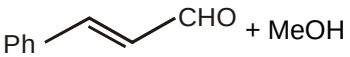
2. Observe the following compound and match the reagents of List - I and List – II

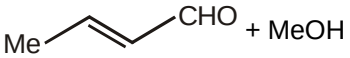


	List-I (Reagents)		**List-II (Functional group oxidised / reduced**
(A)	CrO_3 / Pyridine / CH_2Cl_2	(p)	w
(B)	$NaBH_4$	(q)	z
(C)	Na / C_2H_5OH	(r)	x
(D)	CrO_3 / H^+	(s)	y

3. **Column-I (Reactant and reagents)** **Column-II (Products)**

(A)  (p) 

(B)  (q) 

(C)  (r) 

(D)  (s) 

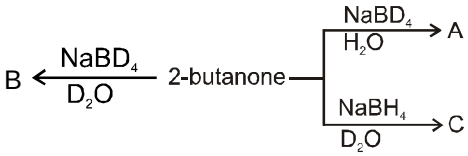
(t) No reaction

Exercise-2

✍ **Marked Questions may have for Revision Questions.**

PART - I : OBJECTIVE QUESTIONS

1. Consider reduction of 2-butanone.



A, B and C are respectively.

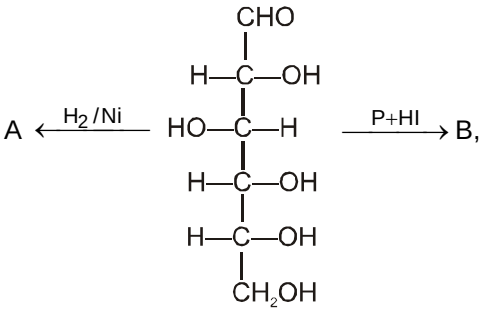
(A) $CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$ in all cases

(B) $CH_3\underset{\underset{D}{|}}{C}OHCH_2CH_3$, $CH_3\underset{\underset{D}{|}}{C}ODCH_2CH_3$, $CH_3\underset{\underset{H}{|}}{C}ODCH_2CH_3$

(C) $CH_3\underset{\underset{D}{|}}{C}OHCH_2CH_3$ in all case

(D) $CH_3\underset{\underset{D}{|}}{C}OHCH_2CH_3$, $CH_3\underset{\underset{H}{|}}{C}OHCH_2CH_3$, $CH_3\underset{\underset{H}{|}}{C}ODCH_2CH_3$

2.



A and B can be :

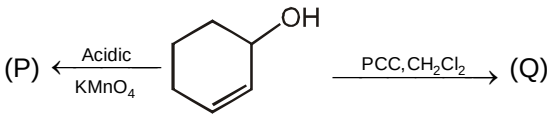
(A) Both are n-Hexane

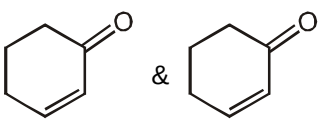
(B) Both are Hexane-1,2,3,4,5,6-hexaol

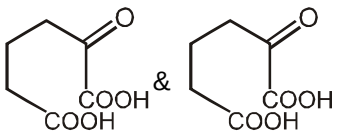
(C) A is n-Hexane B is Hexane-1,2,3,4,5,6-hexaol

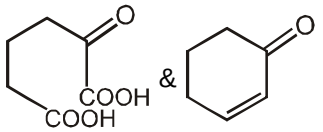
(D) A is Hexane-1,2,3,4,5,6-hexaol and B is n-Hexane

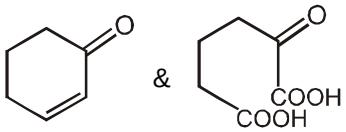
3. Identify (P) and (Q) are respectively in the given reaction ?



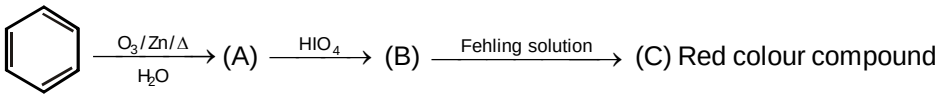
(A)  &

(B)  &

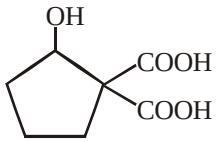
(C)  &

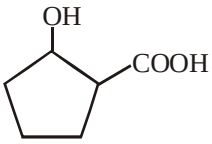
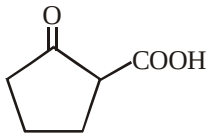
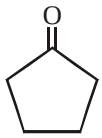
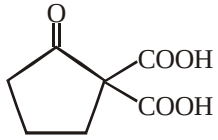
(D)  &

4. In the given reaction compound B will be :

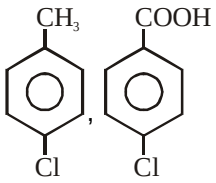
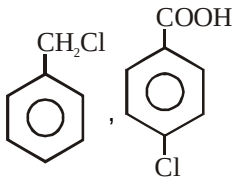


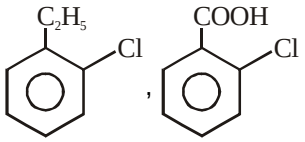
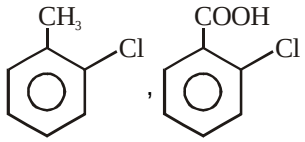
(A)  (B) CH_3–CHO (C) CH_3–COOH (D) H–COOH

5.  $\xrightarrow[(2)\ \Delta]{(1)K_2Cr_2O_7}$ Product is -

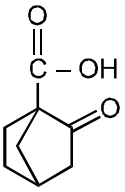
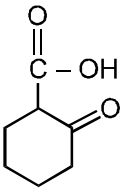
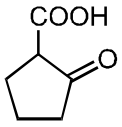
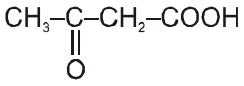
(A)  (B)  (C)  (D) 

6. Compound 'X' (C_7H_7Cl) on oxidation with hot alkaline $KMnO_4$ produces 'Y' ($C_7H_5ClO_2$). Compound 'Y' is found to be strongest acid amongst all its positional isomers. Compound 'X' and 'Y' respectively are :

(A)  (B) 

(C)  (D) 

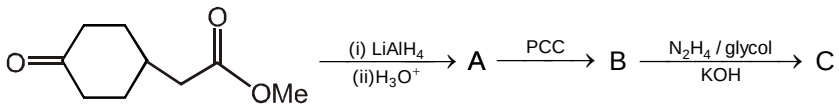
7. Which acid will decarboxylate with greatest difficulty ?

(A)  (B)  (C)  (D) 

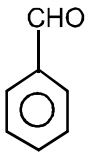
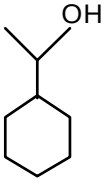
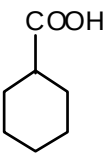
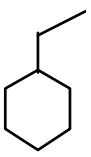
8. But-2-ene can be obtained by electrolysis of an aqueous solution of -

(A) 2, 3-Dimethyl maleic acid (B) 2, 2-Dimethyl butanedioic acid

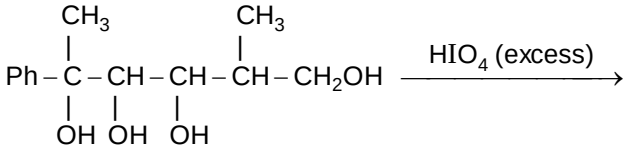
(C) 2-Methylbutanedioic acid (D) 2,3-Dimethylbutanedioic acid

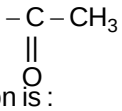
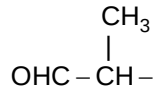
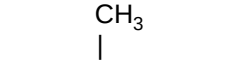
9. 

Product C is -

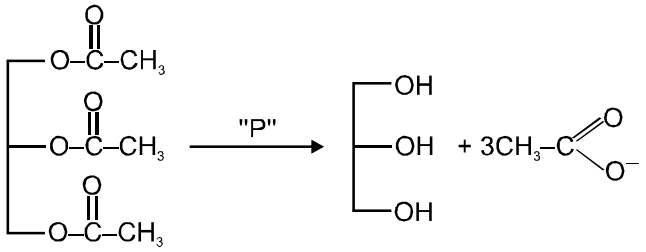
(A)  (B)  (C)  (D) 

10. The product which is not formed in the following reaction ?

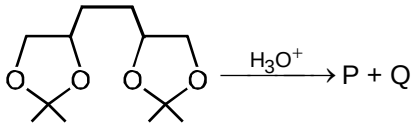


(A) HCOOH (B)  (C)  (D) 

11. Reagent "P" in the given reaction is :



(A) $LiAlH_4$ (B) $NaBH_4$ (C) DIBAL-H (D) OH^-, H_2O

12. 

P and Q are respectively-

(A) Acetone and Hexane-1,2,5,6-tetraol. (B) Acetaldehyde and Acetone.

(C) Acetaldehyde and Hexane-1,2,5,6-tetraol. (D) Acetone and Formaldehyde.

PART - II : SUBJECTIVE QUESTION

1. How many of the following reagent can convert benzaldehyde into benzyl alcohol ?

(i) $LiAlH_4$ (ii) $NaBH_4$ (iii) $SnCl_2$ + HCl (iv) B_2H_6/THF

(v) Zn–Hg/HCl (vi) N_2H_4/alc. KOH (vii) H_2/Ni (viii) Red P + HI

(ix) Na/EtOH

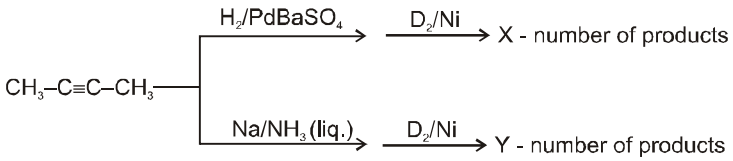
2. How many of the following reagents can convert benzyl alcohol into benzaldehyde?

(i) $KMnO_4$ (ii) $K_2Cr_2O_7$ (iii) PCC

(iv) Cu/Δ (v) Collin's reagent

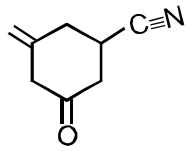
(vi) PDC (vii) MnO_2 (viii) HIO_4

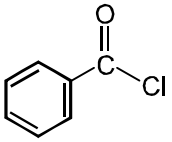
(ix) $AgNO_3 + NH_4OH$

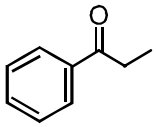
3. 

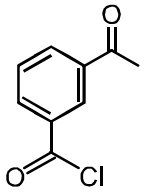
Find the value of x + y

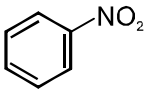
4. Find the number of reactions which give alcohol as product ?

(a)  $\xrightarrow{H_2/Pd}$ ----------

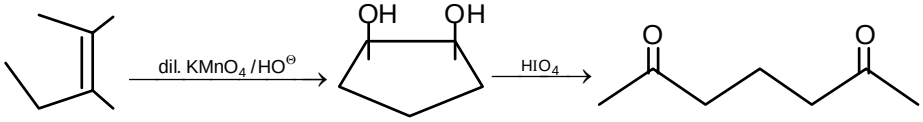
(b)  $\xrightarrow{H_2/Pd/BaSO_4}$ ----------

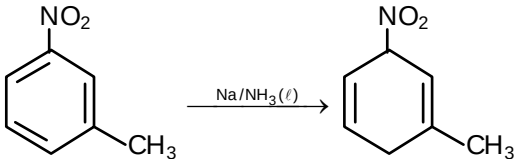
(c)  $\xrightarrow{LiAlH_4/THF}$ ----------

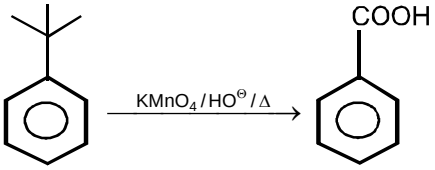
(d)  $\xrightarrow{NaBH_4/THF}$ ----------

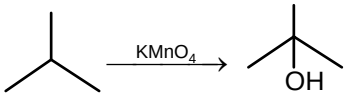
(e)  $\xrightarrow[C_2H_5OH]{Na/NH_3(\ell)}$ ----------

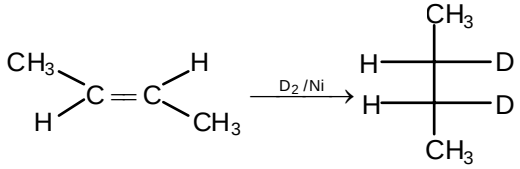
5. How many reactions are correct ?

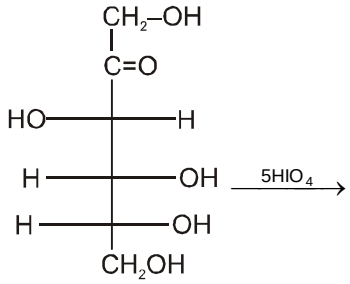
(i) 

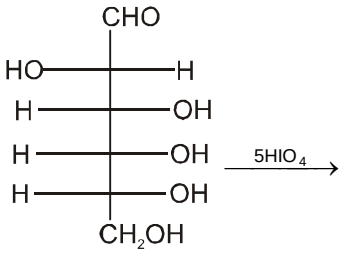
(ii) 

(iii) 

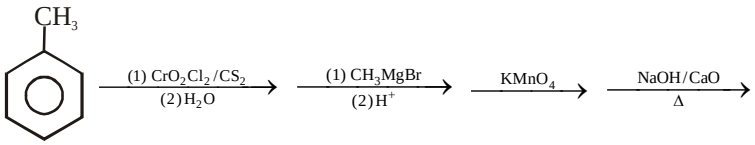
(iv) 

(v) 

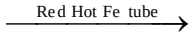
6. (i) 

(ii) 

Sum of moles of formaldehyde obtained in the reaction (i) and reaction (ii) is ?

7. 

How many atoms are present in same plane in the final product ?

8. $Mg_2C_3 \xrightarrow{H^+/H_2O}$ 

The number of carbon atoms present in same plane in the final product is :

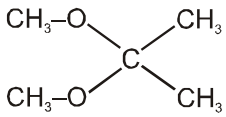
9. How many of following reactants give at least one carbonyl compound on hydrolysis ?

(i) $CH_3–CH_2–CN \xrightarrow{\text{partial hydrolysis}}$

(ii) $CH_3–\underset{\underset{O}{\|}}{C}–OC_2H_5 \xrightarrow{H_3O^+}$

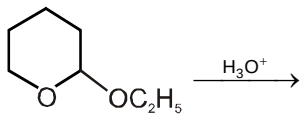
(iii) $CH_3–\underset{\underset{O}{\|}}{C}–NH_2 \xrightarrow{H_3O^+}$

(iv) $CH_3–C\equiv N \xrightarrow{H_3O^+}$

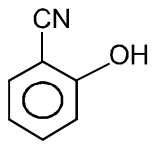
(v) 

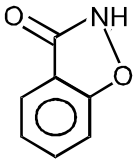
(vi) $CH_3–CH=NH \xrightarrow{H_3O^+}$

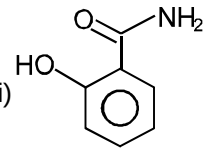
(vii) $CH_2=CH–O–C_2H_5 \xrightarrow{H_3O^+}$

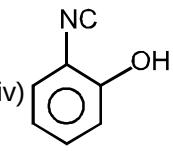
(viii) 

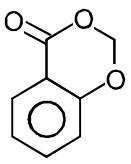
10. How many of the following may produce salicylic acid on hydrolysis under appropriate conditions ?

(i) 

(ii) 

(iii) 

(iv) 

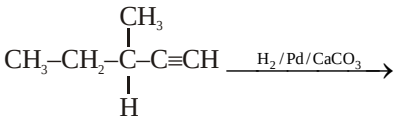
(v) 

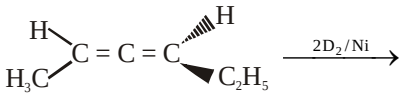
11. How many carboxylic acid isomers (including stereoisomers) having molecular formula $C_6H_{12}O_2$ on heating with sodalime gives isopentane as a major product?

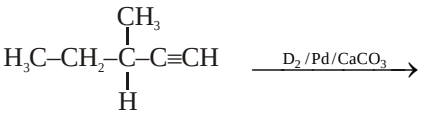
12. How many isomers are obtained when 2-ethyl-2-methyl propanedioic acid is heated ?

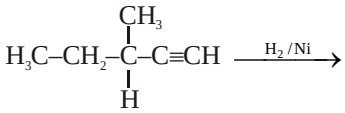
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. In which of the following reactions chiral product is obtained ?

(A) 

(B) 

(C) 

(D) 

2. Which of the following catalysts is/are used for partial reduction of alkyne ?

(A) $Na/NH_3(\ell)$ (B) Ni_2B or P-2catalyst

(C) Lindlar catalyst (D) Rossenmund catalyst

3. Propan-1-ol and propan-2-ol can be best distinguished by -

(A) oxidation with alkaline $KMnO_4$ followed by reaction with H_2O.

(B) oxidation with PCC followed by reaction with Tollen's reagent.

(C) oxidation by heating with copper followed by reaction with idoform test.

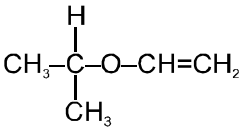
(D) reaction with conc.H_2SO_4 followed by reaction with Fehling solution.

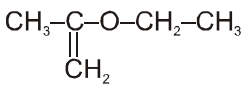
4. Which of the following reduction methods is not suitable for preparing an alcohol ?

(A) $CH_3COOC_2H_5 + NaBH_4 \longrightarrow$ (B) $CH_3COOC_2H_5 + Na/EtOH \longrightarrow$

(C) $CH_3COOC_2H_5 + LiAlH_4 \longrightarrow$ (D) $CH_3COOC_2H_5 + H_2 \xrightarrow{Ni}$

5. $C_5H_{10}O \xrightarrow{H_3O^{\oplus}} B + C$; (B) and (C) both give positive iodoform test. Compound (A) is -
(A)

(A) $CH_3–CH=CH–O–CH_2–CH_3$ (B) 

(C)  (D) None of these

6. $CH_3COONa \xrightarrow[(2)\,H^+]{(1)\,NaOH/CaO,\Delta} (P)$

The correct statements is/are :

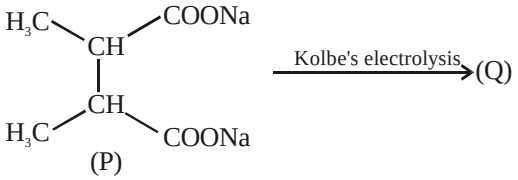
(A) Reaction is known as decarboxylation.

(B) Carbanion is formed as intermediate.

(C) When aqueous solution of reactant is electrolysed, ethane will be obtained at anode.

(D) (P) is marsh gas.

7. Choose the correct statement regarding following reaction ?



(P)

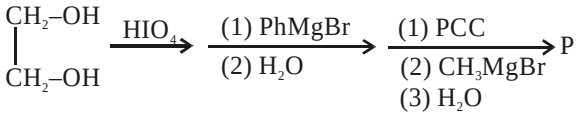
(A) (Q) will give 4 alkenyl halides with NBS.

(B) Compound (Q) on reaction with dilute $KMnO_4$ forms vicinal diol.

(C) Product (Q) is mixture of cis and trans–2–butene.

(D) (P) can exist in four stereoisomeric forms.

8. Which of the following is **correct** for the final product (P) of the given sequence of reaction ?



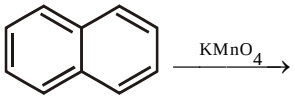
(A) Compound P on oxidation with PCC gives a compound which gives 2,4–DNP test.

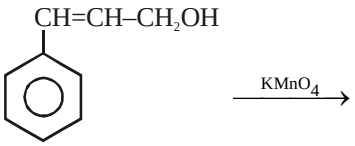
(B) Compound P on reaction with I_2 + NaOH gives yellow ppt.

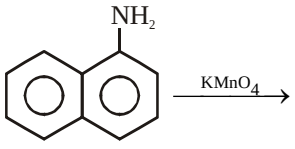
(C) Compound P on reaction with cerric ammonium nitrate gives red colour.

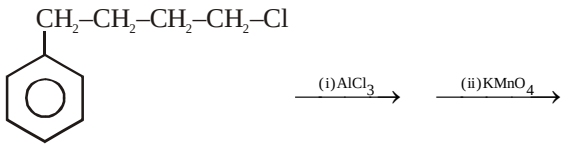
(D) Compound P on reaction with MnO_2 gives carboxylic acid.

9. Which of the following reactions give pthalic acid as a product ?

(A) 

(B) 

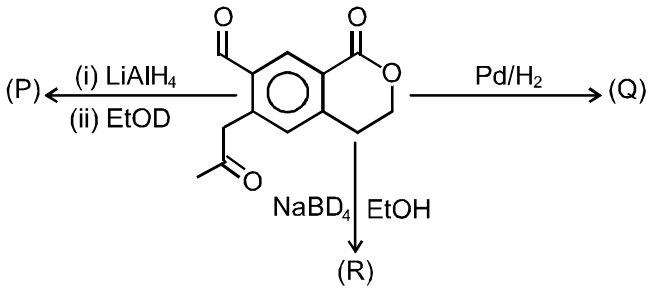
(C) 

(D) 

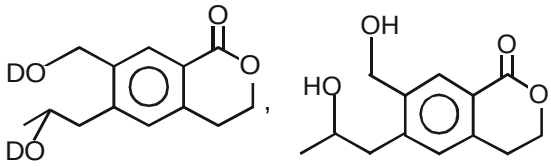
PART - IV : COMPREHENSION

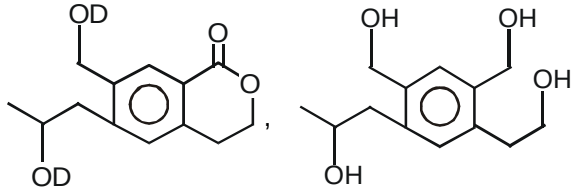
Read the following passage carefully and answer the questions.

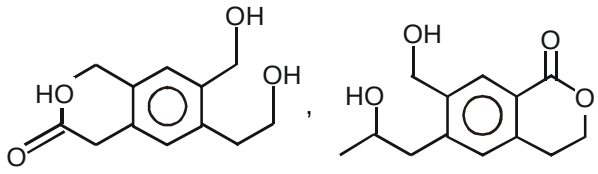
C**omprehension # 1**

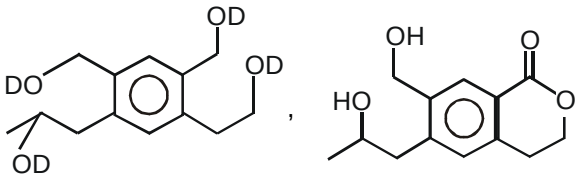


1. (P) and (Q) respectively are

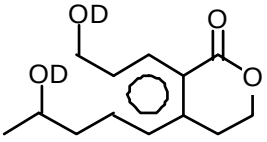
(A) 

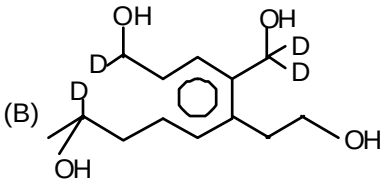
(B) 

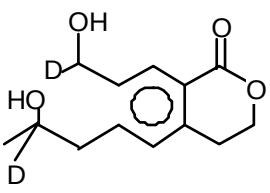
(C) 

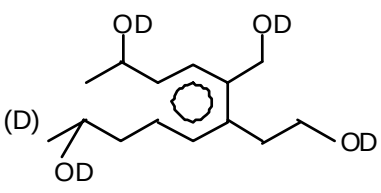
(D) 

2. (R) is

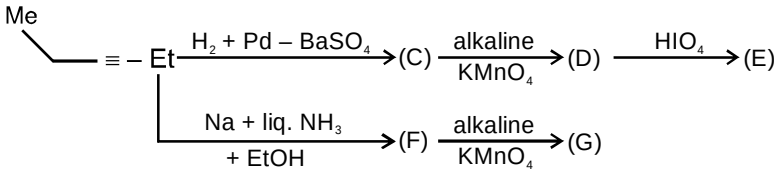
(A) 

(B) 

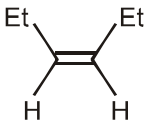
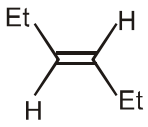
(C) 

(D) 

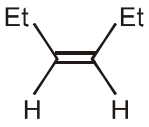
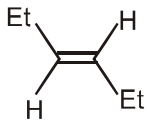
Comprehension # 2



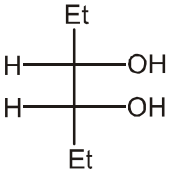
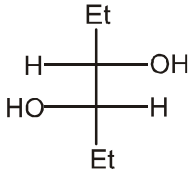
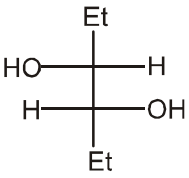
3. The compound (C) is :

(A)  (B)  (C) Et – ≡ – Et (D) Both (A) and (B)

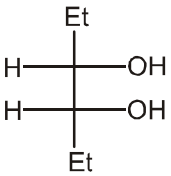
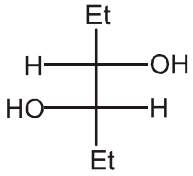
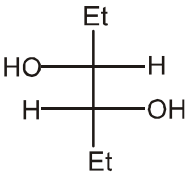
4. The compound (F) is :

(A)  (B)  (C) Et – ≡ – Et (D) Both (A) and (B)

5. The compound (D) is :

(A)  (B)  (C)  (D) Both (B) and (C)

6. The compound (G) is :

(A)  (B)  (C)  (D) Both (B) and (C)

7. The compound (E) is :

(A) Two moles of  . (B) Two moles of  .

(C) One mole of (A) and one mole of (B) (D) No reaction.

Exercise-3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

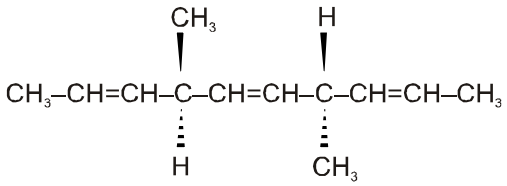
1. Match each of the compounds in **Column I** with its characteristic reaction (s) in **Column II :**

[IIT-JEE- 2009]

	Column-I	**Column-II**
(A)	$CH_3CH_2CH_2CN$	(p) Reduction with $Pd–C/H_2$
(B)	$CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2/HCl$
(C)	$CH_3–CH = CH–CH_2OH$	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(D)	$CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutylaluminium hydride (DIBAL–H)
		(t) Alkaline hydrolysis

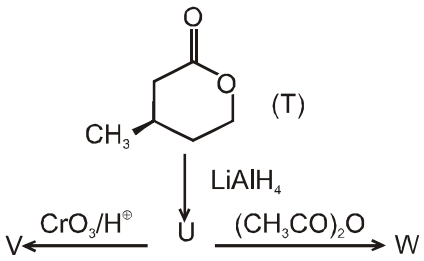
2. The number of optically active products obtained from the **complete** ozonolysis of the given compound is:

[IIT-JEE- 2012]



(A) 0 (B) 1 (C) 2 (D) 4

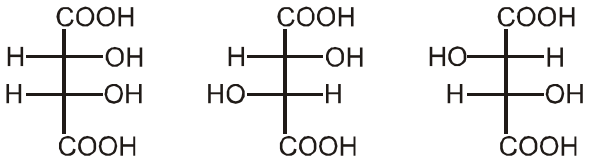
3. With reference to the scheme given, which of the given statments(s) about T, U, V and W is (are) correct?



[JEE - 2012]

(A) T is soluble in hot aqueous NaOH
(B) U is optically active
(C) Molecular formula of W is $C_{10}H_{18}O_4$
(D) V gives effervescence on treatment with aqueous $NaHCO_3$

4. **P** and **Q** are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O. On heating, **P** forms the cyclic anhydride.
Upon treatment with dilute alkaline $KMnO_4$, **P** as well as **Q** could produce one or more than one from **S, T** and **U**. **[JEE Advance- 2013]**



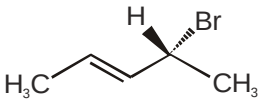
S **T** **U**

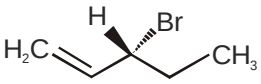
Compounds formed form **P** and **Q** are, respectively
(A) Optically active **S** and optically active pair **(T, U)**
(B) Optically inactive **S** and optically inactive pair **(T, U)**
(C) Optically active pair **(T, U)** and optically active **S**
(D) Optically inactive pair **(T, U)** and optically inactive **S**

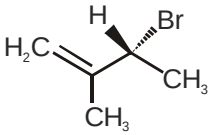
5. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are idependently reacted with $NaBH_4$ (**NOTE :** stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are **[JEE Advance-2014]**

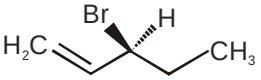
6. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are)

[JEE(Advanced)-2015]

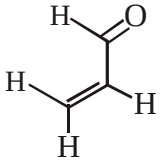
(A) 

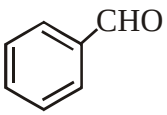
(B) 

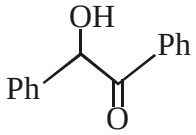
(C) 

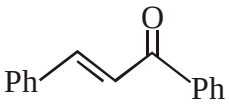
(D) 

7. Positive Tollen's test is observed for **[JEE-Advance 2016]**

(A) 

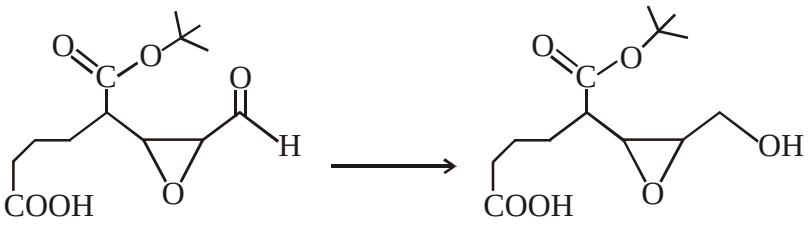
(B) 

(C) 

(D) 

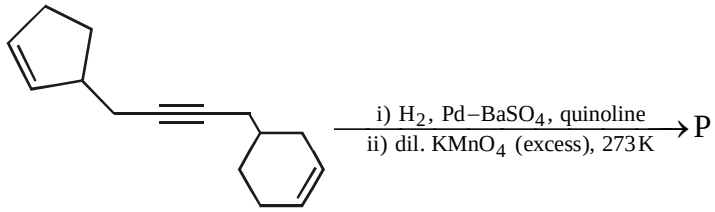
8. Reagent(s) which can be used to bring about the following transformation is(are)

[JEE-Advance 2016]



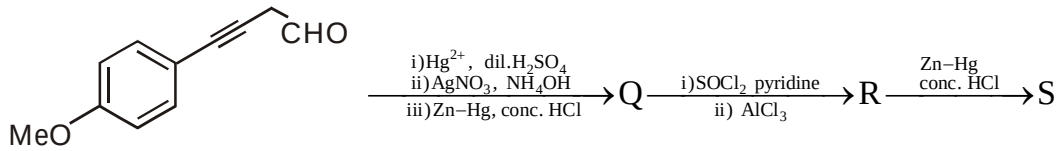
(A) $LiAlH_4$ in $(C_2H_5)_2O$ (B) BH_3 in THF (C) $NaBH_4$ in C_2H_5OH (D) Raney Ni / H_2 in THF

9. Total number of hydroxyl groups present in a molecule of the major product P is ___



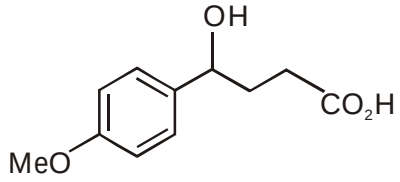
[IIT-2019]

10. Choose the correct option(s) for the following reaction sequence **[IIT-2019]**

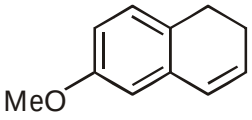


Consider Q, R and S as major products

(A)

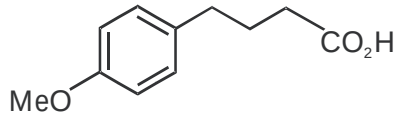


Q

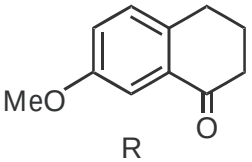


S

(B)

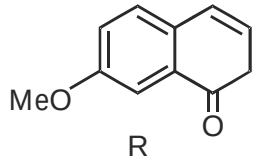


Q

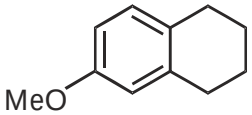


R

(C)

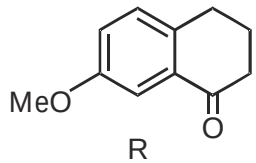


R

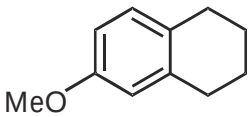


S

(D)



R



S

PART - II : JEE (MAIN) PROBLEMS (PREVIOUS YEARS)

1 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is : **[AIEEE-2010, 4/144]**

(1) propane (2) 1-butene (3) 2-butene (4) ethene

2 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :

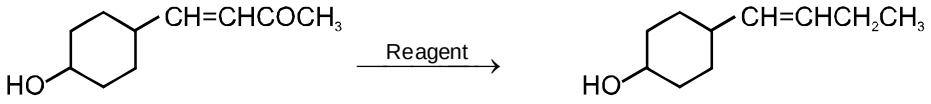
(1) two ethylenic double bonds (2) a vinyl group **[AIEEE-2011, 4/120]**

(3) an isopropyl group (4) an acetylenic triple bond

3. 2– Hexyne gives trans –2–hexene on treatment with : **[AIEEE-2012, 4/120]**

(1) Pt/H_2 (2) Li / NH_3 (3) $Pd/BaSO_4$ (4) $Li AlH_4$

4. In the given transformation, which of the following is the most appropriate reagent ? **[AIEEE-2012, 4/120]**



(1) $NH_2NH_2, \overset{\ominus}{O}H$ (2) Zn–Hg/HCl (3) Na, Liq, NH_3 (4) $NaBH_4$

5. The most suitable reagent for the conversion of $R–CH_2–OH \rightarrow R–CHO$ is : **[JEE Mains-2014, 4/120 M]**

(1) $KMnO_4$ (2) $K_2Cr_2O_7$

(3) CrO_3 (4) PCC (Pyridinium Chlorochromate)

6. In the reaction, the product C is : **[JEE Mains-2014, 4/120 M]**

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.\ KOH} C,$$

(1) Acetaldehyde (2) Acetylene (3) Ethylene (4) Acetyl chloride

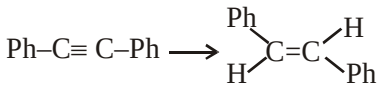
7. In the following sequence of reactions :

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product C is : **[JEE Mains-2015, 4/120 M]**

(1) C_6H_5COOH (2) $C_6H_5CH_3$ (3) $C_6H_5CH_2OH$ (4) C_6H_5CHO

8. The reagent needed for converting **[JEE MAIN ONLINE 2014]**



is :

(1) H_2/Lindlar Cat. (2) Cat. Hydrogenation

(3) $LiAlH_4$ (4) Li/NH_3

9. Bouveault-Blanc reduction reaction involves : **[JEE Main Online 2016]**

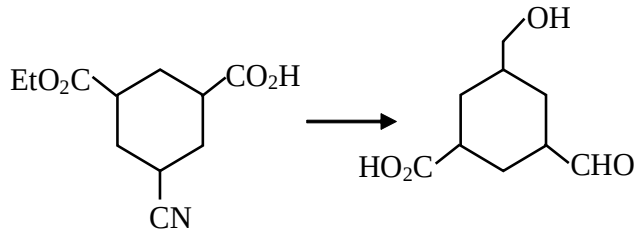
(1) Reduction of an anhydride with $LiAlH_4$.

(2) Reduction of an ester with Na, C_2H_5OH.

(3) Reduction of a carbonyl compound with Na/Hg and HCl.

(4) Reduction of an acyl halide with H_2/Pd.

10. The reagent(s) required for the following conversion are



[JEE Main Online 2018]

(1) (i) $NaBH_4$ (ii) Raney Ni/H_2 (iii) H_3O^+

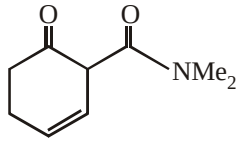
(2) (i) $LiAlH_4$ (ii) H_3O^+

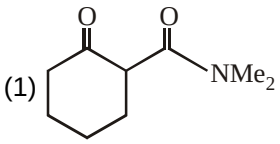
(3) (i) B_2H_6 (ii) DiBAL-H (iii) H_3O^+

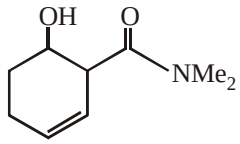
(4) (i) B_2H_6 (ii) $SnCl_2$/HCl(iii) H_3O^+

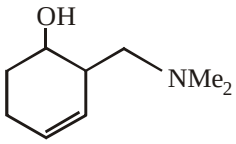
11. The main reduction product of the following compound with $NaBH_4$ in methanol is :-

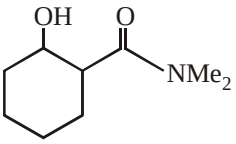
[JEE Main Online 2018]



(1) 

(2) 

(3) 

(4) 

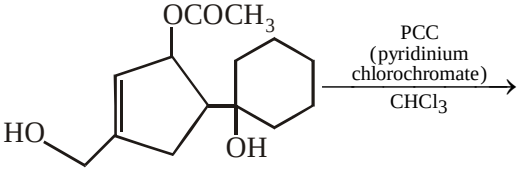
12. When 2-butyne is treated with H_2/Lindlar's catalyst, compound X is produced as the major product and when treated with Na/liq. NH_3 it produces Y as the major product. Which of the following statements is correct ?

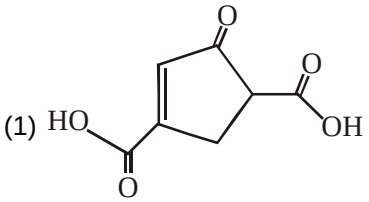
[JEE Main Online 2018]

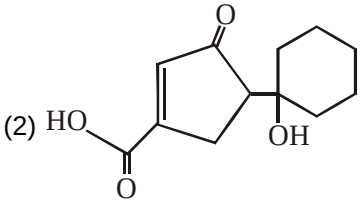
(1) X will have higher dipole moment and higher boiling point than Y.
(2) Y will have higher dipole moment and higher boiling point than X.
(3) X will have higher dipole moment and lower boiling point than Y.
(4) Y will have higher dipole moment and lower boiling point than X.

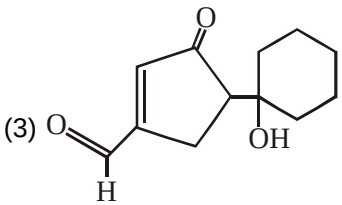
13. The major product formed in the following reaction is :-

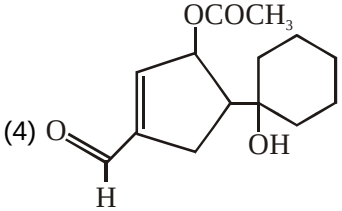
[JEE Main Online 2018]



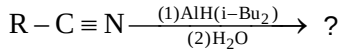
(1) 

(2) 

(3) 

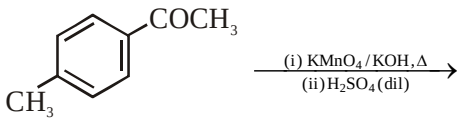
(4) 

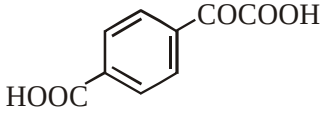
14. The major product of following reaction is : **[JEE Main Online 2019]**

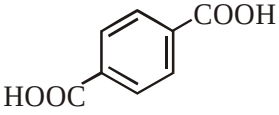


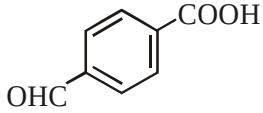
(1) RCHO (2) RCOOH (3) RCH_2NH_2 (4) $RCONH_2$

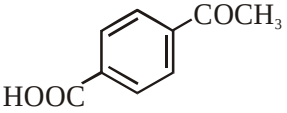
15. The major product of the following reaction is : **[JEE Main Online 2019]**



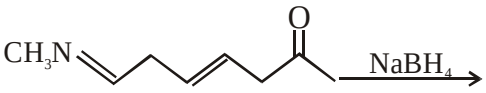
(1) 

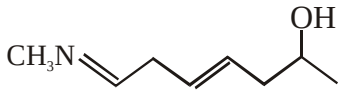
(2) 

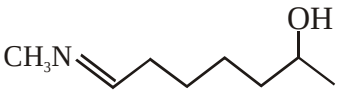
(3) 

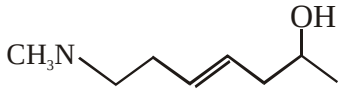
(4) 

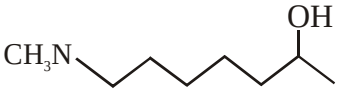
16. The major product of the following recation is: **[JEE Main Online 2019]**



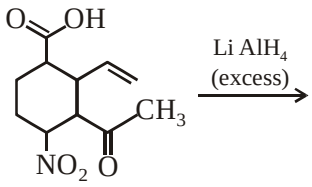
(1) 

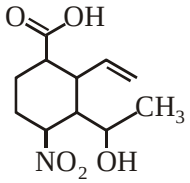
(2) 

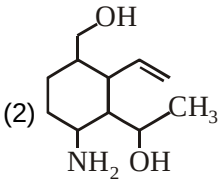
(3) 

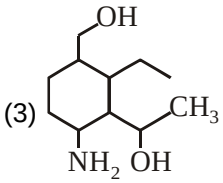
(4) 

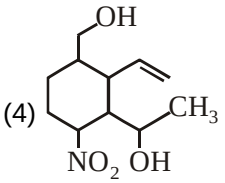
17. The major product obtained in the following reaction is :- **[JEE Main Online 2019]**



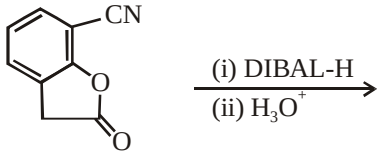
(1) 

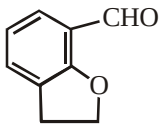
(2) 

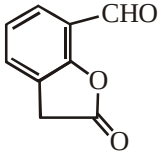
(3) 

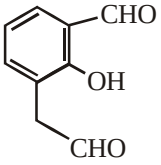
(4) 

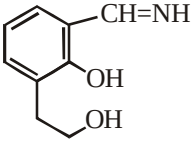
18. The major product of the following reaction is: **[JEE Main Online 2019]**



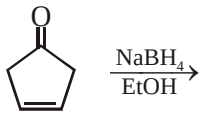
(1) 

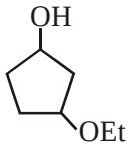
(2) 

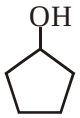
(3) 

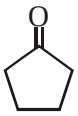
(4) 

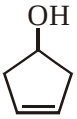
19. The major product of the following reaction is: **[JEE Main Online 2019]**



(1) 

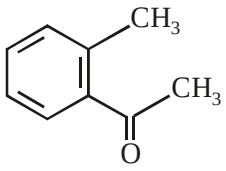
(2) 

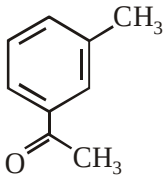
(3) 

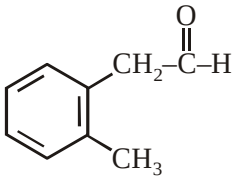
(4) 

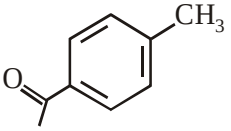
20. Compound A ($C_9H_{10}O$) shows positive iodoform test. Oxidation of A with $KMnO_4$/KOH gives acid B($C_8H_6O_4$). Anhydride of B is used for the preparation of phenolphthalein. Compound A is :-

[JEE Main Online 2019]

(1) 

(2) 

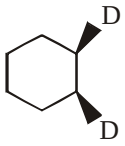
(3) 

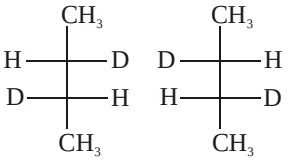
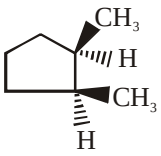
(4) 

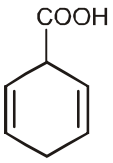
ANSWER KEY

EXERCISE # 1

PART - I

A-1 (a)  (b) 

(c)  (d) 

A-2. (i) $CH_3–CH_2–\underset{\text{trans}}{CH = CH}–(CH_2)_7–CH_2–OH$ (ii) 

A-3. (i) H_2/Pd-$BaSO_4$

(ii) In this conversion –CO– converts into $–CH_2–$ which can be achieved by any one of the following reagents:

(a) $NH_2–NH_2$/KOH/Δ (b) Zn-Hg, Conc HCl, Δ

A-4 (i) (P) = $CH_3–\underset{\underset{OH}{|}}{CH}–CH_3$ (Q) = $CH_3–\underset{\underset{OH}{|}}{CH}–CH_3$

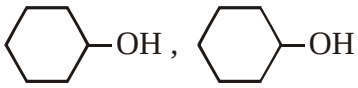
(ii) (P) = $CH_3–CH_2–OH$ (Q) = $CH_3–CH_2–OH$

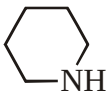
(iii) (P) = No reaction (Q) = $2CH_3–CH_2–OH$

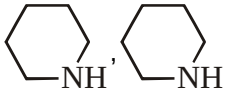
(iv) (P) = No reaction (Q) = $CH_3–CH_2–OH$

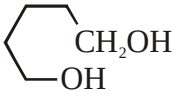
(v) (P) = No reaction (Q) = $CH_3–CH_2–NH_2$

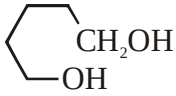
(vi) (P) = No reaction (Q) = No reaction

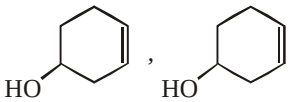
A-5 (i) 

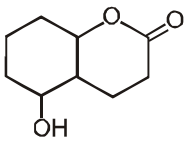
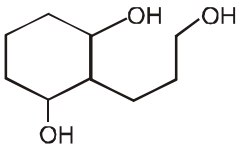
(ii) No reaction, 

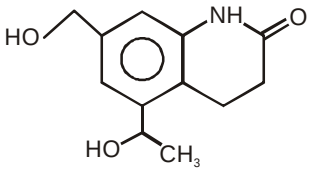
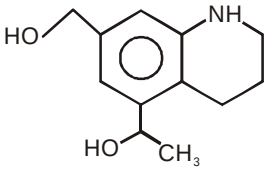
(iii) 

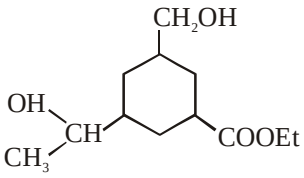
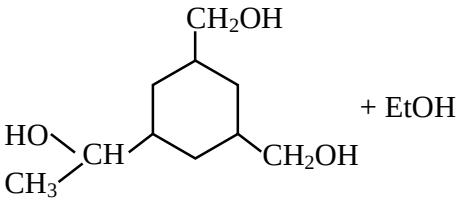
(iv) No reaction, 

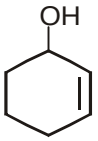
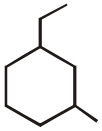
(v) No reaction, 

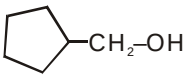
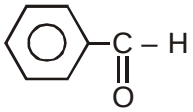
(vi) 

A-6 (i) a :  , b : 

(ii) a :  , b : 

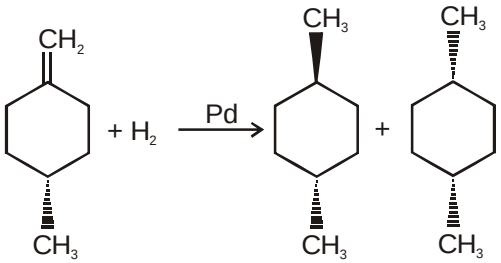
(iii) a :  b :  + EtOH

A-7 (i)  (ii)  (iii) 

A-8 **(a)**  **(b)** 

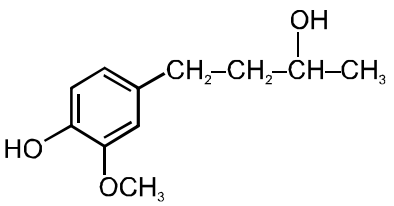
(c) $CH_3 - CHO + CH_3 - CH_2 - OH$

A-9 2

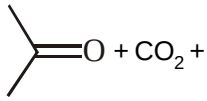


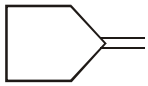
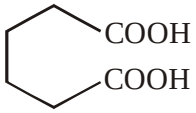
(Trans) (cis)

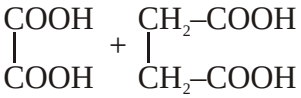
A-10 **49**

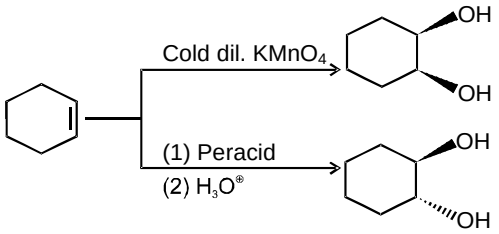
 $(C_{11}H_{16}O_3)$

B-1 (i) $CH_3CH_2\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$ (ii) $CH_3CH_2COOH + HOOCCH_2CH_2CH_3$

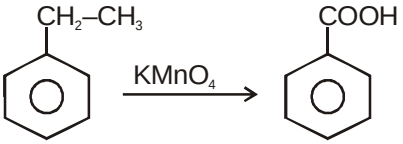
B-2 (i) $CH_3–COOH + CO_2$ (ii)  $+ CO_2 + HOOC–CH_2–CH_2–CH_2–COOH$

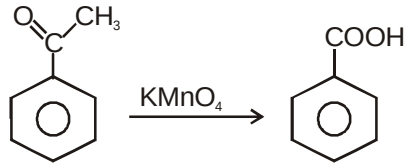
(iii)  $+ CH_3–COOH$ (iv) 

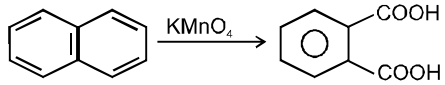
(v) 

B-3 (i) 

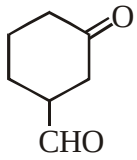
+ Mirror image

(ii) 

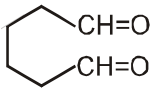
(iii) 

(iv) 

B-4 (i) $CH_3–CH_2–CH_2–COO^-$ (ii) $CH_3–\overset{\overset{O}{\|}}{C}–CH_2–CH_3$

(iii) Ph–CH=CH–CHO (iv) 

(v) $H_2C=CH–CHO$

B-5 (i) 

(ii) 2 HCHO + 2 HCOOH

(iii) $CH_3COOH + CH_3CHO$

(iv) 2Me–COOH

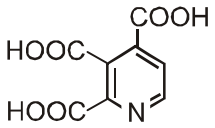
B-6 (i) $Ph–CH_2–CH_2–OH \xrightarrow{Cu/\Delta} Ph–CH_2–CH=O$

(ii) $Ph–\underset{\underset{OH}{|}}{CH}–CH_3 \xrightarrow{Cu/\Delta} Ph–\overset{\overset{O}{||}}{C}–CH_3$

(iii) $Ph–\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}–OH \xrightarrow{Cu/\Delta} Ph–\underset{\underset{CH_3}{|}}{C}=CH_2$

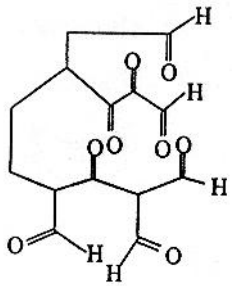
(iv) $CH_3–CHO \xrightarrow[\Delta]{SeO_2} OHC–CHO$

B-7 **3**



(K)

B-8 **5**



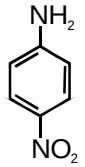
C-1 (a) $CH_3–C\equiv N \xrightarrow{H_3O^{\oplus}} CH_3COOH$

(b) $CH_3NC \xrightarrow{H_3O^{\oplus}} CH_3–\overset{+}{N}H_3 + HCOOH$

C-2 CH_3COCl

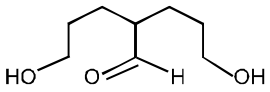
C-3 $CH_3COOH + NH_3$

C-4 Two carboxylic acids

C-5 

C-6 $CH_2=CH-O-CH_3$

C-7 4

C-8 

D-1. $CH_3-CH_2-CH_2-OH \xrightarrow{PCC} CH_3-CH_2-CH=O \xrightarrow{KMnO_4} CH_3-CH_2-COOH \xrightarrow{Ca(OH)_2/\Delta}$

$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

D-2. $CH_3CH_2CH_2-COONa + NaOH \xrightarrow[630K]{CaO} CH_3CH_2CH_3 + Na_2CO_3$

$CH_3-\underset{\underset{CH_3}{|}}{CH}COONa + NaOH \xrightarrow[630K]{CaO} CH_3-CH_2-CH_3 + Na_2CO_3$

D-3. X = 

D-4. 2 **D-5.** **3**

PART - II

A-1.	(A)	**A-2.**	(B)	**A-3**	(C)	**A-4**	(B)	**A-5**	(A)	**A-6**	(D)	**A-7**	(B)
A-8	(D)	**A-9**	(A)	**A-10**	(B)	**A-11**	(C)	**A-12**	(B)	**A-13**	(A)	**A-14**	(D)
B-1.	(C)	**B-2.**	(C)	**B-3.**	(C)	**B-4.**	(B)	**B-5.**	(B)	**B-6.**	(C)	**B-7.**	(C)
B-8.	(B)	**B-9.**	(C)	**B-10.**	(B)	**C-1.**	(D)	**C-2.**	(C)	**C-3.**	(D)	**D-1.**	(A)
D-2.	(A)	**D-3.**	(C)	**D-4.**	(C)	**D-5.**	(A)	**D-6.**	(A)	**D-7.**	(C)	**D-8.**	(D)

PART - III

1. (A) – (p,s) ; (B) – (q); (C)– (r, s); (D) – (q)

2. (A) – (q) ; (B) – (s) ; (C) – (p, s) ; (D) – (q, s)

3. (A) – (p) ; (B) – (q) ; (C) – (t) ; (D) – (s).

EXERCISE # 2

PART - I

1.	(B)	**2.**	(D)	**3.**	(C)	**4.**	(D)	**5.**	(C)	**6.**	(D)	**7.**	(A)
8.	(D)	**9.**	(D)	**10.**	(D)	**11.**	(D)	**12.**	(A)				

PART - II

1.	5 (i), (ii), (iv), (vii) and (ix)	**2.**	5 (iii), (iv), (v), (vi) and (vii)	**3.**	3	**4.**	3		
5.	3 (i, ii, iv)	**6.**	3	**7.**	12	**8.**	9	**9.**	4 (v, vi, vii, viii)
10.	4 (i, ii, iii, v)	**11.**	6	**12.**	2				

PART - III

1.	(ABC)	**2.**	(ABCD)	**3.**	(BC)	**4.**	(AD)	**5.**	(BC)	**6.**	(ABCD)
7.	(ABC)	**8.**	(ABC)	**9.**	(ACD)						

PART - IV

1.	(D)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(A)	**6.**	(D)	**7.**	(A)

EXERCISE # 3

PART - I

1.	(A) - p, q, s, t ; (B) - s, t ; (C) - p ; (D) - r	**2.**	(A)	**3.**	(ACD)						
4.	(B)	**5.**	5	**6.**	(BD)	**7.**	(ABC)	**8.**	(CD)	**9.**	6.00	**10.**	(BD)

PART - II

1	(3)	**2**	(2)	**3.**	(2)	**4.**	(1)	**5.**	(4)	**6.**	(3)	**7.**	(4)
8.	(4)	**9.**	(2)	**10.**	(4)	**11.**	(2)	**12.**	(1)	**13.**	(4)	**14.**	(1)
15.	(2)	**16.**	(3)	**17.**	(2)	**18.**	(3)	**19.**	(4)	**20.**	(1)		

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

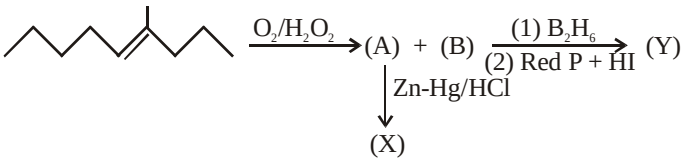
Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1.



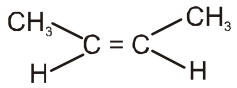
If (A) is ketone then X and Y are respecively :

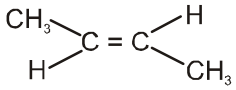
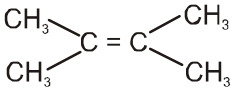
(A) Pentane and Isopentane (B) Isopentane and Pentane

(C) Both are Isopentane (D) Both are Pentane

2. Propyne and propene can be distinguished by :
(A) Conc. H_2SO_4 (B) Br_2 in CCl_4 (C) Dil. $KMnO_4$ (D) $AgNO_3$ in ammonia

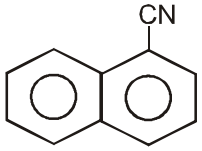
3. The reactivity order towards hydrogenation of the following compounds is

(I) $CH_3 - C \equiv C - CH_3$ (II) 

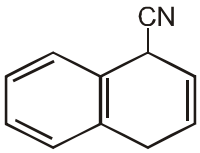
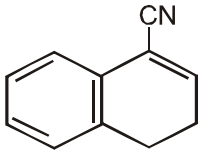
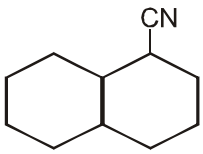
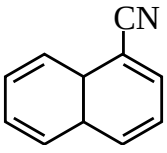
(III)  (IV) 

(A) I > II > III > IV (B) II > III > IV > I (C) III > IV > II > I (D) IV > III > II > I

4.



$\xrightarrow{Na/NH_3(\ell)}$ P, the product can be :

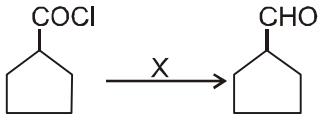
(A)  (B)  (C)  (D) 

5. The product of following reaction is

$$PhCH=CHCH=O \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4}$$

(A) $PhCH_2CH=CHCH_2OH$ (B) $Ph(OH)C=CHCH_3$

(C) $PhCH=CHCH_2OH$ (D) $PhCH_2CH_2CH_2–OH$

6. 

X can be

(A) $NaBH_4$/EtOH (B) $LiAlH_4$/THF (C) Na/EtOH (D) H_2/Pd-$BaSO_4$

7. But-1-ene may be converted to butane by reaction with :

(A) Zn – HCl (B) Sn – HCl (C) Zn – Hg (D) Pd / H_2

8. Which one of the following is reduced with Zn, Hg and HCl acid to give the corresponding hydrocarbon?

(A) Ethyl acetate (B) Butan-2-one (C) Acetamide (D) Acetic acid

9. The best reagent to convert pent-3-en-2-ol into pent-3-ene-2-one is

(A) Pyridinium chloro-chromate (B) Chromic anhydride in glacial acetic acid

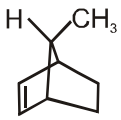
(C) Acidic dichromate (D) Acidic permanganate

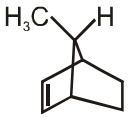
10. The hydrocarbon which can react fastest with sodium in liquid ammonia is :

(A) $CH_3CH_2C\equiv CH$ (B) $CH_3CH=CHCH_3$

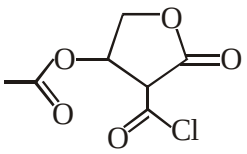
(C) $CH_3CH_2C\equiv CCH_2CH_3$ (D) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$

11. Which undergoes catalytic hydrogenation much faster ?

(A) 

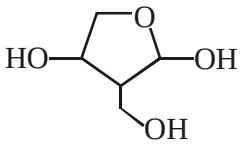
(B) 

(C) equally (D) can't be predicted

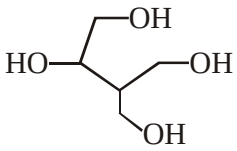
12. 

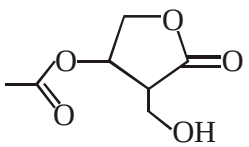
$\xrightarrow{NaBH_4}$ Product

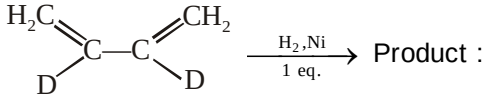
The product is :

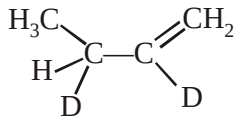
(A) 

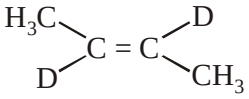
(B) $CH_3–CH_2–OH$

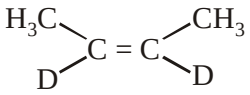
(C) 

(D) 

13.  Product :

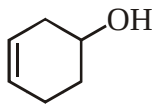
(A) 

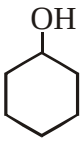
(B) 

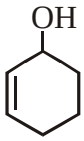
(C) 

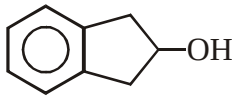
(D) All of these

14. Which of the following can be oxidised by MnO_2 ?

(A) 

(B) 

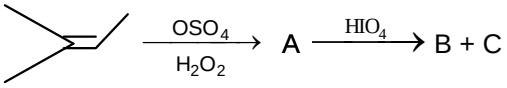
(C) 

(D) 

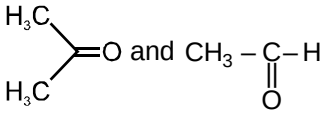
15. Which alkene on heating with alkaline $KMnO_4$ solution gives acetone and a gas, which turns lime water milky –

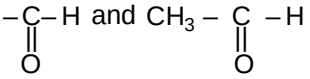
(A) 2–Methyl–2–butene (B) Isobutylene

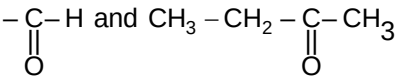
(C) 1–Butene (D) 2–Butene

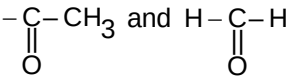
16. 

Product B and C are respectively :

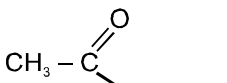
(A) 

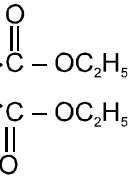
(B) 

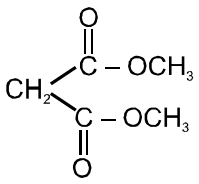
(C) 

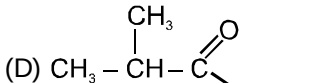
(D) 

17. An organic compound (P) with molecular formula $C_5H_8O_4$ is stable to heat but hydrolyse to (Q) and MeOH by NaOH followed by acidification. (Q) on strong heating gives (R) which with Red P/HI gives ethane. Compound (P) is :

(A) 

(B) 

(C) 

(D) 

18. When acetaldehyde is treated with Fehling's solution, it gives a precipitate of

(A) Cu (B) CuO (C) Cu_2O (D) Cu + Cu_2O + CuO

19. Identify the correct statement about MnO_2/Δ -

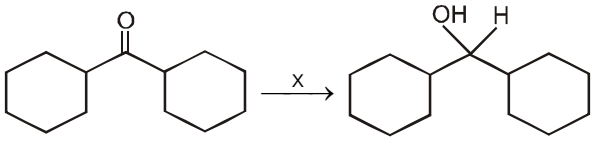
(A) C_6H_5–CHOH–CH_3 as well as CH_3–CH = CH–CH_2OH are oxidised.

(B) C_6H_5–CH_2–CH_2–OH as well as CH_2=CH–CH_2–CH_2–OH are oxidised.

(C) C_6H_5–CHOH–CH_3 is not oxidised but CH_3–CH=CH–CH_2–OH is oxidised.

(D) C_6H_5–CHOH–CH_3 is oxidised but CH_3–CH=CH–CH_2OH is not oxidised.

20.



X is :

(A) $NaBH_4$/EtOH (B) $LiAlH_4$/THF (C) $Al(OiPr)_3$ / CH_3–CH(OH)–CH_3 (D) All of these

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

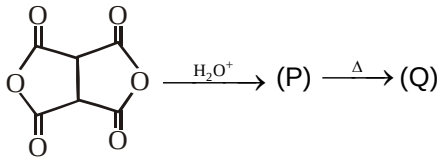
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. How many of the following reagents can convert benzyl alcohol in the benzoic acid ?

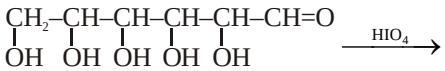
(i) $KMnO_4$	(ii) $K_2Cr_2O_7$	(iii) PCC
(iv) Cu/Δ	(v) Collin's reagent	(vi) PDC
(vii) MnO_2	(viii) HIO_4	(ix) $AgNO_3 + NH_4OH$

22.



The number of carbon atom in final product (Q) is :

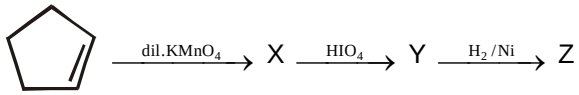
23.



One mole each of all stereoisomers of above compound, when reacts with periodic acid (HIO_4) separately, how many moles of periodic acid will consumed?

24. How many structural isomeric alcohols having molecular formula $C_5H_{12}O$ on reaction with PCC forms ketone?

25.



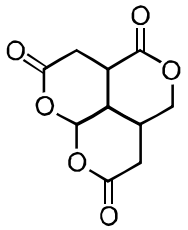
Number of sp^3 carbon atoms in final product Z is :

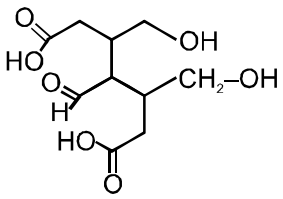
PART - 2 : PAPER JEE (ADVANCED) PATTERN

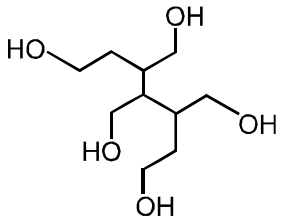
SECTION-I : (Maximum Marks : 12)

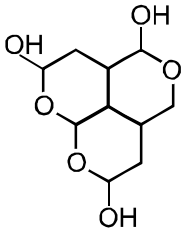
- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	: +3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	: 0	If none of the bubbles is darkened.
Negative Marks	: –1	In all other cases

1.  $\xrightarrow[2.\ LiAlH_4]{1.\ H_3O^+}$ A is

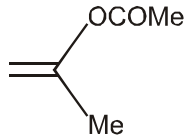
(A) 

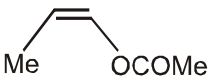
(B) 

(C) 

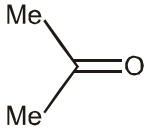
(D) None

2. The products of acid hydrolysis of P and Q can be distinguished by :

(P) $\Rightarrow H_2C$ 

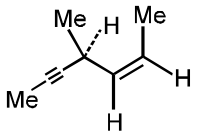
(Q) $\Rightarrow$ 

(A) Lucas reagent (B) 2, 4-DNP (C) Fehling's solution (D) $NaHSO_3$

3.  $+ SeO_2 \longrightarrow$ (P). (P) will not :

(A) reduce Tollens reagent.
(B) give Iodoform test.
(C) form dioxime
(D) give cerric ammonium nitrate test.

4. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives.



(A) an optically active compound
(B) an optically inactive compound
(C) a racemic mixture
(D) a diastereomeric mixture

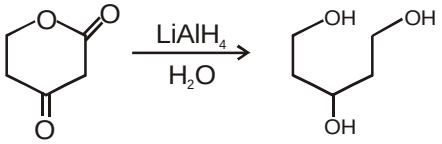
SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

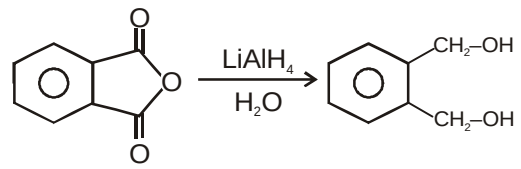
Full Marks	: +4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	: +3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	: +2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	: +1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	: 0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	: –1	In all other cases.

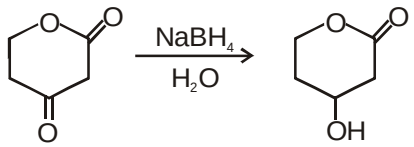
- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5. Which of the following reaction is/are correct ?

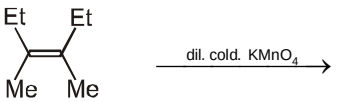
(A) 

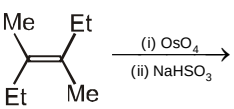
(B) $CH_3–C\equiv N \xrightarrow[H_2O]{LiAlH_4} CH_3–CH_2–NH_2$

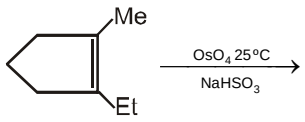
(C) 

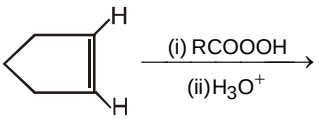
(D) 

6. Which of the following will give syn addition product?

(A) 

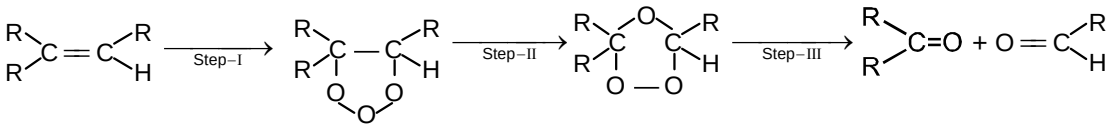
(B) 

(C) 

(D) 

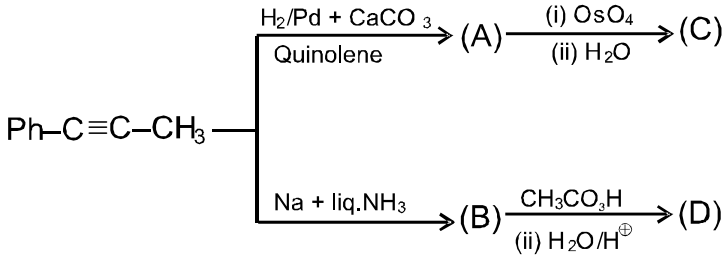
7. Periodic acid is generally used for the oxidation of vicinal diols or α-hydroxycarbonyl compounds. Which of the following statements are correct for this reaction ?
(A) Oxidative cleavage takes place in the above reactions.
(B) Final products are generally carbonyl compounds or carboxylic acids.
(C) HIO_4 reduced into HIO_3
(D) Intermediate of this reaction for a vicinal diol is cyclic per iodate ester.

8. Mechanism of reductive ozonolysis is given below for an alkene.



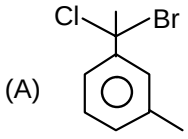
Which is/are correct for the above mechanism
(A) Ozone act as electrophile and as well as nucleophile in this reaction
(B) First step of this reaction is an electrophilic addition
(C) Ozonide is formed in the step-II
(D) When ozonide is cleaved in the presence of reducing agent such as Zn or Me_2S the products will be aldehydes and/or ketones generally.

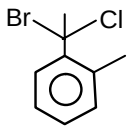
9. Observe the following reaction sequence and choose the correct options.

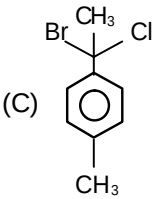


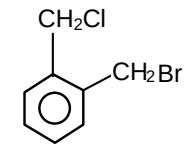
(A) (A) and (B) are diastereomers of each other.
(B) Upon catalytic hydrogenation (A) and (B) give same product
(C) Products (C) and (D) are Identical
(D) Products (C) and (D) are separated by fractional distillation.

10. Hydrolysis of a compound $C_9H_{10}ClBr$ (P) yields $C_9H_{10}O$(Q). (Q) gives positive haloform test Strong oxidation of (Q) yields a dibasic acid which gives two mono-nitro derivative. What is the structure of (P) ?

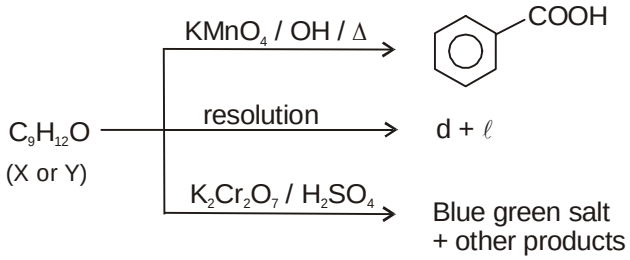
(A) 

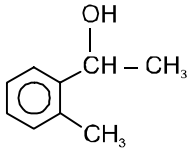
(B) 

(C) 

(D) 

11. Identify the possible structure of X and Y ?



	X	Y
(A)	Ph – CH(OH) – CH_2 – CH_3	Ph – CH_2 – CH(OH) – CH_3
(B)	Ph – C(CH_3)(OH) – CH_2 – OH	Ph – C(CH_3)(OH) – CH_3
(C)		Ph – CH_2 – CH(OH) – CH_3
(D)	Ph – C(CH_3)(H) – CH_2 – OH	Ph – CH(OH) – CH_2 – CH_3

12. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne ?

(A) Sodium metal, CCl_4 (B) H_2, Lindlar catalyst

(C) ammonical $AgNO_3$ solution (D) ammonical Cu_2Cl_2 solution

SECTION-III : (Maximum Marks: 18)

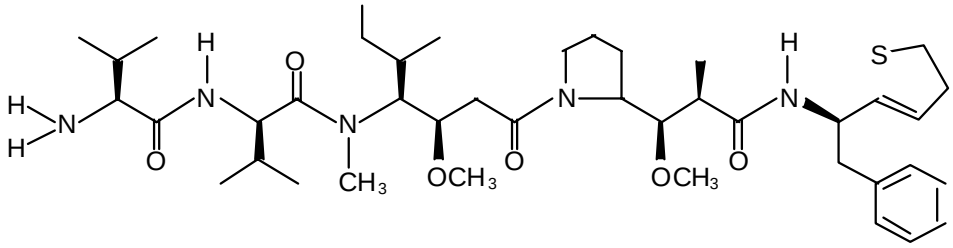
- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

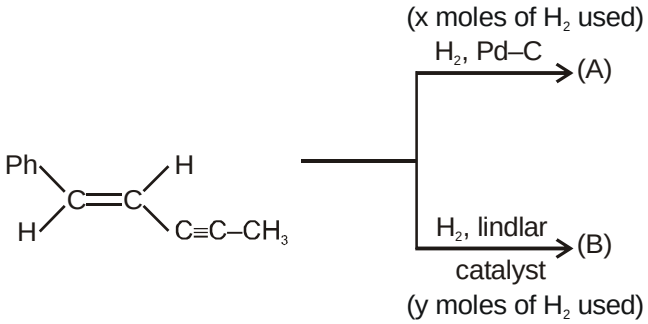
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.

  Zero Marks : 0 In all other cases.

13. Dolastatin is an anti cancer compound isolated from Indian sea have Dobabella ausiculasia. One mole of it on acidic hydrolysis yields how many products are formed?



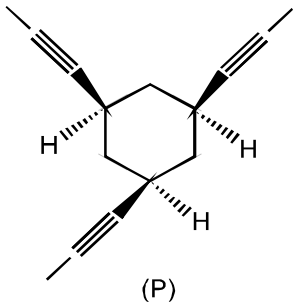
14. Predict the product of following reaction.



Find the value of (x + y).

15_. Compound X gives smallest carboxylic acid & smallest 2º amine on hydrolysis. What is the molecular weight of compound X ?

16.

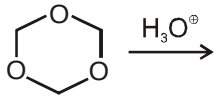


(P)

(P) $\xrightarrow{Na/NH_3(\ell)}$ Product(s)

The product(s) has/have **X** = degree of unsaturation and **Y** = number of isomeric product(s) is/are formed. Then X + Y = ?

17.



How many moles of formaldehyde are obtained when 1,3,5-trioxacylohexane is hydrolysed in acidic medium?

18. How many para substituted benzenoid isomers of $C_8H_8O_2$ gives 1, 4-dihydroxy benzene on hydrolysis ?

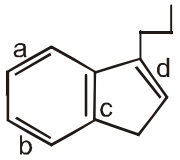
PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. If 2-pentanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O the product will be **[NSEC-2000]**

(A) $CH_3CH(OD)\,CH_2CH_2CH_3$ (B) $CH_3CD\,(OH)\,CH_2CH_2CH_3$

(C) $CH_3CH\,(OH)\,CH_2CH_2CH_3$ (D) $CH_3CD\,(OD)\,CH_2CH_2CH_3$

2. If 1 mole H_2 is reacted with 1 mole of the following compound. **[NSEC-2000]**



Which double bond will be hydrogenated ?

(A) c (B) b (C) a (D) d

3. In the reaction **[NSEC-2001]**

$$CH_3CN + 2H \xrightarrow[\text{ether}]{HCl} X \xrightarrow[\Delta]{H_2O} Y,\ Y \text{ is}$$

(A) acetaldehyde (B) ethanamine (C) dimethylamine (D) acetone

4. If 3-hexanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O, the product will be : **[NSEC-2001]**

(A) $CH_3\,CH_2\,CH\,(OD)\,CH_2\,CH_2\,CH_3$ (B) $CH_3\,CH_2\,CD\,(OH)\,CH_2\,CH_2\,CH_3$

(C) $CH_3\,CH_2\,CH\,(OH)\,CH_2\,CH_2\,CH_3$ (D) $CH_3\,CH_2\,CD\,(OD)\,CH_2\,CH_2\,CH_3$

5. Which of the following can not be obtained when alkenes are oxidised with $KMnO_4$ and then followed by acid hydrolysis ? **[NSEC-2001]**

(A) alkanoic acids (B) alkanals (C) alkanones (D) carbon dioxide

6. The reaction **[NSEC-2001]**

$$R_2CO + 4[H] \xrightarrow[\text{Conc. HCl}]{Zn-Hg} R_2CH_2 + H_2O$$

is well known as :

(A) Wurtz reaction (B) Rosenmund reduction

(C) Kolbe reaction (D) Clemmensen reduction

7. Reduction of an isonitrile gives a **[NSEC-2002]**

(A) primary amine (B) secondary amine (C) tertiary amine (D) quaternary ammonium salt.

8. Methane may be obtained from monochloromethane by **[NSEC-2002]**

(A) reduction with nascent hydrogen (Zn + HCl) (B) reduction with hydrogen (H_2)

(C) heating with sodium metal in dry ether (D) hydrolysis with aqueous NaOH.

9. The compound which does not react with lithium aluminium hydride is **[NSEC-2003]**

(A) 3-penten-2-one (B) methyl benzoate (C) 2 -pentanol (D) propanenitrile

10. The substance that gives a primary amine on hydrolysis is **[NSEC-2004]**

(A) nitroparaffin (B) alkyl cyanide (C) oxime (D) alkyl isocyanide.

11. Reduction of methylbenzoate ($C_6H_5COOCH_3$) to benzyl alcohol ($C_6H_5CH_2OH$) can be accomplished using **[NSEC-2005]**

(A) H_2/Pd (B) $LiAlH_4$ (C) $NaBH_4$ (D)Zn-Hg/HCl

12. Carbonyl compounds can generally be converted to hydrocarbons by **[NSEC-2006]**

(A) H_2 / Pt (B) $LiAlH_4$ (C) N_2H_4 / KOH (D) $K_2Cr_2O_7$ / H_2SO_4

13. To reduce a nitroaldehyde to a nitroalcohol the reducing agent of choice is **[NSEC-2008]**

(A) $LiAlH_4$ (B) $NaBH_4$ (C) Molecular H_2 (D) $SnCl_2$

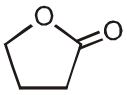
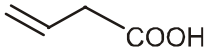
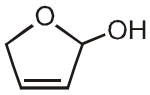
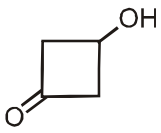
14. An isocyanide on reduction with hydrogen in the presence of plantinum gives : **[NSEC-2009]**

(A) amide (B) primary amine (C) secondary amine (D) alcohol

15. Compound X ($C_5H_{10}O$) is a chiral alcohol. It is catalytically hydrogenated to an achiral alcohol Y ($C_5H_{12}O$) and oxidized by activated MnO_2 to an achiral carbonyl compound Z (C_5H_8O). Compound X is : **[NSEC-2009]**

(A) 1-penten-3-ol (B) 4-penten-2-ol
(C) 3-methyl-2-buten-1-ol (D) 2-methyl-2-buten-1-ol

16. 4-Oxobutanoic acid is reduced with Na-borohydride and the product is treated with aqueous acid. The final product is : **[NSEC-2009]**

(A)  (B)  (C)  (D) 

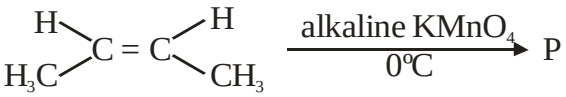
17. Tollen's reagent is **[NSEC-2012]**

(A) Cu_2O (B) $[Cu(OH)_4]^{2-}$ (C) Ag_2O (D) $[Ag(NH_3)_2]^+$

18. Fehlings solution is **[NSEC-2013]**

(A) $AgNO_3$ solution + NaOH solution + NH_4OH
(B) Alkaline solution of Cupric ion complexed with citrate ion
(C) Copper sulphate + sodium potassium tartrate + NaOH
(D) Copper sulphate solution

19. Which of the following statements is true for the reaction given below ? **[NSEC-2013]**

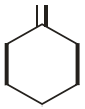
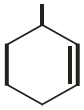


(A) P is a meso compound of 2, 3-butanediol formed by syn addition.
(B) P is meso compound of 2, 3-butanediol formed by anti addition.
(C) P is racemic mixture of d- and ℓ-2, 3-butanediol formed by anti addition.
(D) P is racemic mixture of d- and ℓ-2, 3-butanediol formed by syn addition.

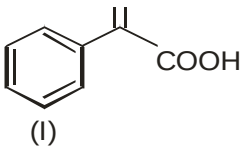
20. Complete catalytic hydrogeneration of naphthalene gives decalin ($C_{10}H_{18}$). The number of isomers of decalin formed and the total number of isomers of decalin possible are respectively. **[NSEC-2016]**

(A) 1, 2 (B) 2, 3 (C) 2, 4 (D) 3, 4

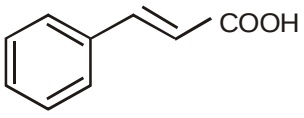
21. Which of the following on treatment with hot concentrated acidified $KMnO_4$ will give 2-methylhexane-1 6-dioic acid as the only organic product? **[NSEC-2017]**

(A)  (B)  (C)  (D) 

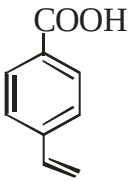
22. An organic compound 'P' with molecular formula $C_9H_8O_2$ on oxidation gives benzoic acid as one of the products. The possible structure/s of 'P' is/are **[NSEC-2017]**



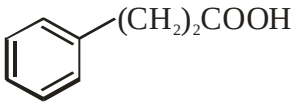
(I)



(II)



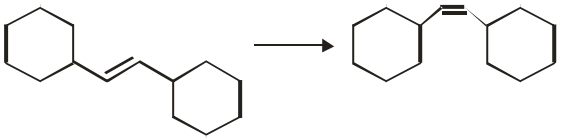
(III)



(IV)

(A) I and III (B) II and IV (C) I and II (D) II only

23. The correct sequence of reagents from those listed below for the following conversion is **[NSEC-2018]**



I. $NaNH_2$ II. Br_2 III. H_2/Pd-C, quinolone IV. H_3O^+

(A) IV–I–III (B) III–IV–I (C) II–I–III (D) I–II–III

RRP ANSWER KEY

PART- 1

1.	(D)	**2.**	(D)	**3.**	(A)	**4.**	(A)	**5.**	(D)	**6.**	(D)	**7.**	(D)
8.	(B)	**9.**	(A)	**10.**	(A)	**11.**	(A)	**12.**	(D)	**13.**	(C)	**14.**	(C)
15.	(B)	**16.**	(A)	**17.**	(C)	**18.**	(C)	**19.**	(A)	**20.**	(D)		
21.	2 (i) and (ii)			**22.**	4	**23.**	80	**24.**	3	**25.**	5		

PART - 2

1.	(B)	**2.**	(C)	**3.**	(D)	**4.**	(B)	**5.**	(ABCD)	**6.**	(ABC)
7.	(ABCD)	**8.**	(ABCD	**9.**	(ABC)	**10.**	(B)	**11.**	(A,D)	**12.**	(ACD)
13.	6	**14.**	4	**15_.**	73	**16.**	5	**17.**	3	**18.**	1

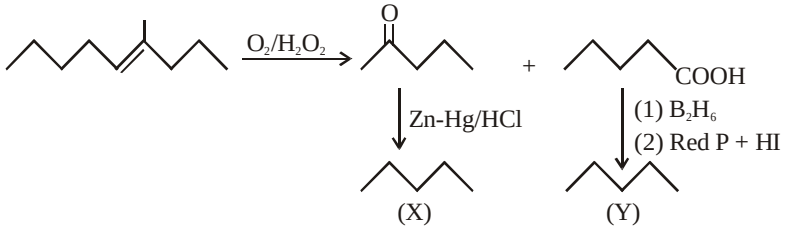
PART - 3

1.	(A)	**2.**	(D)	**3.**	(A)	**4.**	(A)	**5.**	(B)	**6.**	(D)	**7.**	(B)
8.	(A)	**9.**	(C)	**10.**	(D)	**11.**	(B)	**12.**	(C)	**13.**	(B)	**14.**	(C)
15.	(A)	**16.**	(A)	**17.**	(D)	**18.**	(C)	**19.**	(A)	**20.**	(A)	**21.**	(C)
22.	(C)	**23.**	(C)										

RRP SOLUTIONS

PART- 1

1.



2. Terminal alkyne gives white ppt with ammonical silver nitrate.

$$CH_3—C \equiv CH + NH_3 + AgNO_3 \rightarrow \underset{\text{white ppt.}}{CH_3—C \equiv C.Ag} + NH_4NO_3$$

While propene does not give any reaction with ammonical $AgNO_3$ due to absence of acidic hydrogen.

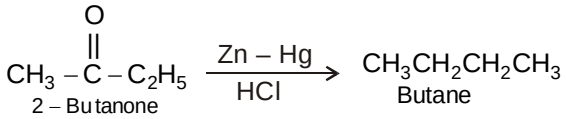
3. Rate of hydrogenation will decreases on increasing steric hinderance at π bond.

4. It is Birch reduction

6. –COCl converts in –CHO by H_2/Pd-$BaSO_4$ (Rosenmund reduction)

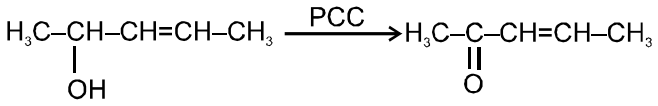
7. $CH_3 – CH_2 – CH = CH_2 \xrightarrow{Pd/H_2} CH_3 – CH_2 – CH_2 – CH_3$

8.



It refers to as Clemensen's reduction

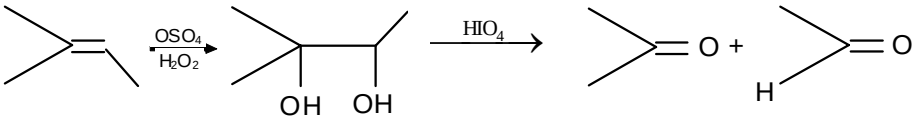
9.



10. $CH_3CH_2\ C{\equiv}CH \xrightarrow[\Delta]{Na/Liq\ NH_3} CH_3CH_2C{\equiv}\overset{-}{C}\overset{+}{N}a$

11. Due to less hinderance A undergoes catalytic hydrogenation much faster.

16.

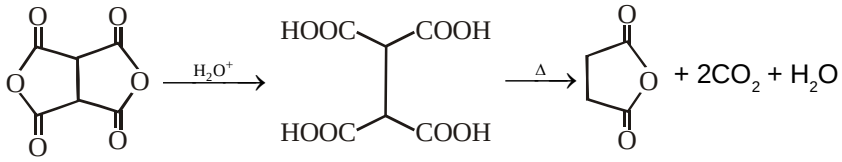


Syn addition

17. (P) on hydrolysis gives propanedioic acid and methanol. Propanedioic acid on strong heating gives acetic acid which when reduced with Red P/HI gives ethane.

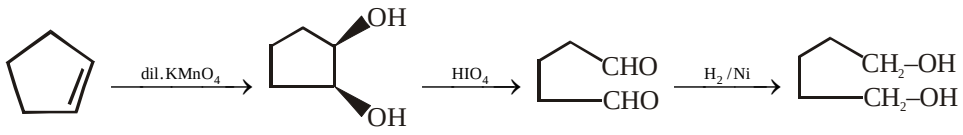
20. X can be $NaBH_4$/EtOH or $LiAlH_4$/THF or $Al(OiPr)_3$ / $CH_3–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$

22.

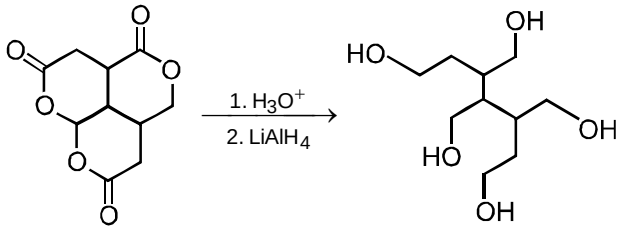


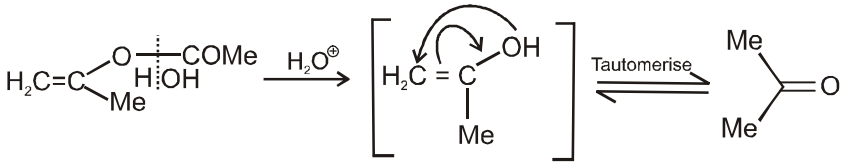
23. 1 mole consumes 5 moles of HIO_4
Total stereoisomer of reactant = 16
Total moles consumes = 16 × 5 = 80

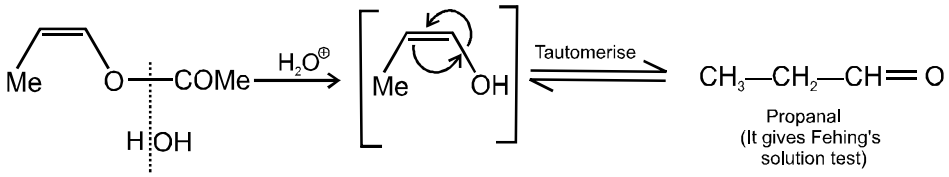
24. $CH_3–\underset{\underset{OH}{|}}{CH}–CH_2–CH_2–CH_3 + CH_3–CH_2–\underset{\underset{OH}{|}}{CH}–CH_2–CH_3 + CH_3–\underset{\underset{CH_3}{|}}{CH}–\underset{\underset{OH}{|}}{CH}–CH_3$

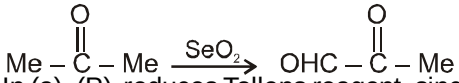
25. 

PART 2

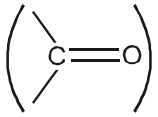
1. 

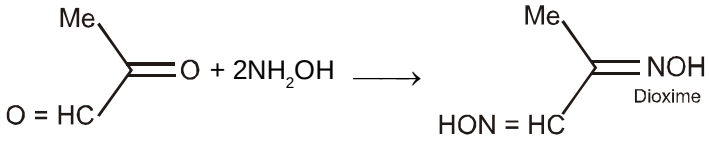
2. 



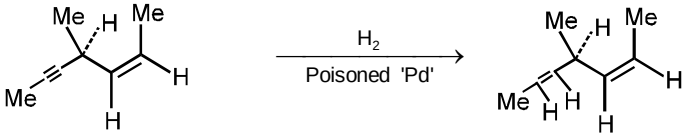
3. 

In (a), (P) reduces Tollens reagent, since it contains (–CHO) group.
In (b), (P) gives iodoform test, since it contains (MeCO–) group.

(P) forms dioxime, since it contains (–CHO) and  groups.



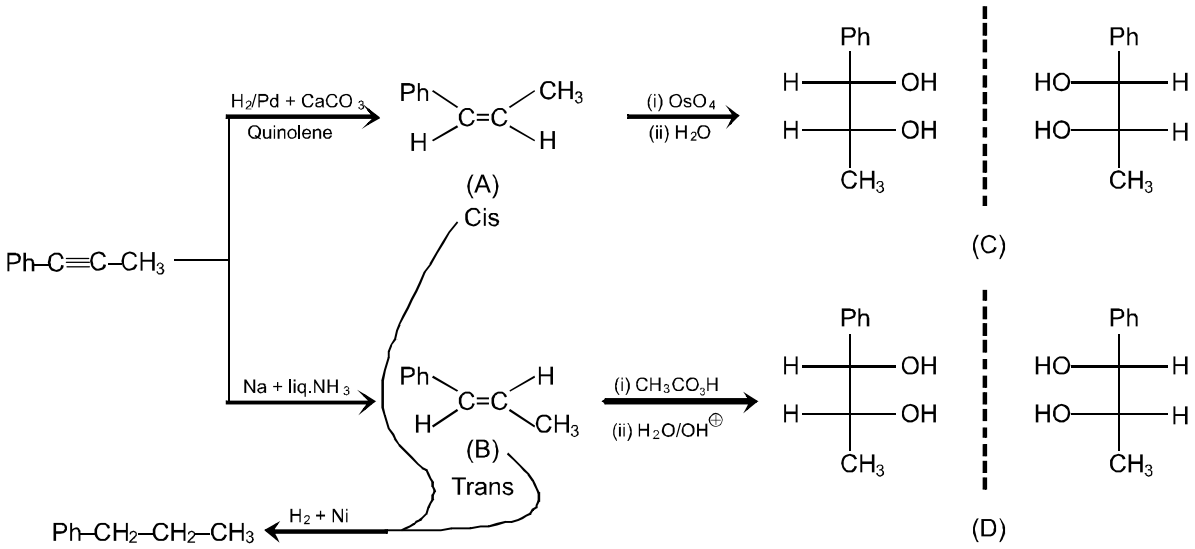
In (d), (P) does not gives cerric ammonium nitrate test, since this test is given by alcohols and (P) does not contain an alcoholic group. So the answer is (D).

4. 

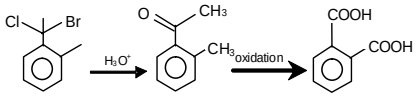
(optical active compound)
By partially hydrogenation of – C ≡ C – alkene is formed.

7. HIO_4 is a mild oxidising agent.
Cyclic intermediate is formed with vicinal diols.

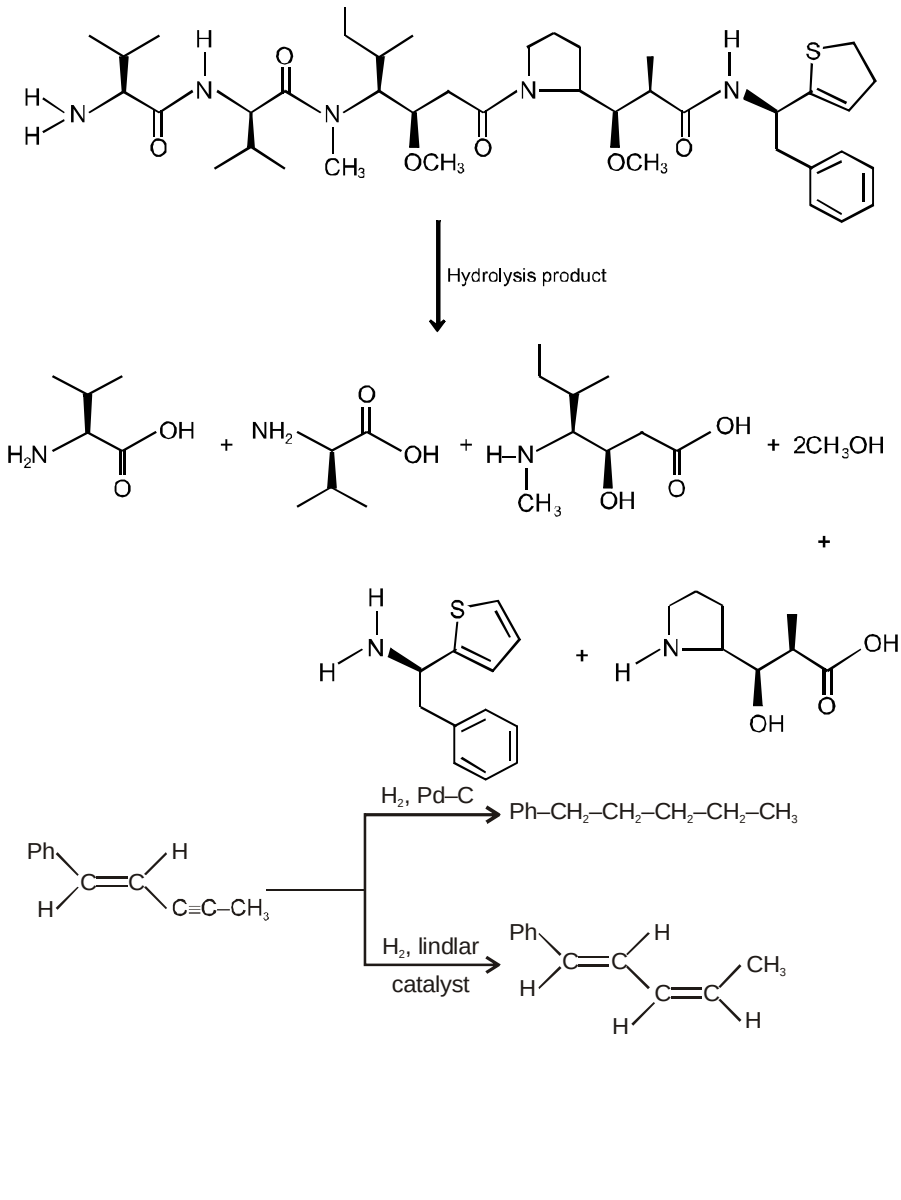
9.



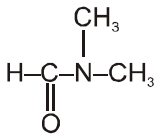
10.

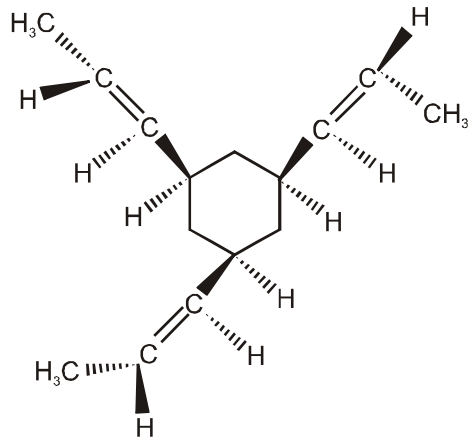


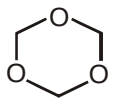
13.

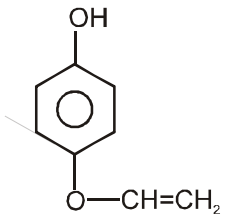
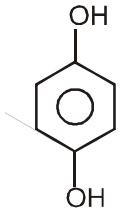


14.

15_.  m.w. is 73

16. (P) $\xrightarrow{Na/NH_3(\ell)}$  D.u. = X = 4 ; Y = 1

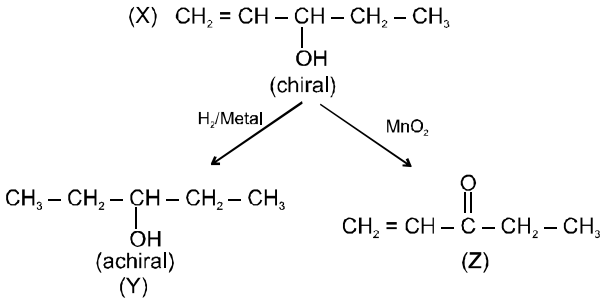
17.  $\xrightarrow{H_3O^{\oplus}}$ 3HCHO

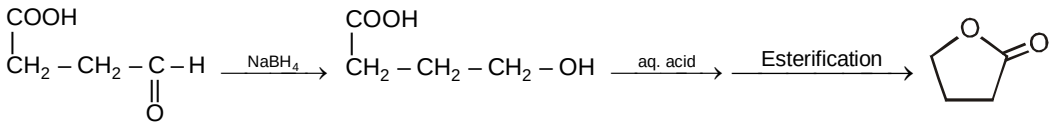
18.  $\xrightarrow{H_3O^+}$  + $CH_2=CH-OH \rightleftharpoons CH_3-CH=O$

1,4-dihydroxy benzene

PART - III

14. $R-NC \xrightarrow{H_2/Pt} R-NH-CH_3$

15. 

16. 

17. Tollen's reagent is ammonical silvernitrate, which has the species $[Ag(NH_3)_2]^+$.

18. Fehling solution is alkaline solution of $CuSO_4$ with Rochelle salt i.e. sodium potassium tartrate.