# REDUCTION, OXIDATION & HYDROLYSIS REACTIONS

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### JEE(Advanced) Syllabus

**Reduction** of Alkenes, Alkynes, Alcohols, Aldehydes, Ketones, Acids, Acid halides, Esters, Amides Cyanide & 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

**Reduction and oxidation** reactions of Alkenes, Alkynes, Alcohols, Aldehydes, Ketones Cyanides, Acids & Acid derivatives.

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# Reduction, Oxidation & Hydrolysis Reactions

### Section (A): Reduction-1

#### Introduction:

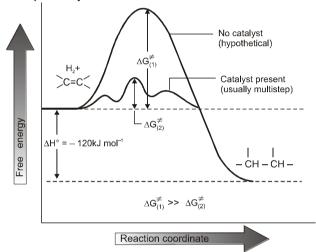
Reduction covers both the addition of hydrogen (or deuterium) to a double bond and the replacement of an atom or group by hydrogen (or deuterium). In other words, reduction means hydrogenation or hydrogenolysis.

Reduction can be carried out in following ways:

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

#### 1.1 Catalytic hydrogenation:

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



Heterogeneous hydrogenation catalysts typically involve finely divided platinum.

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

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

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

#### Facts of catalysis:

- (i) Substrate molecules are assumed to undergo homolysis into atoms at the surface of the catalyst.
- (ii) The substrate is chemisorbed on the surface of the catalyst and hydrogenation takes place.
- (iii) The process is exothermic.

**Note:** (If H<sub>2</sub> and D<sub>2</sub> mixture is used with a Pt catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H<sub>2</sub> and D<sub>2</sub>. (No scrambling occurs in the absence of the catalyst.) The product has both D and H atoms)

### Catalytic Reduction of Functional Groups Using H<sub>2</sub>/Pd(C) or H<sub>2</sub>/Pt or H<sub>2</sub>/Ni

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

Substrate	Product
RCOCI	RCH <sub>2</sub> OH
RNO <sub>2</sub>	RNH <sub>2</sub>
RC≡CR	RCH <sub>2</sub> CH <sub>2</sub> R
RCHO	RCH <sub>2</sub> OH
RCH=CHR	RCH₂CH₂R
RCOR	RCHOHR
RCN	RCH <sub>2</sub> NH <sub>2</sub>



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- Note: (i) Generally RCOOH, RCOOR, RCONH<sub>2</sub> groups are **not reduced** by catalytic hydrogenation. (ii) Stereochemistry of catalytic hydrogenation: The above reaction is syn addition (addition takes
- (ii) Homogeneous catalysis: (catalysts soluble in the reaction medium). It uses reactants and catalyst in the same phase. Both hydrogen atoms usually add from the same side of the molecule. Common example: Use of Wilkinsion catalyst Rh [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>Cl.
- (iii) Lindlar's catalyst : [H<sub>2</sub>/Pd, CaCO<sub>3</sub>, quinoline]

place from the same side of alkene or alkyne).

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

Stereochemistry: Syn addition.

$$CH_3-CH_2-C\equiv C-CH_3 \xrightarrow{H_2 \text{ Lindlar's catalyst}} \text{ or } Ni_2B \xrightarrow{C_2H_5} CH_3 \text{ (syn addition)}$$

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

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

**(iv)** Rosenmund catalyst: [H<sub>2</sub>/Pd, BaSO<sub>4</sub>, quinoline] Hydrogenation in presence of H<sub>2</sub>/Pd/BaSO<sub>4</sub> is called Rosenmund Reduction. It reduces alkyne to alkene and acid halide to aldehyde. It is poisoned palladium catalyst, composed of powdered barium sulphate coated with palladium, poisoned with quinoline or sulphur.

Stereochemistry: Syn addition.

(a) 
$$CH_3-C\equiv C-CH_3$$
  $\xrightarrow{H_2,Pd, BaSO_4, S}$   $\xrightarrow{H_3C}$   $C=C$   $\xrightarrow{CH_3}$   $\xrightarrow{C:s-2-butene}$ 

(b) 
$$CH_3 - C - CI \xrightarrow{H_2,Pd, BaSO_4} CH_3 - CH_0$$

1.2 Metal/proton (acid) reduction:

Reduction by dissolving metals is based on the fact that the metal acts as a source of electrons.

Step-1: Metals give electrons to the electrophilic species and form anion

Step-2: Proton is abstracted from the acidic source.

A-B 
$$\xrightarrow{\overline{e}}$$
 A•+ $\overline{B}$ : or  $\overline{A}$ :+ B•  $\xrightarrow{H^+}$  A•+B-H

A=B  $\xrightarrow{\overline{e}}$  :  $\overrightarrow{A}$ -B• or  $\overrightarrow{A}$ - $\overrightarrow{B}$ : A•-BH

(i) Birch reduction [Na or Li/NH<sub>3</sub>(liq.) or (ethyl alcohol)]:

Alkyne and Aromatic Compounds are reduced by Na or Li/NH<sub>3</sub>.

Alkynes are reduced to trans alkene. Stereochemistry: anti addition.

$$R-C = C-R \xrightarrow{Na/NH_3} R C = C \xrightarrow{H} (anti addition)$$

#### 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.



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

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

#### (ii) Bouvealt-Blanc reduction [Na/C<sub>2</sub>H<sub>5</sub>OH]:

Reduction of aldehydes, ketones, acidhalides, esters or cyanide by means of excess of Na/C<sub>2</sub>H<sub>5</sub>OH is called Bouvealt-Blanc reduction.

Na + C<sub>2</sub>H<sub>5</sub>OH is mild reducing agent.

Reagent	Na/C <sub>2</sub> H <sub>5</sub> OH					
Reactant	Aldehyde	Ketone	Cyanide	Ester	acid halide	
Product	1° alcohol	2° alcohol	1° amine	1° alchol	1° alchol	

CH<sub>3</sub>CHO 
$$\xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}}$$
 CH<sub>3</sub>CH<sub>2</sub>OH Acetaldehyde Ethanol

#### (iii) Stephen's Reductions: [SnCl2/HCl]

When reduction of cyanide is carried out with acidified stannous chloride (SnCl<sub>2</sub>/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.

R-C=N 
$$\begin{array}{c} \text{LiAIH}_4 \text{ or Na/C}_2\text{H}_5\text{OH} \\ \text{(Complete Reduction)} & \text{R-CH}_2\text{NH}_2 \\ \text{(1°Amine)} \\ \hline \text{(i) SnCI}_2 \text{/HCI (ii) H}_2\text{O} \\ \text{(Partial Reduction)} & \text{R-CHO} \\ \text{Aldehyde} \\ \end{array}$$

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

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

$$\begin{array}{c}
C = O \\
\downarrow \\
sp^2
\end{array}
\begin{array}{c}
Conc. \\
CH \\
\downarrow \\
sp^3
\end{array}$$

#### Mechanism:

Mechanism:
$$C = O \xrightarrow{H^{\oplus}} C = \overset{\oplus}{O} - H \xrightarrow{C} C - OH \xrightarrow{Zn \to Zn^{2+}} + 2e^{\Theta} \xrightarrow{C} C - OH \xrightarrow{2H^{\oplus}} C - OH \xrightarrow{Zn \to Zn^{2+}} + 2e^{\Theta} \xrightarrow{C} C - OH \xrightarrow{2H^{\oplus}} C - OH \xrightarrow{2H^{\oplus}} C - OH \xrightarrow{Zn \to Zn^{2+}} + 2e^{\Theta} \xrightarrow{C} C - OH \xrightarrow{2H^{\oplus}} C - OH \xrightarrow{2H^{\oplus}}$$

(a) R – CHO 
$$\xrightarrow{Zn - Hg / \text{ conc. HCl}} A$$
 RCH<sub>3</sub> + H<sub>2</sub>O (b) R – C – R'  $\xrightarrow{Zn - Hg / \text{ conc. HCl}} A$  RCH<sub>2</sub>R' + H<sub>2</sub>O

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



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### Section (B): Reduction-2

#### 1.3 Metal hydrides reduction

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

#### (i) LiAlH<sub>4</sub> (LAH) Lithium aluminium hydride [LiAlH<sub>4</sub>/ Ether or THF]:

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

_					<u> </u>						
	Reagent	LiAIH <sub>4</sub>	LiAlH <sub>4</sub>	LiAIH <sub>4</sub> /Excess	LiAIH <sub>4</sub> /Excess	LiAlH <sub>4</sub>					
Ī	Reactant	Aldehyde	Ketone	Acid	Acidanhydride	Acid chloride	Ester	Cyanide	Amide	Isocyanide	Nitro
Ī	Product	1º alcohol	2º alcohol	1º alcohol	1º alcohol	1º alcohol	1º alcohol	1º amine	1º amine	2º amine	1º amine

Note: Alkene, alkyne, benzene rings are not reduced by LiAlH, in ether but it is reported that

(\*) double bond can be reduced by LiAlH<sub>4</sub> / THF in few cases like :

Ph–CH=CH–CHO 
$$\xrightarrow{\text{(i) LiAIH}_4-\text{THF}}$$
 Ph–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>OH

[Cinnamaldehyde]

#### (ii) Sodium borohydride [NaBH<sub>4</sub> / C<sub>2</sub>H<sub>5</sub>OH or Ether]:

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

Reagent	NaBH <sub>4</sub>	NaBH₄	NaBH₄				
Reactant	Aldehyde	Ketone	Acid chloride				
Product	1º alcohol	2º alcohol	1º alcohol				
O OH							

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

Reagent

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

	Reactant	Ester	Cyanide		
	Product	Aldehyde	Aldehyde		
$\begin{array}{c} \text{LiAlH}_4\text{-THF} \\ \text{H}_2\text{O} \end{array} \rightarrow \text{Ph-CH}_2\text{-CH}_2\text{-CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH} \\ \text{Ph-CH=CH-COOC}_2\text{H}_5$					
		$\frac{\text{DIBAL-H}}{-78^{\circ}\text{C}} \rightarrow \text{Ph-CH=C}$	H—CHO+C₂H₅OH		

DiBAL-H/(-78°C)

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

$$C_6H_5$$
—C-OCH<sub>3</sub>—DIBAL toluene 25°C  $\rightarrow$   $C_6H_5$ CH<sub>2</sub>OH

DIBAL toluene  $-78^{\circ}$ C  $\rightarrow$   $C_6H_5$ CHO

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

$$CH_3-C\equiv N - \begin{array}{c} \text{LiAIH}_4-THF \\ H_2O \end{array} \rightarrow CH_3-CH_2-NH_2$$

$$DIBAL \\ 25^{\circ}C \longrightarrow CH_3-CHO$$



(a)

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DiBAL-H

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### 人

#### 1.4 Miscellaneous reductions:

(i) By Red P & HI:

Used to prepare alkane from carbonyl compounds and alcohols generally.

(a) 
$$R - C - R \xrightarrow{\text{Red P} + \text{HI}} R - \text{CH}_2 - R$$

**(b)** CH<sub>3</sub>CH=O 
$$\xrightarrow{\text{Red P} + \text{HI}}$$
 CH<sub>3</sub>CH<sub>3</sub>

(c) R-CH<sub>2</sub>OH 
$$\xrightarrow{\text{Red P} + \text{HI}}$$
 R-CH<sub>3</sub>

(d) 
$$CH_3 - CH - CH_3 \xrightarrow{\text{Red P} + \text{HI}} CH_3CH_2CH_3$$

(ii) Meerwein-Pondorf-Verley reduction (MPV reduction) (Reduction by isopropyl alcohol and aluminium isopropoxide): It is selective reduction of ketones to alcohol, even in presence of other functional groups using Aluminium isopropoxide in isopropyl alcohol.

$$R - C - R' + CH_3 - CH - CH_3 \xrightarrow{Al(OCHMe_2)_3} R - CH - R' + CH_3 - C - CH_3$$

$$OH OOH OOH$$

(iii) Wolff-kishner reduction [NH<sub>2</sub>NH<sub>2</sub> / KOH]:

Used to prepane alkane from carbonyl compounds

Mechanism:

$$\begin{array}{c}
C = O + H_2 \\
\downarrow \\
Sp^2
\end{array}$$

$$C = N - NH_2 \xrightarrow{\ddot{B}}$$

$$C = N \xrightarrow{\Theta} NH$$

$$C = N \xrightarrow{\Theta} NH$$

$$C = N = NH$$

$$(A)$$

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} CH_2 \leftarrow BH \\ \downarrow \\ sp^3 \end{array} \end{array} \begin{array}{c} \stackrel{\oplus}{CH} \leftarrow N_2 \end{array} \begin{array}{c} \stackrel{\ominus}{CH} - N = N \leftarrow \stackrel{\oplus}{B} \\ -BH \end{array} \begin{array}{c} CH - N = NH \leftarrow \stackrel{\oplus}{BH} \\ -\ddot{B} \end{array}$$

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



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### Section (C): Oxidation-1

#### Introduction

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

or

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

$$RCH_2OH \xrightarrow{(O)} R-CH \xrightarrow{(O)} R-C-OH$$

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

Replacing hydrogen atoms by chlorine atoms is an oxidation

$$Ar-CH_3 \xrightarrow{(O)} ArCH_2CI \xrightarrow{(O)} ArCHCI_2 \xrightarrow{(O)} ArCCI_3$$

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

#### 2.1 Oxidation of alkanes

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

(i) Chemical oxidation with KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>: Alkanes are usually not affected by oxidising agents like KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. However, alkanes having tertiary hydrogen are oxidised by these oxidising agents to an alcohol.

$$\begin{array}{ccc} (CH_3)_3CH & \xrightarrow{KMnO_4} & (CH_3)_3COH \\ (Isobutane) & (Tertiary butyl alcohol) \end{array}$$

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

(ii) CH<sub>4</sub> + O<sub>2</sub> 
$$\xrightarrow{Mo_2O_3}$$
 HCHO + H<sub>2</sub>O

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

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

### 2.2 Oxidation of alkenes and alkynes

(i) Baeyer reagent [cold diluted to 1% alkaline KMnO<sub>4</sub> solution]:

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

Stereochemistry: syn addition.

Both-OH groups are add from same stereochemical side.

Stereochemistry: syn addition.

Ex. 
$$\begin{array}{c} -OH \\ H_2O \\ O \end{array}$$
 + MnO<sub>2</sub> \( + H\_2O \\ OH \\ cis-diol \\ \end{array}



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#### (ii) Osmium tetraoxide in alkaline medium [OsO<sub>4</sub> / NaHSO<sub>3</sub>]:

Similar to Baeyer's reagent.

OsO <sub>4</sub> /NaHSO <sub>3</sub>	OsO <sub>4</sub> /NaHSO <sub>3</sub>	OsO <sub>4</sub> /NaHSO <sub>3</sub>
Reactant	Alkene	Alkyne
Product	Vicinal diol	Diketone
	Δ ΔΩΗ	

Ex.

cis-Cyclohexane-1,2-diol

#### (iii) Oxidation with peroxyacids

An alkene is converted to an epoxide by a peroxyacid.

[a carboxylic acid that has an extra oxygen atom in a -O-O- (peroxy) linkage].

Peroxy benzoic acid

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

General Reaction 
$$> C = C < + R - C - OOH \longrightarrow -C - C - H^+, H_2O \longrightarrow -C - C - U - U OOH (anti addition)$$

Stereochemistry: anti addition in diol formation.

Ex. 
$$(i) \text{ per acid} \longrightarrow OH$$

Cyclohexene

Ex. 
$$(1) \text{ RCO}_3\text{H} \rightarrow H \rightarrow \text{CH}_3$$
  $(2) \text{ H}_3\text{O}^+ \rightarrow H \rightarrow \text{CH}_3$  + Enantiomer

Ex. 
$$(1) RCO_3H H H OH CH_3 OH CH_3$$

Meso

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



$$CH_{3} - C = C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C = C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - C - CH_{2} - CH = CH_{2}$$

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$$CH_{3} - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - CH_{2} - CH = CH_{2}$$

$$CH_{3} - C - CH_$$

#### (iv) Oxidation with acidic KMnO<sub>4</sub>[KMnO<sub>4</sub>/H<sup>+</sup>]: Stereochemistry: syn addition.

When alkene & alkyne heated with KMnO<sub>4</sub> in acidic or in alkaline medium; following changes takes place.

KMnO <sub>4</sub> /H <sup>+</sup>	KMnO <sub>4</sub> /H <sup>+</sup>	KMnO <sub>4</sub> /H <sup>+</sup>			
Reactant	.= CH <sub>2</sub> group	.= CH <b>R</b> group	.= CR <sub>1</sub> R <sub>2</sub> group	.≡ CH group	.≡ CR group
Product	CO <sub>2</sub>	RCOOH	O.= CR <sub>1</sub> R <sub>2</sub> group	CO <sub>2</sub>	RCOOH
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid

**Ex.** RCH=CH<sub>2</sub> 
$$\xrightarrow{[O]}$$
 CO<sub>2</sub> + H<sub>2</sub>O + RCOOH

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

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

w

Ex.

Ex. 
$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{(1) \ KMnO_4, \ NaOH, \ \Delta} CH_3-C=OH + HO-C-CH_2CH_3$$

$$\textbf{Ex.} \qquad \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}\equiv \text{CH} \xrightarrow{ \begin{array}{c} (1) \text{ KMnO}_4, \text{ NaOH, } \Delta \\ \hline \end{array} \end{array} } \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{OH} + \text{CO}_2\uparrow + \text{H}_2\text{O}$$

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

Like permanganate ozone cleaves double at very low temperature ( $\approx -78^{\circ}\text{C}$ ) bonds to give Ketones and aldehydes. However, ozonolysis is milder, and both Ketones and aldehydes can be recovered without further oxidation.

Reductive Ozonolysis Products (O <sub>3</sub> /Zn, H <sub>2</sub> O)							
O <sub>3</sub> /Zn, H <sub>2</sub> O	O <sub>3</sub> /Zn, H <sub>2</sub> O	O <sub>3</sub> /Zn, H <sub>2</sub> O	O <sub>3</sub> /Zn, H <sub>2</sub> O	O <sub>3</sub> /Zn, H <sub>2</sub> O	O <sub>3</sub> /Zn, H <sub>2</sub> O		
Reactant	= CH <sub>2</sub> group	= CH R group	= CR <sub>1</sub> R <sub>2</sub> group	≡ CH group	≡ CR group		
Product	НСНО	O = CHR group	O = CR <sub>1</sub> R <sub>2</sub> group	O     -C - CHO	diketone		
	Formaldehyde	Aldehyde	Ketone	Keto aldehyde	diketone		

Oxidative Ozonolysis Products							
$O_3/H_2O_2$	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	$O_3/H_2O_2$					
Reactant	=CH <sub>2</sub> group	=CH <b>R</b> group	= CR <sub>1</sub> R <sub>2</sub> group	≡CH group	≡CR group		
Product	ct CO <sub>2</sub> RCOOH		O=CR <sub>1</sub> R <sub>2</sub> group	CO <sub>2</sub>	RCOOH		
	Carbon dioxide	Carboxylic acid	Ketone	Carbon dioxide	Carboxylic acid		



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#### Reduction, Oxidation & Hydrolysis



- $C_8H_{10}$  (A)  $\xrightarrow{O_3, H_2O}$   $C_4H_6O_2$  Acid (B). Identify (A) and (B) in the above reaction Ex.
- Sol.
- Ex. A certain hydrocarbon has the formula C<sub>16</sub>H<sub>26</sub>. Ozonolysis followed by hydrolysis gives CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H and succinic acid as the only product. What is hydrocarbon
- Sol. DU = 4
  - Molecular structure must be:  $CH_3(CH_2)_4C = C - CH_2 - CH_2 - C = C(CH_2)_4 - CH_3$ *:*.

### Section (D): Oxidation-2

#### 2.3 Oxidation reaction of alcohols:

Oxidation Product of Alcohol-1							
	We	ak oxidisi	ng agent	Stror	ng oxidising a	gent	
	PCC*	PDC**	CrO₃/Inert medium	CrO <sub>3</sub> in water or H <sub>2</sub> CrO <sub>4</sub>	KMnO <sub>4</sub> /H <sup>+</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sup>+</sup>	
1º alcohol or primary alcohol	Aldehyde			Carboxylic acid			
2º alcohol or secondary alcohol	Ketone		Ketone				
3º alcohol or tertiary alcohol	Not oxidised		Not oxidised				

(a) Pyridinium Chloro Chromate (PCC)

- Pyridinium dichromate (PDC) = (2C<sub>6</sub>H<sub>5</sub>N.CrO<sub>3</sub>) (b)
- (c) Jones reagent = dilute chromic acid + acetone
- (d) Collin's Reagent = CrO<sub>3</sub> + pyridine, CH<sub>2</sub>Cl<sub>2</sub>
- MnO<sub>2</sub> = It is selectively oxidised reagent & oxidised allylic and benzylic alcohol into aldehyde (e) and ketone.

Oxidation Product of Alcohol-2				
Very-Very Strong oxidising agent Copper & he KMnO <sub>4</sub> /H+/Heat as oxidising a				
1º alcohol or Primary alcohol	Carboxylic acid	Aldehyde		
2º alcohol or Secondary alcohol	Mixture of Carboxylic acid	Ketone		
3º alcohol or tertiary alcohol	Mixture of Carboxylic acid	Dehydrate to alkene		

$$\begin{array}{c} CH_3-CH_2-CH_2-OH \xrightarrow{\qquad CU/\Delta \qquad } CH_3-CH_2-CH=O \quad \text{(dehydrogenation)} \\ CH_3-CH-CH_3 \xrightarrow{\qquad CU/\Delta \qquad } CH_3-C-CH_3 \qquad \text{(dehydrogenation)} \\ OH & O \\ CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ CH_3-C-CH_3 & CU/\Delta & CH_3-C=CH_2 \\ OH & O \\ \end{array}$$

#### Oppenaur's oxidation

- (i) This reaction involves the oxidation of a secondary alcohol with a ketone and base to the corresponding ketone.
- (ii) Commonly used bases are aluminium tert-butoxide.

 $R_2$ CHOH + (CH<sub>3</sub>)<sub>2</sub>CO  $\stackrel{Al(OCMe_3)_3}{\longleftarrow}$   $R_2$ CO + CH<sub>3</sub>CH(OH)CH<sub>3</sub> 2º Alcohol Acetone 2º Alcohol Ketone



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#### Rate of Oxidation:

(a) RCH<sub>2</sub>OH > R<sub>2</sub>CHOH > R<sub>3</sub>C-OH (inert)

(b) RCHO > RCH<sub>2</sub>OH

**Ex.** Write the product of following reactions.

$$CH_{3}-CH=CH-CH_{2}-CH_{2}-OH$$

$$OH$$

$$(X)$$

$$X \xrightarrow{K_{2}Cr_{2}O_{7}} CH_{3} - C - OH + HOOC - G - CH_{2} - G - OH$$

$$X \xrightarrow{PCC} CH_{3}-CH=CH-G - CH_{2}-CHO$$

$$X \xrightarrow{Oppenauer \ oxidation} CH_{3}-CH=CH-G - CH_{2}-CHO$$

$$X \xrightarrow{CrO_{3} / aq.} CH_{3}-CH=CH-G - CH_{2}-COOH$$

$$X \xrightarrow{MnO_{2}} CH_{3}-CH=CH-C - CH_{2}-CH_{2}-OH$$

$$X \xrightarrow{MnO_{2}} CH_{3}-CH=CH-C - CH_{2}-CH_{2}-OH$$

### 2.4 Oxidation reaction of carbonyl compound

### (i) Acidic KMnO<sub>4</sub> & K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as oxidising agent :

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

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

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

$$\begin{array}{c}
O \\
| \\
CH_3 - C - CH_3 + [O] \\
\hline
O r KMnO_4 + H^{\oplus}
\end{array}$$

$$\begin{array}{c}
CH_3COOH + CO_2 + H_2O \\
\hline
O r KMnO_4 + H^{\oplus}
\end{array}$$

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

 $\mathsf{CH}_3\mathsf{COCH}_2\mathsf{CH}_3 \xrightarrow{ \ \ [O] \ } \mathsf{2CH}_3\mathsf{COOH} \ ; \ \mathsf{CH}_3\mathsf{COCH}_2\mathsf{CH}_2\mathsf{CH}_3 \xrightarrow{ \ \ [O] \ } \mathsf{CH}_3\mathsf{COOH} + \mathsf{CH}_3\mathsf{CH}_2\mathsf{COOH}$ 

Mechanism (with Cr+6 oxidising agents):

(i) 
$$CrO_3 + H_2O \longrightarrow H_2CrO_4 = HO - Cr - OH$$

$$(ii) R - C - OH + H - O + Cr - OH \longrightarrow H_2O \longrightarrow H_$$



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#### Remarks:

- (1) Primary alcohol forms a chromate ester with chromic acid.
- (2) The chromate ester decomposes in  $2^{nd}$  slow step with the elimination of  $\alpha$ -hydrogen. So the first oxidation product, an aldehyde is obtained.
- (3) In **aqueous medium**, aldehyde forms a gemdiol (hydrated aldehyde). It is further oxidised to an acid by similar mechanism.
- (4) The following reactivity orders can be explained by this mechanism:

#### **Rate of Oxidation**

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

#### (ii) With Tollen's reagent :

RCHO (aldehydes) can be easily oxidised to RCOOH (except HCHO that can be oxidised to CO<sub>2</sub>) by weak oxidising agents like ammonical AgNO<sub>3</sub> (**Tollen's reagent**) hence they are better reducing agents.

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

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

#### (iii) With Fehling solution:

Aldehydes (except benzaldehyde) reduce **Fehling's** solution (Cu<sup>2+</sup> reduced to Cu<sup>+</sup>) which is an alkaline solution of cupric (Cu<sup>2+</sup>) ion complexed with tartrate ion.

RCHO + 
$$2Cu^{2+}$$
 +  $3OH^{-}$   $\xrightarrow{\Delta}$  RCOO<sup>-</sup> +  $Cu_2O$   $\downarrow$  red ppt. +  $2H_2O$ 

Aldehydes also reduce Benedict's solution (Cu<sup>2+</sup> complexed with citrate ion) to Cu<sup>+</sup>

#### (iv) With Benedict's solution

Sodium citrate + NaOH + NaHCO<sub>3</sub> + CuSO<sub>4</sub>

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

RCHO + Hg<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  RCOOH + 2HCl + 2Hg  $\downarrow$  grey ppt.

#### (v) With Schiff's reagent

Schiff's Reagent is aq. solution of following base decolourised by passing SO<sub>2</sub>.

Aldehyde restore pink colour of Schiff's reagent.

$$\begin{array}{c}
NH_2 \\
NH_2
\end{array}$$

$$\begin{array}{c}
NH_2 \\
NH_2
\end{array}$$

$$\begin{array}{c}
SO_2 \\
NH_2CI^{\Theta}
\end{array}$$
Colourless solution (Schiff's Reagent)
$$\begin{array}{c}
RCHO \\
\Delta
\end{array}$$
RCOOH + Pink colour

p-Rosaniline Hydrochloride

Magenta colour (Fuschin)

Ketons are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2, 4 DNP test.



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#### (vi) Oxidation by using SeO<sub>2</sub>

SeO<sub>2</sub> is a selective oxidizing agent with converts –CH<sub>2</sub>–group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.

#### (vii) Baeyer-villiger oxidation

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

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

#### **KETONES ARE DIFFICULT TO OXIDIZE:**

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

Me-C-Me 
$$\xrightarrow{[O]}$$
 MeCOOH + CO<sub>2</sub> + H<sub>2</sub>O

#### 2.5 Oxidation reaction of diols

### (i) HIO<sub>4</sub> oxidation : (Oxidation by lead acetate is similar to HIO<sub>4</sub> oxidation)

#### Mechanism:

#### Remarks

- (1) HIO<sub>4</sub> (periodic acid) oxidises vicinal diols (1, 2-diols).
- (2) It brings about oxidative cleavage of vicinal diol.
- (3) It can also oxidise  $\alpha$ -hydroxy carbonyl compound and  $\alpha$ -dicarbonyl compound.
- (4) HIO<sub>4</sub> forms a cyclic periodate ester as an intermediate. So the two –OH groups should have synconformation.
- (5) In cyclic diols only cis-vicinal diols are oxidised. Trans isomers are not oxidised.

#### Ex. General reaction

Ex.

$$R-CH \stackrel{+}{+} CH \stackrel{+}{+} CH - R \xrightarrow{HIO_4} R-CHO + HCOOH + R-CHO$$

$$OH OH OH$$

$$OH OH OH$$

$$O+HO$$



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### Section (E): Hydrolysis

#### Introduction:

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

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

#### (i) Hydrolysis of an ester:

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

$$\begin{bmatrix} R - C \\ O - R \\ ester linkage \end{bmatrix}$$

(a) Mild acidic medium: Dilute H<sub>2</sub>SO<sub>4</sub>, dilute HCl.

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

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

$$R - C \xrightarrow{O} R \xrightarrow{H \xrightarrow{O} H} R - C \xrightarrow{O} H$$

#### (ii) Hydrolysis of an anhydride:

The hydrolysis of acid anhydride produces two carboxylic acids.

$$R - \stackrel{\bigcirc}{C} \stackrel{\bigcirc}{\downarrow} \stackrel{\bigcirc}{\downarrow} \stackrel{\bigcirc}{\downarrow} \stackrel{\bigcirc}{\longrightarrow} R - \stackrel{\bigcirc}{C} \stackrel{\bigcirc}{\longrightarrow} H + R - \stackrel{\bigcirc}{C} \longrightarrow OH$$

#### (iii) Hydrolysis of acid halide:

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

$$R - C + CI \xrightarrow{H \nearrow O} H \xrightarrow{R} - C \longrightarrow OH + HCI$$

### (iv) Hydrolysis of acid amide:

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

$$R = C + NH_2 + O + R = C - OH + NH_3$$

#### (v) Hydrolysis of cyanides:

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

$$R-C \neq N \xrightarrow{3H} \xrightarrow{O} H, H^{+} R \xrightarrow{O} R \xrightarrow{O} C \xrightarrow{O} OH + NH_{3}$$



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#### (vi) Hydrolysis of isocyanides:

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

$$R - N \neq C$$
 3H  $\xrightarrow{O}$  H, H  $\xrightarrow{O}$  H  $\xrightarrow{O}$  H  $\xrightarrow{O}$  OH + RNH

Note: Alkylisocyanide does not hydrolyse in basic medium.

#### (vii) Hydrolysis of imine:

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

#### (viii) Hydrolysis of ethers:

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

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

### (ix) Hydrolysis of Vinyl ether:

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

### (x) Hydrolysis of phenyl ether:

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

### (xi) Hydrolysis of hemiacetals and acetals:

Hemiacetals and Acetals has R-O-R group.

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

### (xii) Hydrolysis of epoxide:

$$\xrightarrow{H_3O^+} \xrightarrow{OH}$$

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

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# **Exercise-1**

marked questions are recommended for Revision.

#### **PART - I: SUBJECTIVE QUESTIONS**

#### Section (A): Reduction-1

- **A-1.** Write the hydrogenation product of following species with H<sub>2</sub>/Pd.
  - (a) 1,2-Butadiene  $\xrightarrow{H_2/Pd}$

(b) trans-2-butene H<sub>2</sub>/Pd

(c) Benzaldehyde  $\xrightarrow{H_2/Pd}$ 

(d) 
$$\longrightarrow$$
  $CH_2$   $H_2/Pd$  1 eq. (Limonene)

A-2. Write the hydrogenation product of following species

(a) CH<sub>2</sub>=CH-CH<sub>2</sub>-CH<sub>2</sub>-C=C-CH<sub>3</sub> 
$$\xrightarrow{\text{H}_2(\text{excess})}$$

(b) 
$$CH_2=CH-CH_2-CH_2-C\equiv C-CH_3 \xrightarrow{H_2/Pd-BaSO_4}$$

- (c) Benzoylchloride  $\xrightarrow{H_2/Pd/BaSO_4}$
- **A-3.** Complete the following reactions:

(i) CH<sub>3</sub>–CH<sub>2</sub>–C≡C–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>6</sub>–CH<sub>2</sub>OH 
$$\xrightarrow{\text{(i) Na/NH}_3 (I)}$$
  $\xrightarrow{\text{(ii) H}_2O}$ 

A-4. Give reaction conditions (reagents and/or catalyst) for effecting the following conversions :

(i) 
$$CH_3-(CH_2)_7-C\equiv C-(CH_2)_7-CH_3$$
  $\longrightarrow$   $CH_3-(CH_2)_7$   $C=C$ 

$$CH_2)_7$$
  $C=C$   $CH_2$ 

$$(ii) \bigcirc CH_3 \longrightarrow CH_2-CH_3$$

### Section (B): Reduction-2

**B-1.** What is the product of each reaction

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#### B-2. Identify a and b, in the following reactions:

#### **B-3.** Complete the following reactions :

(a) 
$$\begin{array}{c} & & \\$$

#### Section (C): Oxidation-1

- C-1. ★ Write the structural formulas for the products formed when 3-heptyne reacts with KMnO<sub>4</sub> under?
  - (i) neutral condition at room temp.
  - (ii) alkaline or acidic condition at higher temp.

#### C-2. Complete the following reactions:

C-3. When t-Butanol and n-Butanol are separately treated with a few drops of dilute KMnO<sub>4</sub> in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and which is the brown precipitate. [IIT-JEE, 1994]

#### Section (D): Oxidation-2

**D-1.** Complete the following reactions :

(a) 
$$OH \longrightarrow A$$

(b) 
$$\begin{matrix} \mathsf{CH_2-CH-CH-CH_2} \\ \mathsf{I} \end{matrix} \begin{matrix} \mathsf{HIO_4} \end{matrix} \xrightarrow{\Delta}$$

(c) 
$$CH_3-C-CH-CH_3 \xrightarrow{HIO_4}$$
  $\Delta$ 

#### **D-2.** Complete the following reactions :

HO

OH

H'/KMnO<sub>4</sub>/
$$\Delta$$

PCC or Collin's reagent

R

MnO<sub>2</sub>/ $\Delta$ 

S



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#### D-3 Complete the following reactions:

(a) Ph-CH<sub>2</sub>-CH<sub>2</sub>-OH 
$$\xrightarrow{\text{Cu}/\Delta}$$
 ; (b) Ph-CH-CH<sub>3</sub>  $\xrightarrow{\text{Cu}/\Delta}$  ; (c) Ph-CH<sub>3</sub>  $\xrightarrow{\text{Cu}/\Delta}$   $\xrightarrow{\text{Cu}/\Delta}$  ; (d) Ph-CH<sub>3</sub>  $\xrightarrow{\text{Cu}/\Delta}$  ; (e) Ph-CH<sub>3</sub>  $\xrightarrow{\text{Cu}/\Delta}$   $\xrightarrow{\text{Cu}/\Delta$ 

#### Section (E): Hydrolysis

**E-1.** Write the products of following reaction

$$\longrightarrow 0 \longrightarrow H_3O^{\oplus}$$

- **E-2.** Write the products of following reaction
  - (a) CH<sub>3</sub>–C $\equiv$ N  $\xrightarrow{\text{H}_3\text{O}^+}$

- (b) CH<sub>3</sub>NC  $\xrightarrow{\text{H}_3\text{O}^+}$
- **E-3.** Reactant  $\xrightarrow{H_3O^+}$  CH<sub>3</sub>COOH + HCI
- **E-4.** CH<sub>3</sub>CONH<sub>2</sub>  $\xrightarrow{\text{H}_3\text{O}^+}$  Product is :
- **E-5.** The hydrolysis of acid anhydride produces ......

E-6.  $\begin{array}{c} NHCOCH_3 \\ \hline \\ NO_2 \end{array}$  Product is :

**E-7.** Reactant (C<sub>3</sub>H<sub>6</sub>O)  $\xrightarrow{\text{H}_3\text{O}^+}$  CH<sub>3</sub>CHO + CH<sub>3</sub>OH

### **PART - II: ONLY ONE OPTION CORRECT TYPE**

### Section (A): Reduction-1

- **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  $H_2 / Ni$ .



(B)

(C)

(D)

**A-3.** An organic compound with molecular formula  $C_6H_{10}$  is not reduced by  $H_2$  / Pd / BaSO<sub>4</sub>. From the given options, the compounds may be :

(A) I, II (B) I, III

III (C) II, IV

|V (D) II, II

- **A-4.**  $H_{3}C C C_{2}H_{5}$   $C_{2}H_{5} \longrightarrow X, x \text{ is}$   $C_{3}H_{5} \longrightarrow CH_{3}$ 
  - (A) Only (R,R) product

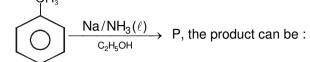
(B) Only (S,S) product

(C) Meso compound

(D) Racemic mixture



A-5.

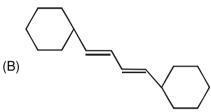






A-6.





(C) Both (A) and (B)

- (D) None of these
- A-7. Which of the following reagents converts both acetaldehyde and acetone to alkanes?
  - (A) Ni/H<sub>2</sub>
- (B) LiAlH<sub>4</sub>
- (C) I<sub>2</sub>/NaOH
- (D) Zn-Hg/conc.HCl

- **A-8.** Stephen reduction (SnCl<sub>2</sub>/ HCl) converts cyanides to
  - (A) Aldehydes
- (B) Ketones
- (C) Amines
- (D) Acids

#### Section (B): Reduction-2

- B-1.2 When benzoic acid is treated with LiAlH4, it forms
  - (A) Benzaldehyde
- (B) Benzyl alcohol
- (C) Benzene
- (D) Toluene

**B-2.** Name the reaction

$$Me- \equiv \begin{array}{c} O \\ \parallel \\ -C-Me \end{array} \xrightarrow[OH]{Al(OCHMe_2)_3} Me- \equiv -CH-Me$$

$$OH \\ \downarrow \\ CH_3-CH-CH_3 \\ \downarrow \\ OH \end{array}$$

- (A) Meervein-Ponndorf-verley reduction
- (B) Wolff-kishner reduction
- (C) Bouveault-Blanc reduction
- (D) Stephen's reduction
- **B-3.** R-C $\equiv$ N  $\xrightarrow{\text{DIBAL-H, H}_2\text{O}}$  Product

The product formed is:

- (A) R-CO-NH<sub>2</sub>
- (B) R-CH<sub>2</sub>-NH<sub>2</sub>
- (C) R-CHO
- (D) R-CH<sub>2</sub>-NO<sub>2</sub>

**B-4.** B  $\leftarrow$  NaBH<sub>4</sub>  $\longrightarrow$  CH<sub>2</sub>-CHO  $\xrightarrow{\text{H}_2/\text{Pd}}$  A

A and B are respectively:



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**B-5.** In the following reaction  $C_2H_5OC_2H_5 + 4H$ 

 $\xrightarrow{\text{Red P+HI}}$  2X + H<sub>2</sub>O, X is

- (A) Ethane
- (B) Ethylene

Y + R' -OH

diisobutyl

- (C) Butane
- (D) Propane

aluminium hydride – 78°C

B-6.

The product Y is

(A) R-CH<sub>2</sub>-OH

R-CO-O-R' -

- (B) R-CHO
- (C) R-COOH
- (D) R-CH<sub>3</sub>

B-7. What are A and B in the following?

$$Q \xleftarrow{\text{Raney Ni, H}_2} \bigcirc \longrightarrow \bigcirc \bigcirc \longrightarrow \bigcirc$$

(D) 
$$P = \bigcap_{Q \in \mathcal{Q}} OH$$
 and  $Q = \bigcap_{Q \in \mathcal{Q}} OH$ 

### Section (C): Oxidation-1

- C-1. Baeyer's reagent decolourises which of the following :
  - (A) Alkane

(B) Alkene only

(C) Alkene and alkyne both

- (D) Benzene
- **C-2.** Ethanol on reaction with alkaline KMnO<sub>4</sub> gives:
  - (A) Ethanal
- (B) Glyoxal
- (C) Acetic acid
- (D) Acrolein.

**C-3.** 1-Butyne  $\xrightarrow{\mathsf{KMnO}_4/\Delta} \mathsf{X} + \mathsf{Y}$ 

Identify X and Y?

(A) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH + O<sub>2</sub>

- (B) CH<sub>3</sub>CH<sub>2</sub>COOH
- (C) CH<sub>3</sub>CH<sub>2</sub>COOH + CO<sub>2</sub> + H<sub>2</sub>O
- (D) CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> + HCOOH
- C-4. An alkyne  $C_7H_{12}$  when reacted with alkaline KMnO<sub>4</sub> followed by acidification by HCl, yielded a mixture of  $CH_3 CH COOH$  &  $CH_3CH_2COOH$ . The alkyne is -

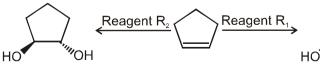
(A) 3-hexyne

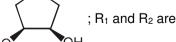
(B) 2-methyl-2-hexyne

(C) 2-methyl-3-hexyne

(D) 3-methyl-2-hexyne

C-5.





- (A) Cold alkaline KMnO<sub>4</sub>, OsO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>
- (B) Cold alkaline KMnO<sub>4</sub>, HCO<sub>3</sub>H & H<sub>3</sub>O<sup>+</sup>
- (C) Cold alkaline KMnO<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>CO<sub>3</sub>H
- (D) C<sub>6</sub>H<sub>5</sub>CO<sub>3</sub>H, HCO<sub>3</sub>H

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#### Section (D): Oxidation-2

- D-1. Glucose as well as fructose are oxidized by periodic acid. The number of moles of HCOOH formed from each mole of glucose and fructose are
  - (A) 5 and 5
- (B) 5 and 4
- (C) 5 and 3
- (D) 4 and 3
- D-2. Secondary alcohols on heating with copper at 300°C give
  - (A) Alkenes
- (B) Aldehydes
- (C) Ketones
- (D) tert-alcohols
- D-3. The reagent, with which both acetaldehyde and acetone react easily is:
  - (A) Tollens reagent
- (B) Schiffs reagent
- (C) H<sub>2</sub>/Ni
- (D) Fehling's solution
- D-4. Which of the following compounds is resistant to periodic acid oxidation?







#### Section (E): Hydrolysis

- E-1. What product is obtained when Benzenecarbonitrile is hydrolysed.
  - (A) Benzoylchloride

(B) Benzenecarboxamide

(C) Benzaldehyde

- (D) Benzoic acid
- E-2. The acid catalysed hydrolysis products in the following reaction are -

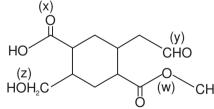
$$\bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \longrightarrow P + C$$

- COOH  $\mathrm{CH_2-OH}$  CHO  $\mathrm{CH_2-OH}$  COOH (B) | & | (C) | & | (D) | COOH CH\_2-OH CHO  $\mathrm{CH_2-OH}$

E-3. Product obtained in above reaction are:

#### **PART - III: MATCH THE COLUMN**

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



			•
	Reagents-I		Functional group oxidised / reduced-II
(A)	CrO <sub>3</sub> / Pyridine / CH <sub>2</sub> Cl <sub>2</sub>	(p)	W
(B)	NaBH <sub>4</sub>	(q)	Z
(C)	Na / C <sub>2</sub> H <sub>5</sub> OH	(r)	X
(D)	CrO₃ / H+	(s)	Υ

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#### 2. Match the following column:

	Column-I			Column-II
	Reactant and reagents			Products
(A)	Ph COOMe _	LiAlH <sub>4</sub> / ether	(p)	Ph OH + MeOH
(B)	Ph COOMe _	(i) DIBAL−H (−78°C) (ii) H <sub>2</sub> O	(q)	Ph CHO + MeOH
(C)	Ph COOMe _	$\stackrel{NaBH_4}{\longrightarrow}$	(r)	Me CHO + MeOH
(D)	Me COOMe _	$H_2+Pd/C$	(s)	Me COOMe
_			(t)	No reaction

# Exercise-2

Marked questions are recommended for Revision.

### PART - I: ONLY ONE OPTION CORRECT TYPE

1. A 
$$\leftarrow$$
 H<sub>2</sub>/Ni HO—C—H Heating with HI  $\rightarrow$  B, H—C—OH H—C—OH H—C—OH H—C—OH CH<sub>2</sub>OH

A and B can be:

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

2. 
$$H_3C - C = C - CH_2 - CH_3$$

$$(X) \qquad H_3C - C = C - CH_2 - CH_3$$

$$(Y) \qquad H_3C - C = C - CH_2 - CH_3$$

$$H_3C - C = C - CH_2 - CH_3$$

In the above reaction the using reagents X and Y are;

- (A) Na/ liq. NH<sub>3</sub> for X
- (B) H<sub>2</sub>, Pd/ BaSO<sub>4</sub> for Y
- (C) BH<sub>3</sub>-THF + CH<sub>3</sub>COOH for Y
- (D) All of these are correct.



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#### 4.3 Consider reduction of 2-butanone.

B 
$$\leftarrow$$
 NaBD<sub>4</sub> 2-butanone  $\rightarrow$  A, B and C are respectively.

NaBH<sub>4</sub>  $\rightarrow$  C

(A) 
$$CH_3CHCH_2CH_3$$
 in all cases  $I$  OH

#### Identify (P) and (Q) respectively in the given reaction: 5.

$$(P) \xleftarrow{\text{Acidic}}_{\text{KMnO}_4} \xrightarrow{\text{PCC}, \text{CH}_2\text{Cl}_2} (Q)$$

#### 6. Which of the following sets of compounds cannot turn clear orange solution of CrO<sub>3</sub> / aq. H<sub>2</sub>SO<sub>4</sub> to greenish opaque solution



8. The product which is not formed in the following reaction:

$$\begin{array}{c|cccc} \operatorname{CH_3} & \operatorname{CH_3} \\ \mid & \mid & | \\ \operatorname{Ph-C-CH-CH-CH-CH_2OH} & \xrightarrow{\quad \operatorname{HIO_4} \text{ (excess)} \\ \mid & \mid & \mid \\ \operatorname{OH} \text{ OH} & \operatorname{OH} \end{array}$$

$$CH_3$$
 | (C) OHC – CH – CH $_2$ OH

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

(A) LiAlH<sub>4</sub>

10.

$$0 \qquad 0 \qquad 0 \qquad \xrightarrow{\mathsf{H}_3\mathsf{O}^+} \mathsf{P} + \mathsf{O}$$

P and Q are respectively.

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

#### PART - II: SINGLE AND DOUBLE VALUE INTEGER TYPE

Find the value of x + y.

2. Number of reactions which give alcohol as product.

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#### Reduction, Oxidation & Hydrolysis

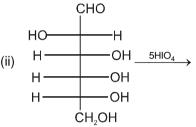


#### 3.3 How many reactions are correct?

$$(i) \qquad \begin{array}{c} \text{dil. KMnO}_4/\text{HO}^{\ominus} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \end{array} \qquad \begin{array}{c} \text{OH} \\ \text{HIO}_4 \\ \text{OH} \\ \end{array} \qquad \begin{array}{c} \text{COOH} \\ \text{KMnO}_4/\text{HO}^{\ominus}/\Delta \\ \text{OH} \\ \end{array} \qquad \begin{array}{c} \text{COOH} \\ \text{KMnO}_4/\text{HO}^{\ominus}/\Delta \\ \text{OH} \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\$$

(i) 
$$HO \longrightarrow H$$
  $OH$   $OH$   $CH_2OH$ 

4.



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

#### How many of following reactions are hydrolysis reactions? 5.

(1) CH<sub>3</sub>–COOH + C<sub>2</sub>H<sub>5</sub>OH 
$$\stackrel{H^+}{\longrightarrow}$$

(2) 
$$\begin{matrix} CH_3-C-OC_2H_5 & \xrightarrow{H_3O^+} \\ O & \\ O \end{matrix}$$
(4) 
$$CH_3-C\equiv N & \xrightarrow{H_3O^+}$$

$$(3) \xrightarrow{CH_3-C-NH_2} \xrightarrow{H_3O^+}$$

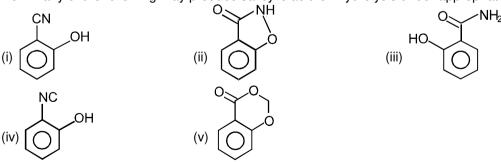
(5) 
$$CH_3-O C CH_3 \longrightarrow CH_3O^+ \longrightarrow CH_3$$

(6) CH<sub>3</sub>–CH=NH 
$$\xrightarrow{\text{H}_3\text{O}^+}$$

(7) CH<sub>2</sub>=CH–O–C<sub>2</sub>H<sub>5</sub> 
$$\xrightarrow{\text{H}_3O^+}$$

(8) 
$$OC_2H_5$$
  $H_3O^+$ 

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





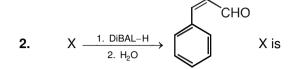
### PART - III: ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- 1. Which of the following catalysts is/are used for partial reduction of alkyne?
  - (A) Na/NH<sub>3</sub>(ℓ)

(B) Ni<sub>2</sub>B or P-2catalyst

(C) Lindlar catalyst

(D) Rossenmund catalyst





Identify the possible structure of X and Y 3.3

$$C_{9}H_{12}O \xrightarrow{resolution} d + \ell$$

$$K_{2}Cr_{2}O_{7}/H_{2}SO_{4} \Rightarrow Blue green salt to other product.$$

other products

		+ other products
	X	Υ
(A)	Ph – CH – CH <sub>2</sub> – CH <sub>3</sub>   OH	Ph – CH <sub>2</sub> – CH – CH <sub>3</sub>   OH
(B)	CH <sub>3</sub>   Ph – CH – CH <sub>2</sub> – OH	CH <sub>3</sub>     Ph – C – CH <sub>3</sub>     OH
(C)	OH     CH - CH <sub>3</sub>   CH <sub>3</sub>	Ph – CH <sub>2</sub> – CH – CH <sub>3</sub>   OH
(D)	CH <sub>3</sub>     Ph – C – CH <sub>2</sub> – OH     H	Ph – CH – CH <sub>2</sub> – CH <sub>3</sub>   OH

- → B + C; (B) and (C) both give +ve iodoform test. Compound (A) is: 4. (A)
  - (A) CH<sub>3</sub>-CH=CH-O-CH<sub>2</sub>-CH<sub>3</sub>

(D) None of these



### **PART - IV: COMPREHENSION**

Read the following passage carefully and answer the questions.

#### Comprehension # 1

$$(P) \xrightarrow{\text{(ii) LiAIH}_4} O \xrightarrow{\text{Pd/H}_2} (Q)$$

$$\text{NaBD}_4 \text{ EtOH}$$

$$(R)$$

1. (P) and (Q) respectively are



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#### 2. (R) is :

$$(A) \quad OD \quad O$$

$$OH \quad O$$

$$(C) \quad D$$

$$(B) \xrightarrow{D} OH$$

$$OH OH$$

$$OD OD$$

$$OD OD$$

$$(D) \longrightarrow OD$$

#### Comprehension # 2

Me
$$\equiv - Et \xrightarrow{H_2 + Pd - BaSO_4} (C) \xrightarrow{alkaline \\ KMnO_4} (D) \xrightarrow{HIO_4} (E)$$

$$\downarrow Na + liq. NH_3 \\ + EtOH \Rightarrow (F) \xrightarrow{alkaline \\ KMnO_4} (G)$$

#### 3.3 The compound (C) is:

(A) 
$$Et$$
  $Et$  (B)  $Et$   $Et$  (C)  $Et - = -Et$  (D) Both (A) and (B)

$$(B) \xrightarrow{Et} \overset{H}{\underset{Et}{H}}$$

(C) Et 
$$- \equiv -$$
 Et

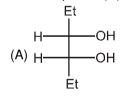
#### 4.3 The compound (F) is:

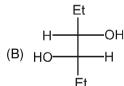
(A) 
$$Et$$
  $Et$   $(B)$   $Et$   $(C)$   $Et - = -Et$   $(D)$  Both (A) and (B)

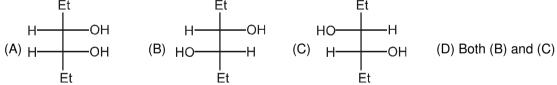
$$(B) \xrightarrow{Et} \overset{H}{\underset{Et}{H}}$$

(C) Et 
$$- \equiv -$$
 Et

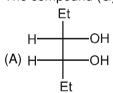
#### 5.3 The compound (D) is:

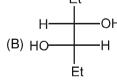


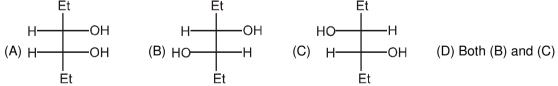




#### The compound (G) is: 6.29







#### 7.3 The compound (E) is:

- (A) Two moles of Me CHO. (B) Two moles of Me COOH. (C) One mole of (A) and one mole of (B) (D) No reaction.

# 人

#### Comprehension #3

Answer Q.8, Q.9 and Q.10 by appropriately matching the information given in the three columns of the following table.

Column-1, 2 and 3 contains starting material, reaction condition and type of reaction respectively.					
00.0	Column-1	1	Column-2	1,7000	Column-3
(I)	CH <sub>3</sub> -C-O-C-CH <sub>3</sub>         O O	(i)	KMnO <sub>4</sub>	(P)	Oxidation
(II)	OPh	(ii)	Cu/Δ	(Q)	Reduction
(III)	CH <sub>3</sub> I CH <sub>3</sub> -C-OH I CH <sub>3</sub>	(iii)	H <sub>3</sub> O <sup>+</sup>	(R)	Hydrolysis
(IV)		(iv)	LiAlH <sub>4</sub>	(S)	Dehydration

**8.** Which of the following combination of reaction result in formation of an alkene.

(A) (I) (iv) Q

(B) (III) (i) S

(C) (III) (ii) S

(D) (II), (iii) R

9. The only correct combination in which product gives position test with sodium bicarbonate is -

(A) (III) (ii) P

(B) (I) (iii) Q

(C) (II) (iii) R

(D) (IV) (i) P

**10.** The reaction and condition which obey bimolecular nucleophilic substitution reaction with respect to tetrahedral intermediate is -

(A) (IV) (i) P

(B) (I) (iv) Q

(C) (II) (iii) R

(D) (III) (ii) S

# Exercise-3

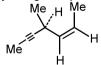
### PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. What would be the major product in the following reaction?

[IIT-JEE 2000(M), 1/100]

$$CH_3 \xrightarrow{H_2} CH_3$$
 Lindlar catalyst

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



[IIT-JEE 2001(S), 1/35]

- (A) an optically active compound
- (B) an optically inactive compound

(C) a racemic mixture

- (D) a diastereomeric mixture
- 3. 1-Propanol and 2-Propanol can be best distinguished by:

[IIT-JEE 2001(S), 1/35]

- (A) oxidation with alkaline KMnO<sub>4</sub> followed by reaction with Fehling solution
- (B) oxidation with acidic dichromate followed by reaction with Fehling solution
- (C) oxidation by heating with copper followed by reaction with Fehling solution
- (D) oxidation with concentrated H<sub>2</sub>SO<sub>4</sub> followed by reaction with Fehling solution



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<sup>\*</sup> Marked Questions may have more than one correct option.



**4. Assertion**: Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds [IIT-JEE-2001(S), 1/35]

Reason: It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates

- (A) Assertion is True, Reason is True; Reason is a correct explanation for Assertion.
- (B) Assertion is True, Reason is True; Reason is NOT a correct explanation for Assertion.
- (C) Assertion is True, Reason is False.
- (D) Assertion is False, Reason is True.
- **5.** Five isomeric para-disubstituted aromatic compounds A to E with molecular formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> were given for identification. Based on the following observations, give structures of the compounds.
  - (i) Both A and B form a silver mirror with Tollen's reagent; also B gives a positive test with FeCl<sub>3</sub> solution.

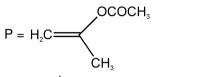
Q =

- (ii) C gives positive iodoform test.
- (iii) D is readily extracted in aqueous NaHCO<sub>3</sub> solution.
- (iv) E on acid hydrolysis gives 1, 4-dihydroxybenzene.

[IIT-JEE-2002(M), 5/60]

**6.** The product of acid hydrolysis of P and Q can be distinguished by :

[IIT-JEE 2003(S), 3/84]



- (A) Lucas reagent
- (C) Fehling's solution

- (B) 2,4-DNP
- (D) NaHSO<sub>3</sub>
- 7. Amongst the following the reagent that would convert 2-hexyne into trans-2-hexene is

[IIT-JEE 2004(S), 3/84]

, ОСОСН3

- (A) H<sub>2</sub>.Pt / O<sub>2</sub>
- (C) Li / NH<sub>3</sub> / C<sub>2</sub>H<sub>5</sub>OH

- (B) H<sub>2</sub>.Pd / SO<sub>4</sub><sup>2</sup>-
- (D) NaBH<sub>4</sub>
- **8.** A compound  $P(C_5H_{10}O)$  reacts with dilute sulfuric acid to give Q and R as the final products. This reaction is about  $10^{15}$  times faster than of ethylene. Both Q and R give positive iodoform test.
  - (a) Identify the structures of P, Q and R.
  - (b) Rationalize the extraordinary reactivity of P.

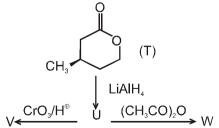
[IIT-JEE-2004(M), 2/60]

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

[IIT-JEE 2009, 8/160]

	Column I		Column II
(A)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN	(p)	Reduction with Pd-C/H <sub>2</sub>
(B)	CH₃CH2OCOCH3	(q)	Reduction with SnCl <sub>2</sub> /HCl
(C)	CH <sub>3</sub> –CH=CH–CH <sub>2</sub> OH	(r)	Development of foul smell on treatment with chloroform and alcoholic KOH.
(D)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	(s)	Reduction with diisobutylaluminium hydride (DIBAL-H)
		(t)	Alkaline hydrolysis

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



[IIT-JEE 2012, 4/136]

- (A) T is soluble in hot aqueous NaOH
- (B) U is optically active
- (C) Molecular formula of W is C<sub>10</sub> H<sub>18</sub>O<sub>4</sub>
- (D) V gives effervescence on treatment with aqueous NaHCO3



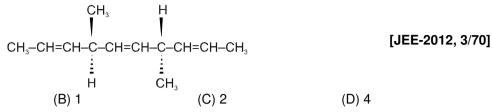
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(A) 0

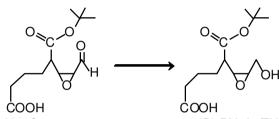


The number of optically active products obtained from the complete ozonolysis of the given compound 11.



- 12. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are idependently reacted with NaBH<sub>4</sub> (Note: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are [JEE(Advance)-2014, 3/120]
- 13.\* Reagent(s) which can be used to bring about the following transformation is(are):

[JEE(Advance)-2016, 3/124]



- (A) LiAlH<sub>4</sub> in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O
- (C) NaBH<sub>4</sub> in C<sub>2</sub>H<sub>5</sub>OH

- (B) BH<sub>3</sub> in THF
- (D) Raney Ni/H2 in THF

### PART - II: JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

#### JEE(MAIN) OFFLINE PROBLEMS

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

(1) Zn-HCl

- (2) Sn-HCl
- (3) Zn-Hg
- [AIEEE-2003, 3/225] (4) Pd/H<sub>2</sub>
- 2. When CH<sub>2</sub>=CH–COOH is reduced with LiAlH<sub>4</sub>, the compound obtained will be: (1) CH<sub>3</sub>–CH<sub>2</sub>–COOH
  - (2) CH<sub>2</sub>=CH-CH<sub>2</sub>OH (3) CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH
- [AIEEE-2003, 3/225] (4) CH<sub>3</sub>-CH<sub>2</sub>-CHO.
- 3. Which one of the following is reduced with Zn, Hg and HCl acid to give the corresponding hydrocarbon? [AIEEE-2004, 3/225]
  - (1) Ethyl acetate
- (2) Butan-2-one
- (3) Acetamide
- (4) Acetic acid
- 4. The best reagent to convert pent-3-en-2-ol into pent-3-ene-2-one is
- [AIEEE-2005, 3/225]

- (1) Pyridinium chloro-chromate
- (2) Chromic anhydride in glacial acetic acid

(3) Acidic dichromate

- (4) Acidic permanganate
- 5. The hydrocarbon which can react with sodium in liquid ammonia is:
- [AIEEE-2008, 3/105]

(1) CH<sub>3</sub>CH<sub>2</sub>C≡CH

(2) CH<sub>3</sub>CH=CHCH<sub>3</sub>

(3) CH<sub>3</sub>CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>3</sub>

- (4) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- In the following sequence of reactions, the alkene affords the compound 'B' 6. [AIEEE-2008, 3/105]  $CH_3CH=CHCH_3 \xrightarrow{\ O_3\ } A \xrightarrow{\ H_2O\ } B,$  The compound B is :
  - (1) CH<sub>3</sub>COCH<sub>3</sub>
- (2) CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub>
- (3) CH<sub>3</sub>CHO
- (4) CH<sub>3</sub>CH<sub>2</sub>CHO
- 7. 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
- 8. 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



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**9.** 2-Hexyne gives trans-2-Hexene on treatment with :

[AIEEE-2012, 4/120]

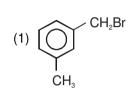
- (1) Pt/H<sub>2</sub>
- (2) Li / NH<sub>3</sub>
- (3) Pd/BaSO<sub>4</sub>
- (4) Li AlH<sub>4</sub>
- 10. In the given transformation, which the following is the most appropriate reagent ? [AIEEE-2012, 4/120]

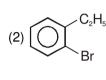


(1) NH<sub>2</sub>NH<sub>2</sub>, ⊖H

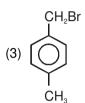
- Reagent →
- (3) Na, Lig, NH<sub>3</sub>
- (4) NaBH<sub>4</sub>
- 11. Compound (A), C<sub>8</sub>H<sub>9</sub>Br, gives a white precipitate when warmed with alcoholic AgNO<sub>3</sub>. Oxidation of (A) gives an acid (B), C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>. (B) easily forms anhydride on heating. Identify the compound (A).

[JEE(Main)-2013, 4/120]





(2) Zn-Hg/HCI



- 12. The most suitable reagent for the conversion of R–CH<sub>2</sub>–OH  $\rightarrow$  R–CHO is : [JEE(Main)-2014, 4/120]
  - (1) KMnO<sub>4</sub>

(2) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

(3) CrO<sub>3</sub>

- (4) PCC (Pyridinium Chlorochromate)
- **13.** In the following sequence of reactions :

Toluene 
$$\xrightarrow{\text{KMnO}_4}$$
 A  $\xrightarrow{\text{SOCl}_2}$  B  $\xrightarrow{\text{H}_2/\text{Pd}}$  C

the product C is:

- (1) C<sub>6</sub>H<sub>5</sub>COOH
- (2) C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>
- (3) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH
- [**JEE(Main)-2015, 4/120**] (4) C<sub>6</sub>H<sub>5</sub>CHO

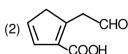
[JEE(Main)-2017, 4/120]

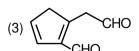
- $(3) O_6 \cap_5 O \cap_2 O \cap (4) O_6 \cap_5 O \cap O$
- **14.** The correct sequence of reagents for the following conversion will be :

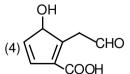
- (1) CH<sub>3</sub>MgBr, H<sup>+</sup>/CH<sub>3</sub>OH, [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>OH<sup>-</sup>
- (2) CH<sub>3</sub>MgBr, [Ag(NH<sub>3</sub>)<sub>2</sub>]+OH-, H+/CH<sub>3</sub>OH
- (3) [Ag(NH<sub>3</sub>)<sub>2</sub>]+OH-, CH<sub>3</sub>MgBr, H+/CH<sub>3</sub>OH
- (4) [Ag(NH<sub>3</sub>)<sub>2</sub>]+OH-, H+/CH<sub>3</sub>OH, CH<sub>3</sub>MgBr
- **15.** The major product obtained in the following reaction is:

[JEE(Main)-2017, 4/120]

$$\begin{array}{c} O \\ \hline \\ COOH \end{array}$$







- **16.** The trans-alkenes are formed by the reduction of alkynes with :
- [JEE(Main)-2018, 4/120]

(1) Na/liq. NH<sub>3</sub>

(2) Sn - HCI

(3) H2-Pd/C, BaSO4

(4) NaBH<sub>4</sub>

#### **JEE(MAIN) ONLINE PROBLEMS**

1. The reagent needed for converting

 $Ph-C=C-Ph \longrightarrow Ph \setminus Ph$ 

[JEE(Main) 2014 Online (11-04-14), 4/120]

(1) Cat. Hydrogenation

(2) H<sub>2</sub>/Lindlar Cat.

(3) Li/NH<sub>3</sub>

- (4) LiAlH<sub>4</sub>
- 2. The gas liberated by the electrolysis of Dipotassium succinate solution is:

[JEE(Main) 2014 Online (11-04-14), 4/120]

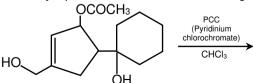
- (1) Ethane
- (2) Ethyne
- (3) Ethene (4) Propene
- 3. Bouveault-Blanc reduction reaction involves:
- [JEE(Main) 2016 Online (09-04-16), 4/120]
- (1) Reduction of an anhydride with LiAlH<sub>4</sub>.
- (2) Reduction of an ester with Na/C<sub>2</sub>H<sub>5</sub>OH.
- (3) Reduction of a carbonyl compound with Na/Hg and HCl.
- (4) Reduction of an acyl halide with H<sub>2</sub>/Pd.
- 4. The reagent(s) required for the following conversion are: [JEE(Main) 2018 Online (15-04-18), 4/120]

$$EtO_2C \xrightarrow{CO_2H} \xrightarrow{OH} \xrightarrow{OH} CHO$$

- (1) (i) NaBH<sub>4</sub> (ii) Raney Ni/H<sub>2</sub> (iii) H<sub>3</sub>O<sup>+</sup>
- (2) (i) LiAlH<sub>4</sub> (ii) H<sub>3</sub>O<sup>+</sup>
- (3) (i) B<sub>2</sub>H<sub>6</sub> (ii) DIBAL-H (iii) H<sub>3</sub>O<sup>+</sup>
- (4) (i) B<sub>2</sub>H<sub>6</sub> (ii) SnCl<sub>2</sub>/HCl (iii) H<sub>3</sub>O<sup>+</sup>
- 5. The main reduction product of the following compound with NaBH<sub>4</sub> in methanol is:

[JEE(Main) 2018 Online (15-04-18), 4/120]

- 6. When 2-butyne is treated with H<sub>2</sub>/Lindlar's catalyst, compound X is produced as the major product and when treated with Na/lig. NH<sub>3</sub> it produces Y as the major product. Which of the following statements is [JEE(Main) 2018 Online (15-04-18), 4/120] correct?
  - (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 lower dipole moment and lower boiling point than Y.
  - (4) Y will have higher dipole moment and lower boiling point than X.
- 7. The major product formed in the following reaction is: [JEE(Main) 2018 Online (15-04-18), 4/120]





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8. The major product of following reaction is:

 $R-C\equiv N \xrightarrow{(1) AIH(i-Bu)_2} ?$ 

- (1) RCONH<sub>2</sub>
- (2) RCH<sub>2</sub>NH<sub>2</sub>
- (3) RCHO
- (4) RCOOH

[JEE(Main) 2019 Online (09-01-19), 4/120]

9. The major product 'X' formed in the following reaction is: [JEE(Main) 2019 Online (10-01-19), 4/120]

$$\xrightarrow{\text{NaBH}_4} X$$
MeOH

CH<sub>2</sub>CH<sub>2</sub>OH

10. The major product of the following reaction is:

> NaBH<sub>4</sub> CH<sub>3</sub>N<sub>3</sub>

- (1) CH<sub>3</sub>NH
- (3) CH<sub>3</sub>N.

[JEE(Main) 2019 Online (10-01-19), 4/120]

[JEE(Main) 2019 Online (11-01-19), 4/120]

11. The major product of the following reaction is:

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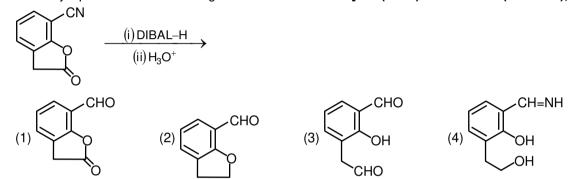


12. The major product obtained in the following reaction is: [JEE(Main) 2019 Online (11-01-19), 4/120]

**13.** The major product of the following reaction is :

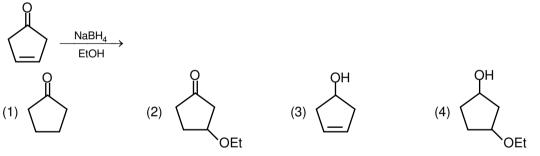
[JEE(Main) 2019 Online (12-01-19), 4/120]

ÓН



**14.** The major product of the following reaction is :

[JEE(Main) 2019 Online (12-01-19), 4/120]



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### **Answers**

### **EXERCISE - 1**

#### PART - I

- **A-1.** (a) Butane
- (b) Butane
- (c) Ph-CH<sub>2</sub>-OH

A-2.

(a) 
$$CH_2=CH-CH_2-CH_2-C=C-CH_3 \xrightarrow{H_2(excess)} CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

(b)  $CH_2=CH-CH_2-CH_2-C\equiv C-CH_3$ 

(c) Benzaldehyde (Benzene carbaldehyde)

A-3.

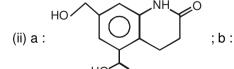
(i) 
$$CH_3-CH_2-CH = CH - (CH_2)_7-CH_2-OH_3$$

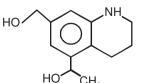


**A-4.** (i) H<sub>2</sub>/Pd-BaSO<sub>4</sub>

- (ii) In this conversion -CO- converts into  $-CH_2-$  which can be achieved by any one of the following reagents :
- (a)  $NH_2-NH_2/KOH/\Delta$
- (b) Zn-Hg, Conc HCl,  $\Delta$
- (c) Red P + HI
- **B-1.** LiAlH<sub>4</sub> and NaBH<sub>4</sub> both gives same products with carbonyl compounds.
  - (i) Ph-CH<sub>2</sub>-OH

B-2.







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$$(b) \xrightarrow{\mathsf{Red} \ \mathsf{P} \ + \ \mathsf{HI}} \longrightarrow \mathsf{CHO}$$

(ii) CH<sub>3</sub>CH<sub>2</sub>COOH + HOOCCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

**C-3.** t-Butanol is not oxidised by dilute  $KMnO_4$ , so it does not give brown-black precipitate of  $MnO_2$ . n-Butanol is oxidised with dil  $KMnO_4$  and  $MnO_4$ -is converted to brown-black precipitate of  $MnO_2$ .

Me OH Dil. KMnO<sub>4</sub> No reaction

Me t-Butanol

OH Dil. KMnO<sub>4</sub> No reaction

Me OH Dil. KMnO<sub>4</sub> CH<sub>3</sub>CH<sub>2</sub>COOH + MnO<sub>2</sub> 
$$\downarrow$$
 (Brown black ppt.) + 2KOH + 2H<sub>2</sub>O

(b) 2 HCHO + 2 HCOOH

(c) CH<sub>3</sub>COOH + CH<sub>3</sub>CHO

**D-3.** (a) 
$$Ph-CH_2-CH_2-OH \xrightarrow{CU/\Delta} Ph-CH_2-CH=O$$
 (b)  $Ph-CH-CH_3 \xrightarrow{CU/\Delta} Ph-C-CH_3$  OH

(c) 
$$Ph$$
 $CH_3$ 
 $Cu/\Delta$ 
 $CH_2$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 



**E-2.** (a) 
$$CH_3-C\equiv N \xrightarrow{H_3O^{\oplus}} CH_3COOH$$

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

### PART – II

(D)

(B)

### PART - III

- 1. (A) (q); (B) (s); (C) (p, s); (D) (q, s)
- **2.** (A) (p); (B) (q); (C) (t); (D) (s).

### **EXERCISE - 2**

### PART - I

- **1.** (D)
- 2.
- (D)
- **3.** (D)
- **4.** (B)
- **5.** (C)

- **6.** (D)
- 7.
- (D)
- **8.** (D)
- **9.** (D)
- **10.** (A)

- **1**. 3
  - **2.** 3
- **3.** 3 (i, ii, iv)

PART - II

- **4.** 3
- **5.** 7

6. 4 (i, ii, iii, v)

#### PART - III

- **1.** (ABCD)
- **2.** (AB)
- **3.** (AD)
- **4.** (BC)
- **5.** (AB)

PART - IV

- **1.** (D)
- (C)
- **3.** (A)
- 4.
- (B)
- **5.** (A)

- **6.** (D)
- 7.

2.

- (A)
- **8.** (C)
- 9.
- (D)
- **10.** (B)

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### **EXERCISE - 3**

### PART - I

1. 
$$CH_2 = C H_3$$

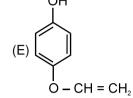
2. (B)

(C) 3.

4. (A)

cis-isomer

(C) COCH<sub>2</sub> (D) ĊOOH



6. (C) 7. (C)

ĊH<sub>2</sub>CHO

$$P = \begin{array}{c} CH_{_{3}} \\ CH \\ CH_{_{3}} \end{array}; Q = \begin{array}{c} O \\ CH_{_{3}} \\ H_{_{3}}C \end{array}; R = HO - CH \\ CH_{_{3}} \end{array}$$

(b) The greater stability of the oxonium ion intermediate is responsible for the extraordinary reactivity. This is demonstrated for the two sets of P, Q, R (cases i and ii above) as follows.

- (A) p, q, s, t; (B) s, t; (C) p; (D) r9.
- (ACD) 10.
- 11. (A)
- 12. 5
- 13. (CD)

#### PART - II

### JEE(MAIN) OFFLINE PROBLEMS

(2)

- 1. (4)
- 2.
- 3.
- 4.

5. (1)

- 6. (3)
- 7. (3)
- 8. (2)
- 9. (2)

(1)

(4)

(3)

(3)

10. (1)

- 11. (4)
- 12. (4)
- 13. (4)
- 14. (4)
- 15. (4)

16. (1)

### **JEE(MAIN) ONLINE PROBLEMS**

- 1. (3)
- 2.
- (3)(3)

(2)

- 3.
- 4.

5. (1)

- 6. (1)
- 7.
- 8.
- (2)(3)
- 9.

- 11. (3)
- 12.
- 13.
- (3)
- 14.

10. (2)

- (1)



### Additional Problems for Self Practice (APSP)

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

### PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time: 1 Hr. Max. Marks: 120

### **Important Instructions**

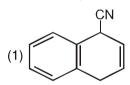
- 1. The test is of 1 hour duration.
- 2. The Test Booklet consists of 30 questions. The maximum marks are 120.
- 3. Each question is allotted 4 (four) marks for correct response.
- **4.** Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
  - 1/4 (one fourth) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- **5.** There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.
- **1.** Propyne and propene can be distinguished by :
  - (1) Conc. H<sub>2</sub>SO<sub>4</sub>

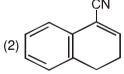
(3) Dil. KMnO<sub>4</sub>

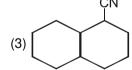
- (2) Br<sub>2</sub> in CCl<sub>4</sub> (4) AgNO<sub>3</sub> in ammonia
- 2. The reactivity order towards hydrogenation of the following compounds is
  - (I) CH3-C=C-CH3

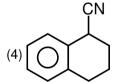
(III) 
$$CH_3$$
  $C = C$ 

- (1) I > II > III > IV
- (2) II > III > IV > I
- $(II) \begin{array}{c} C = C \\ H \\ CH_3 \\ \end{array}$
- (IV)  $CH_3$  C = C  $CH_3$









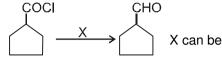
4. The product of following reaction is

- (1) PhCH<sub>2</sub>CH=CHCH<sub>2</sub>OH
- (3) PhCH=CHCH<sub>2</sub>OH

- (2) Ph(OH)C=CHCH<sub>3</sub>
- (4) PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—OH
- 5. The product of the reaction  $Ph_2C=O \xrightarrow{\text{LiAID}_4} \text{is}$ 
  - (1) Ph<sub>2</sub>CD(OH)
- (2) Ph<sub>2</sub>CH(OD)
- (3) Ph<sub>2</sub>CD(OD)
- (4) None

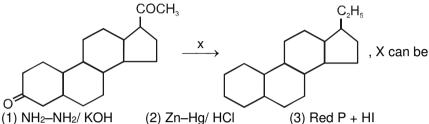


6.



- (1) NaBH<sub>4</sub>/EtOH
- (2) LiAlH<sub>4</sub>/THF
- (3) Na/EtOH
- (4) H<sub>2</sub>/Pd-BaSO<sub>4</sub>
- 7. Hydrogenation of benzoyl chloride in the presence of Pd / BaSO<sub>4</sub> gives
  - (1) benzyl alcohol
- (2) benzaldehyde
- (3) benzoic acid
- (4) phenol
- 8. Which of the following reagent not convert carbonyl compound into alcohol?
  - (1) DiBAL-H
- (2) NH<sub>2</sub>-NH<sub>2</sub>/KOH
- (3) Na-Hg/HCI
- (4) LiAlH<sub>4</sub>

9.



- (2) Zn-Hg/HCI
- (4) All

10. Identify a & b, in the following reaction:

$$\begin{array}{c}
\text{NaBH}_{4} \\
\text{CH}_{3}\text{OH}
\end{array}$$

$$\begin{array}{c}
\text{(i) LiAlH}_{4}, \text{ ether} \\
\text{(ii) } C_{2}\text{H}_{5}\text{OH}
\end{array}$$

- (1) Both are
- (2) Both are

$$OH OH OH$$

$$(4) a = OH (+ EtOH), b = OEt$$

- 11.
  - X is: (2)

- 12. An alkene on ozonolysis yields only ethanal. There is an isomer of this, which on ozonolysis yields:
  - (1) Propanone and methanal

(2) Propanone and ethanal

(3) Ethanal and methanal

- (4) Only propanone
- 13.
- The product 'Y' is

- (1) CH<sub>2</sub>=CH-CH<sub>2</sub>OH
- (3) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>
- (4) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH

- 14. Which of the following will decolorise alkaline KMnO<sub>4</sub> solution?
  - (1) C<sub>3</sub>H<sub>8</sub>
- (2) CH<sub>4</sub>
- (3) CCI<sub>4</sub>
- (4) C<sub>2</sub>H<sub>4</sub>

- **15.** Bayer's reagent is :
  - (1) alkaline permanganate solution
  - (2) acidified permanganate solution
  - (3) neutral permanganate solution
  - (4) aqueous bromine solution

16. (P) 
$$\sim$$
  $\sim$   $\sim$   $\sim$   $\sim$   $\sim$   $\sim$  (A) + E(gas)  $\sim$   $\sim$   $\sim$  (B)  $\sim$   $\sim$   $\sim$  (C)

Select correct options, for identical pairs

- (1) P, A
- (2) A, C
- (3) B, C
- (4) P, C

17. 
$$\frac{OSO_4}{H_2O_2} A \xrightarrow{HiO_4} B + C;$$

 $H_3C$ 

(1) 
$$H_3C$$
 and  $CH_3 - C - H$ 

(3) 
$$H-C-H$$
 and  $CH_3-CH_2-C-CH_3$ 

(2) 
$$CH_3 - CH_2 - C - H$$
 and  $CH_3 - C - H$ 

(4) 
$$CH_3 - C - CH_3$$
 and  $H - C - H$ 

Product B and C are respectively:

$$(4)$$
 CH = CH $\longrightarrow$  OF

- **19.** Fenton's reagent is :
  - (1)  $FeSO_4 + H_2O_2$
- (2)  $HgSO_4 + H_2O_2$
- (3)  $FeSO_4 + H_2O$
- (4) None of these
- **20.** The reagent with which both acetaldehyde and acetone react easily is
  - (1) Tollen's reagent

(2) Schiff's reagent

(3) Grignard reagent

- (4) Fehling reagent
- 21. An organic compound (P) with molecular formula C₅H<sub>8</sub>O<sub>4</sub> 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 :
  - (1) CH<sub>3</sub>-C-O-C-OC<sub>2</sub>H<sub>5</sub>
    0 O
    0
  - (3) CH<sub>2</sub> C OCH<sub>3</sub> C OCH<sub>3</sub>

- (2) CH<sub>3</sub>-C-C-C-OCH<sub>5</sub> 0 0 0 0 0
- 22. When acetaldehyde is treated with Fehling's solution, it gives a precipitate of
  - (1) Cu
- (2) CuO
- (3) Cu<sub>2</sub>O
- (4) Cu + Cu<sub>2</sub>O + CuO

- 23. Identify the correct statement about  $MnO_2/\Delta$ 
  - (1) C<sub>6</sub>H<sub>5</sub>-CHOH-CH<sub>3</sub> as well as CH<sub>3</sub>-CH=CH-CH<sub>2</sub>OH are oxidised
  - (2)  $C_6H_5$ - $CH_2$ - $CH_2$ -OH as well as  $CH_2$ =CH- $CH_2$ - $CH_2$ -OH are oxidised
  - (3)  $C_6H_5$ -CHOH-CH<sub>3</sub> is not oxidised but  $CH_3$ -CH=CH-CH<sub>2</sub>-OH is oxidised.
  - (4)  $C_6H_5$ -CHOH-CH $_3$  is oxidised but  $CH_3$ -CH=CH-CH $_2$ OH is not oxidised.
- 24. Which of the following reaction involves homogeneous reduction?
  - (A)  $CH_2=CH_2 \xrightarrow{H_2/N_i} CH_3-CH_3$
  - (B) CH<sub>3</sub>−C≡C−CH<sub>3</sub> Wilkinson's catalyst CH<sub>3</sub>−CH=CH−CH<sub>3</sub>
  - (C) CH<sub>3</sub>COCI  $\xrightarrow{\text{H}_2/\text{Pd/CaCO}_3/\text{quinoline}}$  CH<sub>3</sub>CHO
  - (D) CH<sub>3</sub>C $\equiv$ CH  $\xrightarrow{\text{H}_2/\text{Pd/CaCO}_3/\text{quinoline}}$  CH<sub>3</sub>CH = CH<sub>2</sub>

X is :

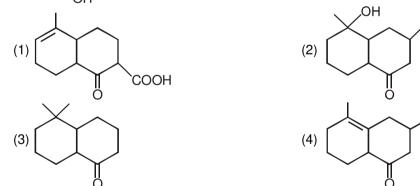
25.

- (1) NaBH<sub>4</sub>/EtOH
- (2) LiAlH<sub>4</sub>/THF
- (3) Al(OiPr) $_3$  / CH $_3$  –CH–CH $_3$  (4) All of these  $I_3$

COOH

COOH

26. Which reducing agent, would you use to carry out the following transformation.



- 28. An unknown compound decolorizes bromine in carbon tetrachloride, and it undergoes catalytic reduction to give decalin. When treated with warm, conc. potassium permangate, this compound give cis—cyclohexane-1,2-dicaboxylic acid and oxalic acid. Possible a structure for the unknown compound is -
  - (1)
- (2)
- (3)
- (4)



29. The reaction, 
$$Ph - CH_2 - CH = CH - CH_3 - CH_3 + CH_2 - CH_3 + CH_2 - CH_3 + CH_3 + CH_2 - CH_3 + CH$$

is known as:

- (1) Wolff-kishner reduction
- (3) Meerwein -Ponndorf reaction
- (2) Oppenauer oxidation
- (4) Clemmensen reduction
- **30.** The reagent used to convert RCOOH  $\rightarrow$  RCH<sub>2</sub>OH is
  - (1) NaBH<sub>4</sub>
- (2) Na/ Alcohol
- (3) Zn/Hg-HCI
- (4) LiAlH<sub>4</sub>

### Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

				<u> </u>		<u> </u>	(0110)			
Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

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

- 1. If 2-pentanone is reacted with NaBH<sub>4</sub> followed by hydrolysis with D<sub>2</sub>O the product will be **[NSEC-2000]** 
  - (A) CH<sub>3</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

(B) CH<sub>3</sub>CD(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

(C) CH<sub>3</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

- (D) CH<sub>3</sub>CD(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- 2. If 1 mole H<sub>2</sub> 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. Which of the following can not be obtained when alkenes are oxidised with KMnO<sub>4</sub> and then followed by acid hydrolysis? [NSEC-2000]
  - (A) alkanoic acids
- (B) alkanals
- (C) alkanones
- (D) carbon dioxide

**4.** In the reaction

[NSEC-2001]

$$CH_3CN + 2H \xrightarrow{HCI} X \xrightarrow{H_2O} Y, Y is$$

- (A) acetaldehyde
- (B) ethanamine
- (C) dimethylamine
- (D) acetone
- 5. A compound is soluble in conc. H<sub>2</sub>SO<sub>4</sub>. It does not declourise bromine in carbon tetrachloride but oxidised by chromic anhydride in aqueous sulphuric acid within two seconds, turning orange solution to blue, green and then opaque. The original compound is:

  [NSEC-2001]
  - (A) an alkane
- (B) a tertiary alcohol
- (C) a primary alcohol
- (D) an ether
- 6. If 3-hexanone is reacted with NaBH<sub>4</sub> followed by hydrolysis with D<sub>2</sub>O, the product will be:

[NSEC-2001]

- (A) CH<sub>3</sub>CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- (B) CH<sub>3</sub>CH<sub>2</sub>CD(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- (C) CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- (D) CH<sub>3</sub>CH<sub>2</sub>CD(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>



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ADVROHO - 43



7. Hydrogenation of benzoyl chloride in the presence of Pd and BaSO<sub>4</sub> gives: [NSEC-2001] (A) benzyl alcohol (B) benzoic acid (C) benzaldehyde (D) toluene  $\xrightarrow{Zn-Hg}$   $R_2CH_2 + H_2O$ The reaction, R<sub>2</sub>CO + 4[H] -8. [NSEC-2001] is well known as: (A) Wurtz reaction (B) Rosenmund reduction (D) Clemmensen reduction (C) Kolbe reaction 9. Acetone will be obtained on ozonolysis of [NSEC-2002] (B) 2-pentene (A) 1-pentene (C) isopentene (D) 2-pentyne 10. The reducing agent for conversion of O2NCH2CH2CH=CH2 to H2NCH2CH2CH=CH2 is: [NSEC-2002] (A) LiAIH<sub>4</sub> (B) H<sub>2</sub>/Pd (C) B<sub>2</sub>H<sub>6</sub> (D) NaBH<sub>4</sub> 11. Reduction of an isonitrile gives a [NSEC-2002] (A) primary amine (B) secondary amine (C) tertiary amine (D) quaternary ammonium salt. 12. Methane may be obtained from monochloromethane by [NSEC-2002] (A) reduction with nascent hydrogen (Zn + HCI) (B) reduction with hydrogen (H<sub>2</sub>) (C) heating with sodium metal in dry ether (D) hydrolysis with aqueous NaOH. The compound which does not react with lithium aluminium hydride is 13. [NSEC-2003] (A) 3-penten-2-one (B) methyl benzoate (C) 2-pentanol (D) propanenitrile The compound that would yield a 5-oxo-2-methylhexanal on ozonolysis is 14. **INSEC-20041** 15. Reduction of methylbenzoate (C<sub>6</sub>H<sub>5</sub>COOCH<sub>3</sub>) to benzyl alcohol (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH) can be accomplished usina [NSEC-2005] (A) H<sub>2</sub>/Pd (B) LiAIH<sub>4</sub> (C) NaBH<sub>4</sub> (D) Zn-Hg/HCI 16. Oxidation of cyclopentanol to cyclopentanone can be accomplished by using [NSEC-2005] (A) Tollen's reagent (B) chromic acid (C) bromine water (D) Fehling's solution. 17. Carbonyl compounds can generally be converted to hydrocarbons by [NSEC-2006] (A) H<sub>2</sub>/Pt (B) LiAIH<sub>4</sub> (C) N<sub>2</sub>H<sub>4</sub>-KOH (D) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> 18. To reduce a nitroaldehyde to a nitroalcohol the reducing agent of choice is **INSEC-20081** (A) LiAlH<sub>4</sub> (B) NaBH<sub>4</sub> (C) Molecular H<sub>2</sub> (D) SnCl<sub>2</sub> 19. Suggest the suitable reagent for the following transformation. [NSEC-2008] reagent (A) meta-chloroperbenzoic acid (B) ozone (C) potassium dichromate (D) alkaline hydrogen peroxide 20. An isocyanide on reduction with hydrogen in the presence of plantinum gives : [NSEC-2009] (A) amide (B) primary amine (D) alcohol (C) secondary amine Compound X (C<sub>5</sub>H<sub>10</sub>O) is a chiral alcohol. It is catalytically hydrogenated to an achiral alcohol Y 21. (C₅H₁2O) and oxidized by activated MnO2 to an achiral carbonyl compound Z (C₅H8O). 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



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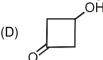
4-Oxobutanoic acid is reduced with Na-borohydride and the product is treated with aqueous acid. The final product is:

[NSEC-2009]



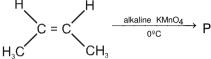
(B) COOH

(C) O



- 23. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of [NSEC-2013]
  (A) sodium atoms (B) sodium hydride (C) sodium amide (D) solvated electrons
- 24. 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 a meso compound of 2,3-butanediol formed by anti addition.
- (C) P is a racemic mixture of d- and I-2,3-butanediol formed by anti addition.
- (D) P is a racemic mixture of d- and I-2,3-butanediol formed by syn addition.
- 25. Complete catalytic hydrogenation of naphthalene gives decalin (C<sub>10</sub>H<sub>18</sub>). 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, 2

  (C) 2, 4

  (D) 3, 4
- Which of the following on treatment with hot concentrated acidified KMnO<sub>4</sub> will give 2-methylhexane-1,6-dioic acid as the only organic product? [NSEC-2017]

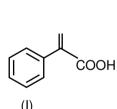




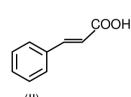




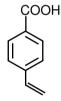
27. An organic compound 'P' with molecular formula C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> on oxidation gives benzoic acid as one of the products. The possible structure/s of 'P' is/are [NSEC-2017]



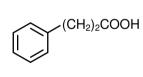
(A) I and III



(II) (B) II and IV



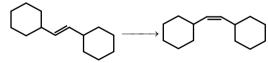
(C) I and II



(IV)

(D) II only

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



I. NaNH<sub>2</sub>

II. Br<sub>2</sub>

III. H<sub>2</sub>/Pd-C, quinolone

IV. H<sub>3</sub>O<sup>+</sup>

(A) IV - I - III

(B) III − IV − I

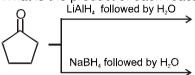
(C) II - I - III

(D) I - II - III

### PART - III: HIGH LEVEL PROBLEMS (HLP)

### SUBJECTIVE QUESTIONS

- 1. An alkene (A) C<sub>16</sub>H<sub>16</sub> on ozonolysis gives only one product (B) C<sub>8</sub>H<sub>8</sub>O. Compound (B) reaction with NaOH / I<sub>2</sub> yields sodium benzoate. Compound (B) reacts with KOH / NH<sub>2</sub>NH<sub>2</sub> yielding a hydrocarbon (C) C<sub>8</sub>H<sub>10</sub>. Write the structures of compound (B) & (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structure and identify the isomer which on catalytic hydrogenation (H<sub>2</sub>/Pd–C) gives a racemic mixture. [JEE-2001. 5/100]
- 2. What is the product of each reaction



3.\_ Which alcohol is prepared from the following ketones via MPV reduction?

4. Complete the following

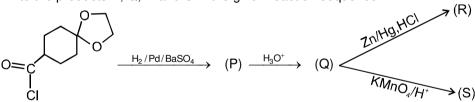
(a) CH<sub>3</sub>-CHO 
$$\xrightarrow{\text{SeO}_2}_{\Delta}$$
 ; (b) H<sub>3</sub>C-CH<sub>2</sub>-C-CH<sub>3</sub>  $\xrightarrow{\text{SeO}_2}_{\Delta}$  ; (c)  $\xrightarrow{\text{SeO}_2}_{\Delta}$ 

5. Complete the following

(a) 
$$\stackrel{\text{HN}}{\underset{\text{NH}}{\longrightarrow}}$$
  $\stackrel{\text{NH}}{\underset{\text{NH}}{\longrightarrow}}$ 

(b) Ph–O–CH=CH<sub>2</sub> 
$$\xrightarrow{\text{H}_3O^{\oplus}}$$
 A + B

6. Write the products P, Q, R and S in the given reaction sequence.



### **ONLY ONE OPTION CORRECT TYPE**

- 7. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne.
  - (A) bromine, CCl<sub>4</sub> (C) dilute H<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub>

- (B) H<sub>2</sub>, Lindlar catalyst
- (D) ammonical Cu<sub>2</sub>Cl<sub>2</sub> solution [JEE-2002, 3/90]

8.

Product obtained in above reaction is:

- (A) 3CH<sub>3</sub>CHO
- (B) 3HCHO
- (C) 3HCOOH
- (D) 3CH<sub>3</sub>OH



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$$\begin{array}{c}
 & H_3O^{\oplus} \\
\hline
 & OEt
\end{array}$$

Product of above reaction is:

### 10.

Which of the following gives  $CH_3$ –OH and  $CH_3$ –C– $CH_3$  on hydrolysis with  $H_3O^+$ .



(B) 
$$CH_3$$
  $CH_2 - CH_3$  (C



### SINGLE AND DOUBLE VALUE INTEGER TYPE

11. In how many reaction CH<sub>3</sub>-CHO is obtained as major product?

(P) CH<sub>3</sub>-C
$$\equiv$$
N  $\xrightarrow{1. \text{SnCl}_2/\text{dil. HCl}}$ 

$$(Q) \xrightarrow[H_3-C]{CH_2} \xrightarrow[H_3O^+]{CH_2} \xrightarrow[H_3O^+]{CH_2}$$

(S) 
$$CH_3-C\equiv N - \frac{1. DIBAL-H}{2. H_3O^+}$$

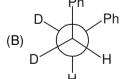
12. Dolastatin is an anti cancer compound isolated from Indian sea have Dobabella ausiculasia. One mole of it on acidic hydrolysis yield how many products are formed.

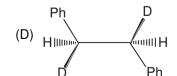
How many para substituted benzenoid isomers of C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> gives 1, 4-dihydroxy benzene on hydrolysis? 13.

### ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

14. The end product of following reaction is / are :

Ph-C=C-Ph 
$$\xrightarrow{\text{H}_2 / \text{Pd} / \text{BaSO}_4 / \text{Quinoline}}$$
  $\xrightarrow{\text{D}_2 / \text{Ni}}$  (2)





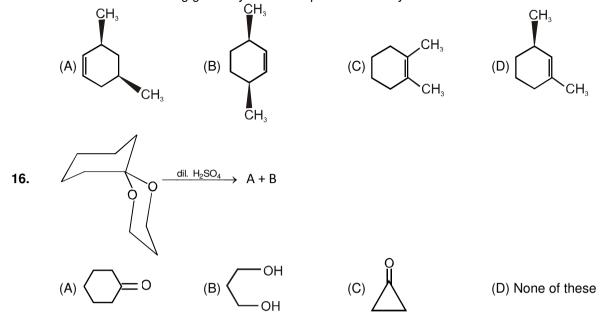


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**15.** Which of the following give only meso compound on catalytic reduction?



### PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time: 1 Hr. Max. Marks: 66

### **Important Instructions**

#### A. General:

- 1. The test is of 1 hour duration.
- 2. The Test Booklet consists of 22 questions. The maximum marks are 66.

#### **B.** Question Paper Format

- 3. Each part consists of five sections.
- 4. Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- 5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- 6. Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- 7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- 8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1: P, Q, R and S; List-2: 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

#### C. Marking Scheme:

- 9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.
- 10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- 11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.



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#### **SECTION-1**: (Only One option correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. 
$$\frac{1. \ H_3O^+}{2. \ \text{LiAlH}_4} \ \text{A is} :$$

$$(C)$$
  $OH$   $OH$   $OH$ 

(D) None

2. 
$$(a) Zn - Hg / HCI \longrightarrow M$$

$$(b) NH_2 - NH_2 / KOH \longrightarrow N$$
Using high boiling solvent
$$(c) HI / P \longrightarrow Y$$

(B) N is

(D) All of these are correct

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

- (A) reduce Tollens reagent.
- (C) form dioxime

- (B) give lodoform test.
- (D) give cerric ammonium nitrate test.

4. 
$$Q \leftarrow \frac{\text{Na/NH}_3(\ell)}{\text{Lindlar catalyst}} \rightarrow F$$

P and Q are:

(B) in both cases

(C) P is I, Q is II

(D) P is II, Q is I



5. Which of the following Reaction is not possible?

(A) 
$$\begin{array}{c} \text{alk.KMnO}_4 \\ \text{CH}_3 \\ \text{CH}_3 - \text{C-CH}_3 \\ \text{(C)} \end{array}$$
(B) 
$$\begin{array}{c} \text{alk.KMnO}_4 \\ \text{A} \\ \end{array}$$
(C) 
$$\begin{array}{c} \text{alk.KMnO}_4 \\ \text{A} \\ \end{array}$$
(D) 
$$\begin{array}{c} \text{alk.KMnO}_4 \\ \text{A} \\ \end{array}$$

6. Hydrolysis of a compound C<sub>9</sub>H<sub>10</sub>ClBr (P) yields C<sub>9</sub>H<sub>10</sub>O(Q)

(Q) gives positive haloform test?

Strong oxidation of (Q) yields a dibasic acid which gives only two mono-nitro derivative. What is the structure of (P) ?

Section-2: (One or More than one options correct Type)

This section contains 5 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

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

(A) 
$$\longrightarrow$$
 LiAlH<sub>4</sub>  $\longrightarrow$  OH OH

(B) CH<sub>3</sub>-C=N  $\longrightarrow$  LiAlH<sub>4</sub>  $\longrightarrow$  CH<sub>3</sub>-CH<sub>2</sub>-NH<sub>2</sub>

(C)  $\longrightarrow$  LiAlH<sub>4</sub>  $\longrightarrow$  CH<sub>2</sub>-OH

(D)  $\longrightarrow$  NaBH<sub>4</sub>  $\longrightarrow$  NaBH<sub>4</sub>  $\longrightarrow$  CH<sub>2</sub>-OH

**8.** Which of the following will give syn addition?

(A) 
$$\stackrel{\text{(i)} \text{ KMnO}_4}{\text{Me}} \stackrel{\text{(i)} \text{ KMnO}_4}{\text{(ii)} \text{ H}_2\text{O}/\text{OH}^-}$$
(B)  $\stackrel{\text{Me}}{\text{Et}} \stackrel{\text{(i)} \text{ OsO}_4}{\text{(ii)} \text{ Na}_2\text{SO}_3}$ 
(C)  $\stackrel{\text{Me}}{\text{Et}} \stackrel{\text{(i)} \text{ RCOOOH}}{\text{(ii)} \text{ H}_3\text{O}^+}$ 



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- 9. Periodic acid is generally used for the oxidation of vicinal diols or  $\alpha$ -hydroxycarboxyl 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<sub>4</sub> reduced into HIO<sub>3</sub>
  - (D) Intermediate of this reaction for a vicinal diol is

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

Which is 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<sub>2</sub>S the products will be aldehydes and/or ketones.
- **11.** Observed the following reaction sequence and choose the correct options.

Ph-C 
$$\equiv$$
 C-CH<sub>3</sub>  $\xrightarrow{\text{Na + liq.NH}_3}$  (A)  $\xrightarrow{\text{(i) OsO}_4}$  (C)

- (A) (A) and (B) are diastereomer's of each other.
- (B) upon catalytic hydrogenation (A) and (B) gives same product
- (C) Product (C) and (D) are Identical
- (D) Product (C) and (D) are separated by fractional distillation.

#### Section-3: (Single/ Double Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

**12.** How many Stereoisomers are formed in following reaction?



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13. Predict the product of following reaction.

$$(x \text{ moles of } H_2 \text{ used})$$

$$H_2, Pd-C \rightarrow (A)$$

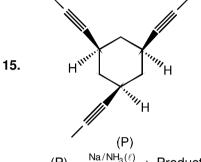
$$H_2, lindlar \rightarrow (B)$$

$$catalyst$$

$$(y \text{ moles of } H_2 \text{ used})$$

Find the value of (x + y).

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



 $\xrightarrow{\text{Na/NH}_3(\ell)} \text{Product(s)}$ 

The product(s) has/have  $\mathbf{X}$  = degree of unsaturation and  $\mathbf{Y}$  = number of isomeric product(s) formed. Then X + Y = ?

#### SECTION-4: Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

#### Paragraph for Questions 16 to 17

#### (Read the paragraph carefully and give the answer of following questions.

Generally, during the clemmenson reduction >C=O group converts into >CH2 after reacting with (conc. HCl + Zn-Hg). But in case of  $\beta$ -diketo compounds, its give unexpected products.



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16. 
$$\frac{\text{(conc. HCl+Zn-Hg)}}{\Delta}$$

 $\xrightarrow{\text{-Hg)}}$  Product (X), (X) will be :

$$\textbf{17.} \qquad \overset{CH_{3}-CH-C-CH_{2}-C-CH_{2}-CH_{3}}{| \quad | \quad |} \overset{Zn-Hg + conc.HCI}{\stackrel{\triangle}{\longrightarrow}} \text{ Product (X), (X) will be :}$$

SECTION-5: Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

18. Match the reducing agents of List-II with the reaction of List-I and select the correct answer using the code given below the lists.

	List-I		List-II
P.	$0 \longrightarrow 0 \longrightarrow H$	1.	DIBAL-H
Q.	$\begin{array}{c} CN \\ \hline \\ CH_2NH_2 \\ \hline \\ \end{array}$	2.	H <sub>2</sub> /Ni, (25°C)
R.	$\bigcirc \bigcirc $	3.	Na / NH <sub>3</sub> (ℓ) / C <sub>2</sub> H <sub>5</sub> OH
S.	CN $OH$ $OH$ $OH$ $OH$ $OH$	4.	H <sub>2</sub> /Pd/BaSO <sub>4</sub> / quinoline
Code			
		P	Q R S
(A) (C)	P Q R S 4 3 1 2 (B) 3 1 2 4 (D)	1 2	Q R S 2 4 3 3 1 4



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# Practice Test-2 ((IIT-JEE (ADVANCED Pattern)) OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18		
Ans.										



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**ADVROHO - 54** 



### **APSP Answers**

PART - I										
1.	(4)	2.	(1)	3.	(1)	4.	(4)	5.	(1)	
6.	(4)	7.	(2)	8.	(2)	9.	(4)	10.	(3)	
11.	(1)	12.	(1)	13.	(2)	14.	(4)	15.	(1)	
16.	(2)	17.	(1)	18.	(1)	19.	(1)	20.	(3)	
21.	(3)	22.	(3)	23.	(1)	24.	(2)	25.	(4)	
26.	(2)	27.	(2)	28.	(4)	29.	(2)	30.	(4)	
				PAF	RT - II					
1.	(A)	2.	(D)	3.	(B)	4.	(A)	5.	(C)	
6.	(A)	7.	(C)	8.	(D)	9.	(C)	10.	(A)	
11.	(B)	12.	(A)	13.	(C)	14.	(B)	15.	(B)	
16.	(B)	17.	(C)	18.	(B)	19.	(D)	20.	(C)	
21.	(A)	22.	(A)	23.	(D)	24.	(A)	25.	(A)	
26.	(C)	27.	(C)	28.	(C)					

### PART - III

1. 
$$C_{6}H_{5} - C = C - C_{6}H_{5} \xrightarrow{O_{3}/Zn} C_{6}H_{5} - C - CH_{3}$$
 $C_{6}H_{5} - C - CH_{3} \xrightarrow{I_{2}/NaOH} C_{6}H_{5} - C - ONa + CHI_{3}$ 
 $C_{6}H_{5} - C - CH_{3} \xrightarrow{I_{2}/NaOH} C_{6}H_{5} - C - ONa + CHI_{3}$ 
 $C_{6}H_{5} - C - CH_{3} \xrightarrow{KOH/NH_{2} - NH_{2}} C_{6}H_{5} - CH_{2} - CH_{3}$ 
 $C_{6}H_{5} \xrightarrow{C} C = C \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} C = C \xrightarrow{C_{6}H_{5}} C = C \xrightarrow{C_{6}H_{5}} CH_{3}$ 
 $C_{6}H_{5} - C - CH_{3} \xrightarrow{C} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$ 
 $C_{6}H_{5} - C - CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$ 
 $C_{6}H_{5} - C - CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$ 
 $C_{6}H_{5} - C - CH_{3} CH_{$ 

Trans isomer give racemic mixture.



Ester group

In (a), the (C=C) bond is not reduced and in (c), the ester (-COOMe) is not reduced in MPV reduction.

(B)

### PART - IV

- **1.** (B)
- 2.
- (D)

1

- 3.
- (D)
- 4.
- 5.

- **6.** (B)
- 7.
- (ABCD)
- 8.
- 9.
- (D) (ABCD)
- **10.** (ABCD)

(C)

5

- **11.** (ABC)
- 12.
- 13.
- (ABC)
- **14.** 73
- 15.

- 16.
- (D)
- 17.
- (D)

2

- 18.
- (A)

## **APSP Solutions**

#### PART - I

**1.** Terminal alkyne gives white ppt with ammonical silver nitrate.

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

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- **2.** Rate of hydrogenation will decreases on increasing steric hinderance at  $\pi$ -bond.
- 3. It is birch reduction
- **6.** –COCI converts in –CHO by H<sub>2</sub>/Pd-BaSO<sub>4</sub> (Rosenmund reduction)
- **8.** Wolf-kishwner reduction (NH<sub>2</sub>–NH<sub>2</sub>/KOH) give alkane after reduction of carbonyl compound.

$$\longrightarrow 0 \xrightarrow{NH_2-NH_2/KOH}$$

- **9.** All reagents are used to convert >C = O to >CH<sub>2</sub>
- 10. Esters are not reduced by NaBH<sub>4</sub>, >C=O (carbonyl) change to -CH(OH) by use of NaBH<sub>4</sub>

11. 
$$C = CH$$

- 12. Alkene  $\xrightarrow{\text{(1) O}_3}$  CH<sub>3</sub>CHO only
- $\textbf{13.} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \text{C} \text{CI} \end{array} \xrightarrow{\begin{array}{c} \text{alco,KOH} \\ \Delta \\ \text{E}_2 \end{array}} \text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \text{CH}_2 \end{array}$

17. 
$$OH OH OH OH OH$$
Syn addition

18. 
$$\bigcirc$$
 CH = CH  $\bigcirc$  R - COO - H  $\bigcirc$  CH - CH  $\bigcirc$ 

- 19. It is fact.
- 21. (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.
- 24. Reduction with Wilkinson's catalyst is homogeneous
- **25.** X can be NaBH<sub>4</sub>/EtOH or LiAlH<sub>4</sub>/THF or Al(OiPr)<sub>3</sub>/CH<sub>3</sub>-CH-CH<sub>5</sub> | OH
- 26. NaBH<sub>4</sub> can not reduces ester.



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- 29. Oppenauer's oxidation, oxidised secondary alcohol into ketone and there is no effect on double bond.
- 30. It is fact.

### **PART - III**

5. (a) 
$$\stackrel{\text{HN}}{\longrightarrow} \stackrel{\text{NH}}{\longrightarrow} \stackrel{\text{H}_3O^{\oplus}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} + \text{NH}_3$$

(b) Ph–O–CH=CH
$$_2$$
  $\xrightarrow{\text{H}_3\text{O}^{\oplus}}$  PhOH + MeCHO

7. 
$$CH_3-CH_2-C \equiv CH \xrightarrow{CU_2Cl_2} CH_3-CH_2-C \equiv CCU + NH_4CI + H_2O$$

- 10. Only C on hydrolysis gives  $CH_3$ –OH and  $CH_3$  C  $CH_3$ .
- 11. All four reactions gives CH<sub>3</sub>-CHO as major product.

12. 
$$\begin{array}{c} H \\ H \\ N \end{array}$$

$$\begin{array}{c} O \\ CH_3 \end{array}$$

$$\begin{array}{c} O \\ O \\ CH_3 \end{array}$$

$$\begin{array}{c} O \\ O \\ CH_3 \end{array}$$

$$\begin{array}{c} O \\ O \\ O \\ O \end{array}$$

$$\begin{array}{c} H \\ O \\ O \\ O \end{array}$$

$$\begin{array}{c} O \\ CH_3 \end{array}$$

$$\begin{array}{c} O \\ O \\ O \\ O \end{array}$$

$$\begin{array}{c} H \\ O \\ O \\ O \end{array}$$

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13. 
$$\begin{array}{c} OH \\ \hline \\ OH \\ \hline \\ O-CH=CH_2 \end{array}$$
 
$$\begin{array}{c} OH \\ \hline \\ OH \\ \hline \\ 1,4-dihydroxy \\ benzene \end{array}$$
 
$$\begin{array}{c} CH_2=CH-OH \\ \hline \\ CH_3-CH=O \end{array}$$

14. Ph-C=C-Ph 
$$\xrightarrow{\text{H}_2 \ / \ \text{Pd} \ / \ \text{BaSO}_4 \ / \ \text{Quinoline}}$$
 Ph-CH=CH-Ph  $\xrightarrow{\text{D}_2 \ / \ \text{Ni}}$  Ph-CHD-CHD-Ph trans meso

**16.** Reaction is hydrolysis of acetal.

### PART - IV

1. 
$$\begin{array}{c}
 & O \\
 & O$$



3. Me – C – Me 
$$\xrightarrow{SeO_2}$$
 OHC – C – Me

In (a), (P) reduces Tollens reagent, since it contains (-CHO) group.

In (b), (P) gives iodoform test, since it contains (MeCO-) group.

In (c), (P) forms dioxime, since it contains (–CHO) and (C—O) groups.

$$O = HC$$

Me

NOH

Dioxime

HON = HC

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. cis-alkene formed by lindlar catalyst and trans-alkene formed by Na/NH<sub>3</sub>.

5. (A) 
$$\xrightarrow{\text{alk.KMnO}_4}$$
  $\xrightarrow{\text{COOH}}$ 

$$(B) \xrightarrow{\text{alk.KMnO}_4} \xrightarrow{\text{HOOC COOH}}$$

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 - \text{C-CH}_3 \\ \text{C)} & \xrightarrow{\text{alk.KMnO}_4} \text{No reaction} \end{array}$$

$$(D) \xrightarrow{NO_2} \xrightarrow{NH_2} \xrightarrow{\text{alk.KMnO}_4} \xrightarrow{NO_2} \xrightarrow{\text{COOH}}$$

**8.** Self explanatory.

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### **9.** HIO<sub>4</sub> is a mild oxidising agent.

Cyclic intermediate is formed with vicinal diols.

12. 
$$\begin{array}{c} CH_2 \\ +H_2 \end{array} \xrightarrow{Pd} \begin{array}{c} CH_3 \\ + CH_3 \end{array} \xrightarrow{CH_3} \begin{array}{c} CH_3 \\ +$$

14. 
$$\begin{array}{c} CH_3 \\ I \\ H-C-N-CH_3 \\ O \end{array}$$
 m.w. is 73

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17. 
$$CH_{3}$$
— $CH$ — $C$ — $CH_{2}$ — $CH_{2}$ — $CH_{3}$ — $CH_{3}$ — $CH_{4}$ — $CH_{4}$