CARBONYL COMPOUND

INTRODUCTION

Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl or oxo group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3.....) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $-\overset{\overset{O}{\|}}{C}-H$ (also known as formyl group). It is a monovalent group

(b) Ketones : The carbonyl group ($>C=O$) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

- Ketones are further classified as :

(i) **Simple or Symmetrical ketones** : Having two similar alkyl groups. $\begin{matrix}R\\R\end{matrix}\!\!>C=O$

(ii) **Mixed or unsymmetrical ketones** : Having two different alkyl groups. $\begin{matrix}R\\R'\end{matrix}\!\!>C=O$

Example : (Ketones) :

Symmetrical	**Unsymmetrical**
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$	$\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!\!>C=O$
(Acetone or Dimethyl ketone)	(Ethyl methyl ketone)
2–Propanone	2–Butanone

Special Point : $-\overset{\overset{O}{\|}}{C}-\ddot{O}H, -\overset{\overset{O}{\|}}{C}-\ddot{X}, -\overset{\overset{O}{\|}}{C}-\ddot{N}H_2, -\overset{\overset{O}{\|}}{C}-\ddot{O}R,$

In all the functional group given above, lone pair of electrons and double bond are in conjugation.

$\left(-\overset{\overset{\curvearrowright O}{\|}}{C}-\ddot{Z}\curvearrowleft\right)$ so resonance occurs. These functional group have $-\overset{\overset{O}{\|}}{C}-$ group still they are not carbonyl compounds because carbonyl group takes part in resonance with the lone pair of electrons.

- **Structure :**

In $>C=O$ compounds C-atom is sp^2 hybridised which forms two σ bonds with C and (H/C) atom respectively and one σ bond with oxygen atom. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen atom give the π bond in $>C=O$ group.

$\left[\begin{matrix}C\\C\end{matrix}\!\!>\overset{sp^2}{C}\overset{\sigma}{=}\underset{\pi}{O}\right]$ The C—C—O and H—C—O bond angles are of approximately 120°.

Due to electro-negativity difference in C & O atoms, the $>C=O$ group is polar.

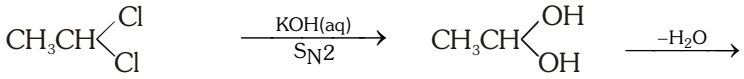
$>\overset{\delta+}{C}=\overset{\delta-}{O}$ Hence aldehydes and Ketones posses dipole moment.

- **GENERAL METHODS OF PREPARATION :**

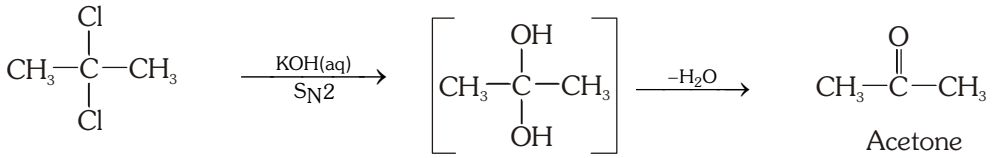
(A) For both Aldehydes and Ketones :

(1) By Hydrolysis of gem dihalides :

Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal dihalides give ketone.

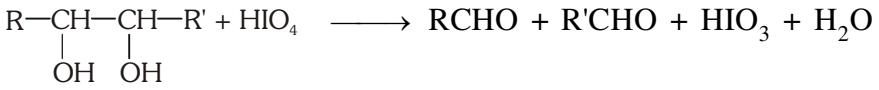


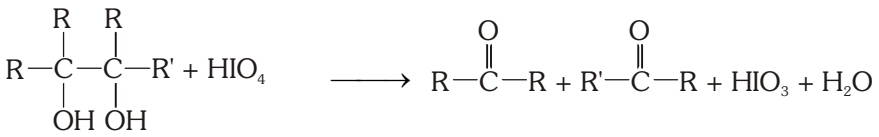
Terminal gem-dihalide [unstable] Acetaldehyde



(2) By Oxidation of diols :

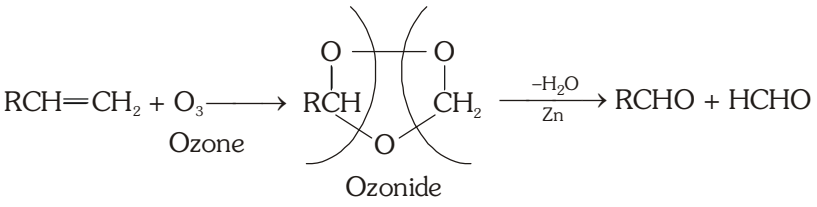
With periodic acid (HIO_4) & lead tetra acetate $(CH_3COO)_4Pb$ vicinal diols gets oxidised to form carbonyl compounds

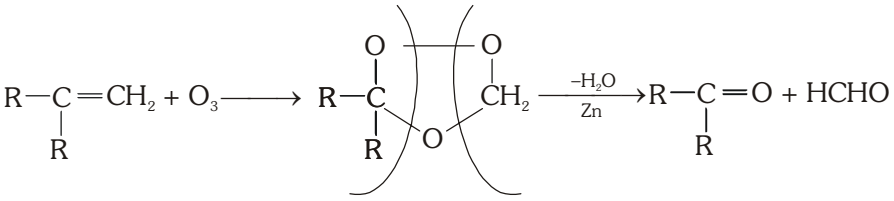




(3) By Ozonolysis of alkenes :

This reaction is used to determine the position of double bond in alkene.





Unbranched alkene	**⟶**	**aldehyde**
Branched alkene	**⟶**	**ketone**

(4) From Alkyne :

(a) Kuchrov reaction (Hydration of alkyne) : With dil H_2SO_4 & 1% $HgSO_4$ at 60-80^{0}C.

$$CH\equiv CH + H_2O \longrightarrow [CH_2=CHOH] \underset{}{\overset{\text{Tauto.}}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\|}{C}}-H$$

In general other alkynes give ketone :

$$CH_3C\equiv CH + H_2O \longrightarrow \underset{\text{(enol)}}{CH_3-\overset{OH}{\overset{|}{C}}=CH_2} \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(b) Hydroboration Oxidation : Reaction with B_2H_6, $2BH_3$ or R_2BH give dialkyl borane.

1 – alkyne gives	**aldehyde**
other alkyne	**ketone**

$$R-C\equiv CH + R_2BH \longrightarrow R-CH=CHBR_2 \xrightarrow[OH^-]{H_2O_2} RCH=CHOH \overset{\text{Tautomerism}}{\rightleftharpoons} R-CH_2-\overset{O}{\overset{\|}{C}}-H + R_2BOH$$

$$CH_3-C\equiv C-CH_3 + R_2BH \longrightarrow \underset{\underset{BR_2}{|}}{CH_3-CH=C-CH_3} \xrightarrow[OH^?]{H_2O_2}$$

$$R_2BOH + \underset{\underset{OH}{|}}{CH_3-CH=C-CH_3} \rightleftharpoons CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + R_2BOH$$

(5) By hydrolysis of carbonyl derivatives :

$$R-CH=N-OH \xrightarrow{H_2O/H^\oplus} R-CHO + NH_2-OH$$

(Aldoxime) (Aldehyde) (Hydroxyl amine)

$$\begin{matrix}R\\R\end{matrix}\!\!>\!C=N-OH \xrightarrow{H_2O/H^\oplus} \begin{matrix}R\\R\end{matrix}\!\!>\!C=O + NH_2-OH$$

(Ketoxime) (Ketone)

$$\begin{matrix}R\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}OR\\OR\end{matrix} \xrightarrow{H_2O/H^\oplus} \begin{matrix}R\\H\end{matrix}\!\!>\!C=O + 2ROH$$

(Acetal) (Aldehyde) (Alcohol)

$$\begin{matrix}R\\R\end{matrix}\!\!>\!C\!<\!\begin{matrix}OR\\OR\end{matrix} \xrightarrow{H_2O/H^\oplus} \begin{matrix}R\\R\end{matrix}\!\!>\!C=O + 2ROH$$

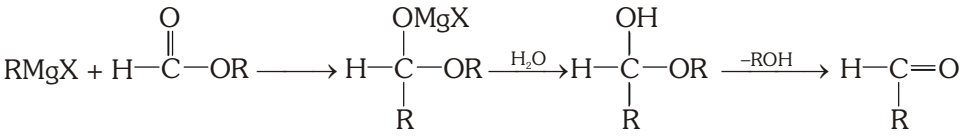
(Ketal) (Ketone) (Alcohol)

(6) From Grignard reagents :

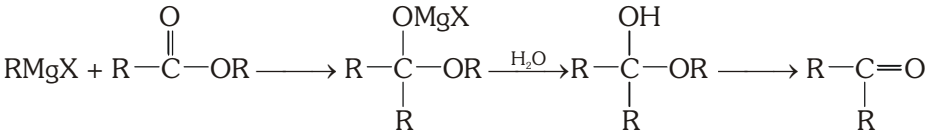
(a) By Cyanides :

$$RMgX + R-C\equiv N \longrightarrow R-\underset{\underset{R}{|}}{C}=N-MgX \xrightarrow{H_2O/H^\oplus} \underset{\text{(Ketone)}}{R-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg\!<\!\begin{matrix}OH\\X\end{matrix}$$

(b) By Esters : HCHO can't be prepared by this method.

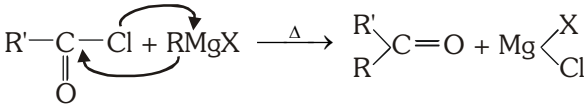


(1 eq.) (Alkyl formate) (Hemiacetal) (Aldehyde)



(1 eq.) (Alkyl Alkanoate) (Hemiacetal) (Ketone)

(c) By acid chlorides :



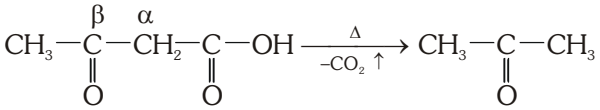
(1 eq.)

(7) From heating of β-keto acids :

The decarboxylation reaction takes place via formation of six membered ring transition state.

(a) $HCOCH_2COOH \xrightarrow[110°C]{\Delta} CH_3CHO + CO_2 \uparrow$

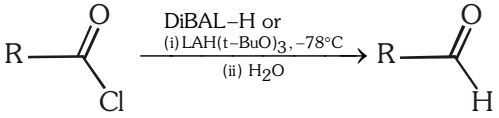
(b)



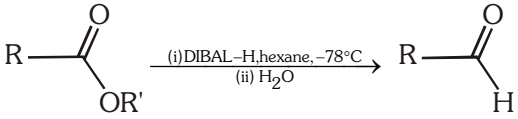
(B) For Aldehydes only :

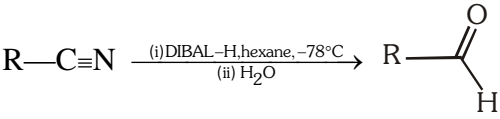
(1) Reduction of acyl halides, esters and nitriles :

(a) Acyl chlorides can be reduced to aldehydes by treating them with lithium-tri-tert-butoxyaluminium hydride, $LiAlH[OC(CH_3)_3]_3$ or with DIBAL–H at – 78°C.



(b) Both esters and nitriles can be reduced to aldehydes by DIBAL-H. Reduction must be carried out at low temperatures. Hydrolysis of the intermediates gives the aldehyde.





(2) Rosenmund's reduction :

Quinoline or sulphur act as a poisoned catalyst, controls the further reduction of aldehyde to alcohols.

$$RCOCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} RCHO + HCl$$

This reaction controls further reduction of aldehyde to alcohols.

In case if only Pd is used, formation of alcohol takes place.

$$RCOCl + H_2 \xrightarrow{Pd} RCHO \xrightarrow{H_2/Pd} RCH_2OH$$

Formaldehyde can not be prepared by this method because HCOCl is highly unstable at room temperature it decompose into CO + HCl.

Example : $C_2H_5COCl + H_2 \xrightarrow[\text{Quinoline or sulphur}]{Pd/BaSO_4} C_2H_5CHO + HCl$

Propionyl Chloride — Propanal

(3) Stephen's reduction :

Alkyl cyanides are reduced by $SnCl_2$ and HCl.

$$R—C\equiv N \xrightarrow{SnCl_2/HCl} R—CH=NH \xrightarrow{H_3O^+} RCHO+NH_3 \uparrow$$

$$C_2H_5—C\equiv N \xrightarrow{SnCl_2/HCl} C_2H_5CH=NH \xrightarrow{H_3O^+} C_2H_5CHO + NH_3 \uparrow$$

(4) Oxo reaction or hydroformylation :

In this reaction symmetrical alkene gives 1^0 aldehyde while unsymmetrical alkene gives isomeric aldehyde (Chain isomers).

$$CH_2=CH_2 + \underbrace{CO+H_2}_{\text{Water gas}} \xrightarrow[125°C/200\,atm]{Co_2(CO)_8} CH_3CH_2CHO$$

$$CH_3—CH=CH_2 + CO + H_2 \xrightarrow[125°C/200\,atm]{Co_2(CO)_8} CH_3CH_2CH_2CHO + \underset{\underset{CHO}{|}}{CH_3—CH—CH_3}$$

(C) For Ketones only :

(1) From dialkyl Cadmium :

RCdR (dialkyl Cadmium) is a organometallic compound.

$$R'COCl + RCdR \longrightarrow RCOR' + RCdCl$$

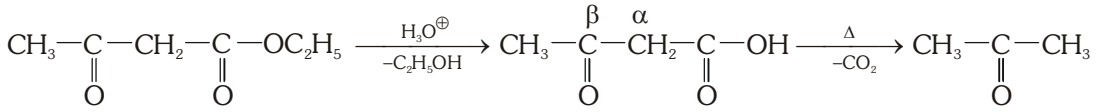
This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.

Example : $CH_3COCl + (C_2H_5)_2Cd \longrightarrow (CH_3)(C_2H_5)C=O + (C_2H_5)Cd(Cl)$

(2) From R_2CuLi [Gilmann's reagent]:

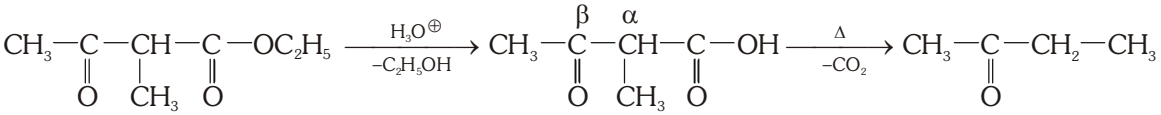
$$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$$

(3) By hydrolysis of Aceto Acetic Ester (AAE) :



(β - keto acid) (Acetone)

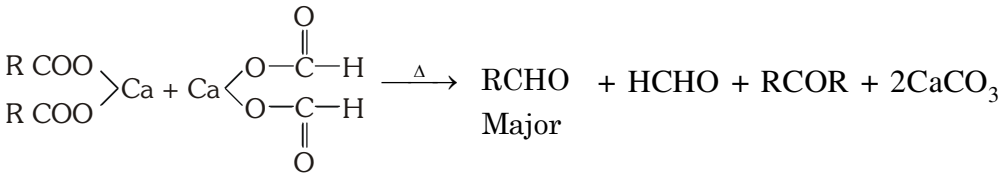
Ex :



(β–keto acid) (Butanone)

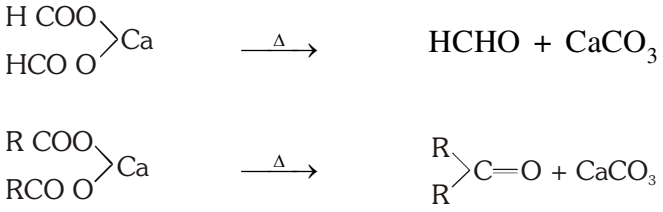
OTHER METHODS FOR ALDEHYDE AND KETONE :

(1) By dry distillation of Ca-salts of carboxylic acid :



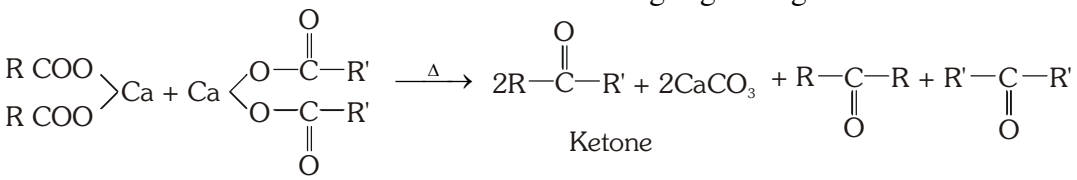
Calcium formate

Note : In this reaction mixture of ketones are formed and usually cross product is major product.



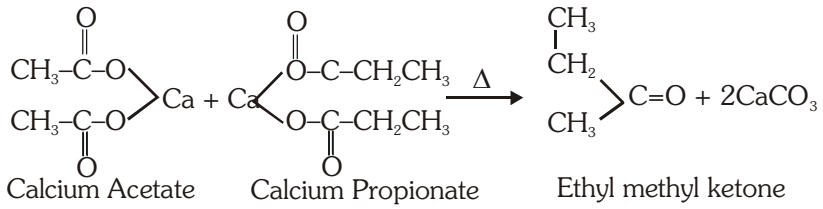
Calcium-alkanoate Ketone

Calcium salts of acids other than formic acid on heating together gives ketone



Ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :



Calcium Acetate Calcium Propionate Ethyl methyl ketone

(2) By Thermal decomposition of carboxylic acids :

Vapour of carboxylic acids when passed over MnO/300^{0}C give carbonyl compounds

$$2\ HCOOH \xrightarrow[300°C]{MnO} HCHO + H_2O + CO_2$$

$$2\ CH_3COOH \xrightarrow[300°C]{MnO} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O + CO_2 + H_2O$$

$$RCOOH + HCOOH \xrightarrow[300°C]{MnO} RCHO + CO_2 + H_2O$$

$$RCOOH + R'COOH \xrightarrow[300°C]{MnO} RCOR' + CO_2 + H_2O$$

(3) Wacker process :

$$CH_2{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + HCl$$

All other alkenes gives ketone.

$$RCH{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + Pd + HCl$$

❑ **Physical Properties :**

◆ **State :**

Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

◆ **Odour :**

Lower aldehydes give unpleasant smell, higher aldehydes and all ketones have pleasant smell.

◆ **Solubility :**

C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $\overset{\delta+}{>}C{=}\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.

$$\overset{\delta+}{>}C{=}\overset{\delta-}{O}\cdots\cdots H{-}O_{\delta-}^{H^{\delta+}} \qquad \text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

H-bonding

◆ **Boiling point :** Boiling point $\propto$ Molecular weight

Boiling point order is - **Alcohol > Carbonyl compounds > Alkane**

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole vander waal force of attraction is present. Alkanes are non polar.

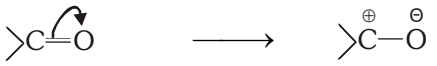
$$\overset{\delta+}{>}C{=}\overset{\delta-}{O}\cdots\cdots\overset{\delta+}{>}C{=}\overset{\delta-}{O}$$

◆ **Density :** Density of carbonyl compounds is lower than water.

CHARACTERISTIC REACTIONS OF ALDEHYDES & KETONES

Nucleophilic addition Reaction:-

Due to strong electronegativity of oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons.

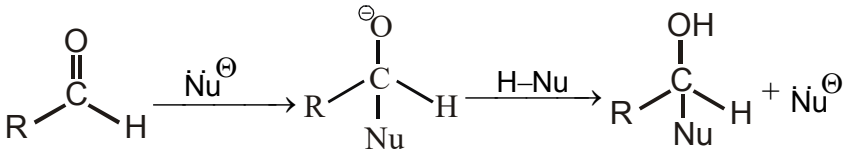


Carbon is thus readily attacked by $\ddot{N}u$. The negatively charged oxygen is attacked by electron deficient (electrophile) E^+, hence carbonyl compound shows NAR.

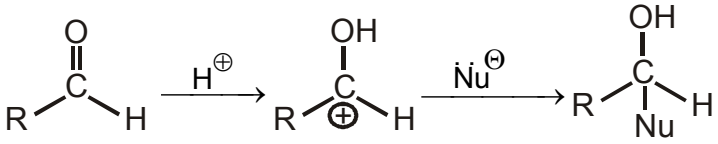
$>C=O$ bond in carbonyl group is stronger than C=C bond in alkanes.

C—O	Bond energy is	84.0 K Cals	C—C	Bond energy is	83.1 K Cals
C=O	Bond energy is	178 K Cals	C=C	Bond energy is	146 K Cals

Base catalysed

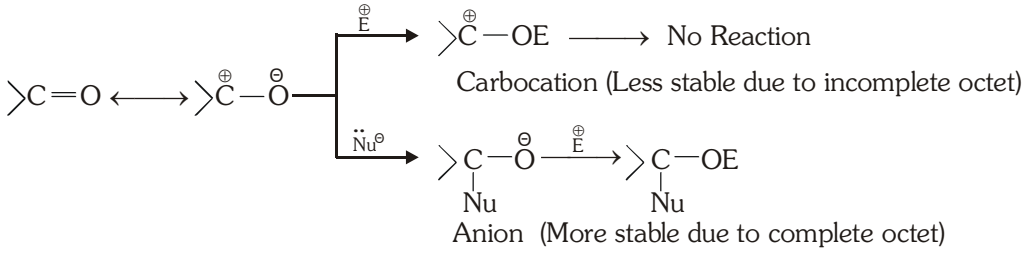


Acid catalysed



Ex : Why carbonyl compound gives nucleophilic addition reaction (NAR) ?

Sol.



(i) Reactivity of carbonyl group $\propto$ Magnitude of +ve charge $\propto$ – I group $\propto \frac{1}{+I\text{group}}$

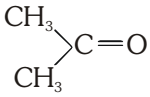
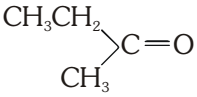
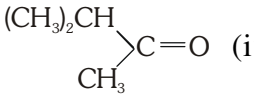
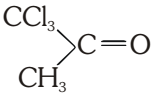
(ii) Reactivity of carbonyl group $\propto \frac{1}{\text{Steric Hindrence on carbonyl group}}$

Ex.1 Arrange the following for reactivity towards NAR in decreasing order

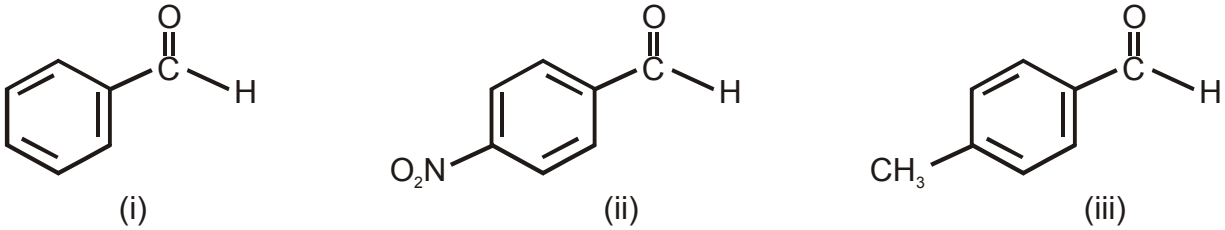
(I) (i) $\begin{matrix}H\\H\end{matrix}\!>\!C=O$ (ii) $\begin{matrix}CH_3\\H\end{matrix}\!>\!C=O$ (iii) $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C=O$

(II) (i) $ClCH_2CHO$ (ii) NO_2CH_2CHO (iii) CH_3CHO (iv) CH_3CH_2CHO

(III) (i) CH_3CHO (ii) $ClCH_2CHO$ (iii) $HCCl_2CHO$ (iv) CCl_3CHO

(IV) (i)  (ii)  (iii)  (iv) 

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

(v) 

(i) (ii) (iii)

Ans. (ii) > (i) > (iii)

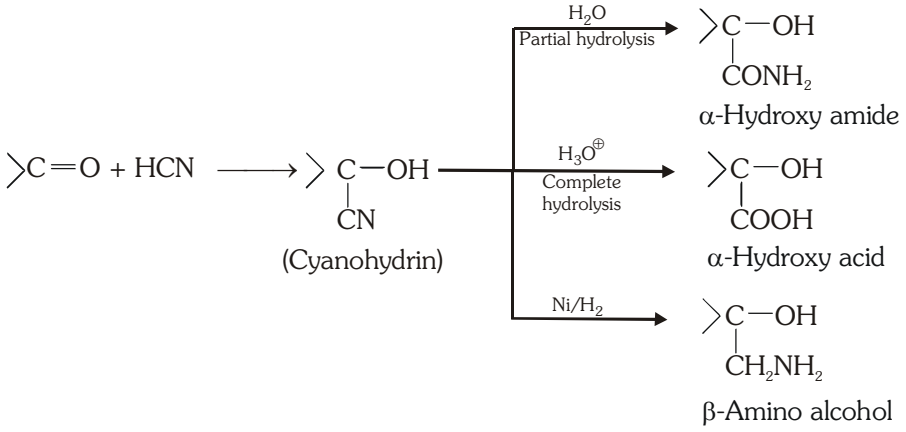
(vi) 

(i) (ii)

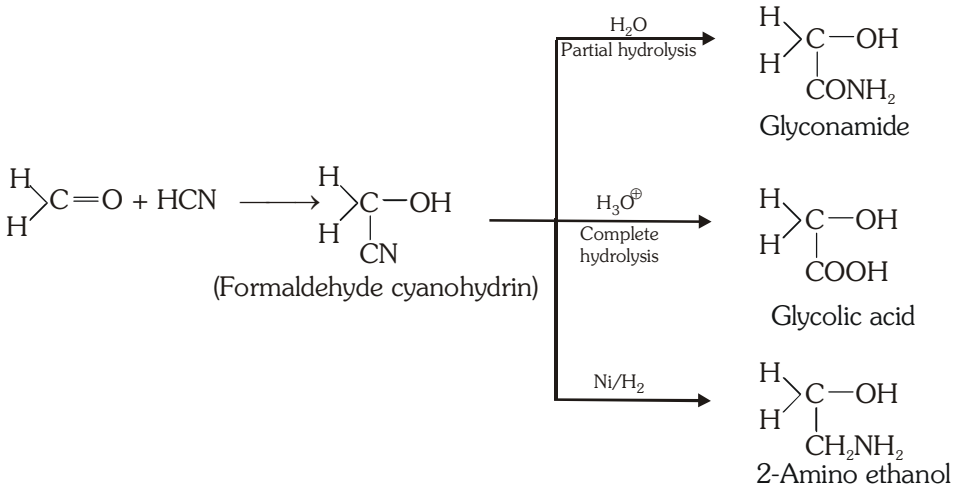
Ans. (i) > (ii)

CHEMICAL REACTION OF NAR

(1) Addition of HCN :



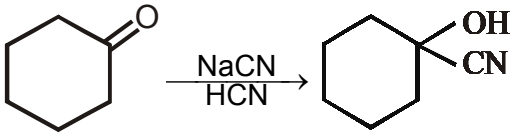
(I)

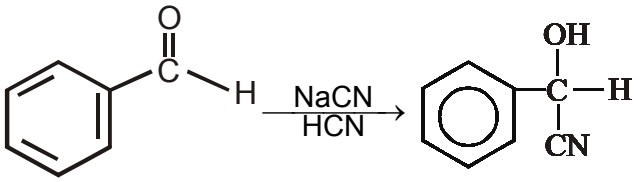


(II) $CH_3CH(H)C{=}O + HCN \longrightarrow CH_3CH(H)C^{*}(OH)CN$

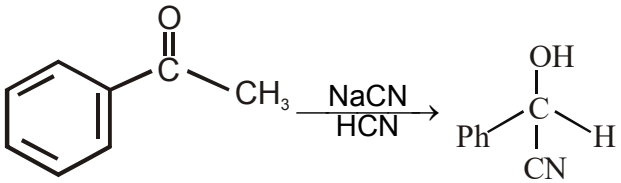
Acetaldehyde Cyanohydrin
*(Racemic mixture)

- $\xrightarrow[\text{Partial hydrolysis}]{H_2O}$ $CH_3CH(H)C(OH)CONH_2$ (+ –)
  Lactamide (2-Hydroxy propanamide)
- $\xrightarrow[\text{Complete hydrolysis}]{H_3O^{\oplus}}$ $CH_3CH(H)C(OH)COOH$ (+ –)
  Lactic acid (2- Hydroxy propanoic acid)
- $\xrightarrow{Ni/H_2}$ $CH_3CH(H)C(OH)CH_2NH_2$ (+ –)
  1-Amino – 2-Propanol

(III) 

(IV) 

(+ –)

(V) 

(+ –)

(2) Addition of $NaHSO_3$: (Reaction is useful in POC)

This reaction is utilized for the separation of carbonyl compounds from non - carbonyl compounds.

$>C{=}O + NaHSO_3 \longrightarrow >C(OH)SO_3Na \xrightarrow{H_3O^{\oplus}}$ Carbonyl compounds. *(Regain)

Sodium bi sulphite — Bisulphite compound (Crystalline) White ppt (soluble in water)

Mechanism : $NaHSO_3 \rightleftharpoons Na^+ + H\bar{S}O_3$

$H\bar{S}O_3 \rightleftharpoons H^+ + SO_3^{-2}$

$>C{=}O + SO_3^{-2} \xrightarrow{\text{Slow}} >C(O^{\ominus})SO_3^{\ominus} \xrightarrow[\text{Fast}]{H^+} >C(OH)SO_3^{\ominus} \xrightarrow{Na^+} >C(OH)SO_3Na$

(3) Reaction with ammonia derivatives :

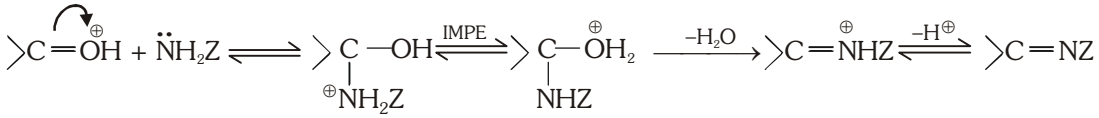
These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.

$$NH_3 + Z \xrightarrow[+Z]{-H} NH_2Z \text{ (Ammonia derivative)}$$

$$>C=O + H_2N-Z \longrightarrow >C=N-Z + H_2O$$

Addition - elimination (Condensation)

Mechanism :

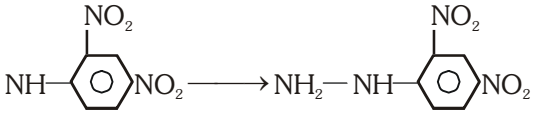


◆ **Ammonia derivatives (NH_2Z) :**

$Z = OH \longrightarrow NH_2OH$ (Hydroxyl amine)

$Z = NH_2 \longrightarrow NH_2NH_2$ (hydrazine)

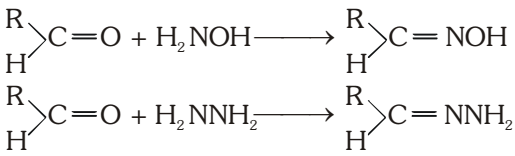
$Z = NHC_6H_5 \longrightarrow NH_2NHC_6H_5$ (Phenyl hydrazine)

$Z =$ 

2, 4–Dinitro phenyl hydrazine (DNP) / Brady's reagent / Borsch reagent.

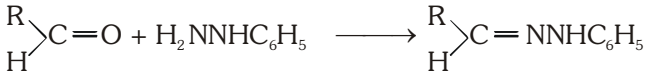
$Z = NHCONH_2 \longrightarrow NH_2NHCONH_2$

Semi Carbazide.

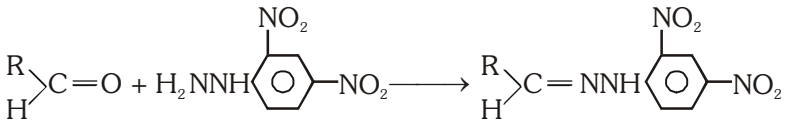


(Aldoxime)

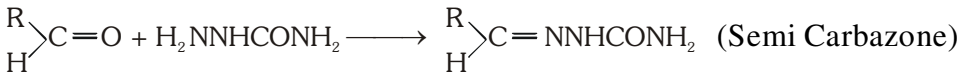
(Hydrazone)



(Phenyl hydrazone)



2,4-DNP (Brady's reagent) (2, 4 - dinitro phenyl hydrazone) (Yellow ppt)



(Semi Carbazone)

Imp. Note :

1. NH_3 gives imine as product with carbonyl compound.

2. 1° amines (primary amines) give ⟶ N-alkyl imine and 2° amines give ⟶ enamine

3. DNP reagent useful in POC to identify carbonyl compound.

(i) $CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{hydrazine}]{NH_2-NH_2} >C=N-NH_2$

(ii) $CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{Phenylhydrazine}]{NH_2-NH-Ph} >C=N-NHPh$

(iii) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[\text{hydroxyl amine}]{NH_2OH} >C=N-OH$

(iv) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[\text{Semicarbazide}]{NH_2-NH-\overset{\overset{O}{\|}}{C}-NH_2} >C=N-NH-\overset{\overset{O}{\|}}{C}-NH_2$

(4) With alcohol and thioalcohol :

$\begin{matrix}H\\R\end{matrix}\!\!>C=O + ROH \xrightarrow{HCl(g)} \begin{matrix}H\\R\end{matrix}\!\!>C<\begin{matrix}OH\\OR\end{matrix} \xrightarrow[HCl(g)]{ROH} \begin{matrix}H\\R\end{matrix}\!\!>C<\begin{matrix}OR\\OR\end{matrix}$

Hemi-acetal Acetal

$\begin{matrix}R\\R\end{matrix}\!\!>C=O + 2ROH \xrightarrow{HCl(g)} \begin{matrix}R\\R\end{matrix}\!\!>C<\begin{matrix}OR\\OR\end{matrix} + H_2O$

Ketal

Tri ethoxy methane $[HC(OC_2H_5)_3]$ remove the water formed during the reaction and so the reaction proceeds in forward direction.

$\begin{matrix}R\\H\end{matrix}\!\!>C=O + 2RSH \xrightarrow[-H_2O]{HCl(g)} \begin{matrix}R\\H\end{matrix}\!\!>C<\begin{matrix}SR\\SR\end{matrix}$

Thioalcohol Mercaptal

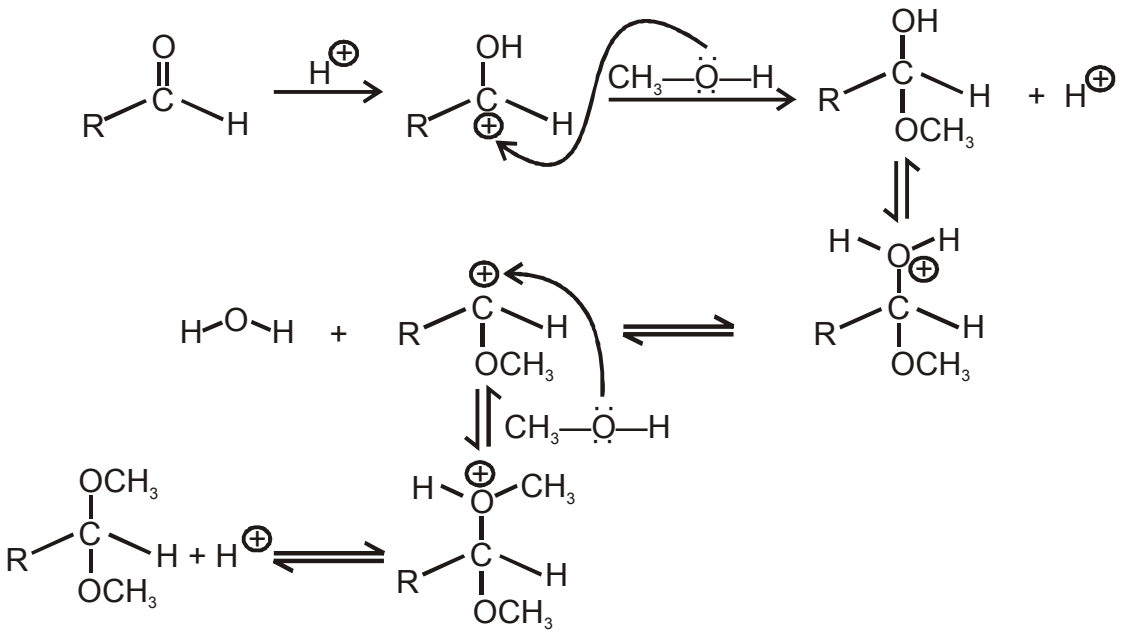
$\begin{matrix}R\\R\end{matrix}\!\!>C=O + 2RSH \xrightarrow[-H_2O]{HCl(g)} \begin{matrix}R\\R\end{matrix}\!\!>C<\begin{matrix}SR\\SR\end{matrix}$

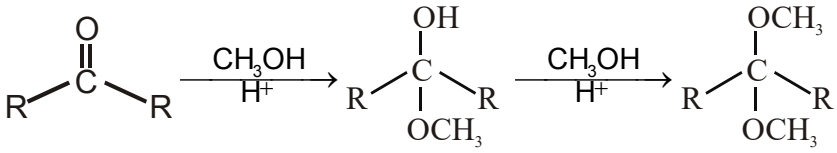
Mercaptal (Thio Ketal)

$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CH_3OH/H^+} R-\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow{CH_3OH/H^+} R-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-H$

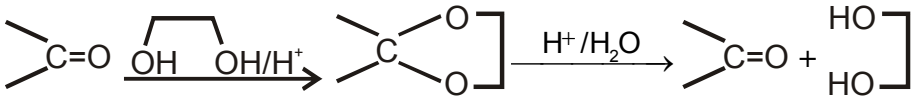
Hemiacetal acetal

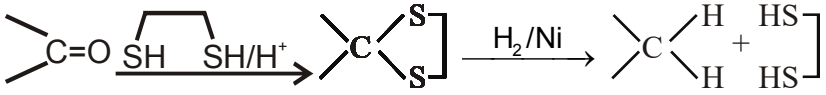
Mechanism :





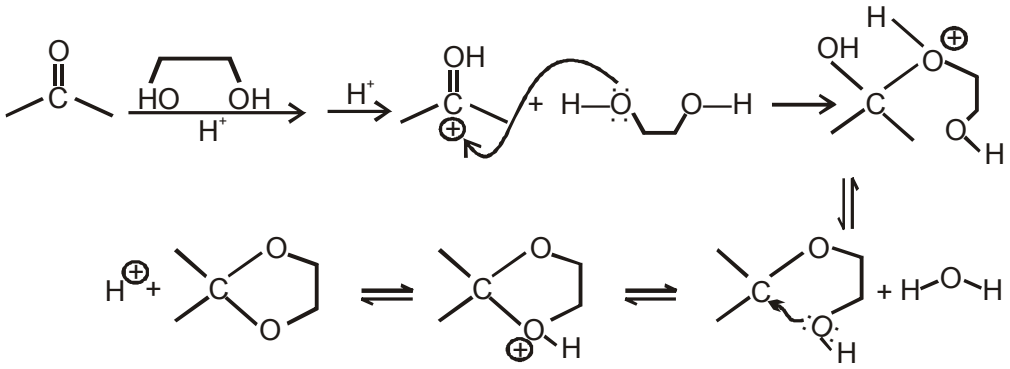
Reactions with diols (Thiols) (Group protection)

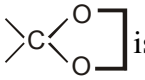
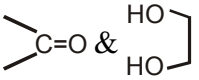




(Mozingo Reduction)

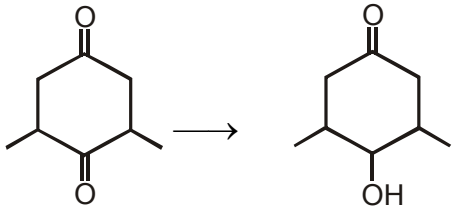
Mechanism



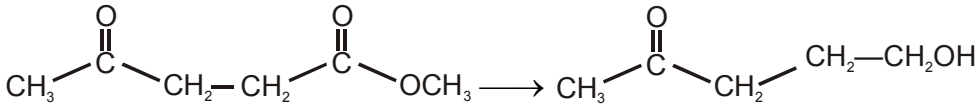
 is stable in basic medium but in aqueous acidic medium it converts to 

Convert

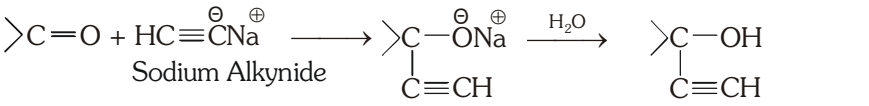
(i)



(ii)



(5) Reaction with sodium alkynide :

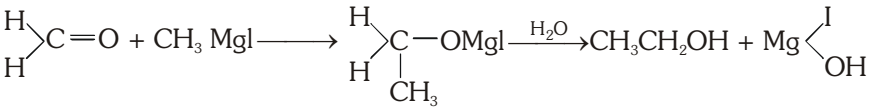


Sodium Alkynide

Acetylinic alcohol

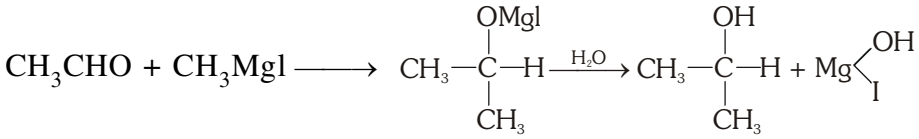
(6) Reaction with Grignard reagent :

Ex.(i)



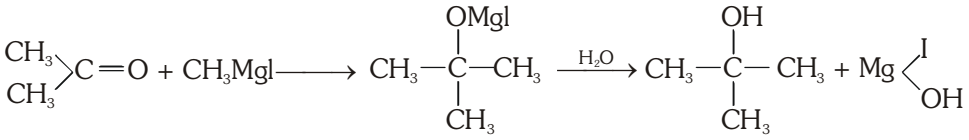
Ethanol (1° alcohol)

(ii)



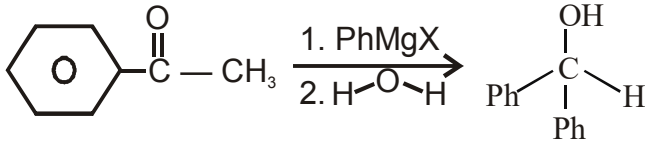
2–Propanol (2° alcohol)

(iii)

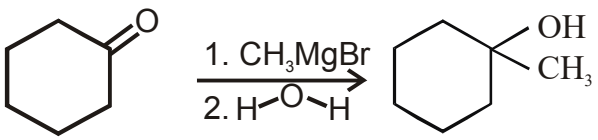


2–Methyl–2–propanol (3° alcohol)

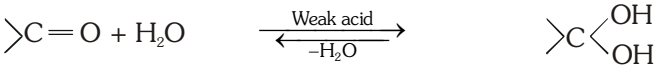
(iv)



(v)



(7) Reaction with H_2O : It is a reversible reaction.



(neutral)

unstable hydrate

Q.1 Which compound form more stable hydrate with H_2O?

(A) HCHO (B) CH_3CHO (C) CH_3COCH_3 (D) $CH_3COC_2H_5$

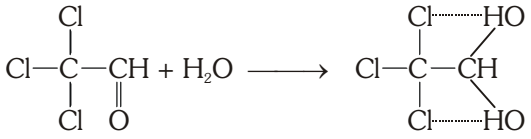
[Hint : HCHO since it is more reactive towards this reaction.]

Ans. (A)

Q.2 Which carbonyl compound not gives reversible reaction with water ?

Sol. Chloral hydrate.

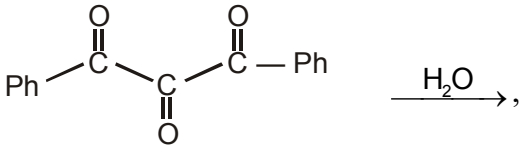
Ex.1



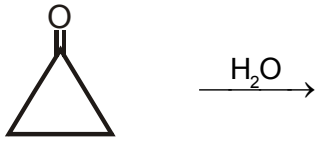
(Chloral) (Chloral hydrate)

Stable by intra molecular hydrogen bonding.

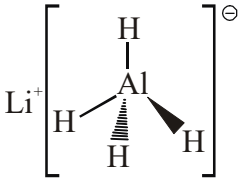
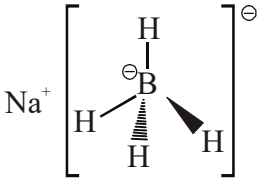
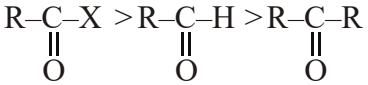
Ex.2

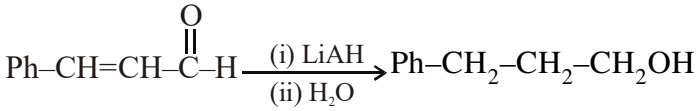


Ex.3

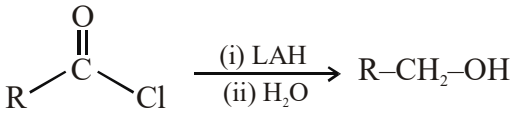


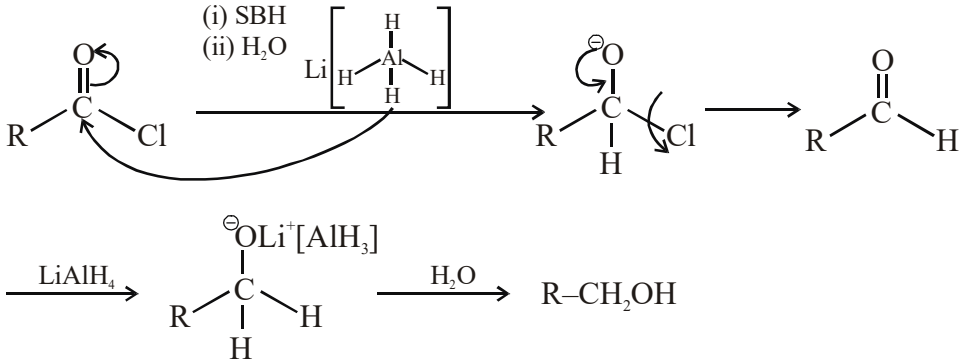
8. REDUCTION BY METALLIC HYDRIDES

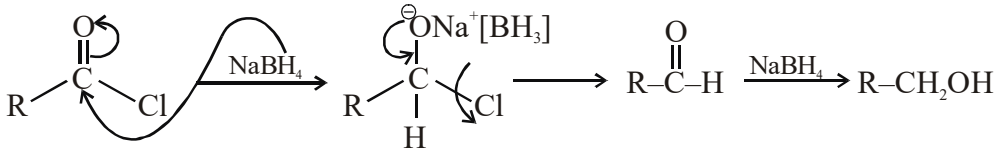
	Lithium aluminium hydride	Sodium borohydride
→	$LiAlH_4$ (LAH)	$NaBH_4$(SBH)
→		
→	Nucleophilic reducing agent	Nucleophilic reducing agent (Weak reducing agent)
→	It reduces most of functional group except	It reduces only
	* Alcohol	
	* Ordinary alkene	
→	It reduces cinamic double bond	

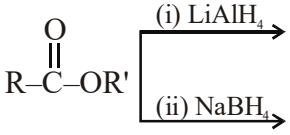


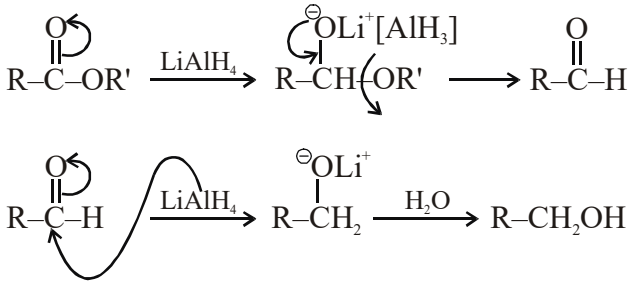
→ Stronger reducing agent

1. 

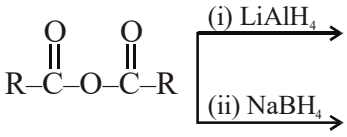
(i) 

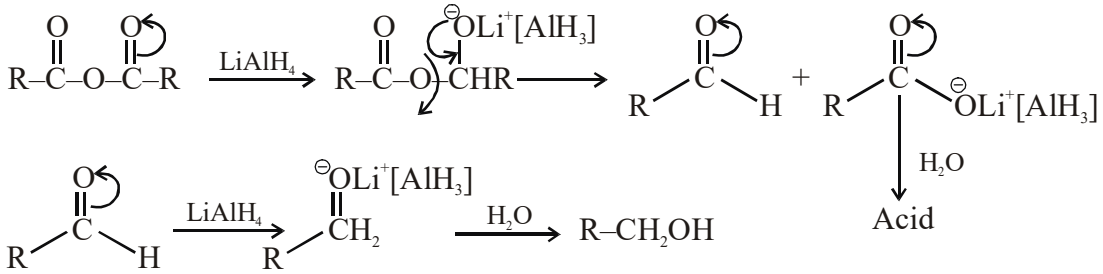
(ii) 

2. 

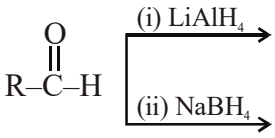
(i) 

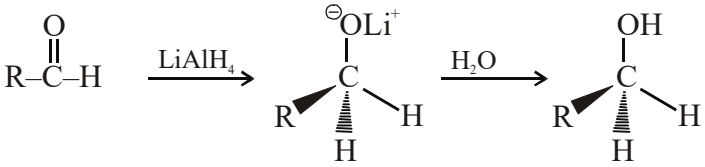
(ii) No reaction

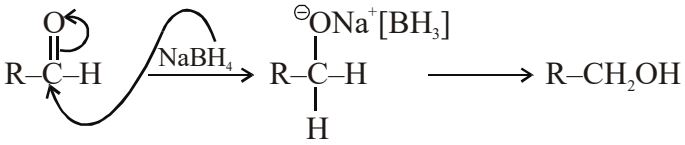
3. 

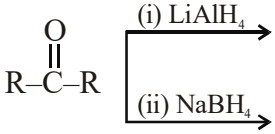
(i) 

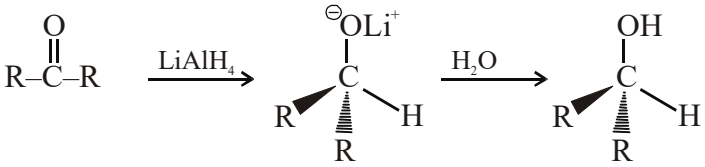
(ii) No reaction

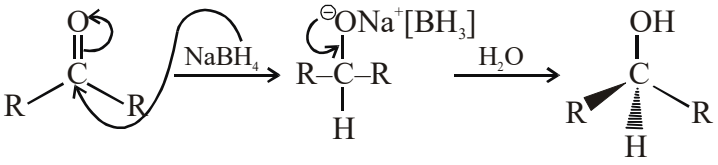
4. 

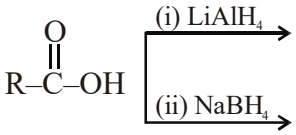
(i) 

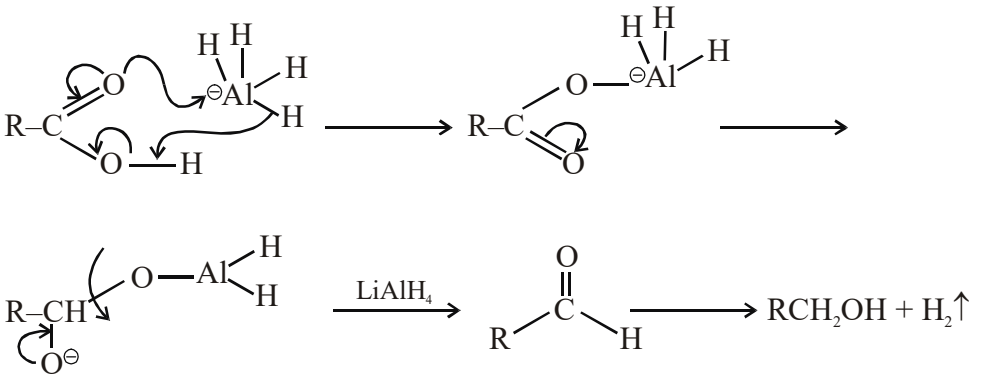
(ii) 

5. 

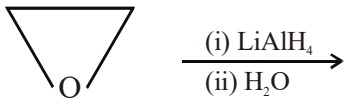
(i) 

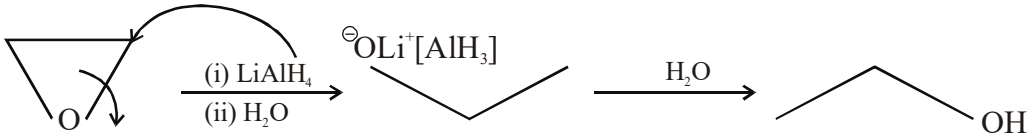
(ii) 

6. 

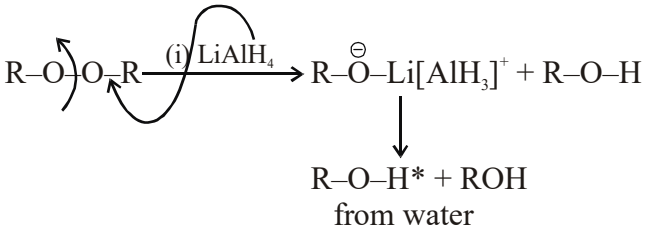
(i) 

(ii) No reaction

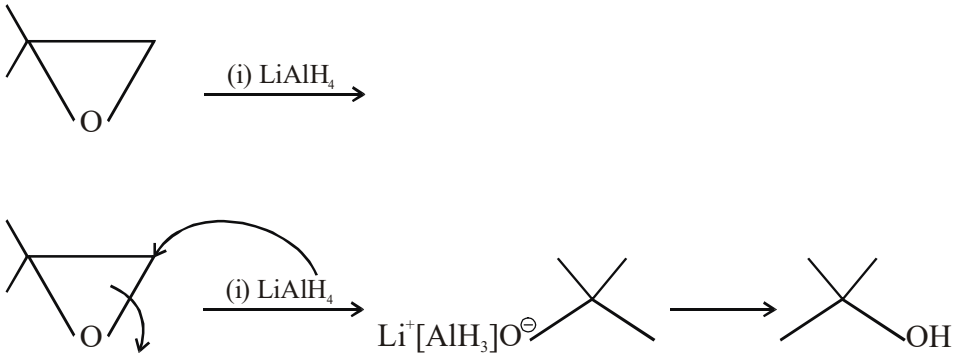
7. 

(i) 

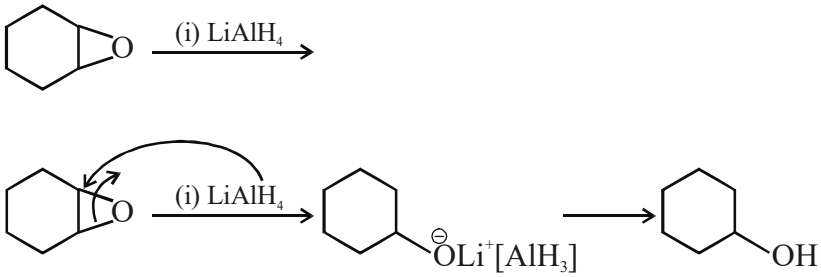
8. $R–O–O–R \xrightarrow{(i)\ LiAlH_4}$



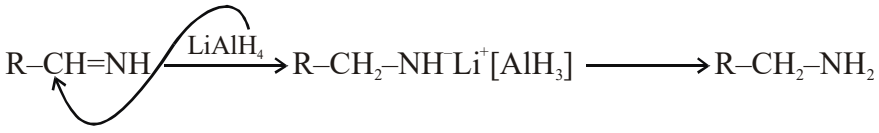
9.



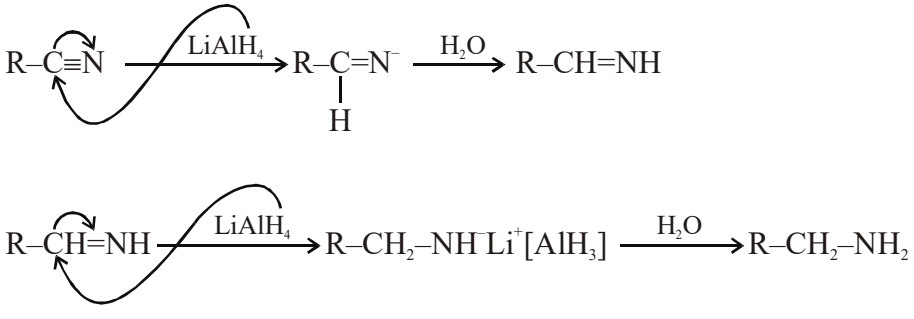
10.



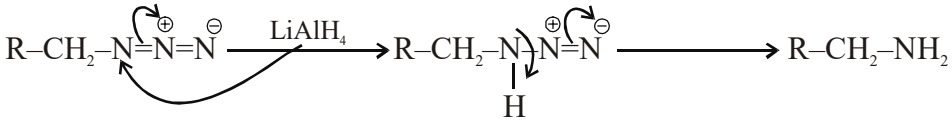
11. $R–CH=NH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$



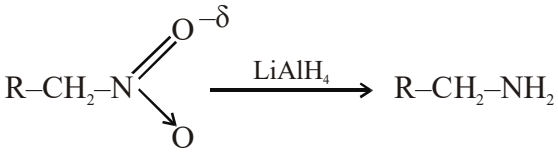
12. $R–C\equiv N \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$



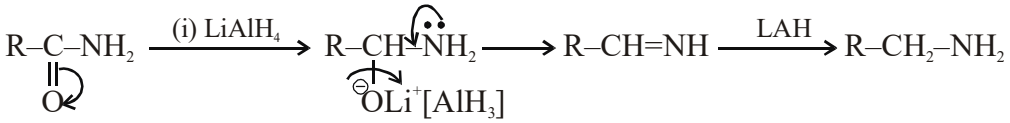
13. $R–CH_2–N_3 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$



14. $R–CH_2–NO_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$



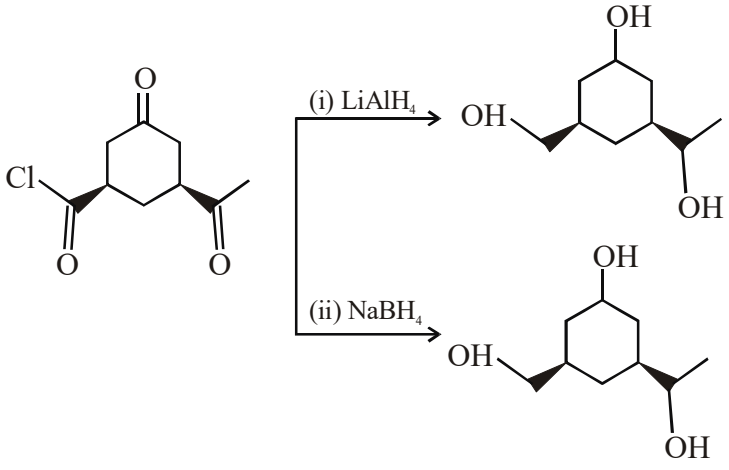
15. $R–\underset{\underset{O}{\|}}{C}–NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2NH_2$



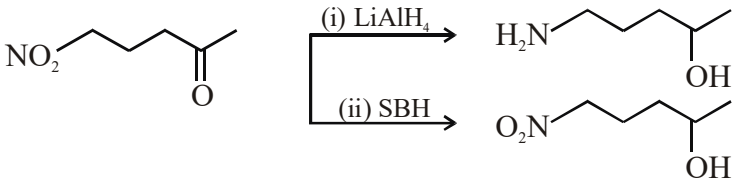
16. $R–\underset{\underset{O}{\|}}{C}–NHR' \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R–CH_2–NHR$

17. $R–\underset{\underset{O}{\|}}{C}–NR_2' \xrightarrow{LAH} R–CH_2–NR_2$

18.



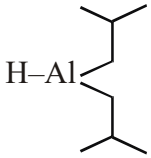
19.



Note: METALLIC HYDRIDE

* Di-iso-butyl aluminium hydride

→ DIBAL-H



$HAl–(CH_2–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_3)_2$

or $H–Al(iBu)_2$

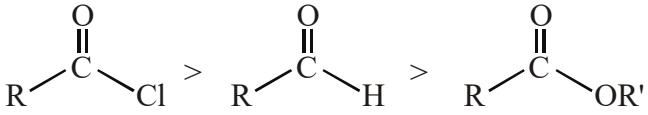
→ Electrophilic reducing agent

→ DIBAL-H is highly reactive

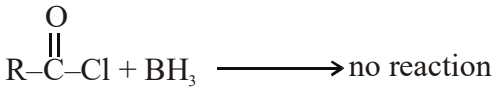
→ Single hydride donor

→ DIBAL-H is used at –78°C

→ Reactivity order

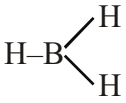


→ One step reducing agent



Borane or diborans

→ BH_3 or B_2H_6



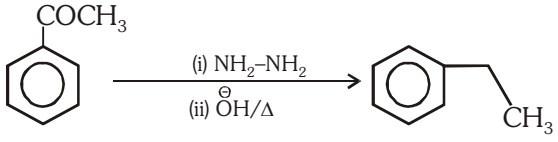
→ electrophilic reducing agent

→ Borane is milder reducing agent.

9. Reduction :

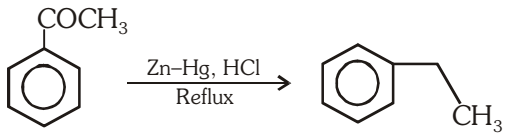
(a) The wolf kishner reduction :

When a ketone or an aldehyde is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group this process is called Deoxygenation because an oxygen is removed from the reactant. The reaction is known as the Wolf-kishner Reduction.



(b) Clemmensen Reduction :

The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction.



The nature of product depends upon the reducing agent used. It can be summarized as.

(i) $>C=O \longrightarrow >CH_2$ Reducing agents are

- Red P/HI at 150°C
- Zn-Hg/HCl [Clemensen's reduction]
- $NH_2—NH_2/C_2H_5OH,OH^{\ominus}$ [Wolff Kishner's reduction]

(ii) $>C=O \longrightarrow >CHOH$ Reducing agents are

- H_2 / Ni, Pd, Pt, Δ
- $LiAlH_4$
- Na/C_2H_5OH (Bouvalt blank)
- NaH/Benzene (Darzen reaction)
- $[(CH_3)_2CHO]_3Al$ / (Aluminium isopropoxide)

$(CH_3)_2$ CHOH (Isopropyl alcohol)

Reduction with aluminium isopropoxide in excess of isopropanol is called MPV **(Meerwein Ponndroff Verley)** reduction.

Note : Other reducible groups are not attacked like —NO_2, —CH=CH_2, —C≡C—.

Example : $\begin{matrix} CH_3 \\ CH_2=CH \end{matrix}\!\!>C=O \xrightarrow{\text{MPV Reduction}} \begin{matrix} CH_3 \\ CH_2=CH \end{matrix}\!\!>CHOH$

Reactions given by only aldehydes :

(1) Polymerisation : It is a reversible process.

Formaldehyde :

(a) $nHCHO \underset{\Delta}{\overset{\text{Evaporation}}{\rightleftharpoons}} (CH_2O)_n,\ H_2O$

Formalin (40% HCHO)

Paraformaldehyde
n = 6–50
Hydrated white crystal

Paraformaldehyde is a linear polymer which show reducing character with Tollen's reagent, Fehling solution etc.

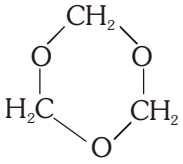
(b) $nHCHO \underset{H_2SO_4\Delta}{\overset{Conc.}{\rightleftharpoons}} (CH_2O)_n\, H_2O$

Poly oxy methylene

n > 100

(c) $3HCHO \xrightarrow[\text{at room temp.}]{\text{Allowed to stand}} (CH_2O)_3$

Meta formaldehyde (Trioxane)
Cyclic polymer (Trioxy methylene)
Cyclic polymer doesn't show reducing character with Tollen's reagent etc.



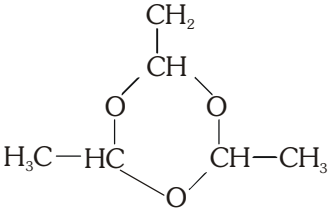
(d) $6HCHO \xrightarrow[\text{or } Ba(OH)_2]{Ca(OH)_2} C_6H_{12}O_6$

Formose sugar
A linear polymer (α -acrose)

(e) $6HCHO \xrightarrow{4NH_3}$ Urotropine

Acetaldehyde :

(a) $3CH_3CHO \xrightarrow[\text{Room temp.}]{\text{Conc. } H_2SO_4} (CH_3CHO)_3$

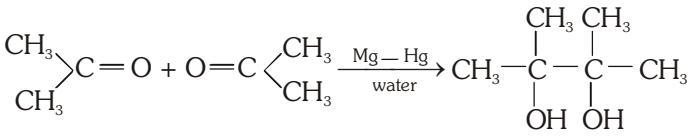


Para acetaldehyde
Paraldehyde (cyclic polymer)
Pleasent smelling liquid
Hypnotic compound

(b) $4CH_3CHO \xrightarrow[0°C]{\text{conc. } H_2SO_4} (CH_3CHO)_4$

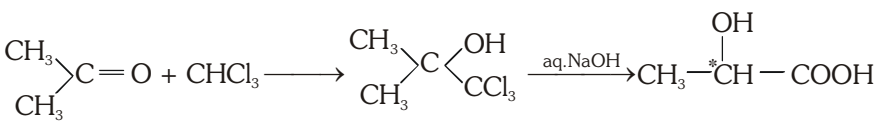
Reaction of only ketones :

(1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



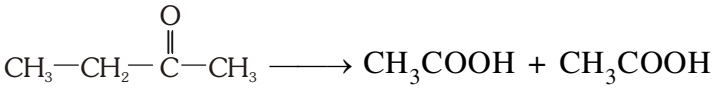
Pinacol

(2) Reaction with chloroform :



(Chloretone) (Lactic acid)
2-Hydroxy propanoic acid

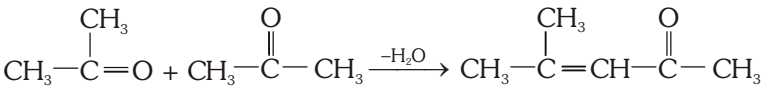
(4) Oxidation reaction : According to popoff's rule $>C=O$ group stays with smaller alkyl group.



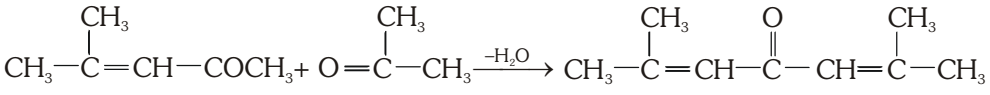
Oxidation of ketone is only possible in vigrous condition with strong oxidising agent.

(5) Condensation reaction :

(a) In presence of dry HCl - aldol condensation takes place

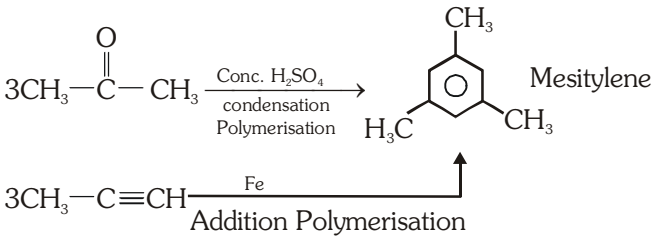


Mesityl oxide

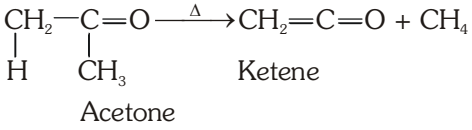


(Phorone) or 2,6–Dimethyl–2,5–hepta diene–4–one

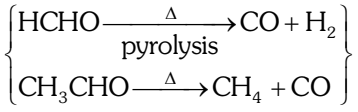
(b) In presence of conc.H_2SO_4



(7) Pyrolysis :



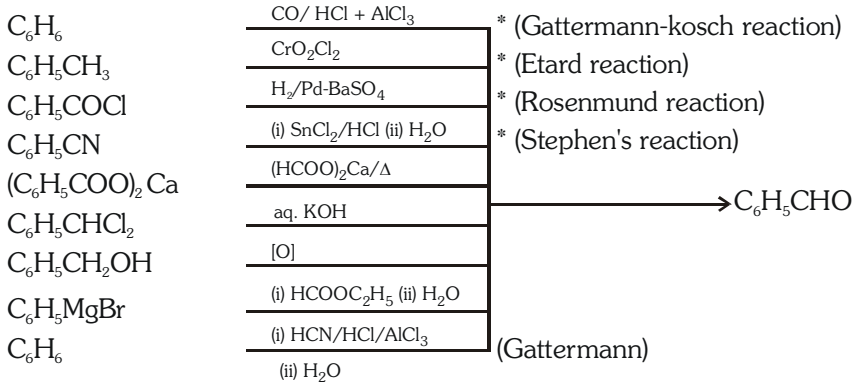
Acetone Ketene



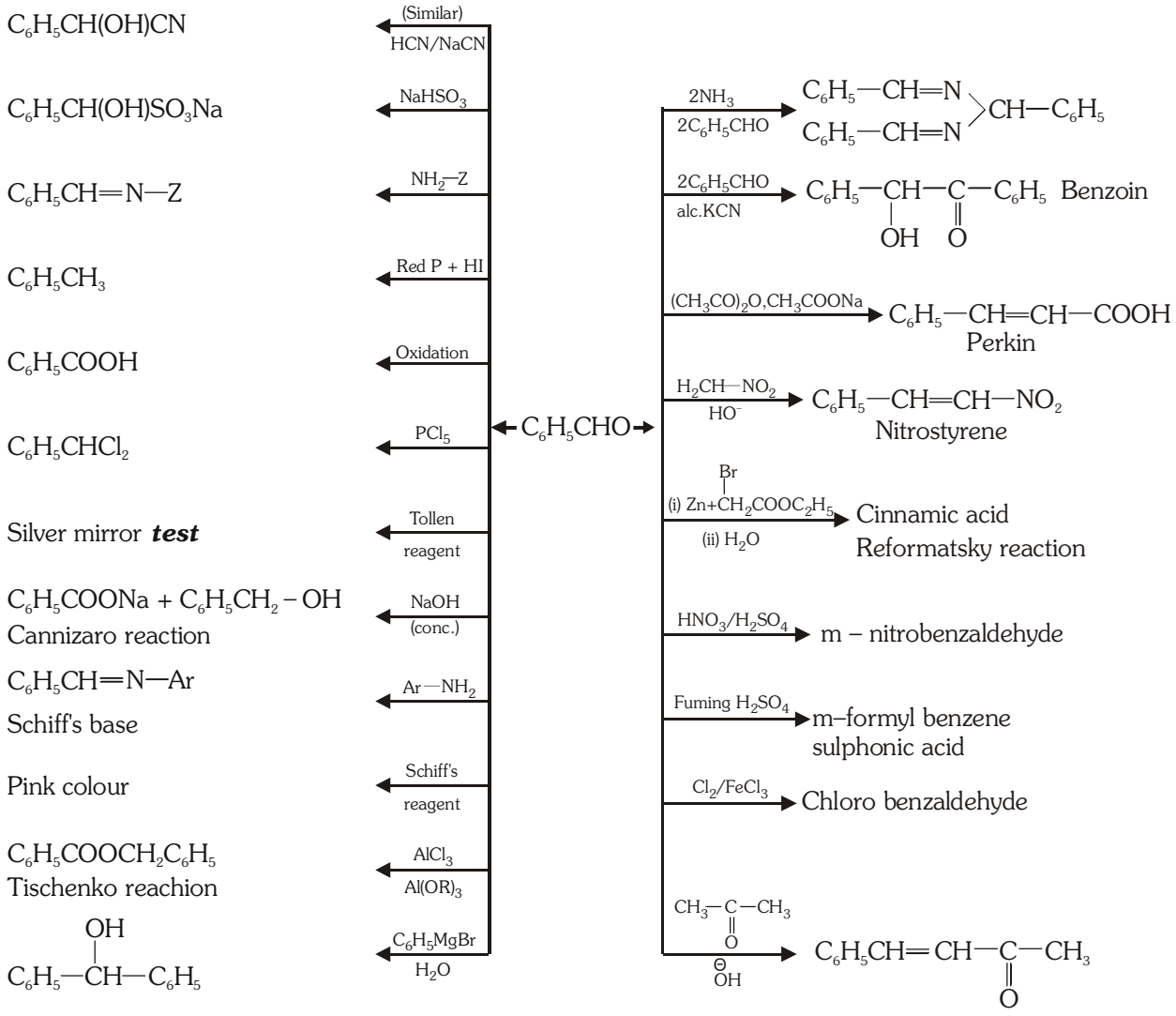
BENZALDEHYDE (C_6H_5CHO)

Oil of bitter almonds

General Method of Preparation :



Chemical properties :



CARBONYL COMPOUND

EXERCISE # O-I

Q.1 Arrange these compounds in decreasing order of reactivity for the nucleophilic attack :

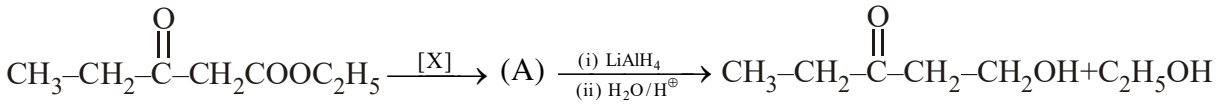
(I) Acid chloride (II) Aldehyde (III) Ketone (IV) Ester

Select the correct answer from the codes given below :

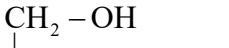
(A) I > II > III > IV (B) IV > III > II > I (C) III > II > I > IV (D) I > IV > II > III

CL0001

Q.2 In the given reaction

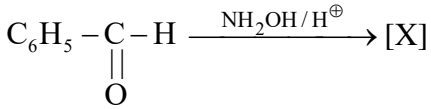


[X] will be :

(A) HCHO (B)  (C) (D) HCN

CL0002

Q.3 In the given reaction:



[X] will be:

(A) Only syn oxime (B) Only anti oxime

(C) Mixture of syn and anti oxime (D) Secondary amide **CL0003**

Q.4 Acetophenone can be obtained by the distillation of :

(A) $(C_6H_5COO)_2Ca$ s (B) $(CH_3COO)_2Ca$

(C) $(C_6H_5COO)_2Ca$ and $(CH_3COO)_2Ca$ (D) $(C_6H_5COO)_2Ca$ and $(HCOO)_2Ca$ **CL0004**

Q.5 Gem dihalide on hydrolysis gives :

(A) Vic diol (B) Gem diol

(C) Carbonyl compound (D) Carboxylic acid **CL0005**

Q.6 Acetal or ketal is:

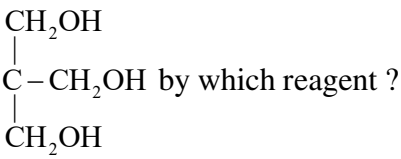
(A) Vic dialkoxy compound (B) α, ω-dialkoxy compound

(C) α-alkoxy alcohol (D) Gem dialkoxy compound **CL0006**

Q.7 Cross cannizzaro reaction is example of :

(A) Redox reaction (B) Disproportionation

(C) Both (A) and (B) (D) Only oxidation **CL0007**

Q.8 Acetaldehyde can be converted into  by which reagent ?

(A) KOH (B) KOH followed by LAH

(C) excess of HCHO and KOH (D) KCN followed by SBH **CL0008**

Q.9 Which one of the combinations will give propanaldehyde on dry distillation ?

(A) $(C_6H_5COO)_2Ca$ and $(HCOO)_2Ca$ (B) $(CH_3COO)_2Ca$ and $(CH_3CH_2–COO)_2Ca$

(C) $(CH_3–CH_2–COO)_2Ca$ and $(HCOO)_2Ca$ (D) $(CH_3COO)_2Ca$ and $(CH_3COO)_2Ca$

CL0009

Q.10 In the given reaction :

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Distillation}]{\text{Conc.}H_2SO_4} [X]$$

[X] will be :

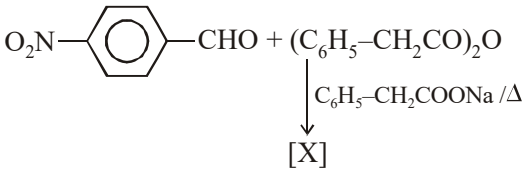
(A) Methyl oxide (B) Phorone

(C) 1, 3, 5-Trimethylbenzene (D) 2-Butyne **CL0010**

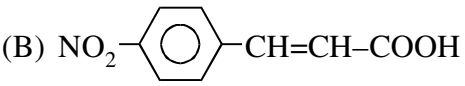
Q.11 Grignard reagents can not give carbonyl compounds with :

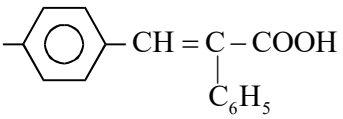
(A) CO_2 (B) RCOCl (C) RCN (D) RCOOR **CL0011**

Q.12 The product of the reaction :



will be :

(A) $C_6H_5–CH=CH–COOH$ (B) 

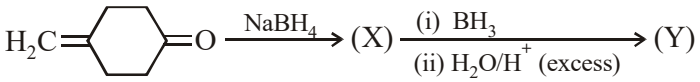
(C) $C_6H_5-CH=\underset{\underset{CH_3}{|}}{C}-COOH$ (D)  **CL0012**

Q.13 Cyanohydrin of which compound on hydrolysis will give lactic acid ?

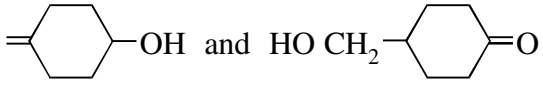
(A) C_6H_5CHO (B) HCHO (C) CH_3CHO (D) $CH_3–CH_2–CHO$

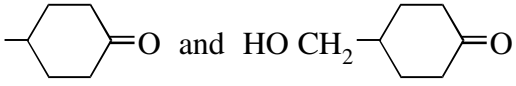
CL0013

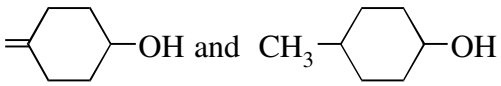
Q.14 In the given reaction :

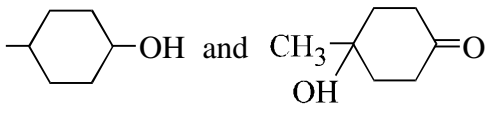


(X) and (Y) are :

(A) 

(B) 

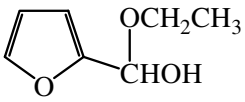
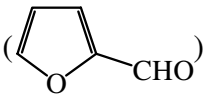
(C) 

(D)  **CL0014**

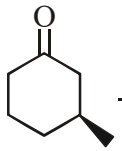
Q.15 Acetaldehyde cannot give :

(A) Iodoform test (B) Lucas test (C) Benedict test (D) Tollens test

CL0015

Q.16 Compound  formed by the reaction of furfural () with ethanol is :

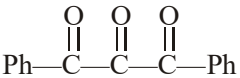
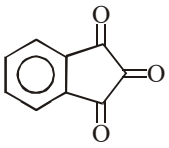
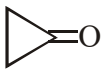
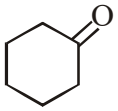
(A) an aldol (B) an acetal (C) a ketal (D) a hemiacetal **CL0016**

Q.17  $\xrightarrow[(2)\ H_2O]{(1)\ NaBH_4}$ A + B

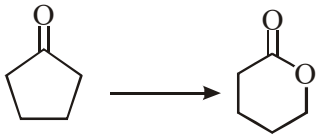
Identify relationship between A & B products ?

(A) Diastereoisomers (B) Enantiomers (C) Positional isomer (D) Identical **CL0017**

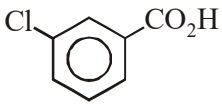
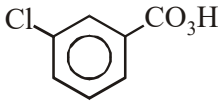
Q.18 Which of the following does not form a stable hydrate by the addition of H_2O?

(A)  (B)  (C)  (D)  **CL0018**

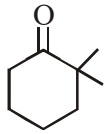
Q.19 The conversion



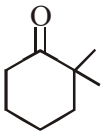
can be effected by using the reagent

(A) Tollen's reagent (B) O_3 (C)  (D) 

CL0019

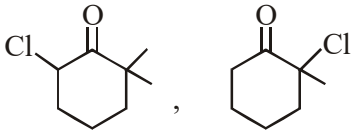
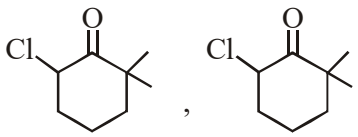
Q.20 (I)  + Cl_2 $\xrightarrow{NaOH}$ P

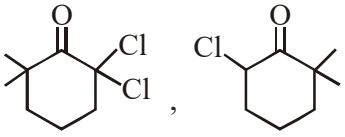
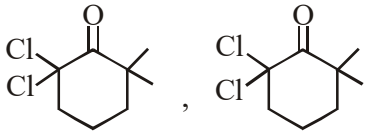
1 (mole) : 1 (mole)

(II)  + Cl_2 $\xrightarrow{CH_3COOH}$ Q

1 (mole) : 1 (mole)

Organic product P & Q are respectively -

(A)  (B) 

(C)  (D) 

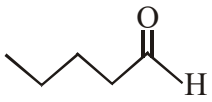
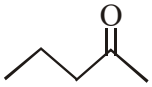
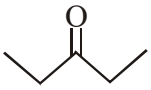
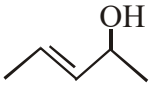
CL0020

Q.21 Total number of stereoisomers of major product (Q) are :

$$CH_3–CHO + 4HCHO \xrightarrow[-HCOONa]{NaOH} (P) \xrightarrow[H^{\oplus}]{2CH_3–CHO} (Q)$$

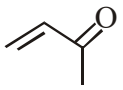
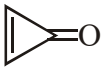
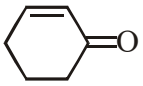
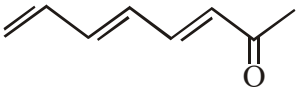
(A) 0 (B) 4 (C) 8 (D) 2 **CL0021**

Q.22 An organic compound (A), $C_5H_{10}O$, reacts with hydrazine to form a hydrazone derivative (B). The hydrazone (B) on being heated with KOH at about 180ºC, gives n-pentane. The compound (A) does not respond positively to Tollen's reagent and to the iodoform test. The compound (A) is

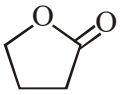
(A)  (B)  (C)  (D) 

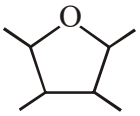
CL0022

Q.23 The compound having the highest dipole moment is :

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

CL0023

Q.24  $\xrightarrow[(2)\ H_2O]{(1)\ \text{Excess MeMgCl}}$ (A) $\xrightarrow[H_2SO_4]{\text{conc.}}$ 'B' Identify 'B' product ?

(A)  (B)  (C)  (D)  **CL0024**

Question No. 25 to 27 (3 questions)

An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only product (B) C_8H_8O. (B) also can be obtained by hydrolysis of the product obtained by reaction between cyano benzene and CH_3MgBr. (A) can show geometrical isomerism and it can decolourise Br_2 water. (B) on treatment with SeO_2 produces (C)

Q.25 Which is not correct about (A) ?

(A) A is optically inactive

(B) On catalytic hydrogenation 'trans' form of A produces racemic mixture

(C) A can be prepared by Witting reaction on acetophenone with $Ph_3P = C(CH_3)Ph$.

(D) On treatment with per acid followed by hydrolysis 'trans' form of A produces racemic mixture

CL0025

Q.26 Which is not correct about B ?

(A) It gives iodoform test

(B) On treatment with $LiAlH_4$, H_2O it produces a compound which also responds to iodoform test.

(C) It gives Tollen's test

(D) On treatment with NH_2NH_2 followed by alc. KOH at high temperature, it produces ethyl benzene

CL0026

Q.27 Which is not correct about C?

(A) On treatment with $NaBH_4$ it will produce a diol.

(B) On treatment with OH^- (conc.) followed by acidification racemic mixture of a carboxylic acid is obtained

(C) It gives Tollen's test

(D) It can take part in aldol condensation **CL0027**

(Question No. 28 & 29)

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) If both (A) and (R) are true and (R) is the correct explanation of (A)

(B) If both (A) and (R) are true but (R) is not correct explanation of (A)

(C) If (A) is true but (R) is false

(D) If (A) is false and (R) is true

Q.28 **Assertion** : Benzaldehyde with HCN gives two isomeric compounds

Reason : Both nitrile and isonitrile compounds are possible when HCN reacts with carbonyl group.

CL0028

Q.29 **Assertion :** $Cl_3C-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NaOH} Cl_3C—CH_2OH + Cl_3C—COONa$

Reason : There are no α–H in this compound, so it can't give aldol. **CL0029**

EXERCISE # O-II

Q.1 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :

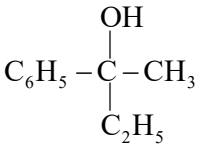
(A) I_2 / NaOH (B)$NaSO_3H$ (C) NaCN / HCl (D) 2,4-DNP **CL0030**

Q.2 An optically inactive alcohol (A) $C_6H_{12}O$ is oxidized by MnO_2 to produce optically inactive carbonyl compound while reduction of (A) by H_2/Ni produces optically active compound. Possible structure(s) of alcohol is/are

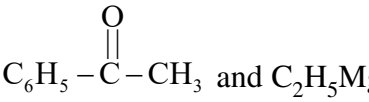
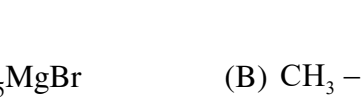
(A) Hex-2-ene-1- ol (B) Hex-3-ene-2- ol

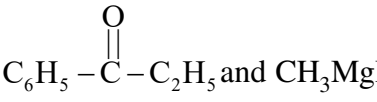
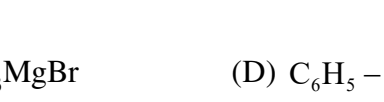
(C) 2-Methyl pent-2 - ene-1-ol (D) 3-Methyl pent-2 - ene-1-ol **CL0031**

Q.3 Consider the structure of given alcohol:



This alcohol can be prepared from:

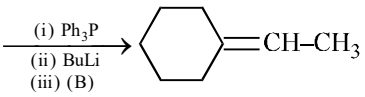
(A)  and C_2H_5MgBr (B)  and C_6H_5MgBr

(C)  and CH_3MgBr (D)  and C_2H_5MgCl **CL0032**

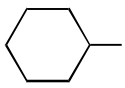
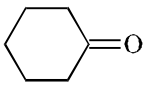
Q.4 Which of the following compounds will not give aldol condensation :

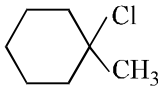
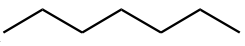
(A) Acetaldehyde (B) Formaldehyde (C) Pivaldehyde (D) Crotonaldehyde

CL0033

Q.5 (A) 

In above reaction (A) and (B) will respectively be

(A)  & CH_3CHO (B) CH_3CH_2Cl & 

\ (C)  & HCHO (D)  & CH_3CHO

CL0034

Q.6 Stability of hydrates of carbonyl compounds depends on:

(A) Steric hindrance (B) Presence of –I group on gemdiol carbon

(C) Intramolecular hydrogen bonding (D) angle strain in carbonyl compound

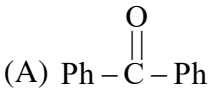
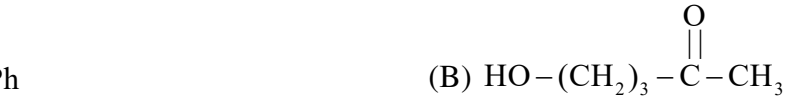
CL0035

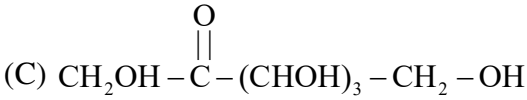
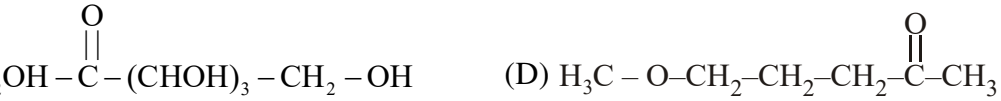
Q.7 Which of the following can be used for protection of carbonyl group

(A) $CH_2OH–CH_2OH$ / $H^{\oplus}$ (B) $CH_2OH–CH_2–CH_2OH$ / $H^{\oplus}$

(C) $HS–(CH_2)_3–SH$ (D) $CH_2OH–CH_2–CHO$ **CL0036**

Q.8 Which of the following(s) will form stable hemiketal :

(A)  (B) 

(C)  (D) 

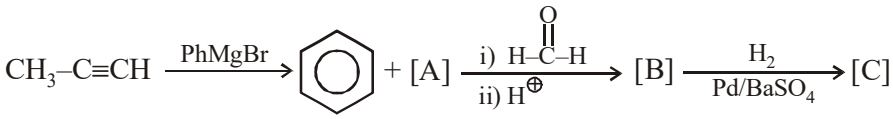
CL0037

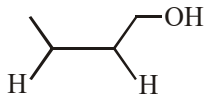
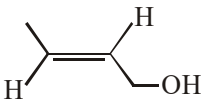
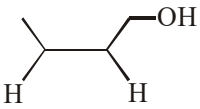
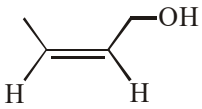
Q.9 Mixture of Ph–CHO & HCHO is treated with NaOH then Cannizzaro reaction involves:

(A) Oxidation of HCHO (B) Reduction of HCHO

(C) Oxidation of Ph–CHO (D) Reduction of Ph–CHO **CL0038**

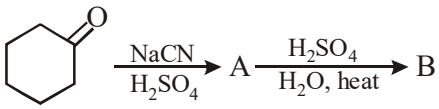
Q.10 Final product in the given reaction sequence is :



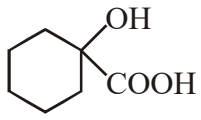
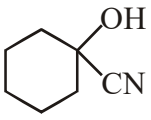
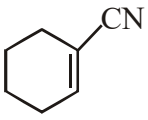
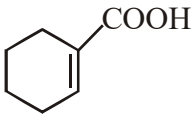
(A)  (B)  (C)  (D) 

CL0039

Q.11 Consider the following sequence of reactions.

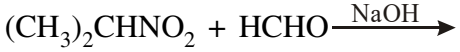


The major product (B) is :

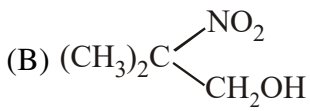
(A)  (B)  (C)  (D) 

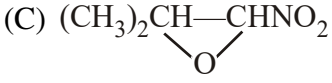
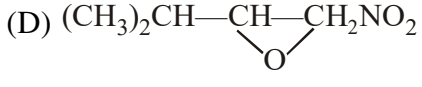
CL0040

Q.12 In the reaction

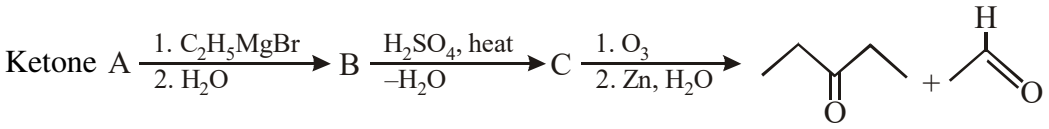


the major product is

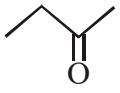
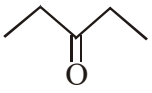
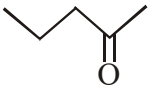
(A) $(CH_3)_2CHCH_2ONO_2$ (B) 

(C)  (D)  **CL0041**

Q.13 Consider the following sequence of reactions.



The ketone (A) is :

(A)  (B)  (C)  (D)  **CL0042**

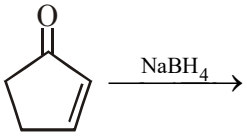
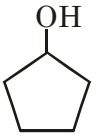
Q.14 Which of the following reactions will give(s) 2° alcohol as a major product :

(A) $CH_3—CH_2—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow[(ii)\ NaNO_2/HCl]{(i)\ LAH}$ (B) $H—\overset{O}{\overset{\|}{C}}—OR \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgX(excess)}$

(C) $H_3C—HC(\diagdown O \diagup)—CH_2 \xrightarrow[(ii)\ H^+]{(i)\ RMgX}$ (D) $CH_3—\overset{O}{\overset{\|}{C}}—Cl \xrightarrow[H^+]{CH_3MgX\ (excess)}$

CL0043

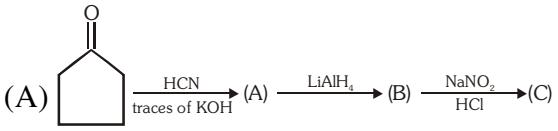
Q.15 Match list-I with list-II :

List - I	**List - II**
(A) 	(P) Acetal
(B) $C_6H_5CHO + Ph–NH_2 \xrightarrow{H^\oplus}$	(Q) Schiff's base
(C) $C_6H_5COCH_3+CH_3–CH_2–NH_2 \xrightarrow{H^\oplus}$	(R) 
(D) $RCHO + 2RCH_2OH \xrightarrow{H^\oplus}$	(S) Imine

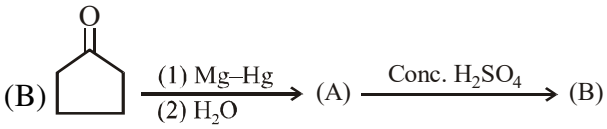
CL0044

EXERCISE # S-I

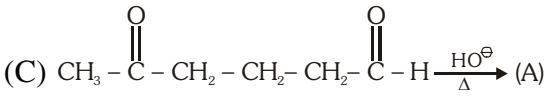
Q.1 **Column - I** **Column - II**

(A) 

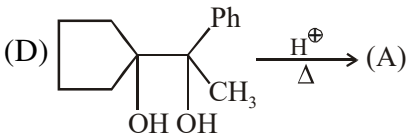
(P) Formation of six member ring takes place

(B) 

(Q) Final product is Ketone

(C) 

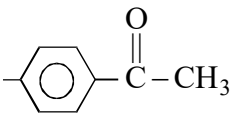
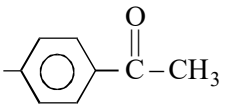
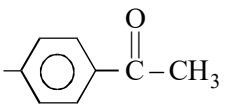
(R) Final product formed will give positive Idoform test

(D) 

(S) Final product formed will react with 2,4-DNP. (2,4-Di-nitrophenyl hydrazine)

CL0045

Q.2 Arrange the following compounds in decreasing order of $K_{eq.}$ for hydrate formation.

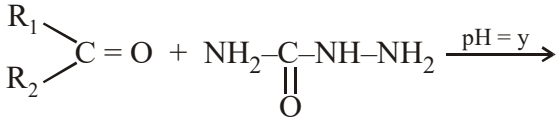
(1) $C_6H_5COCH_3$ (2)  (3)  (4) 

CL0046

Paragraph for Q. 03 to 04

Two reactions which are example of nucleophilic attack are given as below .

Reaction - I : 

Reaction - II : 

Q.3 Value of x is :

(A) $x \leq 4.5$ (B) $x = 6$ (C) $x > 7$ (D) Can't decide

CL0047

Q.4 Value of y is :

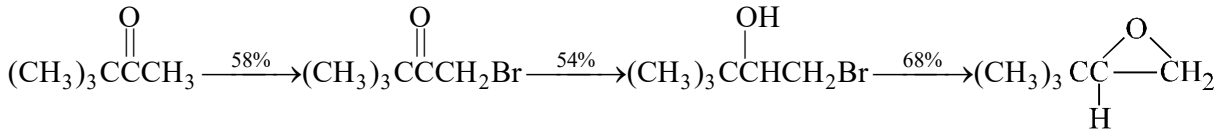
(A) $x = 4.5$ (B) $x = 1.5$ (C) $x = 7$ (D) $x = 9$

CL0047

Q.5 Some Grignard reagents react with ethyl orthoformate, followed by acidic hydrolysis, to give aldehydes. Propose mechanisms for the two steps in this synthesis.

CL0048

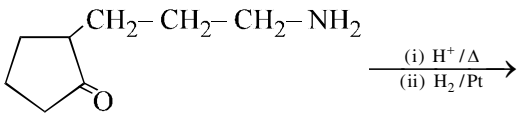
Q.6 A synthesis that begins with 3,3-dimethyl-2-butanone gives the epoxide shown. Suggest reagents appropriate for each step in the synthesis.

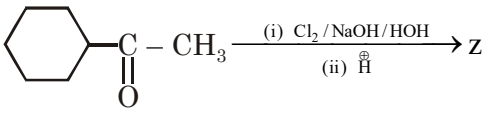


CL0049

Q.7 Predict the organic products :

(a) 

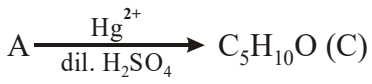
(b) 

(c) 

CL0050

Paragraph for Q.No.8 to 9

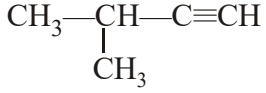
A(Hydrocarbon) (C ⇒ 88.24%) [Molecular weight of A = 68]

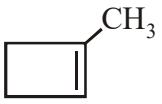


Q.8 'A' can be :

(A) $H_3C–H_2C–C\equiv C–CH_3$

(B) $CH_3–CH_2–CH_2–C\equiv C–H$

(C) 

(D) 

CL0051

Q.9 Correct statement reagarding C is.

(A) C reacts with fehling solution to give red ppt.

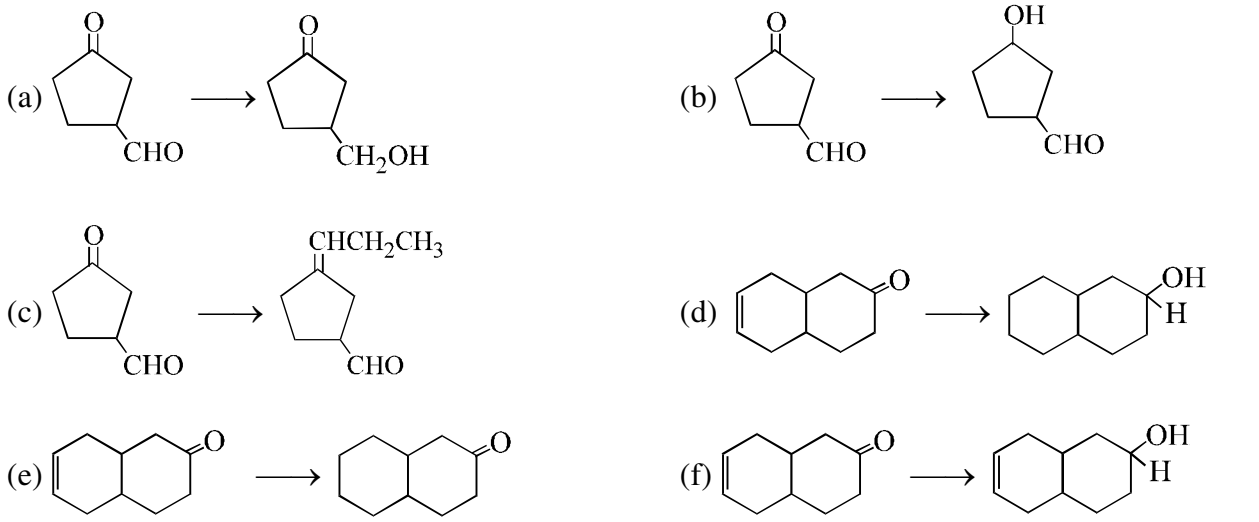
(B) C gives +ve iodoform test

(C) C give –ve 2, 4, D.N.P test

(D) C is aldehyde

CL0051

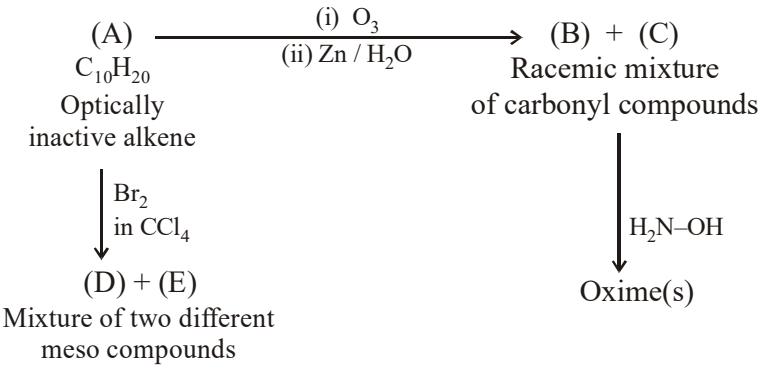
Q.10 Show how you would accomplish the following syntheses efficiently and in good yield. You may use any necessary reagents.



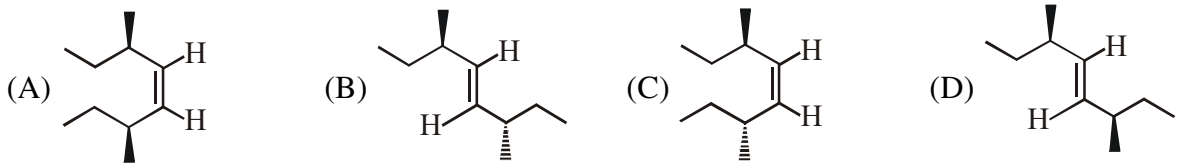
CL0052

Paragraph for Q.No. 11 to 12

In given reaction sequence



11. Alkene A is :



CL0053

12. How many total oxime(s) is/are obtained

(A) 1 (B) 2 (C) 3 (D) 4 **CL0053**

EXERCISE # (MAINS)

1. When $CH_2 = CH–COOH$ is reduced with $LiAlH_4$, the compound obtained will be - **[AIEEE-2003]**

(1) $CH_3–CH_2–CH_2OH$ (2) $CH_3–CH_2–CHO$

(3) $CH_3–CH_2–COOH$ (4) $CH_2=CH–CH_2OH$ **CL0054**

2. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE-2004]**

(1) Phenol (2) Benzaldehyde (3) Butanal (4) Benzoic acid **CL0055**

3. Which one of the following is reduced with Zn-Hg/HCl to give the corresponding hydrocarbon **[AIEEE-2004]**

(1) Butan-2-one (2) Acetic acid (3) Acetamide (4) Ethyl acetate **CL0056**

4. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[AIEEE-2004]**

(1) $CH_3COOC_2H_5 + NaCl$ (2) $CH_3COONa + C_2H_5OH$

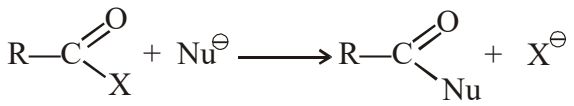
(3) $CH_3COCl + C_2H_5OH + NaOH$ (4) $CH_3Cl + C_2H_5COONa$ **CL0057**

5. The best reagent to convert pent–3–en–2–ol into pent –3–en –2–one is - **[AIEEE-2005]**

(1) Acidic dichromate (2) Acidic permanganate

(3) Pyridinium chloro-chromate (4) Chromic anhydride in glacial acetic acid **CL0058**

6. Rate of the reaction- **[AIEEE-2005]**

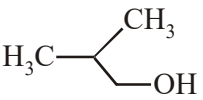


is fastest when X is -

(1) NH_2 (2) Cl (3) OCOR (4) OC_2H_5 **CL0059**

7. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is-

(1) $CH_3CH_2CH(OH)CH_2CH_3$ (2) $C_6H_5CH_2CH_2OH$ **[AIEEE-2006]**

(3)  (4) $PhCHOHCH_3$ **CL0060**

8. In the following sequence of reactions

$CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[Ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$, then compound 'D' is - **[AIEEE-2007]**

(1) Butanal (2) n–Butyl alcohol

(3) n–Propyl alcohol (4) Propanal **CL0061**

9. In the following sequence of reactions, the alkene affords the compound 'B' :- **[AIEEE-2008]**

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is

(1) CH_3CH_2CHO (2) CH_3COCH_3 (3) $CH_3CH_2COCH_3$ (4) CH_3CHO **CL0062**

10. Bakelite is obtained from phenol by reacting with **[AIEEE-2008]**
(1) $(CH_2OH)_2$ (2) CH_3CHO (3) CH_3COCH_3 (4) HCHO **CL0063**

11. Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE-2009]**
(1) CH_2ClCH_2Cl (2) CH_3CHCl_2 (3) CH_3COCl (4) CH_3CH_2Cl **CL0064**

12. In Cannizzaro reaction given below :- **[AIEEE-2009]**

$$2PhCHO \xrightarrow{:\overset{\ominus}{O}H} PhCH_2OH + PhCO_2^{\ominus}$$

the slowest step is :-
(1) The abstraction of proton from the carboxylic group
(2) The deprotonation of $PhCH_2OH$
(3) The attack of $:\overset{\ominus}{O}H$ at the carboxyl group
(4) The transfer of hydride to the carbonyl group **CL0065**

13. 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]**
(1) Ethene (2) Propene (3) 1-Butene (4) 2-Butene **CL0066**

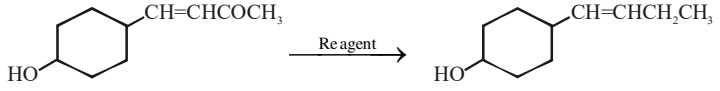
14. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- **[AIEEE-2011]**
(1) An isopropyl group (2) An acetylenic triple bond
(3) Two ethylenic double bonds (4) A vinyl group **CL0067**

15. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : - **[AIEEE-2011]**
(1) 2-Methyl - 1- pentene (2) 1-Pentene
(3) 2-Pentene (4) 2-Methyl-2-pentene **CL0068**

16. Trichloroacetaldehyde was subjected to assumed Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is :-
(1) 2,2,2–Trichloropropanol (2) Chloroform **[AIEEE-2011]**
(3) 2,2,2–Trichloroethanol (4) Trichloromethanol **CL0069**

17. Silver Mirror test is given by which one of the following compounds? **[AIEEE-2011]**
(1) Formaldehyde (2) Benzophenone (3) Acetaldehyde (4) Acetone **CL0070**

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



(1) $NaBH_4$ (2) $NH_2NH_2, \overset{\ominus}{O}H$ (3) Zn – Hg / HCl (4) Na, Liq.NH_3 **CL0071**

19. Iodoform can be prepared from all except :- **[AIEEE-2012]**
(1) Isobutyl alcohol (2) Ethyl methyl ketone
(3) Isopropyl alcohol (4) 3-Methyl–2–butanone **CL0072**

20. The major organic compound formed by the reaction of 1, 1, 1–trichloroethane with silver powder is :- **[JEE(Main)-2014]**

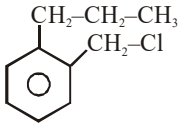
(1) 2-Butyne (2) 2-Butene (3) Acetylen (4) Ethene **CL0073**

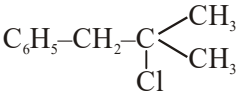
21. The most suitable reagent for the conversion of $R - CH_2 - OH \rightarrow R - CHO$ is :- **[JEE(Main)-2014]**

(1) CrO_3 (2) PCC (Pyridinium chlorochromate)

(3) $KMNO_4$ (4) $K_2Cr_2O_7$ **CL0074**

22. A compound A with molecular formula $C_{10}H_{13}Cl$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is : **[JEE(Main)-2015]**

(1) 

(2) 

(3) $C_6H_5–CH_2–CH_2–CH_2–CH_2–Cl$

(4) 

CL0075

23. In the reaction sequence **[JEE(Main)-2015]**

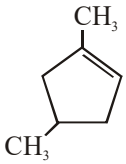
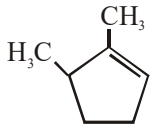
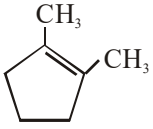
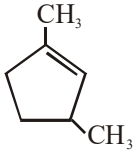
$2CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B$; the product B is:-

(1) $CH_3–CH=CH–CHO$ (2) $CH_3–CH_2–CH_2–CH_3$

(3) $CH_3–CH_2–CH_2–CH_2–OH$ (4) 

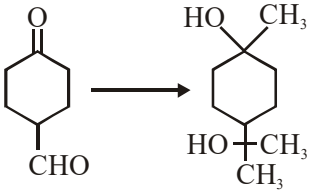
CL0076

24. Which compound would give 5-keto-2-methyl hexanal upon ozonlysis? **[JEE(Main) 2015]**

(1)  (2)  (3)  (4) 

CL0077

25. The correct sequence of reagents for the following conversion will be :- **[JEE(Main)-2017]**



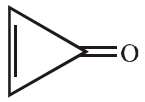
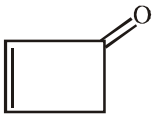
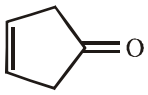
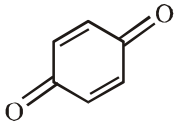
(1) $[Ag(NH_3)_2]^+ OH^-$, H^+/CH_3OH, CH_3MgBr

(2) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+ OH^-$

(3) CH_3MgBr, $[Ag(NH_3)_2]^+ OH^-$, H^+/CH_3OH

(4) $[Ag(NH_3)_2]^+ OH^-$, CH_3MgBr, H^+/CH_3OH **CL0078**

26. Which of the following compounds will show highest dipole moment ? **[JEE(Main-on-line)-2017]**

(I)  (II)  (III)  (IV) 

(1) (II) (2) (III) (3) (I) (4) (IV) **CL0079**

27. Glucose on prolonged heating with HI gives : **[JEE(Main)-2018]**

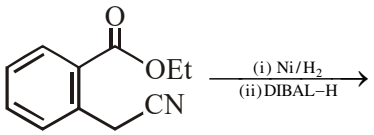
(1) 1–Hexene (2) Hexanoic acid (3) 6-iodohexanal (4) n-Hexane **CL0080**

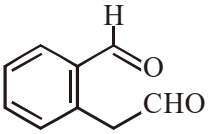
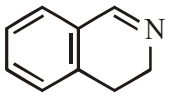
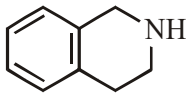
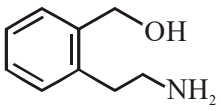
28. Which of the following compounds will most readily be dehydrated to give alkene under acidic condition? **[JEE(Main-on-line)-2018]**

(1) 4-Hydroxypentan-2-one (2) 2-Hydroxycyclopentanone

(3) 3-Hydroxypentan-2-one (4) 1-Pentanol **CL0081**

29. The major product of the following reaction is: **[JEE-Main(January)-2019]**



(1)  (2)  (3)  (4) 

CL0082

30. In the following reaction **[JEE-Main(January)-2019]**

Aldehyde + Alcohol $\xrightarrow{HCl}$ Acetal

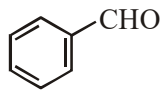
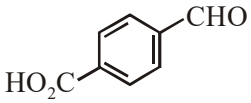
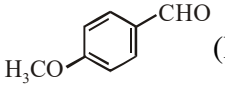
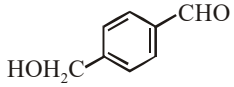
Aldehyde	Alcohol
HCHO	^{t}BuOH
CH_3CHO	MeOH

The best combinations is :

(1) HCHO and MeOH (2) HCHO and ^{t}BuOH

(3) CH_3CHO and MeOH (4) CH_3CHO and ^{t}BuOH **CL0083**

31. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are : **[JEE-Main(January)-2019]**

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

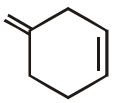
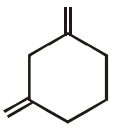
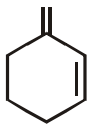
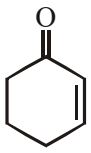
(1) (B), (C), (D) (2) (B), (D) (3) (B), (C) (4) (C), (D) **CL0084**

32. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenattion, and also gives following reaction : **[JEE-Main(Jan)-2020]**

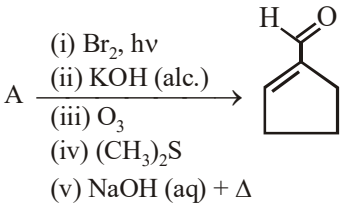
$X \xrightarrow[Zn/H_2O]{O_3} A \xrightarrow{[Ag(NH_3)_2]^+}$

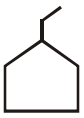
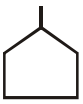
B(3 - oxo - hexanedicarboxylic acid)

X will be :-

(1)  (2)  (3)  (4)  **CL0085**

33. In the following reaction A is : **[JEE-Main(Jan)-2020]**



(1)  (2)  (3)  (4)  **CL0086**

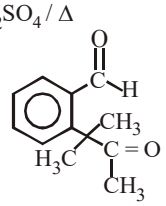
34. Consider the following reactions **[JEE-Main(Jan)-2020]**

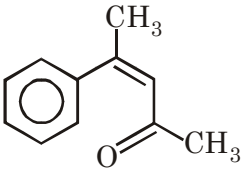
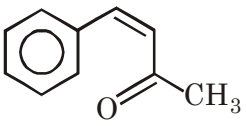
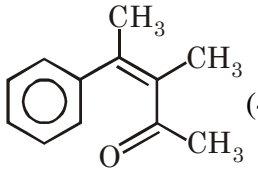
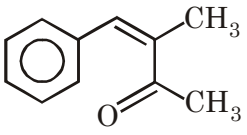
$$A \xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr} B \xrightarrow[573K]{Cu} \text{2-methyl}$$

2-butene

The mass percentage of carbon in A is _____. **CL0087**

35. Identify (A) in the following reaction sequence : **[JEE-Main(Jan)-2020]**

(A) Gives positive iodoform test $\xrightarrow[(ii)\ H^+, H_2O \\ (iii)\ \text{Conc. } H_2SO_4 / \Delta]{(i)\ CH_3MgBr}$ (B) $\xrightarrow{O_3 / Zn, H_2O}$ 

(1)  (2)  (3)  (4) 

CL0088

36. The major product (Y) in the following reactions is : **[JEE-Main(Jan)-2020]**

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv CH \xrightarrow[H_2O]{HgSO_4,H_2SO_4} X \xrightarrow[(ii)\text{Conc. } H_2SO_4/\Delta]{(i)C_2H_5MgBr,H_2O} Y$$

(1) $H_3C-\underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle CH_2}{\overset{\|}{C}}-CH}}-CH_3$

(2) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$

(3) $CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}=C}}-CH_3$

(4) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH_2$ **CL0089**

EXERCISE-(IIT QUESTIONS)

Q.1 Which of the following has the most acidic hydrogen: **[IIT 2000]**

(A) 3-hexanone (B) 2,4-hexanedione

(C) 2,5-hexanedione (D) 2,3-hexandione **CL0090**

Q.2 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

(A) benzyl alcohol and sodium formate (B) sodium benzoate and methyl alcohol

(C) sodium benzoate and sodium formate (D) benzyl alcohol and methyl alcohol **[IIT 2001]**

CL0091

Q.3 1-propanol & 2-propanol can be best distinguished by : **[IIT 2001]**

(A) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

(B) Oxidation with acidic dichromate followed by reaction with Fehling solution

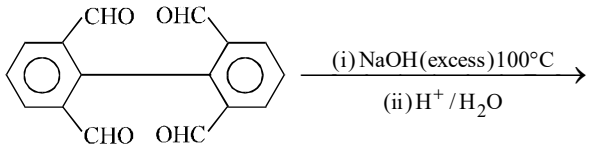
(C) Oxidation by heating with copper followed by reaction with Fehling solution

(D) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution **CL0092**

Q.4 Compound A (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product B (molecular formula C_3H_6O). B forms a shining silver mirror on warming with ammonical silver nitrate. B when treated with an aqueous solution of $H_2NCONHNH_2$. HCl and sodium acetate gives a product C. Identify the structure of C. **[IIT 2002]**

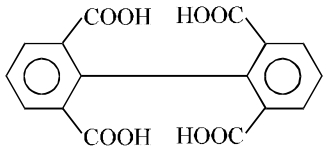
(A) $CH_3CH_2CH = NNHCONH_2$ (B) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=NNHCONH_2$

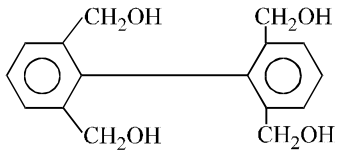
(C) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=NCONHNH_2$ (D) $CH_3CH_2CH=NCONHNH_2$ **CL0093**

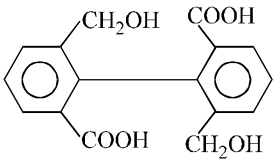
Q.5 

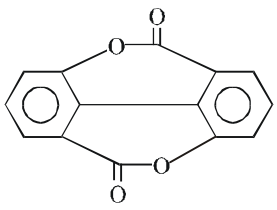
[IIT 2003]

any one of the products formed is :

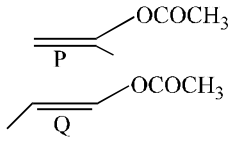
(A) 

(B) 

(C) 

(D) 

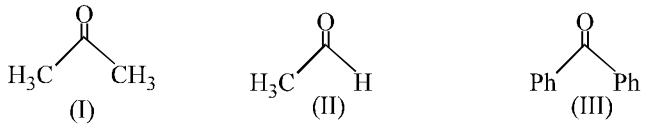
CL0094

Q.6  Products formed by P & Q can be differentiated by: **[IIT 2003]**

(A) 2, 4 DNP (B) Lucas reagent ($ZnCl_2$) conc. HCl

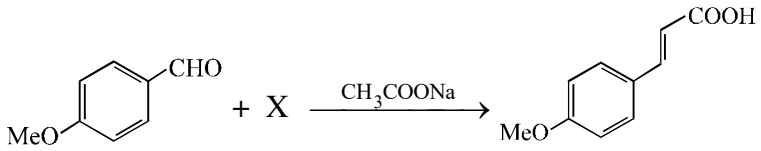
(C) $NaHSO_3$ (D) Fehlings solution **CL0095**

Q.7 The order of reactivity of phenyl Magnesium Bromide with the following compounds is **[IIT 2004]**



(A) II > III > I (B) I > III > II (C) II > I > III (D) All react with the same rate

CL0096

Q.8  **[IIT 2005]**

What is X?

(A) CH_3COOH (B) $BrCH_2$, COOH (C) $(CH_3CO)_2O$ (D) CHO–COOH

CL0097

Q.9 The smallest ketone and its next homologue are reacted with NH_2OH to form oxime.

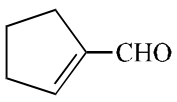
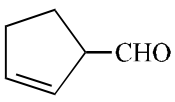
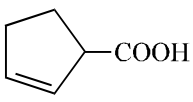
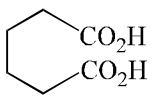
(A) Two different oximes are formed (B) Three different oximes are formed

(C) Two oximes are optically active (D) All oximes are optically active **[IIT 2006]**

CL0098

Q.10 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is

[IIT-JEE(ADV.)- 2007]

(A)  (B)  (C)  (D)  **CL0099**

Q.11 **Statement-1 :** Glucose gives a reddish-brown precipitate with Fehling's solution.

because

Statement-2 : Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False. **[IIT-JEE(ADV.)- 2007]**

(D) Statement-1 is False, Statement-2 is True. **CL0100**

Q.12 Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

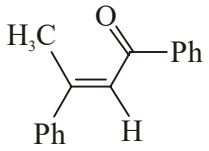
[IIT-JEE(ADV.)- 2007]

Column I	**Column II**
(A) C_6H_5CHO	(P) gives precipitate with 2,4-dinitrophenylhydrazine
(B) $CH_3C{\equiv}CH$	(Q) gives precipitate with $AgNO_3$
(C) CN^-	(R) is a nucleophile
(D) I^-	(S) is involved in cyanohydrin formation

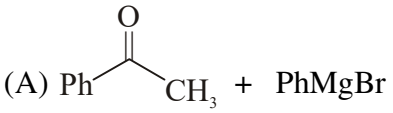
CL0101

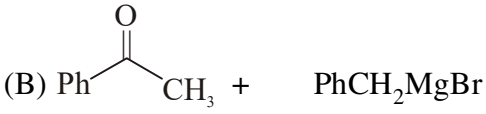
Paragraph for Question No. 13 to 15

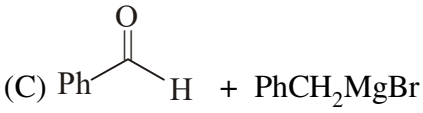
A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

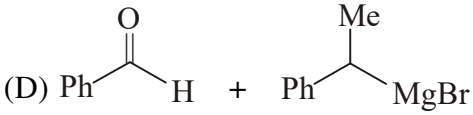
M = 

Q.13 Compound **H** is formed by the reaction of **[IIT-JEE(ADV.)- 2008]**

(A) 

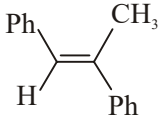
(B) 

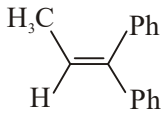
(C) 

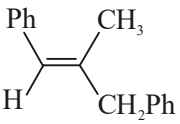
(D) 

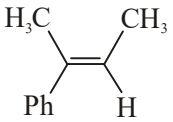
CL0102

Q.14 The structure of compound **I** is **[IIT-JEE(ADV.)- 2008]**

(A) 

(B) 

(C) 

(D) 

CL0102

Q.15 The structures of compounds **J**, **K** and **L**, respectively, are **[IIT-JEE(ADV.)- 2008]**

(A) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(B) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

(C) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

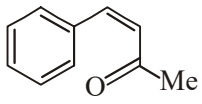
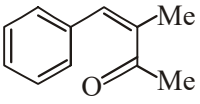
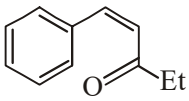
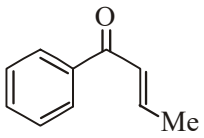
(D) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$ **CL0102**

Paragraph for Question Nos. 16 to 38

A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

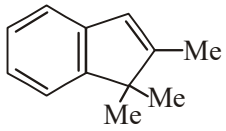
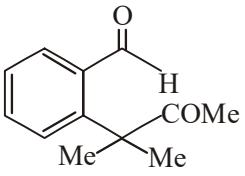
$$\mathbf{P} \xrightarrow[2.H^+,H_2O \\ 3.H_2SO_4,\Delta]{1.MeMgBr} \mathbf{Q} \xrightarrow[2.\ Zn,H_2O]{1.\ O_3} \mathbf{R} \xrightarrow[2.\ \Delta]{1.\ OH^-} \mathbf{S}$$

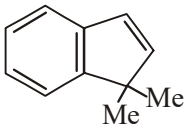
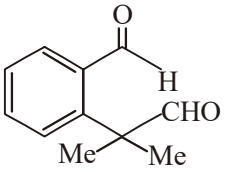
Q.16 The structure of the carbonyl compound **P** is **[IIT-JEE(ADV.)- 2009]**

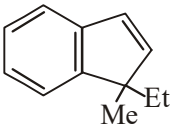
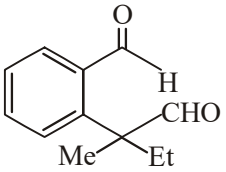
(A)  (B)  (C)  (D) 

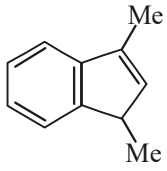
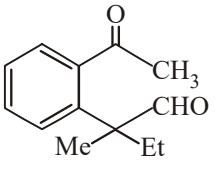
CL0103

Q.17 The structure of the products **Q** and **R**, respectively, are **[IIT-JEE(ADV.)- 2009]**

(A)  , 

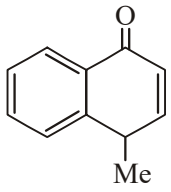
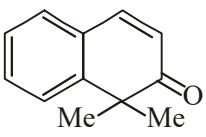
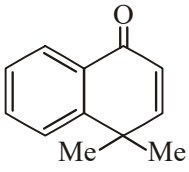
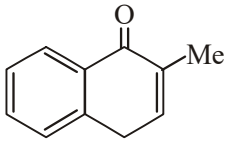
(B)  , 

(C)  , 

(D)  , 

CL0103

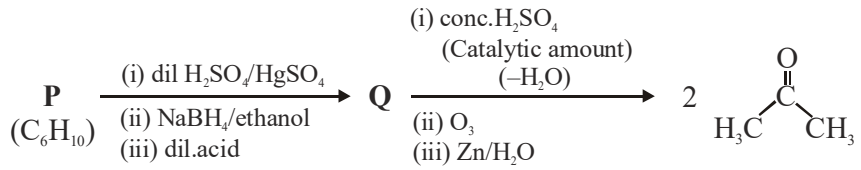
Q.18 The structure of the product **S** is **[IIT-JEE(ADV.)- 2009]**

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

CL0103

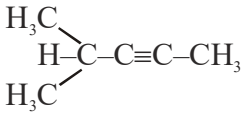
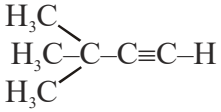
Paragraph for Questions Nos. 19 to 20

An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in the which Q is an intermediate organic compound.

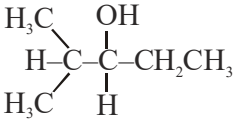
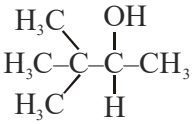
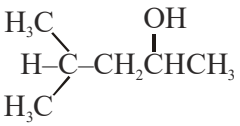
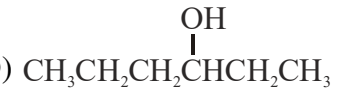


Q.19 The structure of compound P is - **[IIT-JEE(ADV.)- 2011]**

(A) $CH_3CH_2CH_2CH_2–C\equiv C–H$ (B) $H_3CH_2C\equiv C–CH_2CH_3$

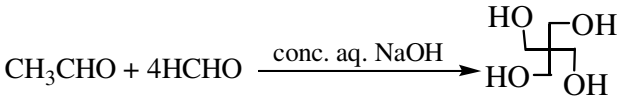
(C)  (D)  **CL0104**

Q.20 The structure of the compound Q is - **[IIT-JEE(ADV.)- 2011]**

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

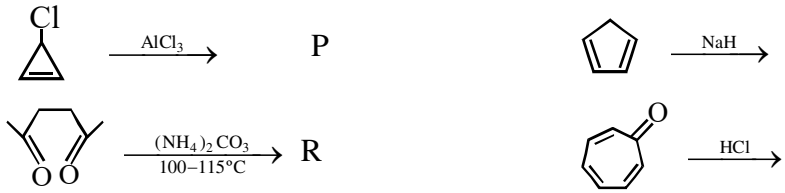
CL0104

Q.21 The number of aldol reaction(s) that occurs in the given transformation is **[IIT-JEE(ADV.)- 2012]**



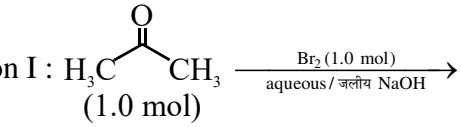
(A) 1 (B) 2 (C) 3 (D) 4 **CL0105**

Q.22 Among P, Q, R and S, the aromatic compound(s) is / are : **[IIT-JEE(ADV.)- 2013]**

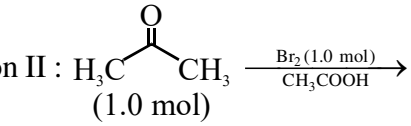


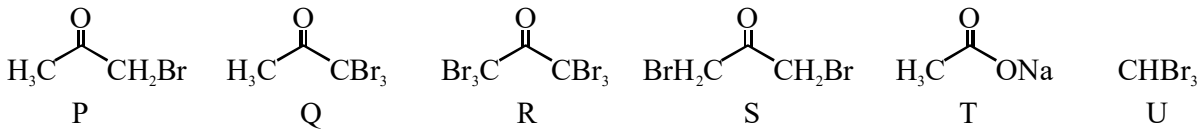
(A) P (B) Q (C) R (D) S **CL0106**

Q.23 After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

Reaction I : 

[IIT-JEE(ADV.)- 2013]

Reaction II : 



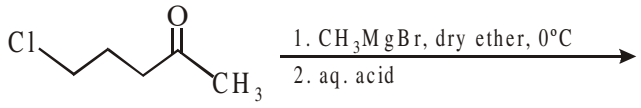
(A) Reaction I : P and Reaction II : P

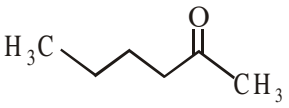
(B) Reaction I : U, acetone and Reaction II : Q acetone

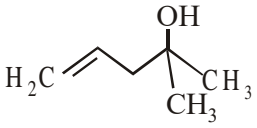
(C) Reaction I : T, U, acetone and Reaction II : P

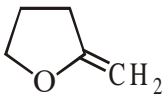
(D) Reaction I : R, acetone and Reaction II : S acetone **CL0107**

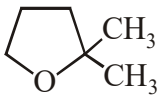
Q.24 The major product in the following reaction is **[IIT-JEE(ADV.)- 2014]**



(A) 

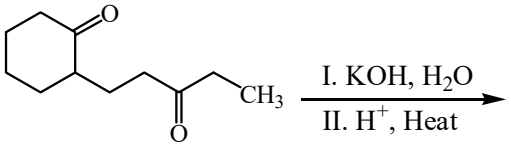
(B) 

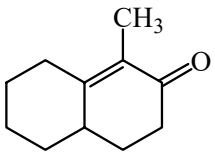
(C) 

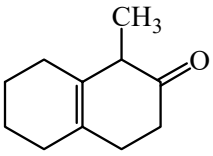
(D) 

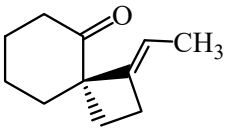
CL0108

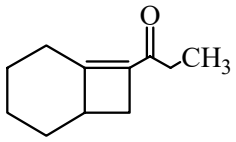
Q.25 The major product of the following reaction is - **[IIT-JEE(ADV.)- 2015]**



(A) 

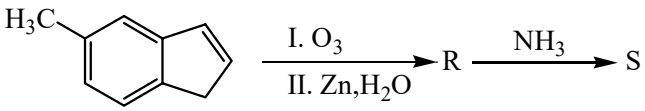
(B) 

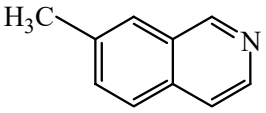
(C) 

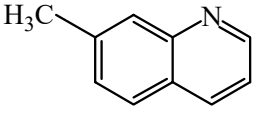
(D) 

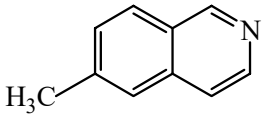
CL0109

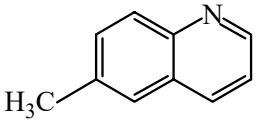
Q.26 In the following reactions, the product S is - **[IIT-JEE(ADV.)- 2015]**



(A) 

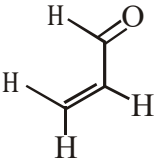
(B) 

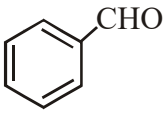
(C) 

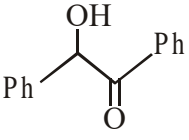
(D) 

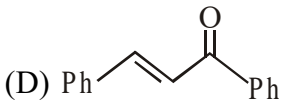
CL0110

Q.27 Positive Tollen's test is observed for : **[IIT-JEE(ADV.)- 2016]**

(A) 

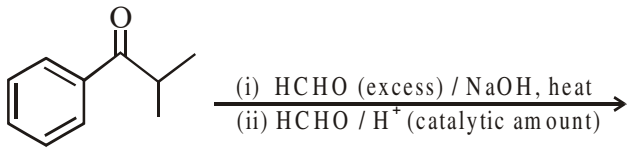
(B) 

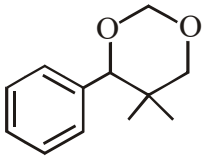
(C) 

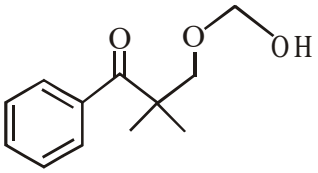
(D) 

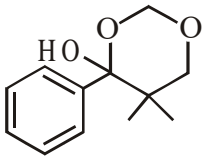
CL0111

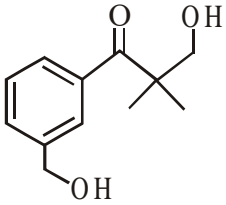
Q.28 The major product of the following reaction sequence is : **[IITJEE(ADV.)-2016]**



(A) 

(B) 

(C) 

(D) 

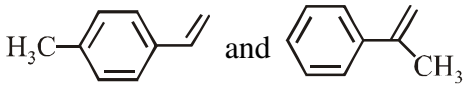
CL0112

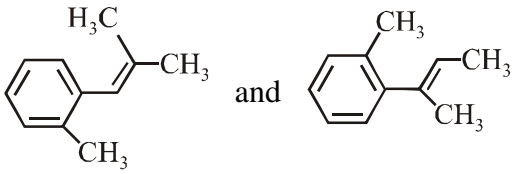
Q.29 Compound **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is C_8H_8O. **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction : **[IIT-JEE(ADV.)- 2017]**

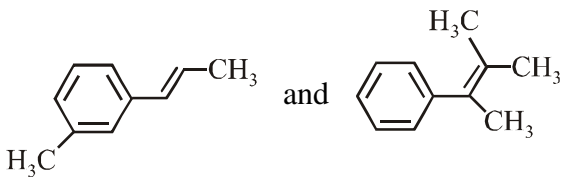
(i) P $\xrightarrow[\text{(ii) } Zn / H_2O]{\text{(i) } O_3 / CH_2Cl_2}$ Q (C_8H_8O)

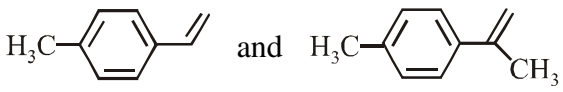
(ii) R $\xrightarrow[\text{(ii) } Zn / H_2O]{\text{(i) } O_3 / CH_2Cl_2}$ S (C_8H_8O)

The option(s) with suitable combination of P and R, respectively, is(are)

(A) 

(B) 

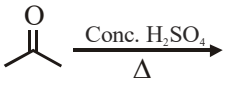
(C) 

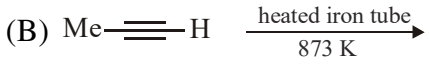
(D) 

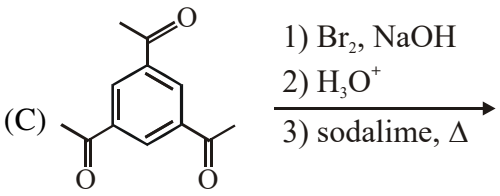
CL0113

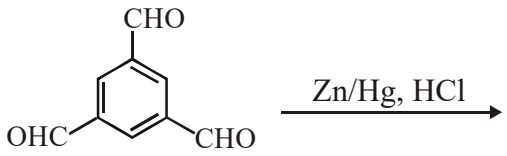
30. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

[IIT-JEE(ADV.)- 2018]

(A) 

(B) 

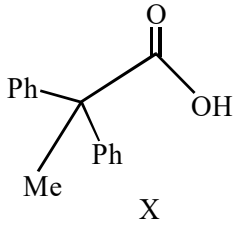
(C) 

(D) 

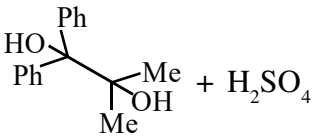
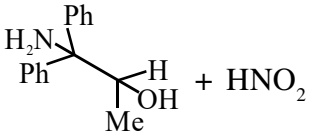
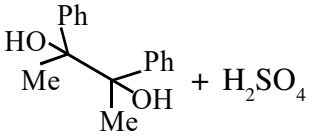
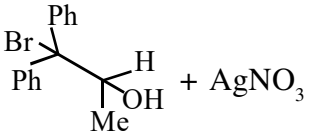
CL0114

31. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. **[IIT-JEE(Adv.)-2018]**

(given, order of migratory aptitude: aryl > alkyl > hydrogen)



X

LIST-I	**LIST-II**
P.  + H_2SO_4	1. I_2, NaOH
Q.  + HNO_2	2. $[Ag(NH_3)_2]OH$
R.  + H_2SO_4	3. Fehling solution
S.  + $AgNO_3$	4. HCHO, NaOH
	5. NaOBr

The correct option is

(A) P → 1; Q → 2,3; R → 1,4; S → 2,4 (B) P → 1,5; Q → 3,4; R → 4,5; S → 3

(C) P → 1,5; Q → 3,4; R → 5; S → 2,4 (D) P → 1,5; Q → 2,3; R → 1,5; S → 2,3

CL0115

ANSWER-KEY-EXERCISE # O-I

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

EXERCISE # O-II

1	**Ans.** (A,B)	2	**Ans.** (C,D)	3	**Ans.** (A,B,C)	4	**Ans.** (B,C)
5	**Ans.** (A,B)	6	**Ans.** (A,B,C,D)	7	**Ans.** (A,B,C)	8	**Ans.** (B,C)
9	**Ans.** (A,D)	10	**Ans. (D)**	11	**Ans.** (D)	12	**Ans.** (B)
13	**Ans.** (B)	14	**Ans. (A,B,C)**	**15**	**Ans. (A)→R ; (B)→Q,S ; (C)→S ; (D)→P**		

EXERCISE # S-I

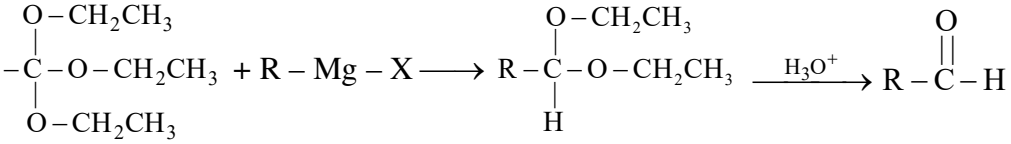
1. **Ans. (A) P,Q,S ; (B) P,Q,S ; (C) P,Q,S ; (D) P,Q,S**

2. **Ans. 3 > 2 > 1 > 4**

3. **Ans.** (C)

4. **Ans.** (A)

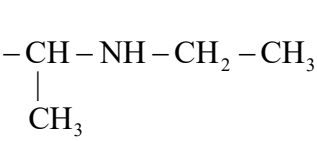
5. **Ans.**



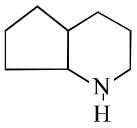
Ethyl orthoformate Acetal aldehyde

6. **Ans.** H^+/Br_2 ; H_2 / Ni ; NaOH

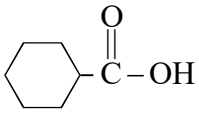
7. **Ans.** (a)



(b)



(c)

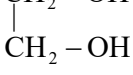


8. **Ans.** (B,C)

9. **Ans.** (B)

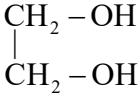
10. **Ans.**

(a) (i) $KMnO_4$, (ii)



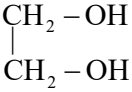
, (iii) $LiAlH_4$, (iv) $H_3O^{\oplus}$

(b) (i)



, (ii) $NaBH_4$, (iii) H_3O^+,

(c) (i)



, (ii) Ph_3P=CH–Et

(d) (i) H_2, Ni (e) NH_2NH_2/H_2O_2 (f) $NaBH_4$

11. **Ans. (B)** **12.** **Ans. (D)**

EXERCISE # (MAINS)

1. **Ans. (4)** **2.** **Ans. (2)** **3.** **Ans. (1)** **4.** **Ans.** (2)

5. **Ans.** (4) **6.** **Ans.** (2) **7.** **Ans. (4)** **8.** **Ans.** (3)

9. **Ans.** (4) **10.** **Ans.** (4) **11.** **Ans.** (2) **12.** **Ans.** (4)

13. **Ans.** (4) **14.** **Ans.** (4) **15.** **Ans.** (4) **16.** **Ans.** (3)

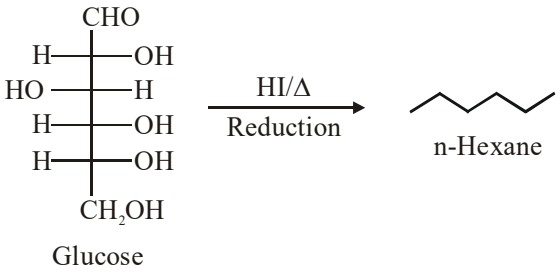
17. **Ans.** (1 , 3) **18.** **Ans.** (2) **19.** **Ans.** (1) **20.** **Ans.** (1)

21. **Ans.** (2) **22.** **Ans.** (2) **23.** **Ans. (1)** **24.** **Ans. (4)**

25. **Ans. (1)** **26.** **Ans. (3)**

27. **Ans. (4)**

Sol.

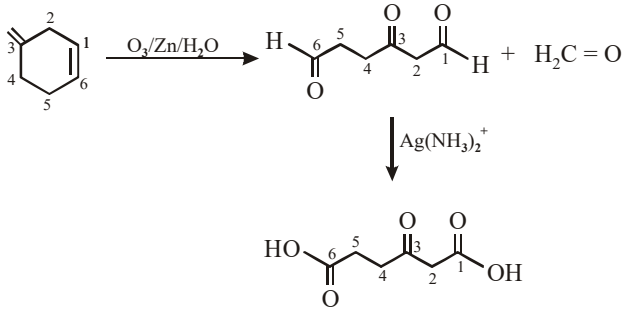


Glucose

28. **Ans. (1)** **29.** **Ans. (2)** **30.** **Ans. (1)** **31.** **Ans. (2)**

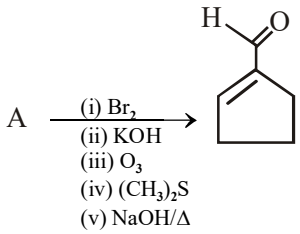
32. **Ans. (1)**

Sol.



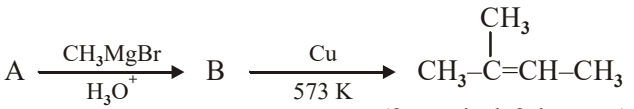
33. **Ans. (3)**

Sol.

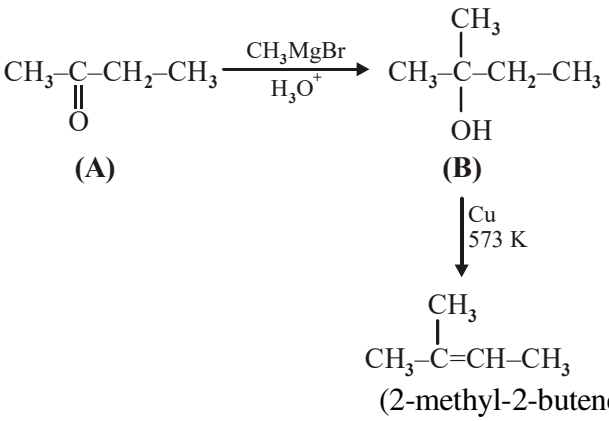


34. **Ans. (66.65 to 66.70)**

Sol.



(2-methyl-2-butene)



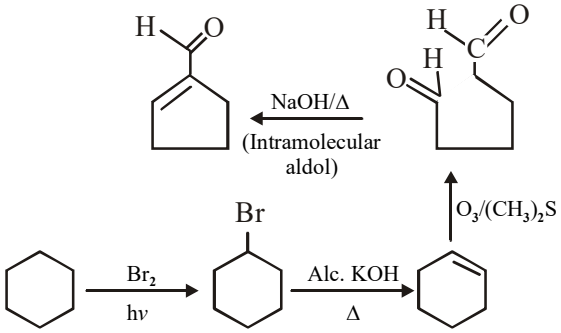
C ⇒ 12 × 4 = 48

H ⇒ 8 × 1 = 8

O ⇒ 16 × 1 = 16

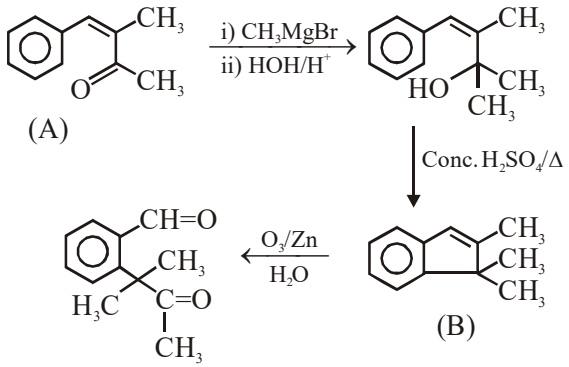
Total 72

$$\% \text{ of C} = \frac{48}{72} \times 100 = 66.66\%$$



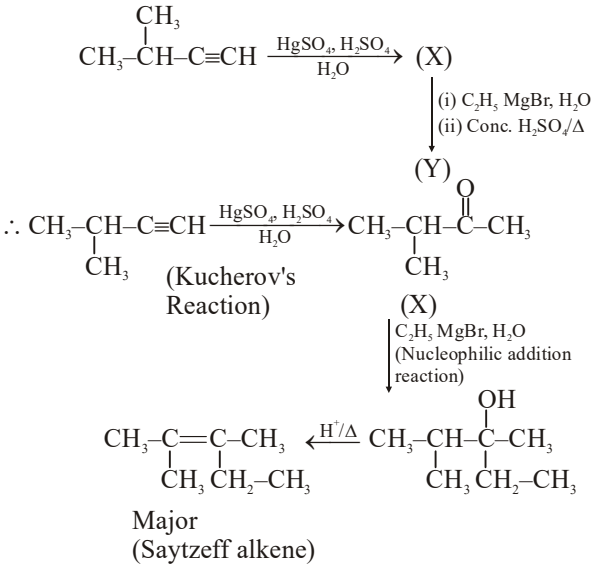
35. Ans. (4)

Sol.



36. Ans. (3)

Sol.

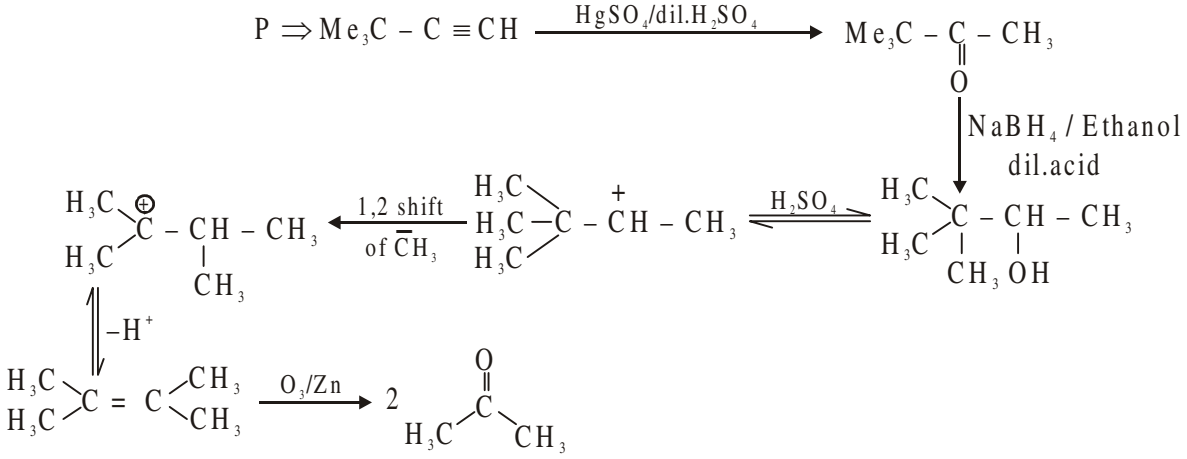


EXERCISE-#(IIT QUESTIONS)

1.	**Ans.** (B)	**2.**	**Ans.** (A)	**3.**	**Ans.** (C)	**4.**	**Ans. (A)**
5.	**Ans.** (C)	**6.**	**Ans.** (D)	**7.**	**Ans.** (C)	**8.**	**Ans.** (C)
9.	**Ans.** (B)	**10.**	**Ans. (A)**	**11.**	**Ans.** (C)		
12.	**Ans.** (A) P,S; (B) Q; (C) Q,R,S; (D) Q,R			**13.**	**Ans. (B)**	**14.**	**Ans. (A)**
15.	**Ans.** (D)	**16.**	**Ans.** (B)	**17.**	**Ans. (A)**	**18.**	**Ans.** (B)

19. Ans. (D)

20. Ans.(B)



21. Ans. (C)

Sol. $CH_3CH=O + \bar{O}H \rightleftharpoons \bar{C}H_2-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} H_2C-CH(CH_2OH)-CH=O$

(1 time aldol)

$\xrightleftharpoons{\bar{O}H} CH_2(CH_2OH)-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} HOH_2C-CH(CH_2OH)-CH=O$

(2 time aldol)

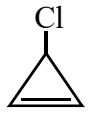
$\xrightleftharpoons{\bar{O}H} HOH_2C-C(CH_2OH)_2-CH=O \xrightleftharpoons{H-\overset{O}{\overset{\|}{C}}-H} HOCH_2-C(CH_2OH)_2-CH=O$

(3 times aldol)

$H-\overset{O}{\overset{\|}{C}}-H + \overset{\ominus}{O}H \rightleftharpoons HOH_2C-C(CH_2OH)_2-CH_2OH + H-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

(crossed cannizaro product)

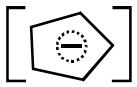
22. Ans. (A,B,C,D)

Sol. 

$\xrightarrow{A\ell Cl_3}$  $A\ell Cl_4^{\ominus}$

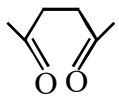
(P)

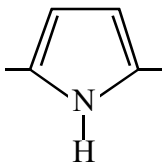
2π electron (delocalised)
(Aromatic Nature)


$\xrightarrow{NaH}$  $Na^+ + \frac{1}{2}H_2$

(Q)

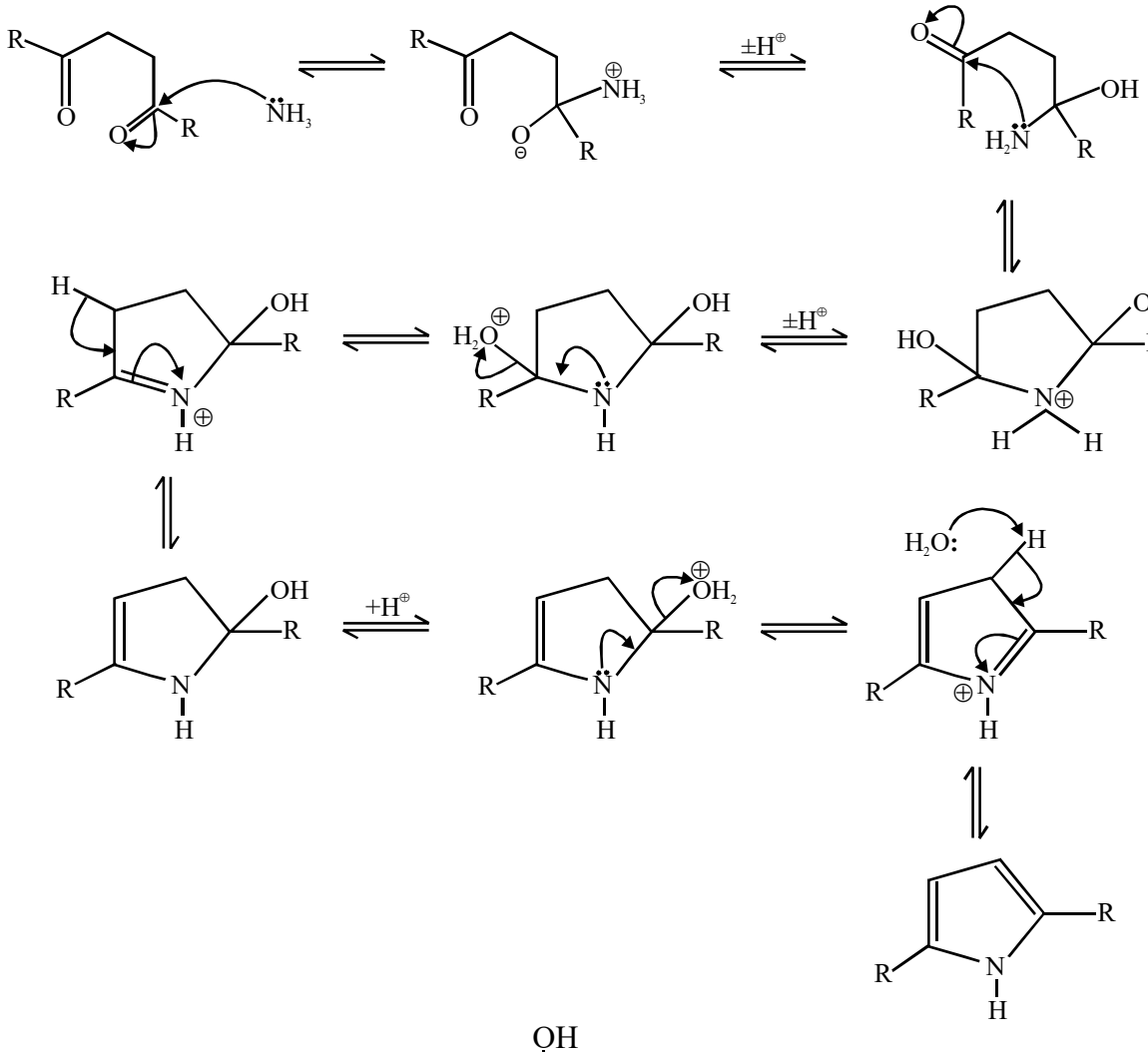
6π electron (delocalised)
(Aromatic Nature)

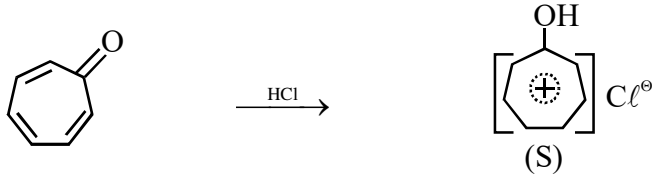


$\xrightarrow[100-115°C]{(NH_4)_2CO_3}$ 

(R) 6π-electron (delocalised)
(Aromatic nature)

Mechanism :

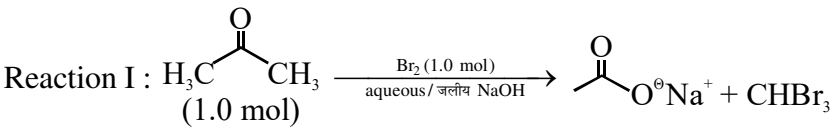




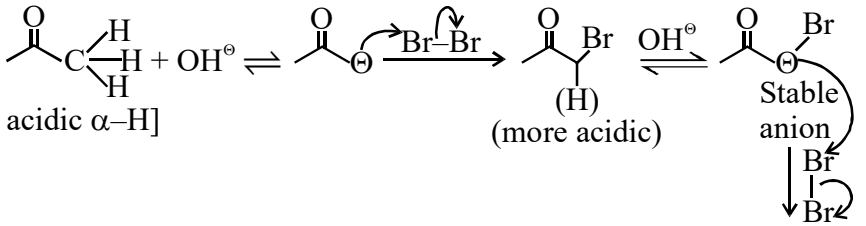
(S)

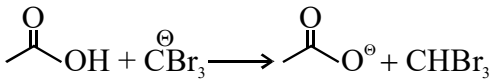
6π electron (delocalised)
(Aromatic Nature)

23. **Ans.** (C)

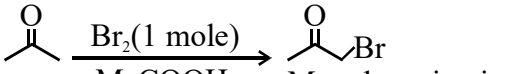
Sol. Reaction I : 

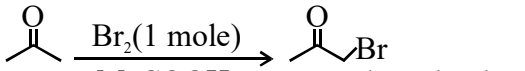
Mechanism

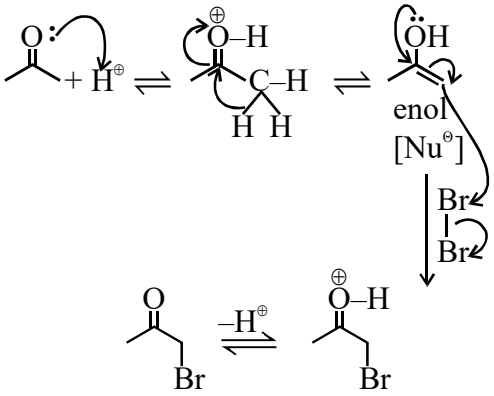




In basic medium halogenation dose not stop with replacement of just one hydrogen and poly halogenation takes place because α-haloketones are more reactive towards base and haloform reaction takes place In above reaction Br_2 is limiting agents.

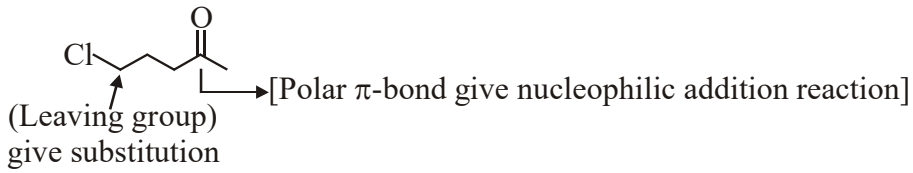
Reaction II : 

Mechanism : 



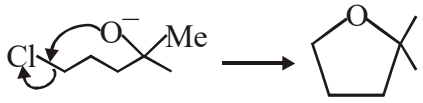
Further bromination is less favourable because of less amount of Br_2

24. Ans. (D)

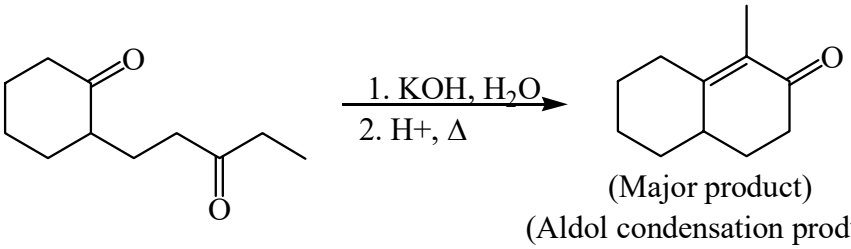


(i) Grignard prefer to give nucleophilic addition on polar π-bond and form anion intermediate.

(ii) In next step anion give intramolecular nucleophilic substitution reaction & form 5 membered ring.

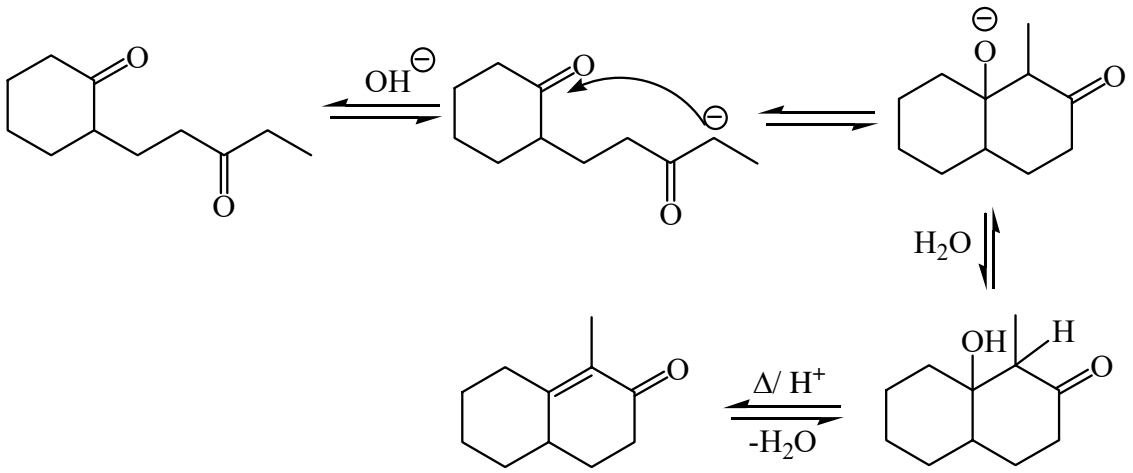


25. Ans. (A)



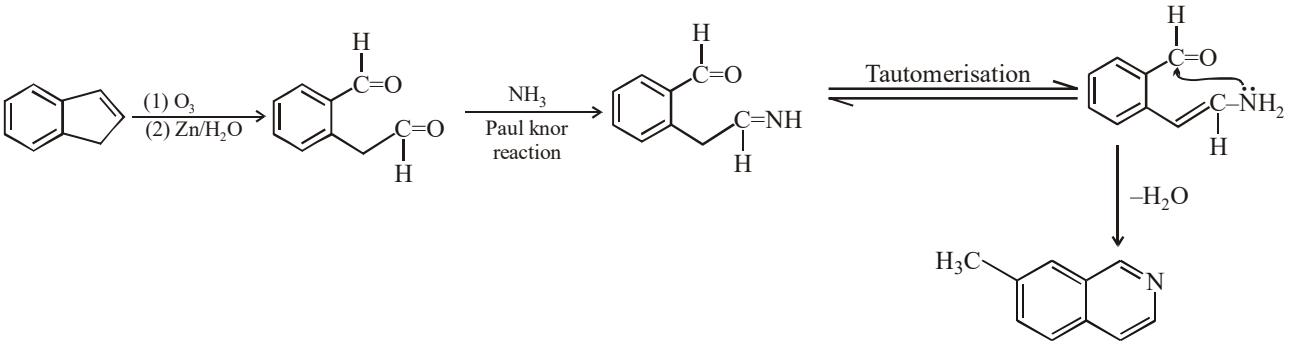
(Major product)
(Aldol condensation product)

Mechanism :



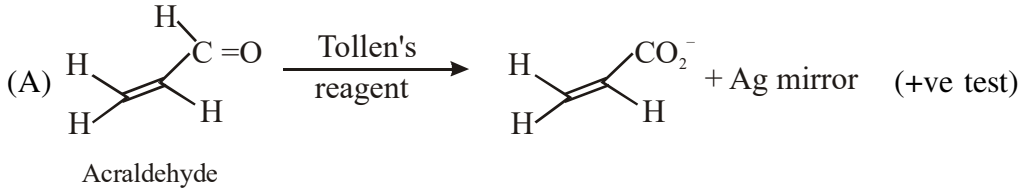
26. Ans.(A)

Sol.

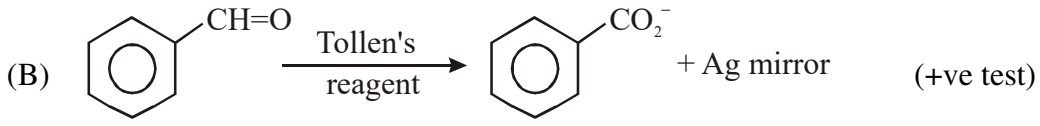


27. Ans. (A,B,C)

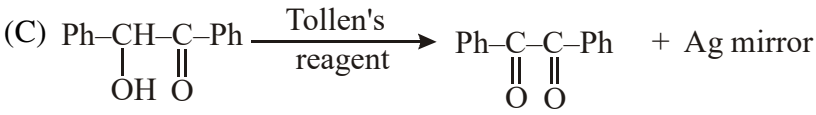
Sol. Tollens's test is given by compounds having aldehyde group. Also α-hydroxy carbonyl gives positive tollen's test.



Acraldehyde

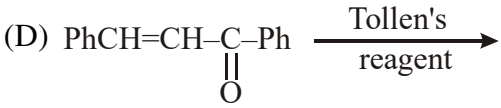


Benzaldehyde

(C) 

(+ve test)

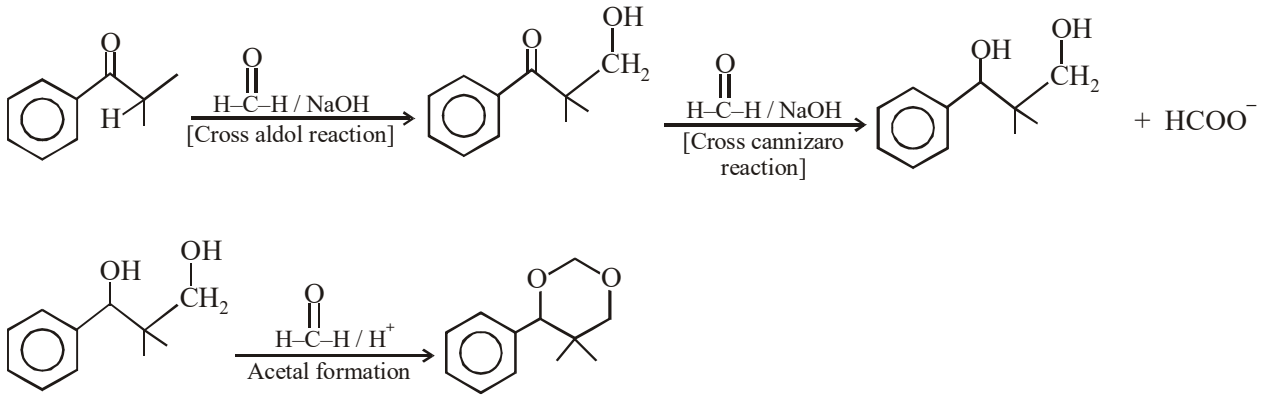
Benzoin

(D) 

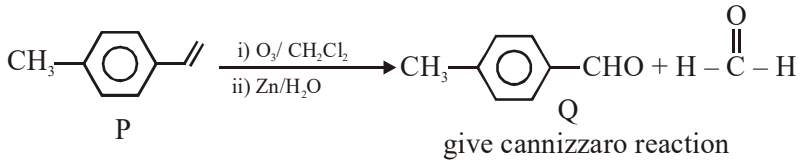
(–ve test)

28. Ans. (A)

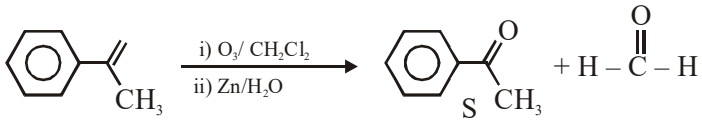
Sol.



29. Ans. (A,C)

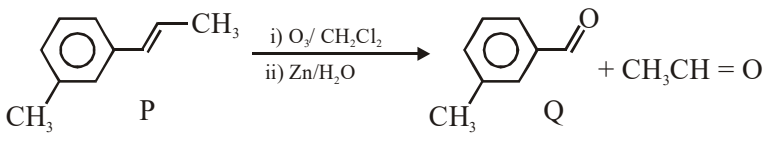
Sol. **(A)** 

give cannizzaro reaction
but no haloform

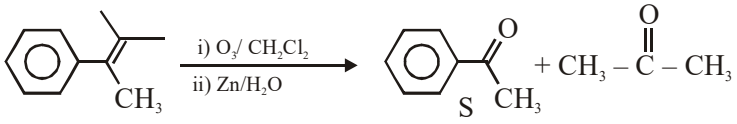


no cannizzaro
but give haloform

(B) Product of ozonolysis of R is having 9 carbon.

(C) 

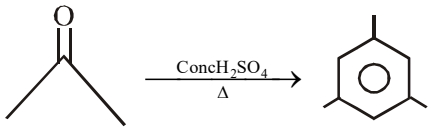
give cannizzaro reaction
but no haloform

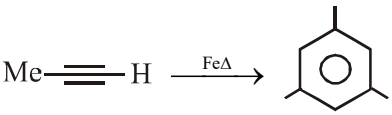


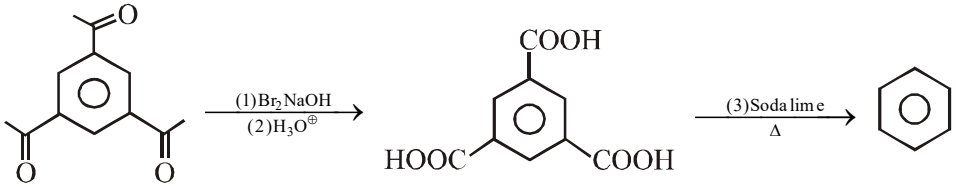
no cannizzaro
but give haloform

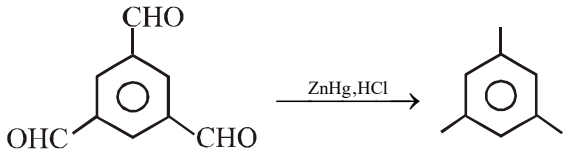
(D) Product of ozonolysis of R is having 9 carbon.

30. Ans. (A,B,D)

Sol. (A) 

(B) 

(C) 

(D) 

31. Ans. (D)