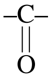
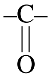
CHAPTER 3

Carbonyl Compounds

INTRODUCTION

- Organic compounds in which  $-\underset{\underset{O}{\|}}{C}-$ group is present, are called '**Aldehyde and Ketone**'.
- The group,  $-\underset{\underset{O}{\|}}{C}-$ is called as carbonyl group. So the compounds containing this group are also called carbonyl compounds.
- If H atom is attached with this carbonyl group, then compound is called **aldehyde**, and if alkyl group is present on both sides then compound is called **Ketone**.
- In ketone if both alkyl groups are same then they are called simple ketone, if different then the compound is called mixed ketone.
- The general formula of carbonyl compounds is $C_nH_{2n}O$. Hybridisation state of carbon is sp^2 and C=O bond length is 1.23 Å.
- The ratio of C, H, and O in formaldehyde is 1:2:1 (CH_2O).
- Aldehyde shows chain and functional isomerism.
- Ketone shows chain, position, functional isomerism, and also metamerism.
- Aldehyde and ketone both are functional isomer with each other.

PHYSICAL PROPERTIES

- Aldehydes are colourless liquid with pungent smell, while ketones are pleasant smelling liquids; but formaldehyde is gaseous in nature.
- Lower carbonyl compounds are soluble in water. It is due to polarity in carbonyl group.
- Higher carbonyl compounds are insoluble in water due to more covalent character.
- $\boxed{\text{Boiling point} \propto \text{Molecular mass} \propto \frac{1}{\text{Number of branches}}}$
- Aldehydes and ketones have higher boiling points than those of non-polar compounds of comparable molar mass, but have lower boiling points than those of alcohols and carboxylic acids due to the absence of H-bonding.

Order of boiling point

(a) Aldehyde < Ketone

(b) The boiling point of unbranched aldehydes increases with the increase in the molecular weight.

Methanal < ethanal < propanal

(c) Order of boiling point of methyl ketones.

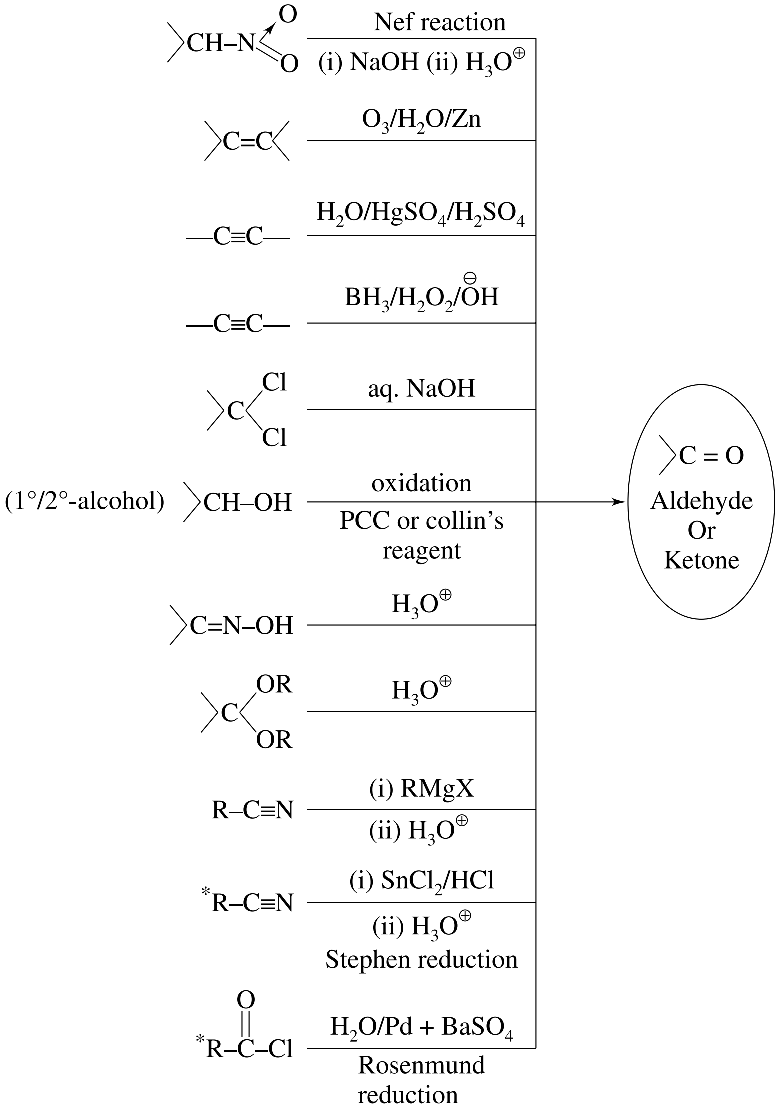
Propanone < butanone < 2-pentanone

(d) Branched carbonyl compounds < unbranched carbonyl compounds
3-methyl butanal < Pentanal
2-pentanone > 3-methyl-2-butanone

- 40% solution of formaldehyde is known as '**FORMALIN**' (40% HCHO, 54–56% H_2O, 4–6% methanol). It is used in preserving dead bodies.
- Mixture of formaldehyde and lactose sugar is called '**FORMAMINT**' which is used in medicine of throat infection.
- Boiling point of carbonyl compounds is as under:

S. No.	Compound	Boiling Point
1.	Formaldehyde	−21°C
2.	Acetaldehyde	+21°C
3.	Acetone	+56°C

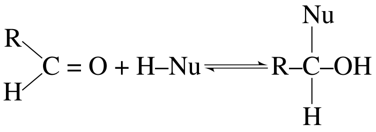
METHODS OF PREPARATION OF CARBONYL COMPOUDNS



*only used for prepration of aldehyde.

NUCLEOPHILIC ADDITION TO THE CARBON–OXYGEN DOUBLE BOND

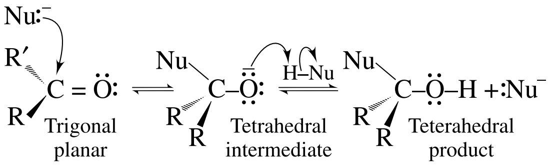
The most characteristic reaction of aldehydes and ketones is nucleophilic addition to the carbon–oxygen double bond.



$$\mathrm{RHC{=}O + H{-}Nu \rightleftharpoons R{-}C(Nu)(H){-}OH}$$

When the reagent is a strong nucleophile (Nu), addition usually takes place in the following way, converting the trigonal planar aldehyde or ketone into a tetrahedral product.

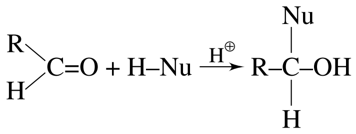
If the nucleophile attacks the carbonyl group, the hybridisation state of carbon changes from sp^2 to sp^3.



Nucleophilic addition can take place either under acidic or basic conditions.

(1) Acid catalysed mechanism of nucleophilic additions to the carbon–oxygen double bonds:

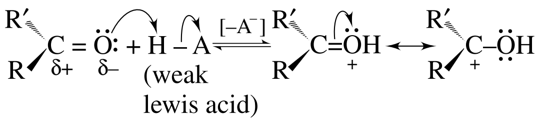
A poor nucleophile requires an acid catalyst to make the nucleophilic addition reaction occur at a reasonable rate. The acid protonates the carbonyl oxygen, which increases the susceptibility of the carbonyl carbon to the nucleophilic attack.



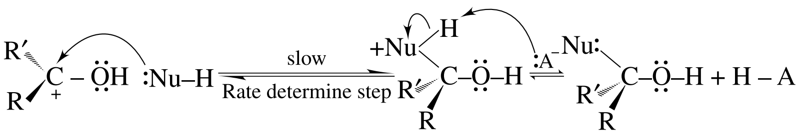
$$\mathrm{RHC{=}O + H{-}Nu \xrightarrow{H^{\oplus}} R{-}C(Nu)(H){-}OH}$$

The mechanism of **acid-catalysed** reaction is as follows:

Step-I

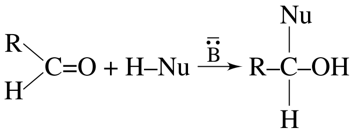


Step-II



(2) Base catalysed mechanism of nucleophilic additions to the carbon–oxygen double bonds:

If the attacking atom of the nucleophile (such as Oxygen nucleophile and nitrogen nucleophile) has a pair of nonbonding electrons in the addition product, water will be eliminated from the addition product. This is called a **nucleophilic addition–elimination** reaction.



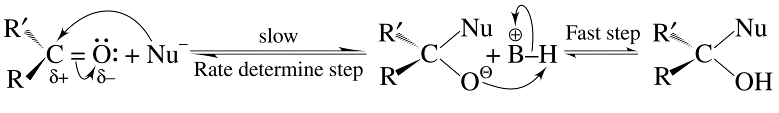
$$\mathrm{RHC{=}O + H{-}Nu \xrightarrow{\bar{\ddot{B}}} R{-}C(Nu)(H){-}OH}$$

The mechanism for **base-catalysed** reaction is as follows:

Step-I

$$\ddot{B} + H{-}Nu^{-} \rightleftharpoons \overset{\oplus}{B}H + \overset{\ominus}{Nu}$$

Step-II



Intermediate

Reactivity of Aldehydes and Ketones for Nucleophilic Addition Reactions

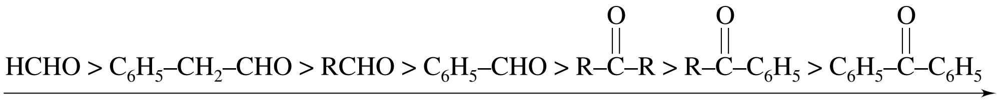
The reactivity of the carbonyl group for nucleophilic addition depends mainly on three factors.

(1) Ability of carbonyl oxygen to carry a negative charge

(2) Nature of the groups attached to the carbonyl carbon atom

(3) Size of the substituent groups (steric factor).

Reactivity of different carbonyl compounds in decreasing order is as follows:

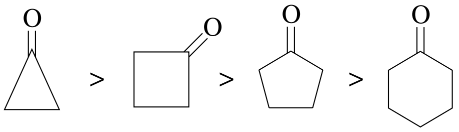


$$\mathrm{HCHO > C_6H_5{-}CH_2{-}CHO > RCHO > C_6H_5{-}CHO > R{-}\overset{\overset{O}{\|}}{C}{-}R > R{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5 > C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5}$$

Reactivity in decreasing order

Reactivity of Cyclic Ketones

In case of cyclic ketones the reactivity order is as follows:



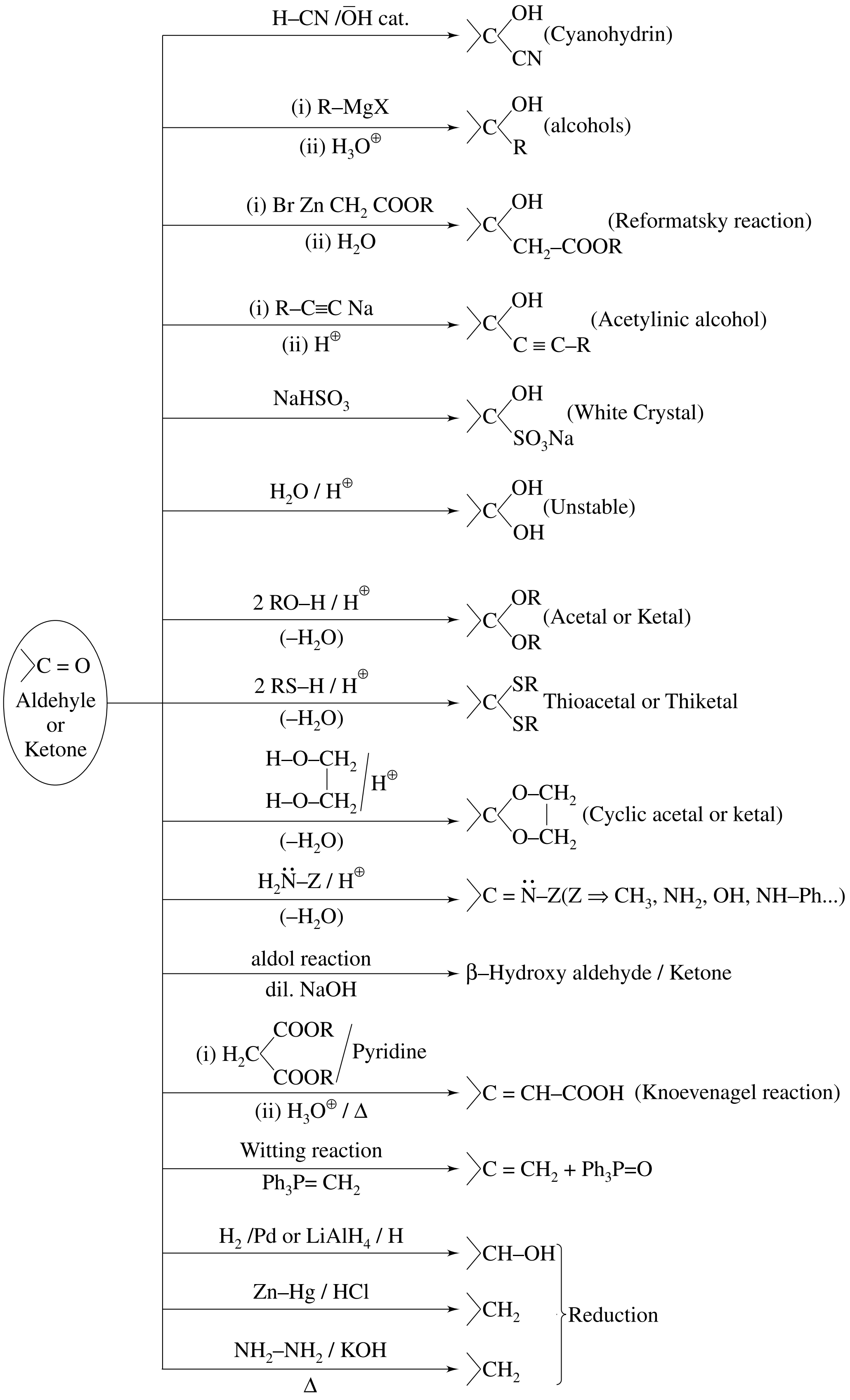
Thus more is the angle strain in the cyclic ketones more is their reactivity for nucleophilic addition reaction.

Conclusion

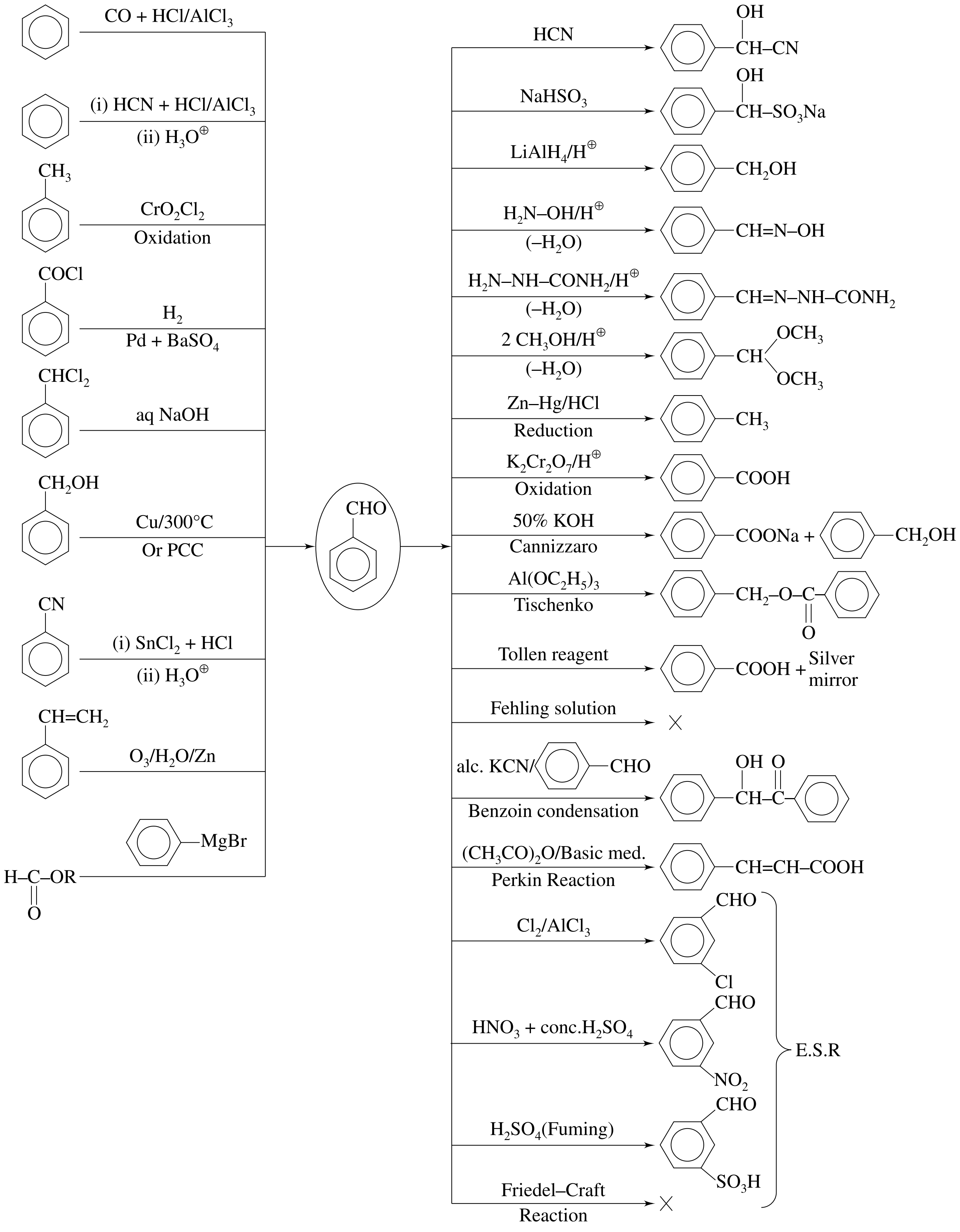
(i) Steric hindrance and more alkyl substituents make carbonyl compounds less reactive towards any nucleophile.

(ii) Electron-withdrawing groups and small rings make carbonyl compounds more reactive towards any nucleophile.

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS



METHODS OF PREPARATION AND CHEMICAL PROPERTIES OF BENZALDEHYDE: (OIL OF BITER ALMONDS)

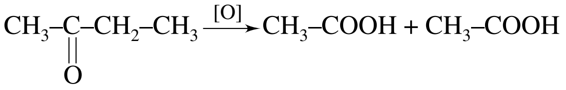


SPECIAL POINTS

1. Distinction between formaldehyde, acetaldehyde and acetone:

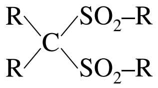
S. No.	Reagent/Test	HCHO	CH_3CHO	CH_3COCH_3
1	Brady reagent/DNP	Coloured crystal	Coloured crystal	Coloured Crystal
2	Tollen's reagent	Silver mirror	Silver mirror	×
3	Fehling's solution	Red	Red	×
4	Benedict's solution	Red	Red	×
5	Corrosive sublimate ($HgCl_2$)	Black	Black	×
6	Schiff's reagent	Pink	Pink	×
7	Iodoform test	×	Yellow	Yellow
8	Pyrogallol test	White	×	×
9	Legal test (Sodium nitroprusside/NaOH)	×	Red	Red
10	m-dinitrobenzaldehyde test	×	×	Blue

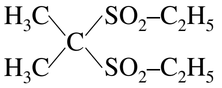
2. **Chloral** (CCl_3CHO) is an important intermediate in the manufacture of chloroform and D.D.T.
3. **Popoff's rule:** Oxidation of unsymmetrical ketones largely take place in such a way that the smaller alkyl group remains attached to the CO group during the formation of two molecules of acids.

e.g., 

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_3 \xrightarrow{[O]} CH_3{-}COOH + CH_3{-}COOH$$

4. Formaldehyde is used in preparation of urotropine (Hexamethylene tetramine), a urinary antiseptic and bakelite (phenol–formaldehyde resin) polymer, formamint, throat lozenges (formalin + lactose).
5. Formaldehyde is used as disinfectant and preservative for biological specimens in the form of **formalin.**
6. Acetaldehyde is used in preparation of polymers and dyes; metaldehyde is used as solid fuel and paraldehyde as mild hypnotic. Some more hypnotics are.


sulphonal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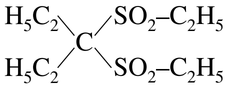

tetronal

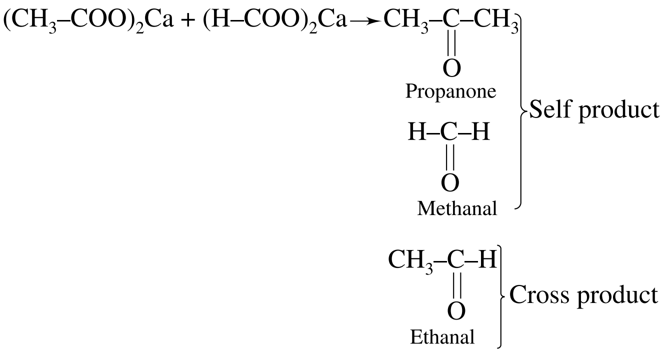
7. Acetaldehyde is used as an antiseptic.
8. Acetone is used as a solvent for cellulose, nail polish, varnish and silk.

SOLVED EXAMPLE

1. Which of the following will not be formed when calcium formate is distilled with calcium acetate?

(1) Propanone (2) Propanal
(3) Ethanal (4) Methanal

Sol. **[2]**



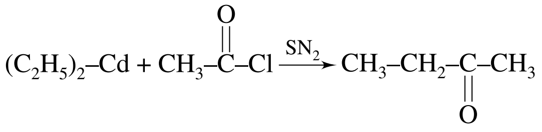
$$(CH_3{-}COO)_2Ca + (H{-}COO)_2Ca \rightarrow CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3,\quad H{-}\underset{\underset{O}{\|}}{C}{-}H,\quad CH_3{-}\underset{\underset{O}{\|}}{C}{-}H$$

Thus, propanal is not formed.

2. When diethyl cadmium [$(C_2H_5)_2Cd$] is treated with acetyl chloride [CH_3COCl], the main product is likely to be:

(1) acetone (2) methyl ethyl ketone
(3) diethyl ketone (4) acetaldehyde

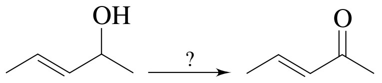
Sol. **[2]**



$$(C_2H_5)_2{-}Cd + CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow{SN_2} CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

Methly ethyl ketone

3. Which one among the following is the best reagent for the conversion of pent-3-en-2-ol into pent-3-en-2-one?



(1) $KMnO_4/H_2SO_4$ (2) $K_2Cr_2O_7/H_2SO_4$

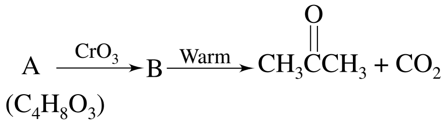
(3) CrO_3/CH_3COOH (4)  $\overset{+}{N}H\ ClCrO_3^-$

Sol. **[4]**


$\overset{+}{N}H\ ClCrO_3^-$

P.C.C. is selective oxidising agent which does not affect the oxidation of $>C=C<$

4. Consider the following sequence of reactions



$$\underset{(C_4H_8O_3)}{A}\xrightarrow{CrO_3}B\xrightarrow{Warm}CH_3\overset{\overset{O}{||}}{C}CH_3+CO_2$$

The compound (A) is:

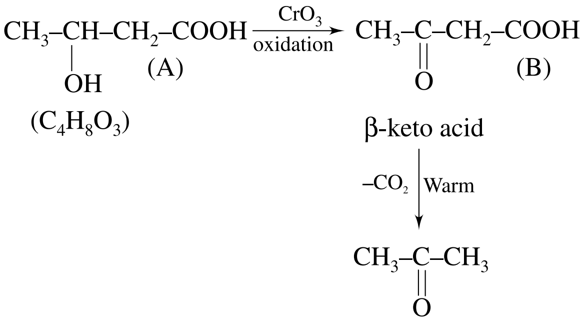
(1) $HOCH_2CH_2CH_2COOH$

(2) $CH_3CH(OH)CH_2COOH$

(3) $CH_3CH_2CH(OH)COOH$

(4) $(CH_3)_2C(OH)COOH$

Sol. **[2]**



$$\underset{(C_4H_8O_3)}{CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-COOH}\ (A)\xrightarrow[oxidation]{CrO_3}CH_3-\underset{\underset{O}{||}}{C}-CH_2-COOH\ (B)$$

β-keto acid

$$\Big\downarrow{\scriptstyle -CO_2\ \text{Warm}}$$

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

5. Which of the following compounds does not react with sodium bisulphate?

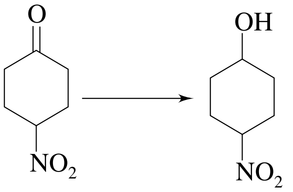
(1) Propanone (2) Propionaldehyde

(3) 3-pentanone (4) 2-pentanone

Sol. **[3]**

All aldehydes and only aliphatic methyl ketones give white precipitate with $NaHSO_3$

3-pentanone, $CH_3-CH_2-CO-CH_2-CH_3$, does not give white precipitate because it is not methyl ketone.

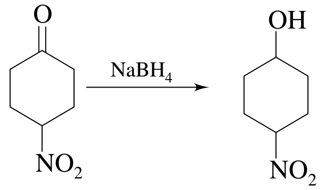
6. 

Above conversion can be achieved by

(1) $LiAlH_4$ (2) H_2,Ni

(3) $NaBH_4$ (4) All

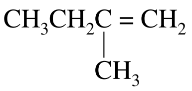
Sol. **[3]**



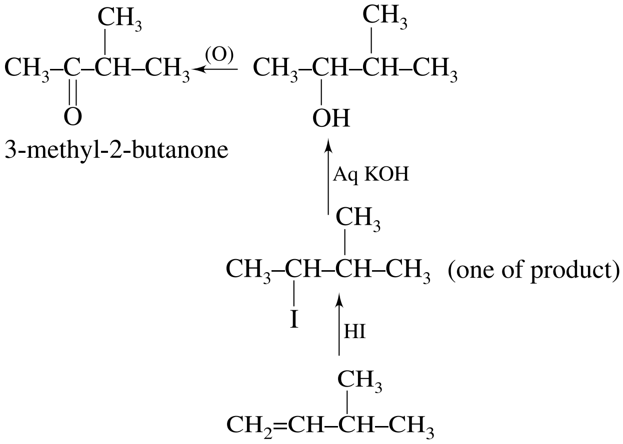
→ $-NO_2$ group not reduced by $NaBH_4$

7. A hydrocarbon reacts with HI to give (X) which on being treated with aqueous KOH gives (Y). Oxidation of (Y) gives 3-methyl-2-butanone. The hydrocarbon is

(1) $CH_3CH=C(CH_3)_2$ (2) $CH_2=CHCH(CH_3)_2$

(3)  $CH_3CH_2\underset{\underset{CH_3}{|}}{C}=CH_2$ (4) $HC\equiv C-CH(CH_3)_2$

Sol. **[2]**



$$CH_3-\underset{\underset{O}{||}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_3\xleftarrow{(O)}CH_3-\underset{\underset{OH}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

3-methyl-2-butanone

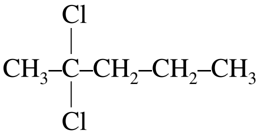
$$\Big\uparrow{\scriptstyle \text{Aq KOH}}$$

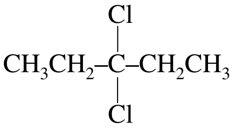
$$CH_3-\underset{\underset{I}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3\ \text{(one of product)}$$

$$\Big\uparrow{\scriptstyle HI}$$

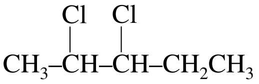
$$CH_2=CH-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

8. A compound $A(C_5H_{10}Cl_2)$ on hydrolysis gives $C_5H_{10}O$ which reacts with NH_2OH, forms iodoform but does not give Fehling test A is

(1)  $CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2-CH_2-CH_3$

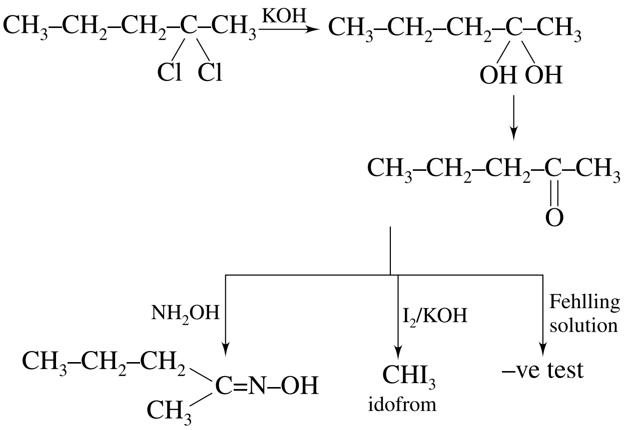
(2)  $CH_3CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$

(3)  $CH_3CH_2CH_2CH_2\overset{\overset{Cl}{|}}{C}H-Cl$

(4)  $CH_3-\overset{\overset{Cl}{|}}{C}H-\overset{\overset{Cl}{|}}{C}H-CH_2CH_3$

Sol. **[1]**

$C_5H_{10}O$ must be methyl ketone because it gives iodoform. Also ketone does not answer Fehling's solution.

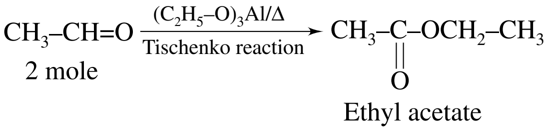


9. Acetaldehyde on being treated with aluminium ethoxide forms

(1) $CH_3CHOHCH_2CHO$ (2) $CH_3COCH_2CH_3$

(3) $CH_3COCH_2COOC_2H_5$ (4) $CH_3COOC_2H_5$

Sol. **[4]**



$$\underset{\text{2 mole}}{CH_3-CH=O} \xrightarrow[\text{Tischenko reaction}]{(C_2H_5-O)_3Al/\Delta} \underset{\text{Ethyl acetate}}{CH_3-\underset{\underset{O}{||}}{C}-OCH_2-CH_3}$$

10. Which of the following cannot be used to convert RCHO into RCH_2OH?

(1) H_2/Pd

(2) $LiAlH_4$

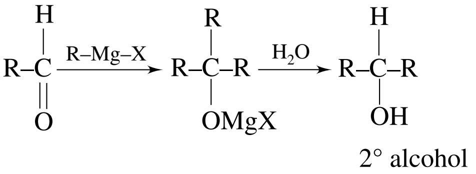
(3) $NaBH_4$

(4) Reaction with RMgX followed by hydrolysis

Sol. **[4]**

H_2/Pd, $LiAlH_4$, $NaBH_4$ will convert R–CH=O into R–CH_2OH by reduction.

Aldehyde is converted into 2° alcohol with Grignard reagent.



$$R-\overset{\overset{H}{|}}{\underset{\underset{O}{||}}{C}} \xrightarrow{R-Mg-X} R-\overset{\overset{R}{|}}{\underset{\underset{OMgX}{|}}{C}}-R \xrightarrow{H_2O} \underset{\text{2° alcohol}}{R-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-R}$$

11. A compound (X) of molecular formula C_3H_6O forms bisulphate complex, gives iodoform test but does not reduce Tollens reagent. (X) on reaction with CH_3MgBr/H_3O^+ gives a compound (Y) that cannot

(1) give red colour with CAN

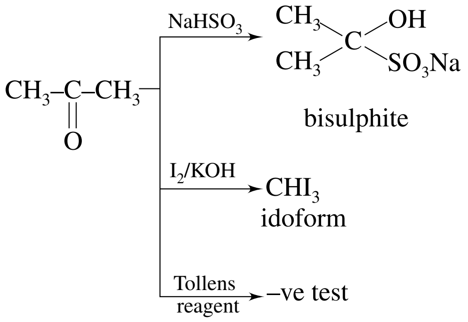
(2) give white turbidity immediately with Lucas reagent

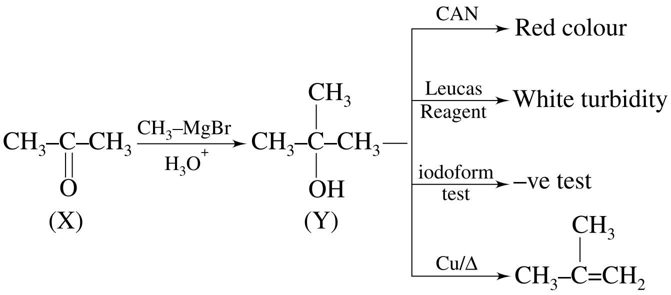
(3) give iodoform test

(4) be dehydrated to alkene on reaction with heated Cu

Sol. **[3]**

In given condition $X(C_3H_6O)$ should be methyl ketone.





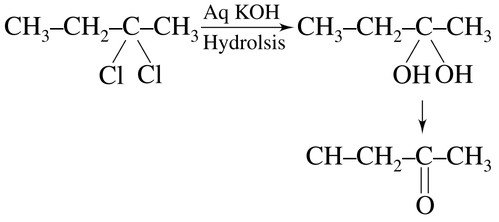
12. A compound (A), $C_4H_8Cl_2$, on hydrolysis gives a product (B) which forms a 2, 4-DNP derivative but does not reduce Tollens reagent. The compound (A) has the structure

(1) $CH_3CH_2CHClCH_2Cl$ (2) $CH_3CH_2CCl_2CH_3$

(3) $CH_3CH_2CH_2CHCl_2$ (4) $CH_3CHClCHClCH_3$

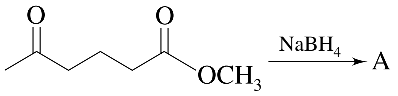
Sol. **[2]**

Ketone group forms 2, 4, DNP derivative but do not reduces Tollens' reagent. Hence $A(C_4H_8Cl_2)$ must be non-terminal geminal di chloride.

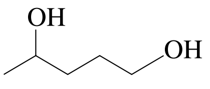


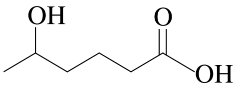
$$CH_3-CH_2-C(Cl)(Cl)-CH_3 \xrightarrow[\text{Hydrolsis}]{\text{Aq KOH}} CH_3-CH_2-C(OH)(OH)-CH_3 \rightarrow CH-CH_2-\underset{\underset{O}{||}}{C}-CH_3$$

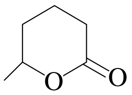
13. Consider the following reaction:

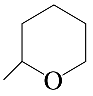


The product (A) is:

(1) 

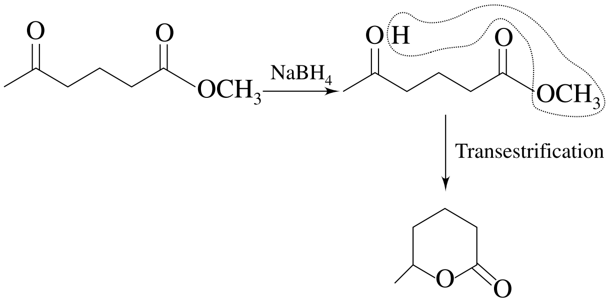
(2) 

(3) 

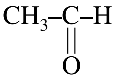
(4) 

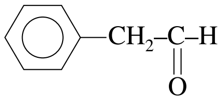
Sol. **[3]**

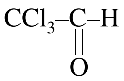
Reduction of ester group is not affected by weak reducing agent $NaBH_4$



14. Which of the following gives Cannizzaro reaction?

(1) 
$CH_3-\underset{\underset{O}{\|}}{C}-H$

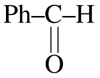
(2) 

(3) 
$CCl_3-\underset{\underset{O}{\|}}{C}-H$

(4) Ph–CH=O

Sol. **[4]**

Aldehydes having no α-H give Cannizzaro reaction. Chloral gives nucleophilic substitution reaction so that derivative of formic acid is formed. Thus only


$Ph-\underset{\underset{O}{\|}}{C}-H$ no –H (gives Cannizzaro reaction)

15. A water soluble $C_6H_{14}O_2$ compound is oxidised by lead tetraacetate (or periodic acid) to a single C_3H_6O carbonyl compound. Which of the following would satisfy this fact?

(1) meso-2, 3-dimethoxybutane

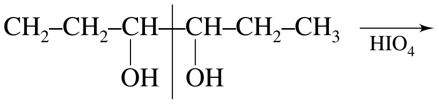
(2) 1, 2-diethoxyethane

(3) meso-2, 5-hexanediol

(4) meso-3, 4-hexanediol

Sol. **[4]**

Only vicinal diol cleaved by periodic acid

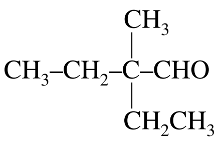

$CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow[HIO_4]{}$

Meso 3,4 hexane diol

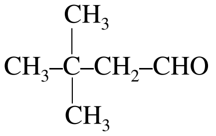
$CH_3-CH_2-CH=O\ (C_3H_6O)$

16. Which of the following would undergo aldol condensation?

(1) HCHO

(2) 
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-CHO$

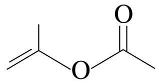
(3) CCl_3CHO

(4) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CHO$

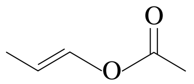
Sol. **[4]**

Only α-H containing substances undergo aldol condensation.

17. Consider the structures (P) and (Q)



(P)

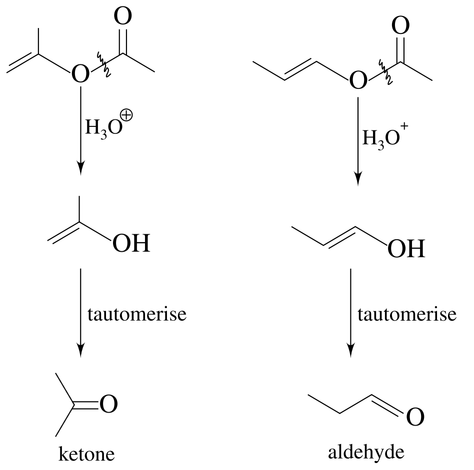


(Q)

The products of acid-catalysed hydrolysis of (P) and (Q) can be distinguished by

(1) Lucas reagent	(2) 2,4-DNP
(3) Fehling's solution	(4) $NaHSO_3$

Sol. **[3]**

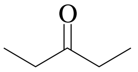


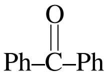
(Negative test with Fehling's solution)

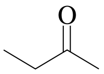
(Postivie test with Fehling's solution)

18. Compound 'A' give positive test with 2,4-DNP and with I_2/NaOH. Compound 'A' may be:

(1) Ph–CHO

(2) 

(3) 
$Ph-\overset{\overset{O}{\|}}{C}-Ph$

(4) 

Sol. **[4]**

- positive DNP test indicating that compound (A) must have carbonyl group
- positive iodoform test indicating that (A) must be methyl ketone

19. Which of the following reduce Fehling's solution?

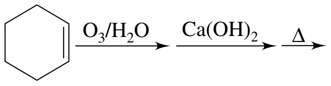
(1) Fructose	(2) Benzaldehyde
(3) Sucrose	(4) Amylose

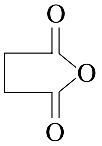
Sol. **[1]**

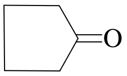
$$\text{Fructose} \xrightarrow[\text{Solution}]{\text{Fehling's}} \text{positive test}$$

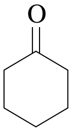
α-Hydroxy ketone will also reduce Fehling's solution.

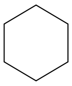
20. End product in the following sequence of reaction is:



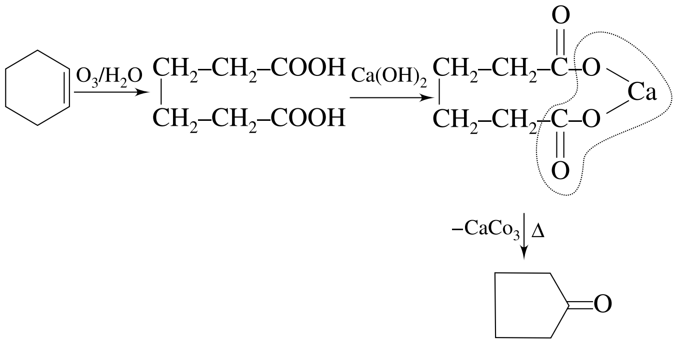
(1) 

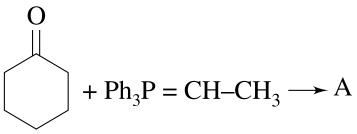
(2) 

(3) 

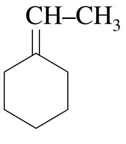
(4) 

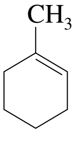
Sol. **[2]**

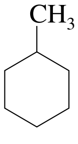


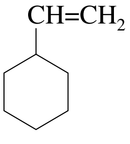
21. 

A is:

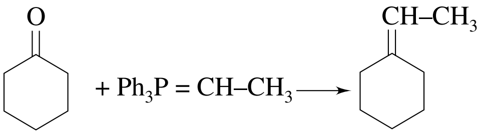
(1) 

(2) 

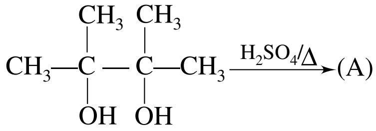
(3) 

(4) 

Sol. **[1]**

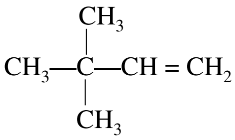


Wittig reaction

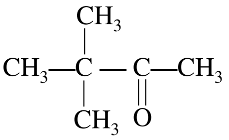
22. 

$$\mathrm{CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3} \xrightarrow{H_2SO_4/\Delta} (A)$$

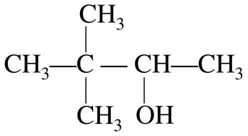
Product A is:

(1) 

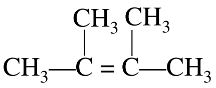
$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2}$

(2) 

$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\overset{\|}{O}}{C}-CH_3}$

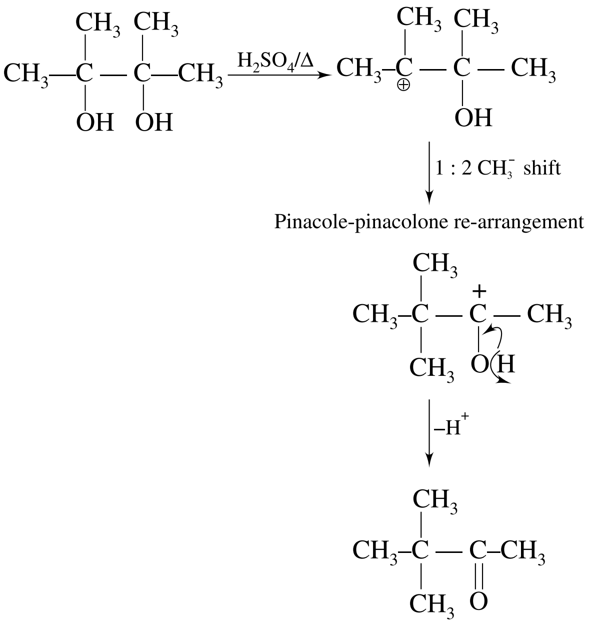
(3) 

$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3}$

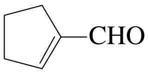
(4) 

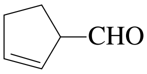
$\mathrm{CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3}$

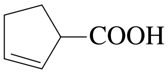
Sol. **[2]**

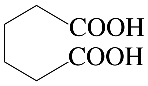


23. Cyclohexene on treatment with O_3, followed by reaction with zinc dust and water gives a compound (E). The compound (E) on further treatment with aqueous KOH yields a compound (F). The compound (F) is

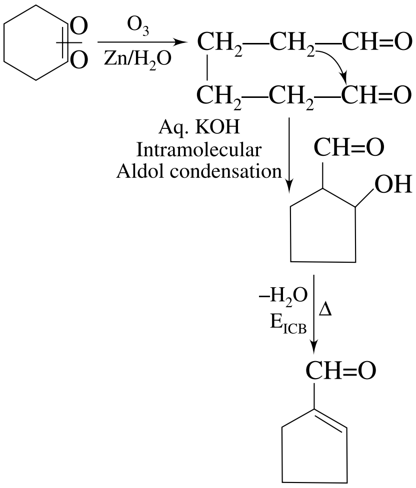
(1) 

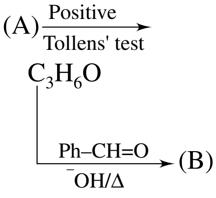
(2) 

(3) 

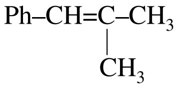
(4) 

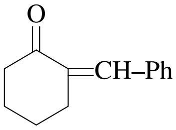
Sol. **[1]**

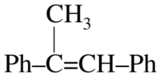


24. 

Product (B) is:

(1) 
$Ph–CH=\underset{\displaystyle CH_3}{\underset{|}{C}}–CH_3$

(2) 

(3) 
$Ph–\overset{\displaystyle CH_3}{\overset{|}{C}}=CH–Ph$

(4) Ph–CH=CH–CH=O

Sol. **[4]**

(A) must be aldehyde,

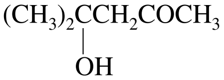
$$CH_3–CH=O \xrightarrow[\overline{O}H/\Delta]{Ph–CH=O} Ph–CH=CH–CH=O$$

(positive Tollens' test)

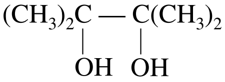
Claisen condensation

25. Propanone on reaction with magnesium amalgam in benzene and subsequent hydrolysis forms:

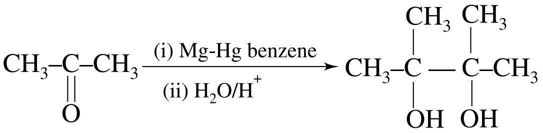
(1) $CH_3CHOHCH_3$

(2) 
$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2COCH_3$

(3) $(CH_3)_2C=CHCOCH_3$

(4) 
$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}—\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2$

Sol. **[4]**


$$CH_3–\underset{\displaystyle O}{\underset{||}{C}}–CH_3 \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) Mg-Hg benzene}} CH_3–\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}—\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}–CH_3$$

(Reductive Dimerisation)

EXERCISE 1

1. Consider the following sequence of reactions

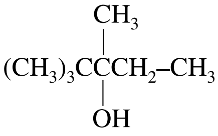
$$CH_3CH_2I \xrightarrow[\text{2. CuI}]{\text{1. Li/Et}_2\text{O}} A$$

$$(CH_3)_3CCOCl + A \longrightarrow B$$

The final product (B) is:

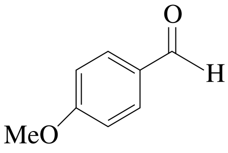
(1) $(CH_3)_3CCOCH_2–CH_3$

(2) $(CH_3)_3CCH(OH)CH_2–CH_3$

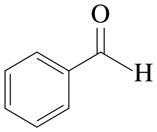
(3) 
$(CH_3)_3C\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_2–CH_3$

(4) $(CH_3)_3CCOOCH_2–CH_3$

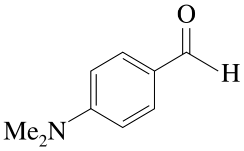
2. The $K_{eq.}$ values in HCN addition to following aldehydes are in the order:



I



II



III

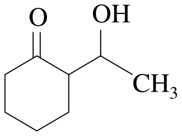
(1) I > II > III
(2) II > III > I
(3) III > I > II
(4) II > I > III

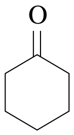
3. Consider the following sequence of reactions:

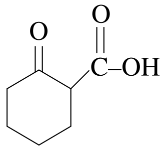
$$CH_3CHO + HCN \rightarrow CH_3CHOHCN \xrightarrow[\text{heat}]{H_3O^+} CH_3CHOHCOOH$$

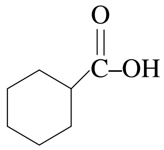
The acid formed as the final product will be obtained as:

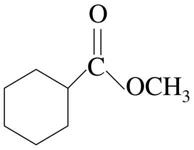
(1) an L-isomer
(2) a D-isomer
(3) 20% D-isomer and 80% L-isomer
(4) 50% D-isomer and 50% L-isomer

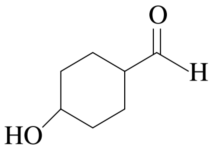
4.  $\xrightarrow[\Delta]{NaOI} \xrightarrow{H^+} \xrightarrow{\Delta}$ A, A is

(1) 

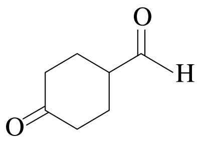
(2) 

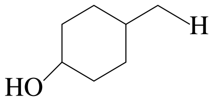
(3) 

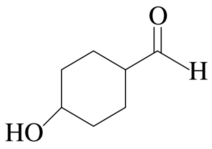
(4) 

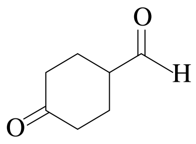
5.  $\xrightarrow[LiAlH_4]{Ag_2O,\ NH_4OH}$ (P)

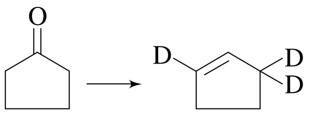
Product (P) is:

(1) 

(2) 

(3) 

(4) 

6. 

Arrange the follwing reagent in the correct order in which above transformation is carried out:

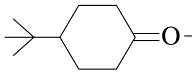
(1) KOD/D_2O, H^+/Δ, $LiAlH_4$

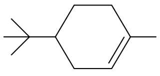
(2) H^+/Δ, KOD/D_2O, $LiAlH_4$

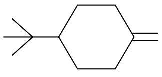
(3) KOD/D_2O, $LiAlH_4$, H^+/Δ

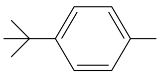
(4) $LiAlH_4$, H^+/Δ, KOD/D_2O

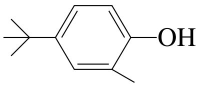
7. Identify the major product in the following reaction.

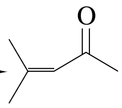
 $\xrightarrow[\text{2. } H_3O^+]{\text{1. MeMgBr}}$ 3. H_2SO_4

(1) 

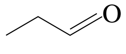
(2) 

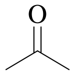
(3) 

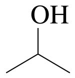
(4) 

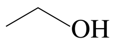
8. (X) $\xrightarrow[\Delta]{\text{dil. KOH}}$ 

Structure of (X) is

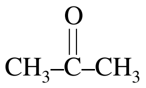
(1) 

(2) 

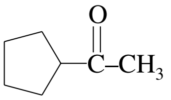
(3) 

(4) 

9. Which of the following ketones/aldehydes can undergo haloform reaction?

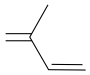
(1)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(2) CH_3-CHO

(3) 

(4) All of these

10. Monomer of trioxane is

(1) 

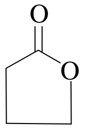
(2) $H_2C = O$

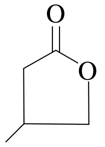
(3) Me(H)C = O

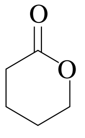
(4) $Me_2C = O$

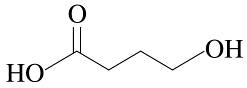
11.  $HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2-CHO$ $\xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$ (A) $\xrightarrow{\Delta}$ (B)

Structure of B will be:

(1) 

(2) 

(3) 

(4) 

12. $CH_3-C\equiv N \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) DIBAL-H}} X \xrightarrow[\Delta]{SeO_2} Y \xrightarrow[\Delta]{\overset{\ominus}{O}H} Z$, Z is:

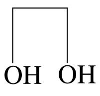
(1) $CH_2(OH)-COO^{\ominus}$

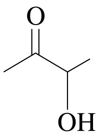
(2) $CH_3-COO^{\ominus}$

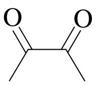
(3) $HOOC-COO^{\ominus}$

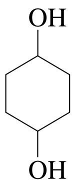
(4) $CH_2(OH)-CH_2(OH)$

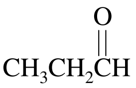
13. Which of the following compound not reacts with HIO_4?

(1) 

(2) 

(3) 

(4) 

14. $CH_3CH=CH_2 \xrightarrow{X} \xrightarrow{Y}$  $CH_3CH_2\overset{O}{\overset{\|}{C}}H$

X and Y are, respectively:

(1) H_3O^+, MnO_4^-/H^+

(2) H_3O^+, CrO_3/Pyridine

(3) BH_3. THF/H_2O_2, OH^-, CrO_3/pyridine

(4) BH_3. THF/H_2O_2, OH^-,$Cr2O_7^{2-}/H_3O^+$

15. Which type of reaction in the reduction of carbonyl compound with LAH and $NaBH_4$ occurs, and which nucleophile takes part in the reaction?

(1) Nucleophilic addition and $AlH_4^{\ominus}$ or $BH_4^{\ominus}$

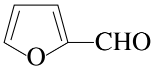
(2) Nucleophilic addition and $H^{\ominus}$

(3) Nucleophilic substitution and $AlH_4^{\ominus}$ or $BH_4^{\ominus}$

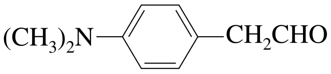
(4) Nucleophilic substitution and $H^{\ominus}$

16. Which of the following aldehydes does not undergo a Cannizzaro reaction?

(1) C_6H_5–CHO

(2) 

(3) $(CH_3)_2$–CH–CHO

(4) 

17. Reagent that can distinguish a set of benzaldehyde and formaldehyde is

(1) I_2/NaOH (2) Tollens' reagent

(3) Fehling's solution (4) Baeyer's reagent

18. In the reaction $PhCN \xrightarrow[\text{2. } H_2O\text{. heat}]{\text{1. } SnCl_2/HCl}$ the modification of the functional group and the change in hybridisation of the functional carbon are, respectively

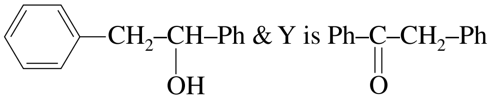
(1) –CN to –CH_2NH_2, sp^2 to sp^3

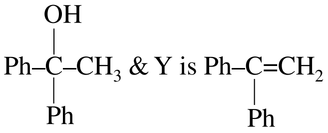
(2) –CN to –$CONH_2$, sp to sp^2

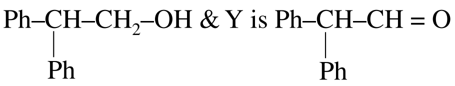
(3) –CN to –COOH, sp^2 to sp^3

(4) –CN to –CHO, sp to sp^2

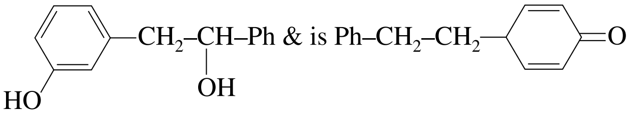
19. A compound 'X' ($C_{14}H_{14}O$) on mild oxidation yields $C_{14}H_{12}O$ (Y). If X is treated with a dehydrating agent, it loses a molecule of H_2O and resulting product on vigorous oxidation yield two molecule of benzoic acid. Identify the structure of X and Y.

(1) 
Xis —CH_2–$\underset{OH}{CH}$–Ph & Y is Ph–$\underset{O}{\underset{\|}{C}}$–$CH_2$–Ph

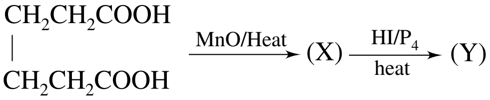
(2) 
X is Ph–$\overset{OH}{\underset{Ph}{C}}$–$CH_3$ & Y is Ph–$\underset{Ph}{C}$=CH_2

(3) 
X is Ph–$\underset{Ph}{CH}$–CH_2–OH & Y is Ph–$\underset{Ph}{CH}$–CH = O

(4) X is



20. Consider the following reaction sequence.


$$\begin{array}{l} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array} \xrightarrow{\text{MnO/Heat}} (X) \xrightarrow[\text{heat}]{HI/P_4} (Y)$$

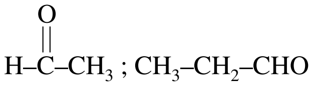
The product (Y) is–

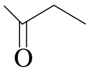
(1) cyclobutane (2) cyclopentane

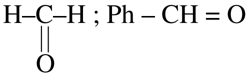
(3) cyclopentanone (4) cyclobutanone

21. Which of the following pairs is differentiated by iodoform and Tollens' reagent?

(1) $PhCOCH_3$; Ph–CHO

(2) 
H–$\overset{O}{\overset{\|}{C}}$–$CH_3$; CH_3–CH_2–CHO

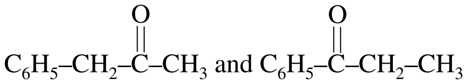
(3)  ; CH_3–CH_2–CHO

(4) 
H–$\underset{O}{\underset{\|}{C}}$–H ; Ph – CH = O

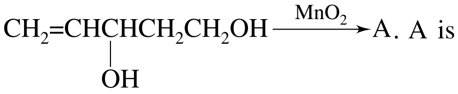
22. Schiff's reagent is used for the differentiation between:

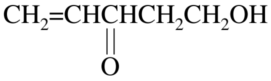
(1) HCHO and CH_3CHO

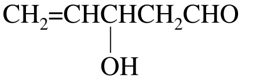
(2) CH_3COCH_3 and CH_3CHO

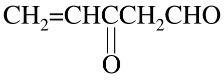
(3) 
C_6H_5–CH_2–$\overset{O}{\overset{\|}{C}}$–$CH_3$ and C_6H_5–$\overset{O}{\overset{\|}{C}}$–$CH_2$–$CH_3$

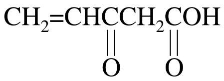
(4) HCHO and C_6H_5CHO

23. 
CH_2=$CH\underset{OH}{C}HCH_2CH_2OH \xrightarrow{MnO_2}$ A. A is

(1) 
CH_2=$CH\underset{O}{\underset{\|}{C}}HCH_2CH_2OH$

(2) 
CH_2=$CH\underset{OH}{C}HCH_2CHO$

(3) 
CH_2=$CH\underset{O}{\underset{\|}{C}}CH_2CHO$

(4) 
CH_2=$CH\underset{O}{\underset{\|}{C}}CH_2\underset{O}{\underset{\|}{C}}OH$

24. In the reaction $PhCOCH_3 \xrightarrow{CH_3CO_3H}$ A, the product (A) is:

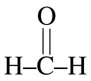
(1) $PhCOOCH_3$ (2) CH_3COOPh

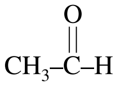
(3) $PhCO_2H$ (4) $PhCOOCOCH_3$

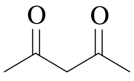
25. Aniline undergoes condensation reaction with benzaldehyde to from benzalaniline. The latter is known as:

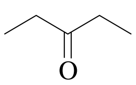
(1) a Mannich base (2) a Schiff base
(3) Schiff reagent (4) Benedict's reagent

26. Which of the following will give negative Tollens' but positive iodoform test?

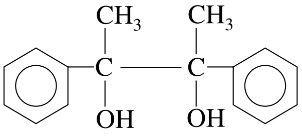
(1) 
$H-\overset{O}{\overset{\|}{C}}-H$

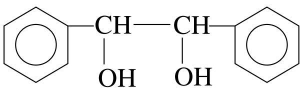
(2) 
$CH_3-\overset{O}{\overset{\|}{C}}-H$

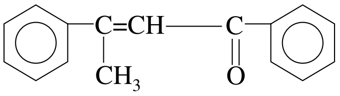
(3) 

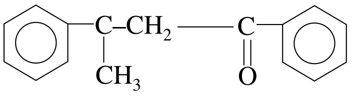
(4) 

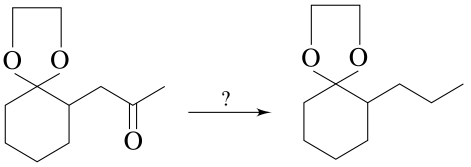
27. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure:

(1) 

(2) 

(3) 

(4) 

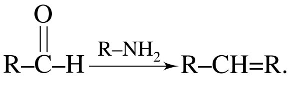
28. 

Above conversion can be carried out by:

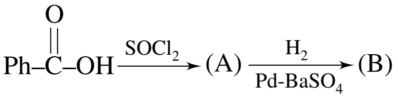
(1) Clemmensen reduction
(2) Wolff–Kishner reduction
(3) $LiAlH_4$
(4) $NaBH_4$

29. When a nucleophile encounters a ketone, the site of attack is:

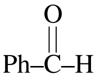
(1) The carbon atom of the carbonyl
(2) The oxygen atom of the carbonyl
(3) Both the carbon and oxygen atoms, with equal probability
(4) No attack occurs as ketones do not react with nucleophiles

30. 
$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{R-NH_2} R-CH=R$. This reaction gives the best yield at:

(1) pH 1–2 (2) pH 4–5
(3) pH 10–11 (4) pH 13–14

31. 
$Ph-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} (A) \xrightarrow[Pd\text{-}BaSO_4]{H_2} (B)$

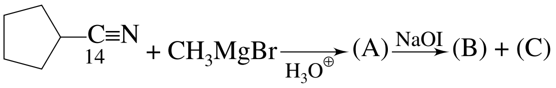
Product (B) is:

(1) 
$Ph-\overset{O}{\overset{\|}{C}}-H$
(2) $Ph-CH_2-OH$
(3) $Ph-CH_2-Cl$ (4) $Ph-CH=CH_2$

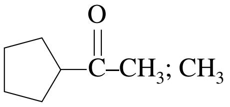
32. $Ph-CH_3 \xrightarrow{CrO_2Cl_2} (A) \xrightarrow{\text{conc. KOH}} Ph-CH_2OH + (B)$

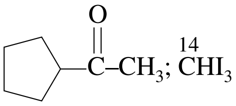
Product (B) of above the reaction is:

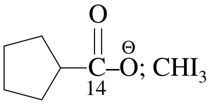
(1) $Ph-CO_2H$ (2) $Ph-CO_2^-$
(3) $Ph-CHO$ (4) $Ph-CH_3$

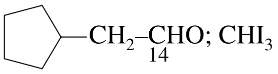
33. 

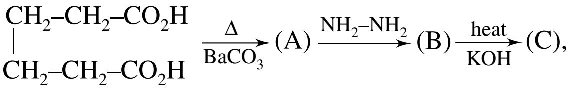
Products (A) and (C) are:

(1) 

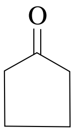
(2) 

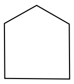
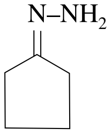
(3) 

(4) 

34. 
$\begin{matrix} CH_2-CH_2-CO_2H \\ | \\ CH_2-CH_2-CO_2H \end{matrix} \xrightarrow[BaCO_3]{\Delta} (A) \xrightarrow{NH_2-NH_2} (B) \xrightarrow[KOH]{heat} (C),$

Product (C) obtained is:

(1) $CH_3-CH=CH-CH_2$ (2) 

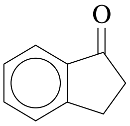
(3)  (4) 

35. $(A) \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} (B) \xrightarrow{LiAlH_4} \underset{\text{Racemic mixture}}{(C)}$

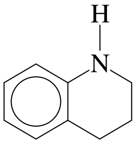
Reactant (A) is:

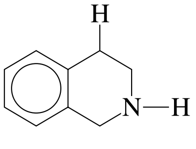
(1) $CH_3-C\equiv CH$ (2) $HC\equiv CH$
(3) $CH_3-C\equiv C-CH_3$ (4) $Ph-CH=CH_2$

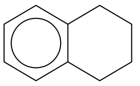
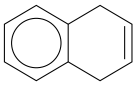
EXERCISE 2

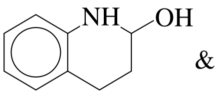
1. 

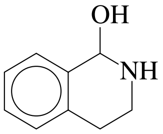
$\xrightarrow[\text{(2) H}^+\text{,D} \quad \text{(3) LiAlH}_4]{\text{(1) NH}_2\text{OH}}$ (A) + (B). Product (A) & (B) are:

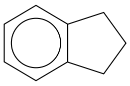
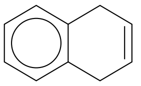
(1) 

& 

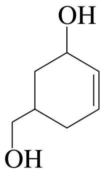
(2) 
& 

(3) 

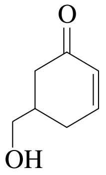
& 

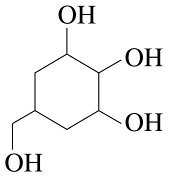
(4) 
& 

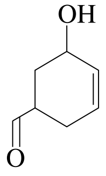
2. Give the major product of the following reaction–

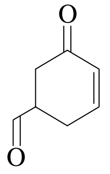


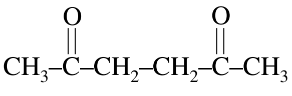
$\xrightarrow{\text{MnO}_2}$ Major product

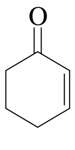
(1) 

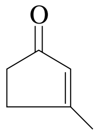
(2) 

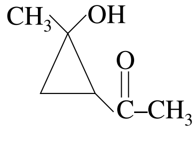
(3) 

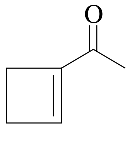
(4) 

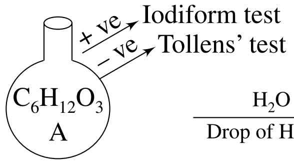
3. 
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\text{(ii) }\Delta]{\text{(i) dil. NaOH}}$ Major product will be–

(1) 

(2) 

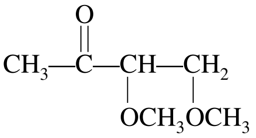
(3) 

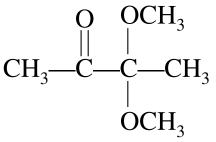
(4) 

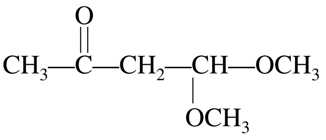
4. 

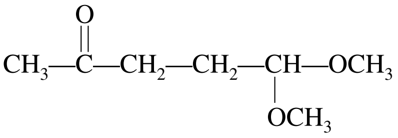
$\xrightarrow[\text{Drop of H}_2\text{SO}_4]{\text{H}_2\text{O}}$ Positive Tollens' test

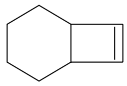
Compound (A is):

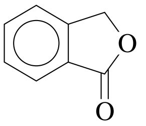
(1) 
$CH_3-\overset{\overset{O}{||}}{C}-\underset{\underset{OCH_3}{|}}{CH}-\underset{\underset{OCH_3}{|}}{CH_2}$

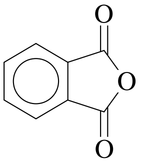
(2) 
$CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-CH_3$

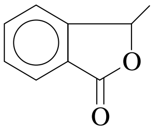
(3) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{OCH_3}{|}}{CH}-OCH_3$

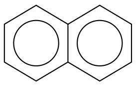
(4) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-\underset{\underset{OCH_3}{|}}{CH}-OCH_3$

5. 
$\xrightarrow[\text{Zn}]{\text{O}_3}$ (A) $\xrightarrow{\text{Conc. KOH}}$ (B) $\xrightarrow[\Delta]{\text{H}^+}$ (C); Product (C) is

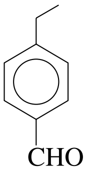
(1) 

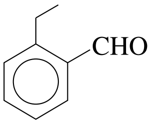
(2) 

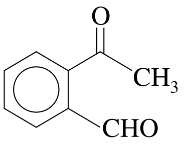
(3) 

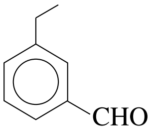
(4) 

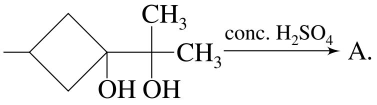
6. An organic compound with the molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction, on $KMnO_4$ oxidation it gives 1, 2-benzenedicarboxylic acid. Structure of organic compound is

(1) 

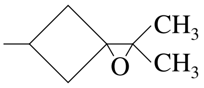
(2) 

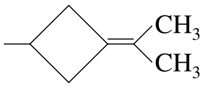
(3) 

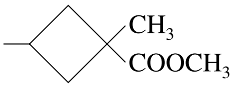
(4) 

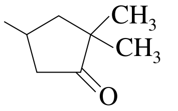
7. In the given reaction 

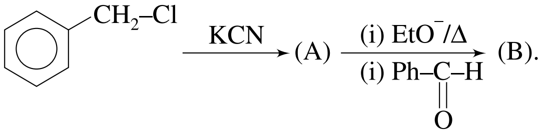
The product A is

(1) 

(2) 

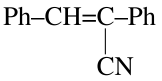
(3) 

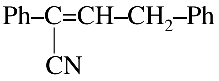
(4) 

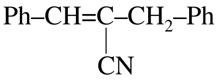
8. 

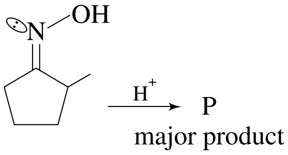
Product (B) of the reaction is

(1) Ph–CH$_2$–CH=CH–Ph

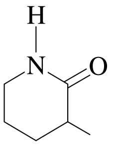
(2) 
$Ph-CH=\underset{\underset{CN}{|}}{C}-Ph$

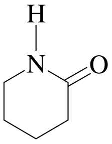
(3) 
$Ph-\underset{\underset{CN}{|}}{C}=CH-CH_2-Ph$

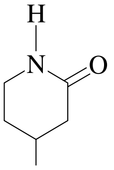
(4) 
$Ph-CH=\underset{\underset{CN}{|}}{C}-CH_2-Ph$

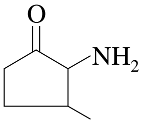
9. 

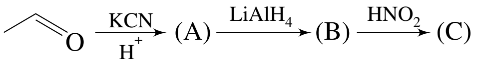
Identify the structure of 'P'

(1) 

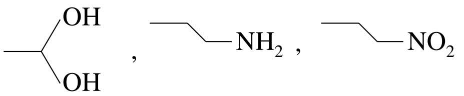
(2) 

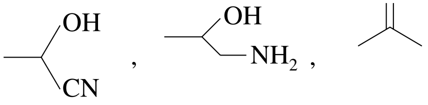
(3) 

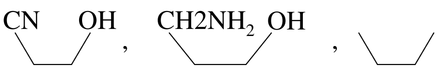
(4) 

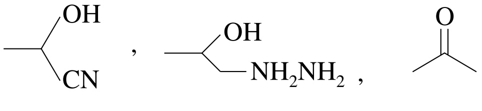
10. 

The products A, B and C, respectively, are:

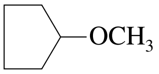
(1) 

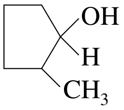
(2) 

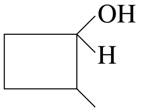
(3) 

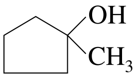
(4) 

11. An organic compound A (molecular formula $C_6H_{12}O$) does not change the colour of acidic dichromate solution. Compound A on treatment with H_2SO_4 produces alkene, which on oxidative ozonolysis gives a molecule ($C_6H_{10}O_3$) which gives positive iodoform test. Find the structure of A

(1) 

(2) 

(3) 

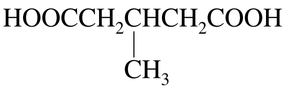
(4) 

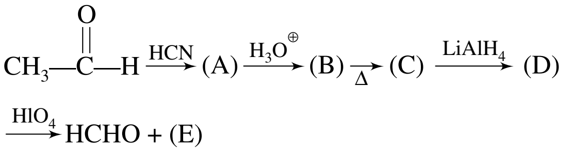
12. Acetaldehyde on being heated with malonic acid in the presence of pyridine produces

(1) $CH_3CH=C(COOH)_2$

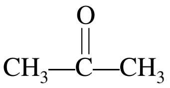
(2) CH_3COOH

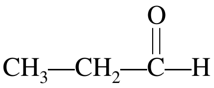
(3) $CH_3CH=CHCOOH$

(4) 
$HOOCCH_2\underset{\underset{CH_3}{|}}{C}HCH_2COOH$

13. 
$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{HCN} (A) \xrightarrow{H_3O^{\oplus}} (B) \xrightarrow[\Delta]{} (C) \xrightarrow{LiAlH_4} (D) \xrightarrow{HIO_4} HCHO + (E)$

Compound (C) can show geometrical isomerism. Product (E) of the reaction will be:

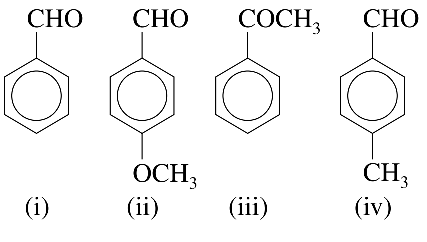
(1) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(2) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

(3) CH_3-CHO

(4) HCHO

14. Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaction.



(1) ii > iii > i > iv

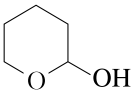
(2) ii > i > iv > iii

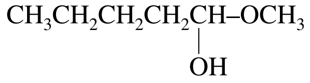
(3) iii > ii > i > iv

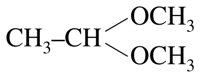
(4) i > iv > ii > iii

15. Which of the following compounds will not give positive Tollens' test?

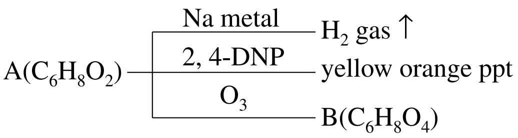
(1) CH_3CHO

(2) 

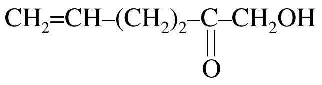
(3) 
$CH_3CH_2CH_2CH_2CH(OH){-}OCH_3$

(4) 
$CH_3{-}CH(OCH_3)_2$

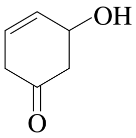
16. The compound A gives following reactions:

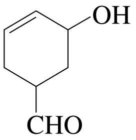


Its structure can be:

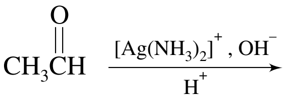
(1) 
$CH_2{=}CH{-}(CH_2)_2{-}\overset{\overset{\textstyle O}{||}}{C}{-}CH_2OH$ (C=O drawn below)

(2) OHC–(H_2C_2)$_2$–HC–COOH

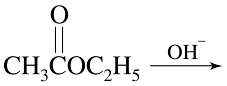
(3) 

(4) 

17. Consider the following reactions:

I. 
$CH_3\overset{O}{\overset{||}{C}}H \xrightarrow[H^+]{[Ag(NH_3)_2]^+,\ \bar{O}H}$

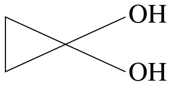
II. $CH_3CCl_3 \xrightarrow{\bar{O}H}$

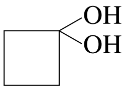
III. 
$CH_3\overset{O}{\overset{||}{C}}OC_2H_5 \xrightarrow{\bar{O}H}$

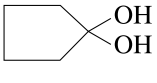
The final product is acid in:

(1) I, II, III	(2) I, III
(3) I, II	(4) I

18. Arrange their stabilities of given gem-diols in decreasing order.

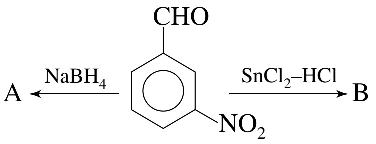
(I) 

(II) 

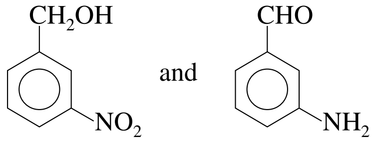
(III) 

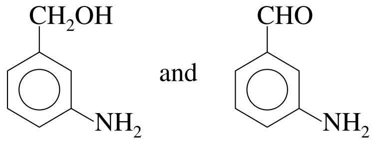
(1) I > II > III	(2) III > II > I
(3) I > III > II	(4) III > I > II

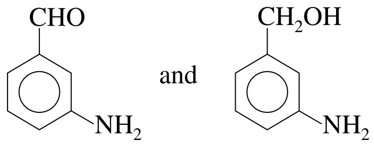
19. Consider the following two reactions:

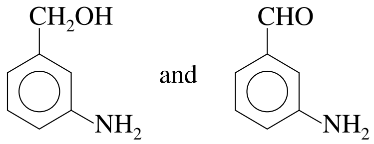


The two major products (A) and (B) are, respectively:

(1) 

(2) 

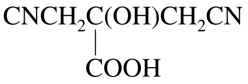
(3) 

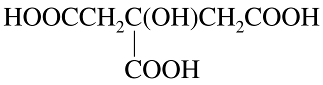
(4) 

20. Consider the following sequence of reactions

$$ClCH_2COCH_2Cl \xrightarrow{HCN} A \xrightarrow{KCN(excess)} B \xrightarrow{H_3O^+} C$$

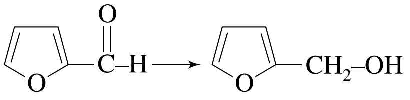
The end product (C) is

(1) 
$CNCH_2C(OH)(COOH)CH_2CN$

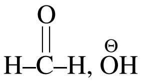
(2) 
$HOOCCH_2C(OH)(COOH)CH_2COOH$

(3) $CNCH_2COCH_2CN$

(4) $HOOCCH_2COCH_2COOH$

21. 

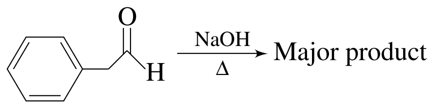
Identify the reagents that can perform this conversion successfully

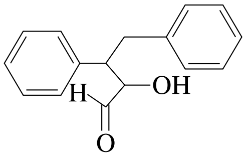
(I) H_2, Raney Ni, Δ	(II) HI/P_4
(III) $NaBH_4$, H_2O	(IV)  $H{-}\overset{O}{\overset{||}{C}}{-}H,\ \overset{\ominus}{O}H$

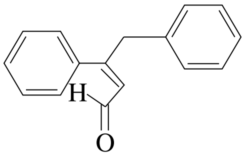
Select the correct code

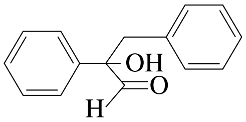
(1) I and II	(2) II and III
(3) III and IV	(4) II and IV

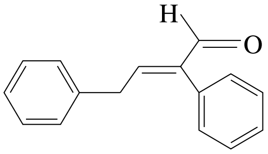
22. Give the major product of the following reaction:

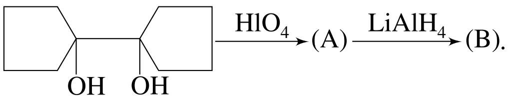


(1) 

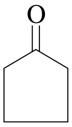
(2) 

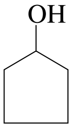
(3) 

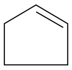
(4) 

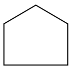
23. 

Product (B) is

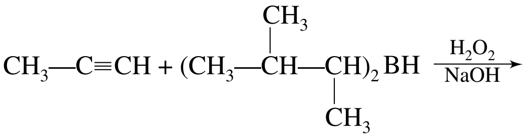
(1) 

(2) 

(3) 

(4) 

24. In which of the following reactions, an aldehyde is not formed as major product?

(1) 

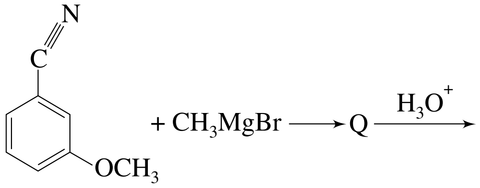
$CH_3—C\equiv CH + (CH_3—\underset{}{\overset{CH_3}{\overset{|}{C}H}}—\underset{\underset{CH_3}{|}}{C}H)_2BH \xrightarrow[NaOH]{H_2O_2}$

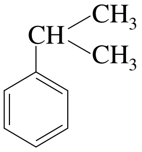
(2) $CH_3—CH_2—C\equiv CH + KMnO_4 \xrightarrow[Cold]{H_2O}$

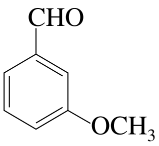
(3) $CH_3—CH_2CH_2CH_2—OH + Cu \xrightarrow{\Delta}$

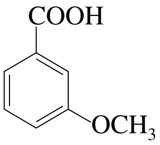
(4) $CH_3—CH_2CH_2CH_2—COOH + HCOOH \xrightarrow[Heat]{MnO}$

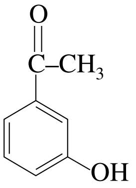
25. The product P in the reaction:



(1) 

(2) 

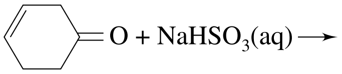
(3) 

(4) 

EXERCISE 3

One and More Than One Option Correct Type Question

1. Consider the reaction given below:



The correct observation regarding the above reaction is/are:

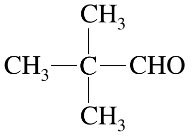
(1) Precipitate formation takes place

(2) Racemic mixture of salts are formed

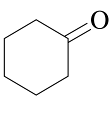
(3) Salts on acid hydrolysis give back the original reactant

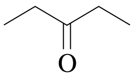
(4) If $NaHSO_3$ is in limited amount, no precipitation occurs

2. Which of the following form enamine on heating with a secondary amine in weakly acidic medium?

(1) 

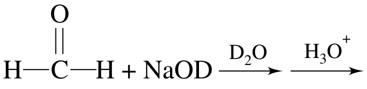
$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO$

(2) 

(3) 

(4) $C_6H_5CH_2–CH=O$

3. In the Cannizzaro reaction mentioned below



$H—\overset{\overset{O}{||}}{C}—H + NaOD \xrightarrow{D_2O} \xrightarrow{H_3O^+}$

the possible product(s) is/are

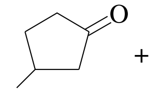
(1) CH_3OH

(2) CH_3OD

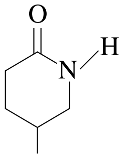
(3) $HCOOD$

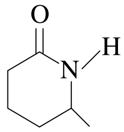
(4) H_2CDOH

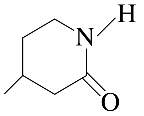
4. In the reaction given below

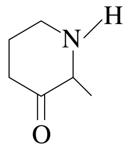
 + $H_2N—OH \xrightarrow{H^{\oplus}}$

expected product(s) is/are

(1) 

(2) 

(3) 

(4) 

5. Consider the reaction sequence give below.

$H_3C—CH_2Cl \xrightarrow[\text{(ii) } C_4H_9Li]{\text{(i) } Ph_3P} X \xrightarrow{CH_3CHO} Y$

The correct statements regarding the above reaction is/are:

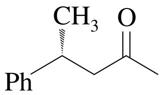
(1) X is $CH_3—CH=PPh_3$

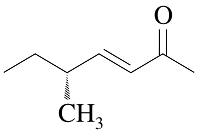
(2) Y is $CH_3—CH=CH—CH_3$

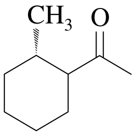
(3) Y is $CH_3—CH_2—CH=CH_2$

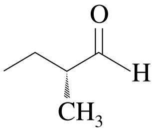
(4) Y is a mixture of diastereomers

6. The carbonyl compound(s) that will undergo racemisation on treatment with aqueous KOH is (are):

(1) 

(2) 

(3) 

(4) 

7. Which of the following are correct statements?

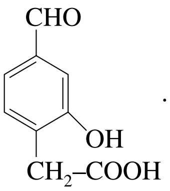
(1) Acetophenone does not give a red colour precipitate with Fehling's solution

(2) Benzaldehyde gives a red coloured precipitate with Fehling's solution

(3) Benzaldehyde gives silver mirror with Tollens' reagent

(4) Benzaldehyde gives a black grey precipitate with mercuric chloride solution

8. An organic compound has the structure



.

It will give

(1) ceric ammonium nitrate test

(2) give brisk effervescence with sodium bicarbonate

(3) it will give a characteristic colouration with neutral ferric chloride after decarboxylation and reduction by Clemmensen's method

(4) It will give silver mirror test

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

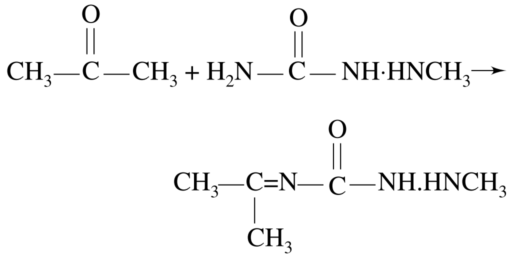
9. **Statement-I:** Fehling solution can oxidise aliphatic aldehyde but cannot oxidise aromatic aldehyde.

Statement-II: Tollens' reagent can oxidise aliphatic and aromatic aldehyde both.

10. **Statement I:** When a mixture of ethanal and propanal is treated with aqueous Na_2CO_3, four aldol (excluding stereoisomers) compounds are formed.

Statement-II: In mixed aldol condensation, two self and two cross condensation products are always formed.

11. **Statement-I:** Consider the reaction given below,

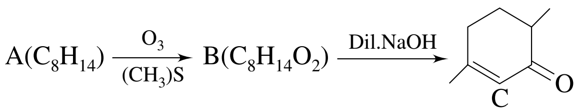


$$CH_3—\overset{O}{\overset{\|}{C}}—CH_3 + H_2N—\overset{O}{\overset{\|}{C}}—NH{\cdot}HNCH_3 \rightarrow CH_3—\underset{CH_3}{\underset{|}{C}}=N—\overset{O}{\overset{\|}{C}}—NH.HNCH_3$$

Statement-II: Aldehydes and ketones react with semicarbazide to form semicarbazone.

Comprehension Type Question

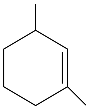
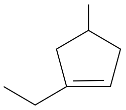
Passage Based Questions (Q. 12–14)

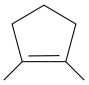
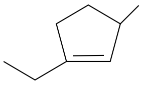


$A(C_8H_{14}) \xrightarrow[(CH_3)S]{O_3} B(C_8H_{14}O_2) \xrightarrow{\text{Dil.NaOH}}$ C

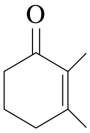
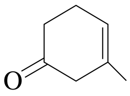
A is optically active and C is one of the several aldol possible in the above reaction.

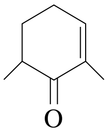
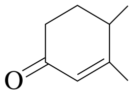
12. The structure of A satisfying above criteria is

(1) 
(2) 

(3) 
(4) 

13. Besides C, the other six membered cyclic aldol formed in the above reaction is

(1) 
(2) 

(3) 
(4) 

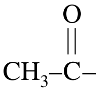
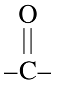
14. The product B is stereomeric. If a mixture containing all stereoisomers of B is treated with excess of $LiAlH_4$ followed by the acidification will give how many different isomeric diols?

(1) 2 (2) 4

(3) 6 (4) 8

Column Matching Type Question

15.

Column-I	**Column-II**
(A) $-COOH$	(p) Tollens' reagent
(B) $-CHO$	(q) Sodium bisulphite
(C)  $CH_3-\overset{O}{\overset{\|}{C}}-$	(r) Sodium bicarbonate
(D)  $-\overset{O}{\overset{\|}{C}}-$	(s) Sodium hypo iodite
(E) $-COOCH_3$	(t) Sodium hydroxide

(1) A→r; B→p; C→s; D→q; E→t

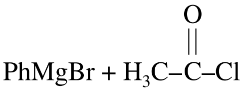
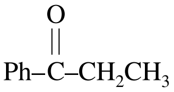
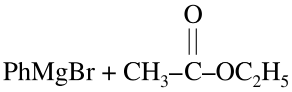
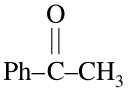
(2) A→p; B→s; C→t; D→q; E→r

(3) A→s; B→q; C→p; D→r; E→t

(4) A→q; B→t; C→s; D→p; E→r

Sol. **[1]**

16.

Column-(I)	**Column-(II)**
(a) $PhMgBr + Cl{-}NH_2$	(P) $Ph{-}CN$
(b) $PhMgBr + Cl{-}CN$	(Q) $Ph{-}NH_2$
(c)  $PhMgBr + H_3C-\overset{O}{\overset{\|}{C}}-Cl$	(R)  $Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_3$
(d)  $PhMgBr + CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$	(S)  $Ph-\overset{O}{\overset{\|}{C}}-CH_3$

(1) a→Q; b→P; c→S; d→R

(2) a→Q; b→P; c→R; d→S

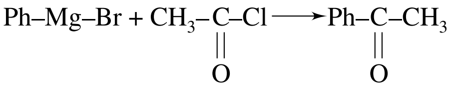
(3) a→P; b→Q; c→R; d→S

(4) a→Q; b→P; c→R; d→S

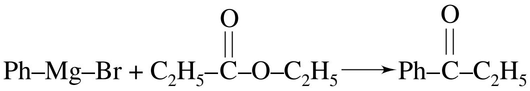
Sol. **[1]**

$$Ph{-}Mg - Br + Cl{-}NH_2 \longrightarrow Ph - NH_2$$

$$Ph{-}Mg{-}Br + Cl{-}C{=}N \longrightarrow Ph{-}CN$$



$$Ph{-}Mg{-}Br + CH_3-\underset{O}{\underset{\|}{C}}-Cl \longrightarrow Ph-\underset{O}{\underset{\|}{C}}-CH_3$$



$$Ph{-}Mg{-}Br + C_2H_5-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-C_2H_5$$

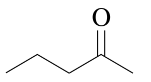
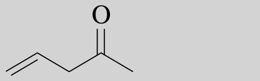
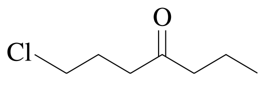
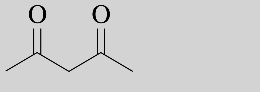
17. Match the compounds given in List-I with those in List-II and select the suitable option using the code given blow:

List-I		**List-II**	
(a)	Benzaldehyde	(i)	Phenolphthalein
(b)	Phthalic anhydride	(ii)	Benzoin condensation
(c)	Phenyl benzoate	(iii)	Oil of wintergreen
(d)	Methyl salicylate	(iv)	Fries rearrangement

Code:

	a	**b**	**c**	**d**
(1)	(ii)	(i)	(iv)	(ii)
(2)	(iv)	(i)	(iii)	(ii)
(3)	(iv)	(ii)	(iii)	(i)
(4)	(ii)	(iii)	(iv)	(i)

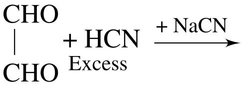
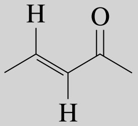
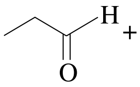
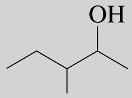
18. Match the reactants from Column I with the reagents and expected outcomes from Column II. Mark the correct option form the codes given below.

Column I		**Column II**	
i.		p.	$LiAlH_4$-racemic mixture of products.
ii.		q.	$[(CH_3)_2CHO]_3$ Al-racemic mixture of products.
iii.		r.	Zn(Hg)–HCl- suitable for selective reduction of carbonyl group
iv.		s.	N_2H_4/NaOH/Heat- suitable for selective reduction of carbonyl group.

Codes:

	i	ii	iii	iv
(1)	p, q, r, s	p, q, s	q, r	p, q, r, s
(2)	p, r	q, r	s	r, r
(3)	q, r	r, s	p, s	s
(4)	p, r	q	r, s	s

19. Match the reaction from Column I with the properties of products from Column II. Mark the correct option form the codes given below.

	Column I		Column II
i.	 $\begin{matrix}\text{CHO}\\ \vert\\ \text{CHO}\end{matrix} + \underset{\text{Excess}}{\text{HCN}} \xrightarrow{+\text{NaCN}}$	p.	Racemic mixture
ii.	 $+ \text{NaHSO}_3\text{(aq.)} \longrightarrow$	q.	Pair of diastereomers
iii.	 $+ CH_3MgBr \rightarrow \xrightarrow{H_3O^+}$	r.	Meso isomer
iv.	 $\xrightarrow[H^+]{K_2Cr_2O_7} \xrightarrow{NaBH_4} \xrightarrow{H_3O^+}$ (+) 3-methyl-2pentanol	s.	Product mixture can be separated into two fractions by chromatography

Codes

	i	ii	iii	iv
(1)	p, q, r, s	q, s	p	q, s
(2)	q, s	p, s	p, q	r, q
(3)	p, q	q	r, q	s
(4)	p, q, r	r, s	r	p

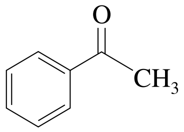
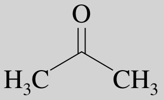
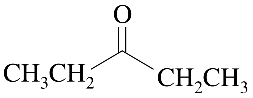
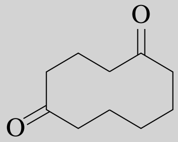
20. Match the reactions of Column I with the type of reactions from Column II. Mark the correct option form the codes given below.

	Column I		Column II
i.	$CH_3CHO + CH_2O \text{ (excess)} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	p.	Aldol condensation
ii.	$\text{F—CHO} + \text{Conc. NaOH} \xrightarrow{H_3O^+}$	q.	Cannizzaro reaction
iii.	$(CH_3)_2CH\text{—}CHO \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	r.	Claisen reaction
iv.	$CH_3CHO + C_6H_5CHO \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	s.	Tischenko reaction

Codes:

	i	ii	iii	iv
(1)	p, q	s	r	p
(2)	p, q	q	p, q	p, q, r
(3)	p	q	r	s
(4)	p	q	r	s

21. Match the Column I with Column II and mark the correct option form the codes given below.

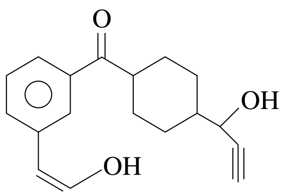
	Column I		Column II
i.		p.	Gives just one aldol only
ii.		q.	Gives yellow precipitate with I_2/NaOH
iii.		r.	Produces isomeric oximes with $HONH_2$
iv.		s.	more than 4 u in molar mass on treatment with NaOD/D_2O
		t.	Gives more than one aldol.

Codes:

	i	ii	iii	iv
(1)	p, q	q	r, t	s, t
(2)	q, r, t	p, q, s	t	r, s, t
(3)	t, r, q	p, q, s	p, r	q
(4)	q, s, t	p, r	r, s, q	s, r, t

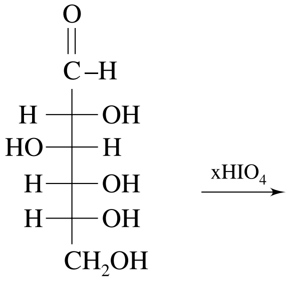
Single Digit Integer Type Question

22. How many reagents (i to viii) are successively reacted with the following it compound



(i) $NaHCO_3$	(ii) 2, 4, DNP
(iii) Na metal	(iv) $AgNO_3$ + OH
(v) Fehling's solution	(vi) Cu_2Cl_2 + HCl
(vii) Br_2/H_2O	(viii) $NaNO_2$ + HCl

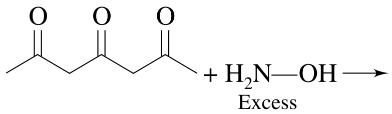
23. How many moles of HIO_4 are consumed by given compound when it reacts with HIO_4?



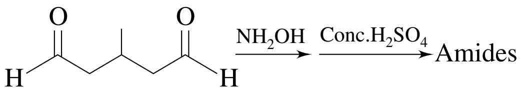
(D-Glucose)

24. How many different alcohol isomers with molecular formula $C_5H_{12}O$ can be oxidised to ketones using $K_2Cr_2O_7$–H_2SO_4?

25. In the following reaction, how many isomers of tri-oximes are formed?

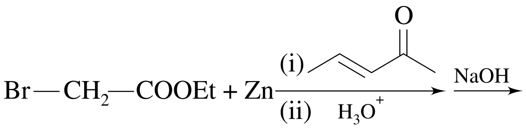


26. In the reaction



How many different amides are expected?

27. Consider the following two step synthesis:

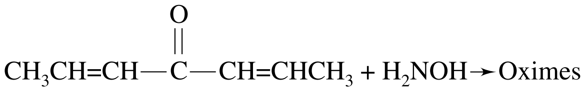


A cyclic diketone X

If x is finally treated with excess of $NaBH_4$ followed by acid work-up, how many different isomers of diols would be formed?

28. In reaction of $C_6H_5COCH_3$ with KOH-I_2 to form iodoform, how many moles of KOH are consumed per mole of ketone?

29. In the reaction given below, how many different oximes would be formed?



$$CH_3CH{=}CH—\overset{\overset{\displaystyle O}{\|}}{C}—CH{=}CHCH_3 + H_2NOH \rightarrow \text{Oximes}$$

30. If all the aldehyde isomers of $C_5H_{10}O$ is independently treated with HCN/NaCN solution, how many of them will of them will give racemic mixture of cyanohydrin?

EXERCISE 4

1. 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

2. 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

3. The increasing order of the rate of HCN addition to compounds A–D is **[AIEEE-2006]**

(a) HCHO (b) CH_3COCH_3

(c) $PhCOCH_3$ (d) $PhCOC_6H_5$

(1) d < b < c <a (2) d < c < b < a

(3) c < d < b < a (4) a < b < c < d

4. Which of the following on heating with aqueous KOH produces acetaldehyde? **[AIEEE-2009]**

(1) CH_3COCl (2) CH_3CH_2Cl

(3) CH_2ClCH_2Cl (4) CH_3CHCl_2

5. Among the following the order of reactivity toward nucleophilic addition is **[JEE-Main Online-2012]**

(1) $HCHO > CH_3CHO > CH_3COCH_3$

(2) $CH_3CHO > HCHO > CH_3COCH_3$

(3) $CH_3CHO > CH_3COCH_3 > CH_3COCH_3$

(4) $CH_3COCH_3 > CH_3CHO > HCHO$

6. The reaction **[JEE-Main Online-2012]**

$$CH_3CHO - \xrightarrow[\text{Zn(Hg/Conc. HCl)}]{[H]} CH_3CH_3 \text{ is:}$$

(1) Cannizzaro reaction

(2) Wolf–Kishner reduction

(3) Rosenmund reduction

(4) Clemmensen reduction

7. Formaldehyde can be distinguished from acetaldehyde by the use of **[JEE-Main Online-2013]**

(1) Schiff's reagent (2) Tollens' reagent

(3) I_2/Alkali (4) Fehling's solution

8. Clemmensen reduction of a ketone is carried out in the presence of:– **[JEE-Main Online-2013]**

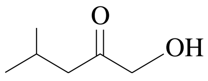
(1) $LiAlH_4$

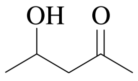
(2) Zn–Hg with HCl

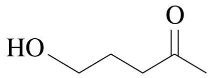
(3) Glycol with KOH

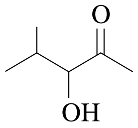
(4) H_2 with Pt as catalyst

9. Which of the following is the product of aldol condensation? **[JEE-Main Online-2013]**

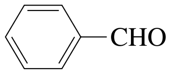
(1) 

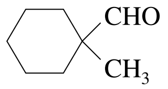
(2) 

(3) 

(4) 

10. Cannizzaro reaction is not given by– **[JEE-Main Online-2013]**

(1) 

(2) 

(3) CH_3CHO

(4) HCHO

11. Which is the major product formed when acetone is heated with iodine and potassium hydroxide? **[JEE-Main Online-2014]**

(1) Iodoacetone

(2) Acetic acid

(3) Iodoform

(4) Acetophenone

12. Tishchenko reaction is a modification of: **[JEE-Main Online-2014]**

(1) Aldol

(2) Claisen condensation

(3) Cannizzaro reaction

(4) Pinacol–pinacolone reaction

13. In the following sequence of reactions **[JEE-Main-2015]**

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

The product C is:

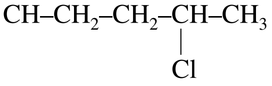
(1) C_6H_5COOH

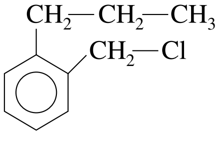
(2) $C_6H_5CH_3$

(3) $C_6H_5CH_2OH$

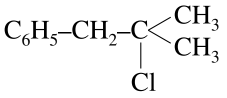
(4) C_6H_5CHO

14. 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 Cannizzaro reaction but not aldol condensation. D gives aldol condensation but not Cannizzaro reaction. A is: **[JEE-Main Online-2015]**

(1) 
$CH\text{–}CH_2\text{–}CH_2\text{–}\underset{\underset{\displaystyle Cl}{|}}{CH}\text{–}CH_3$

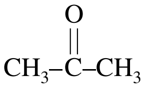
(2) 

(3) $C_6H_5\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Cl$

(4) 
$C_6H_5\text{–}CH_2\text{–}\underset{\underset{\displaystyle Cl}{|}}{C}(CH_3)_2$

15. In the reaction sequence **[JEE-Main Online-2015]**

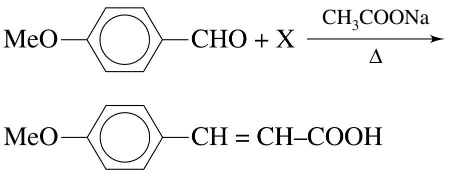
$$2\,CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B, \text{ the product B is}$$

(1) 
$CH_3\text{–}\overset{\overset{\displaystyle O}{||}}{C}\text{–}CH_3$

(2) $CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_3$

(3) $CH_3\text{–}CH\text{=}CH\text{–}CHO$

(4) $CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}OH$

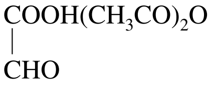
16. 

[IIT-2005]

The X in the given reaction is

(1) CH_3COOH

(2) $BrCH_2\text{–}COOH$

(3) 
$\underset{\underset{\displaystyle CHO}{|}}{COOH}(CH_3CO)_2O$

(4) $(CH_3CO)_2O$

17. How will you convert butan-2-one to propanoic acid? **[IIT-2005]**

(1) Tollens' reagent

(2) Fehling's solution

(3) $NaOH/I_2/H^+$

(4) $NaOH/NaI/H^+$

18. Butan-2-one can be converted to propanoic acid by which of the following?

(2006, Only One Option Correct Type)

(1) $NaOH,\ NaI/H^+$

(2) Fehling's solution

(3) $NaOH,\ I_2/H^+$

(4) Tollens' reagent

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

(2006, Only One Option Correct Type)

(1) Two different oximes are formed

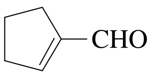
(2) Three different oximes are formed

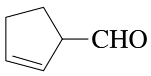
(3) Two oximes are optically active

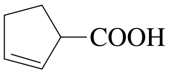
(4) All oximes are optically active

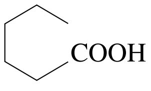
20. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is

(2007, Only One Option Correct Type)

(1) 

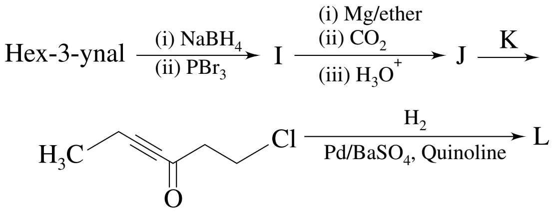
(2) 

(3) 

(4) 

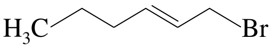
Passage Based Questions: (Q. 21–23)

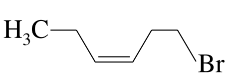
In the following sequence, product I, J and L are formed. K represents a reagent.

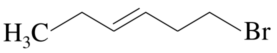


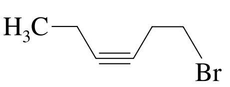
(2008 Comprehension Type)

21. The structure of the product I is

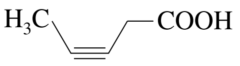
(1) 

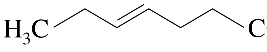
(2) 

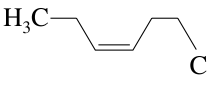
(3) 

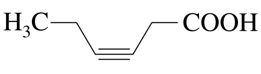
(4) 

22. The structure of compounds J and K, respectively, are

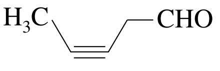
(1)  and $SOCl_2$

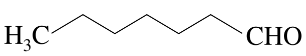
(2)  and $SOCl_2$

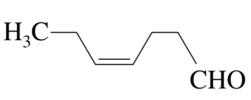
(3)  and SO_2Cl_2

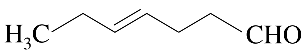
(4)  and CH_3SO_2Cl

23. The structure of product L is

(1) 

(2) 

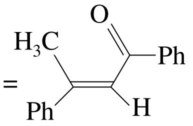
(3) 

(4) 

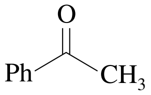
Passage Based Questions: (Q. 24 and 25)

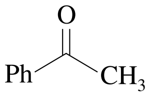
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on react ion with KOH gives only M.

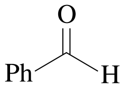
(2008 Comprehension Type)

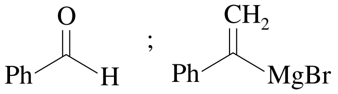
M = 

24. Compound H is formed by the react ion of

(1)  ; PhMgBr

(2)  ; $PhCH_2MgBr$

(3)  ; $PhCH_2MgBr$

(4) 

25. The structures of compounds J, K and L, respectively, are

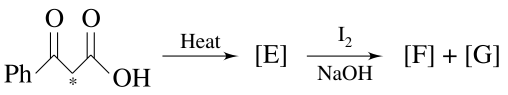
(1) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

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

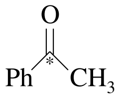
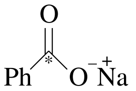
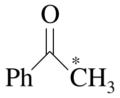
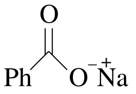
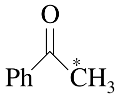
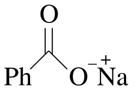
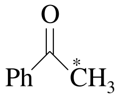
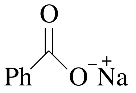
(3) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

(4) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

26. In the following reaction sequence, the correct structures of E, F and G are **[IIT-2008]**



(* implies ^{13}C labeled carbon)

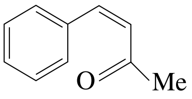
	E	F	G
(1)			CHI_3
(2)			CHI_3
(3)			CHI_3
(4)			$\overset{*}{C}H_3I$

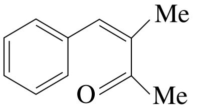
Passage Based Questions: (Q. 27–29)

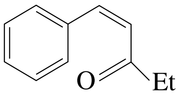
A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly S. **(2009 Comprehension Type)**

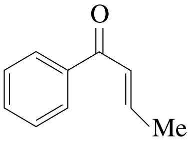
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4/Heat}]{1.\ MeMgBr} Q \xrightarrow{O_3/Zn\text{-}H_2O} R \xrightarrow[Heat]{\overline{O}H} S$$

27. The structure of the carbonyl compound P, is

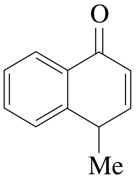
(1) 

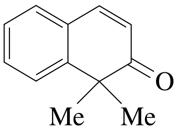
(2) 

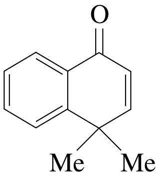
(3) 

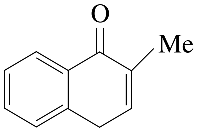
(4) 

28. The structure of the product S, is

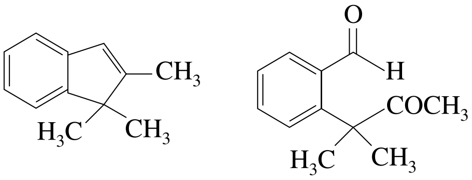
(1) 

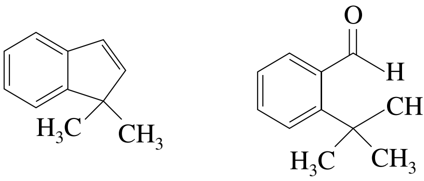
(2) 

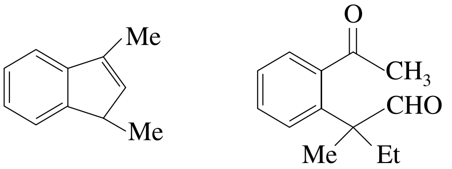
(3) 

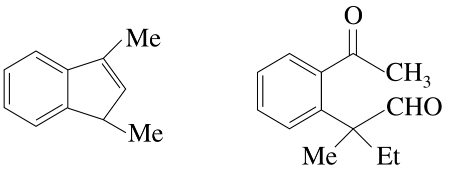
(4) 

29. The structures of the products Q and R, respectively, are

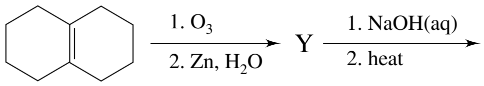
(1) 

(2) 

(3) 

(4) 

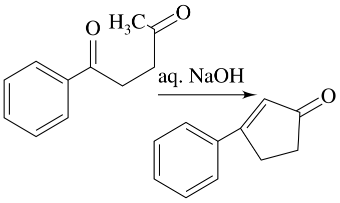
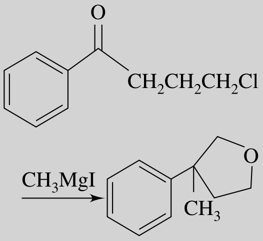
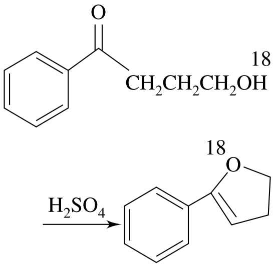
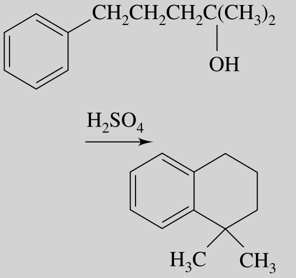
30. In the scheme given below, the total number of intra-molecular aldol condensation products form (Y) is **[IIT-2010]**



(1) 1 (2) 2

(3) 3 (4) 4

31. Match the reactions in column I with appropriate type of steps/reactive intermediate involved in these reactions as given in column II and give a correct answer **[IIT-2011]**

	Column-I		**Column-II**
(A)		(p)	Nucleophilic substitution
(B)		(q)	Electrophilic Substitution
(C)		(r)	Dehydration
(D)		(s)	Nucleophilic addition
		(t)	Carbanion

(1) A → r, t, s; B → p, s, t; C → r, s; D → r, q

(2) A → r, t, s; B → r, s; C → p, s; D → r, s

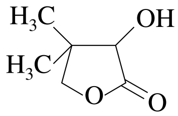
(3) A → p, s, t; B → r, s, t; C → r, s; D → q, r

(4) A → q, r, ; B → p, s, t; C → q, t; D → r, s

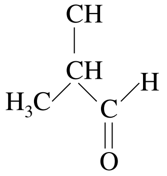
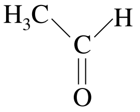
Passage Based Questions: (Q. 32–34)

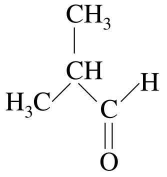
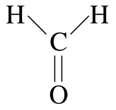
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below.

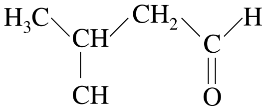
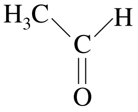
(2012 Comprehension Type)

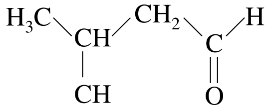
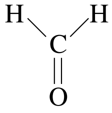


32. The compounds P and Q, respectively, are

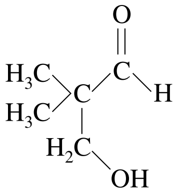
(1)  and 

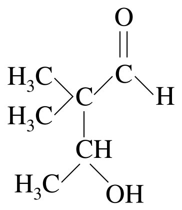
(2)  and 

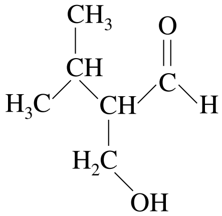
(3)  and 

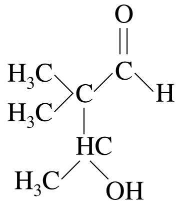
(4)  and 

33. The compound R is

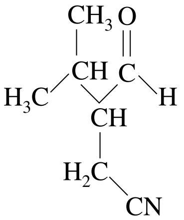
(1) 

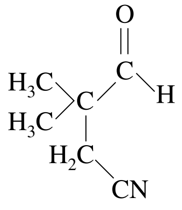
(2) 

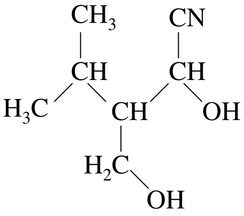
(3) 

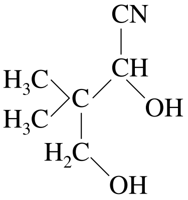
(4) 

34. The compound S is

(1) 

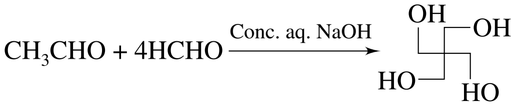
(2) 

(3) 

(4) 

35. The number of aldol reaction (s) that occurs in the given transformation is

(2012 Only One Option Correct Type)



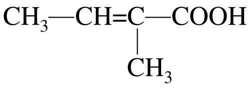
(1) 1 (2) 2

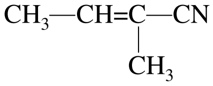
(3) 3 (4) 4

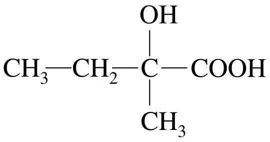
36. The major product H in the given reaction sequence is

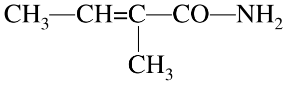
(2012 Only One Option Correct Type)

$CH_3{-}CH_2{-}CO{-}CH_3 \xrightarrow{^{-}CN} G \xrightarrow{95\%\ H_2SO_4} H$

(1) 
$CH_3{-}CH{=}\underset{CH_3}{C}{-}COOH$

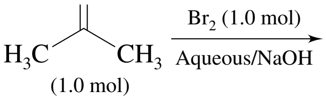
(2) 
$CH_3{-}CH{=}\underset{CH_3}{C}{-}CN$

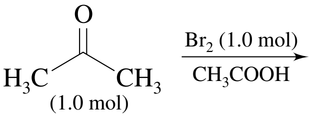
(3) 
$CH_3{-}CH_2{-}\overset{OH}{\underset{CH_3}{C}}{-}COOH$

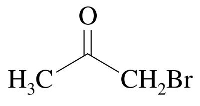
(4) 
$CH_3{-}CH{=}\underset{CH_3}{C}{-}CO{-}NH_2$

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

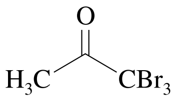
(JEE Adv.-2013)

Reaction-I: 

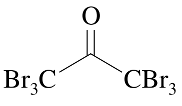
Reaction-II: 



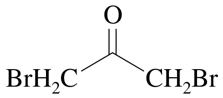
(P)



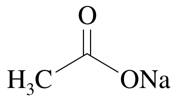
(Q)



(R)



(S)



(T)

$CHBr_3$

(U)

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

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

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

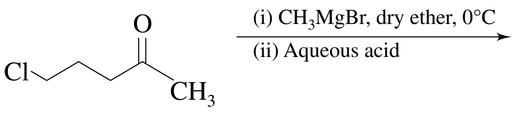
(4) Reaction I: R, acetone and Reaction II: S, acetone

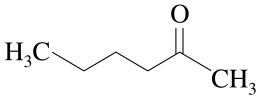
38. Consider all possible isomeric ketones including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$. The total number of ketones that give a racemic product(s) is/are

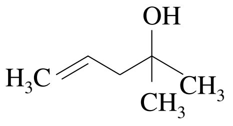
(2014 Adv., Integer Type)

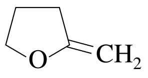
39. The major product in the following reaction is

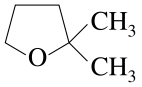
(2014 Adv., Only One Option Correct Type)



(1) 

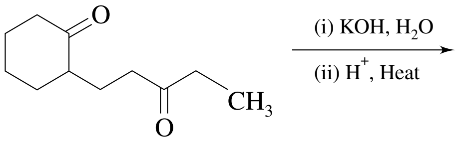
(2) 

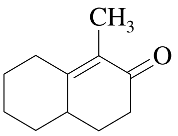
(3) 

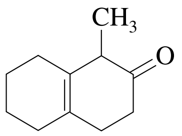
(4) 

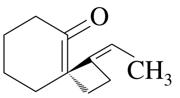
40. The major product of the following reaction is

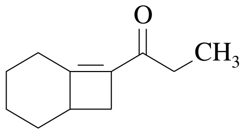
(2014 Adv., Only One Option Correct Type)



(1) 

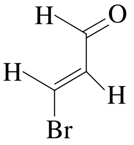
(2) 

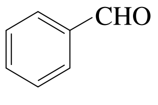
(3) 

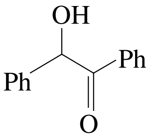
(4) 

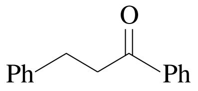
41. Positive Tollens' test is observed for

[IIT Adv.-2016]

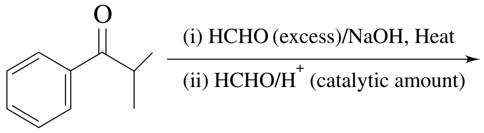
(1) 

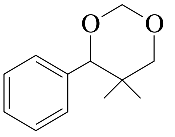
(2) 

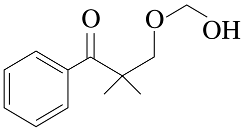
(3) 

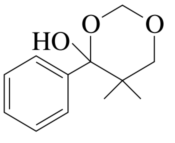
(4) 

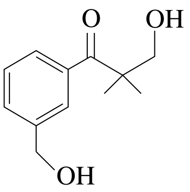
42. The major product of the following reaction sequence is **[IIT Adv.-2016]**



(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1.	(1)	2.	(4)	3.	(4)	4.	(1)	5.	(2)
6.	(3)	7.	(1)	8.	(2)	9.	(4)	10.	(2)
11.	(1)	12.	(1)	13.	(4)	14.	(3)	15.	(2)
16.	(4)	17.	(3)	18.	(4)	19.	(1)	20.	(2)
21.	(3)	22.	(2)	23.	(1)	24.	(2)	25.	(2)
26.	(3)	27.	(3)	28.	(2)	29.	(1)	30.	(2)
31.	(1)	32.	(2)	33.	(3)	34.	(3)	35.	(3)

EXERCISE # 2

1.	(1)	2.	(1)	3.	(2)	4.	(3)	5.	(1)
6.	(2)	7.	(4)	8.	(2)	9.	(1)	10.	(2)
11.	(4)	12.	(3)	13.	(3)	14.	(4)	15.	(4)
16.	(3)	17.	(4)	18.	(1)	19.	(1)	20.	(2)
21.	(3)	22.	(4)	23.	(2)	24.	(2)	25.	(4)

EXERCISE # 3

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

EXERCISE # 4

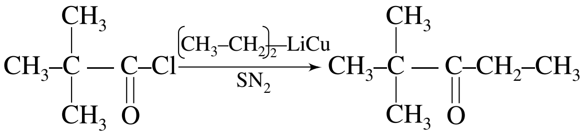
1.	(2)	2.	(4)	3.	(2)	4.	(4)	5.	(1)
6.	(4)	7.	(3)	8.	(2)	9.	(2)	10.	(3)
11.	(3)	12.	(3)	13.	(4)	14.	(3)	15.	(3)
16.	(4)	17.	(3)	18.	(3)	19.	(2)	20.	(2)
21.	(4)	22.	(1)	23.	(3)	24.	(2)	25.	(4)
26.	(4)	27.	(2)	28.	(2)	29.	(1)	30.	(1)
31.	(1)	32.	(2)	33.	(1)	34.	(4)	35.	(3)
36.	(1)	37.	(3)	38.	(5)	39.	(4)	40.	(1)
41.	(1,2,3)	42.	(1)						

HINT AND SOLUTION

EXERCISE # 1

1. [1]

$$CH_3-CH_2-I \xrightarrow[\text{(ii) CuI}]{\text{(i) Li/Et}_2\text{O}} (CH_3-CH_2)_2LiCu$$



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\displaystyle \overset{\|}{O}}{C}-Cl \xrightarrow[SN_2]{(CH_3-CH_2)_2LiCu} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\displaystyle \overset{\|}{O}}{C}-CH_2-CH_3$$

2. [4]

Rate of nucleophilic addition or HCN addition $\propto$ EWG. $\propto \frac{1}{\text{ERG}}$

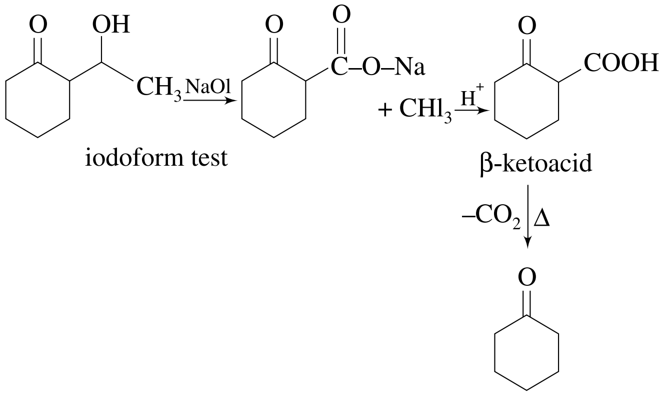
ERG ($-NMe_2$) > ERG($-OMe$)

3. [4]

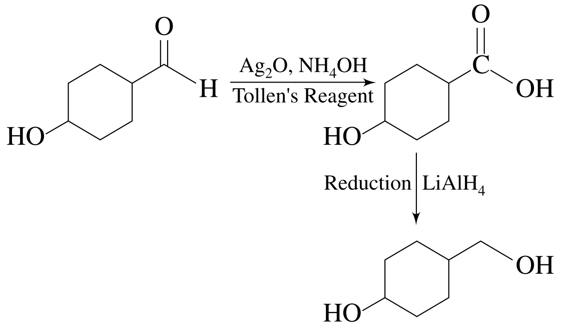
⇒ Final product has chiral C

⇒ So that equal amount of d and l isomer is present

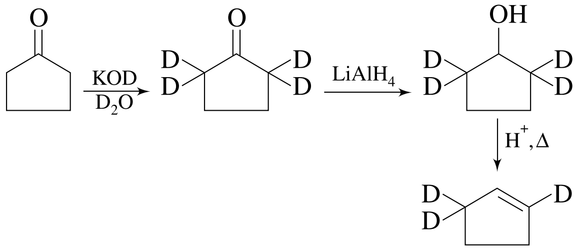
4. [1]



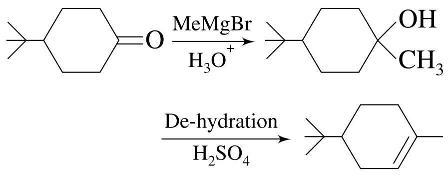
5. [2]



6. [3]

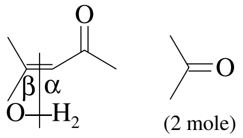


7. [1]

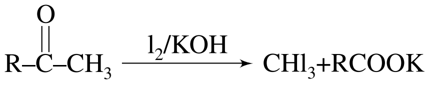


8. [2]

Given product is α, β unsaturated ketone so it is formed by aldol condensation reaction.



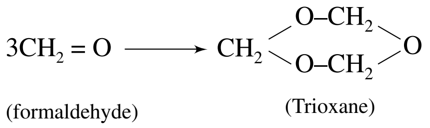
9. [4]



$$R\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3 \xrightarrow{I_2/KOH} CHI_3 + RCOOK$$

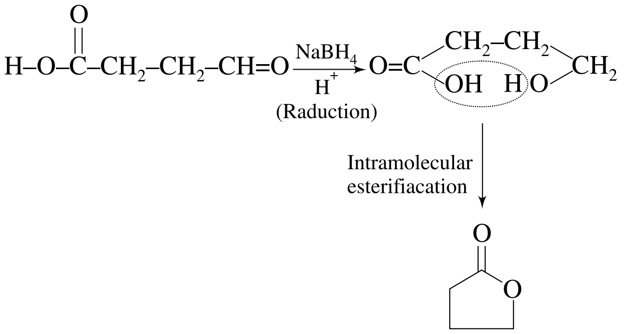
R=H, alkyl, etc.

10. [2]

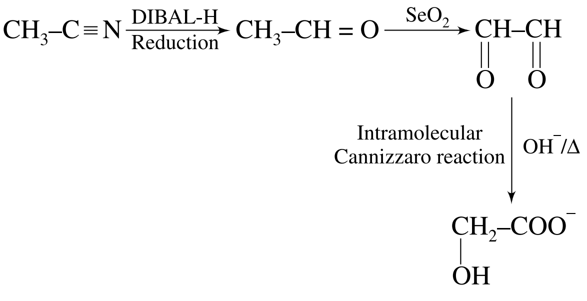


11. [1]

By using $NaBH_4$ reduction of only aldehyde group takes place.



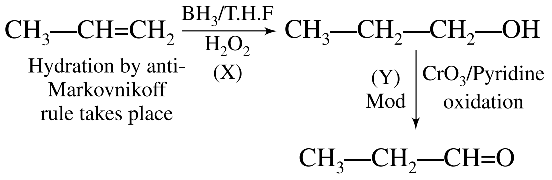
12. [1]



13. [4]

1, 4 diol not cleaved by HIO_4

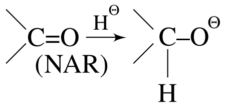
14. [3]



15. [2]

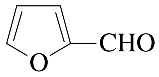
$LiAlH_4$ (LAH) $\rightarrow \overset{\oplus}{Li} + Al\overset{\oplus}{H_4} + \rightarrow AlH_3 + \overset{\oplus}{H}$

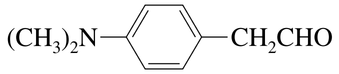
$NaBH_4 \rightarrow Na^+ + B\overset{\ominus}{H_4} \rightarrow BH_3 + \overset{\ominus}{H}$



16. [4]

Compound having no α-H undergoes Cannizzaro reaction.

- C_6H_5–CHO and 

  no α-H undergoes Cannizzaro reaction.
- $(CH_3)_2CH$–CH = O gives both Cannizzaro reaction and aldol condensation reaction.
-  It have α-H so that gives only aldol condensation reaction.

17. [3]

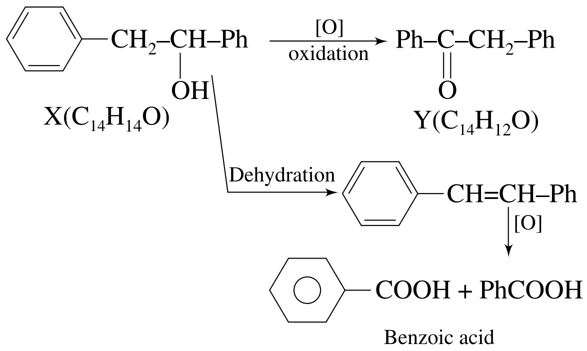
$$Ph\text{–}CH{=}O \xrightarrow{\text{Fehling solution}} -\text{ve test}$$

$$H\text{–}CH{=}O \xrightarrow{\text{Fehling solution}} +\text{ve test}$$

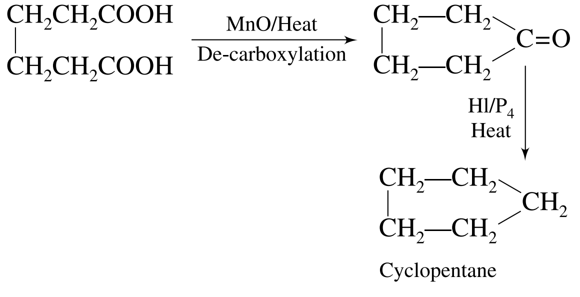
18. [4]

$$\underset{sp}{PhCN} \xrightarrow[\text{2. }H_2O\text{, heat}]{\text{1. }SnCl_2/HCl} Ph\text{–}\underset{sp^2}{CH} = O$$

19. [1]



20. [2]



21. [3]

(methyl ketone)
Positive Iodoform
Negative Tollens' reagent

(aldehyde)
Negative Iodoform
Positive Tollens' reagent

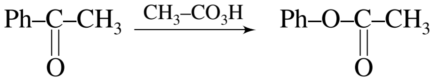
22. [2]

By Shiff reagent distinction between aldehyde (–CHO) & ketone $\left(>CO\right)$ group takes place.

23. [1]

With MnO_2, oxidation of only allylic alcohol takes place.

24. [2]

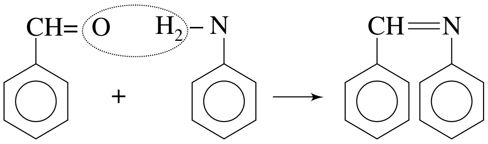


$$Ph{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{CH_3{-}CO_3H} Ph{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

Baeyer–Villegar oxidation, migration aptitude order for oxygen atom.

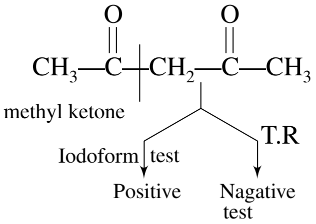
3° > Ph > 2° > 1°

25. [2]



(Shiff base)

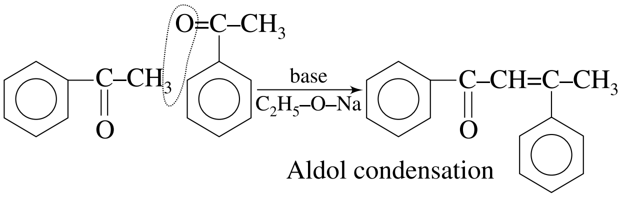
26. [3]



→ Negative Tollens' test indicating that compound have ketone group.

→ Positive iodoform test indicating that A must be methyl ketone or having acidic CH.

27. [3]

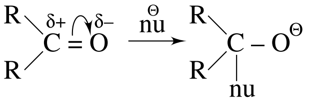


Aldol condensation

28. [2]

Geminal ethers are stable in basic medium. Hence give conversion carried in basic medium so that $NH_2{-}NH_2$ on reagent is most suitable (wolf krishner reduction).

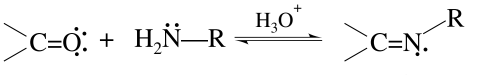
29. [1]



nucleophilic attack on the +vely charged carbon of carbonly group.

30. [2]

A general equation for the formation of an imine from a primary amine and an aldehyde or ketone is shown here. Imine formation is acid catalysed, and the product can from as a mixture of (*E*) and (*Z*) isomers.



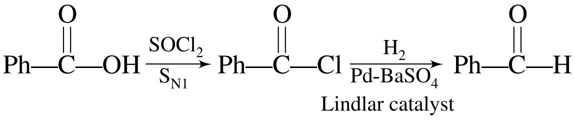
Aldehyde or ketone

1° Amine

Imine [(E) and (Z) isomer]T

Imine formation generally takes place fastest between **pH 4 and 5** and is slow at very low or very high pH. We can understand why an acid catalyst is necessary if we consider the mechanism that has been proposed for imine formation. The important step is the step in which the protonated amino alcohol loses a molecule of water to become an iminium ion. By protonating the alcohol group, the acid converts a poor leaving group (an —OH group into a good one (an $—OH_2^+$ group.).

31. [1]

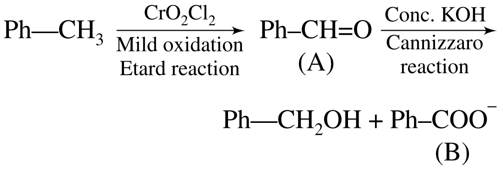


$$Ph{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow[S_{N1}]{SOCl_2} Ph{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} Ph{-}\overset{\overset{O}{\|}}{C}{-}H$$

Lindlar catalyst

Rosenmund's reduction

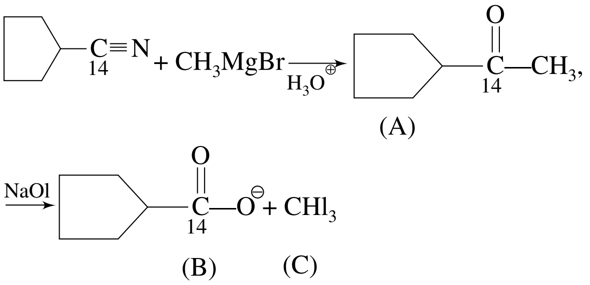
32. [2]



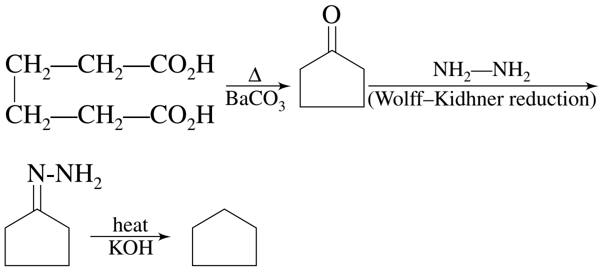
$$Ph{-}CH_3 \xrightarrow[\text{Mild oxidation}]{CrO_2Cl_2} \underset{(A)}{Ph{-}CH{=}O} \xrightarrow[\text{Cannizzaro reaction}]{\text{Conc. KOH}} Ph{-}CH_2OH + \underset{(B)}{Ph{-}COO^-}$$

Etard reaction

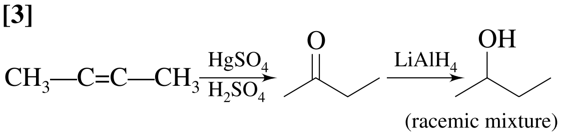
33. [3]



34. [3]

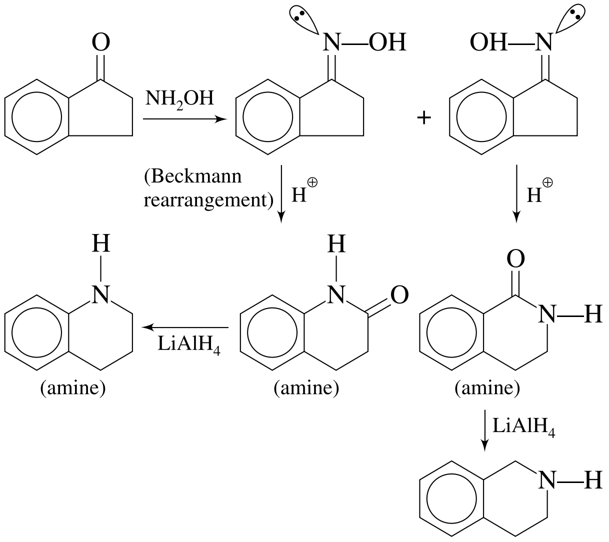


35. [3]

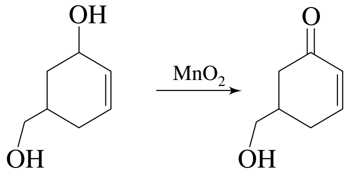


EXERCISE # 2

1. [1]

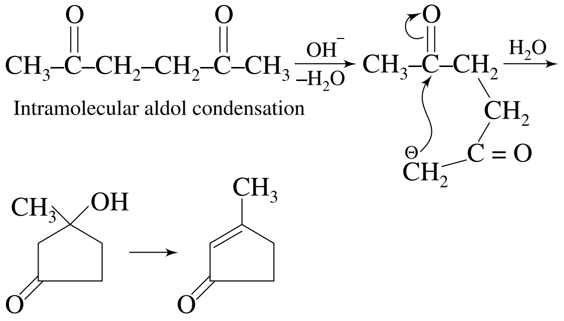


2. [1]

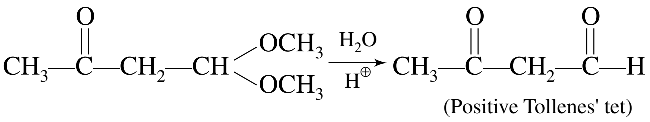


MnO_2 oxidises only allylic and Benzyllic alcohol

3. [2]



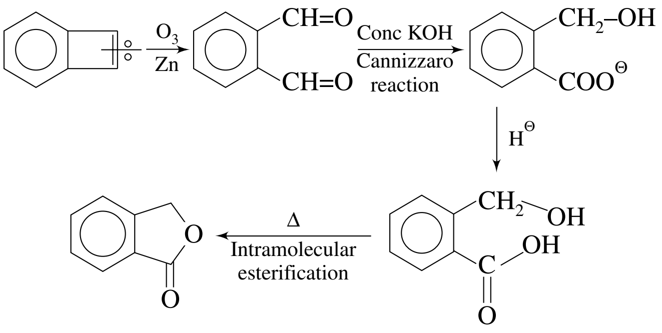
4. [3]



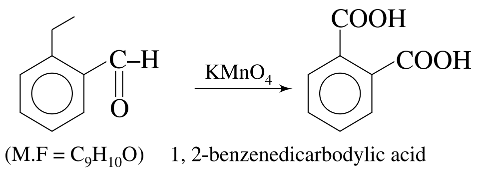
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH\begin{matrix}OCH_3\\OCH_3\end{matrix}\xrightarrow[H^{\oplus}]{H_2O}CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

(Positive Tollenes' tet)

5. [1]

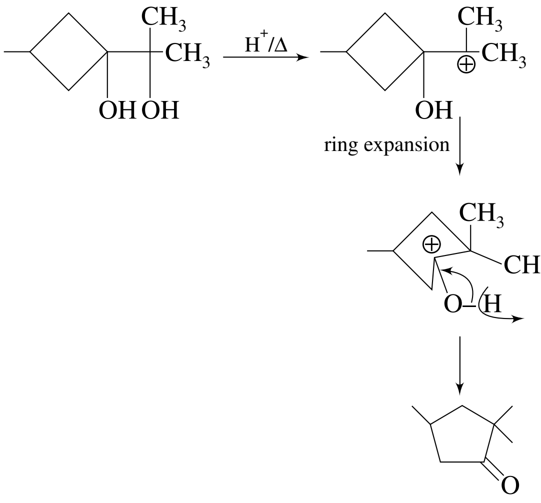


6. [2]



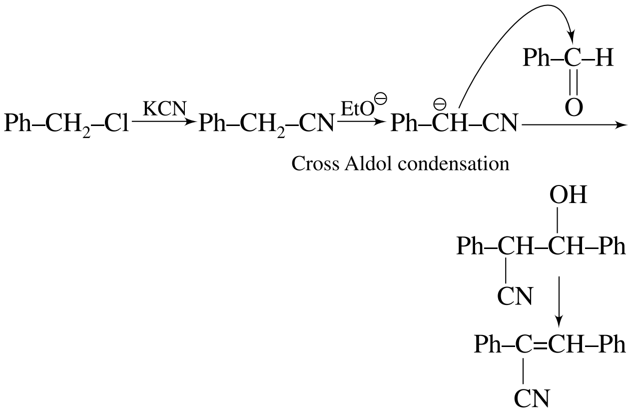
given strueture have CH = O group hence will give 2, 4 DNP test, Tollen's reagent and Cannizzaro reaction

7. [4]

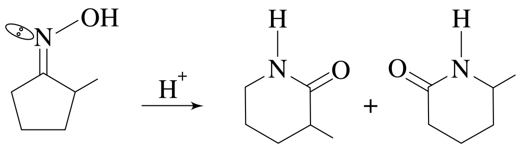


This is pinacole–pinacolone rearrangement

8. [2]

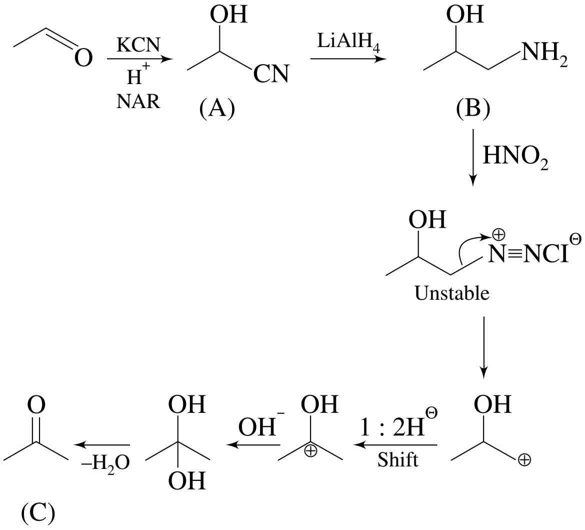


9. [1]



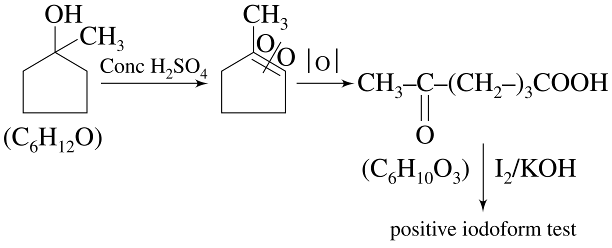
Beckmann re-arrangement (refer mechanism)

10. [2]



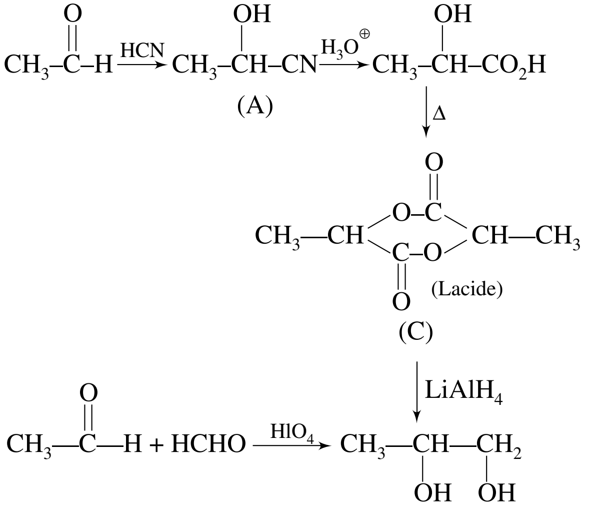
11. [4]

A→Must be 3° alcohol because dichromate test do not given by 3° alcohol



12. [3]

13. [3]



14. [4]

(i) Reactivity in NAR $\propto \xrightarrow[\text{Steric hindrance}]{1}$

Thus aldehyde is more reactive than ketone.

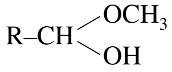
(ii) Reactivity in NAR ∝ +ve charge at the carbon of $>$C=O group $\propto$ EWG $\propto \xrightarrow[\text{ERG}]{1}$

We know that ERG Power (—O—CH$_3$) > (—CH$_3$)
ERG

Hence order of reactivity in NAR
(i) > (iv) > (ii) > (iii)

15. [4]

Aldehyde and hemiacetal gives positive test with Tollens' reagent.


$\text{R–CH}\begin{smallmatrix}\text{OCH}_3\\ \text{OH}\end{smallmatrix}$ type substance known as hemiacetal, they will convert into corresponding aldehyde in basic medium, Hence also give positive test with tollen's reagent.

16. [3]

A (C$_6$H$_8$O$_2$) $\xrightarrow{\text{Na/metal}}$ H$_2$ gas

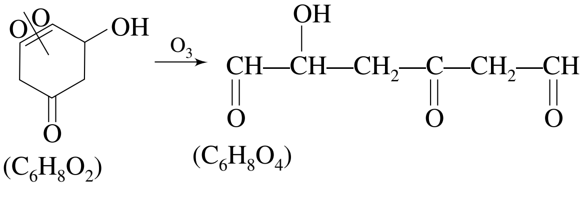
It indicates presence of –OH group.

A (C$_6$H$_8$O$_2$) $\xrightarrow{\text{2, 4 DNP}}$ yellow orange solution

It indicates presence Carbonyl group $\left(>\text{C=O}\right)$

A (C$_6$H$_8$O$_2$) $\xrightarrow{\text{O}_3}$ B (C$_6$H$_8$O$_4$)

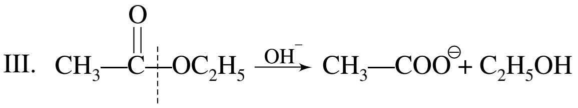
No loss of carbon atom indicating that, A must have double bond around the ring.



17. [4]

$$\text{I. } CH_3\text{—}CH{=}O \xrightarrow[H^+]{[Ag(NH_3)_2]^+,\ OH^-} \underset{\text{(Acid)}}{CH_3\text{—}COOH}$$

$$\text{II. } CH_3\text{—}CCl_3 \xrightarrow{OH^-} CH_3\text{—}COO^{\ominus}$$

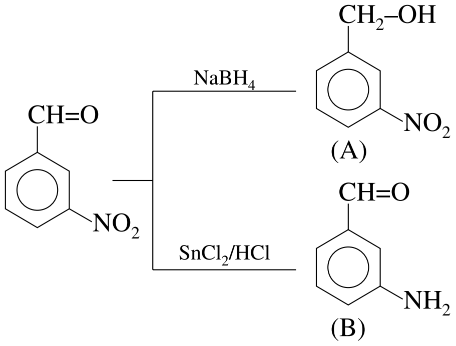


$$\text{III. } CH_3\text{—}\overset{O}{\overset{||}{C}}\text{—}OC_2H_5 \xrightarrow{OH^-} CH_3\text{—}COO^{\ominus} + C_2H_5OH$$

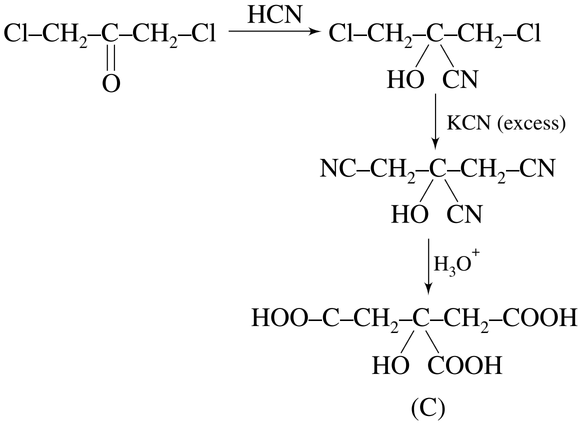
18. [1]

Refer angle strain.

19. [1]



20. [2]



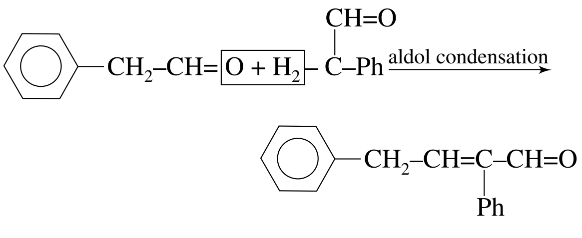
21. [3]

The given conversion is achieved by

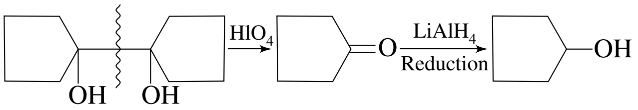
$NaBH_4/H_2O$ ⟶ Reduction

$HCH = O/OH^-$ ⟶ Intermolecular Cannizzaro reaction

22. [4]



23. [2]



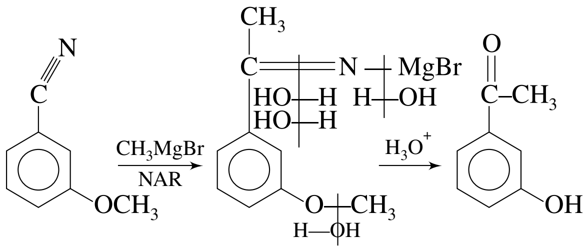
Cleavage of vicinal diol takes place

24. [2]

In option (2), aldehyde is not formed. When a terminal alkyne is oxidised with $KMnO_4$ formation of carboxylic acid is always formed.

All options are preparation of aldehydes.

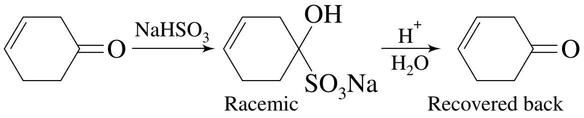
25. [4]



EXERCISE # 3

1. [1,2,3,4]

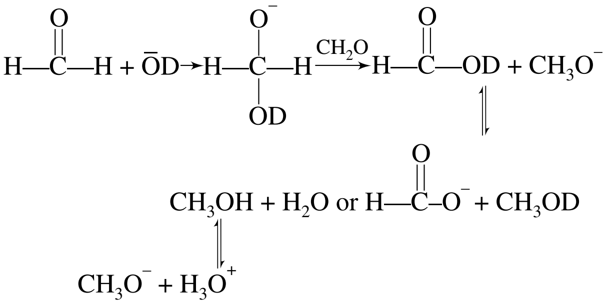
Aldehydes and ketones form bisulphite salt with $NaHSO_3$ which is insoluble in concentrated $NaHSO_3$ solution due to common ion effect. Hence, if $NaHSO_3$ is in limited quantity, precipitation may not take place.



2. [2,3,4]

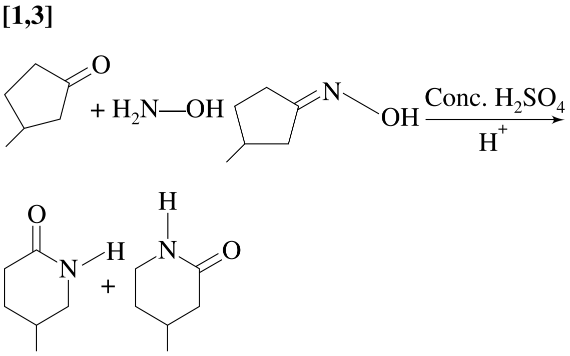
Aldehydes and ketones containing α-H form enamines when treated with secondary amine in slightly acidic medium.

3. [1,2,3]



However, C—D bond is not formed in this reaction.

4. [1,3]



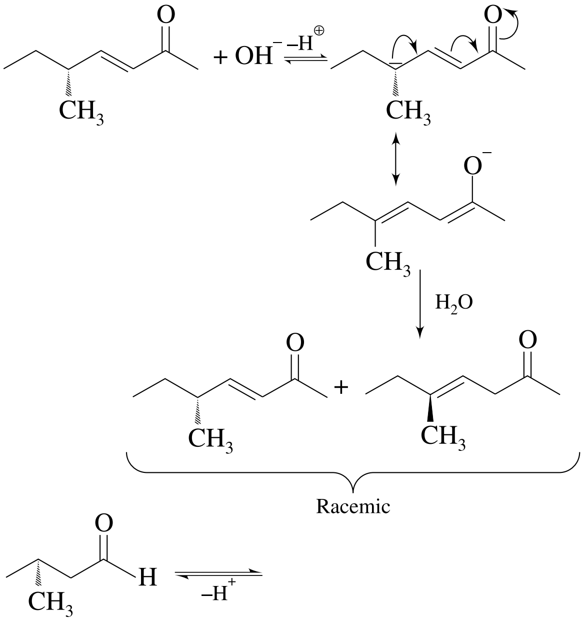
5. [1, 2, 4]

Wittig reaction

$$\mathrm{CH_3{-}CH_2Cl \xrightarrow{Ph_3P} \xrightarrow{BuLi} \underset{X}{CH_3{-}CH{=}PPh_3} \xrightarrow{CH_3CHO} \underset{Y}{CH_3{-}CH{=}CH{-}CH_3}}$$

Both diastereomers (*cis* and *trans*) of Y are formed.

6. [2,4]



7. [1,3,4]

8. [2,3,4]

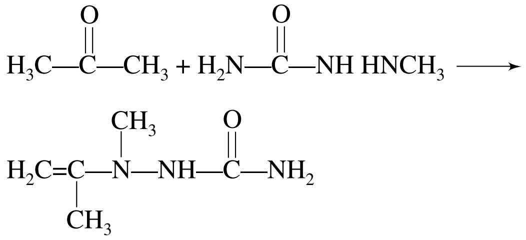
9. [2]

10. [3]

Statement I is correct but Statement II is false, It would be true only if both carbonyls are capable of forming enolates, i.e., if both possess α-H

11. [4]

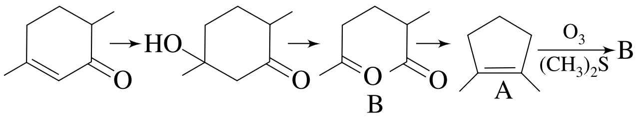
Nucleophilic attack occurs from aminic nitrogen not from amidic nitrogen.



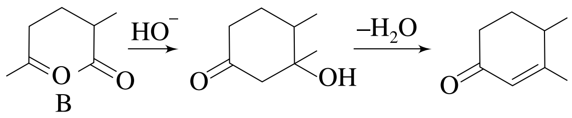
$$\mathrm{H_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + H_2N{-}\overset{\overset{O}{\|}}{C}{-}NH\,HNCH_3 \longrightarrow H_2C{=}\underset{\underset{CH_3}{|}}{C}{-}\overset{\overset{CH_3}{|}}{N}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH_2}$$

12. [3]

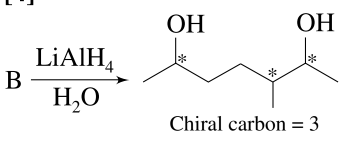
Reversing the final product gives



13. [4]



14. [4]



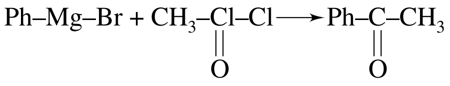
So O.I = 2^3 = 8

15. [1]

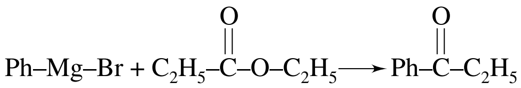
16. [2]

$\mathrm{Ph{-}Mg - Br + Cl - NH_2 \longrightarrow Ph - NH_2}$

$\mathrm{Ph{-}Mg{-}Br + Cl - C{\equiv}N \longrightarrow Ph{-}CN}$



$$\mathrm{Ph{-}Mg{-}Br + CH_3{-}\underset{\underset{O}{\|}}{C}{-}Cl \longrightarrow Ph{-}\underset{\underset{O}{\|}}{C}{-}CH_3}$$



$$\mathrm{Ph{-}Mg{-}Br + C_2H_5{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_5 \longrightarrow Ph{-}\overset{\overset{O}{\|}}{C}{-}C_2H_5}$$

17. [1]

18. [1]

(i) It has carbonyl carbon that turns chiral on reduction with hydrides. Hence, with $LiAlH_4$ or aluminium isopropoxide, gives racemic mixture. Also, it has no other functional groups, either Clemmensen reduction or Wolf–Kishner reduction can be used.

(ii) It has an olefinic double bond. Clemmensen reduction would not be suitable for selective reduction of carbonyl group.

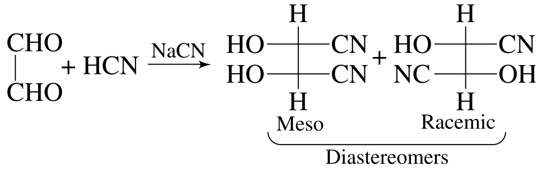
(iii) $LiAlH_4$ also reduces primary halide but aluminium isopropoxide does not. Wolf–Kishner reduction would not be suitable because HO^- reacts with halide group (S_N2 or E2).

(iv) Same reasons as in (i).

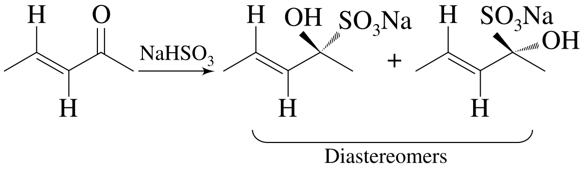
Hence, (i) → (p, q, r, s); (ii) → (p, q, s); (iii) → (q, r); (iv) → (p, q, r, s)

19. [1]

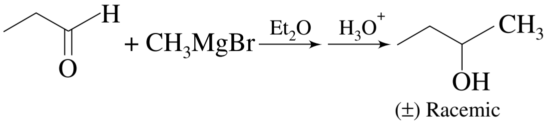
(i)



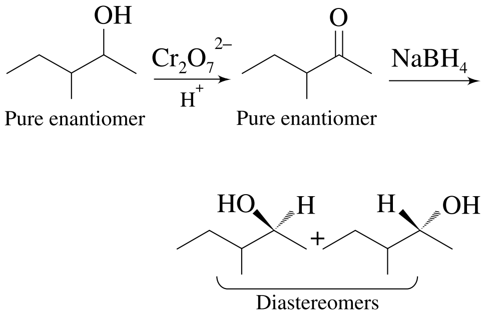
(ii)



(iii)



(iv)



Hence, (i) → (p, q, r, s); (ii) → (q, s); (iii) → (p); (iv) → (q, s)

20. [2]

(i) Initially, aldol reaction followed by Cannizzaro reaction gives $C(CH_2OH)_4$ + HCOOH.

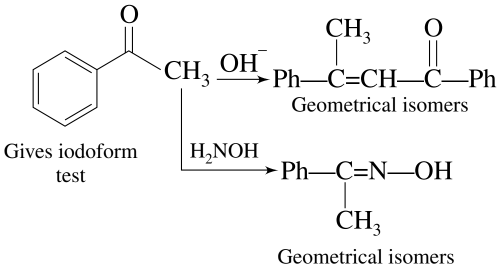
(ii) F—CHO undergoes Cannizzaro reaction due to absence of α-H.

(iii) It has difficulty ion aldol condensation, hence undergo Cannizzaro reaction predominantly.

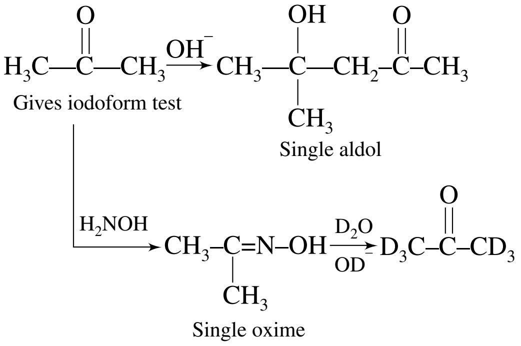
(iv) All aldol, Cannizzaro and Claisen reaction occur.

21. [2]

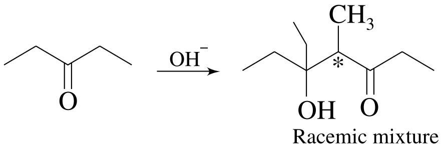
(i)



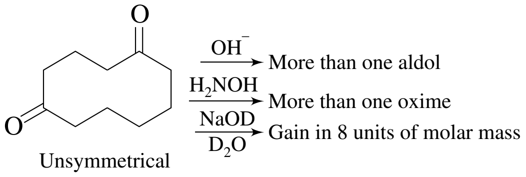
(ii)



(iii)



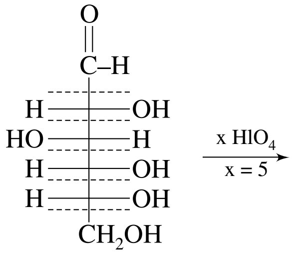
(iv)



Hence (i) → (q, r, t); (ii) → (p, q, s); (ii) → (t); (iv) → (r, s, t)

22. [6]

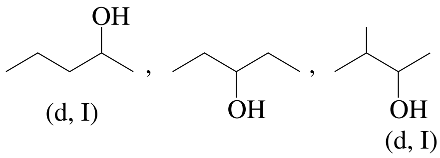
23. [5]



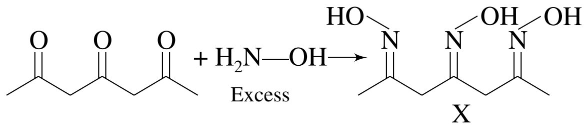
Each C–C bond cleavage requires 1 mole HIO_4

24. [5]

All secondary alcohol isomers can be oxidised to ketones.

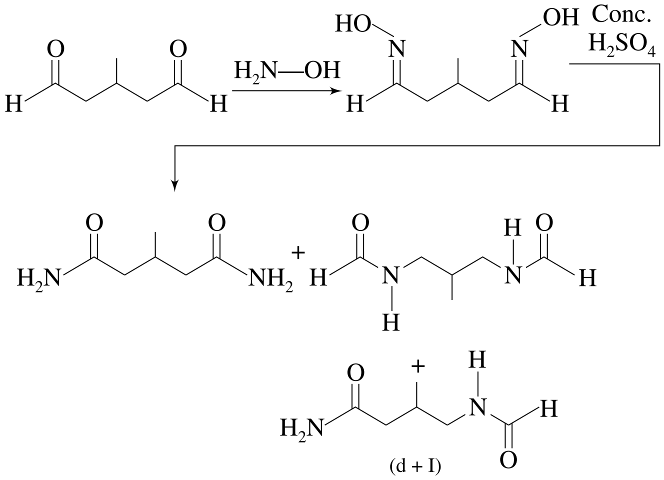


25. [6]

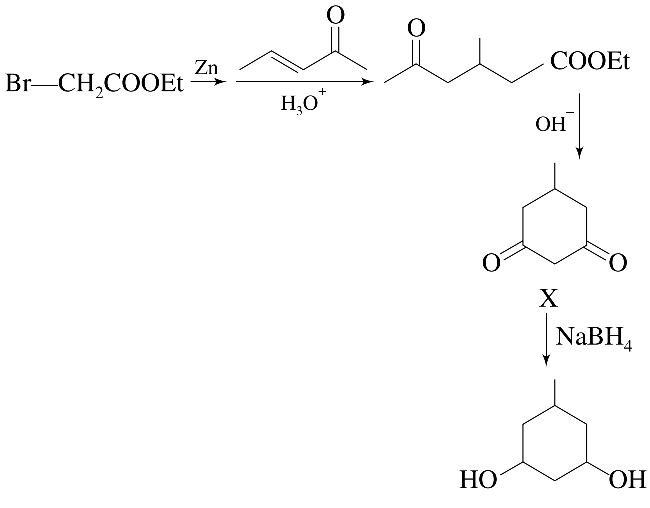


Six isomers (stereoisomers) are possible for X.

26. [4]

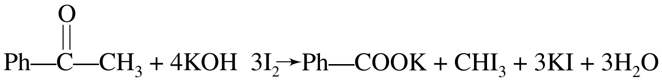


27. [4]



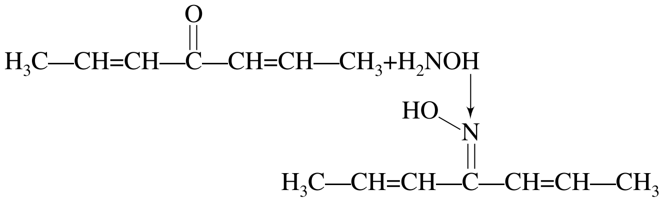
Has two chiral carbons

28. [4]



$$Ph-\overset{\overset{O}{\|}}{C}-CH_3 + 4KOH\ 3I_2 \rightarrow Ph-COOK + CHI_3 + 3KI + 3H_2O$$

29. [6]

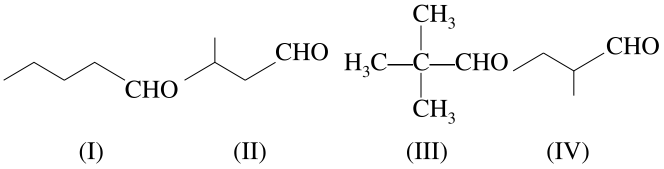


$$H_3C-CH{=}CH-\overset{\overset{O}{\|}}{C}-CH{=}CH-CH_3 + H_2NOH \rightarrow H_3C-CH{=}CH-\overset{\overset{HO\diagdown N}{\|}}{C}-CH{=}CH-CH_3$$

(I)

Four stereoisomers exist for 1, *cis-cis*, *trans-trans* and *cis-trans* with OH *syn* to *cis* and OH *anti* to *cis*.

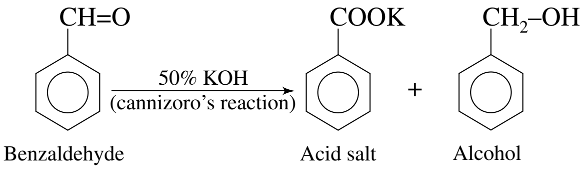
30. [3]



IV is enantiomeric, its pure enantiomer, with HCN/NaCN, would produce pair of diastereomers.

EXERCISE # 4

1. [2]



2. [4]

Only suitable reagent is chromic anhydride in glacial acetic acid.

Option (1) and (2) will also affect (C=C) bond.

Option (3) is more suitable reagent for preparation of aldehyde.

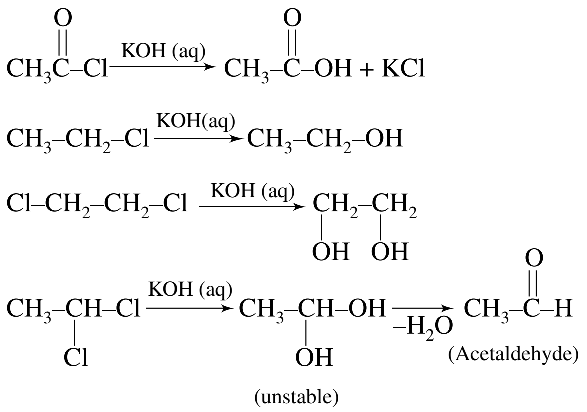
3. [2]

Reactivity towards nucleophilic substitution ∝ positive charge at the carbon of carbonyl group

$$\propto \frac{1}{\text{Steric hidrance}}$$

$PhCOC_6H_5 < PhCOCH_3 < CH_3COCH_3 < HCHO$

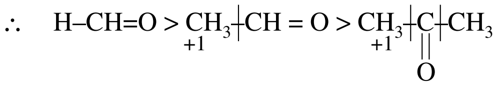
4. [4]



5. [1]

Reactivity towards nucleophilic substitution ∝ positive charge at the carbon of carbonyl group

$$\propto \frac{1}{\text{Steric hidrance}}$$



$$\therefore\quad H–CH=O > \underset{+1}{CH_3}\!-\!CH = O > \underset{+1}{CH_3}\!-\!\underset{\underset{O}{\|}}{C}\!-\!CH_3$$

6. [4]

It is Clemmensen reduction

7. [3]

$$H–CH=O \xrightarrow{I_2/KOH} \text{–ve test}$$

$$CH_3–CH=O \xrightarrow{I_2/KOH} \text{+ve test } (CHI_3)$$

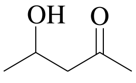
Hence I_2/alkali is suitable reagent.

8. [2]

Zn–Hg/HCl

9. [2]

Compound having α-H gives aldol condensation and β-hydroxy carbonyl Compound is formed.

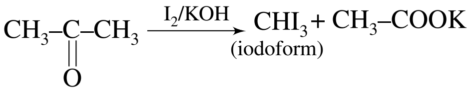
In option (2) 

β-hydroxy ketone

10. [3]

CH_3–CH=O has α-H so it does not give Cannizzaro reaction.

11. [3]

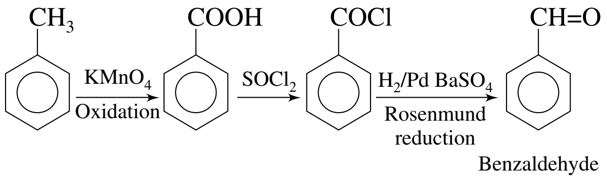


$$CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow{I_2/KOH} \underset{\text{(iodoform)}}{CHI_3} + CH_3–COOK$$

12. [3]

Tishchenko reaction is a modification of Cannizzaro reaction.

13. [4]



14. [3]

$$C_6H_5–CH_2–CH_2–CH_2–CH_2–Cl \xrightarrow{\text{Alc. KOH}}$$

(A)

$(C_{10}H_{13}Cl)$

$$C_6H_5–CH_2–CH_2–CH=CH_2$$

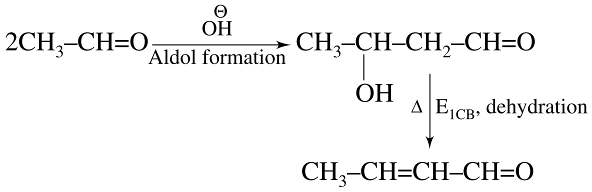
(B)

ozonolysis $\Big\downarrow$ O_3Zn/H_2O

$$\underset{(C)}{H–CH = O} + \underset{(D)}{C_6H_5–CH_2–CH_2–CH=O}$$

(C)	(D)
no α-H It gives Cannizaro but not aldol condensation	α-H present It gives aldol condensation not Cannizaro

15. [3]



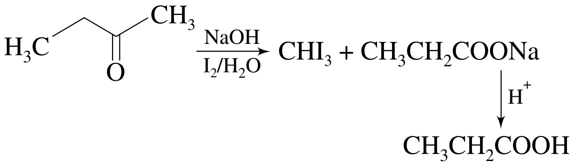
$$2CH_3–CH=O \xrightarrow[\text{Aldol formation}]{\overset{\ominus}{OH}} CH_3–\underset{\underset{OH}{|}}{CH}–CH_2–CH=O$$

$$\xrightarrow{\Delta,\ E_{1CB},\ \text{dehydration}} CH_3–CH=CH–CH=O$$

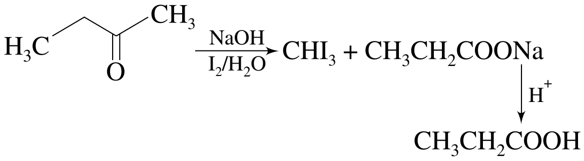
16. [4]

It is Perkin condensation reaction.

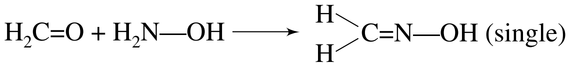
17. [3]



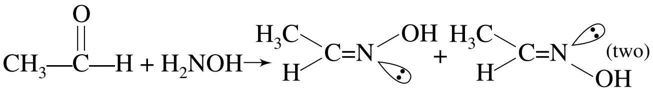
18. [3]



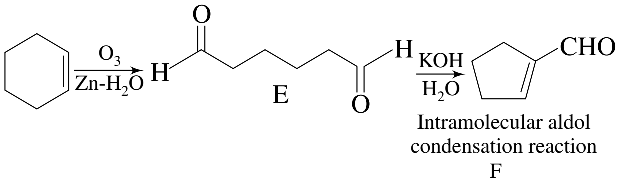
19. [2]



$$H_2C=O + H_2N—OH \longrightarrow \begin{matrix}H\\H\end{matrix}\!>\!C=N—OH \text{ (single)}$$



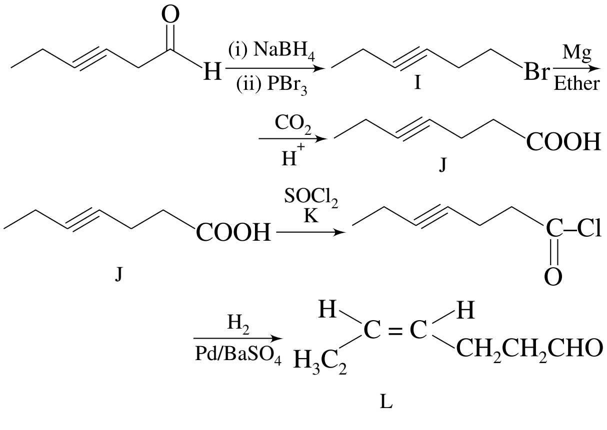
20. [2]



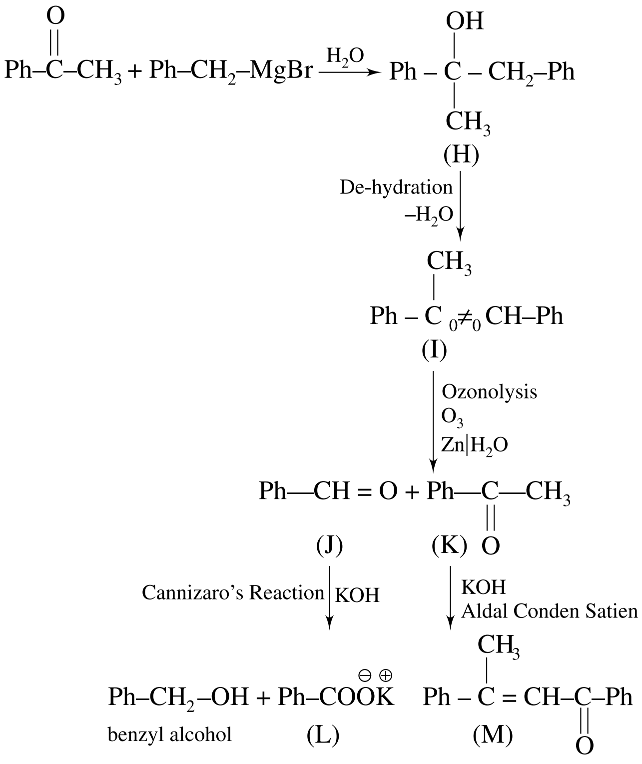
21. [4]

22. [1]

23. [3]



24. [2]



$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 + Ph-CH_2-MgBr \xrightarrow{H_2O} \underset{(H)}{Ph-\overset{OH}{\underset{CH_3}{C}}-CH_2-Ph}$$

$$\xrightarrow[-H_2O]{\text{De-hydration}} \underset{(I)}{Ph-\overset{CH_3}{C}\,{}_0{\neq}_0\,CH-Ph} \xrightarrow[Zn|H_2O]{\text{Ozonolysis } O_3} \underset{(J)}{Ph-CH=O} + \underset{(K)}{Ph-\underset{O}{\underset{\|}{C}}-CH_3}$$

$$(J) \xrightarrow[KOH]{\text{Cannizaro's Reaction}} \underset{\text{benzyl alcohol}}{Ph-CH_2-OH} + \underset{(L)}{Ph-CO\overset{\ominus}{O}\overset{\oplus}{K}}$$

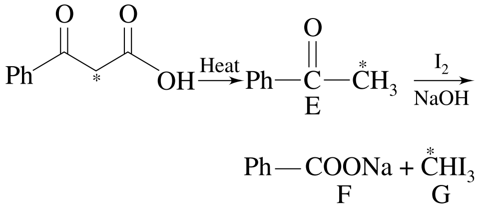
$$(K) \xrightarrow[\text{Aldal Conden Satien}]{KOH} \underset{(M)}{Ph-\overset{CH_3}{C}=CH-\underset{O}{\underset{\|}{C}}-Ph}$$

Since H is tertiary alcohol and gives de-hydration hence H is formed by treatment of grignard reagent having with ketone as shown above.

25. [4]

As per above reaction.

26. [4]

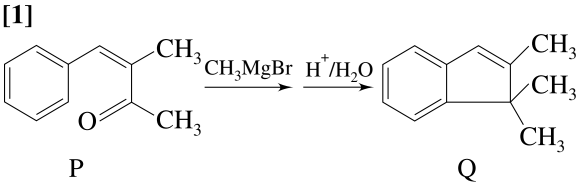


$$\xrightarrow{Heat} Ph-\underset{E}{\overset{O}{\overset{\|}{C}}}-\overset{*}{C}H_3 \xrightarrow[NaOH]{I_2} \underset{F}{Ph-COONa} + \underset{G}{\overset{*}{C}HI_3}$$

27. [2]

28. [2]

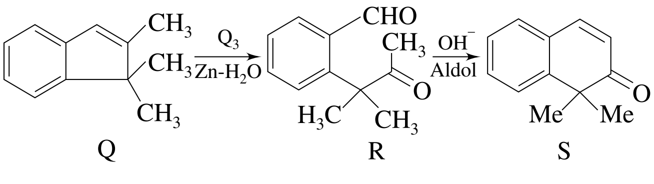
29. [1]



P

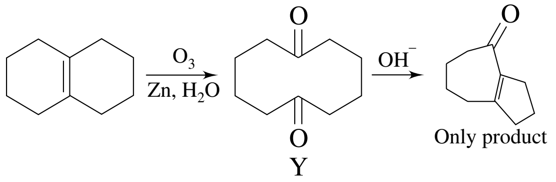
(Gives positive iodoform test)

Q



Q R S

30. [1]



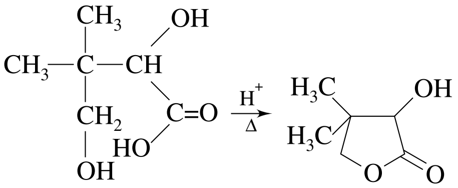
31. [1]

32. [2]

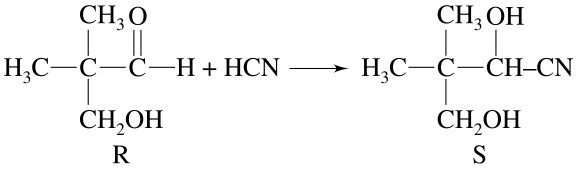
33. [1]

34. [4]

The given product is an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin.

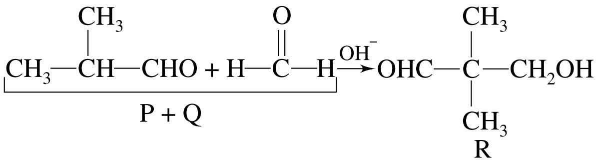


Acid above is obtained by acid hydrolysis of cyanohydrin S as



$$\underset{R}{H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{O}{\overset{\|}{C}}-H} + HCN \longrightarrow \underset{S}{H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{OH}{CH}-CN}$$

R is obtained by treatment of P and Q with aqueous K_2CO_3 through aldol condensation reaction as

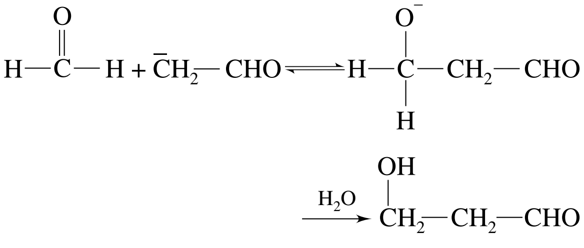


$$\underbrace{CH_3-\overset{CH_3}{CH}-CHO + H-\overset{O}{\overset{\|}{C}}-H}_{P+Q} \xrightarrow{OH^-} \underset{R}{OHC-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH}$$

35. [3]

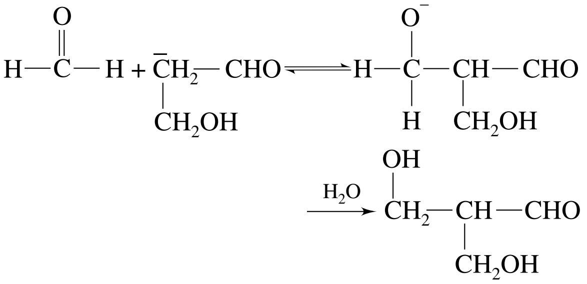
The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.

Step I $CH_3CHO + OH^- \longrightarrow \bar{C}H_2-CHO + H_2O$



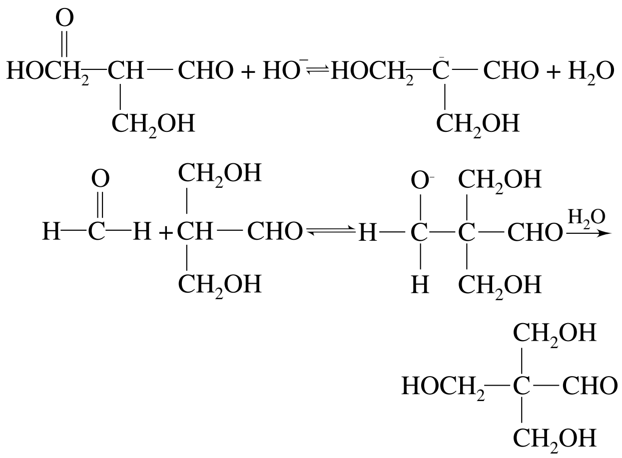
$$H-\overset{O}{\overset{\|}{C}}-H + \bar{C}H_2-CHO \rightleftharpoons H-\overset{O^-}{\underset{H}{C}}-CH_2-CHO \xrightarrow{H_2O} \overset{OH}{CH_2}-CH_2-CHO$$

Step II $HOCH_2-CH_2-CHO + HO^- \rightleftharpoons HO-CH_2-\bar{C}H-CHO + H_2O$



$$\mathrm{H{-}CO{-}H + {}^{-}CH(CH_2OH){-}CHO \rightleftharpoons H{-}CH(O^-){-}CH(CH_2OH){-}CHO \xrightarrow{H_2O} HOCH_2{-}CH(CH_2OH){-}CHO}$$

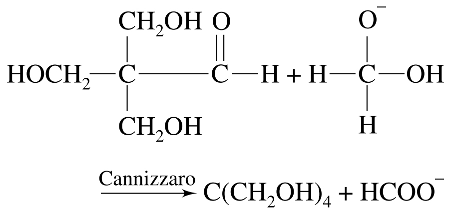
Step III



$$\mathrm{HOCH_2{-}CH(CH_2OH){-}CHO + HO^- \rightleftharpoons HOCH_2{-}\bar{C}(CH_2OH){-}CHO + H_2O}$$

$$\mathrm{H{-}CO{-}H + {}^{-}C(CH_2OH)_2{-}CHO \rightleftharpoons H{-}CH(O^-){-}C(CH_2OH)_2{-}CHO \xrightarrow{H_2O} HOCH_2{-}C(CH_2OH)_2{-}CHO}$$

Step IV

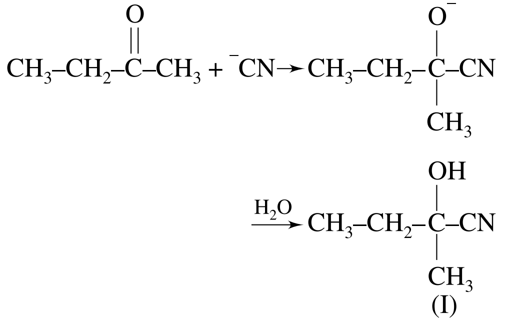


$$\mathrm{HOCH_2{-}C(CH_2OH)_2{-}CO{-}H + H{-}C(O^-)(OH){-}H \xrightarrow{Cannizzaro} C(CH_2OH)_4 + HCOO^-}$$

In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

36. [1]

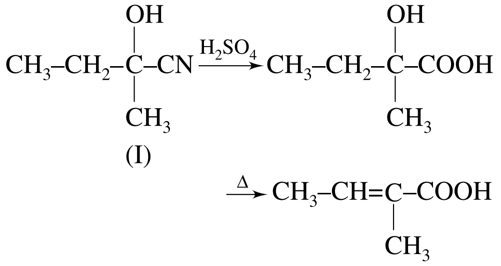
The first step is cyanohydrin reaction.



(I)

$$\mathrm{CH_3{-}CH_2{-}CO{-}CH_3 + {}^{-}CN \to CH_3{-}CH_2{-}C(O^-)(CH_3){-}CN \xrightarrow{H_2O} CH_3{-}CH_2{-}C(OH)(CH_3){-}CN}\ \text{(I)}$$

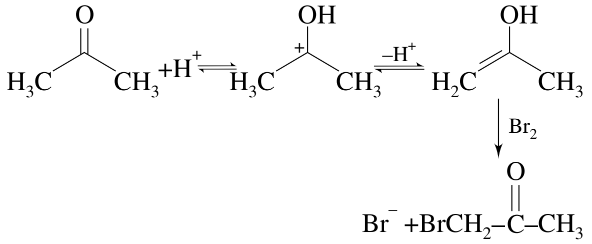
In the second step, the —CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc. H_2SO_4.



(I)

$$\mathrm{CH_3{-}CH_2{-}C(OH)(CH_3){-}CN \xrightarrow{H_2SO_4} CH_3{-}CH_2{-}C(OH)(CH_3){-}COOH \xrightarrow{\Delta} CH_3{-}CH{=}C(CH_3){-}COOH}$$

37. [3]

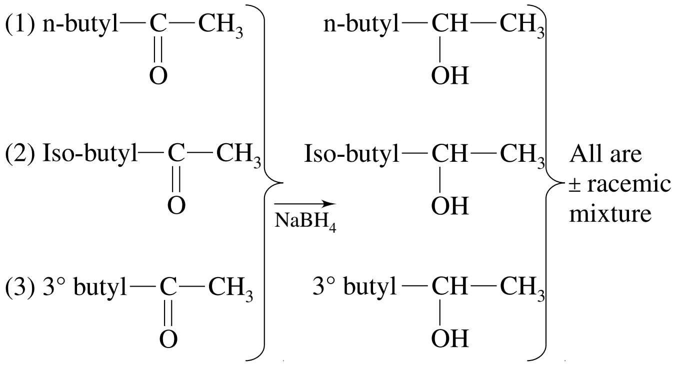


$$\mathrm{CH_3COCH_3 + H^+ \rightleftharpoons CH_3C^+(OH)CH_3 \overset{-H^+}{\rightleftharpoons} H_2C{=}C(OH)CH_3 \xrightarrow{Br_2} Br^- + BrCH_2{-}CO{-}CH_3}$$

38. [5]

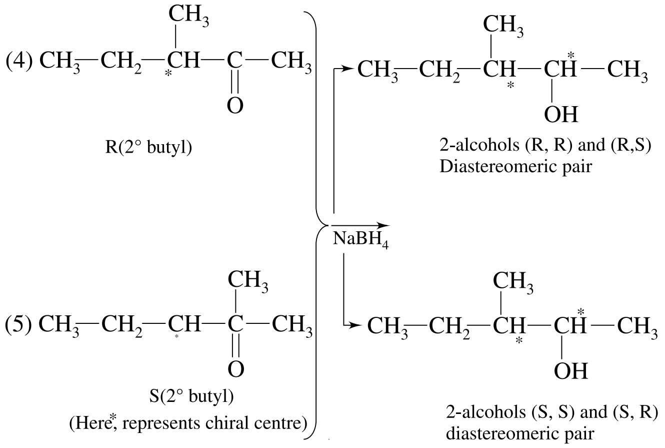
Molecular weight of the ketone is 100.

So, molecular formula = $C_6H_{12}O$



$$\text{(1) n-butyl}{-}\mathrm{CO{-}CH_3},\ \text{(2) Iso-butyl}{-}\mathrm{CO{-}CH_3},\ \text{(3) 3° butyl}{-}\mathrm{CO{-}CH_3} \xrightarrow{NaBH_4} \text{n-butyl}{-}\mathrm{CH(OH){-}CH_3},\ \text{Iso-butyl}{-}\mathrm{CH(OH){-}CH_3},\ \text{3° butyl}{-}\mathrm{CH(OH){-}CH_3}$$

All are ± racemic mixture



$$\text{(4) }\mathrm{CH_3{-}CH_2{-}\overset{*}{C}H(CH_3){-}CO{-}CH_3},\ \text{(5) }\mathrm{CH_3{-}CH_2{-}CH(CH_3){-}CO{-}CH_3} \xrightarrow{NaBH_4} \mathrm{CH_3{-}CH_2{-}\overset{*}{C}H(CH_3){-}\overset{*}{C}H(OH){-}CH_3}$$

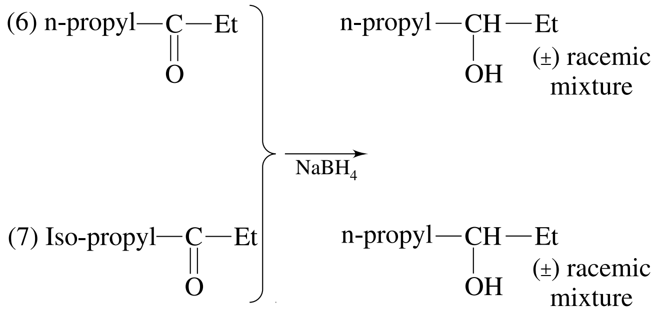
R(2° butyl)

2-alcohols (R, R) and (R,S) Diastereomeric pair

S(2° butyl)

(Here*, represents chiral centre)

2-alcohols (S, S) and (S, R) diastereomeric pair

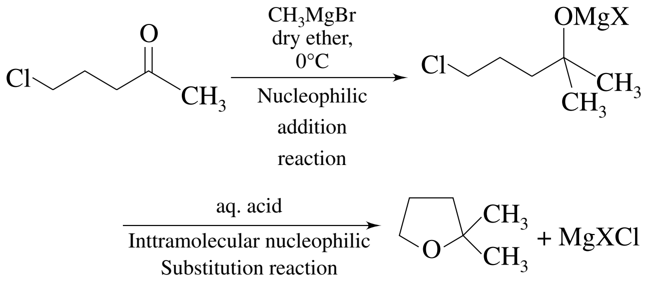


While in case of (4) and (5), they do not produce enantiomer due to the presence of stereogenic centre on ketone.

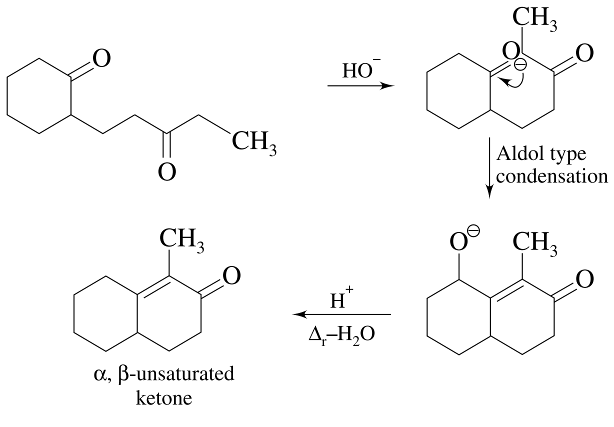
39. [4]

This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

Complete reaction sequence is as shown below



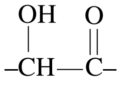
40. [1]



41. [1, 2, 3]

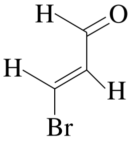
$$\underset{\text{(Tollen's reagent)}}{\text{RCHO} + \text{Ag}_2\text{O}} \xrightarrow{\text{OH}^-} \underset{\text{(Silver mirror)}}{\text{RCOOH} + 2\text{Ag}}$$

Tollens' test is given by all aldehydes and all reducing sugars as glucose, fructose and α-hydroxy ketones



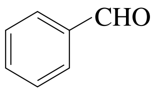
$$-\overset{\overset{\large\text{OH}}{|}}{\text{CH}}-\overset{\overset{\large\text{O}}{||}}{\text{C}}-$$

(1)



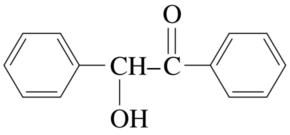
having an aldehyde group gives Tollens' test

(2)

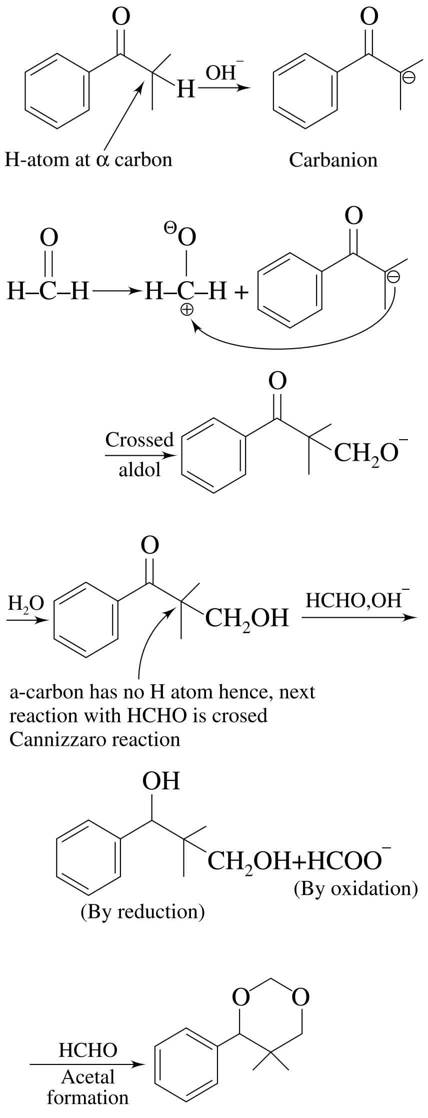


Aldehyde

(3)



42. [1]



Comment: Please check, α-carbon should be α-carbon