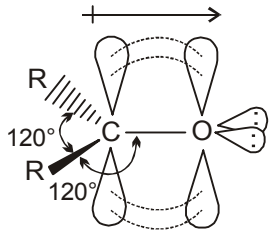
Aldehydes and Ketones

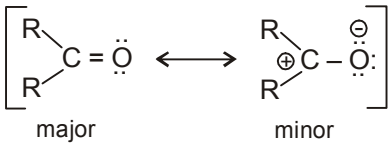
1. Introduction

Aldehydes & ketones have general formula $C_nH_{2n}O$ and contains >C = O group. Thus aldehydes (R–CHO) and ketones (R–CO–R) are collectively called as carbonyl compounds. Aldehyde is always at terminal position while ketone is never at terminal position.

2. Strucutre and bonding in aldehydes and ketones

The carbonyl carbon atom is sp^2 hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized.
Orbital diagram for the formation of carbonyl group is as follows:





This polarity confirms that there is nucleophilic addition reaction takes place in carbonyl compound.
The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.
Carbonyl carbon act as an electrophile (Lewis acid)
Carbonyl oxygen act as a nucleophile (Lewis base)

3. Preparation methods of Aldehydes and Ketones :

3.1 By oxidation of alcohols :

Primary alcohols $\xrightarrow{[O]}$ Aldehydes

Secondary alcohols $\xrightarrow{[O]}$ Ketones

3.2 By dehydrogenation of alcohols :

Dehydrogenation means removal of hydrogen and reagent used is heated copper.

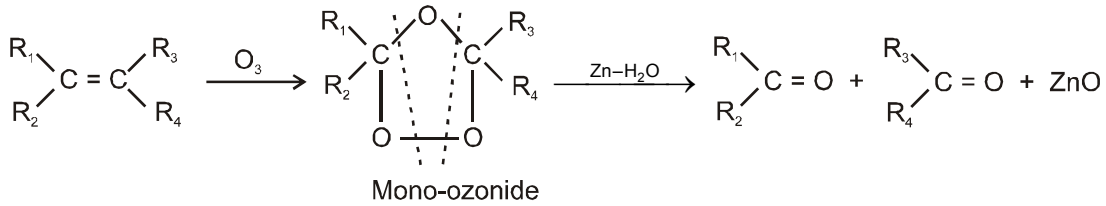
1° alcohol (RCH_2OH) $\xrightarrow[-H_2]{Cu/300^\circ C}$ Aldehyde (R–CH = O)

2° alcohol (R_2CHOH) $\xrightarrow[-H_2]{Cu/300^\circ C}$ Ketone ($R_2C = O$)

3° alcohol $\xrightarrow[-H_2O]{Cu/300^\circ C}$ Alkene

3.3 Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



Note : (i) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.
(ii) By this method we can locate double bond in olefin or exact structrue of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen atoms of two carbonyl compounds.
(iii) Among the three molecules of carbonyl compounds.
(a) If one molecule contains two carbonyl groups, then hydrocarbon will be alkadiene.
(b) If all the three molecules contain two carbonyl group then hydrocarbon will be cycloalkatriene.

3.4 Wacker process :

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

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

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

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

3.5 Hydration of alkynes :

$$\underset{\text{Ethyne}}{CH \equiv CH} \xrightarrow[H_2SO_4/HgSO_4]{H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

Other alkynes give ketones in this reaction.

$$R - C \equiv C - H \xrightarrow[H_2O]{Hg^{++}/H_2SO_4} R - \overset{O}{\overset{\|}{C}} - CH_3$$

3.6 Hydroboration of alkyne :

It is used to get aldehyde from terminal alkyne. Here reagent is (i) diborane (B_2H_6) (ii) H_2O_2,OH^-

$$R - C \equiv C - H \xrightarrow[(ii)H_2O_2/OH^-]{(i)\ B_2H_6} R - CH_2 - CH = O$$

In this reaction Borane (BH_3) is act as electrophile.

3.7 Dry distillation of calcium salt of acid :

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

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

calcium acetate

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

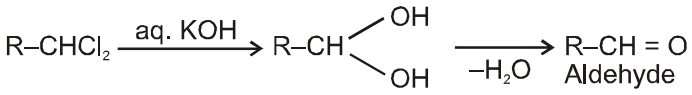
3.8 On passing vapours of fatty acids over Mangnous oxide at 300ºC :

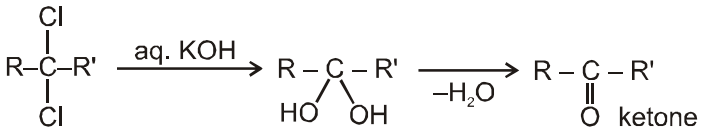
$$\underset{\text{(Vap)}}{2\ RCOOH} \xrightarrow{MnO\ /\ 300^oC} \underset{\text{Ketone}}{R - \overset{O}{\overset{\|}{C}} - R} + CO_2 + H_2O$$

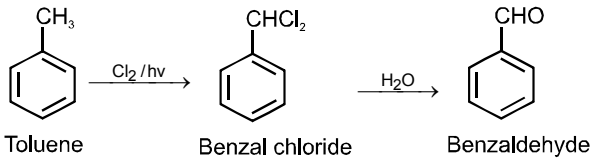
On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

3.9 On aqueous alkali hydrolysis of gem-dihalides :

Terminal gemdihalides will give aldehyde while non-terminal will give ketone as follows



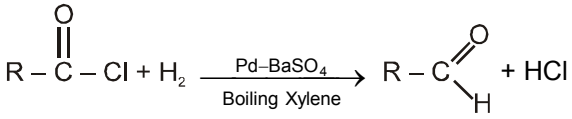




4. Methods used for the preparation of Aldehydes only.

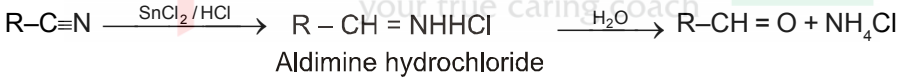
4.1 Rosenmund's reduction :

Here acid chlorides are reduced to aldehyde with H_2 in boiling xylene using palladium as a catalyst supported on barium sulphate.



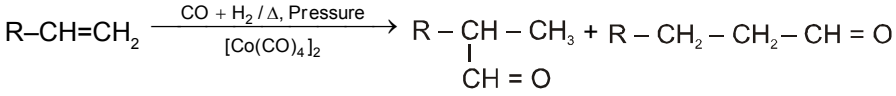
Note : (a) Pd Catalyst is poisoned by $BaSO_4$ to check further reduction of aldehyde to alcohol.
(b) Formaldehyde cannot be obtained by this method because HCOCl is unstable at common temperature.
(c) Reaction with acid chloride and dialkyl cadmium we can obtain ketone.

4.2 Stephen's reduction :



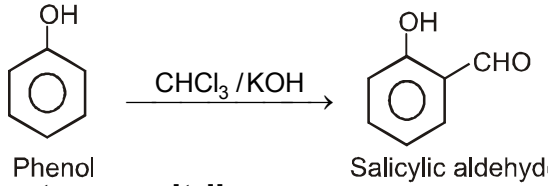
4.3 Oxo-process :

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

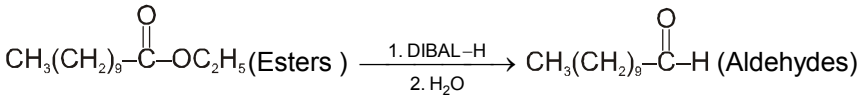


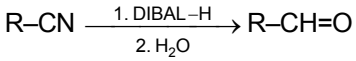
4.4 Reimer-Teimann Reaction :

By this method phenolic aldehyde is prepared



4.5 From esters or nitrile :

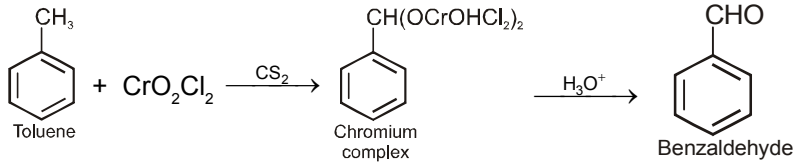




DIBAL–H : Diisobutyl aluminium hydride [AlH(i-Bu)$_2$] is a reducing agent.

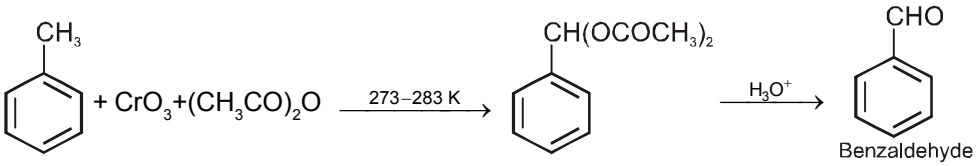
4.6 From hydrocarbons :

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



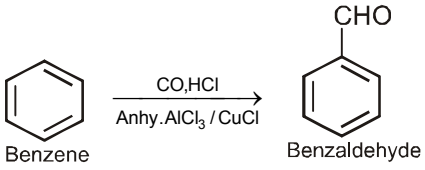
This reaction is called **Etard reaction.**

4.7 By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride:



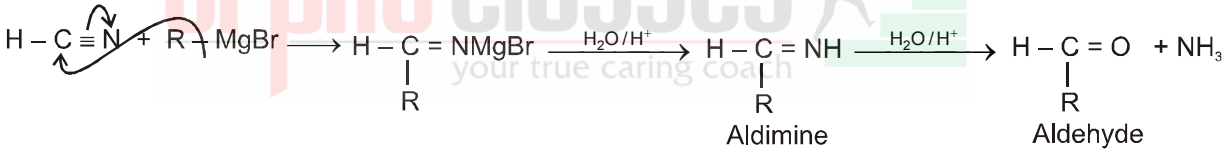
4.8. By Gatterman-Koch reaction :

Benzene or its derivative $\xrightarrow[\text{Anhy.}AlCl_3/CuCl]{CO,HCl}$ Benzaldehyde or substituted benzaldehyde



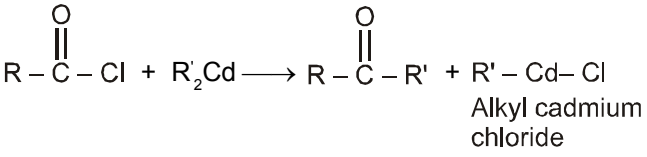
4.9 By hydrogen cyanide :

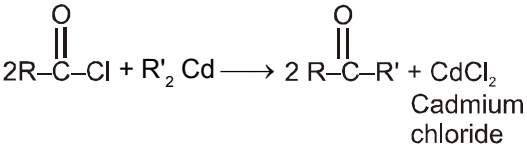
Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via aldimine.



5. Methods used for the preparation of Ketones only

5.1 Using alkanoylchloride and dialkyl cadmium :





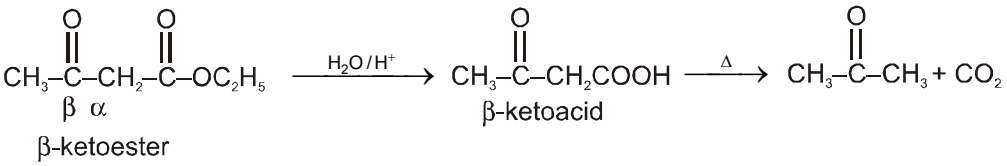
5.2 By acylation or benzoylation of aromatic hydrocarbon (Friedel-Craft Reaction)

$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COCH_3 + HCl$$
Acetophenone

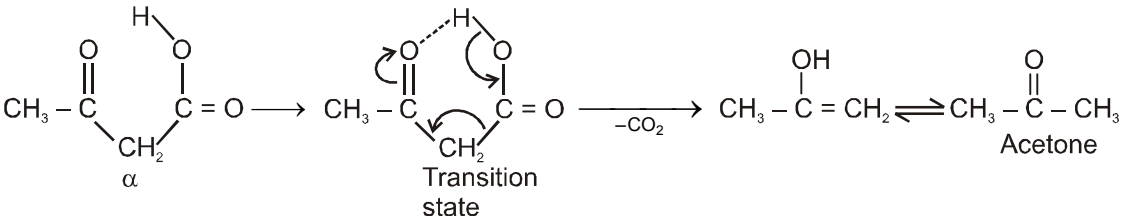
$$C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCl$$
Benzophenone

$$\underset{\text{excess}}{C_6H_6} + COCl_2 \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCl$$
Benzophenone

5.3 By acid hydrolysis followed by heating of β-Ketoester :

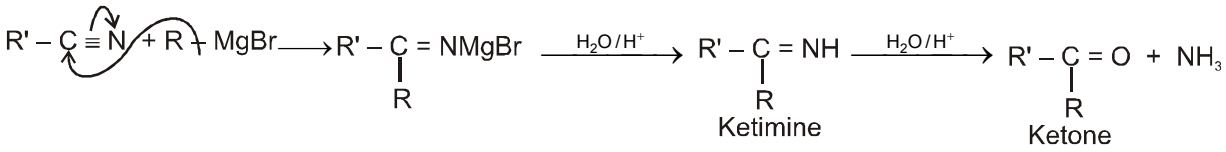


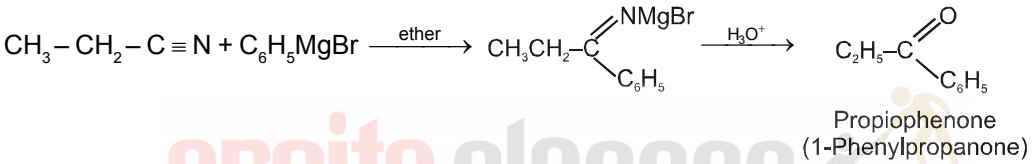
Note : It is β-ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.



5.4 From nitriles :

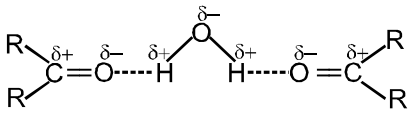
Treatment of nitrile with Grignard reagent followed by hydrolysis gives a ketone.





6. Physical properties of Aldehydes and Ketones :

- Methanal - Gas at room temperature
- Ethanal - Volatile liquid
- Other aldehydes and ketones - Liquid or solid at room temperature
- Boling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.
  Reason : Weak molecular association in aldehydes and ketones, arising out of the dipole-dipole interactions
- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
  Reason : Absence of intermolecular hydrogen bonding
- Lower members of aldehydes and ketones are miscible with water in all proportions.
  Reason : They form hydrogen bonds with water.



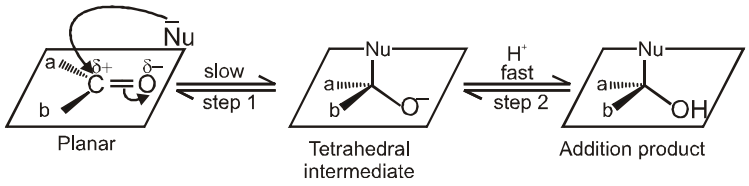
- Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc.
- Lower aldehydes have sharp pungent odours.
- As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

7. Chemical Reactions

7.1 Nucleophilic addition reactions :

Addition of a nuceophile and a proton across the (C = O) double bond. The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

Mechanism :

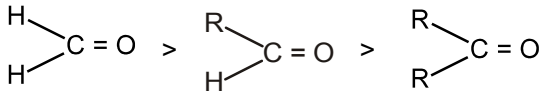


Nucleophile (Nu^-) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon.

In the process, hybridisation of carbon changes from sp^2 to sp^3.

A tetrahedral alkoxide is formed as intermediate.

Reactivity : Aldehydes are more reactive than ketones in nucleophilic addition reactions.



There are two factors which influence the reactivity of ketone and aldehyde.

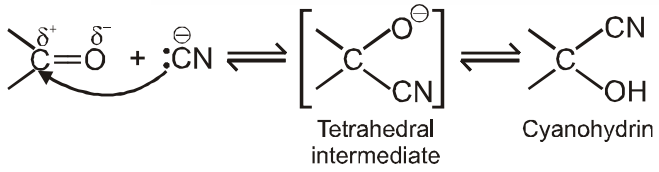
(i) Inductive effect (ii) steric factor

(i) + I effect of alkyl group decrease the amount of charge on C^+ ($C^+ – O^-$). in ketones.

(ii) Steric effect also causes the less reactivity of carbonyl group.

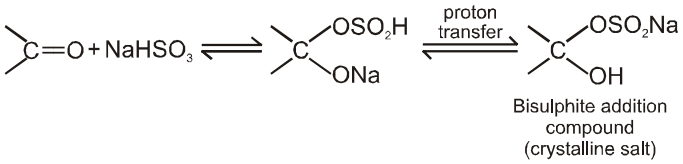
(I) Addition of hydrogen cyanide (HCN)

$HCN + OH^- \longleftrightarrow :\bar{C}N + H_2O$

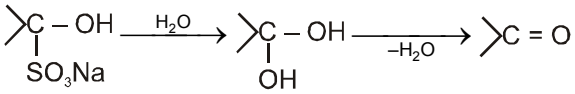


Note : (i) Addition of HCN over aldehyde and ketones gives cyanohydrin.
(ii) Cyanohydrin on acid hydrolysis gives α-hydroxy acid.
(iii) Cyanohydrin on treating with $NH_3(l)$ followed by acid hydrolysis gives α-amino acid.
(iv) In case of ketone cyanohydrin formation is reversible due to bulky group of ketone which hinder the formation.

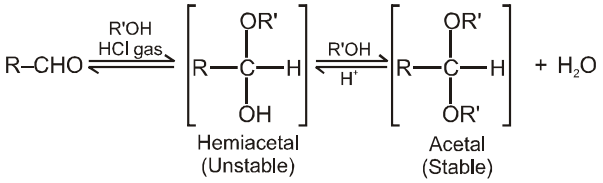
(II) Addition of sodium hydrogen sulphite ($NaHSO_3$)

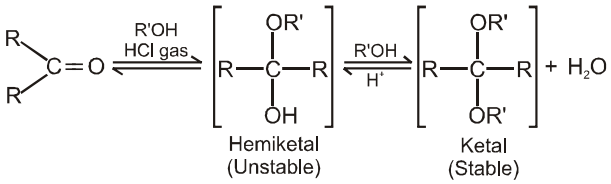


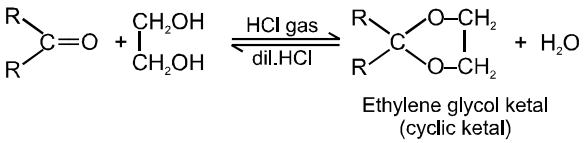
salt on hydrolysis gives carbonyl compounds again, this reaction is used to separate the aldehydes from mixture.



(III) Addition of alcohols (ROH) :





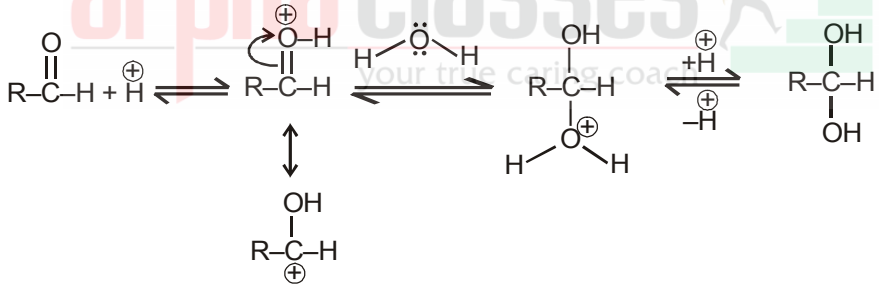


Note : (i) Acetal is formed to protect aldehyde for a long time.
(ii) Acetal has functional groups ether.
(iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
(iv) On treating with ethyleneglycol we get cyclic acetal or ketal.
(v) Acetal formation is found to be more favourable than ketal formation if both the carbonyl groups are present within the molecule.

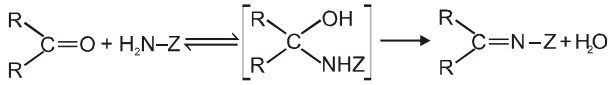
(IV) Addition of water :

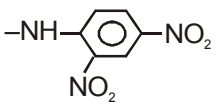
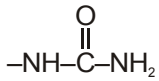
Aldehyde or ketone reacts with water to form gem-diols. Water is a poor nucelophile and therefore adds relatively slowly to the carbonyl group, but the rate of reaction can be increased by an acid catalyst.

Mechanism:

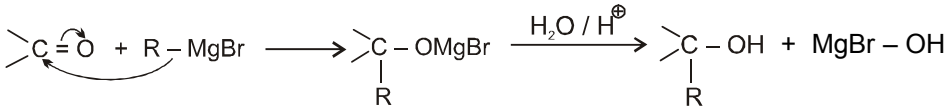


(V) Addition of ammonia and its derivatives (addition elimination reactions) :

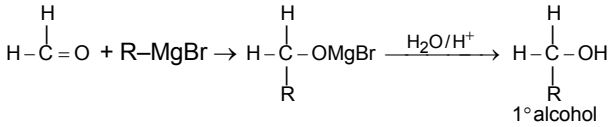


If Z are	Reagents Name	Products
–OH	Hydroxylamine	Oxime
$-NH_2$	Hydrazine	Hydrazone
$-NH-C_6H_5$	Phenylhydrazine	Phenylhydrazone
	2,4-dinitrophenylhydrazine (Brady's reagent) or 2,4-DNP	2,4-dinitrophenylhydrazone (Solid orange precipitate)
	Semicarbazide	Semicarbazone

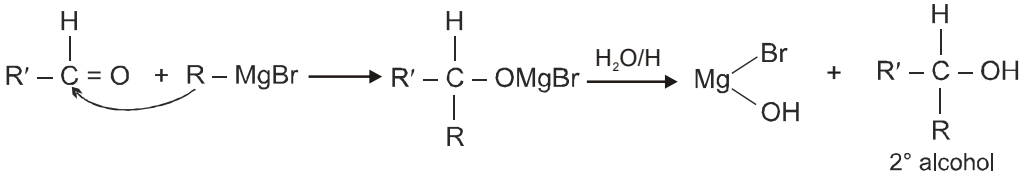
(VI) Addition of Grignard reagents (Preparation of alcohol) :



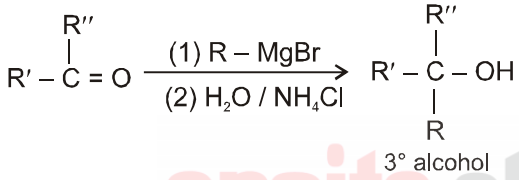
(a) When formaldehyde is treated with Grignard reagent followed by acid hydrolysis primary alcohol is obtained.



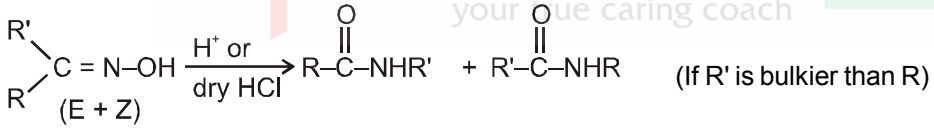
(b) When aldehyde except formaldehyde is treated with grignard reagent followed by hydrolysis 2° alcohol is obtained.



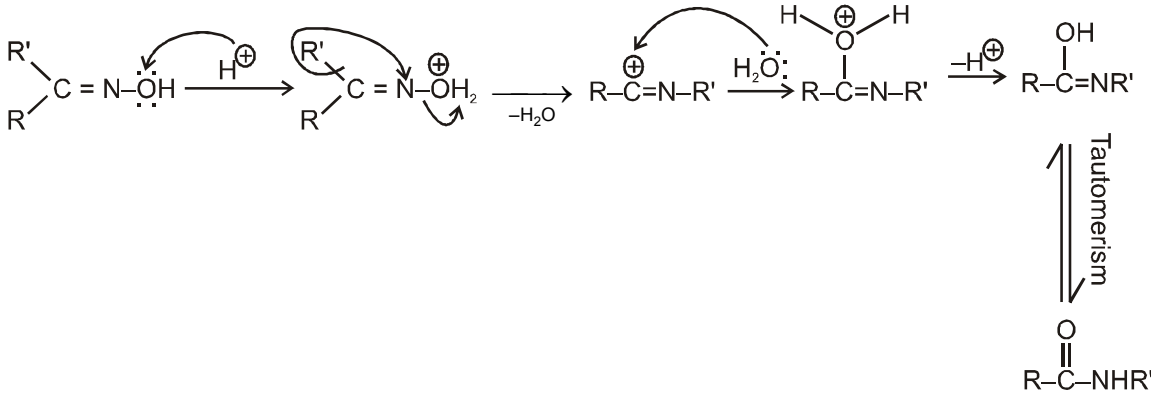
(c) When ketone is treated with grignard reagent followed by acid hydrolysis 3° alcohol is obtained.



7.2 Beckmann rearrangement in Oxides:

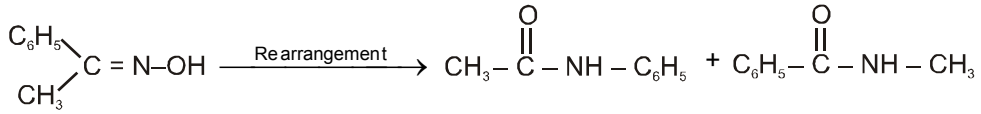


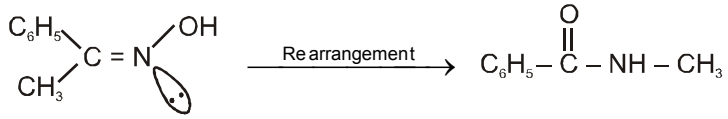
Mechanism :



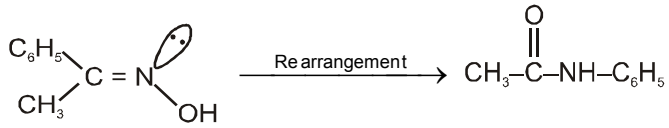
Note : (i) Oxime undergoes Beckmann rearrangement to give its isomer amide.
(ii) In this reaction the group which is anti to –OH group migrates.

Ex.





(–CH_3 is anti to –OH)

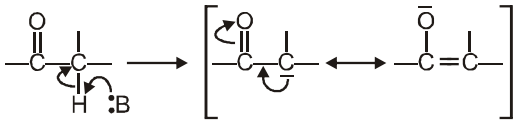


(–C_6H_5 is anti to –OH)

7.3 Reactions due to α-Hydrogen

α-Hydrogen of aldehydes and ketones are acidic: They undergo a number of reactions due to the acidic nature of α-hydrogen.

Reason for the acidity of α-hydrogen: Strong electron-withdrawing effect of the carbonyl group, and resonance stabilisation of the conjugate base

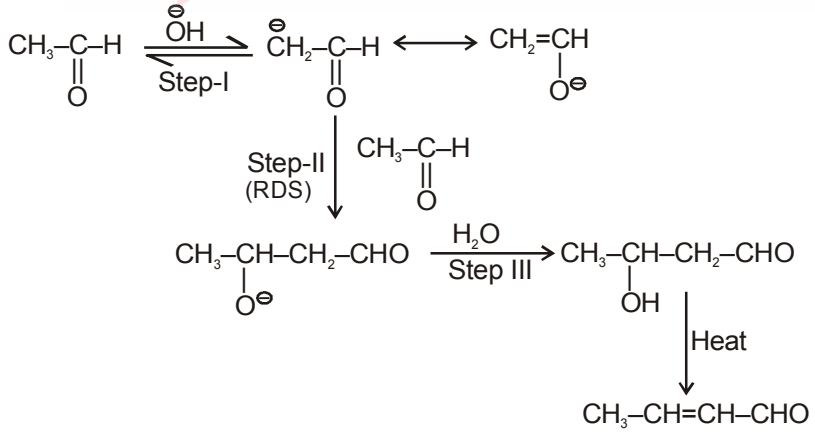


Resonating structure of conjugate base

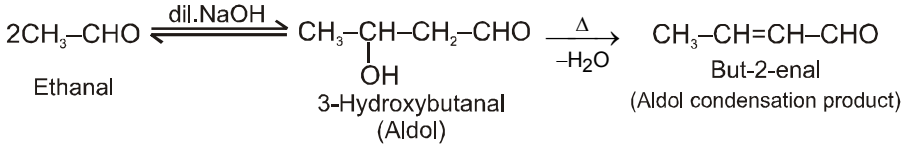
(I) Aldol condensation (or aldol reaction)

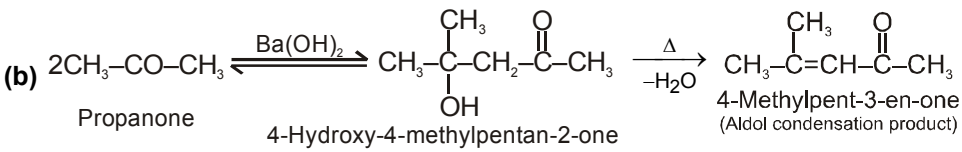
Aldehydes and ketones with at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.

Mechanism



Ex.

(a) 

(b) 

(II) Cross-Aldol condensation :

On using two types of carbonyl compounds both having α-hydrogen atoms we get a mixture of four condensed product because two types of carbonyl compounds will give two type of carbanions which will be nucleophile for itself and other molecule.

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH}$$

$CH_3–CH=CH–CHO$ (Simple or self aldol products)

+

$CH_3–CH_2–CH=C(CH_3)–CHO$ (Simple or self aldol products)

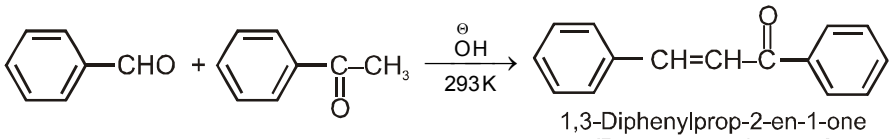
+

$CH_3–CH=C(CH_3)–CHO$ (Cross aldol products)

+

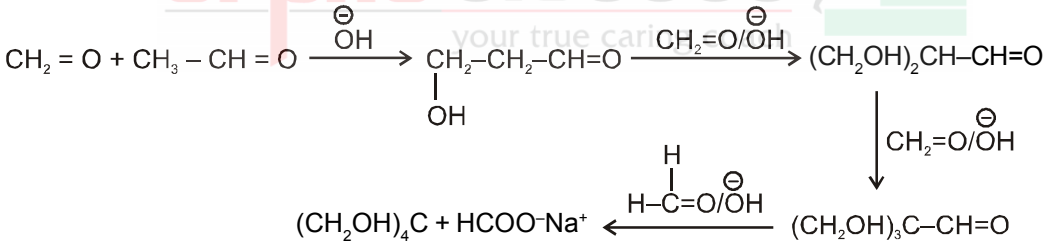
$CH_3–CH_2–CH=CH–CHO$ (Cross aldol products)

Ketones can also be used as one component in cross-aldol reactions.



1,3-Diphenylprop-2-en-1-one
{Benzalacetophenone}
{Major product}

Note : On using formaldehyde and acetaldehyde during crossed aldol all the α-hydrogen atom of acetaldehyde are replaced one by one by hydroxymethyl group because of smaller size of formaldehyde to give trihydroxymethylacetaldehyde which undergoes crossed cannizaro's reaction with formaldehyde to give tetrahydroxymethyl methane and formate ion as a final product.

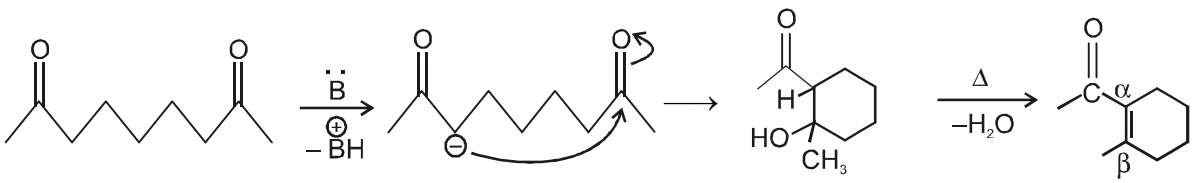


Ex. Show how cinnamaldehyde is prepared by crossed aldol condensation ?

Sol. $C_6H_5CHO + CH_3CHO \xrightarrow[(-H_2O)]{OH^{\ominus}} C_6H_5CH=CH–CHO + H_2O$

(III) Intramolecular aldol condensation :

If two carbonyl groups with α-hydrogen atoms are present within the same molecule, then we get cyclic α, β-unsaturated aldehyde / ketones via the formation of cyclic-β-hydroxy aldehyde / ketone in presence of basic medium.

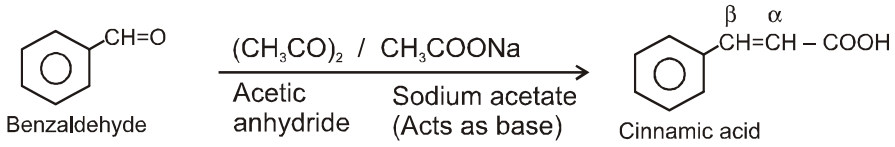


Cyclic β-hydroxy-ketone

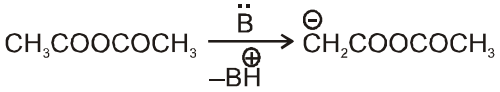
By knowing product we can get reactant as in case of intermolecular aldol condensation :

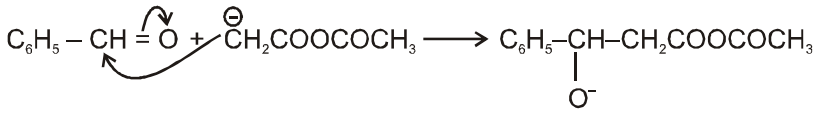
7.4 Perkin reaction :

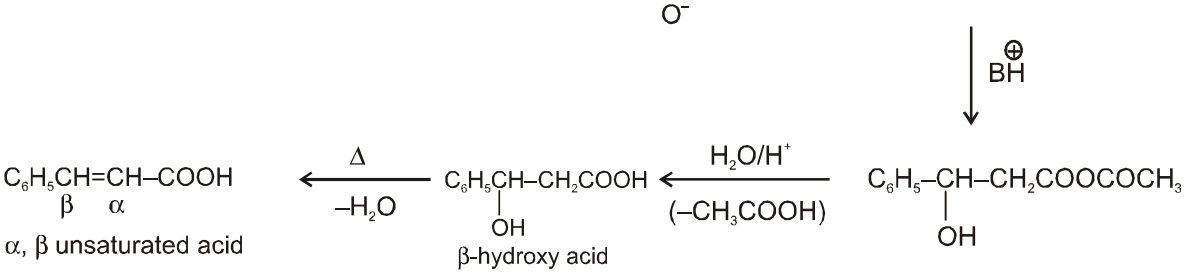
When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get α, β-unsaturated acid.



Mechanism :



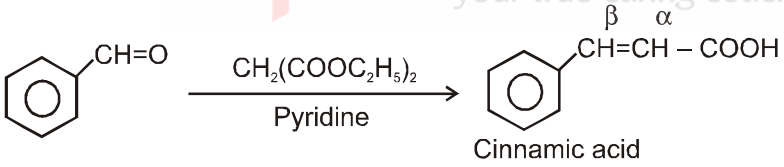




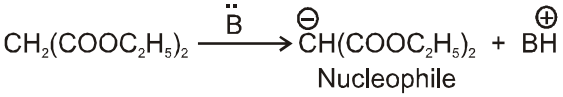
Note : By knowing α, β-unsaturated acid we can get idea about the anhydride used in perkin reaction. This can be done by keeping 'H' at α and –OH at β-carbon atom followed by breaking α, β carbon. By this we can know about acid and it will be anhydride of this acid only.

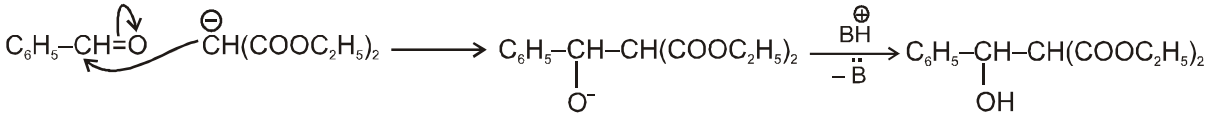
7.5 Knoevenagel reaction :

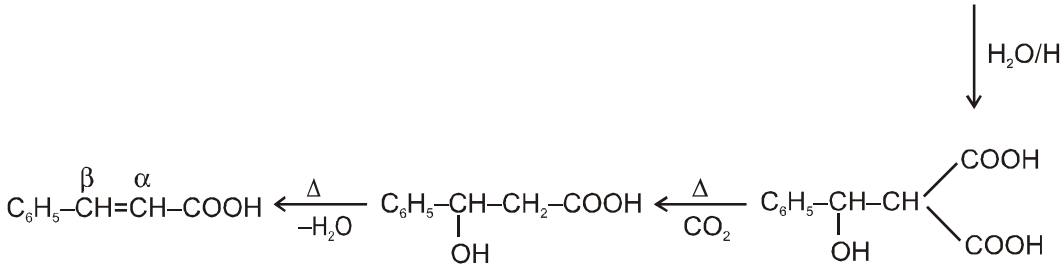
It is preparation of α, β-unsaturated acid with carbonyl compound using malonic ester in the presence of pyridine base.



Mechanism :

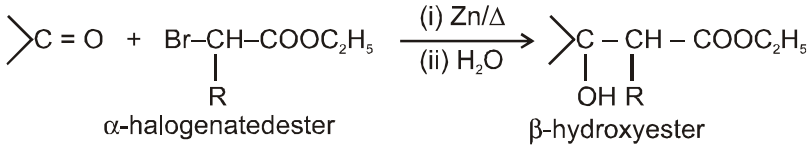




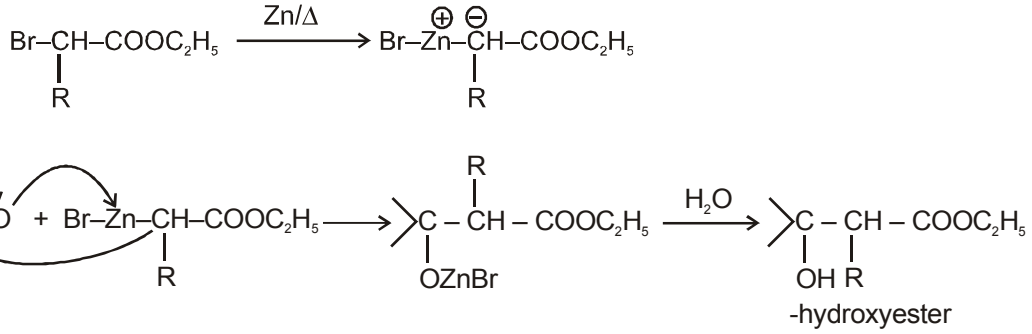


7.6 Reformatsky reaction :

When carbonyl compound and α-halogenated ester are heated with zinc followed by treating with water we get β-hydroxyester.



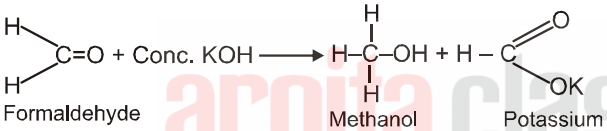
This reaction can be represented as –



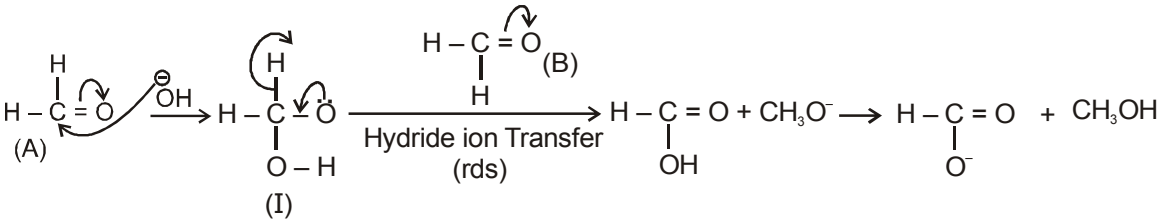
7.7 Cannizzaro reaction :

Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with a concentrated alkali.

Ex.



Mechanism :

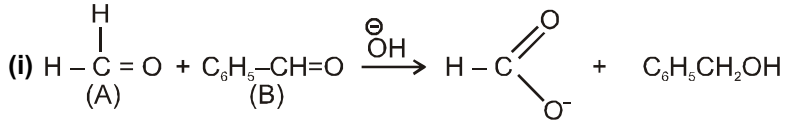


By this mechanism it is clear that acid corresponds to that carbonyl compound over which $\overset{\ominus}{O}H$ can attack easily as nucleophile.

Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Crossed Cannizzaro reaction :

On using two types of carbonyl compounds not having α-hydrogen atom, acid salt will be corresponding to that aldehyde over which $\overset{\ominus}{O}H$ will approach without any hindrence.

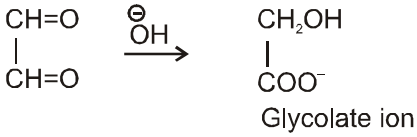


(ii) $(CH_2OH)_3C-CH=O$ (A) + $H-C(=O)-H$ (B) $\xrightarrow{\ominus OH}$ $(CH_2OH)_3C-CH_2OH + H-C(=O)-O^-$

in case (i) $\overset{\ominus}{O}H$ will easily go to (A) and in case (ii) it will go to (B) hence acid salt will be formate ion in both the cases.

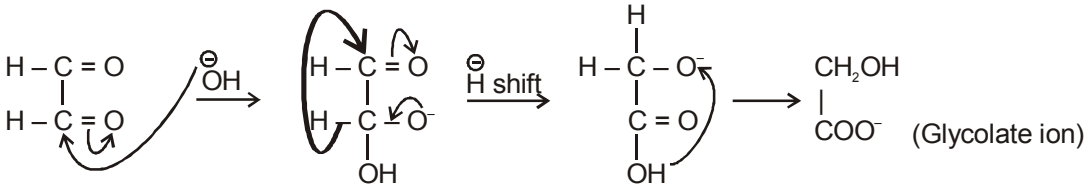
Intramolecular Cannizzaro reacion :

Here two carbonyl groups (without α-hydrogen atom) are present within the same molecule.



Glycolate ion

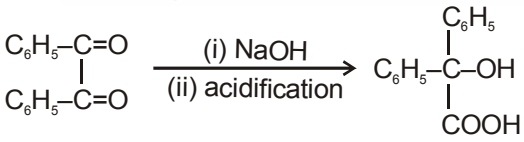
Mechanism :



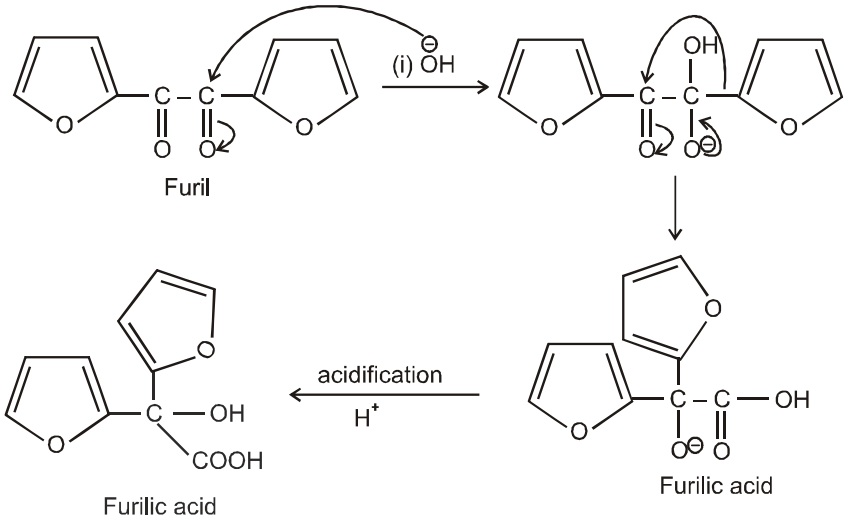
(Glycolate ion)

Ex. $C_6H_5-C(=O)-H$ $\xrightarrow{\ominus OH}$ $C_6H_5-CHOH-COO^-$ (mendalic acid ion)

7.8 Benzil-benzilic acid rearrangement:

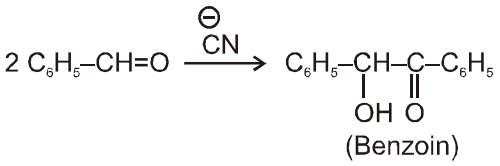


Conversion of furil to furilic acid with mechanism :

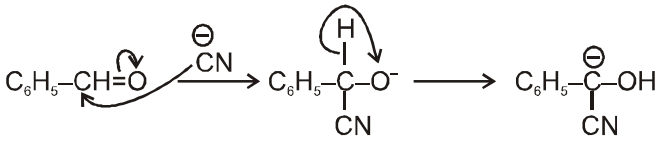


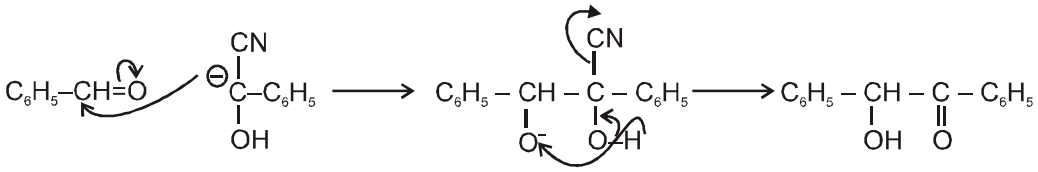
7.9 Benzoin Condensation :

During this reaction benzoin is obtained when an ethanolic solution of benzaldehyde is heated with strong alkali potassium cyanide or sodium cyanide.



Mechanism :

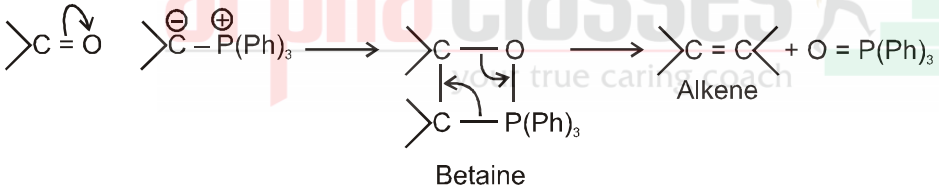




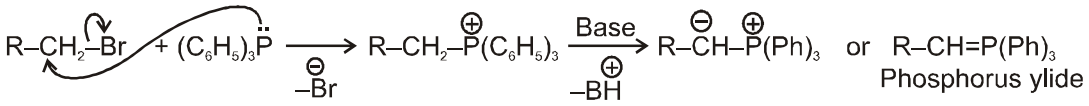
7.10 Wittig reaction :

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.

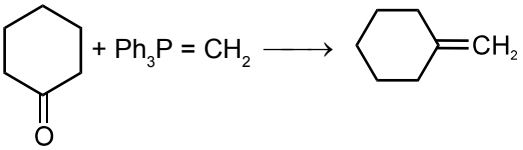
Mechanism :



Note : Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –



Ex.



7.11 Reduction reactions

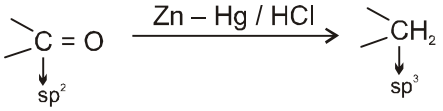
(I) Reduction to alcohols :

Aldehydes $\xrightarrow[\text{or Catalytic hydrogenation}]{NaBH_4 \text{ or } LiAlH_4}$ Primary alcohols

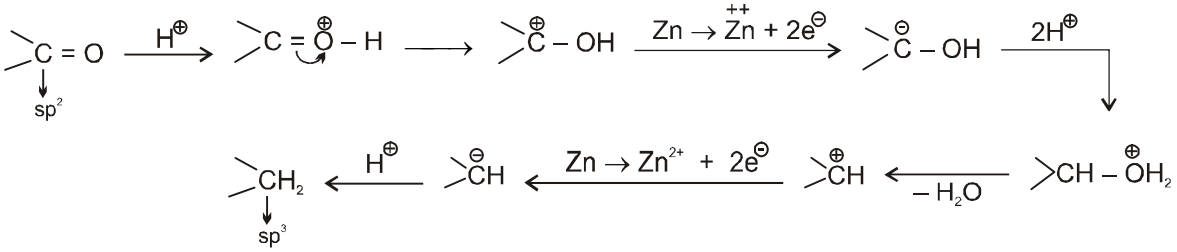
Ketones $\xrightarrow[\text{or Catalytic hydrogenation}]{NaBH_4 \text{ or } LiAlH_4}$ Secondary alcohols

(II) Clemmensen reduction :

Used to get alkane from carbonyl compounds.



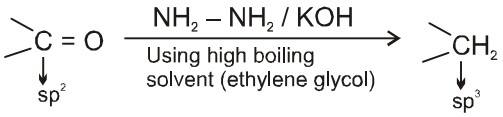
Mechanism :



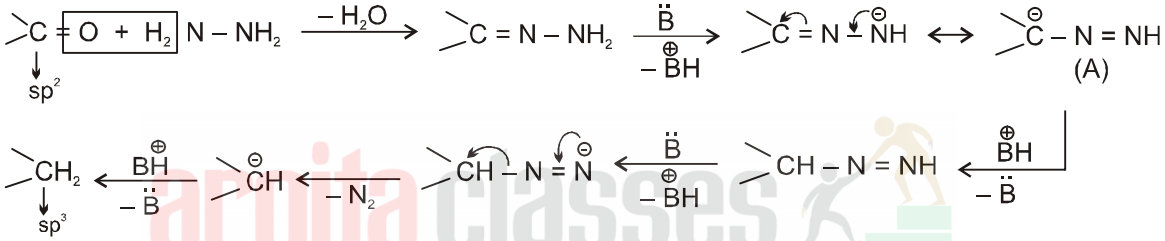
Note : Generally this reaction is avoid if **acid sensitive** groups are present in the carbonyl compounds.

(III) Wolf-Kishner reduction :

Used to get alkane from carbonyl compounds.



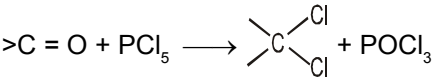
Mechanism :

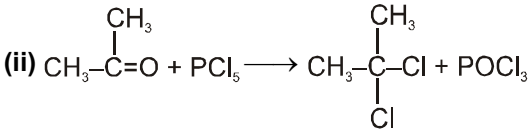


Note : Generally this reaction is avoid if **base sensitive** groups are present in the carbonyl compounds

(IV) Reaction with PCl_5 :

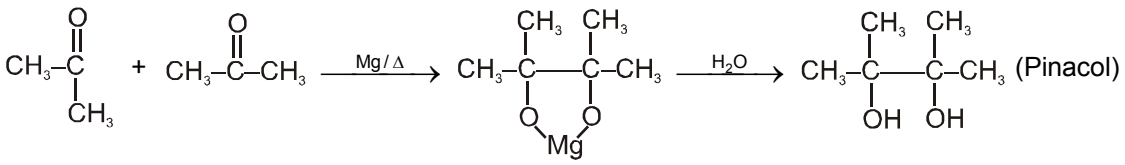
Carbonyl compounds give gemdihalides



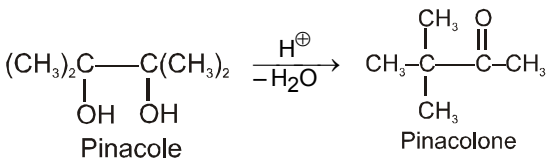
(i) $CH_3CH = O + PCl_5 \longrightarrow CH_3–CHCl_2 + POCl_3$ **(ii)** 

(V) Pinacol-Pinacolone rearrangement :

Pinacole is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.



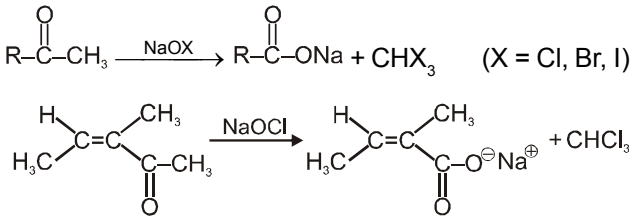
Pinacole undergoes rearrangement in acidic media to give pinacolone

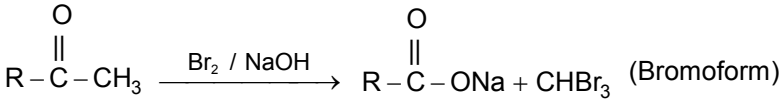


7.12 Oxidation reactions

(I) Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2, Br_2 or I_2) in the presence of alkali to give haloform and acid salt.

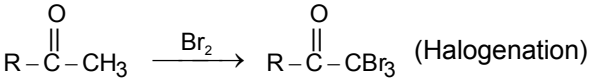


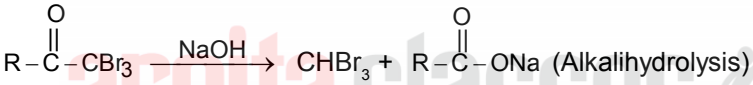


In this reaction $-CH_3$ of $CH_3-\overset{O}{\overset{\|}{C}}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

Preparation of haloform from methylketone involves two steps.

(a) Halogenation **(b) Alkalihydrolysis**

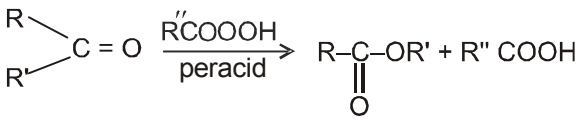




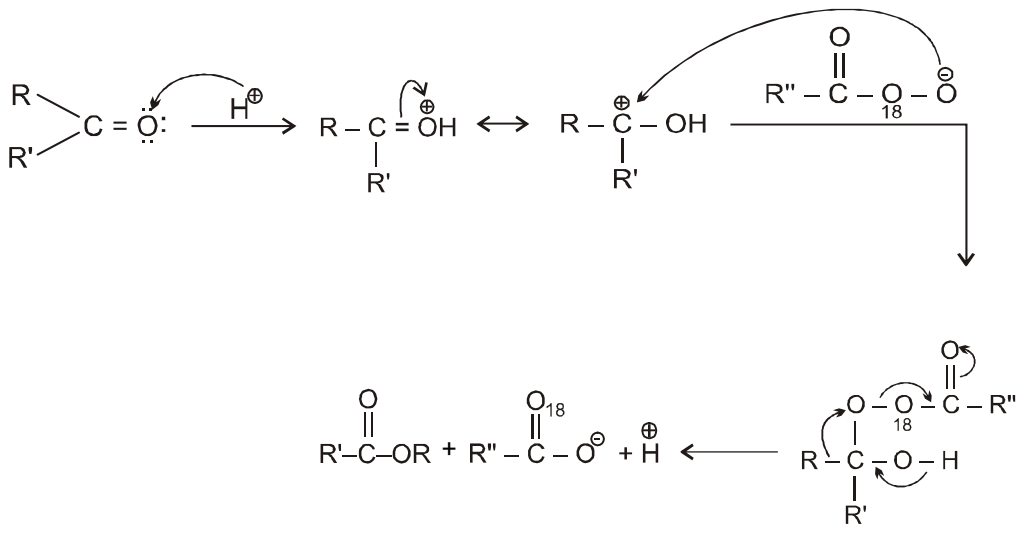
Note : This reaction is used to distinguish the presence of $CH_3-\overset{O}{\overset{\|}{C}}-$ group.

(II) Baeyer-Villiger oxidation :

It is preparation of ester from ketone using peracid.



Mechanism :



(III) Oxidation of Aldehydes :

- Aldehydes are oxidised to carboxylic acids by common oxidising agents such as $KMnO_4$, HNO_3, $K_2Cr_2O_7$, etc.

$$R–CHO \xrightarrow{[O]} RCOOH$$

- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On the other hand, ketones are not oxidised by mild oxidising agents.
- Ketones are oxidised under vigorous conditions, i.e., by strong oxidising agents and at elevated temperatures. It involves carbon-carbon bond cleavage.

$$R\overset{1}{C}H_2–\overset{2}{C}(=O)–\overset{3}{C}H_2–R' \xrightarrow{[O]} \underset{\text{(By cleavage of } C_1–C_2 \text{ bond)}}{R–COOH + R'–CH_2COOH} \quad \text{and} \quad \underset{\text{(By cleavage of } C_2–C_3 \text{ bond)}}{R–CH_2COOH + R'–COOH}$$

(a) Tollen's reagent :

It is ammonical silver nitrate solution, prepared by adding ammonium hydroxide to $AgNO_3$ solution. During reaction, first Ag_2O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]OH} + 3H_2O$$

Tollen's reagent is weak oxidising agent. It gives Ag mirror test with aldehyde.

$$R – CH = O + 2Ag(NH_3)_2^{\oplus} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + 2Ag + 2NH_3 + 2H_2O$$

$$R – CH = O + Ag_2O \longrightarrow R – COOH + 2Ag \text{ (Silver mirror)}$$

(b) Fehling's solution :

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate.
There are two solutions in Fehling solution
Solution (A) $CuSO_4$ solution and
Solution (B) Alkaline solution of sodium potassiumtartarate.
When these two solutions are mixed we get deep blue coloured solution.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 + \underset{\substack{\text{HO – CH – COOK}\\ \text{Roschelle salt}}}{\begin{matrix}\text{HO – CH – COONa}\\ |\\ \text{HO – CH – COOK}\end{matrix}} \longrightarrow \underset{\text{(Blue coloured compound)}}{Cu\begin{matrix}\text{O – CH – COONa}\\ |\\ \text{O – CH – COOK}\end{matrix}}$$

Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

$$R – CHO + \underset{\text{Blue}}{2CuO} \longrightarrow RCOOH + Cu_2O \text{ (Red ppt)}$$

$$RCHO + 2Cu^{2+} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + \underset{\text{(Red ppt)}}{2Cu^{\oplus}} + 2H_2O$$

(c) Benedict solution :

It also consists of two solutions.
Solution (A) $CuSO_4$ solution and
Solution (B) Alkaline solution of sodium Citrate.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 + \begin{matrix}CH_2COONa\\ |\\ HO – C – COONa\\ |\\ CH_2 – COONa\end{matrix} \longrightarrow \underset{\text{(Blue colour)}}{\begin{matrix}CH_2COONa\\ |\\ HO – Cu – O – C – COONa\\ |\\ CH_2COONa\end{matrix}}$$

Aldehyde gives positive test with Benedict solution.

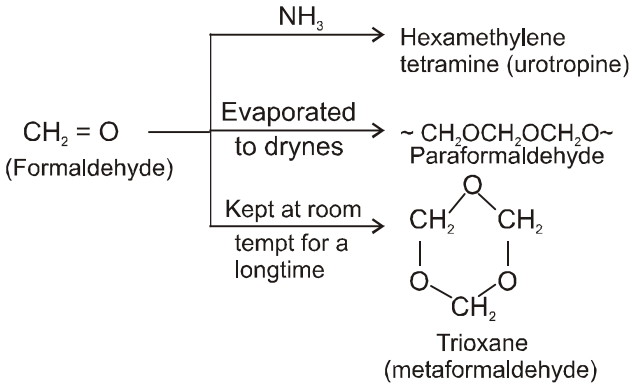
$$RCH=O + 2Cu^{2+} + 3OH^{\ominus} \longrightarrow RCOO^{\ominus} + 2Cu^{\oplus} + 2H_2O$$
(blue) (Red ppt.)

(d) Schiff's reagent :

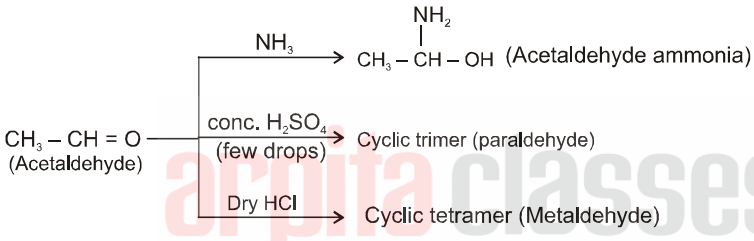
It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2. Aldehyde restores pink colour when treated with schiff's reagent (Magenta solution in H_2SO_3).

7.13 Other miscellaneous reactions :

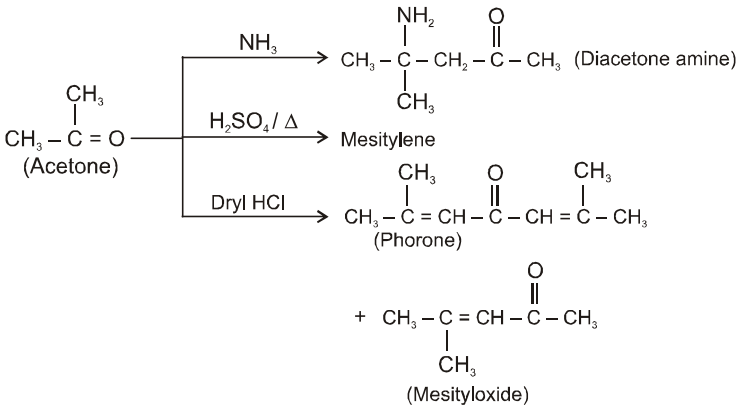
(I)



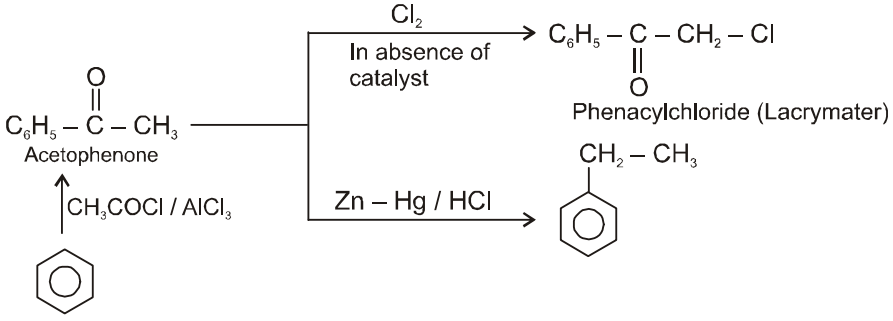
(II)



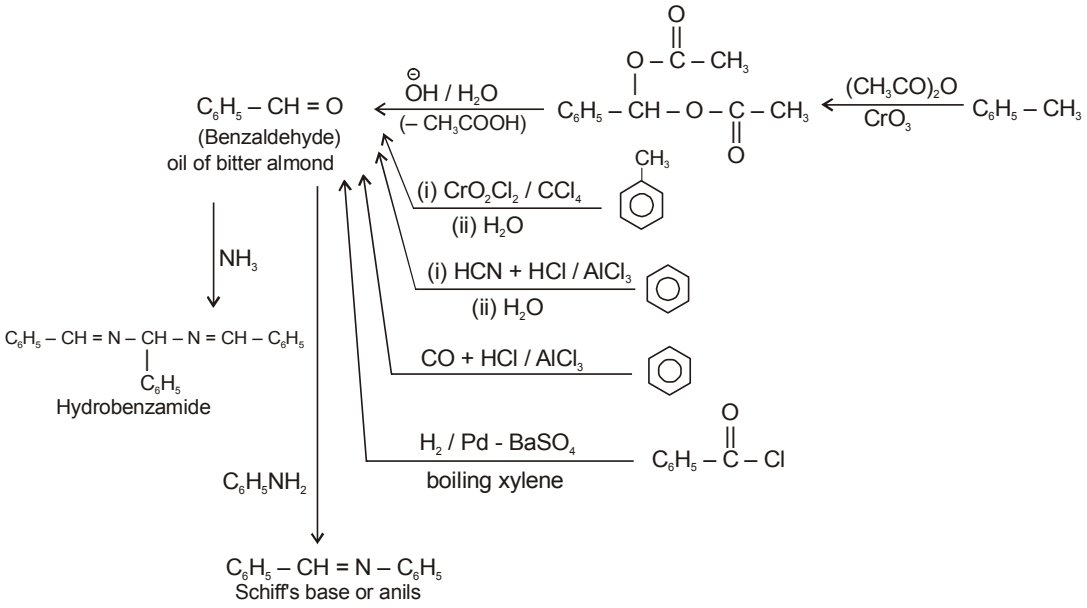
(III)



(IV)



(V)



8. Uses of Aldehydes and Ketones

- Act as solvents.
- Act as starting materials and reagents for the synthesis of other products.
- Formalin (40% solution of formaldehyde)- Used for preserving biological specimens, bakelite, urea , formaldehyde glues and other polymers products.
- Acetaldehyde used in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde used in perfumery and in dye industries.
- Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- Acetone and ethyl methyl ketone are common industrial solvents.

9. Grignard reagent

9.1 Introduction of Organometallic compounds :

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond.

For example C – M or $\overset{\ominus}{C}$ $\overset{\oplus}{M}$ (R-MgX, R_2CuLi, R_2Zn, RNa, RLi)

(Where C is a carbon atom of an organic molecule and M is a metal atom)

If the metal atom is attached to oxygen, nitrogen. sulphur, etc., then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.

RONa (Sodium alkoxide). CH_3COONa (Sodium acetate), CH_3COOAg (Silver acetate), RSK (Potassium mercaptide) RNHK (N-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc.

Note : It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

Most important examples of organometallic compound are **Grignard's reagents.** In Grignard's reagent, the carbon and magnesium atom are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.

C – $\overset{\oplus}{Mg}$ $\overset{\ominus}{X}$ (Functional part of a Grignard's reagent molecule)

Examples of Grignard's reagent :

1. Saturated Aliphatic Grignard's reagent

R – MgX (Alkylmagnesium halide)

CH_3 – MgI (Methylmagnesium iodide)

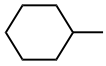
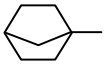
2. Unsaturated Aliphatic Grignard's reagent

(i) Alkenyl Grignard's reagent : $CH_2 = CH - CH_2 - MgX$ (Allylmagnesium halide)

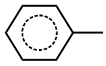
(ii) Alkynyl Grignard's reagent : $CH \equiv C - CH_2 - MgX$ (Propargylmagnesium halide)

(iii) CH≡C–MgBr (Ethyl magnesium bromide)

3. Alicyclic Grignard's reagent

 MgX (Cyclohexylmagnesium halide,  MgX

4. Aromatic Grignard's reagent

 MgX (Phenylmagnesium halide)

$C_6H_5CH_2MgCl$ (Benzylmagnesium halide)

9.2 Preparation :

$$RX + Mg \xrightarrow[\text{Ether}]{\text{Dry and pure}} RMgX$$

Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard's reagent (G.R.) by completing the octet on magnesium atom.

Process : To an etherial solution of alkyl halide Mg metal is added at very low temp. (0 – 5°C). A vigorous reaction takes place , and a solution of G.R. is obtained. It cannot be evaporated to get it in solid state because reaction will be explosive. It is stable only in solution state.

Reactivity order with respect to X (For preparation of RMgX)

$$R - X : R - I > \underbrace{R - Br}_{\text{Most commonly used}} > R - Cl > \underset{\downarrow}{R - F}$$

(No G.R. formation)

Iodides forms organometallic compounds at the fastest rate.

Structural stability of G.R.

If the alkyl part has more stable negative charge, then RMgX is more stable. It will be less reactive

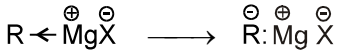
Ex. (1) CH_3–CH_2–MgX ; (2) CH_2=CH–MgX ; (3) $CH_3C\equiv C$–MgX

Reactivity order : 1 > 2 > 3

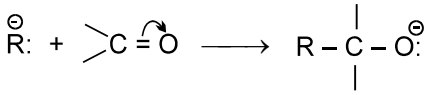
Stability order : 1 < 2 < 3

9.3 Reactivity of Grignard Reagent :

It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of Grignard's reagent. Therefore, there is a tendency of forming carbanion by heterolysis of this polar bond as follows.



If Grignard reagent is regarded as the attacking reagent, then the nucleophilic carbanion of Grignard's reagent will attack on the other compound taken as substrate.



Reactivity order of Grignard's reagent

On having same hydrocarbon radical, the order of reactivity of Grignard's reagent will be as follows :

* RMgI > RMgBr > RMgCl

Reactivity order with different alkyl part is

* RMgX : 3° > 2° > 1° > CH_3 > C=C > C≡C

Reactivity order with respect to different reactants (Substrate)

* Acidic hydrogen > – CHO > R – CO – R > R – COOR' > R – X

Note : Except X (halogen) all other functional groups must be absent in the alkyl group otherwise G.R. will be destroyed by internal reactions. [– NO_2, – CN must also be absent]

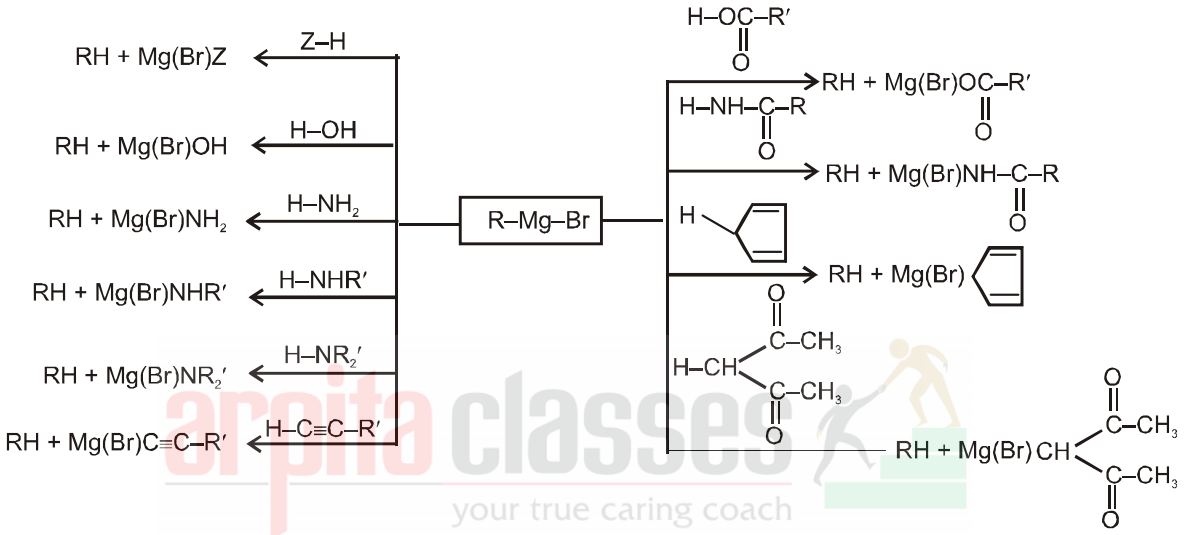
9.4 Chemical Reactions

(I) Reaction with acidic Hydrogen (H)

Compounds having reactive or acidic hydrogen gives acid base reaction.

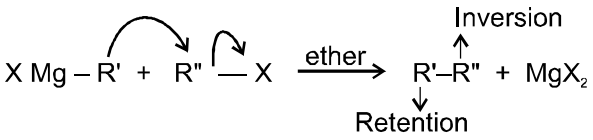
$$Z - H + R - MgX \longrightarrow R - H + Z - MgX$$

Example :



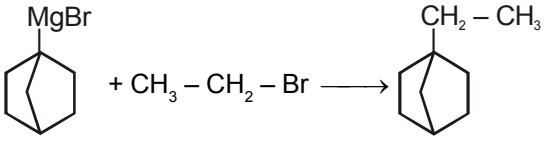
(II) Reaction with alkyl halide :

Coupling between a Grignard reagent and alkyl halide containing a reactive halogen atom can be effected directly ; this reaction is probably S_N^2.

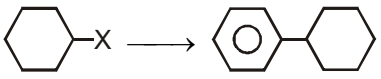


The yield is very good if R" is allyl, benzyl.

Ex.



Ex. Ph – MgX +

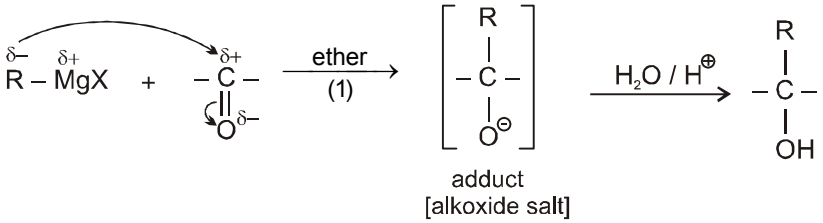


(III) Reactions involving addition on polar π-Bond (Nucleophilic Addition Reaction):-

Grignard's reagents form adducts by addition on the following type of π bonds.

$>C = O$, $>C = S$, $>C = N$ and $-C\equiv N$, $-N = O$, $>S = O$

Nucleophilic Addition Reaction With $>C=O$

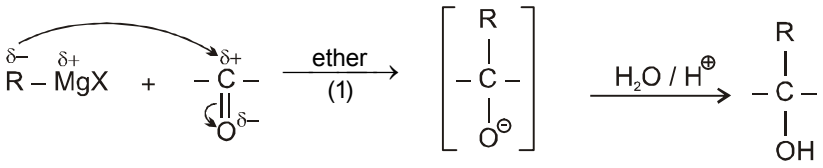


adduct
[alkoxide salt]

Reactivity order : HCHO > RCHO > RCOR
RCHO > ArCHO
RCOR > RCOAr > ArCOAr

(i). E.R.G at >C=O decreases rate
(ii) Crowding of R Group at >C=O decreasing rate

Ex.



adduct
[alkoxide salt]

(a) $R-MgX + HCHO \xrightarrow[(1)]{\text{ether}} R-CH_2-OMgX \xrightarrow{H_2O/H^{\oplus}} R-CH_2-OH$ (1° Alcohol)

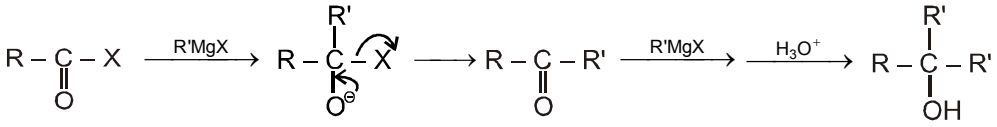
(b) $R-MgX + RCHO \xrightarrow[(1)]{\text{ether}} R-CH(R')-OH$ (2° Alcohol)

(c) $R-MgX + RCOR' \xrightarrow[(1)]{\text{ether}} R-C(R')(R'')-OMgX \xrightarrow{HOH} R-C(R')(R'')-OH$ (3° Alcohol)

(IV) S_N2 Th (Substitution nucleophilic bimolecular with tetrahedral intermediate)

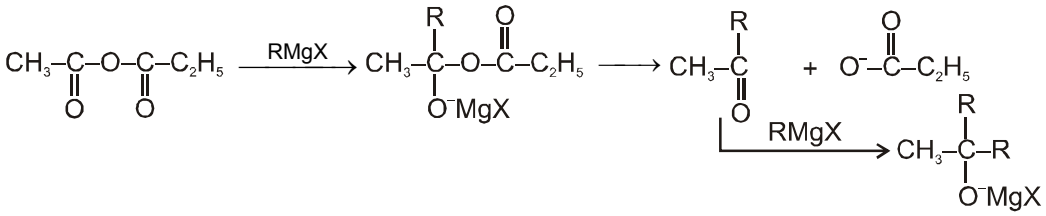
Acid derivatives gives S_N2Th reaction with grignard reagent.

(i) Reaction with $R-\overset{\overset{O}{\|}}{C}-X$ **(Acid halide)**



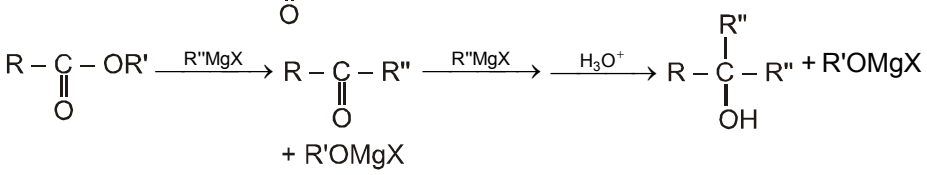
(ii) Reaction with $R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$ **(anhydride)**

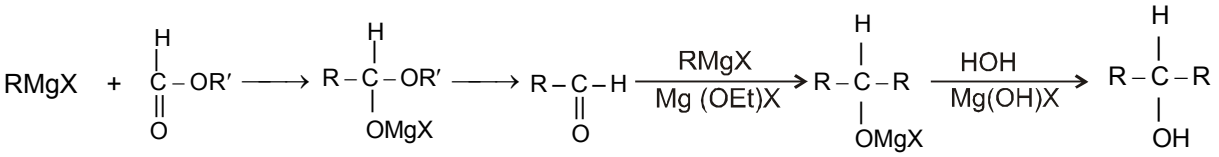
Ex.



(iii) Reaction with $R-\underset{\underset{O}{\|}}{C}-OR'$ **(Ester)**

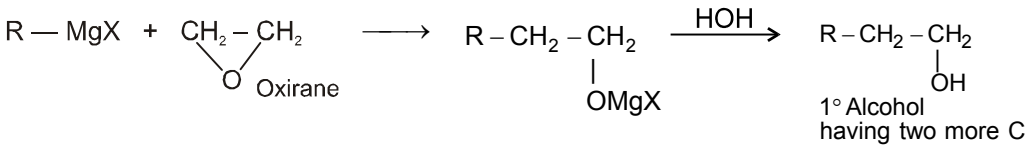
Ex



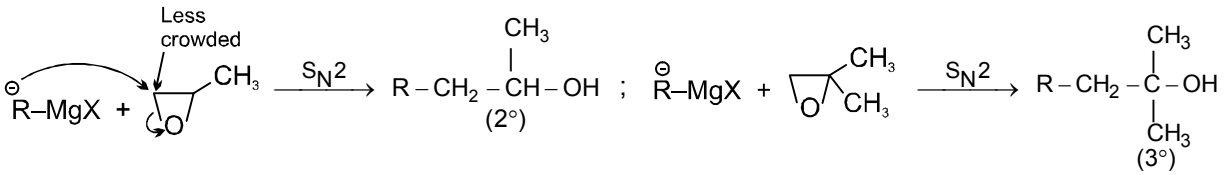


Various alcohols can be prepared by changing R in the above synthesis.

(V) Reaction with Epoxides



Ex.



(VI) Reaction with Oxygen

$$R-MgX + O=O \longrightarrow R-O-O-MgX$$

$$R-O-O-MgX + R-MgX \longrightarrow 2R-O-MgX$$

$$R-O-MgX + HOH \longrightarrow R-O-H + Mg(OH)X$$

Primary, secondary and tertiary alcohols can be obtained by above reaction.

Phenol is obtained on hydrolysis of the product obtained by reaction of arylmagnesium bromide with oxygen.

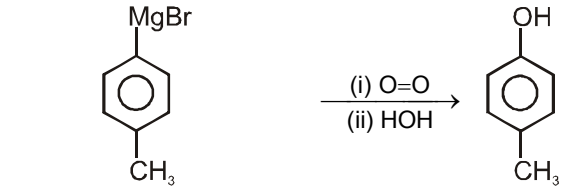
$$C_6H_5MgBr + O=O \longrightarrow C_6H_5O-OMgBr$$

$$C_6H_5O-OMgBr + C_6H_5MgBr \longrightarrow 2C_6H_5-OMgBr$$

$$C_6H_5-OMgBr + H_2O \longrightarrow C_6H_5-OH + Mg(OH)Br$$

Other phenols can be prepared by taking any aryl (Ar) group in place of phenyl group.

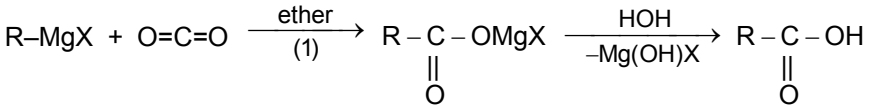
For example, on taking p-toluenemagnesium bromide p-cresol is formed.



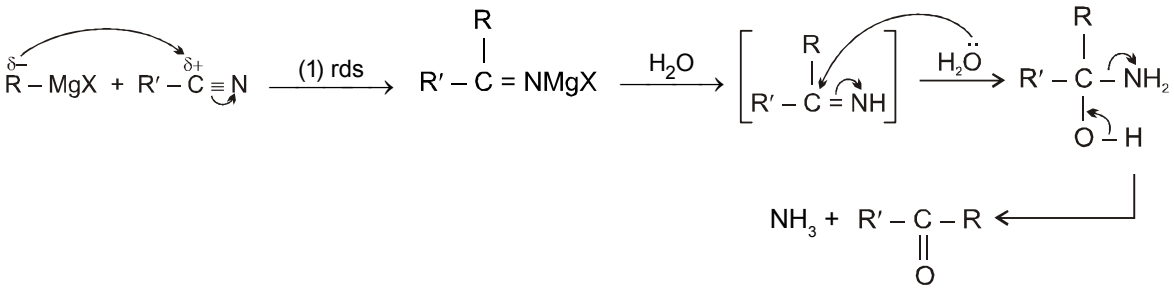
(p-Toluenemagnesium bromide) (p-Cresol)

(VI) Reaction with CO_2 (Synthesis of carboxylic acids)

A carboxylic acid is formed on hydrolysis of the adduct formed by passing carbon dioxide in the etherial solution of a Grignard's reagent.



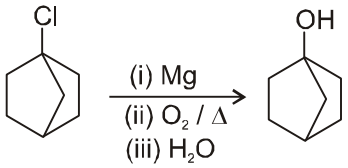
(VIII) Reaction with R – C ≡ N



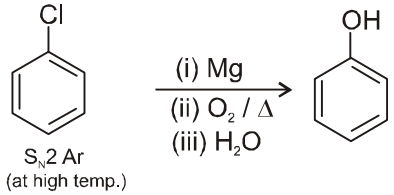
Applications :

G.R. is used to prepare alcohols or phenol from those alkyl halides / aryl halides which do not give normal S_N reactions

Ex. (i)



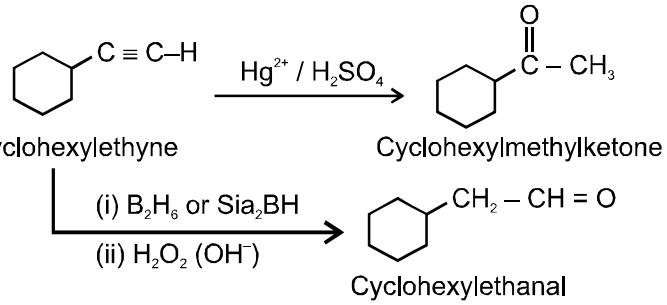
(ii)



MISCELLANEOUS SOLVED PROBLEMS

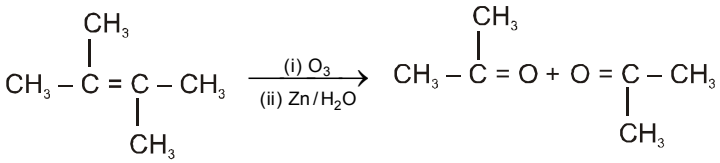
1. What will be hydration and hydroboration product for Cyclohexylethyne.

Sol.

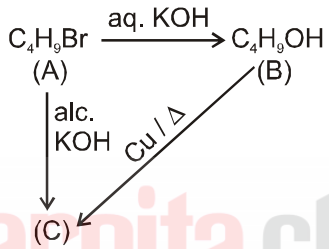


2. Which hydrocarbon on ozonolysis gives acetone only ?

Sol. Acetone only, means two moles of acetone.

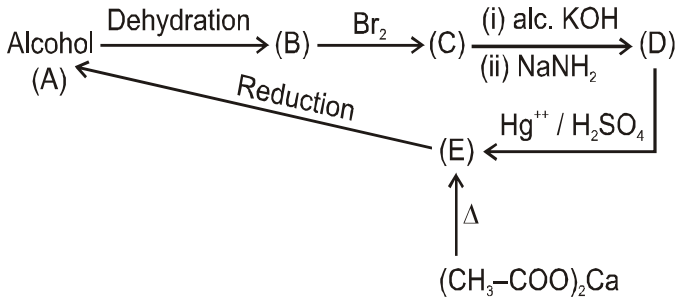


3. Predict the structure of (A) in the following sequence :

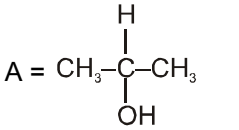


Sol. Since (B) is alcohol and (C) is alkene hence (B) is 3° alcohol only according to question (It is known that alkene can only be obtained from 3° alcohol when heated with copper). Thus structure of (B) is $(CH_3)_3C–OH$ and its corresponding. alkyl bromide will be $(CH_3)_3C–Br$ (tertiarybutylbromide)

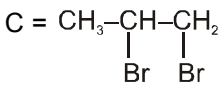
4. Find out unknown in following reactions.



Sol. Since E is obtained on dry distillation of calcium salt of acetic acid hence E will be $CH_3–\overset{\overset{O}{\|}}{C}–CH_3$. Thus other unknowns are



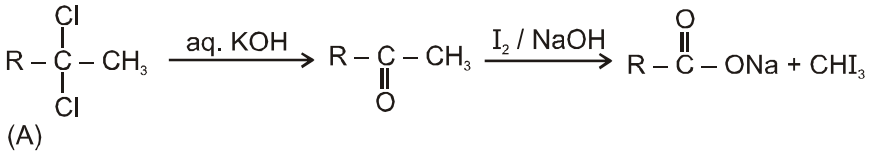
$B = CH_3 – CH = CH_2$



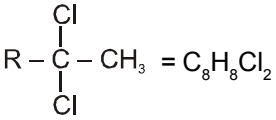
$D = CH_3 – C \equiv C – H$

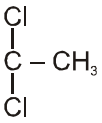
5. What will be structure of aromatic $C_8H_8Cl_2$ (A), which on aqueous alkalihydrolysis gives product (B). (B) gives positive iodoform test.

Sol. Since (B) is showing iodoform test hence it will be methylketone only as it is obtained on aqueous alkali hydrolysis of (A) which will be non-terminal gem dihalides as –

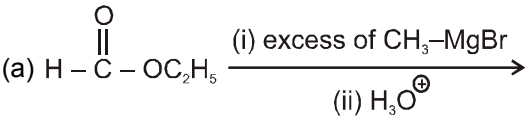


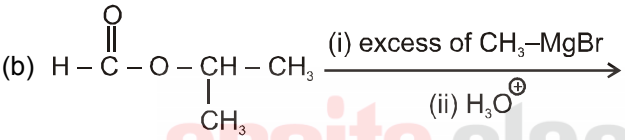
Now unknown 'R' can be known as :

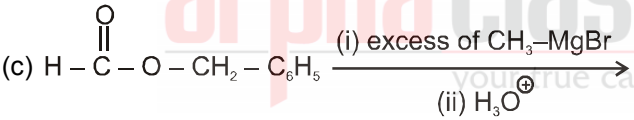


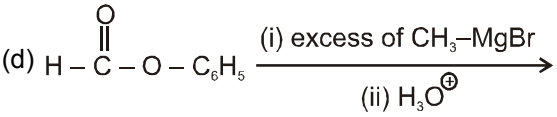
$R = C_8H_8Cl_2 - C_2H_3Cl_2 = C_6H_5$ Hence 'A' is 

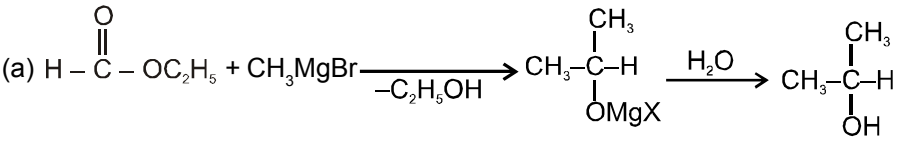
6. Write the products of the following reactions.

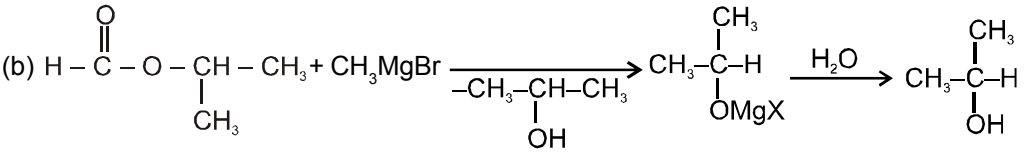


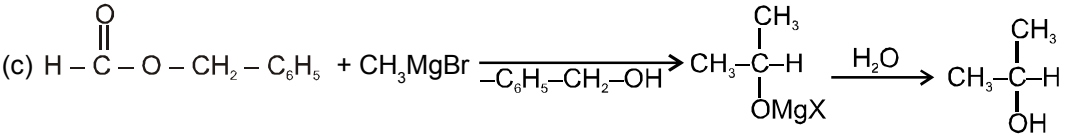


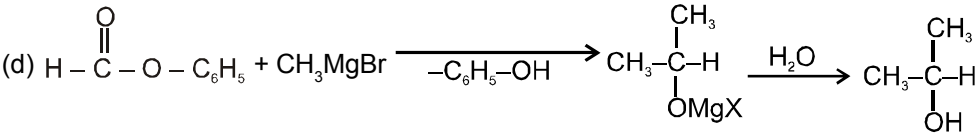




Sol. (a) 

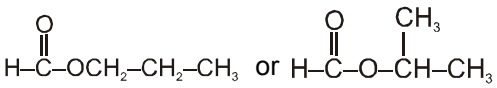
(b) 

(c) 

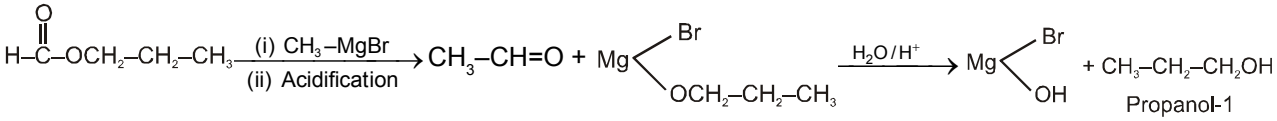
(d) 

7. What will be structure of $C_4H_8O_2$ which on treating with excess CH_3–MgBr followed by acidification gives sole alcohol (A). (A) on treating with sodium hypoiodite solution gives positive iodoform test.

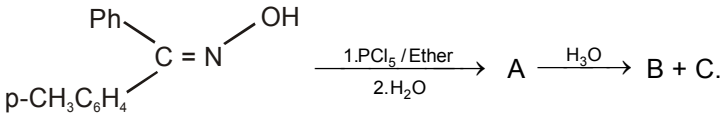
Sol. Since (A) gives positively iodoform test hence it will be alkanol-2. 2º alcohol can be obtained only when alkylformate is treated with Grignard's reagent via aldehyde where alkyl part is alkyl part of Grignard's reagent. As Grignard's reagent is CH_3–MgBr hence 2º alcohol will be $CH_3–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}–OH$ (propanol-2). Thus $C_4H_8O_2$ is either



Reactions :



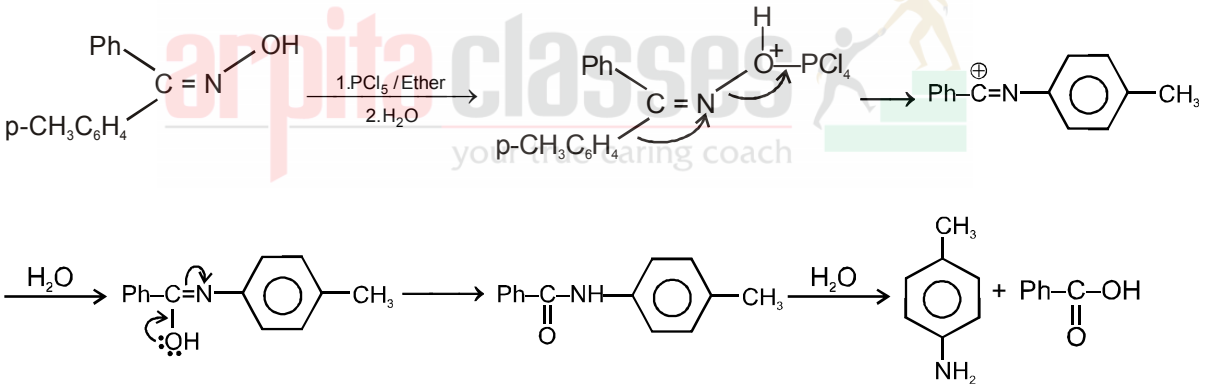
Here we get two alcohols propanol-2 and propanol-1. Alkyl part of formic acid ester which gives propanol-2 will be isopropyl only. Thus structure of $C_4H_8O_2$ is $H-\overset{\displaystyle O}{\overset{\|}{C}}-OCH(CH_3)_2$

8. 

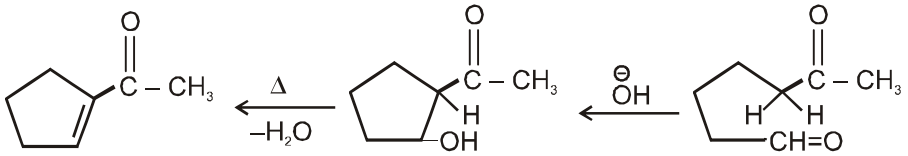
A , B , C are

(A) PhCONH-p - $CH_3C_6H_4$ (B) PhCOOH (C) p$CH_3C_6H_4NH_2$ (D) PhCHO

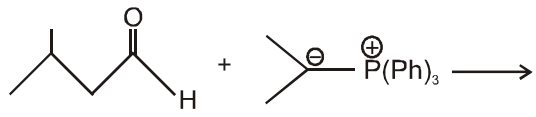
Sol. (A,B,C)

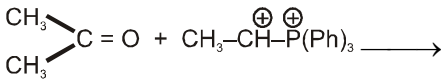


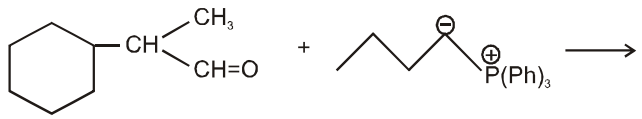
9. Which carbonyl compound on heated with dilute alkali gives 1- acetylcyclopentene.

Sol. 

10. Predict the product for the followings :

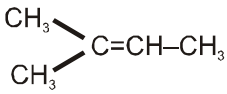
(i) 

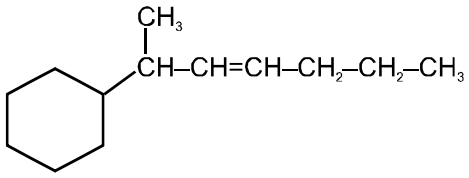
(ii) 

(iii) 

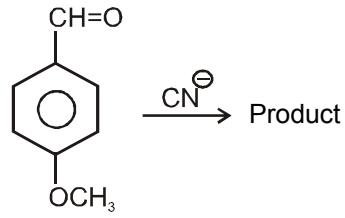
Sol. Witting reaction

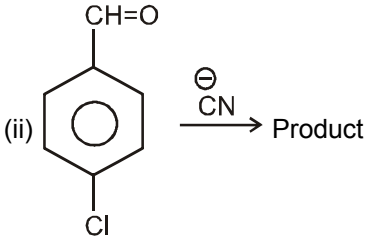
(i) 

(ii) 

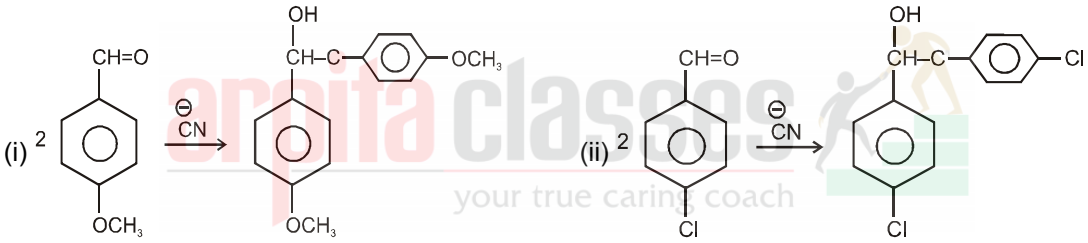
(iii) 

11. Predict Product –

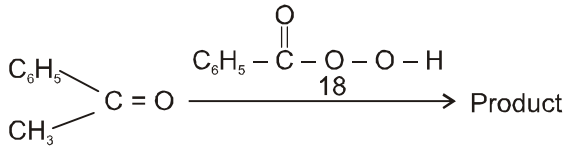
(i) 

(ii) 

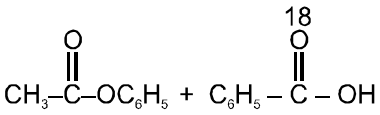
Sol. Benzoin condensation reaction

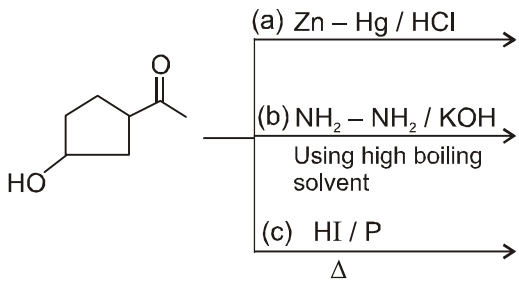


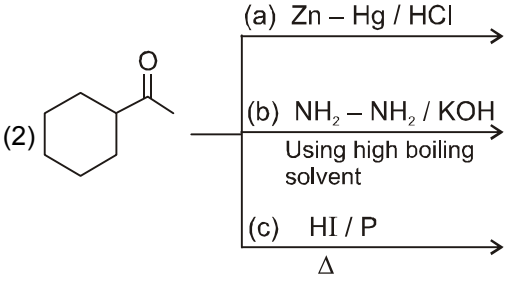
12. Predict product for the following

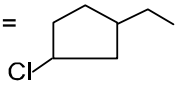


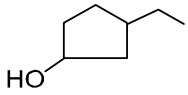
Sol. Baeyer-villiger oxidation

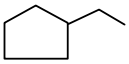


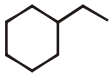
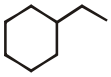
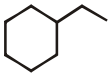
13. (1) 

(2) 

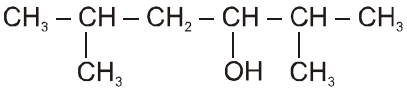
Sol. **(1)** (a) = 

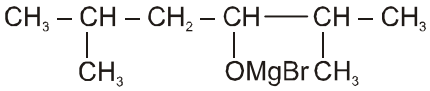
(b) = 

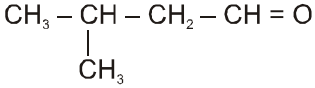
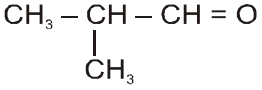
(c) = 

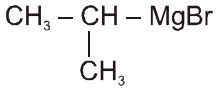
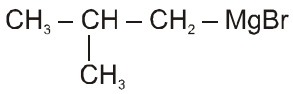
(2) (a) = 
(b) = 
(c) = 

14. (A) on treating with (B) in the presence of dry ether gives (C) which on acids hydrolysis gives (D). (D) on oxidation gives 2,5-dimethylhexan-3-one.

Sol. By knowning structure of given product (D) will be  hence (C) will be

 and finaly A & B will have following two structures.

A =  or A = 

B =  or B = 

Board Level Exercise

Type (I) : Very Short Answer Type Questions : **[01 Mark Each]**

1. Write the structure of 4-Oxopentanal?

2. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions. Ethanal, Propanal, Propanone, Butanone.

3. Arrange the following compounds in increasing order of their reactivity with HCN : Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone.

4. Arrange the following compounds in increasing order of their boiling points. CH_3CHO, CH_3CH_2OH, CH_3COCH_3, $CH_3CH_2CH_3$

5. How will you distinguish between Propanal and Propanone?

6. How will you distinguish between Benzoic acid and Ethyl benzoate?

7. How will you distinguish between Ethanal and Propanal?

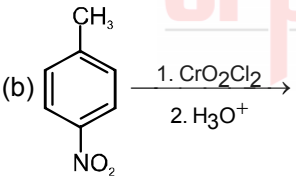
Type (II) : Short Answer Type Questions : **[02 Marks Each]**

8. Show how each of the following compounds can be converted to benzoic acid?
(i) Bromobenzene **(ii)** Phenylethene (Styrene)

9. How Semicarbazone are synthesis by carbonyl compound?

10. What is meant by the following terms? Give an example of the reaction in each case?
(i) 2,4-DNP-derivative **(ii)** Schiff's base

11. Write the structures of products of the following reactions :
(a) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

(b) 

Type (III) : Long Answer Type Questions: **[03 Marks Each]**

12. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.
(i) PhMgBr and then H_3O^+ **(ii)** Tollen's reagent
(iii) Zinc amalgam and dilute hydrochloric acid

13. How will you convert ethanal into the following compounds?
(i) Butane-1, 3-diol **(ii)** But-2-enal **(iii)** But-2-enoic acid

14. Write short note on Cannizzaro reaction ?

Type (IV) : Very Long Answer Type Questions: **[05 Marks Each]**

15. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

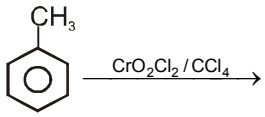
Section (A) : Preparation of Carbonyl Compounds

A-1. Write the products of following reactions

(a) $2CH_3COOH \xrightarrow{MnO,\ \Delta}$

(b) $PhCN + CH_3MgBr \xrightarrow{Ether} \xrightarrow{H_2O}$

(c) $CH_3-\underset{CH_3}{\overset{}{C}}=\underset{CH_3}{\overset{}{C}}-CH_3 \xrightarrow{O_3/Zn}$

(d)  $\xrightarrow{CrO_2Cl_2/CCl_4}$

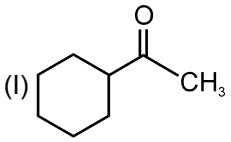
Section (B) : Nucleophilic addition reactions

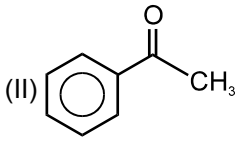
B-1. Why aldehydes are more reactive than ketones (among isomers) towards nucleophilic addition reaction.

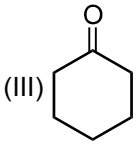
B-2. Arrange the following compounds in decreasing order of rate of nucleophilic addition with RMgBr.

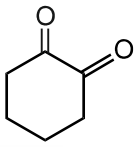
(I) $Ph–CO–CH_3$ (II) $Ph–CHO$ (III) CH_3CHO (IV) CCl_3CHO

B-3. Arrange the following compounds in decreasing orders of nucleophilic addition with semicarbazide $NH_2NHCONH_2$ i.e., $\ddot{N}H_2-\ddot{Z}:$

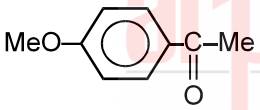
(I) 

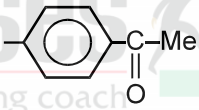
(II) 

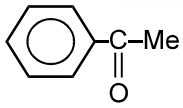
(III) 

(IV) 

B-4. Arrange the following compounds in decreasing order of rate of addition of HCN.

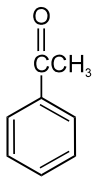
(a) 

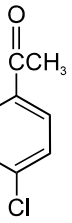
(b) 

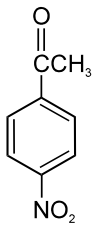
(c) 

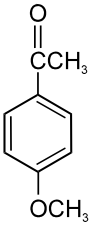
(d) CH_3CHO

B-5. Arrange the following compounds in decreasing orders of K_{eq} for hydrate formation.

(a) 

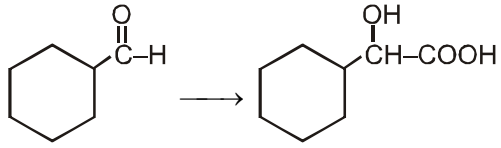
(b) 

(c) 

(d) 

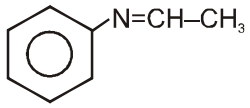
B-6. Show how you would do the following conversions ?

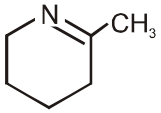
(a) Acetophenone $\longrightarrow$ Acetophenone cyanohydrin

(b) 

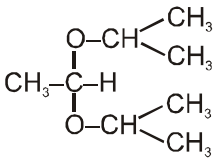
B-7. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not. Explain why ?

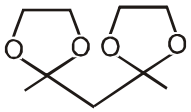
B-8. Give the structure of the carbonyl compound and amine used to form the following imines.

(a) 

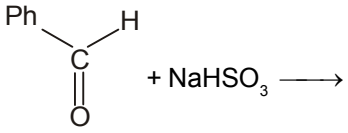
(b) 

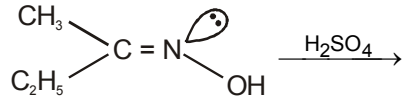
B-9. Show which alcohol and carbonyl compound react to give each of the following product.

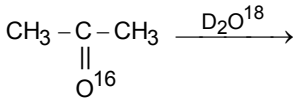
(a) 

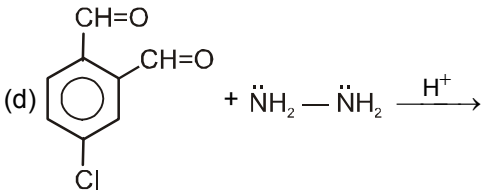
(b) 

B-10. Write the product of following reaction :

(a) 

(b) 

(c) 

(d) 

Section (C) : Condensation reactions

C-1. Predict the product of following aldol condensation reaction :

(a) $CH_3–CH_2–CHO \xrightarrow{OH^- / \Delta}$

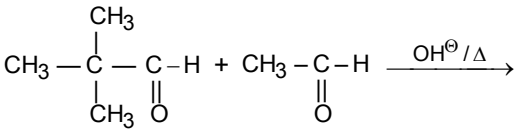
(b) $Ph–CH_2–CHO \xrightarrow{OH^- / \Delta}$

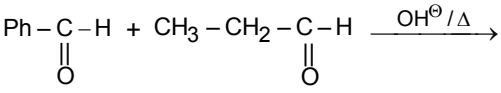
(c) $Ph–CO–CH_3 \xrightarrow{OH^- / \Delta}$

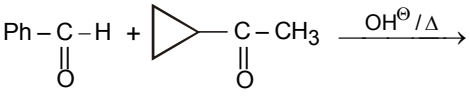
C-2. Indicate the starting aldehyde or ketone from which each of the following compounds are formed by an aldol condensation reaction.
(a) 2–Ethyl – 3–hydroxy hexanal ; (b) 4–Hydroxy–4–methyl–2–pentanone

C-3. When acetone is treated with excess of benzaldehyde in the presence of base, the crossed condensation add two equivalents of benzaldehyde and expels two equivalent of water and forms [X]. Identify the structure of [X] when [X] reacts with NH_2OH how many stereoisomers are formed.

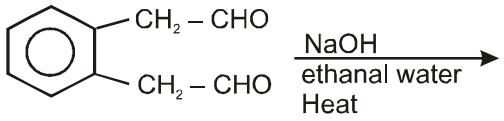
C-4. Predict the products of following cross condensation reaction,

(a) 

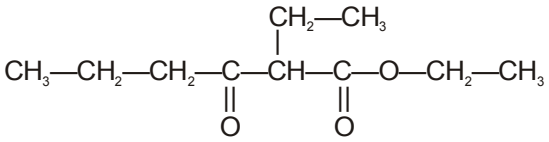
(b) 

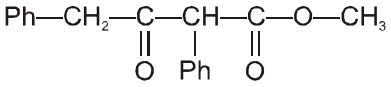
(c) 

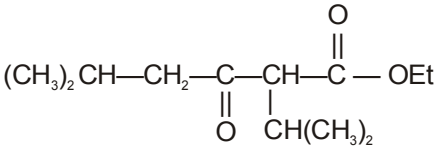
C-5. What is the principal product of the follwoing reaction ?



C-6. Show which esters would undergo claisen condensation to give the following β–ketoester.

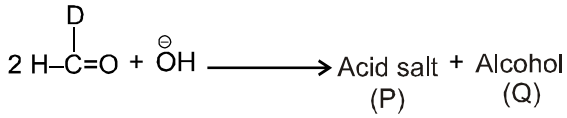
(a) 

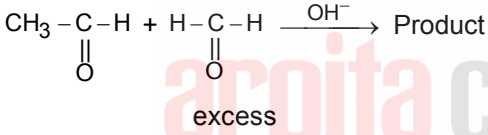
(b) 

(c) 

Section (D) : Cannizzaro's reactions

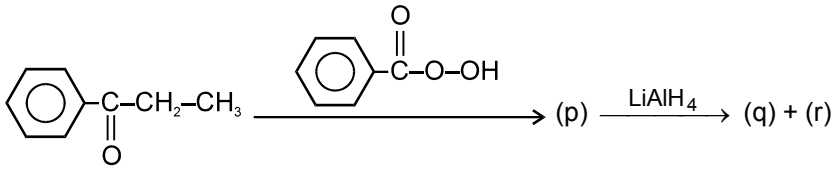
D-1. Identify the products in the following disproportionation reaction and also mention rate determining step.

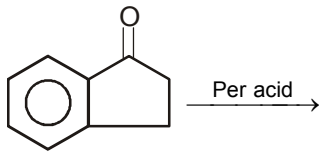


D-2. 

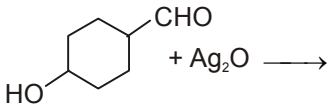
Section (E) : Redox reactions

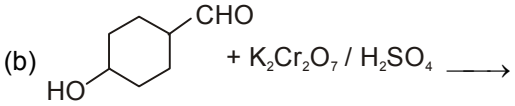
E-1. Write the product of following reaction,

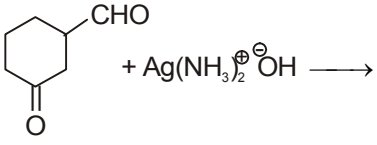
(a) 

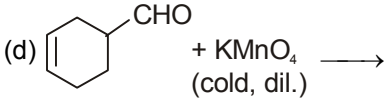
(b) 

E-2. Write the product of following reaction :

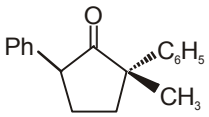
(a) 

(b) 

(c) 

(d) 

Section (F) : α-Halogenation, haloform, α-deuteration reactions

F-1.  $\xrightarrow{Br_2 / OH^{\ominus}}$ Products and mention stereochemical relation

F-2. Write the product of following reaction,

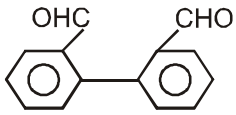
(a) $CH_3–CH_2–OH \xrightarrow{I_2 / KOH}$

(b) $Ph–CH_2–CO–CH_3 \xrightarrow{I_2 / KOH}$

(c) $(Me)_3C–CO–CH_3 \xrightarrow{I_2 / KOH}$

Section (G) : Miscellanious reactions

G-1. $CH_3I + Ph_3P \longrightarrow \xrightarrow[\text{benzene}]{CH_3CH_2CH_2CH_2–Li} \xrightarrow{Ph_2C=O}$

G-2.  $\xrightarrow{Al(OEt)_3}$ Product.

G-3. Compound (X) with molecular formula $C_9H_{10}O$ forms a semicarbazone and gives negative Tollen's and Iodoform tests. Upon reduction it gives n-propyl benzene. Deduce the structure of X.

Section (H) : GRIGNARD REAGENT

H-1. Which of the following compounds are suitable solvents for Grignard reagent ?

(a) n-Hexane (b) $C_2H_5 – O – C_2H_5$ (c) $CHCl_3$

(d) Cyclohexane (e) Benzene (f) $CH_3 – O – CH_2 – CH_2 – O – CH_3$

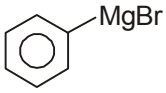
(g)  THF

(h)  1, 4-dioxane

H-2. Predict the product of the following reactions

(a) Methylmagnesium iodide + $D_2O \longrightarrow$?

(b) Isobutylmagnesium iodide + Phenylacetylene $\longrightarrow$?

(c)  + $DOCH_3 \longrightarrow$

H-3. Give the reaction of C_2H_5MgBr with 2-butanone followed by acid hydrolysis.

H-4. Bring about the following conversions

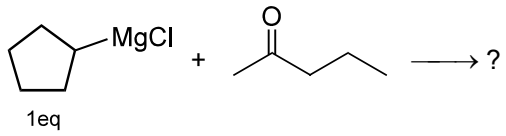
(i) Acetone to 2-Methylpropane -2-ol.

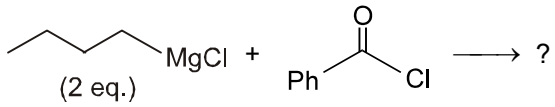
(ii) Ethyl magnesium chloride to propane-1-ol.

H-5. Predict the structure of X and Y.

$X \xrightarrow[THF]{Mg} CH_2 = CH – MgBr \xrightarrow{Y}$ propene.

H-6. Draw the organic products you would expect to obtained from the following reactions (after hydrolysis).

(a) 

(b) 

(c) CH_3MgBr (excess) + H–COOPh $\xrightarrow[(2)H_3O+]{(1)\ Ether}$

PART - II : OBJECTIVE QUESTIONS

*** Marked Questions are having more than one correct option.**

Section (A) : Preparation of Carbonyl Compounds

A-1. On heating calcium propionate, the product formed is

(A) 3-Pentanone (B) 2-Pentanone
(C) 3-Methyl-2-butanone (D) Propanone

A-2. A mixed salt of calcium acetate formate on dry distillation gives

(A) ethanal (B) methanal (C) propanone (D) All the three above.

A-3. Acetic acid when heated (300°C) with MnO gives

(A) formaldehyde (B) acetaldehyde (C) acetone (D) butaone

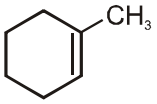
A-4. In which of the following reaction ketone is formed :

(A) $CH_3–CH_2–OH \xrightarrow{KMnO_4/H^{\oplus}}$ (B) $CH_3–CH_2–OH \xrightarrow{Cu/\Delta}$

(C) $CH_3–\underset{\displaystyle CH_3}{\overset{}{CH}}–OH \xrightarrow{Cu/\Delta}$ (D) $CH_3–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}–OH \xrightarrow{Cu/\Delta}$

A-5. Ethylidene chloride on treatment with aq. KOH gives

(A) CH_3CHO (B) $CH_2OH.CH_2OH$ (C) HCHO (D) CHO. CHO

A-6. 

On reductive ozonolysis yields

(A) 6-oxoheptanal (B) 6-oxoheptanoic acid
(C) 6-hydroxyheptanal (D) 3-hydroxypentanal

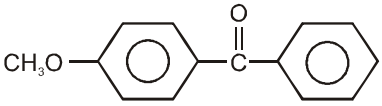
Section (B) : Nucleophilic addition reactions

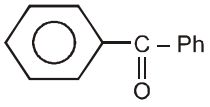
B-1. Arrange the following compounds in decreasing orders of rate of exchange of O^{18} with H_2O^{18}

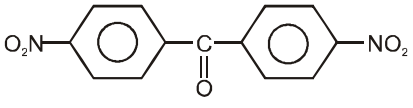
(X) CCl_3CHO (Y) CH_3CHO (Z) CH_3COCH_3 (W) CF_3CHO

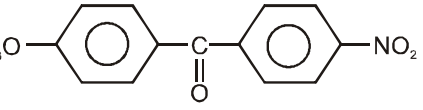
(A) W > Z > X > Y (B) W > X > Y > Z (C) W > Y > Z > X (D) W > Z > Y > X

B-2. Which of the following compound has the largest equilibrium constant for the addition of water ?

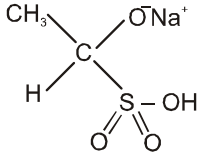
(A) 

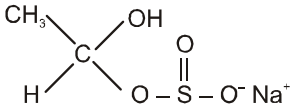
(B) 

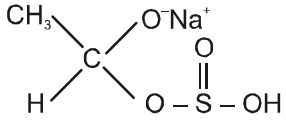
(C) 

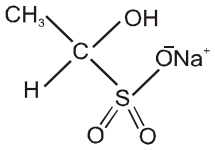
(D) 

B-3. Acetaldehyde on reaction with sodium hydrogen sulphite produces

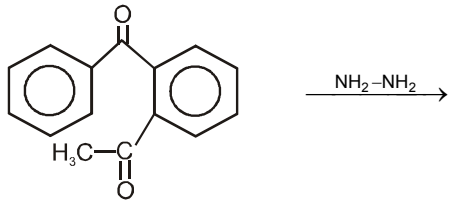
(A) 

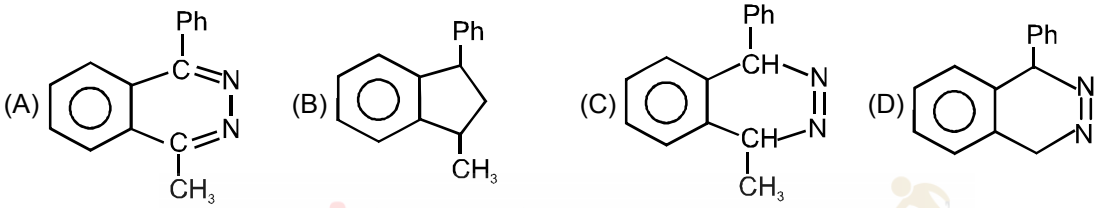
(B) 

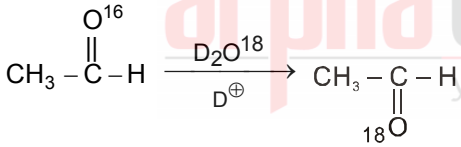
(C) 

(D) 

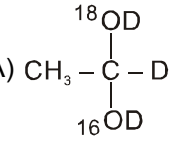
B-4. Write the product of following reaction :

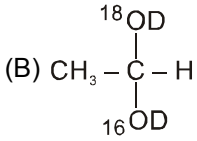


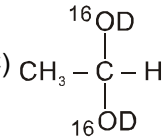


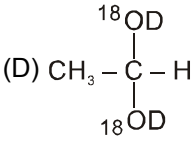
B-5. 

The intermediate is :

(A) 

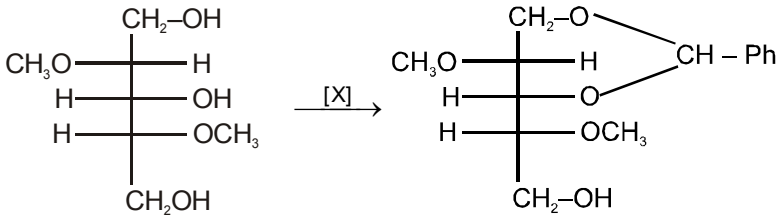
(B) 

(C) 

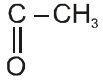
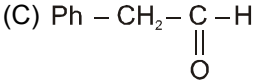
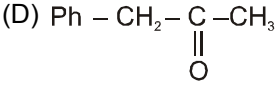
(D) 

B-6. Aromatic carbonyl compounds having molecular formula C_8H_8O react with NH_2OH how many oximes can be formed :

(A) 8 (B) 10 (C) 12 (D) 6

B-7. 

Compound (X) in the above reaction.

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

B-8. The correct order of reactivity of PhMgBr with following compounds will be.

$(C_6H_5)_2CO$, $CH_3 - CH = O$, $(CH_3)_2 C = O$

(1) (2) (3)

(A) 1 > 2 > 3 (B) 2 > 3 > 1 (C) 3 > 2 > 1 (D) 1 > 3 > 2

B-9. The cyanohydrin of a carbonyl compound on hydrolysis gives lactic acid. The carbonyl compound is

(A) HCHO (B) CH_3CHO (C) CH_3COCH_3 (D) $CH_3COCH_2CH_3$

Section (C) : Condensation reactions

C-1. Which of the following will not undergo aldol condensation ?

(A) CH_3CHO (B) CH_3CH_2CHO (C) CD_3CHO (D) PhCHO

C-2. (X) is the product of cross aldol condensation between benzaldehyde (C_6H_5CHO) and acetone What is its structure ?

(A) $C_6H_5–CH=CH–\overset{\overset{O}{\|}}{C}–CH_3$ (B) $C_6H_5–CH=C–(CH_3)_2$

(C) $C_6H_5–CO–CH_2–C=(CH_3)_2$ (D) None of these

C-3. In which of the following compounds the methylene hydrogens are the most acidic ?

(A) $CH_3COCH_2CH_3$ (B) $CH_3CH_2COOC_2H_5$ (C) $CH_3CH_2CH(COOC_2H_5)_2$ (D) CH_3COCH_2CN.

C-4. $PhCHO + (CH_3CO)_2O \xrightarrow[(2)\text{hydrolysis},\Delta]{(1)CH_3COONa} A \xrightarrow{HBr} B$

The product B is :

(A) $PhCH = CHCH_2Br$ (B) $\underset{\underset{Br}{|}}{PhCH} – CH_2– COOH$ (C) $PhCH_2 CH(Br) COOH$ (D) $PhCH = CH – COBr$

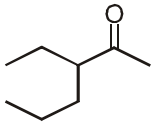
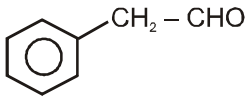
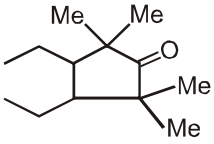
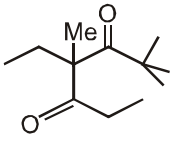
C-5. In the given reaction the product is :

$$CH_3–CH_2–\overset{\overset{O}{\|}}{C}–OCH_3 + CH_3–\overset{\overset{O}{\|}}{C}–OCH_3 \xrightarrow[(2)\ CH_3OH]{(1)\ CH_3O^{\ominus}\ Na^{+}} \xrightarrow[\Delta]{H_2O}$$

(A) $CH_3–CH_2–\overset{\overset{O}{\|}}{C}–CH_2–\overset{\overset{O}{\|}}{C}–OCH_3$ (B) $CH_3–\overset{\overset{O}{\|}}{C}–\underset{\underset{CH_3}{|}}{CH}–COOCH_3$

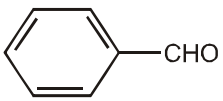
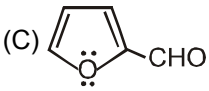
(C) $H–\overset{\overset{O}{\|}}{C}–CH_2–\underset{\underset{CH_3}{|}}{CH}–COOCH_3$ (D) $CH_3 – \overset{\overset{O}{\|}}{C} – CH_2 – CH_3$

C-6.* The compounds that undergo Aldol condensation is :

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

Section (D) : Cannizzaro's reactions

D-1. Cannizzaro reaction does not take place with

(A) $(CH_3)_3CCHO$. (B)  (C)  (D) CH_3CHO.

D-2. In the reaction, $(CH_3)_3CCHO + HCHO \xrightarrow[\text{heat}]{NaOH} A + B.$

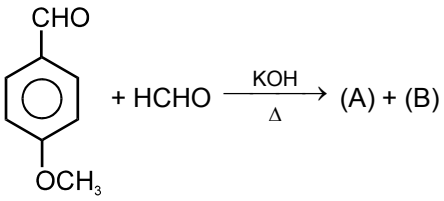
the products (A) and (B) are respectively :

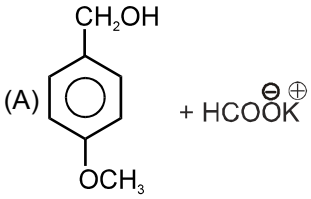
(A) $(CH_3)_3CCH_2OH$ and $HCOO^- Na^+$.

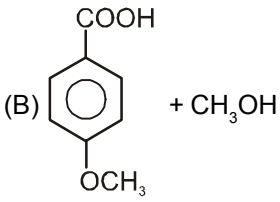
(B) $(CH_3)_3CCOONa$ and CH_3OH.

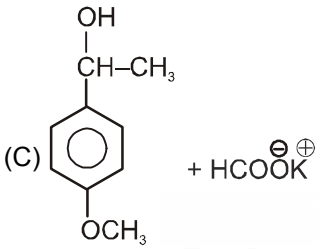
(C) $(CH_3)_3CCH_2OH$ and CH_3OH.

(D) $(CH_3)_3COONa$ and $HCOO^- Na^+$.

D-3. 

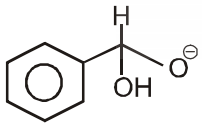
(A) 

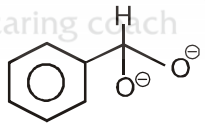
(B) 

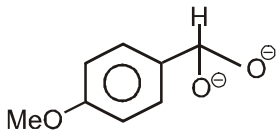
(C) 

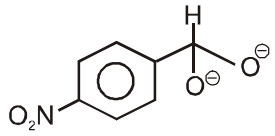
(D) Both (A) and (B),

D-4. In the cannizzaro's reaction the intermediate that will be the best hydride donar ?

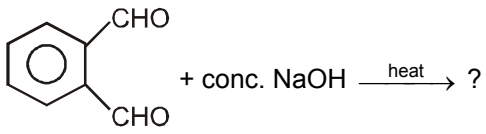
(A) 

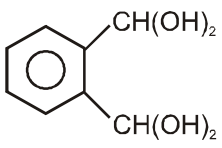
(B) 

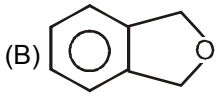
(C) 

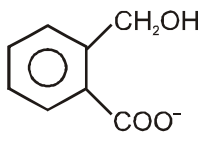
(D) 

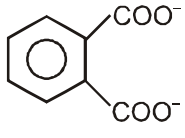
D-5. Product of following reaction is

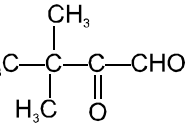


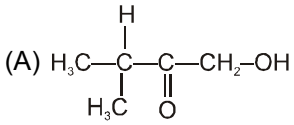
(A) 

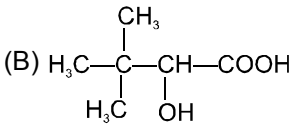
(B) 

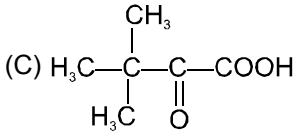
(C) 

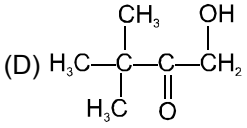
(D) 

D-6. In the given reaction  Product is

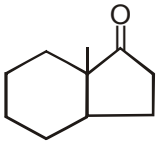
(A) 

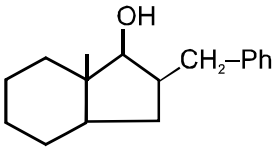
(B) 

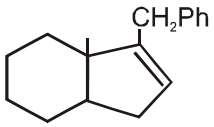
(C) 

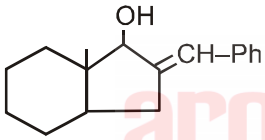
(D) 

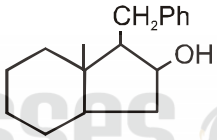
Section (E) : Redox reactions

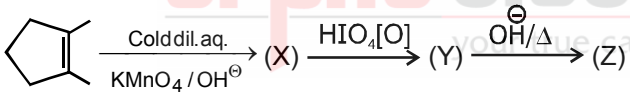
E-1.  [X], Product (X) in this reaction is :

(A) 

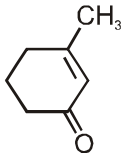
(B) 

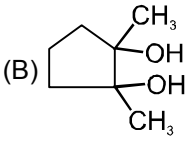
(C) 

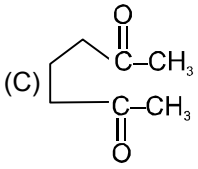
(D) 

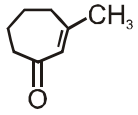
E-2.* 

The products of the above reaction is / are :

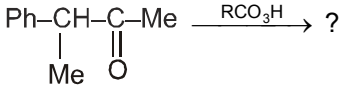
(A) 

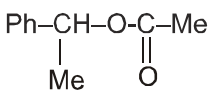
(B) 

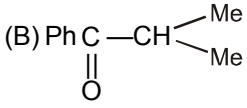
(C) 

(D) 

E-3. What will be the product of the following reaction



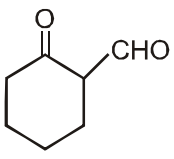
(A) 

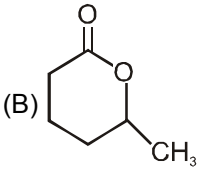
(B) 

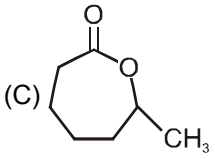
(C) PhCH(Me)OCOOMe

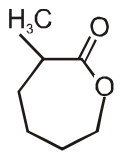
(D) None of these

E-4. 2-Methyhlcyclohexanone is allowed to react with metachloroperbenzoic acid. The major product in the reaction is

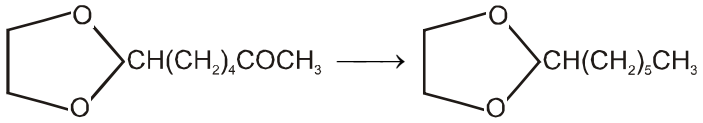
(A) 

(B) 

(C) 

(D) 

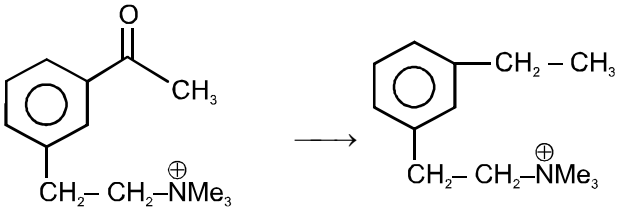
E-5. In the following conversion



Which of the following regents is suitable ?

(A) NH_2NH_2,KOH, DMSO (B) $NaBH_4$ (C) Zn-Hg, concentrated H_2SO_4 (D) $LiAlH_4$

E-6.



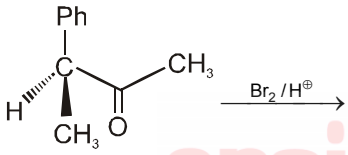
Above conversion can be achieved by

(A) NH_2–NH_2/ NaOH (B) Zn–Hg/HCl

(C) $LiAlH_4$ (D) $NaBH_4$.

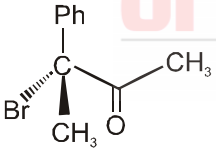
Section (F) : α-Halogenation, haloform, α-deuteration reactions

F-1.

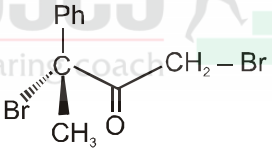


Major Product is :

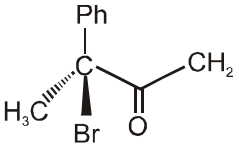
(A)



(B)

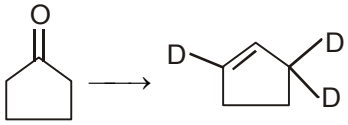


(C)



(D) A and C both

F-2.

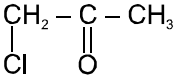


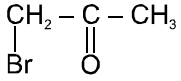
The above conversion is carried out

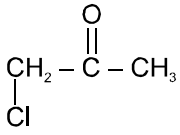
(A) KOD /D_2O, $H^{\oplus}/\Delta$, $LiAlH_4$ (B) $H^{\oplus}/\Delta$ / KOD, D_2O, $LiAlH_4$

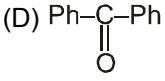
(C) KOD/ D_2O, $LiAlH_4$, $H^{\oplus}/\Delta$ (D) $LiAlH_4$, $H^{\oplus}\Delta$,KOD/H_2O

F-3.* Which of the following gives haloform reaction

(A) 

(B) 

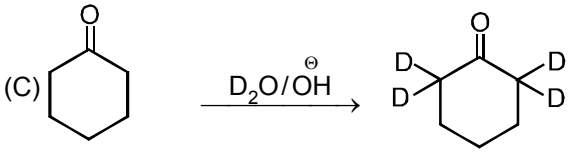
(C) 

(D) 

F-4.* In which of the following reaction deuterium exchange is observed ?

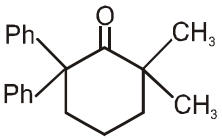
(A) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[\text{excess}]{D_2O/\overset{\Theta}{O}H} CD_3-\underset{\underset{O}{\|}}{C}-CD_2-CH_3$

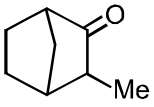
(B) $CH_3-\underset{\underset{Ph}{|}}{CH}-\underset{\underset{O}{\|}}{C}-H \xrightarrow{D_2O/\overset{\Theta}{O}H} CH_3-\underset{\underset{Ph}{|}}{CD}-\underset{\underset{O}{\|}}{C}-H$

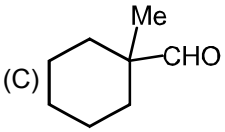
(C) 

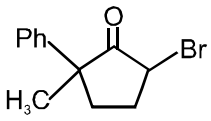
(D) $H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{D_2O/\overset{\Theta}{O}H} D-\underset{\underset{O}{\|}}{C}-D$

F-5.* In which of the following reaction deuterium exchange is not observed ?

(A) 

(B) 

(C) 

(D) 

Section (G) : Miscellaneous reactions

G-1. The major product formed in the reaction.

$C_6H_5CHO + CH_3NO_2 \xrightarrow[\text{heat}]{NaOH} (X)$

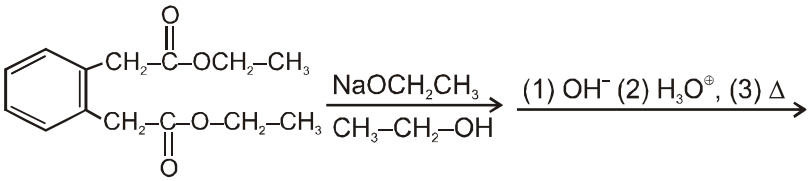
(A) $C_6H_5-CH-CH-NO_2$ (O bridge)

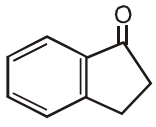
(B) $C_6H_5CHCH_2NO_2$ (OH)

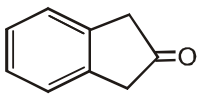
(C) $C_6H_5CH=CH-NO_2$

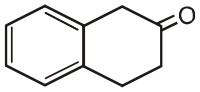
(D) $C_6H_5CH(CH_2NO_2)_2$.

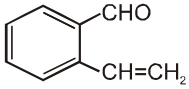
G-2. What is the final product of this sequence of reactions ?

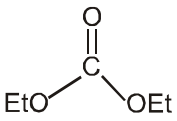


(A) 

(B) 

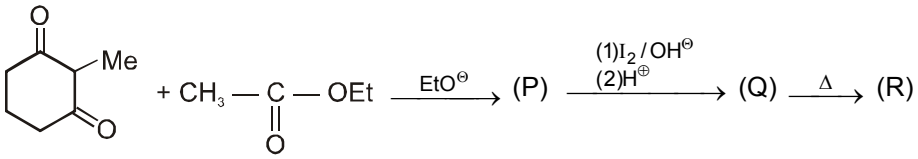
(C) 

(D) 

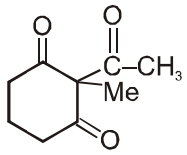
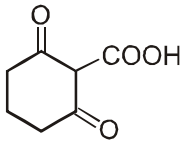
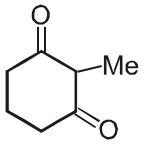
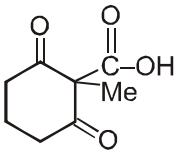
G-3. $Ph-CH_2-COOEt +$  $\xrightarrow[EtOH]{NaOEt}$ (A) $\xrightarrow{H_2O,\,\Delta}$ (B)

Product B is :

(A) $Ph-CH_2-COOH$ (B) $Ph-CH_2-COOEt$ (C) $Ph-CH(COOH)_2$ (D) None of these

G-4.* 

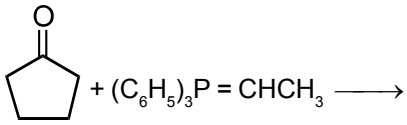
The products of the above reaction is / are :

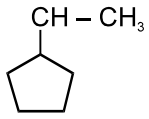
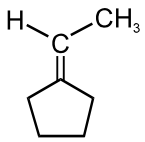
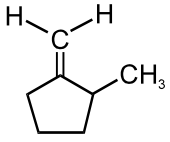
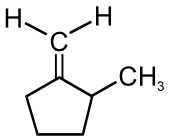
(A)  (B)  (C)  (D) 

G-5. 2-pentanone can be distinguished from 3- pentanone by the reagent ?

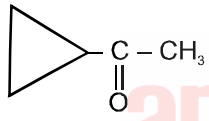
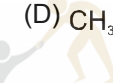
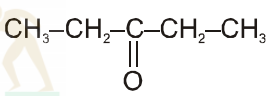
(A) 2, 4- Dinitrophenyl hydrazine (B)Tollen's reagent

(C) I_2 and dilute NaOH (D) $NaHSO_3$

G-6. 

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

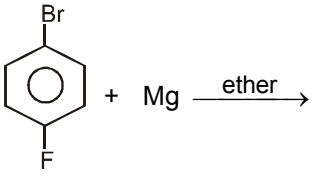
G-7.* Which of the following will gives iodoform with NaOI ?

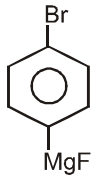
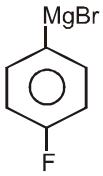
(A)  (B)  (C)  (D) 

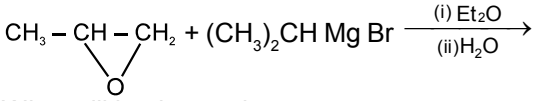
Section (H) : GRIGNARD REAGENT

H-1. $C_6H_5COOH + CH_3MgI \longrightarrow$?

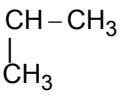
(A) $C_6H_5COOMgI$ (B) CH_4 (C) Both A & B (D) none

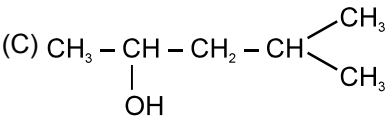
H-2. 

(A)  (B)  (C) Both (D) None of these

H-3. 

What will be the product :

(A) $CH_3-(CH_2)_4-CH_2-OH$ (B) 

(C)  (D) 

H-4.*_ Analyse the following reaction. If

$$HOCH_2CH_2COCH_2CH_2CO_2Et \xrightarrow{1\ CH_3MgX} P \xrightarrow{1\ CH_3MgX} Q \xrightarrow{1\ CH_3MgX} R$$

a : $EtO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2OMgX$

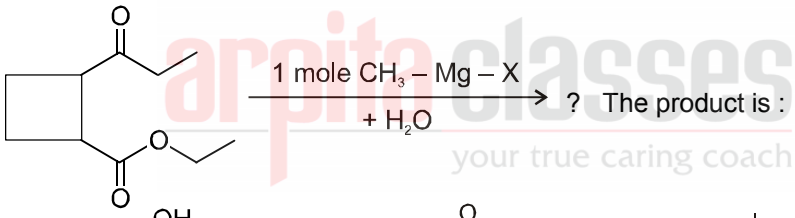
b : $EtO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{OMgX}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2OMgX$

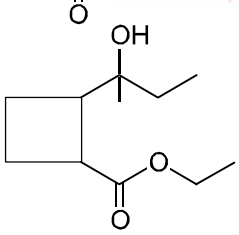
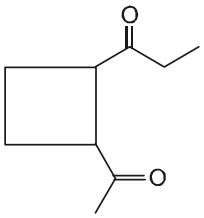
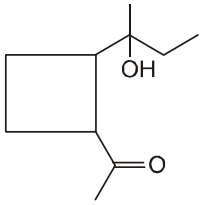
c : $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-OMgX$

d : $CH_3-\overset{\overset{OMgX}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-OMgX$

which is/are correct.

(A) P is a (B) Q is c (C) R is not d (D) Q is b

H-5. 

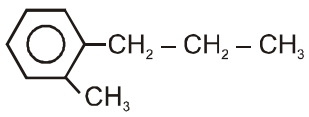
(A)  (B)  (C)  (D) All of these

H-6. $(CH_3)_3CMgCl$ on reaction with D_2O, produces :
(A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD_3)_3CD$ (D) $(CD_3)_3COD$

H-7. $Ph-MgBr + (CH_3)_2CH-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow [X] \xrightarrow{Zn-Hg/HCl} [Y]$
1 mole

Identify strucutre of [Y].

(A) $Ph-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (B) $Ph-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

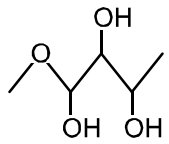
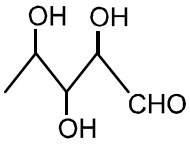
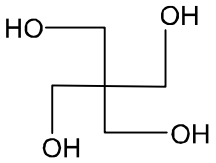
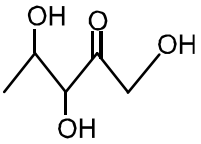
(C) $Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (D) 

H-8. Predict the major product in the following reaction:

$C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)}$

(A) $Ph–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$ (B) $C_6H_5 – CH_2 – \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} – CH_3$ (C) $Ph–CH_2–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_3$ (D) $Ph–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_3$

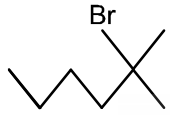
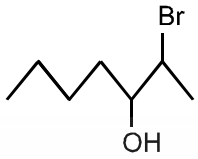
H-9. A compound X ($C_5H_{12}O_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).

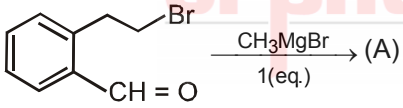
(A)  (B)  (C)  (D) 

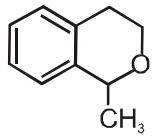
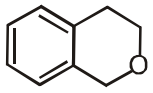
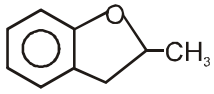
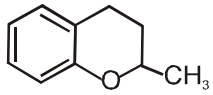
H-10. $CH_3–CH_2–CH_2–CH_2–CH_2–Br \xrightarrow[Ether]{Mg} X \xrightarrow[(ii)\ HOH/H^+]{(i)\ CH_2–CH_2 \diagdown O \diagup} Y \xrightarrow{PBr_3} Z$

Identify Z

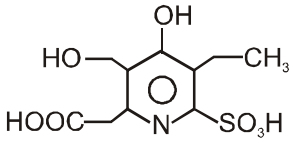
(A)  (B) 

(C)  (D) 

H-11. 

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

H-12. How many functional group produced CH_4 gas by the reaction of compound (I) with CH_3MgBr.



(I)

(A) 3 (B) 4 (C) 5 (D) 6

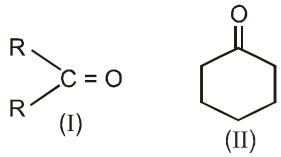
PART - III : ASSERTION / REASONING

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

(A) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is correct explanation for STATEMENT-1
(B) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is not correct explanation for STATEMENT-1
(C) STATEMENT-1 is true, STATEMENT-2 is false
(D) STATEMENT-1 is false, STATEMENT-2 is true
(E) Both STATEMENTS are false

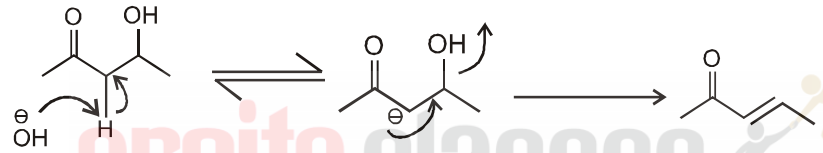
1. **Statement-1 :** Aldehyde and ketone undergo nucleophilic addition reaction with carbon nucleophile and underog nucleophilic addition-elimination reaction with nitrogen Nucleophile.
Statement-2 : Addition of nucleophile on aldehyde and ketone form tetrahedral intermediate, in case of tetrahedral intermediate of nitrogen nucleophile non bonding electrons are present on nitrogen which cause water molecule to eliminate while in case of carbon and hydrogen nucleophile non bonding electron are not present.

2. **Statement-1 :** The rate of addition reaction of alcohol on aldehyde can be increased by adding small amount of base.
Statement-2 : Addition of alcohols to an aldehyde form acetal.

3. **Statement-1 :** 

Compound II is more reactive towards nucleophilic addition reaction.
Statement-2 : Cyclic ketones are more reactive than acyclic ketone due to less steric hinderance and compact structure of cyclic ketone.

4. **Statement-1 :** $NaHSO_3$ is used in seperation and purification of aldehydes.
Statements-2 : $NaHSO_3$ is reducing agent.

5. **Statement -1 :** Dehydration of aldol takes place by the following mechanism.


Statement -2 : It is due to acidity of α – H and stability of conjugated double bond

6. **Statement-1 :** Cinnamaldehyde (Ph–CH = CH – CHO) fails to undergo aldol condensation.
Statement 2: This is due to the fact that cinnamaldehyde does not have acidic α – H.

7. **Statement-1 :** Grignard reagent can be prepared in all nonpolar solvent.
Statement-2 : Diethyl ether solvates the Grignard reagent.

8. **Statement-1 :** CH_3MgBr is prepared in cold aqueous solution.
Statement-2 : Water molecules stablise grignard molecules by H–bonding.

9. **Statement-1 :** CCl_3CHO forms an isolable crystalline hydrate.
Statement-2 : Electron withdrawing chlorine atoms stabilise hydrate by intramolecular H-bonding.

10. **Statement-1 :** Acetal are easily coverted to parent carbonyl compound. This easy interconverision make acetal attractive as protecting group to prevent carbonyl compound.
Statement-2 : Acetal are easily hydrolysed in acidic as well as basic medium.

11. **Statement-1 :** Acetaldehyde react with nitromethane in presence of dil. NaOH to give 1-nitro-2-propanol.
Statement-2 : The hydrogen atom of acetaldehyde are more acidic than nitromethane.

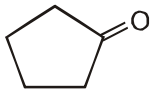
12. **Statement-1 :** The addition of ammonia derivative to a carbonyl compound is carried out in weakly acidic medium.
Statement-2 : In weakly acidic medium attacking nucleophile is also protonated.

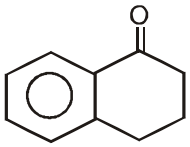
13. **Statement-1 :** HCHO is always oxidized in the crossed cannizzaro reaction.
Statement-2 : HCHO is the most reactive aldehyde, it exist in aqueous $OH^{\ominus}$ solution as the conjugate base of its hydrate $H_2C(OH)(O^{\ominus})$, there is also a statistical factor because HCHO has two aldehydic hydrogen available for transfer while in other aldehyde hydrate anion has only one such hydrogen atom.

Exercise # 2

PART - I : SUBJECTIVE QUESTIONS

1. Write the product of the following reaction

(a)  $+ HO - NH_2 \xrightarrow{H^{\oplus}}$

(b)  $+ NH_2 - NH_2 \xrightarrow{H^{\oplus}}$

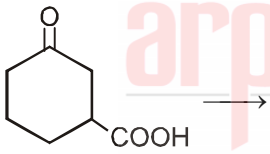
(c) $Ph - CH_2 - CH_2 - CHO + H_2\ddot{N} - \overset{\overset{O}{\|}}{C} - NH - NH_2 \longrightarrow$

(d) $Ph - \overset{\overset{O}{\|}}{C} - Ph + Ph - NH - NH_2 \longrightarrow$

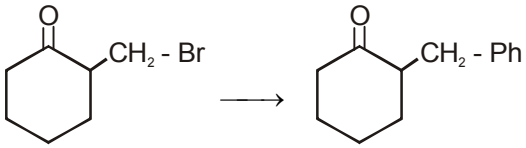
2. When semicarbazide reacts with a ketone (or aldehyde) to form semicarbazone. Only one nitrogen atom of semicarbazide acts as a nucleophile and attack the carbonyl carbon of the ketone. The product of the reaction consequently is $R_2C=N-NH-CONH_2$ rather than $R_2C=NCONH-NH_2$. What factor account for the fact that two nitrogen atoms of semicarbazide are relatively non nucleophilic ?

3. Cyclopropanone exists as the hydrate in water but 2-hydroxy ethanal does not exist as its hemiacetal expalin why ?

4. Show how would you accomplish the following synthesis

(a) 

(b) $Br - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3 \longrightarrow HC \equiv C - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$

(c) 

5. (a) Cis-1, 2-Cyclopentanediol reacts with acetone in the presence of dry HCl to yield compound K, $C_8H_{14}O_2$, which is resistant to boiling alkali, but which is readily converted into the starting material by aqueous acids. What is structure of K ?
(b) Trans-1, 2-Cyclopentanediol does not form an analogous compound. Explain why ?

6. On the basis of following reaction answer the following questions.

$$Ph - \overset{*}{C}H - CH = O + NH_2.NH - \overset{\overset{O}{\|}}{C} - NH - \overset{\overset{H}{|}}{\overset{*}{C}} - CH_2 - CH_3 \xrightarrow{H^+}$$

(dℓ mixture) (pure optical isomer)

(a) How many stereoisomers will be formed ?
(b) How many pair(s) of enantiomers are formed ?

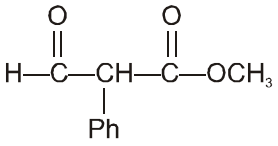
7. Predict the product from claisen condensation of the following pair of esters.

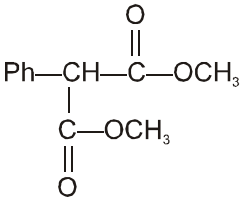
(a) $Ph-CH_2-\underset{\underset{O}{\|}}{C}-OCH_3 + Ph-\underset{\underset{O}{\|}}{C}-OCH_3 \xrightarrow{EtO^{\ominus}}$

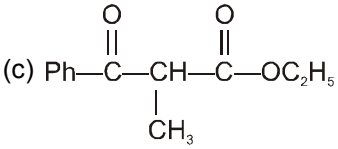
(b) $Ph-CH_2-\underset{\underset{O}{\|}}{C}-OCH_3 + CH_3-\underset{\underset{O}{\|}}{C}-OCH_3 \xrightarrow{EtO^{\ominus}}$

(c) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 + C_2H_5O-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[2.\ H_2O/\Delta]{1.\ EtO^{\ominus}}$

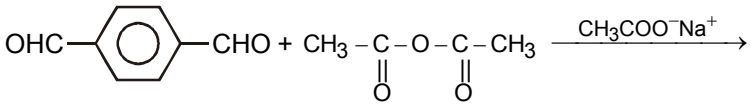
8. Write the components which on crossed claisen condensation could be used to prepare the following esters.

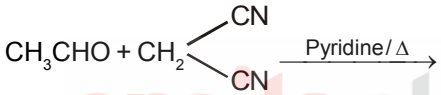
(a) 

(b) 

(c) 

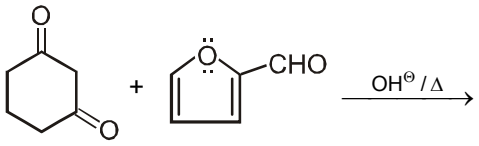
9. Predict the product for each of the following reactions,

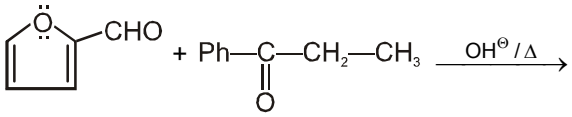
(a) 

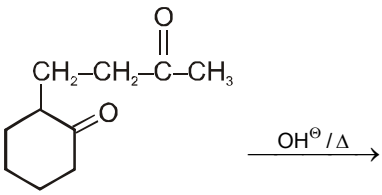
(b) 

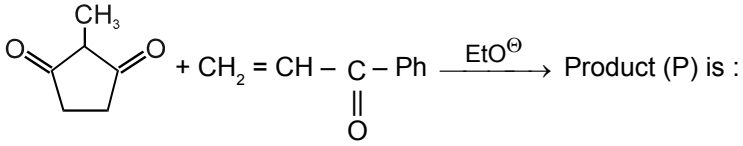
(c) 

10. Predict the product for each of the following reactions.

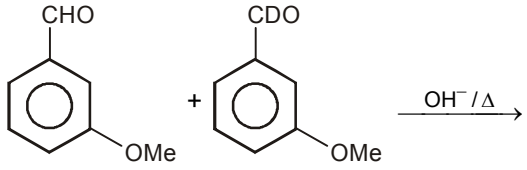
(a) 

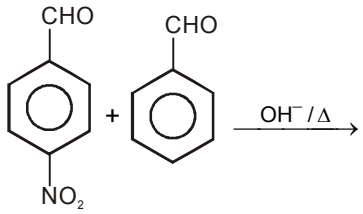
(b) 

(c) 

11.  Product (P) is :

12. Write the product of the following reaction,

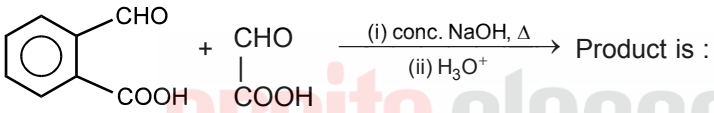
(a) 

(b) 

13. $PhCOCHBr_2 \xrightarrow{OH^-} A \xrightarrow{OH^-} B \xrightarrow{H^+} C$

The compound 'C' is :

14. Glyoxal (CHOCHO) on being heated with concentrated NaOH forms.

15.  Product is :

16. The compound $C_4H_8Cl_2$ (A) on hydrolysis gives a compound C_4H_8O, (B). The compound (B) reacts with hydroxylamine and gives a negative test with Tollen's reagent. What are (A) and (B) Support your answer with proper reasoning and give the equations of reactions.

17. An alcohol (A), 0.22 gm of this alcohol librates 56 ml of CH_4 at STP on reaction with CH_3MgBr. Write the molecular formula of alcohol which satisfy these conditions.

18. An organic compound which have molecular formula $C_4H_4O_3$, gives 3 mole of CH_4 gas on treatment with methyl magnesium bromide. Give structure of the compound.

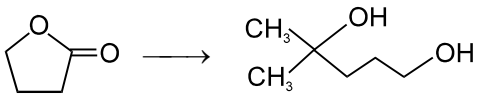
19. $\underset{(X)}{C_{10}H_{21}Br} \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ Mg} Y \xrightarrow{Cl_2}$ Give 5 types of structural monochloro product

Y has only 1° and 2° carbon atoms and X is 1° alkyl halide. Give structure of X & Y.

20. Show that how could be the following transformations carried out.

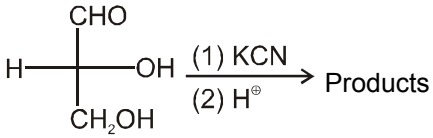
(a) Phenylethyne $\longrightarrow$ $C_6H_5C \equiv C\,C(OH)\,(CH_3)_2$

(b)  $\longrightarrow$ $Ph(CH_3)_2COH$

(c) 

PART - II : OBJECTIVE QUESTIONS

Single choice type

1. 

Products obtained in the reaction is-

(A) Diastereomer (B) Racemic mixture (C) Meso compound (D) Optically pure enantiomer

2. $CH_2O \xrightarrow[H_3O^{\oplus}]{CHD_2MgI} X \xrightarrow[\Delta]{Conc.H_2SO_4} Y$

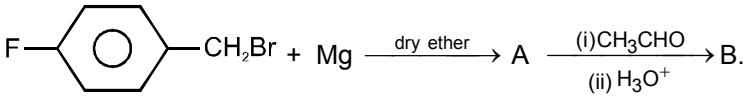
In the above reaction compound X & Y respectively will be

(A) $\overset{OH}{\overset{|}{C}}HD - CH_2 - OH$, $CHO - CHO$

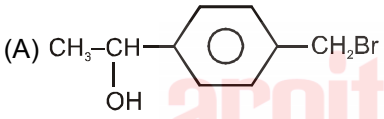
(B) $CHD_2 - CH_2 - OH$, $CHO - CHO$

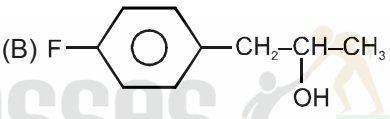
(C) $CHD_2 - CH_2 - OH$, $CD_2 = CH_2$

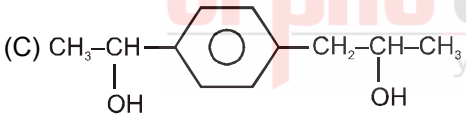
(D) $\overset{OH}{\overset{|}{C}}HD - CH_2 - OH$, $CD_2 = CH_2$

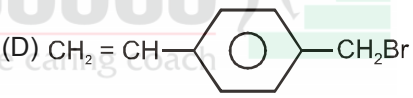
3. For the given reaction 

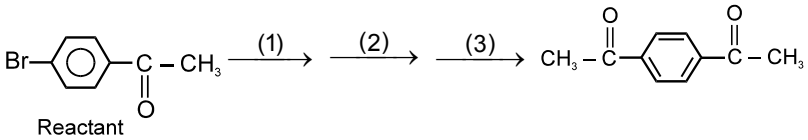
product B is :

(A) 

(B) 

(C) 

(D) 

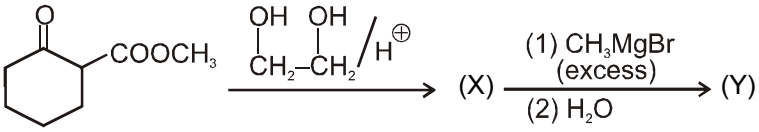
4. 

(A) (1) $\left.\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix}\right/H^{\oplus}$ (2) Mg /  (3) $H-\overset{O}{\overset{\|}{C}}-O-H$ / H^+

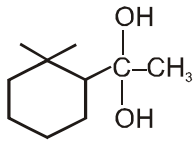
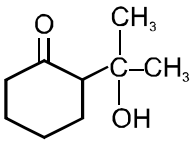
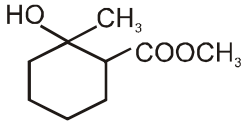
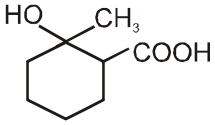
(B) (1) $\left.\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix}\right/H^{\oplus}$ (2) Mg /  (3) $CH_3-\overset{O}{\overset{\|}{C}}-O-Et$ / H^+

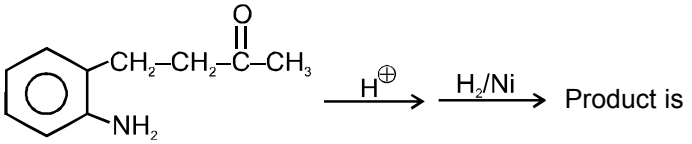
(C) (1) $\left.\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix}\right/H^{\oplus}$ (2) Mg / THF (3) $CH_3-\overset{O}{\overset{\|}{C}}-O-Et$ / H^+

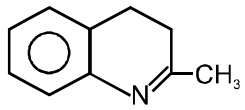
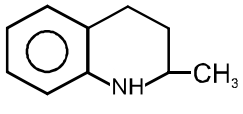
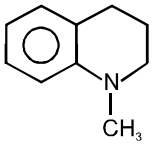
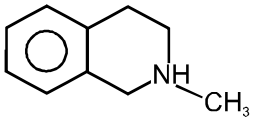
(D) (1) $\left.\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix}\right/H^{\oplus}$ (2) Mg / THF (3) $H-\overset{O}{\overset{\|}{C}}-O-H$ / H^+

5. In the given reaction, 

(Y) is

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

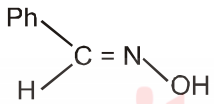
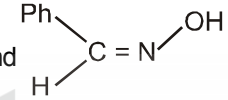
6. 

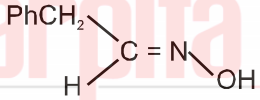
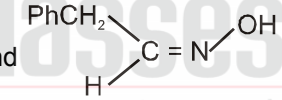
(A)  (B)  (C)  (D) 

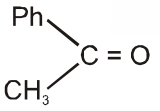
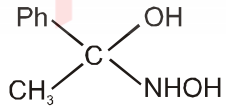
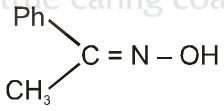
7. Consider the following sequence of reactions-.

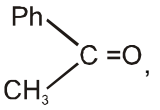
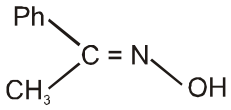
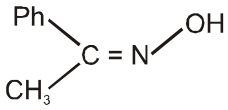
$$PhC \equiv CH \xrightarrow[dil.H_2SO_4]{HgSO_4} A \xrightarrow{NH_2OH} B + C.$$

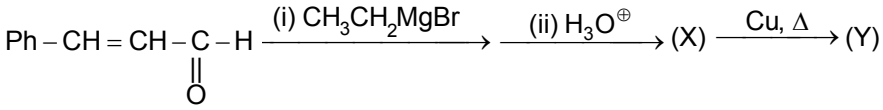
The products (A), (B) and (C) are respectively,

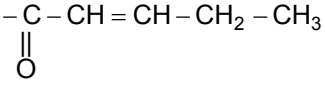
(A) PhCHO,  and 

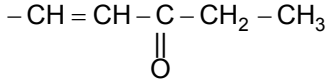
(B) $PhCH_2CHO$,  and 

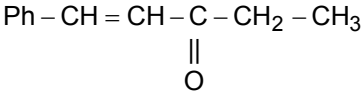
(C)  ,  and 

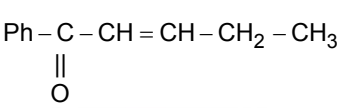
(D)  ,  and 

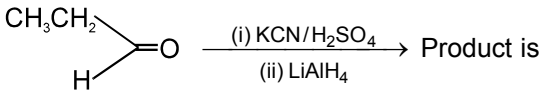
8. 

(A) X is 1, 4-addition product ; Y is 

(B) X is 1, 2-addition product ; Y is 

(C) X is 1, 4-addition product ; Y is 

(D) X is 1, 2-addition product ; Y is 

9.  Product is

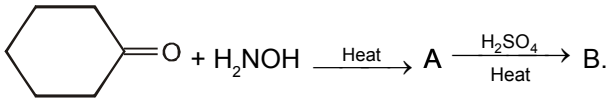
(A) $CH_3CH_2-CH(OH)-CH_2NH_2$

(B) $CH_3-CH_2-CH(OH)-CH_2-NH-CH_3$

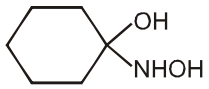
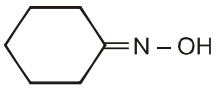
(C) $CH_3CH_2-CH(OH)-CN$

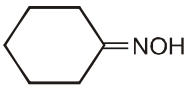
(D) $CH_3CH_2-CH_2-CH(OH)-NH_2$

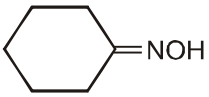
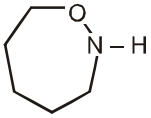
10. Consider the following sequence of reactions :

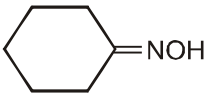
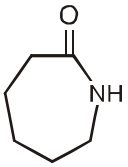


The products (A) and (B) are, respectively :

(A)  and 

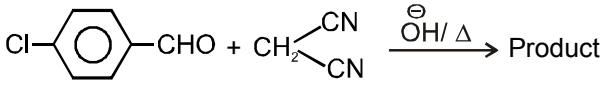
(B)  and 

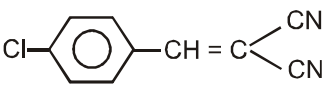
(C)  and 

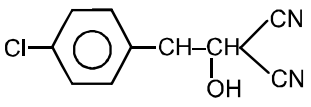
(D)  and 

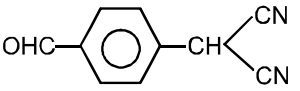
11. Compound (X) $C_9H_{10}O$ gives yellow coloured ppt with 2,4 DNP but does not give red coloured ppt with Fehling's solution. (X) on treatment with NH_2OH/H^+ gives compound (Y) $C_9H_{11}NO$. (Y) when treated with PCl_5 gives isomeric compound (Z). (Z) on hydrolysis gives propanoic acid and aniline. What will be the correct structure of (X), (Y) and (Z) ?

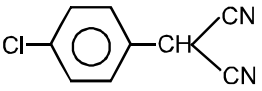
	(X)	(Y)	(Z)
(A)	$C_6H_5-C(=O)-C_2H_5$;	$C_6H_5-C(=N-OH)-C_2H_5$;	$C_6H_5-C(=O)-NH-C_2H_5$
(B)	$C_6H_5-C(=O)-C_2H_5$;	$C_6H_5-C(=N-OH)-C_2H_5$;	$C_2H_5-C(=O)-NH-C_6H_5$
(C)	$C_6H_5-CH_2-C(=O)-CH_3$;	$C_6H_5-CH_2-C(=N-OH)-CH_3$;	$CH_3-C(=O)-CH_2-NH-C_6H_5$
(D)	$C_6H_5-C(=O)-C_2H_5$;	$C_6H_5-C(=N-OH)-C_2H_5$;	$C_6H_5-C(=O)-NH-C_2H_5$

12.  Product

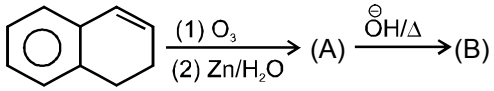
(A) 

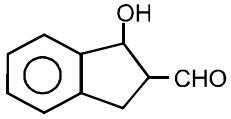
(B) 

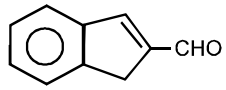
(C) 

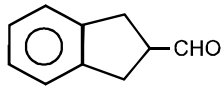
(D) 

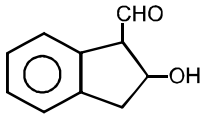
13. In the given reaction sequence B is

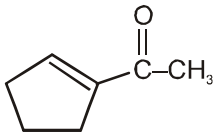


(A) 

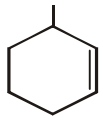
(B) 

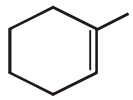
(C) 

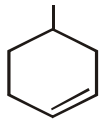
(D) 

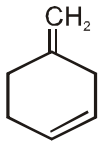
14. (A) $\xrightarrow[]{O_3/Zn/H_2O}$ (B) $\xrightarrow[\Delta]{NaOH}$ 

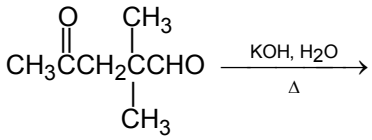
The reactant (A) will be :

(A) 

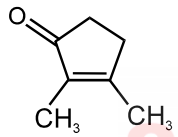
(B) 

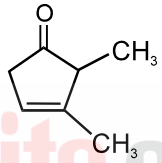
(C) 

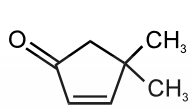
(D) 

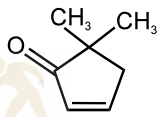
15. 

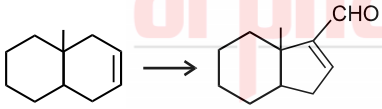
Product ($C_7H_{10}O$) :

(A) 

(B) 

(C) 

(D) 

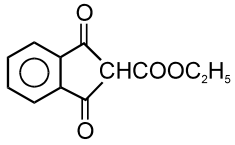
16. 

(A) $\xrightarrow[(1)]{O_3/Zn,H_2O}$ $\xrightarrow[(2)]{OH^{\ominus}}$ $\xrightarrow[(3)]{\Delta}$

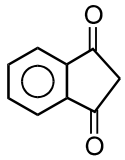
(B) $\xrightarrow[(1)]{CrO_3}$ $\xrightarrow[(2)]{H^{\oplus}}$

(C) $\xrightarrow[(1)]{N_2H_4}$ $\xrightarrow[(2)]{OH^{\ominus}}$ $\xrightarrow[(3)]{\Delta}$

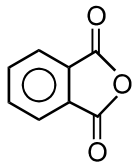
(D) $\xrightarrow[(1)]{KMnO_4/H^+}$ $\xrightarrow[(2)]{OH^{\ominus}}$

17. In the following reaction, A + B $\xrightarrow{C_2H_5\overset{\ominus}{O}\,Na^{\oplus}}$ 

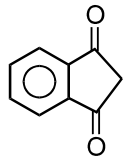
A and B respectively are :

(A) 

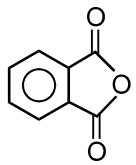
+ $CH_3COOC_2H_5$

(B) 

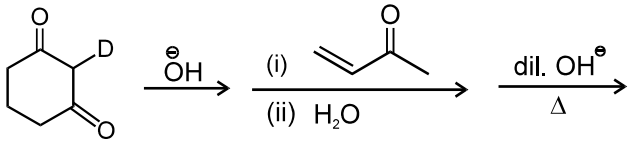
+ $CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5$

(C) 

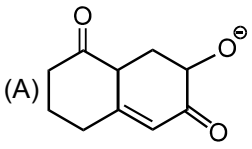
+ $C_2H_5O-\underset{\underset{O}{\|}}{C}-OC_2H_5$

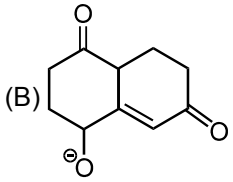
(D) 

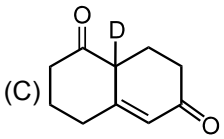
+ $C_2H_5O-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5$

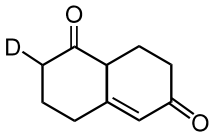
18. 

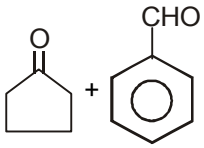
(X) Identify.

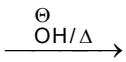
(A) 

(B) 

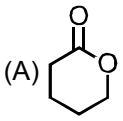
(C) 

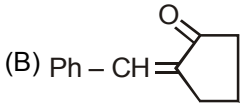
(D) 

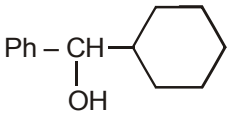
19. 

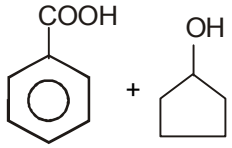


Product is.

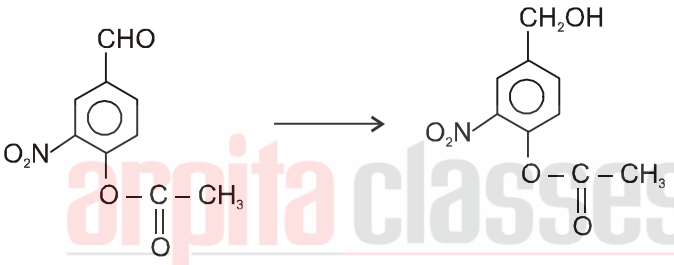
(A) 

(B) 

(C) 

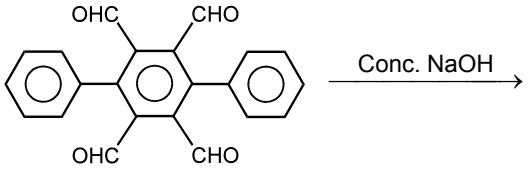
(D) 

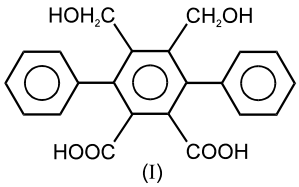
20. The suitable reagent for the following reaction is :



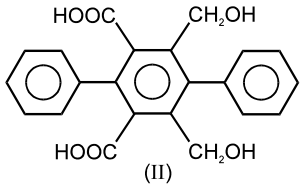
(A) $LiAlH_4$ (B) Na / C_2H_5OH (C) H_2 / Ni (D) $CH_2 = O / OH^{\ominus}$

21. Which of the following can be the product/s of following reaction.

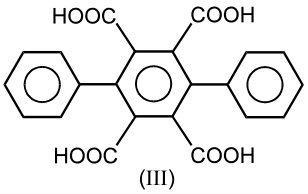




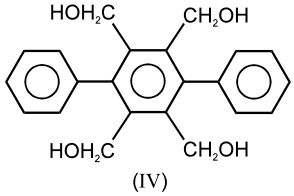
(I)



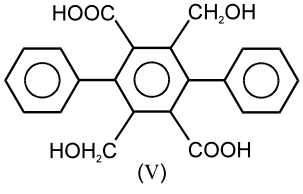
(II)



(III)

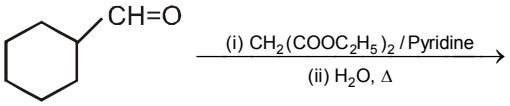


(IV)

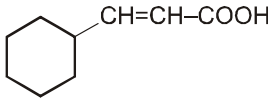


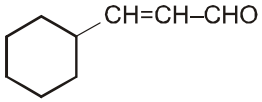
(V)

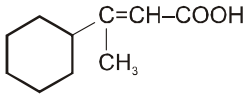
(A) I, II, IV (B) III, IV (C) II, V (D) I, V

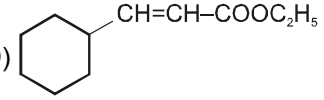
22. 

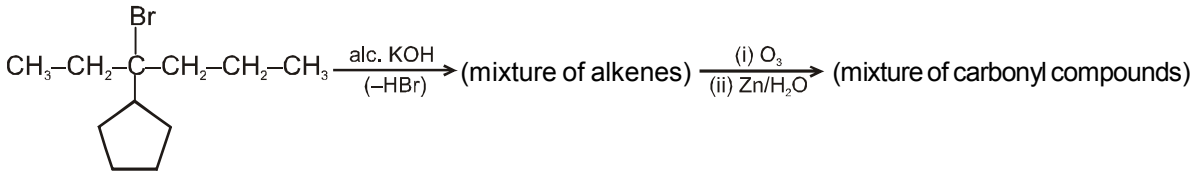
(P) is

(A) 

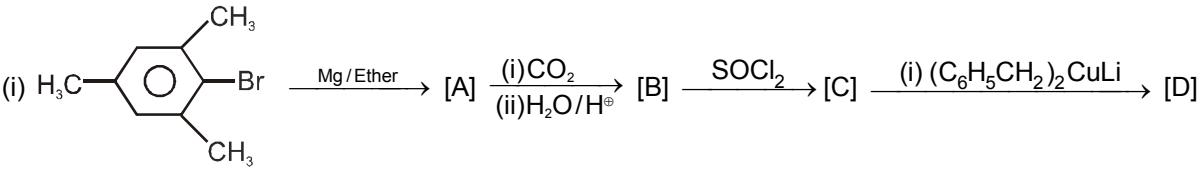
(B) 

(C) 

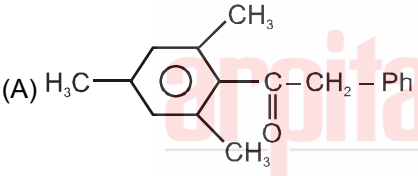
(D) 

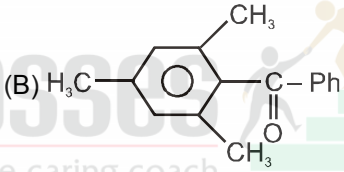
23. 

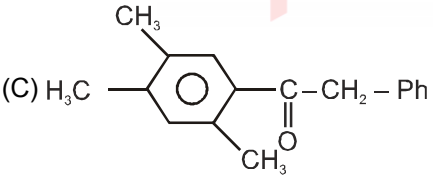
The incorrect statement is
(A) Total five alknes are obtained
(B) Total six different carbonly compounds are obtained on ozonolysis
(C) All carbonly compounds can give aldol reaction when treated with dil KOH
(D) Only two carbonly compounds give positive iodoform test

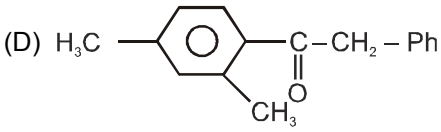
24. 

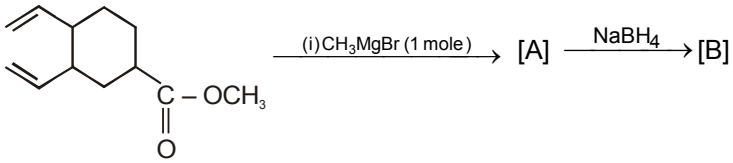
Identify (D) in the following sequence of reaction.

(A) 

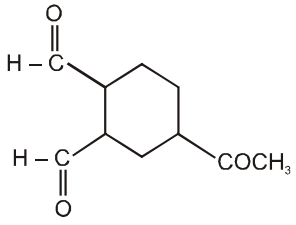
(B) 

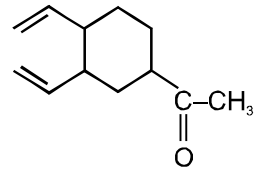
(C) 

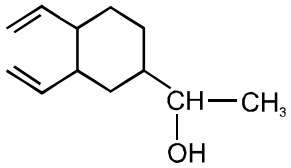
(D) 

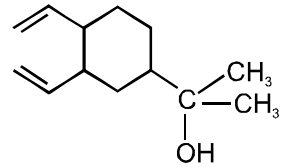
25. 

Identify the structure of [B] in following sequence of reactions.

(A) 

(B) 

(C) 

(D) 

26. $Cl-CH_2-\underset{\underset{O}{\|}}{C}-OEt + 2CH_3MgI \xrightarrow[\text{by } H_2O]{\text{Followed}}$ product.

What is the product.

(A) $HO-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (B) $Cl-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-OEt$ (C) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OEt$ (D) $Cl-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

27. $2CH_2=CH-CH_2-Cl \xrightarrow[\text{Ether}]{Mg} X \xrightarrow[\text{Followed by } H_2O]{Y} (CH_2=CH-CH_2)_2CH-OH + CH_3-CH_2-OH$

In the above chemical reaction, Y may be

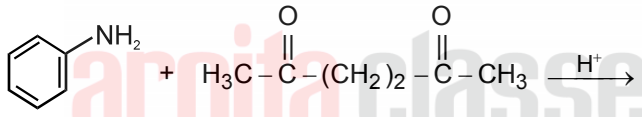
(A) Ethyl formate (B) Methyl formate (C) Isopropyl methanoate (D) Ethanoylchloride

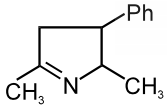
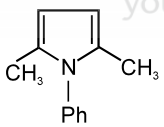
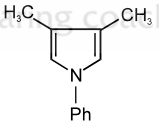
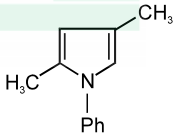
28. The reaction, $BrCH_2CH_2CH_2Br + Mg \xrightarrow{Et_2O}$
produces mainly.

(A) $CH_3CH_2CH_3$ (B) $BrMgCH_2CH_2CH_2MgBr$

(C) (D) $CH_3CH=CH_2$

29. What will be the product of the following reaction

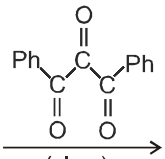


(A)  (B)  (C)  (D) 

More than one choice type

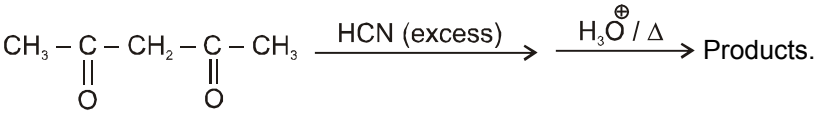
30. Which of the following correctly indicate(s) the rate.

(A) $CH_3CH(CN)(OH) \xleftarrow[\text{(very fast)}]{CH_3CHO} KCN + HCl \xrightarrow[\text{slow}]{} Me-C_6H_4-CH(OH)(CN)$

(B) (hydrate) $\xleftarrow[\text{(fast)}]{CH_3CH=O} H_2O/H^+ \xrightarrow[\text{(slow)}]{}$  hydrate

(C) Cyanohydrin $\xleftarrow[\text{slow}]{HCN/OH^{\ominus}} C_2H_5CHO \xrightarrow[\text{fast}]{CH_3MgBr}$ Adduct formation

(D) All of these

31. Observe the following reaction  Products.

The correct statement is

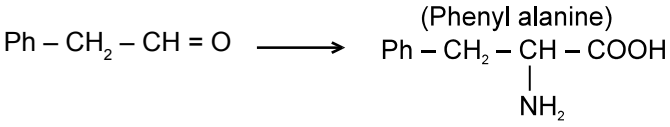
(A) The product is a mixture of two compounds

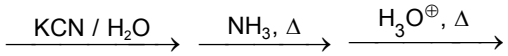
(B) The product is optically inactive

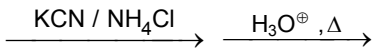
(C) The product is a mixture of two chiral and one achiral stereoisomer

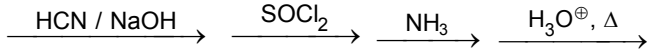
(D) The product is a mixture of three stereoisomers.

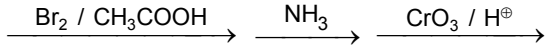
32. The following conversion is/are possible by



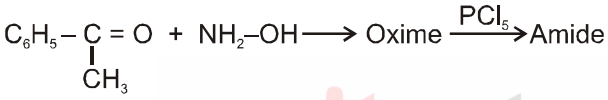
(A) 

(B) 

(C) 

(D) 

33. In the given reaction which one of the following statement is correct –



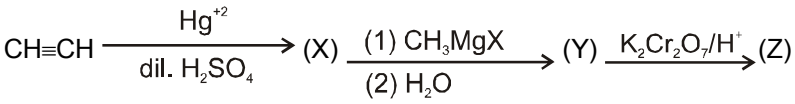
(A) Oxime may be E/Z.

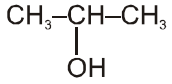
(B) Amide on hydrolysis gives a mixture acetic acid, benzoic acid, Aniline and methylamine.

(C) Preparation of oxime is nucleophilic addition followed by elimination reaction.

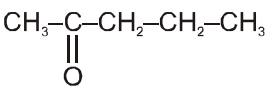
(D) Oxime and amides are isomers.

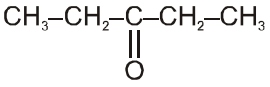
34. In the given reaction

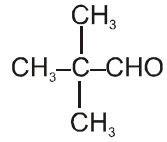


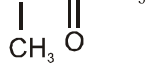
(A) X is CH_3CHO (B) Y is  (C) Z is  (D) Z is CH_3COOH

35. A compound (A) $C_5H_{10}O$ forms a phenyl hydrozone and gives negative tollen's and positive iodoform test compound can be :

(A) 

(B) 

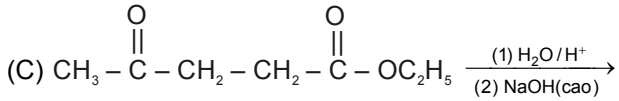
(C) 

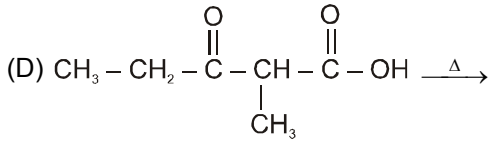
(D) 

36. Which of the following will give 3–pentanone.

(A) $(CH_3 - CH_2COO)_2 Ca \xrightarrow{\Delta}$

(B) $CH_3 - CH_2 - C \equiv N \xrightarrow[(2)\ H_3^{\oplus}O]{(1)\ CH_3-CH_2-MgBr}$

(C) 

(D) 

37. Which of the following reactions is / are correct to get cinnammic acid :

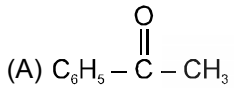
(A) C_6H_5-CH=O $\xrightarrow{(CH_3CO)_2O/CH_3COONa}$

(B) C_6H_5-CH=O $\xrightarrow[\text{Pyridine}]{CH_2(COOC_2H_5)_2}$

(C) C_6H_5-CH=O $\xrightarrow{CH_3COOC_2H_5/OH^-}$

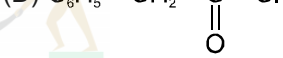
(D) C_6H_5-CH=O $\xrightarrow[(ii)\ H_2O/H^+/\Delta]{(i)BrCH_2-COOC_2H_5/Zn/\Delta}$

38. Identify product in the following reaction sequence

(A) 

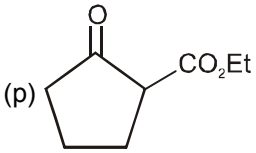
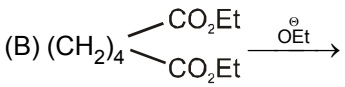
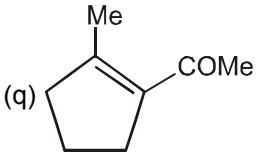
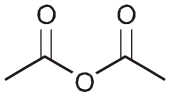
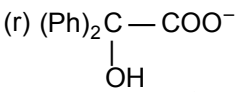
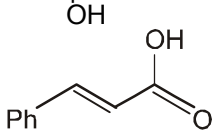
(B) 

(C) 

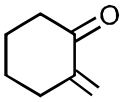
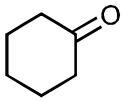
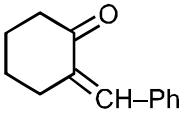
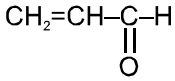
(D) 

PART - III : MATCH THE COLUMN

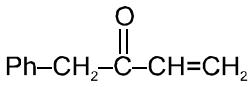
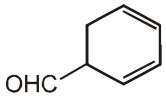
1. Match the column

Column I	**Column II**
(A) $MeCO(CH_2)_4COMe \xrightarrow[(ii)\ H^+/\Delta]{(i)\ OH^{\ominus}}$	(p) 
(B) 	(q) 
(C) PhCHO +  $\xrightarrow{CH_3COO^-}$	(r) 
(D) PhCOCOPh $\xrightarrow{OH^{\ominus}}$	(s) 

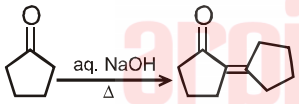
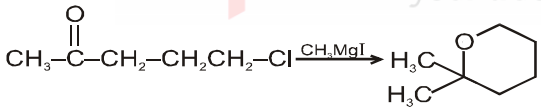
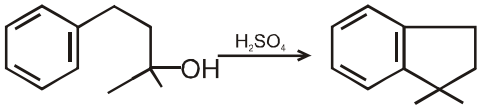
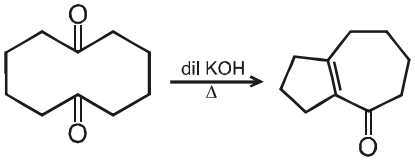
2.

Column-I **Aldol product**	**Column-II** **Reactant required**
(A) 	(p) 
(B) 	(q) HCHO
(C) 	(r) Ph–CHO
(D) Ph–CH=CH–CHO	(s) CH_3–CHO

3.

Column-I	**Column-II**
(A) 	(p) 1, 4-addition
(B) 	(q) Tautomerism
(C) CH_3–CH=CH–CH = CH_2	(r) $AgNO_3$ / NH_4OH

4.

Column-I	**Column-II**
(A) 	(p) Nucleophilic substitution
(B) 	(q) electrophilic substitution
(C) 	(r) Dehydration
(D) 	(s) Nucleophilic addition
	(t) carbanion intermediate

5. Match the product of **Column- II** with the reaction given in **Column- I.**

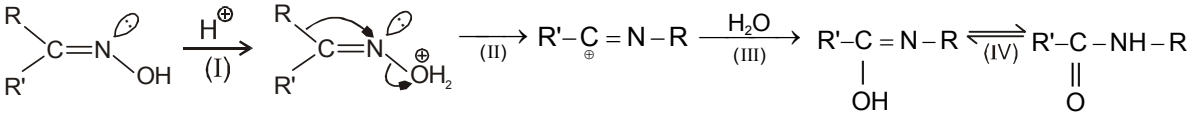
Column- I	**Column- II**
(A) RMgI + Acetonitrile ($CH_3C \equiv N$)	(p) Alkanone
(B) RMgI + Carbon disulphide	(q) Ester
(C) RMgI.(1eq) + Ethyl chloroformate	(r) 1° Alcohol
(D) RMgI + Oxirane	(s) Dithionic acid

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

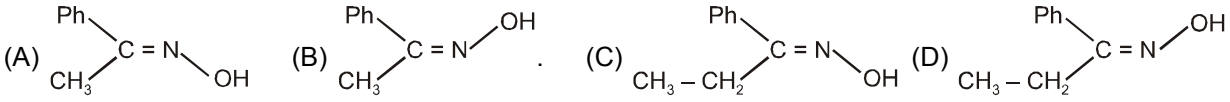
Comprehension # 1

Aldehydes and Ketones reacts with NH_2OH to form Aldoximes and Ketoximes respectively. Configuration of these can be determined by Beckmann rearrangement as that group migrates which is anti w.r.t –OH.



1. [X] $\xrightarrow{H_2SO_4}$ $\xrightarrow{H_2O}$ $Ph-NH_2 + CH_3-\underset{\underset{O}{\|}}{C}-OH$

Identify the configuration of [X] compound :



2. Which step is Rate determening step ?

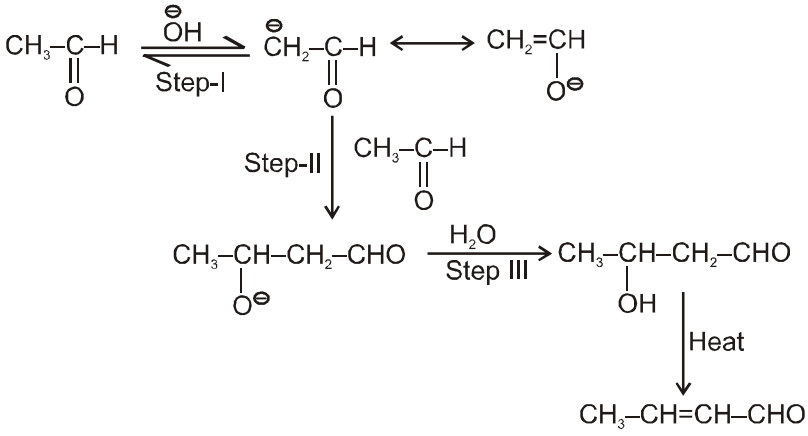
(A) I (B) II (C) III (D) IV

3.  $\xrightarrow{NH_2OH}$ (A) $\xrightarrow[(2)\text{hydrolysis}]{(1)H_2SO_4}$ (B).

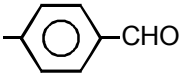
The product (B) is :

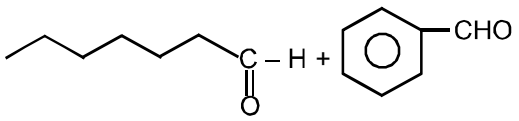
Comprehension # 2

Carbonyl compound which contains α–H gives aldol condenation reaction in presence of alkaline medium. The reaction between two molecules of acetaldehyde take place as follows in presence of base.



4. Aldol condensation reaction is given by

(A) C_6H_5–CHO (B) CX_3-CHO (C) O_2N–  –CHO (D) $C_6H_5-CH_2-CHO$

5. 

(A) Ph – CH = CH – $(CH_2)_5$ – CHO

(B) Ph – $(CH_2)_5$ – CH = CH – CHO

(C) Ph – CH = CH – $(CH_2)_4$ – CHO
CHO

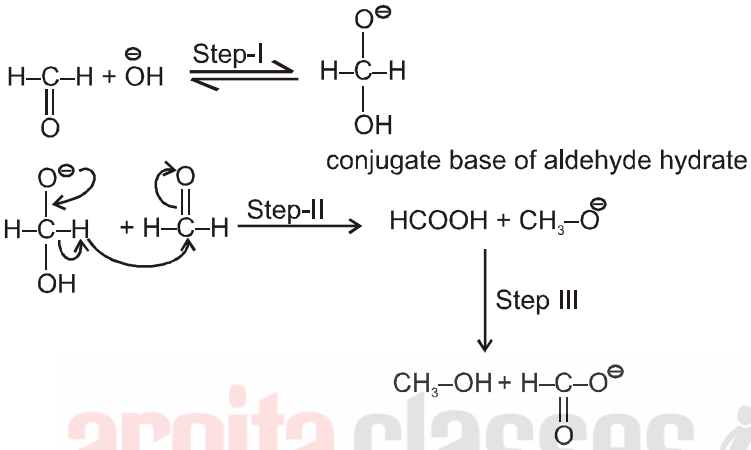
(D) Ph – CH = CH – $(CH_2)_4$ – CH_3
CHO

6. Intramolecular aldol condensation reaction is given by

(A) 1,4 diketone (B) 1,6 diketone (C) 1,5 and 1,7 diketone (D) All of these

Comprehension # 3

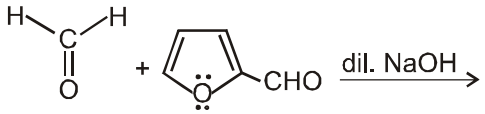
The conversion of aldehyde having no alpha hydrogen to a mixture of carboxylic acid and primary alcohol is known as cannizzaro reaction. The most important feature of this reaction is the conjugate base of hydrate of aldehyde.

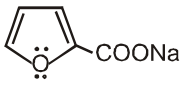


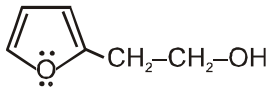
7. Which step is rate determining step

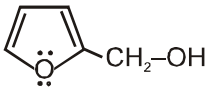
(A) step I (B) step II (C) step III (D) step I and II both

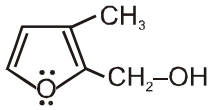
8. In the given reaction final product is



(A) CH_3OH + 

(B) HCOONa + 

(C) HCOONa + 

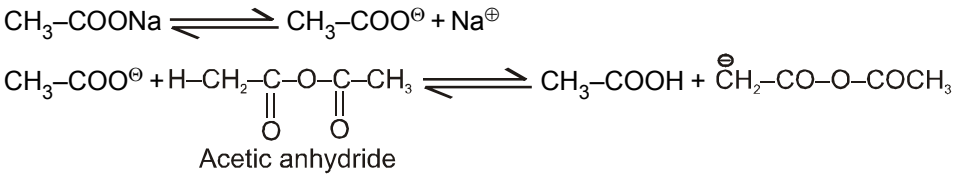
(D) HCOONa + 

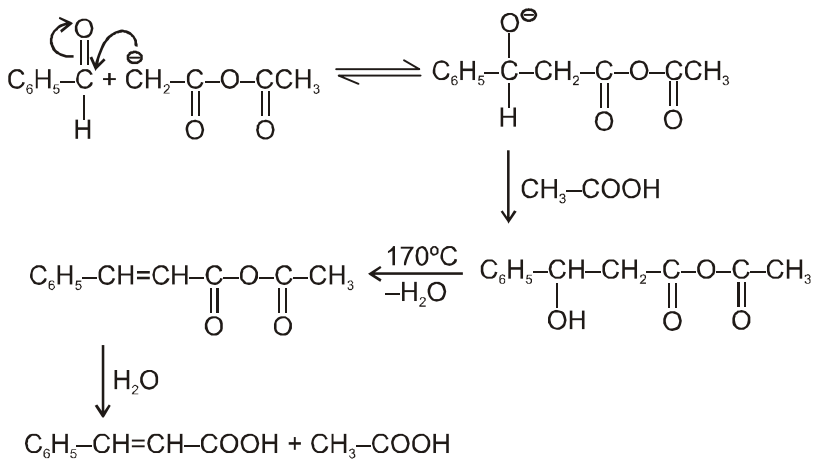
Comprehension # 4

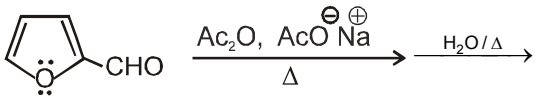
Perkin reaction is the condensation reaction between aromatic aldehyde and aliphatic acid anhydride in the presence of sodium or potasium salt of the acid of the corresponding anhydride to yield α, β unsaturated aromatic acid.

$$Ph–CHO + (CH_3CO)_2O \xrightarrow[170\text{-}180^oC]{AcONa} Ph–CH=CH–COOH + CH_3–COOH$$

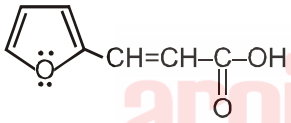
Mechanism

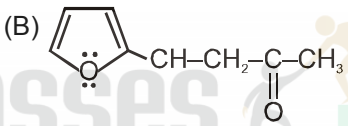


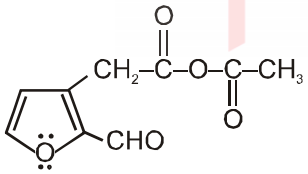


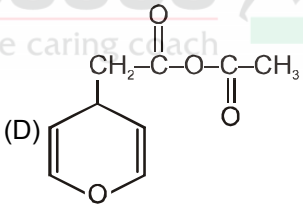
9. 

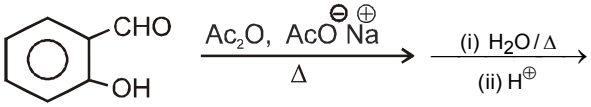
Product is

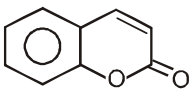
(A) 

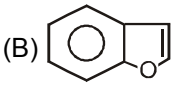
(B) 

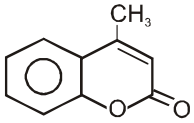
(C) 

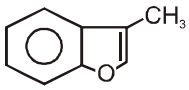
(D) 

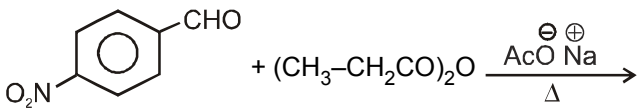
10. 

(A) 

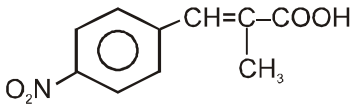
(B) 

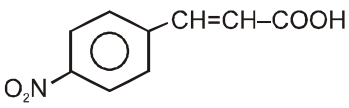
(C) 

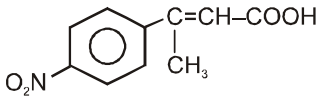
(D) 

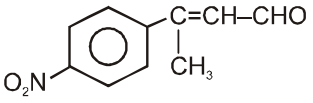
11. 

Product is

(A) 

(B) 

(C) 

(D) 

Comprehension # 5

Ester having α-hydrogen on treatment with a strong base eg. C_2H_5ONa undergoes self condensation to produce β-keto esters.This is called claisen condensation.

$$C_2H_5O^- + H - CH_2COOC_2H_5 \rightleftharpoons C_2H_5OH + \overset{\ominus}{\underset{\cdot\cdot}{C}}H_2 - COOC_2H_5$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OEt + \overset{\ominus}{\underset{\cdot\cdot}{C}}H_2 - COOC_2H_5 \rightleftharpoons CH_3-\overset{O^{\ominus}}{\overset{|}{C}}(OEt)-CH_2-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt + C_2H_5O^-$$

12. $C_6H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[(2)\ H^{\oplus}]{(1)\ C_2H_5O^{\ominus}Na^{\oplus}}$

(A) $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH$

(B) $C_6H_5-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH$

(C) $C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH$

(D) None of these

13. $EtO-\overset{O}{\overset{\|}{C}}-OEt + Ph-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[(2)\ H_2O,\ \Delta]{(1)\ C_2H_5ONa}$ product is

(A) $CH_3-\underset{Ph}{\underset{|}{CH}}-COOH$

(B) $Ph-\underset{COOH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-COOH$

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

(D) $Ph-CH_2-COOH$

14. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[(2)\ CH_3-I]{(1)\ C_2H_5ONa} \xrightarrow[(2)\ \Delta]{(1)\ H_2O^-}$

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

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

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

(D) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOH$

Comprehension # 6

Study following mechanism of haloform reaction.

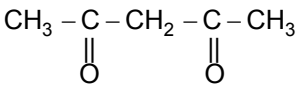
$$R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}-H + HO^{\ominus} \underset{a}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}(H)-H \xrightarrow[b]{I-I} R-\overset{O}{\overset{\|}{C}}-\overset{I}{\overset{|}{C}}-H \xrightarrow[C]{(1)\ HO^{\ominus},\ (2)\ I_2} R-\overset{O}{\overset{\|}{C}}-\overset{X}{\overset{|}{C}}-X$$

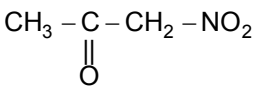
$$CHX_3 \uparrow + R-\overset{O}{\overset{\|}{C}}-\overset{X}{\overset{|}{C}}-O^{\ominus} \xleftarrow{f} R-\overset{O}{\overset{\|}{C}}-OH + {}^{\ominus}CX_3 \underset{e}{\overset{HO^{\ominus}}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-\overset{X}{\overset{|}{C}}-X \xleftarrow[(2)\ I_2]{(1)\ HO^{\ominus}\ d}$$

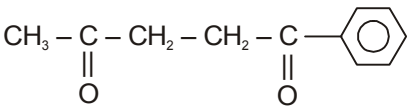
15. Which step is RDS

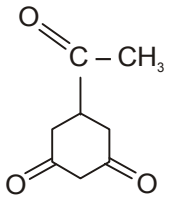
(A) a (B) b (C) c (D) f

16. Which of the following compounds gives haloform reaction ?

(A) 

(B) 

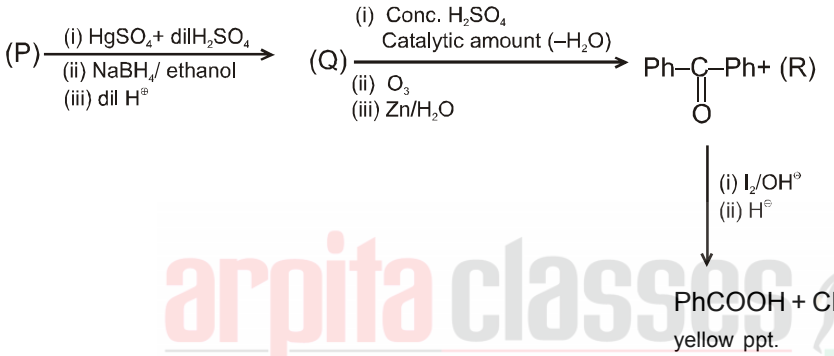
(C) 

(D) 

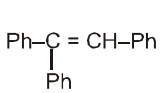
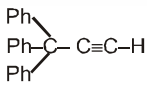
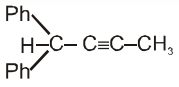
17. Which step produces most acidic compound

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

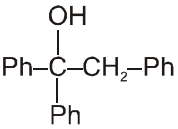
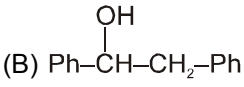
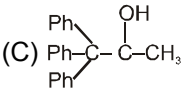
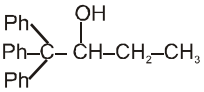
Comprehension # 7



18. The structure of compound P is

(A)  (B)  (C)  (D) Ph–C≡C–Ph

19. The structure of the compound Q is .

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

20. The incorrect statement about compound R is :

(A) It gives positive test with 2, 4–DNP

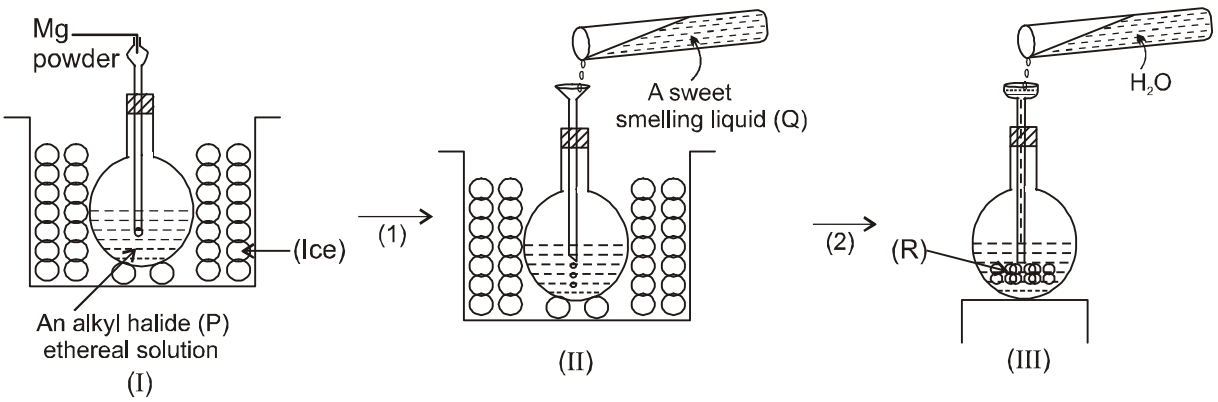
(B) It gives aldol reaction with dil NaOH

(C) It gives cannizzaro reaction with conc. KOH/Δ

(D) It shows D-exchange when treated $OD^{\ominus}/D_2O$ excess

Comprehension-8

Observe the following experiment



21. If the reactant 'P' is ethyl chloride then the product R can be

(A) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

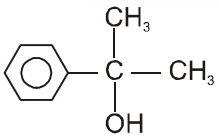
(B) $CH_3CH_2-O-CH_2CH_3$

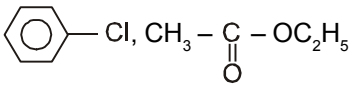
(C) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}}-CH_2-CH_3$

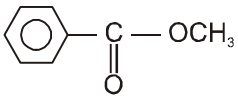
(D) $CH_3CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

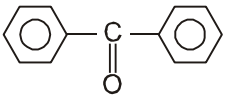
22. If the liquid Q is $H-\overset{\overset{O}{\|}}{C}-OC_2H_5$ then the product R can be (P can be any other halide)

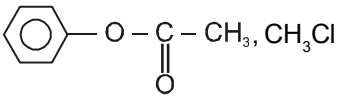
(A) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ (B) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (C) $H-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-C_2H_5$ (D) $C_2H_5-\underset{\underset{OH}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-C_2H_5$

23. If R is  then P and Q can be respectively.

(A) 

(B) CH_3-Cl, 

(C) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$, 

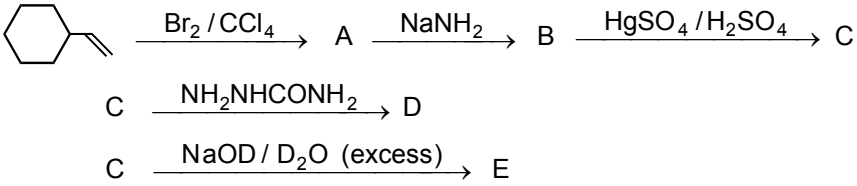
(D) 

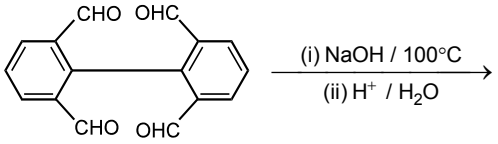
Exercise # 3

PART - I : IIT-JEE PROBLEMS (LAST 10 YEARS)

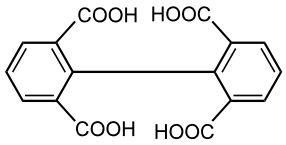
*** Marked Questions are having more than one correct option.**

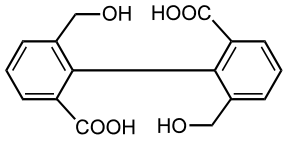
1. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures : **[JEE 2001, 5/100]**

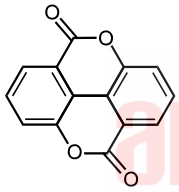


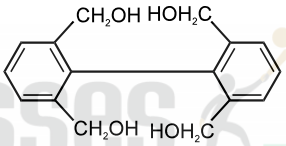
2. 

Major Product is **[JEE 2003, 3/84]**

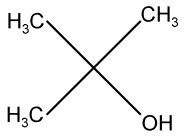
(A) 

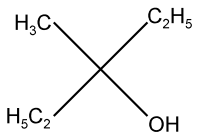
(B) 

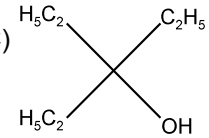
(C) 

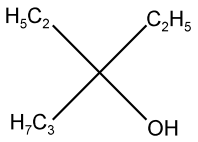
(D) 

3. Ethylester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be **[JEE-2003, 3/84]**

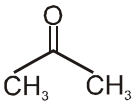
(A) 

(B) 

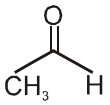
(C) 

(D) 

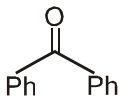
4. The order or reactivity of phenyl magnesium bromide with the following compounds is : **[JEE-2004, 3/84]**



I



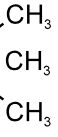
II

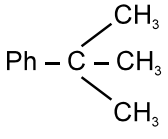


III

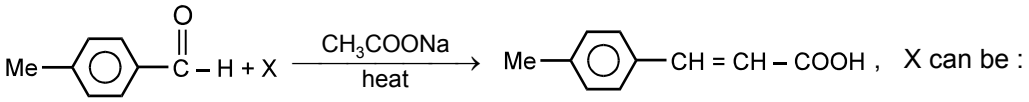
(A) (II) > (III) > (I) (B) (I) > (III) > (II) (C) (II) > (I) > (III) (D) all react with the same rate

5. Phenyl magnesium bromide reacting with t-Butyl alcohol gives **[JEE-2005, 3/60]**

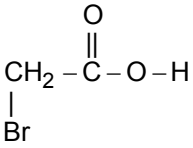
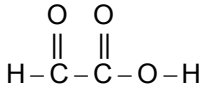
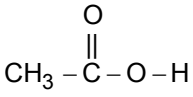
(A) Ph – OH (B) Ph – H (C) 

(D) 

6. In the following reaction **[JEE 2005, 3/84]**



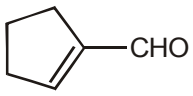
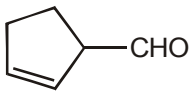
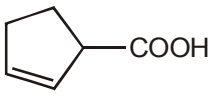
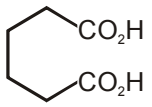
X can be :

(A)  (B)  (C)  (D) $(CH_3CO)_2O$

7. In conversion of 2-butanone to propanoic acid which reagent is used. **[JEE 2005, 3/84]**

(A) NaOH, NaI / $H^{\oplus}$ (B) Fehling solution (C) NaOH, I_2 / $H^{\oplus}$ (D) Tollen's reagent

8. 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 : **[JEE 2007, 3/162]**

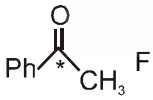
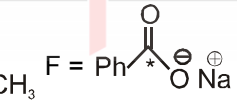
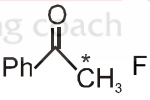
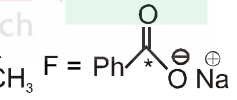
(A)  (B)  (C)  (D) 

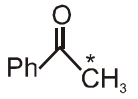
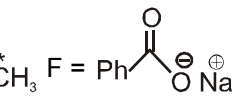
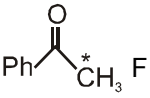
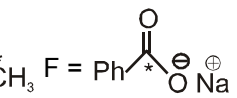
9. Match the compounds/ions in Column I with their properties/reactions in Column II. **[JEE 2007, 8/162]**

	Column I		**Column II**
(A)	C_6H_5CHO	(p)	gives precipitate with 2,4 dinitrophenylhydrazine.
(B)	$CH_3C \equiv CH$	(q)	gives precipitate with $AgNO_3$.
(C)	CN^-	(r)	is a nucleophile.
(D)	I^-	(s)	is involved in cyanohydrin formation.

10. In the following reaction sequence, the correct structures of E, F and G are **[JEE 2008, 3/163]**

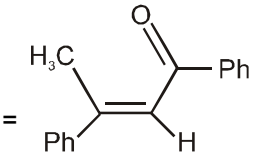
(*implies ^{13}C labelled carbon)

(A) E =  F =  G = CHI_3 (B) E =  F =  G = CHI_3

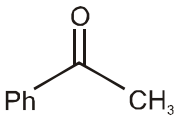
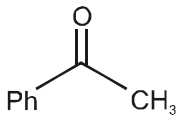
(C) E =  F =  G = $\overset{*}{C}HI_3$ (D) E =  F =  G = CH_3I

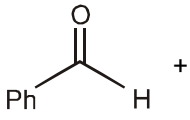
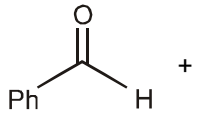
Comprehension (Q. 11 to 13)

A tetriary 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 compound **L**, whereas **K** on reaction with KOH gives only **M**.

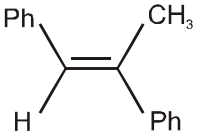
M = 

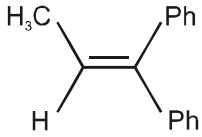
11. Compound **H** is formed by the reaction of **[JEE 2008, 4/163]**

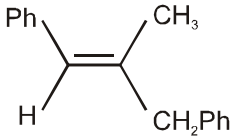
(A)  + PhMgBr (B)  + $PhCH_2MgBr$

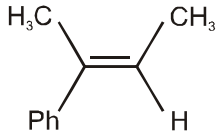
(C)  + $PhCH_2MgBr$ (D) 

12. The structure of compound **I** is **[JEE 2008, 4/163]**

(A) 

(B) 

(C) 

(D) 

13. The structure of compounds **J**, **K** and **L** respecitvely, are : **[JEE 2008, 4/163]**

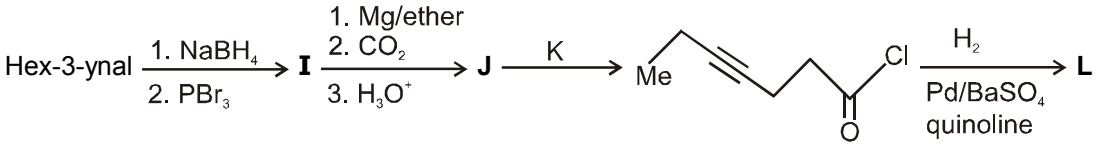
(A) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$ (B) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

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

Comprehension (Q. 14 to 16)

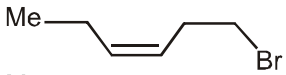
In the following reaction sequence, product **I**, **J** and **L** are formed. **K** represents a reagent.

[JEE-2008, 12/163]



14. The structure of the product **I** is ; **[JEE-2008, 4/163]**

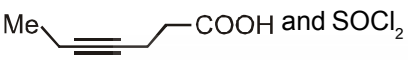
(A) 

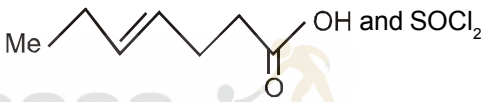
(B) 

(C) 

(D) 

15. The structures of compound **J** and **K**, respectively, are : **[JEE-2008, 4/163]**

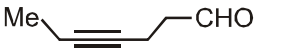
(A) 

(B) 

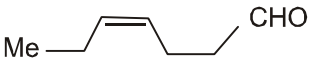
(C) 

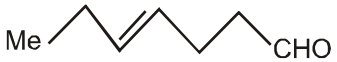
(D) 

16. The structure of product **L** is : **[JEE-2008, 4/163]**

(A) 

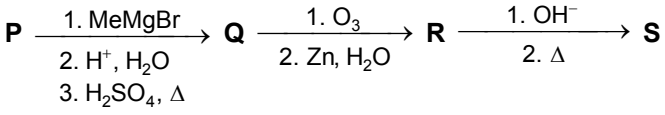
(B) 

(C) 

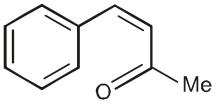
(D) 

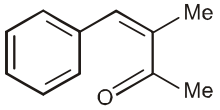
Comprehension (Q. 17 to 19)

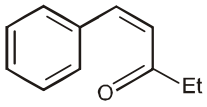
A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

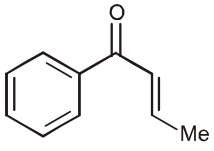


17. The structure of the carbonyl compound **P** is : **[JEE 2009, 4/160]**

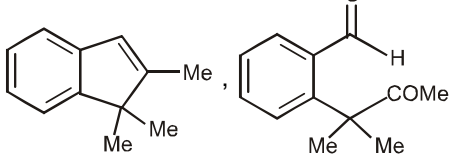
(A) 

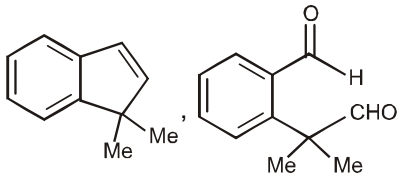
(B) 

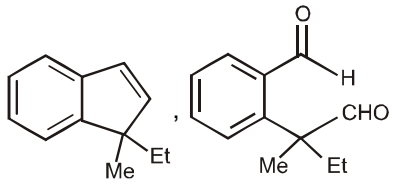
(C) 

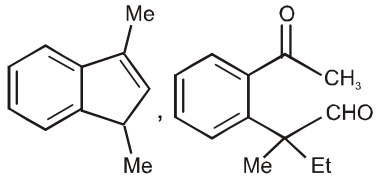
(D) 

18. The structures of the products **Q** and **R**, respectively, are : **[JEE 2009, 4/160]**

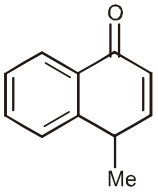
(A) 

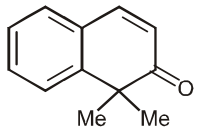
(B) 

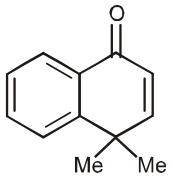
(C) 

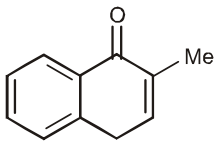
(D) 

19. The structure of the product **S** is : **[JEE 2009, 4/160]**

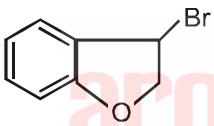
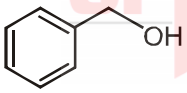
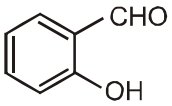
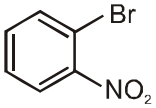
(A) 

(B) 

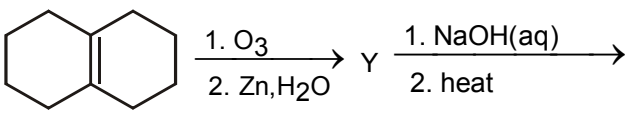
(C) 

(D) 

20. Match each of the compounds given in **Column I** with the reaction(s), that they can undergo, given in **column II.** **[JEE-2009, 8/160]**

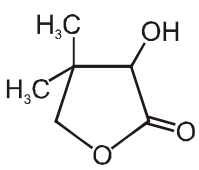
	Column I		**Column II**
(A)		(p)	Nucleophilic substitution
(B)		(q)	Elimination
(C)		(r)	Nucleophilic addition
(D)		(s)	Esterification with acetic anhydride
		(t)	Dehydrogenation

21. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is: **[JEE 2010, 3/163]**

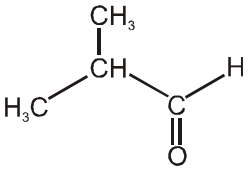
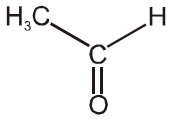


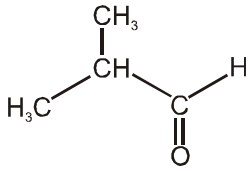
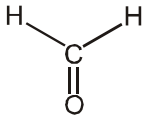
Comprehension (Q. 22 to 24)

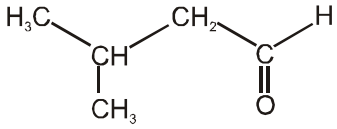
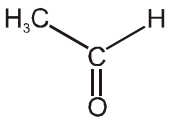
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below :

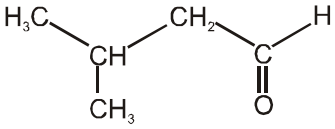
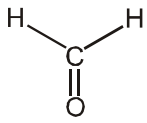


22. The compounds P and Q respectively are : **[JEE 2010, 3/163]**

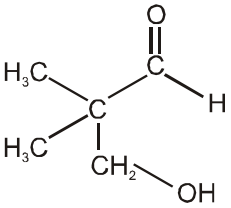
(A)  and 

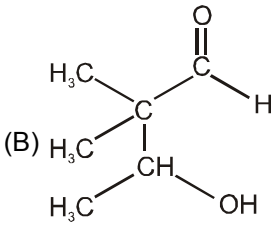
(B)  and 

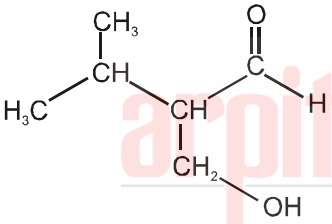
(C)  and 

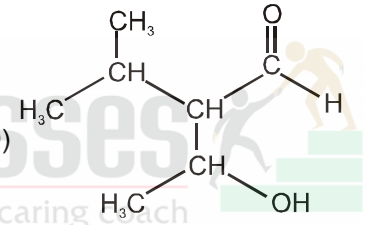
(D)  and 

23. The compound R is : **[JEE 2010, 3/163]**

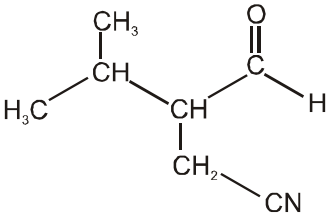
(A) 

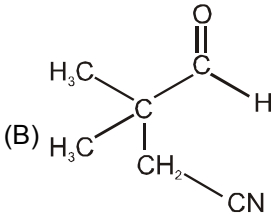
(B) 

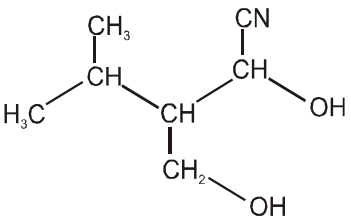
(C) 

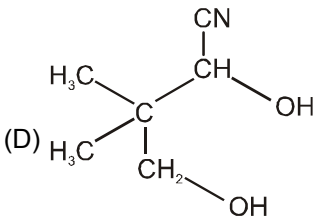
(D) 

24. The compound S is : **[JEE 2010, 3/163]**

(A) 

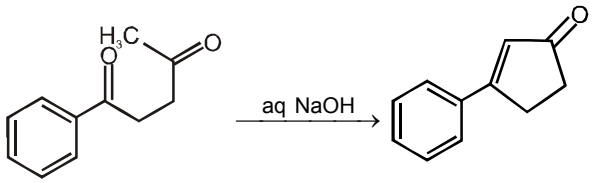
(B) 

(C) 

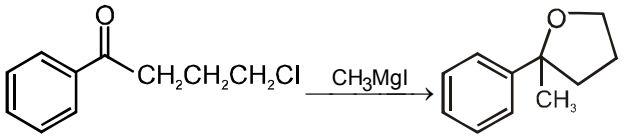
(D) 

25. Match the reactions in **column I** with appropriate type of steps/reactive intermediate involved in these reactions as given in **column II**

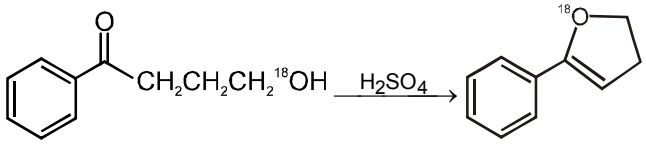
Column I **Column II** **[JEE 2011]**

(A) 

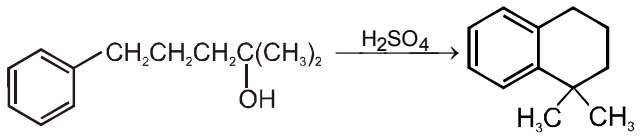
(p) Nucleophilic substitution

(B) 

(q) Electrophilic substitution

(C) 

(r) Dehydration

(D) 

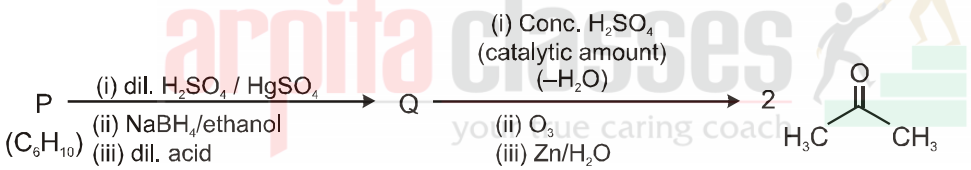
(s) Nucleophilic addition

(t) Carbanion

Comprehension (Q. 26 to 27)

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

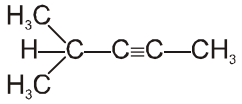
[JEE 2011]

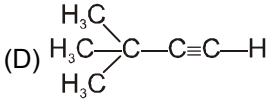


26. The structure of compound **P** is **[JEE 2011]**

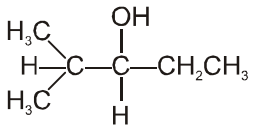
(A) $CH_3CH_2CH_2CH_2–C\equiv C–H$

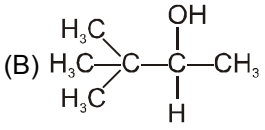
(B) $H_3CH_2C–C\equiv C–CH_2CH_3$

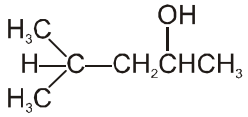
(C) 

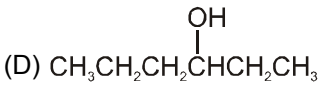
(D) 

27. The structure of the compound **Q** is **[JEE 2011]**

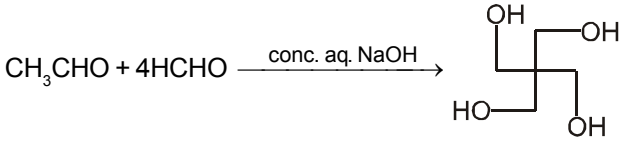
(A) 

(B) 

(C) 

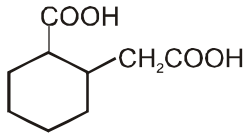
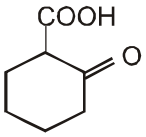
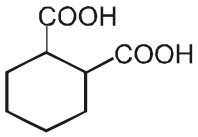
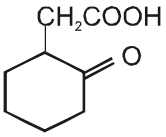
(D) 

28. The number of aldol reaction (s) that occurs in the given transformation is : **[IIT-JEE 2012, 3/136]**



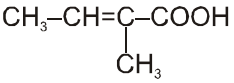
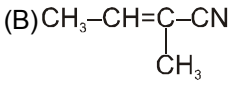
(A) 1 (B) 2 (C) 3 (D) 4

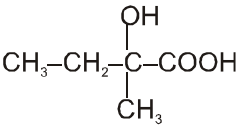
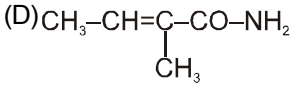
29. The compound that undergoes decarboxylation most readily under mild condition is **[IIT-JEE 2012, 3/136]**

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

30. The major product H in the given reaction sequence is **[IIT-JEE 2012, 3/136]**

$$CH_3–CH_2–CO–CH_3 \xrightarrow{\ominus CN} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

(A)  (B) 

(C)  (D) 

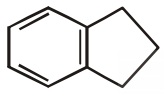
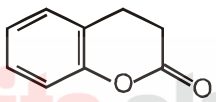
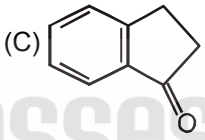
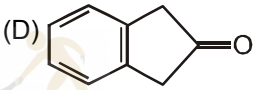
Comprehension (Q. 31 to 32)

In the following reactions sequence, the compound J is an intermediate.

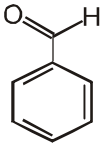
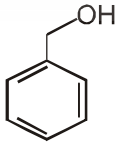
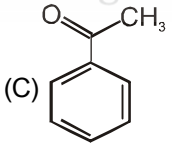
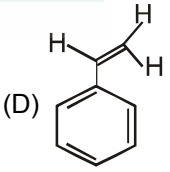
$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\text{(ii) anhyd. } AlCl_3]{\text{(i) } H_2, Pd/C;\ \text{(ii) } SOCl_2} K$$

J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test

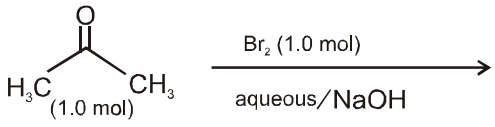
31. The compound K is **[IIT-JEE 2012, 3/136]**

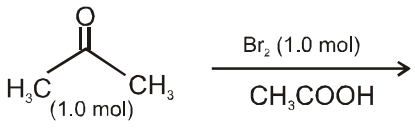
(A)  (B)  (C)  (D) 

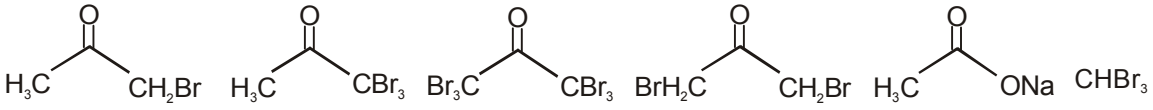
32. The compound I is **[IIT-JEE 2012, 3/136]**

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

33. After completion of the reactions (**I** and **II**), the organic compound(s) in the reaction mixtures is (are) **[JEE (Advance) 2013, 3/360]**

Reaction **I** : 

Reaction **II** : 



P **Q** **R** **S** **T** **U**

(A) Reaction **I** : **P** and Reaction **II** : **P**
(B) Reaction **I** : **U**, acetone and Reaction **II** : **Q**, acetone
(C) Reaction **I** : **T**, **U**, acetone and Reaction **II** : **P**
(D) Reaction **I** : **R**, acetone and Reaction **II** : **S**, acetone

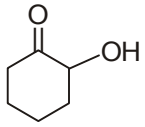
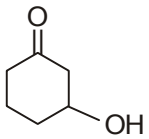
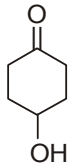
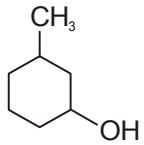
PART - II : AIEEE PROBLEMS (LAST 10 YEARS)

1. On vigorous oxidation by permangnate solution $(CH_3)_2C = CHCH_2CHO$ gives **[AIEEE-2002]**

(1) $(CH_3)_2CO$ and $OHCCH_2CHO$ (2) $(CH_3)_2C(OH)-CH(OH)CH_2CHO$

(3) $(CH_3)_2CO$ and $OHCCH_2COOH$ (4) $(CH_3)_2CO$ and $CH_2(COOH)_2$

2. Maximum dehydration takes place in : **[AIEEE-2002]**

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

3. CH_3MgI is an organometallic compound due to : **[AIEEE-2002]**

(1) Mg – I bond (2) C – I bond (3) C – Mg bond (4) C – H bond

4. Which one of the following is reduced with Zn, Hg and HCl acid to give the corresponding hydrocarbon? **[AIEEE-2004]**

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

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

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

6. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives **[AIEEE-2004]**

(1) Acetone (2) Acetamide (3) 2-Methyl-2-propanol (4) Acetyl iodide

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

(1) Pyridinium chloro-chromate (2) Chromic anhydride in glacial acetic acid
(3) Acidic dichromate (4) Acidic permanganate

8. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as **[AIEEE-2005]**

(1) an amine (2) an imine (3) an enamine (4) a Schiff's base

9. The decreasing order of the ratio of HCN addition to compounds A to D is **[AIEEE-2006]**

(1) HCHO (2) CH_3COCH_3 (3) $PhCOCH_3$ (4) PhCOPh

(1) d > b > c > a (2) d > c > b > a (3) c > d > b > a (4) a > b > c > d

10. In the following sequence of reactions, **[AIEEE-2007, 3/120]**

$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[Ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$. The compound 'D' is

(1) n-propyl alcohol (2) propanal (3) butanal (4) n-butyl alcohol

11. In the following sequence of reactions, the alkene affords the compound 'B' **[AIEEE-2008, 3/105]**

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

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

12. The treatment of CH_3MgX with $CH_3C\equiv C-H$ produces **[AIEEE-2008]**

(1) $CH_3C\equiv C-CH_3$ (2) $CH_3-CH=CH-CH_3$ (3) CH_4 (4) $CH_3-CH=CH_2$

13. In Cannizzaro reaction given below **[AIEEE-2009, 4/144]**

$2Ph\,CHO \xrightarrow{\overset{\Theta}{:OH}} PhCH_2OH + PhC\ddot{O}_2^{\Theta}$

the slowest step is :

(1) the transfer of hydride to the carbonyl group (2) the abstraction of proton from the carboxylic group

(3) the deprotonation of $PhCH_2OH$ (4) the attack of $:\overset{\Theta}{O}H$ at the carboxyl group

14. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is : **[AIEEE 2011, 4/120]**

(1) 2, 2, 2–Trichloroethanol (2) Trichloromethanol

(3) 2, 2, 2–Trichloropropanol (4) Chloroform

15. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : **[AIEEE 2011, 4/120]**

(1) 1-Pentene (2) 2-Pentene

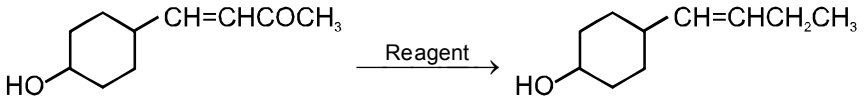
(3) 2-Methyl-2-pentene (4) 2-Methyl-1-pentene

16. Iodoform can be prepared from all except : **[AIEEE 2012, 4/120]**

(1) Ethyl methyl ketone (2) Isopropyl alcohol

(3) 3–Methyl–2–butanone (4) Isobutyl alcohol

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



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

PART - III : CBSE PROBLEMS (LAST 10 YEARS)

1. A organic compound (A) which has a characteristic odour, on treatment with NaOH form two compound (B) and (C). Compound (B) has the molecular formula C_7H_8O which on oxidation gives back compound (A). Compound (C) is the sodium salt of an acid. (C) when heated with sodalime yields an aromatic hydrocarbon (D). Deduce the structures of (A), (B), (C) and (D). **[CBSE 1999]**

2. You are provided with four reagents :

$LiAlH_4$, I_2 / NaOH, $NaHSO_3$ and Schiff's reagent.

Write which two reagents can be used to distinguish between the compounds in each of the following pairs. **[CBSE 1999]**

(i) CH_3CHO and CH_3COCH_3 (ii) CH_3CHO and C_6H_5CHO (iii) $C_6H_5COCH_3$ and C_6H_5CHO

3. How are the following conversions carried out ?

Acetophenone to benzoic acid **[CBSE 2000]**

4. Write the reaction of semicarbanzide with formaldehyde **[CBSE 2002]**

5. How will you convert **[CBSE 2002]**

(i) Benzoyal chloride to benzaldehyde

(ii) Propanone to 2-propanol

6. How will you convert 2-propanone into 2-methyl-2-propanol. **[CBSE 2003]**

7. Propose the mechanism for the following reaction :

$$CH_3CHO + HCN \xrightarrow{H^+} H_3C - \underset{\displaystyle OH}{\underset{|}{CH}} - CN$$ **[CBSE 2004]**

8. Predict the products of and ballance the following reactions : **[CBSE 2005]**

$C_6H_5CHO + KOH\ (conc.) \longrightarrow$

9. An organic compound A contains 69.77% carbon, 11.63% hydrogen and the rest it oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition product with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Write the possible structure of the compound A. **[CBSE 2008]**

10. How are the following conversions carried out? **[CBSE 2010, 1 Mark]**
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol

11. How would you convert the following : **CBSE 2010, 1 Mark]**
(i) Phenol to benzoquinone

12. Illustrate the following name reactions by giving a chemical equation in each case : **[CBSE 2010, 1 Mark]**
Cannizaro's reaction

13. Illustrate the following name reactions :
Wolff-Kishner reduction reaction **[CBSE 2010, 1 Mark]**

14. Illustrate the following name reactions : **[CBSE 2011, 2 Mark]**
(i) Cannizzaro's reaction
(ii) Clemmensen reduction

15. Give chemical tests to distinguish between **[CBSE 2011, 2 Mark]**
(i) Propanal and propanone, (ii) Benzaldehyde and acetophenone.

16. How would you obtain **[CBSE 2011, 1 Mark]**
But -2- enal from ethanal,

17. Describe the following giving linked chemical equations : **[CBSE 2011, 1 Mark]**
(i) Cannizzaro reaction

18. Arrange the following compounds in an increasing order of their property as indicated :
Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactitivity towards HCN) **[CBSE 2012, 1 Mark]**

19. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions :
ethanal, propanal, propanone, butanone. **[CBSE 2012, 1 Mark]**

20. Illustrate the following name reactions giving suitable example in each case : **[CBSE 2012, 1 Mark]**
(i) Clemmensen reduction

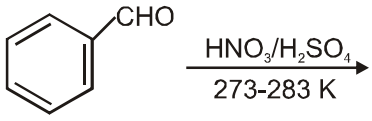
21. Give simple tests to distinguish between the following pairs of compounds. **[CBSE 2012, 1 Mark]**
(i) Pentan-2-one and Pentan-3-one

22. How will you convert Ethanal to propan –2–ol ? **[CBSE 2013, 1 Mark]**

23. How will you bring about the following conversions ? **[CBSE 2013, 3 Mark]**
(i) Propanone to propane
(ii) Benzoyl chloride to benzaldehyde
(iii) Ethanal to but-2-enal

24 (a) Complete the following reactions : **[CBSE 2013, 3 Mark]**

(i) $2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc.KOH}}$

(ii) 

(b) Give simple chemical tests to distinguish between Ethanal and propanal :

BOARD LEVEL EXERCISE : HINT & SOLUTIONS

1. $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CHO$

2. The electron density at the carbonyl carbon increases with the increase in the +I effect. As a result, the chances of attack by a nucleophile decrease. Hence, the increasing order of the reactivities of the given carbonyl compounds in nucleophilic addition reactions is:
Butanone < Propanone < Propanal < Ethanal

3. The +I effect is more in ketone than in aldehyde. Hence, acetophenone is the least reactive in nucleophilic addition reactions. Among aldehydes, the +I effect is the highest in *p*-tolualdehyde because of the presence of the electron-donating —CH_3 group and the lowest in *p*-nitrobezaldehyde because of the presence of the electron-withdrawing -NO_2 group. Hence, the increasing order of the reactivities of the given compounds is:
Acetophenone < *p*-tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

4. The molecular masses of the given compounds are in the range 44 to 46. CH_3CH_2OH undergoes extensive intermolecular H-bonding, resulting in the association of molecules. Therefore, it has the highest boiling point. CH_3CHO is more polar than CH_3COCH_3 and so CH_3CHO has stronger intermolecular dipole - dipole attraction than CH_3COCH_3· $CH_3CH_2CH_3$ has only weak van der Waals force. Thus, the arrangement of the given compounds in the increasing order of their boiling points is given by:
$CH_3CH_2CH_3 < CH_3COCH_3 < CH_3CHO < CH_3CH_2OH$

5. Propanal and propanone can be distinguished by the following tests.
(a) Tollen's test :
Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But, propanone being a ketone does not reduce Tollen's reagent.

$$CH_3CH_2CHO + 2\,[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + Ag\downarrow + 4NH_3 + 2H_2O$$

Propanal Tollen's reagent Propanoate ion Silver mirror

(b) Fehling's test :
Aldehydes respond to Fehling's test, but ketones do not.
Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu_2O, but propanone being a ketone does not.

$$CH_3CH_2CHO + 2\,Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + Cu_2O\downarrow + 3H_2O$$

(c) Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom respond to iodoform test. They are oxidized by sodium hypoiodite (NaOI) to give iodoforms. Propanone being a methyl ketone responds to this test, but propanal does not.

$$CH_3COCH_3 + 3\,NaOI \longrightarrow CH_3COONa + CHI_3 + 2NaOH$$

Propanone Sodium acetate Iodofrom (yellow ppt.)

6. Benzoic acid and Ethyl benzoate can be distinguished by sodium bicarbonate test.
Sodium bicarbonate test :
Acids react with $NaHCO_3$ to produce brisk effervescence due to the evolution of CO_2 gas.
Benzoic acid being an acid responds to this test, but ethylbenzoate does not.

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$$

Benzoic acid Sodium benzoate

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No effervescence due to evolution of } CO_2 \text{ gas.}$$

7. Ethanal and propanal can be distinguished by iodoform test.

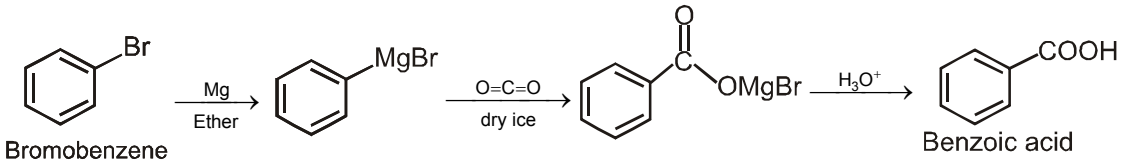
Iodoform test

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom responds to the iodoform test. Ethanal having one methyl group linked to the carbonyl carbon atom responds to this test. But propanal does not have a methyl group linked to the carbonyl carbon atom and thus, it does not respond to this state.

$$CH_3CHO + 3NaOI \longrightarrow HCOONa + CHI_3 + 2NaOH$$

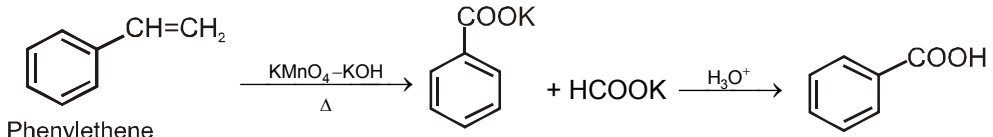
Ethanal — Sodium methanoate — Iodoform (yellow ppt)

8. (i)



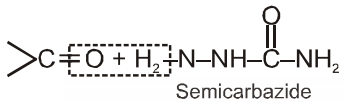
Bromobenzene — Benzoic acid

(ii)

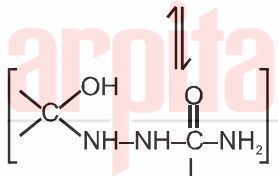


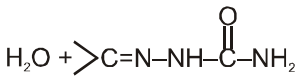
Phenylethene — Benzoic acid

9. Semicarbazones are derivatives of aldehydes and ketones produced by the condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazide



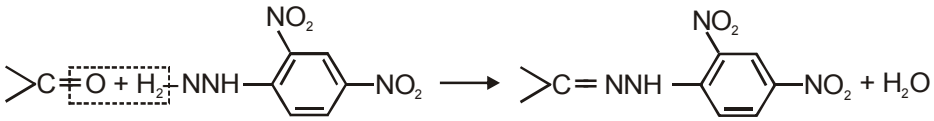


Semicarbazone

Semicarbazones are useful for identification and characterization of aldehydes and ketones.

10. **(i) 2, 4-DNP-derivative :**

2, 4-dinitrophenylhydrazones are 2, 4-DNP-derivatives, which are produced when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in a weakly acidic medium.



2, 4-Dinitrophenylhydrazine — 2, 4-Dinitrophenylhydrazone

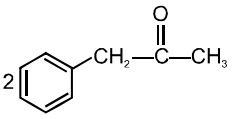
To identify and characterize aldehydes and ketones, 2, 4-DNP derivatives are used.

(ii) Schiff's base :

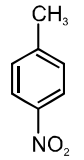
Aldehydes and ketones on treatment with primary aliphatic or aromatic amines in the presence of trace of an acid yields a Schiff's base.

$$R–CH{=}O + H_2{-}N—R' \xrightarrow{\text{Trace of } H^+} R–CH{=}N—R' + H_2O$$

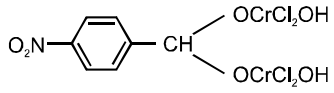
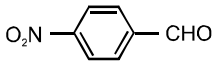
Aldehyde — 1°amine — Schiff's base

11. (a) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2$  $+ CdCl_2$

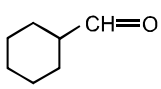
1–Phyenylpropanone

(b) 

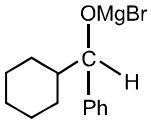
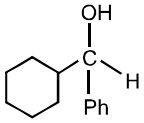
p-Nitrotoluene

$\xrightarrow[2.CS_2]{1.\ CrO_2Cl_2}$  $\xrightarrow{H_3O^+}$ 

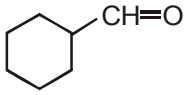
p-Nitrobenzaldehyde

12. (i) 

Cyclohexane Carbaldehyde

$\xrightarrow[\text{Dry ether}]{Ph-MgBr}$  $\xrightarrow[\text{Hydrolysis}]{H_3O^+}$ 

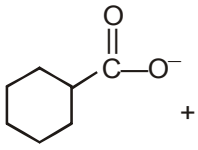
Cyclohexylphenylcarbinol

(ii) 

Cyclohexane carbaldehyde

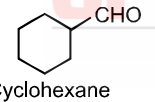
$+ \ 2\,[Ag(NH_3)_2]^+ + 3OH^-$

Tollen's reagent

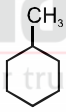
$\longrightarrow$  $+ \ 2\,Ag\downarrow + 4NH_3 + 2H_2O$

Cyclohexane carboxylate ion

Silver mirror

(iii) 

Cyclohexane carbaldehyde

$\xrightarrow[\text{(Clemmensen reduction)}]{Zn/Hg-HCl}$ 

Methylcyclohexane

13. **(i)** On treatment with dilute alkali, ethanal produces 3-hydroxybutanal gives butane-1, 3-diol on reduction.

$CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\underset{OH}{CH}-CH_2-CHO \xrightarrow[\text{(Reduction)}]{NaBH_4} CH_3-\underset{OH}{CH}-CH_2-CH_2-OH$

Ethanal — 3-Hydroxybutanal — Butane-1, 3-diol

(ii) On treatment with dilute alkali, ethanal produces 3-hydroxybutanal gives bute-2-enal on heating.

$CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\underset{OH}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$

Ethanal — 3-Hydroxybutanal — But-2-enal

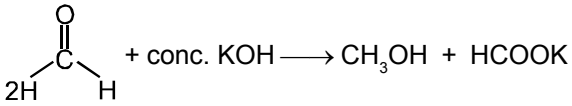
(iii) When treated with Tollen's reagent, But-2-enal produced in the above reaction produces but-2-enoic acid.

$CH_3-CH=CH-CHO \xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+OH^-} CH_3-CH=CH-COOH$

But-2-enal — But-2-enoic acid

14. **Cannizzaro reaction :**

The self oxidation-reduction (disproportionation) reaction of aldehydes having no α-hydrogens on treatment with concentrated alkalis is known as the Cannizzaro reaction. In this reaction, two molecules of aldehydes participate where one is reduced to alcohol and the other is oxidized to carboxylic acid.



Hydride transfer is the rate determing step.

15. % of carbon = 69.77 %

% of hydrogen = 11.63 %

% of oxygen = {100 - (69.77 + 11.63)}% = 18.6 %

$$C:H:O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

$$= 5.81 : 11.63 : 1.16$$

$$= 5 : 10 : 1$$

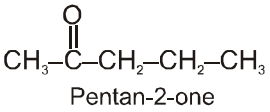
Therefore, the empirical formula of the compound is $C_5H_{10}O$.

Now, the empirical formula mass of the compound = 5 × 12 + 10 ×1 + 1 × 16 = 86.

Molecular mass of the compound = 86

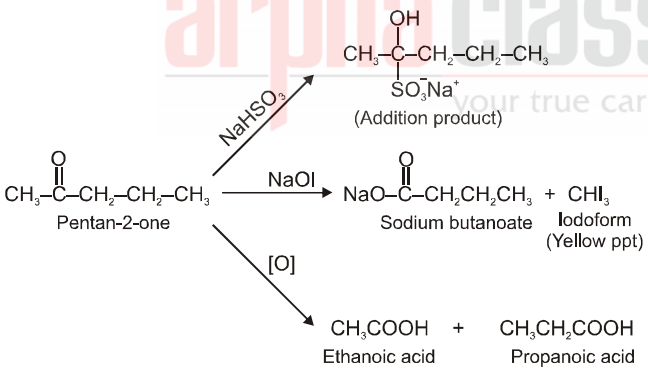
Therefore, the molecular formula of the compound is given by $C_5H_{10}O$.

Hence, the given compound is pentan-2-one.



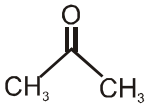
Pentan-2-one

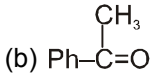
The given reactions can be explained by the following equations:



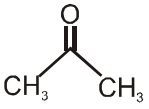
EXERCISE - 1

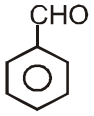
PART - I

A-1. (a) 

(b) 

+ NH_3 + Mg(OH)I

(c) 

(d) 

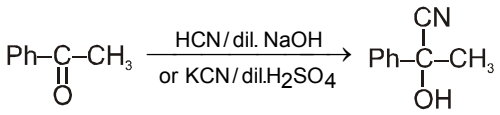
B-1. The reactivity of carbonyl group towards nucleophilic reagent depends upon the extent of positive charge present on the carbon. In ketones two alkyl group attach to the carbon reduce the positive charge on the carbonyl carbon due to their electron repelling nature while in aldehyde the positive charge on carbonyl carbon is reduced to lesser extent because only one alkyl group is present.
Also, In ketones steric hinderance is more than aldehyde.

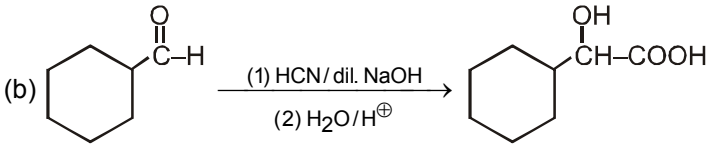
B-2. IV > III > II > I

B-3. IV > III > I > II

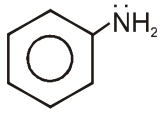
B-4. d > b > c > a

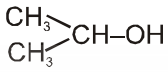
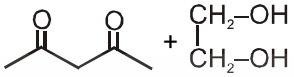
B-5. c > b > a > d

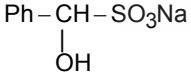
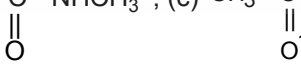
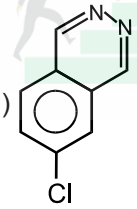
B-6. (a) 

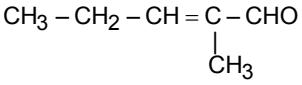
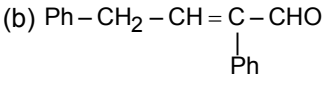
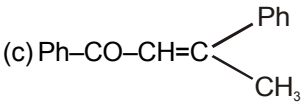
(b) 

B-7. Cyanohydrin is formed by nucleophilic attack on carbonyl group (C=O), 2, 2, 6-trimethylcyclohexanone has more steric crowding and three methyl groups in tri methyl cyclohexanone which nearly neutralise the positive charge on carbon hence CN^- nucleophile does not react with 2,2,6-trimethylcyclohexanone.

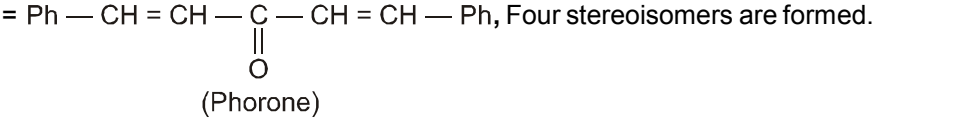
B-8. (a)  $+ CH_3–CHO$ (b) $H_2N – CH_2 – CH_2–CH_2–CH_2–CO–CH_3$

B-9. **(a)** $CH_3–CHO +$  **(b)** 

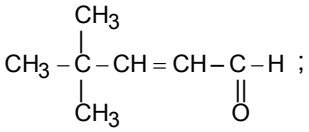
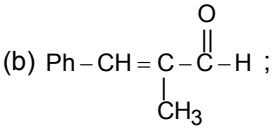
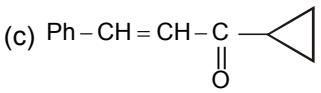
B-10. (a)  ; (b)  ; (c) ; (d) 

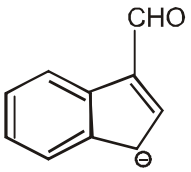
C-1. (a)  (b)  (c) 

C-2. (a) $CH_3CH_2CH_2CHO$; (b) CH_3COCH_3

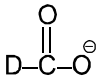
C-3. [X] =  , Four stereoisomers are formed.

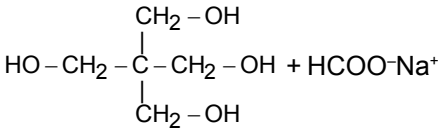
(Phorone)

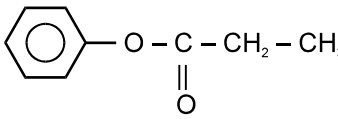
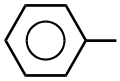
C-4. (a)  ; (b)  ; (c) 

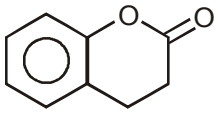
C-5. 

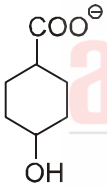
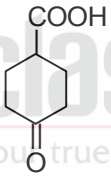
C-6. (a) $CH_3CH_2CH_2COOEt$; (b) $PhCH_2COOCH_3$; (c) $(CH_3)_2CHCH_2COOEt$

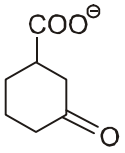
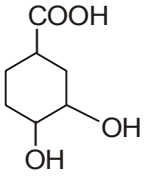
D-1. (P) =  (Q) = $D–CH_2–OH$

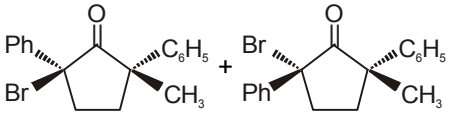
D-2. 

E-1. (a) (p)  , (q)  , (r) $CH_3 – CH_2 – CH_2OH$

(b) 

E-2. (a)  ; (b)  ;

(c)  ; (d) 

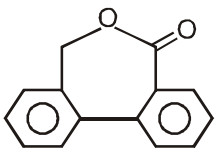
F-1.  , (Diastereomer).

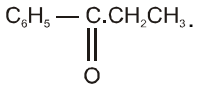
F-2. (a) $CHI_3 + HCOO^{\ominus}Na^{\oplus}$

(b) $CHI_3 + PhCH_2COO^{\ominus}Na^{\oplus}$

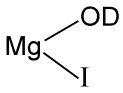
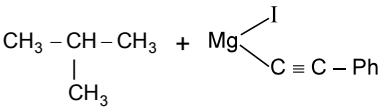
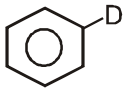
(c) $CHI_3 + (Me)_3C–COO^{\ominus}Na^{\oplus}$

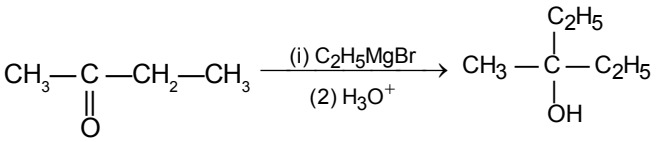
G-1. $Ph_2C = CH_2$

G-2I. 

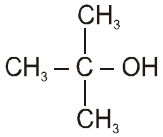
G-3. X $\Rightarrow$ 

H-1. b, f, g, h

H-2. (a) $CH_3 - D$ +  (b)  (c) 

H-3. 

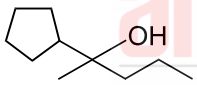
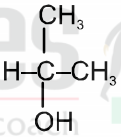
3-Methylpentan-3-ol

H-4. (i) 

2-Methyl-2-propanol

(ii) $CH_3CH_2CH_2OH$

H-5. X = CH_2=CH–Br, Y = CH_3Br

H-6. (a)  (b)  (c) 

PART - II

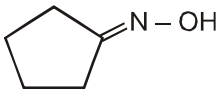
A-1.	(A)	**A-2.**	(A)	**A-3.**	(C)	**A-4.**	(C)	**A-5.**	(A)
A-6.	(A)	**B-1.**	(B)	**B-2.**	(C)	**B-3.**	(D)	**B-4.**	(A)
B-5.	(B)	**B-6.**	(B)	**B-7.**	(B)	**B-8.**	(B)	**B-9.**	(B)
C-1.	(D)	**C-2.**	(A)	**C-3.**	(D)	**C-4.**	(B)	**C-5.**	(D)
C-6.*	(A,B,D)	**D-1.**	(D)	**D-2.**	(A)	**D-3.**	(A)	**D-4.**	(C)
D-5.	(C)	**D-6.**	(B)	**E-1.**	(A)	**E-2.***	(A,B,C)	**E-3.**	(A)
E-4.	(C)	**E-5.**	(A)	**E-6.**	(B)	**F-1.**	(A)	**F-2.**	(C)
F-3.*	(A,B,C)	**F-4.***	(A,B,C)	**F-5.***	(A,C)	**G-1.**	(C)	**G-2.**	(B)
G-3.	(A)	**G-4.***	(A,C,D)	**G-5.**	(C)	**G-6.**	(B)	**G-7.***	(A,B,C)
H-1.	(C)	**H-2.**	(B)	**H-3.**	(C)	**H-4.*_**	(A,C,D)	**H-5.**	(A)
H-6.	(A)	**H-7.**	(A)	**H-8.**	(B)	**H-9.**	(C)	**H-10.**	(A)
H-11.	(A)	**H-12.**	(B)						

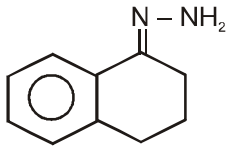
PART - III

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

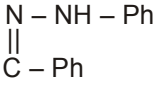
EXERCISE - 2

PART - I

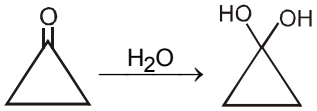
1. (a) 

(b) 

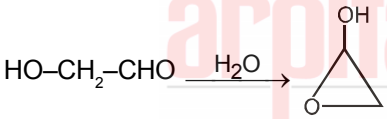
(c) $Ph–CH_2–CH_2–CH=N–NH–\overset{\overset{O}{\|}}{C}–NH_2$

(d) 

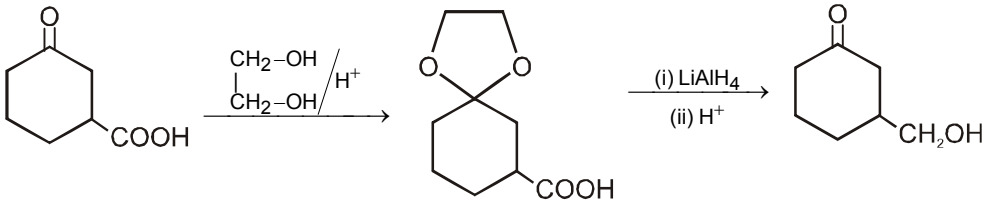
2. Two nitrogen atoms of semicarbazide that are adjacent to the (C=O) group have their lone pair present in conjugation so nucleophilicity decreases.

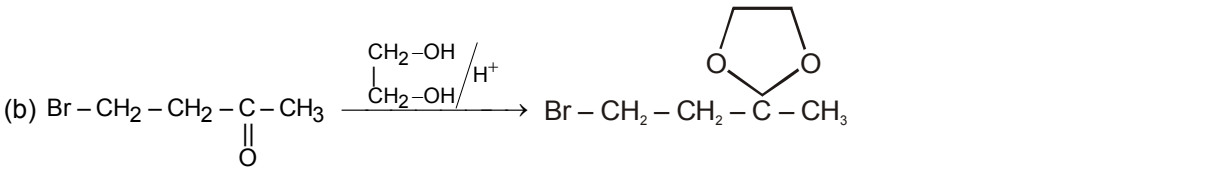
3. 

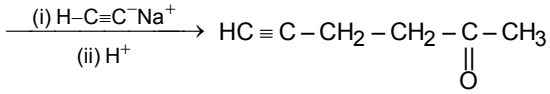
In cyclopropanone angle strain decreases after addition of water, while cyclic hemiacetal structure of 2-hydroxy ethanal will develope angle strain.

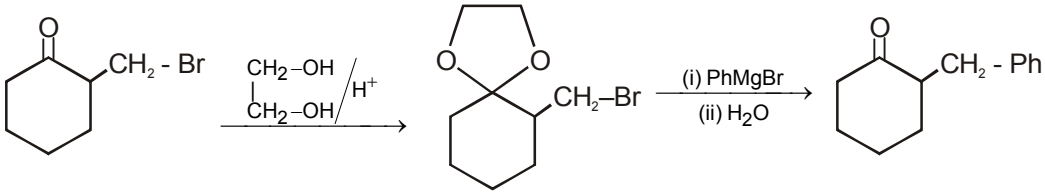


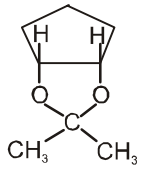
Hemiacetal
(Not form due to angle strain)

4. (a) 

(b) 

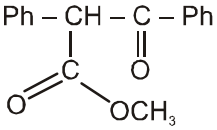
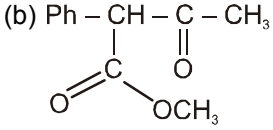


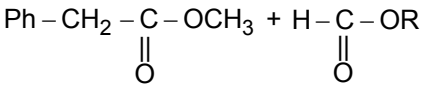
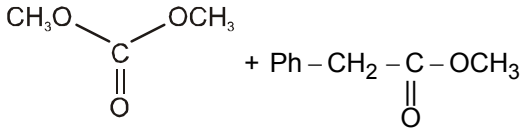
(c) 

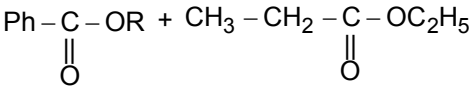
5. (a) 
A cyclic ketal

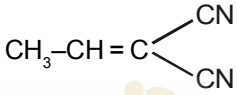
(b) The – OH groups in the trans isomer are too far apart to form cyclic structure.

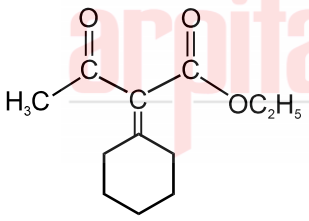
6. (a) 4 (b) 0

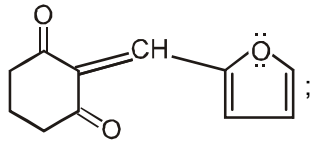
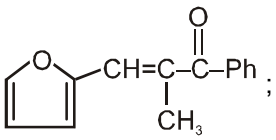
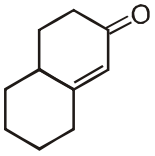
7. (a)  (b)  (c) CH_3CH_2COOH

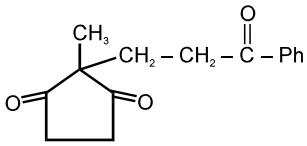
8. (a)  (b) 

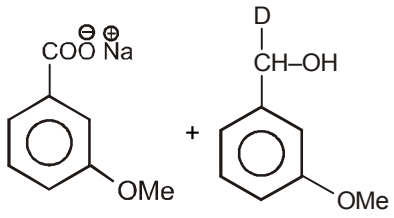
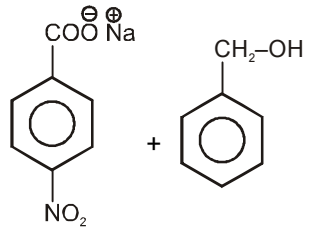
(c) 

9. (a)  (b) 

(c) 

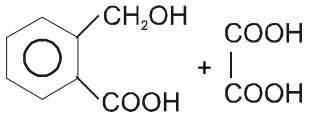
10. (a)  ; (b)  ; (c)  ;

11. 

12. (a)  (b) 

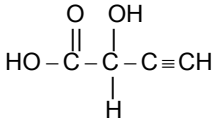
13. PhCH(OH)COOH

14. $HO-CH_2-COONa$.

15. 

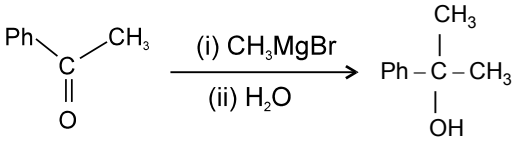
16. **A =** $CH_3CCl_2CH_2CH_3$, **B =** $CH_3COCH_2CH_3$.

17. C_5H_{11}–OH

18. 

19. $X = CH_3(CH_2)_8CH_2Br$; $Y = CH_3(CH_2)_8CH_3$

20. (a) $Ph–C\equiv CH + CH_3MgBr \longrightarrow CH_4 + Ph-C\equiv CMgBr \xrightarrow[(ii)\ H_2O]{(i)\ CH_3-\underset{\underset{O}{\|}}{C}-CH_3} Ph-C\equiv C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(b) 

(c) 

PART - II

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

PART - III

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

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

3. (A) - p, q, s ; (B) - p, q, r, s ; (C) - p ; (D) - q, r, s

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

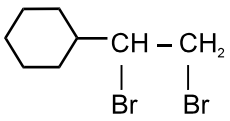
5. (A) - (p) ; (B) - (s) ; (C) - (q) ; (D) - (r)

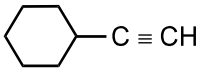
PART - IV

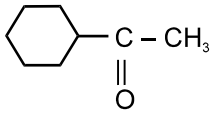
1.	(A)	**2.**	(B)	**3.**	(A)	**4.**	(D)	**5.**	(D)
6.	(D)	**7.**	(B)	**8.**	(C)	**9.**	(A)	**10.**	(A)
11.	(A)	**12.**	(A)	**13.**	(D)	**14.**	(A)	**15.**	(A)
16.	(C)	**17.**	(B)	**18.**	(B)	**19.**	(C)	**20.**	(C)
21.	(C)	**22.**	(A)	**23.**	(B)				

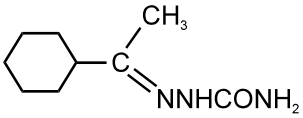
EXERCISE - 3

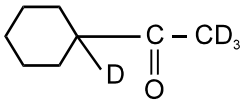
PART - I

1. (A) = 

(B) = 

(C) = 

(D) = 

(E) = 

2.	(B)	**3.**	(A)	**4.**	(C)	**5.**	(B)	**6.**	(D)
7.	(C)	**8.**	(A)	**9.**	(A) – (p, q, s) ; (B) – (q) ; (C) – (q, r, s) ; (D) – (q, r)				
10.	(C)	**11.**	(B)	**12.**	(A)	**13.**	(D)	**14.**	(D)
15.	(A)	**16.**	(C)	**17.**	(B)	**18.**	(A)	**19.**	(B)
20.	(A) - p, q, t ; (B) - p, s, t ; (C) - r, s ; (D) - p			**21.**	1	**22.**	(B)	**23.**	(A)
24.	(D)	**25.**	(A-r, s, t) ; (B-p, s) ; (C-r, s) ; (D-q, r)			**26.**	(D)	**27.**	(B)
28.	(C)	**29.**	(B)	**30.**	(A)	**31.**	(C)	**32.**	(A)
33.	(C)								

PART - II

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

PART - III

1. The molecular formula of the compound is C_7H_8O therefore, it is an aromatic compound. Since on heating with NaOH it yields an alcohol, therefore, it is nothing but benzaldehyde and the alcohol is benzyl alcohol.

$$\underset{\text{(A)}}{C_6H_5CHO} \xrightarrow[\Delta]{NaOH} \underset{\text{(B)}}{C_6H_5CH_2OH} + C_6H_5COONa$$

Banzaldehyde — Benzyl alcohol

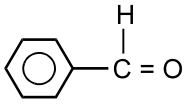
(B) On oxidation yields back (A) (∵ B alcohols on oxidation give aldehydes)

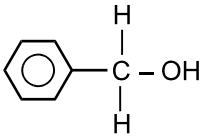
$$\underset{\text{(B)}}{C_6H_5CH_2OH} \xrightarrow{[O]} \underset{\text{(A)}}{C_6H_5CHO} + H_2O$$

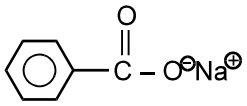
Since (C) is a sodium salt of an acid and gives a hydrocarbon (D) on heating with soda lime therefore, (C) is sodium benzoate and (D) is benzene as illustrated below :

$$\underset{\text{(C)}}{C_6H_5COONa} \xrightarrow[\Delta]{NaOH / CaO} \underset{\text{(D)}}{C_6H_6} + Na_2CO_3$$

Structure of A, B, C and D are :

(A) 

(B) 

(C) 

(D) 

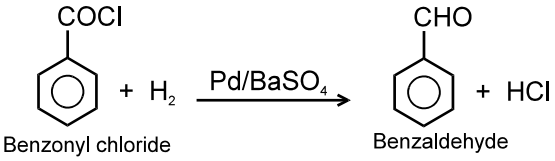
2. (i) Schiff's reagent

(ii) I_2 / NaOH

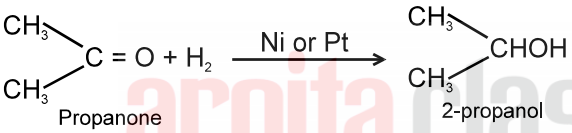
(iii) I_2 / NaOH and $NaHSO_3$.

3. $PhCOCH_3 \xrightarrow{I_2 / OH^-} CHI_3 + PhCOO^{\ominus}\ Na^{\oplus}$

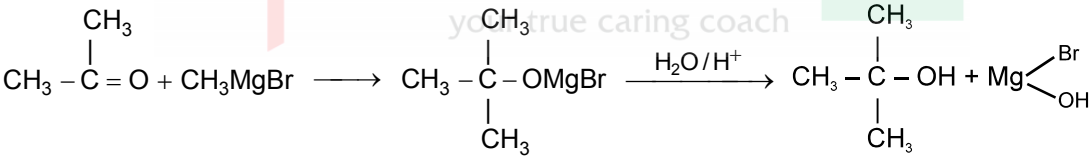
4. $\underset{\text{formaldehyde}}{HCHO} + \underset{\text{semicarbazide}}{H_2NNHCONH_2} \xrightarrow{-H_2O} \underset{\substack{\text{formaldehyde}\\\text{semicarbazone}}}{HCN=NNHCONH_2}$

5. (i) 

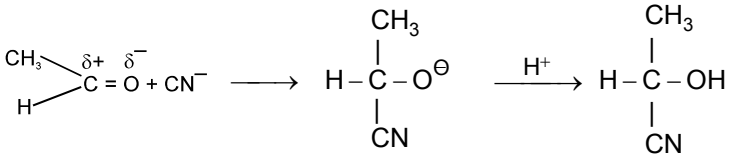
Benzonyl chloride — Benzaldehyde

(ii) 

Propanone — 2-propanol

6. 

2-Methyl-2-propanol

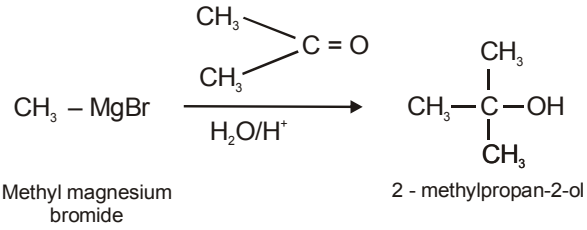
7. 

8. $\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + KOH \xrightarrow{\Delta} \underset{\text{Pot. benzoate}}{C_6H_5COO^{\ominus}K^{\oplus}} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$

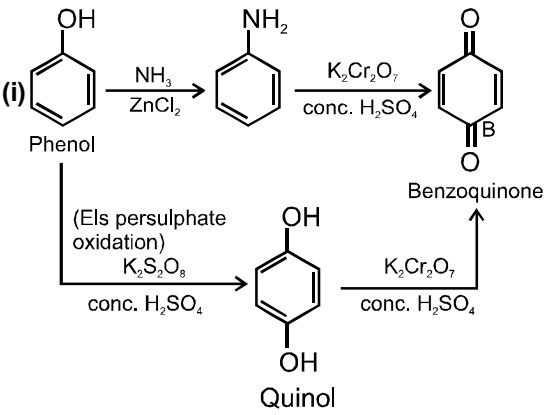
9. $A = C_5H_{10}O$

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 \xrightarrow{\text{Oxidation}} CH_3COOH + CH_3CH_2COOH$

10. (ii)



11. (i)



12. **Cannizaro's reaction :** When aldehyde having no α-hydrogen reacts in presence of conc. NaOH, sodium salt of acid and alcohol is formed.

$$2HCHO \xrightarrow{50\%\ NaOH} HCOONa + CH_3OH$$

$$C_6H_5CHO + HCHO \xrightarrow{50\%\ NaOH} C_6H_5CH_2OH + HCOONa$$

13. **Wolff-Kishner reduction :** When aldehydes and ketones are reduced with hydrazine and KOH, hydrocarbons are formed.

$$CH_3-\underset{\underset{H}{|}}{C}=O \xrightarrow{NH_2-NH_2} \underset{\text{Ethanal hydrazone}}{CH_3CH=N-NH_2} \xrightarrow[\text{glycol}]{KOH} CH_3-CH_3+N_2$$

14. **(i) Cannizzaro reaction :** Aldehydes which do not contain an α -hydrogen atom, when treated with concentrated alkali solution undergo self oxidation - reduction. As a result, one molecule of the aldehyde is reduced to the corresponding alcohol which is oxidised to the corresponding carboxylic acid. This reaction is called Cannizzaro reaction.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. benzoate}}{C_6H_5COONa}$$

(ii) Clemmensen Reduction : When aldehydes and ketones are reduced with Zn(Hg) and conc. HCl, hydrocarbons are formed.

$$CH_3CHO + 4[H] \xrightarrow[HCl]{Zn(Hg)} CH_3-CH_3 + H_2O$$

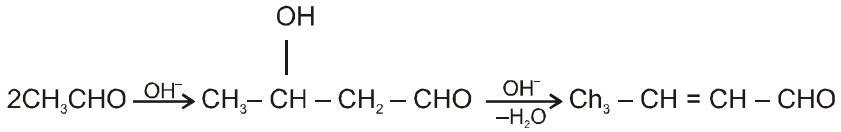
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 4[H] \xrightarrow[\text{conc. HCl}]{Zn(Hg)} CH_3-CH_2-CH_3 + H_2O$$

15. (i) Fehling solution test : Warm each compound with few drops of Fehling solution. Propanal gives a red precipate of cuprous oxide.

$$CH_2CH_2CHO + \underbrace{2Cu^{2+} + 5OH^-}_{\text{Fehling solution}} \longrightarrow CH_3CH_2COONa + \underset{\text{red ppt.}}{Cu_2O} + 3H_2O$$

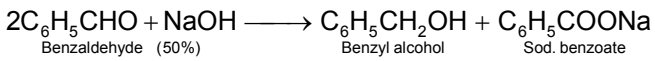
(ii) Iodoform Test : Warm each compound with iodine and sodium hydroxide solution on a water bath. Acetophenone ($C_6H_5COCH_3$) gives yellow precipitate of iodoform Benzaldehyde doe not give this test.

16.



Ethanal — But-2-enal

17. **(i) Cannizzaro reaction :** Aldehydes which do not contain an α -hydrogen atom, when treated with concentrated alkali solution undergo self oxidation - reduction. As a result, one molecule of the aldehyde is reduced to the corresponding alcohol which is oxidised to the corresponding carboxylic acid. This reaction is called Cannizzaro reaction.

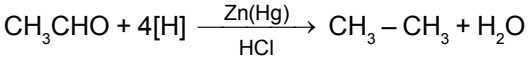


Benzaldehyde (50%) — Benzyl alcohol — Sod. benzoate

18. **(i)** Methyl tert-butyl ketone < Acetone < Acetaldehyde

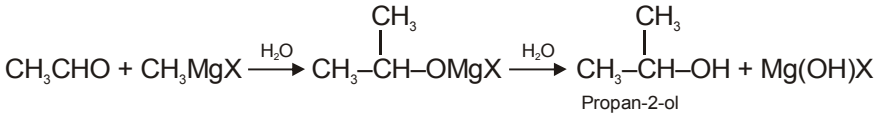
19. Butanone < Propanone < Propanal < Ethanal.

20. (**i) Clemmensen reduction** = When aldehydes and ketones are reduced with Zn (Hg) and conc. HCl, hydrocarbons are formed.



21. **Add I_2 and NaOH =** Pentan-2one will give yellow ppt. of iodoform whereas pentan – 3 – one will not react.

22.



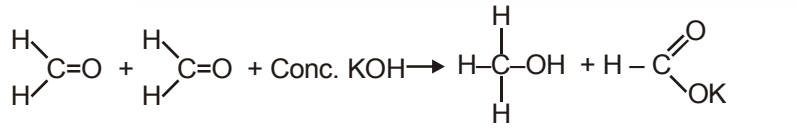
Propan-2-ol

23. (i) $CH_3–CO–CH_3 \xrightarrow{NH_2–NH_2, Conc.KOH} CH_3–CH_2–CH_3$ (It is the Wolff Kishner reduction)

(iii) $2CH_3CHO \xrightarrow[(ii)\ H^+, \Delta]{(i)\ dil.\ NaOH} CH_3CH = CHCHO$ (It is the aldol condensation reaction)

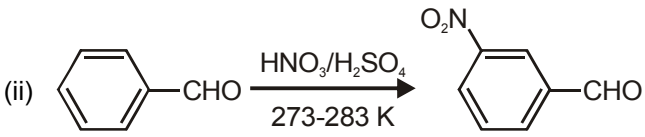
Ethanal — But-2-enal

24 (i)



Formaldehyde — Methanol — Potassium formate

(ii)



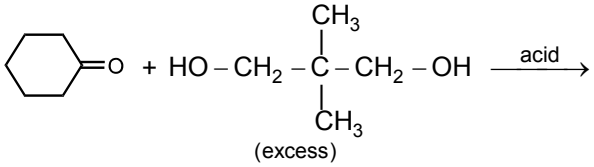
Benzaldehyde — m-Nitrobenzaldehdye

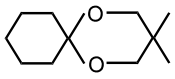
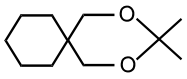
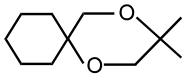
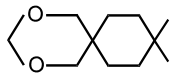
(b) Ethanal gives iodoform test but propanal can not give iodoform test

PART - I : OBJECTIVE QUESTIONS

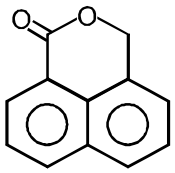
Single choice type

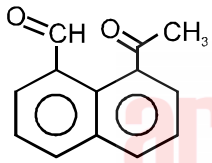
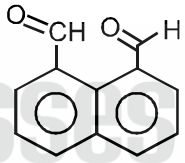
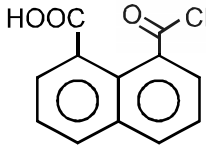
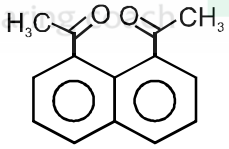
1. Which of the following will be product of following reactions ?

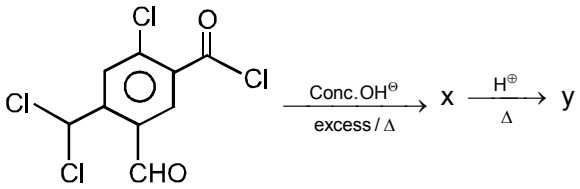


(A) 
(B) 
(C) 
(D) 

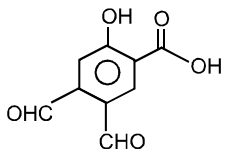
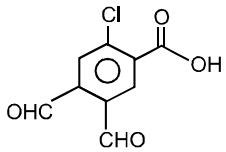
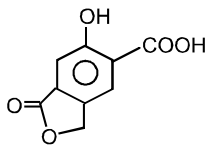
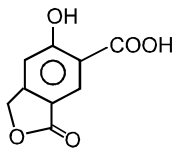
2. Which of the following compounds on reaction with conc. NaOH followed by $\overset{\oplus}{H}$ gives following cyclic ester.



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

3. 

The major product (y) in the above reaction :

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

4. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives :
(A) Potassium m-chlorobenzoate and m-hydroxybenzaldehyde
(B) m-hydroxybenzaldehyde and m-chlorobenzyl alcohol
(C) m-chlorobenzyl and m-hydroxybenzyl alcohol
(D) Potassium m-chlorobenzoate and m-chlorobenzyl alcohol.

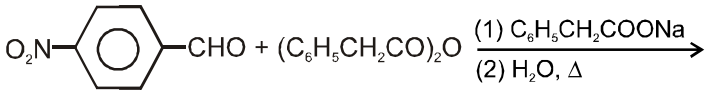
5. Under Wolf Kishner reduction conditions, the conversions which may be brought about is ?
(A) Benzaldehyde into Benzyl alcohol (B) Cyclohexanol into Cyclohexane
(C) Cyclohexanone into Cyclohexanol (D) Benzophenone into Diphenylmethane

6. Hydrogenation of benzoylchloride in presence of Pd and $BaSO_4$ gives
(A) Benzyl alcohol (B) Benzaldehyde (C) Benzoic acid (D) Phenol

7. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is :
(A) MeCOCl (B) MeCHO (C) MeCOOMe (D) MeCOOCOMe

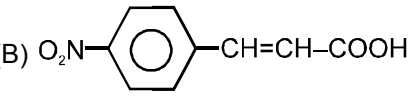
8. An organic compound C_3H_6O does not give a precipitate with 2, 4-dinitrophenyl hydrazine reagent also does not react with metallic sodium it could be :
(A) $CH_3–CH_2–CHO$ (B) $CH_3–COCH_3$ (C) $CH_2=CH–CH_2–OH$ (D) $CH_2=CH–OCH_3$

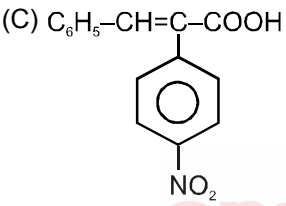
9. The product of the reaction

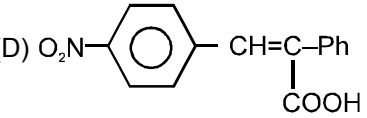


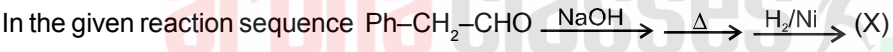
(X) will be :

(A) $C_6H_5CH=CH–COOH$

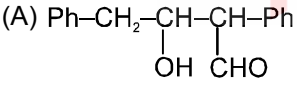
(B) 

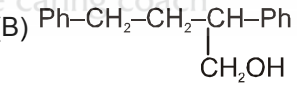
(C) 

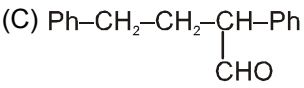
(D) 

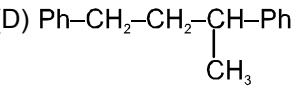
10. In the given reaction sequence 

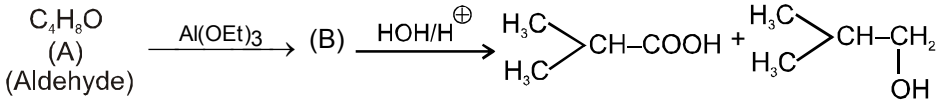
Product (X) will be :

(A) 

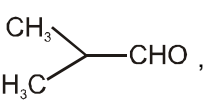
(B) 

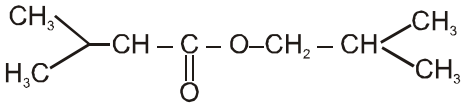
(C) 

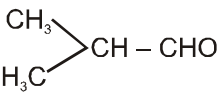
(D) 

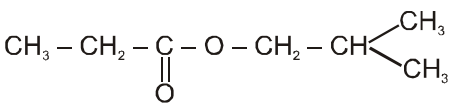
11. 

A and B are :

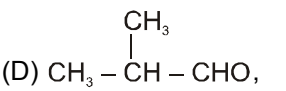
(A) 

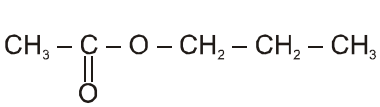
, 

(B) 

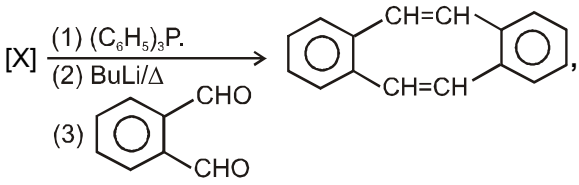


(C) Both 'a' and 'b'

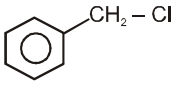
(D) 

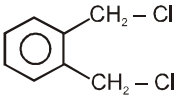


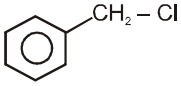
12. In the given reaction



, [X] is :

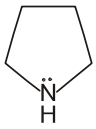
(A) 2 Mole 

(B) 

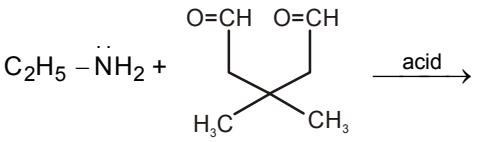
(C) 

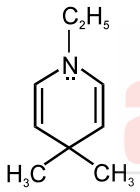
(D) All of these

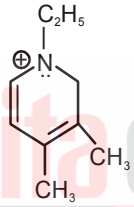
13. Among the following compounds which one will react with acetone to give a product that contains carbon-nitrogen double bond ?

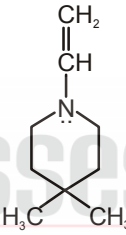
(A) $C_6H_5\ddot{N}HC_6H_5$ (B) $(CH_3)_3\ddot{N}$ (C)  (D) $C_6H_5\ddot{N}H\ddot{N}H_2$.

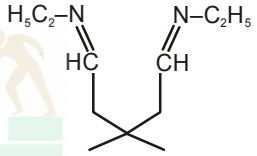
14. The final product of the following reaction is :

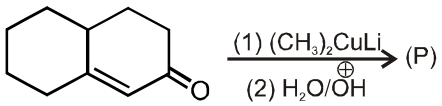


(A) 

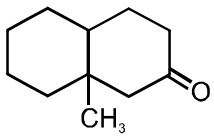
(B) 

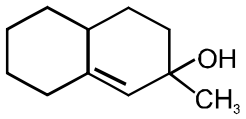
(C) 

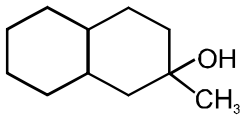
(D) 

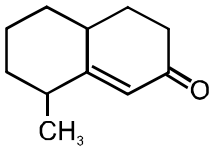
15. In the given reaction 

P will be :

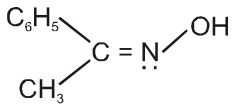
(A) 

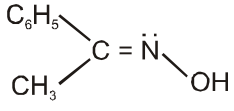
(B) 

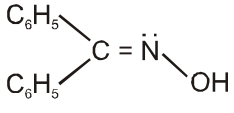
(C) 

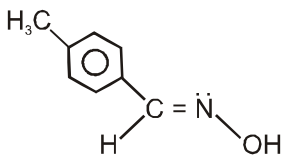
(D) 

16. A compound (X) on treatment with $SOCl_2$ produces another compound (Y). The latter on hydrolysis yields a mixture of benzoic acid and methylamine. The compound (X) is :

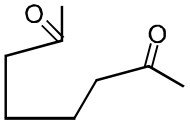
(A) 

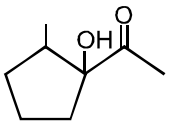
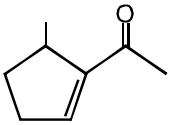
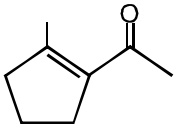
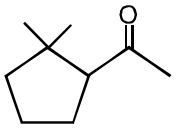
(B) 

(C) 

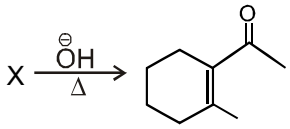
(D) 

17. Compound 'A' given below can undergo intramolecular aldol condensation reaction.

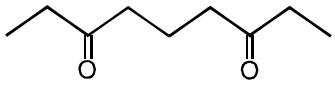
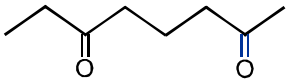
A =  product formed is :

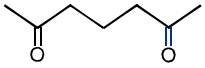
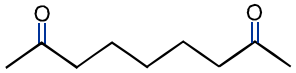
(A)  (B)  (C)  (D) 

18. Consider following intramolecular aldol condensation reaction.

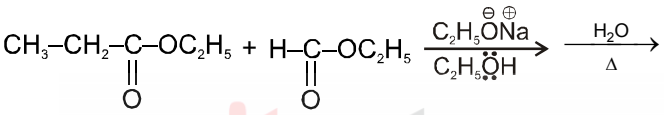


X can be :

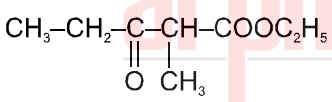
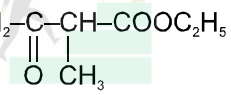
(A)  (B) 

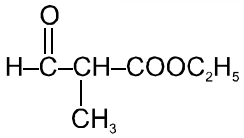
(C)  (D) 

19 In the given reaction

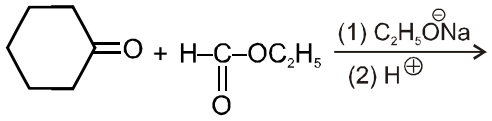
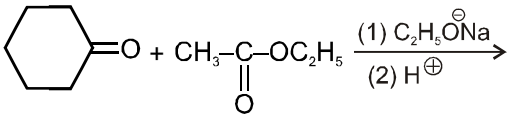


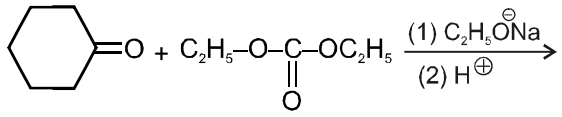
the major product will be

(A)  (B) 

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

20. Which of the following reaction will give β-keto aldehyde as the final product ?

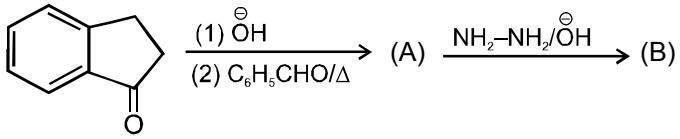
(A)  (B) 

(C)  (D) All of these

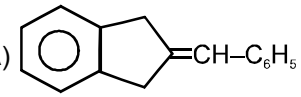
21. An organic compound X on treatment with acidified $K_2Cr_2O_7$ gives compound Y which reacts with I_2 and sodium carbonate to form Triiodomethane. The compound X can be :

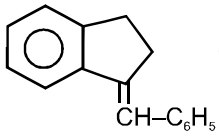
(A) CH_3OH (B)  (C) CH_3CHO (D) $CH_3CH(OH)CH_3$.

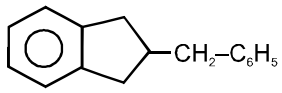
22. In the given reaction sequence

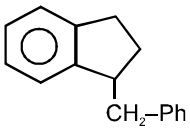


Compound (B) is :

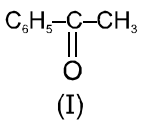
(A) 

(B) 

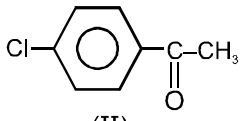
(C) 

(D) 

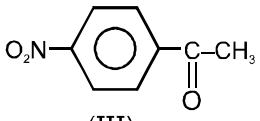
23. Arrange the following compound in decreasing order of K_{eq} for hydrate formation.



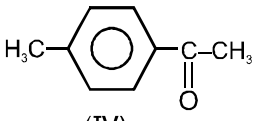
(I)



(II)

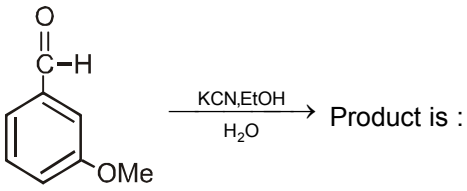


(III)

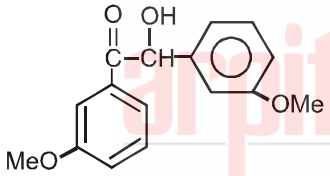


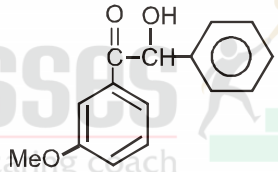
(IV)

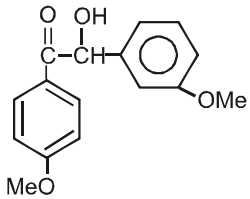
(A) III > II > I > IV (B) I > II > III > IV (C) II > III > I > IV (D) III > IV > II > I

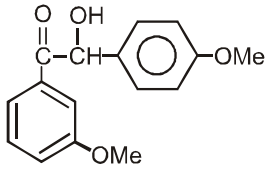
24. 

Product is :

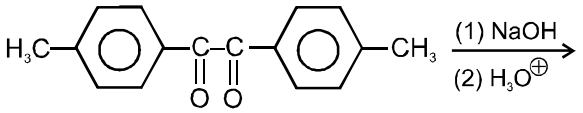
(A) 

(B) 

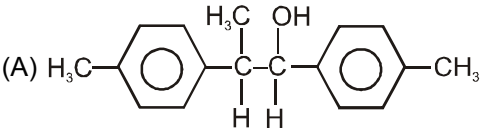
(C) 

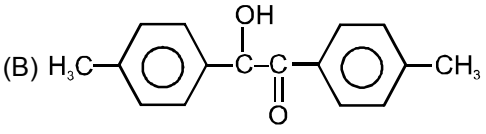
(D) 

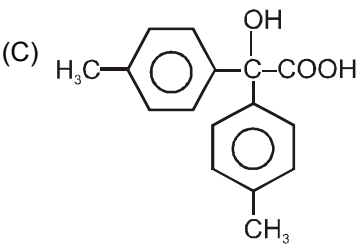
25. In the given reaction

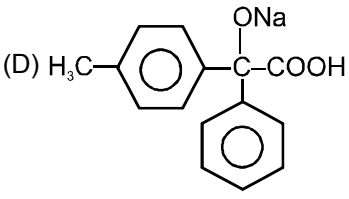


(X), (X) will be :

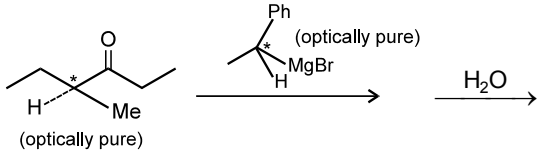
(A) 

(B) 

(C) 

(D) 

26. The number of stereoisomeric products formed in the following reaction is



(A) 1 (B) 8 (C) 4 (D) 2

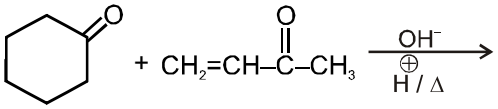
27. In the Cannizzaro reaction given below :

$$2Ph - CHO \xrightarrow{{}^{\ominus}OH} Ph - CH_2OH + PhCO_2^-$$

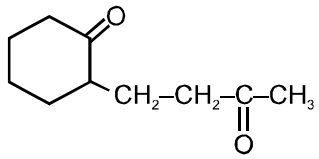
The slowest step is :

(A) The attack of ${}^{\ominus}OH$ at the carbonyl group
(B) The transfer of hydride to the carbonyl group
(C) The abstraction of proton from the carboxylic acid
(D) The disproportionation of $Ph - CH_2OH$

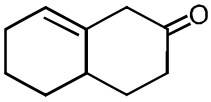
28.



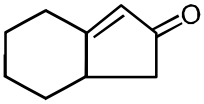
(A)



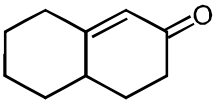
(B)



(C)



(D)

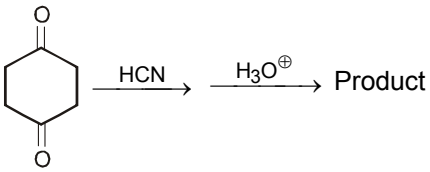


29. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives :
(A) Benzyl alcohol and sodium formate (B) Sodium benzoate and methyl alcohol
(C) Sodium benzoate and sodium formate (D) Benzyl alcohol and methyl alcohol

30. 1-Propanol and 2-Propanol can be best distinguished by
(A) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(B) oxidation with acidic dichromate followed by reaction with Fehling solution
(C) oxidation by heating with copper followed by reaction with Fehling solution
(D) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

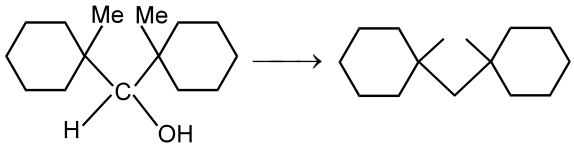
More than one choice type

31.



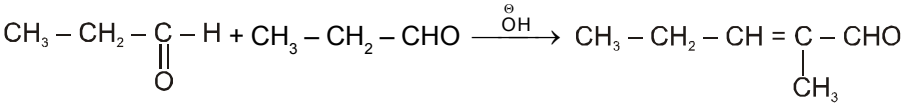
The correct statement about product is
(A) The product is optical inactive
(B) The product is meso compound
(C) The product is mixture of two enantiamer
(D) Product exist is two diastereomer forms

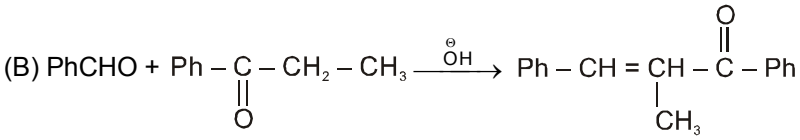
32. The sutabile reagent of the following reaction is :

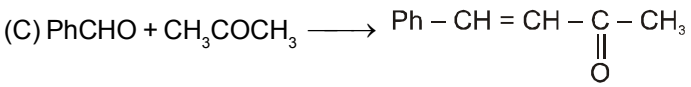


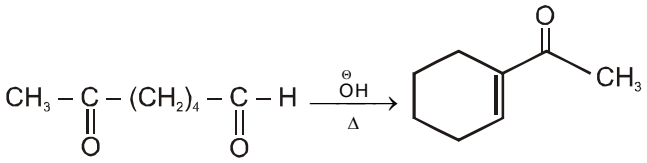
(A) $K_2Cr_2O_7 / H^{\oplus}$
(B) $N_2H_4 / OH^{\ominus}$
(C) $CrO_3 / H^{\oplus}$, Zn-Hg/ Con. HCl
(D) $CrO_3 / H^{\oplus}$, $N_2H_4 / OH^{\ominus}$, Δ

33. Which of the following aldol reaction product is correctly mention :

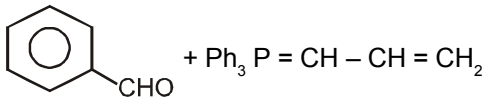
(A) 

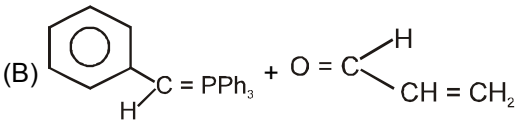
(B) 

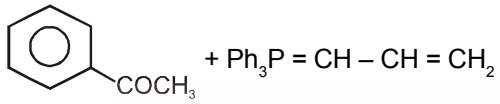
(C) 

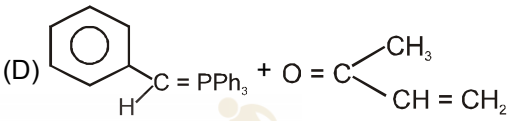
(D) 

34. Which of the following is possible combination to prepare 1 -phenyl 1,3 butadiene from Wittig reaction ?

(A) 

(B) 

(C) 

(D) 

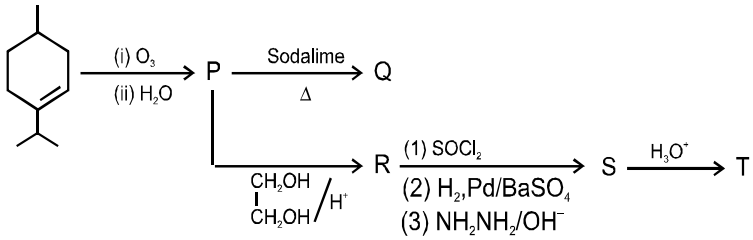
35. Stability of hydrates of carbonyl compound depends on

(A) Steric hindrance

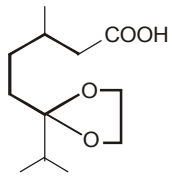
(B) presence of –I group on gemdiol carbon

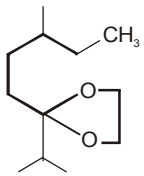
(C) Intramolecular hydrogen bonding

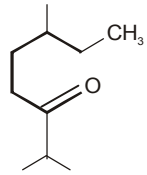
(D) Angle strain in carbonyl compound

36. 

The correct statements are :

(A) R = 

(B) S = 

(C) Q = 

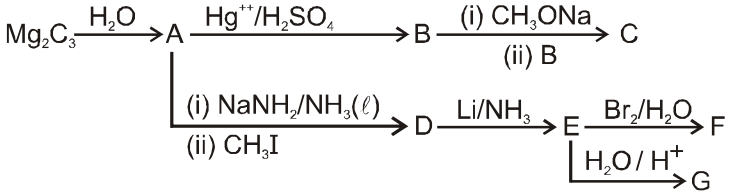
(D) Q and T are homologues.

37. Among the following compounds, which will react with acetone to give a product containing > C = N – :
[JEE-98, 3M]

(A) $C_6H_5NH_2$ (B) $(CH_3)_3N$ (C) $C_6H_5NHC_6H_5$ (D) $C_6H_5NHNH_2$

PART - II : SUBJECTIVE QUESTIONS

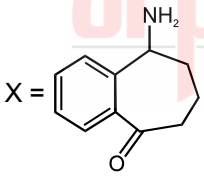
1.



2. (A) on hydration gives (B) which gives positive iodoform test. Also (A) gives white precipitate with Tollen's reagent. (B) is also obtained from acetyl chloride on treating with benzene in the presence of anhydrous $AlCl_3$

3. An alkene C_6H_{12} after ozonolysis yielded two products. One of these gave a positive iodoform reaction but a negative Tollen's test. The other gave a positive Tollen's test but negative iodoform test. The structure of C_6H_{12} is.

4. The calcium salt of an acid A ($C_6H_{10}O_4$) on dry distillation produced B (C_5H_8O). When B is reacted with Bromine solution in acetic acid, 'C' (C_5H_7OBr) is obtained. 'C' is reacted with anhydrous acidic glycol ($HOCH_2CH_2OH$) solution and PhMgBr is added to this solution carefully and then its is subjected to dilute HCl solution then compound 'D' ($C_{11}H_{12}O$) is formed. 'D' reacted with hydroxylamine hydrochloride to give 'E' and 'F' having molecular formula ($C_{11}H_{13}NO$). 'E' on heating with small amount of H_2SO_4 produced G which on hydrolysis produced 'H'. F under the same treatment yields I and J compounds respectively. E, F, G and I all are isomeric and have molecular formula ($C_{11}H_{13}NO$). H have two α hydrogen atom while J have only one α hydrogen atom. Identify compounds A to J. 'H' on reaction with $SOCl_2$ followed by treatment with anhydrous $AlCl_3$ gives the following compound 'X'.

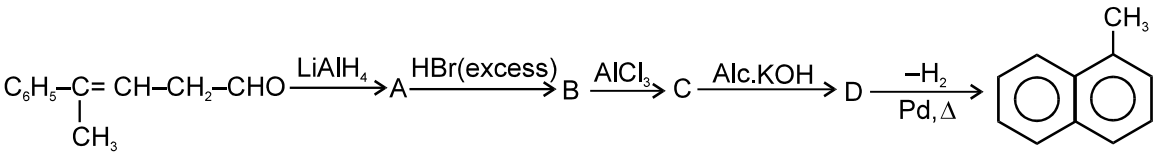


5. $A \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ B_2H_6} B \xrightarrow{HCl,\ ZnCl_2} C \xrightarrow{Mg/Et_2O} CH_3CH_2CH_2MgCl \xrightarrow[(2)\ H_3O^{\oplus},\ \Delta]{(1)\ Ph-CHO} D$

6. An organic compound (A) C_4H_9Cl on reaction with aqueous KOH gives (B). (A) on reaction with alcoholic KOH gives (C) which is also formed on passing the vapours of (B) over heated copper. The compound (C) readily decolourise bromine water. Ozonolysis of (C) gives two compounds (D) and (E). Compound (D) reacts with NH_2OH to give (F) and compound (E) reacts with NaOH to give an alcohol (G) and sodium salt (H) of an acid. (D) can also be prepared from propyne on treatment with water in presence of Hg^{+2} and H_2SO_4. Indentify (A) to (H) with proper reasoning.

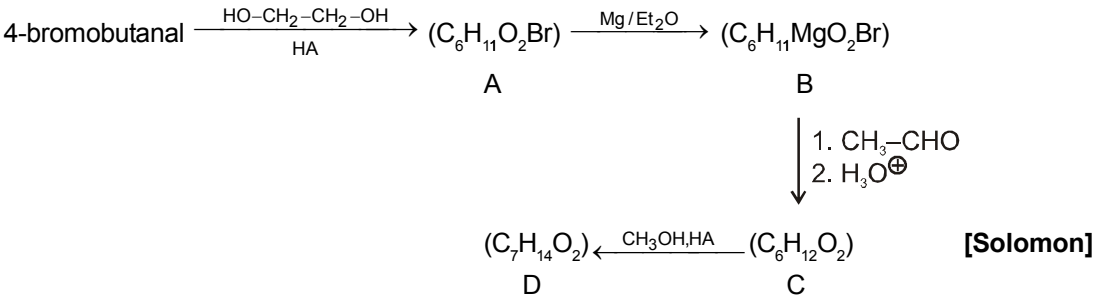
7. An organic compound (A) contains 40% carbon and 67% Hydrogen. Its vapour density is 15. (A) on reaction with a concentrated solution of KOH gives two compound (B) and (C). When (B) is oxidised original compound (A) is obtained. When 'C' is treated with concentrated HCl, it gives a compound (D) which reduces ammonical. $AgNO_3$ solution and also gives effervescences with sodium bicarbonate solution. Write structure (A), (B), (C) and (D).

8. $CH_3–CH=CH–CHO \xrightarrow[OH^-]{HCN} A \xrightarrow{\text{Alkaline hydrolysis}} \xrightarrow{(H_3O^+)} B$

9. 

10. An organic compound (A) $C_9H_{10}O$ reacts with NH_2OH to give two isomers B & C with same moleculer formula $C_9H_{10}ON$.The compound B and C isomerizes to D and E respectively on treating with small amount of H_2SO_4. Compound (F) $C_8H_8O_2$ is formed either by (A) on treating with I_2/KOH followed by acidification or by acid hydrolysis of (D). Hydrolysis of (E) gives ortho–methylaniline. identify the structure from (A) to (E).

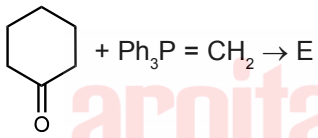
11. Compound A to D do not gives tollens test however compound C does. Give the structure of A to D.

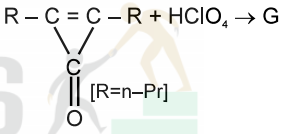


[Solomon]

12. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structure of the oximes.

13. Complete the following giving the structures of the principal organic products.

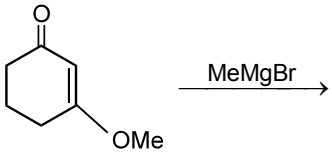
(a) 

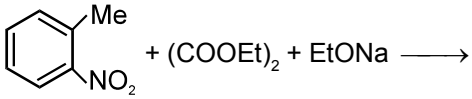
(b) 

(c) $ClCH_2CH_2CH_2COPh + KOH + MeOH \rightarrow I$

(d) $H_3CCOCOC_6H_5 + NaOH / H_3O^+ \rightarrow J$

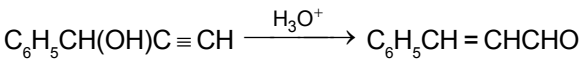
14. How many asymmetric cabon atoms are created during the complete reduction of benzil (PhCOCOPh) with $LiAlH_4$? Also write the number of possible stereoisomer of the possible product.

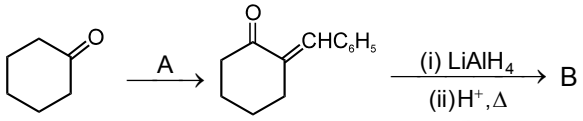
15. 

16. 

17. An aldehyde (A) ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two mole of (B) on ozonolysis. Compound (B), on oxidation with silver ion, gives oxalic acid. Identify the compound (A) and (B). **[JEE-98, 2M]**

18. Write the intermediate steps for each of the following reactions **[JEE-98, 2M]**



19. 

[JEE 98, 2M]

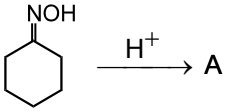
20. Compound 'A' (C_8H_8O) on treatment with NH_2OH . HCl gives 'B' and 'C' . 'B' and 'C' rearrange to give 'D' and 'E' respectively on treatment with acid . 'B' , 'C' , 'D' , and 'E' are all isomers of molecular formula C_8H_9NO . When 'D' is boiled with alcoholic KOH , an oil 'F' (C_6H_7N) separates out . 'F' reacts rapidly with CH_3COCl to give back 'D' . 'E' on boiling with alkali , followed by acidification gives a white solid 'G' ($C_7H_6O_2$) Identify 'A' to 'G'.

21. Carry out the following transformation in not more than three steps :

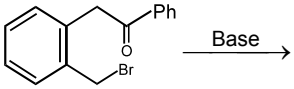
$$CH_3 - CH_2 - C \equiv C - H \longrightarrow CH_3 - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$$

22. Two different Grignard reagents, (X) and (Y) produce $C_6H_5CH_2C(CH_3)_2OH$ on reaction with (P) and (Q) respectively. Give structures of (X), (Y), (P) and (Q).

23.



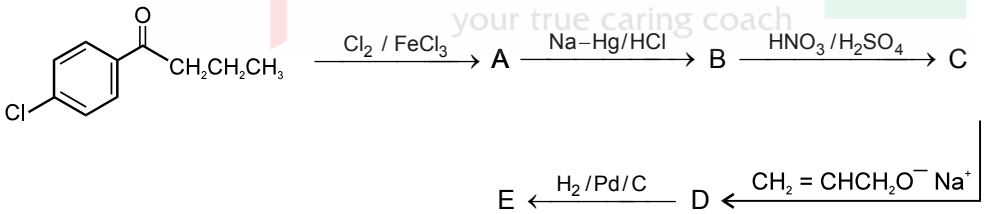
24.



25. An organic compound (A), $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound (B). The compound (B) on treatment with PCl_5, followed by reaction with H_2/ $Pd(BaSO_4)$ gives compound (C), which on reaction with hydrazine gives a cyclised compound (D) ($C_{14}H_{10}N_2$). Identify (A), (B), (C) and (D). Explain the formation of (D) from (C).

26. An organic compound A, $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.

27. Write structures of the products A, B, C, D and E in the following scheme.



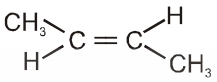
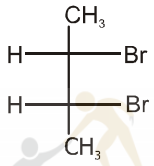
Answers

PART - I

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

PART - II

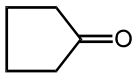
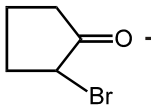
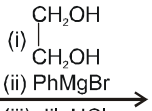
1. A = Propyne B = $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ C = $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ (aldol product)

D = $CH_3-C\equiv C-CH_3$ E =  F = 

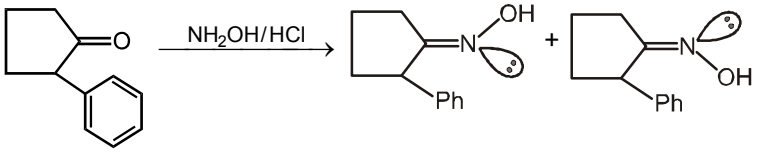
G = $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

2. (A) $C_6H_5-C\equiv C-H$ (B) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

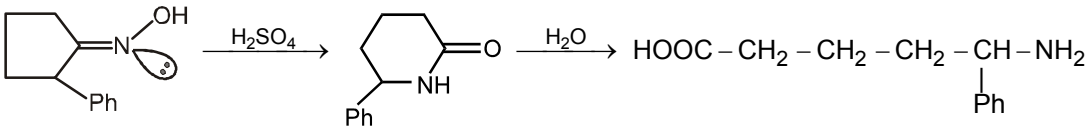
3. $CH_3-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$ or $CH_3-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_3$

4. $\begin{matrix}CH_2-CH_2-COOH\\ |\\ CH_2-CH_2-COOH\end{matrix}$ $\xrightarrow{\text{Dry distillation}}$  $\xrightarrow{Br_2/CH_3COOH}$  $\xrightarrow[\text{(ii) PhMgBr}]{\text{(i) } \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$ 

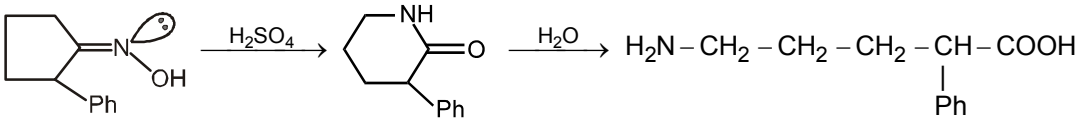
(A) (B) (C)



(D) (E) (F)

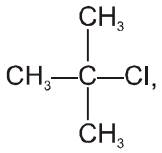
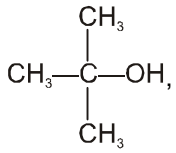
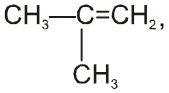
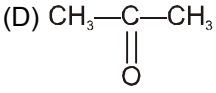


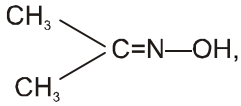
(E) (G) (H)



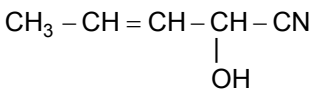
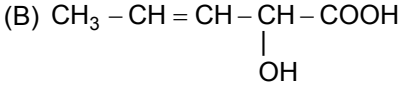
(F) (I) (J)

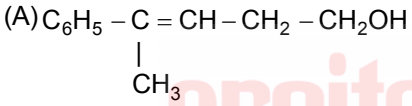
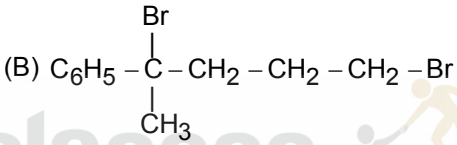
5. (A) $CH_3CH=CH_2$ (B) $CH_3CH_2CH_2OH$ (C) $CH_3CH_2CH_2Cl$ (D) $PhCH=CHCH_2CH_3$

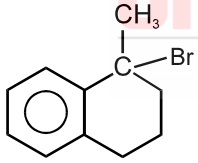
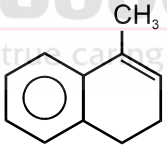
6. (A)  (B)  (C)  (D) 

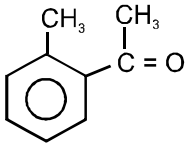
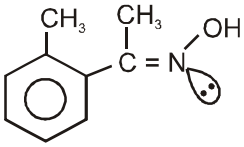
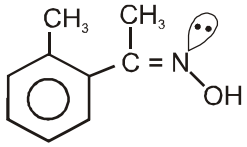
(E) HCHO, (F)  (G) CH_3OH, (H) HCOONa

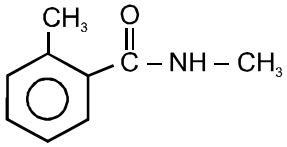
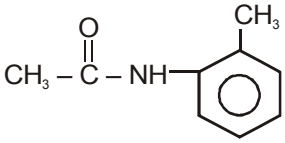
7. (A) 2HCHO, (B) CH_3OH, (C) HCOONa, (D) HCOOH

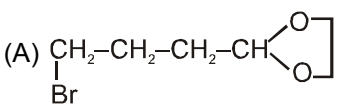
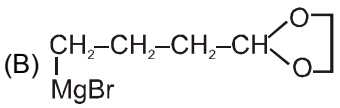
8. (A)  , (B) 

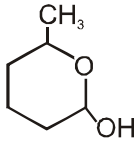
9. (A)  (B) 

(C)  (D) 

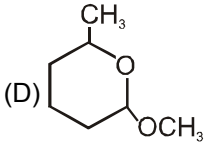
10. (A)  (B)  (C) 

(D)  (E) 

11. (A)  (B) 

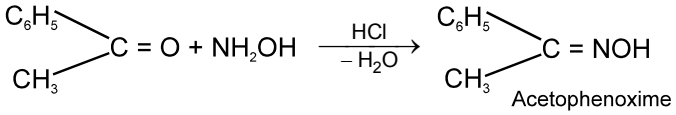
(C) 

Hemiacetal

(D) 

acetal

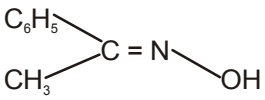
12.



Acetophenoxime

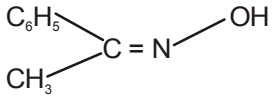
It shows two isomers which are geometrical isomers to each other and represented as follow :

(i)



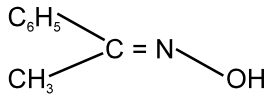
Syn-methyl anti-Syn-phenyl Ketoxime

(ii)



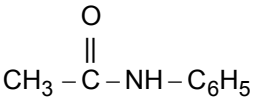
Syn-phenyl anti Syn-methyl Ketoxime

Their configuration may be identified with the help of Backmann's Rearrangement

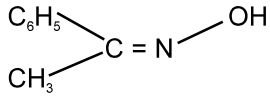


(i) isomer

Presence of acid or PCl_5 or Acid anhydride

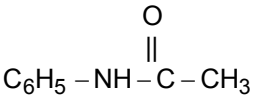


N – phenyl acetamide



(ii) isomer

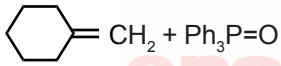
Presence of acid or PCl_5 or Acid anhydride



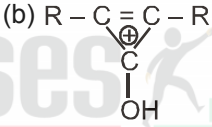
N – phenyl acetamide

Therefore both isomers give different product with different configturation.

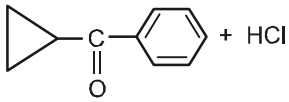
13. (a)



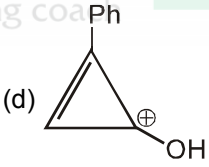
(b)



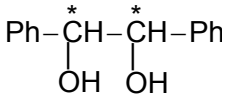
(c)



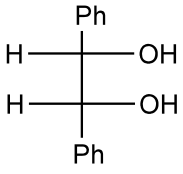
(d)



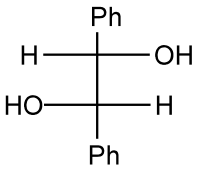
14.



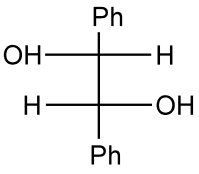
two chiral C atoms ; total 3 isomers :



(meso)

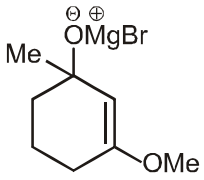


(d)

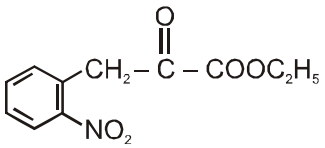


(l)

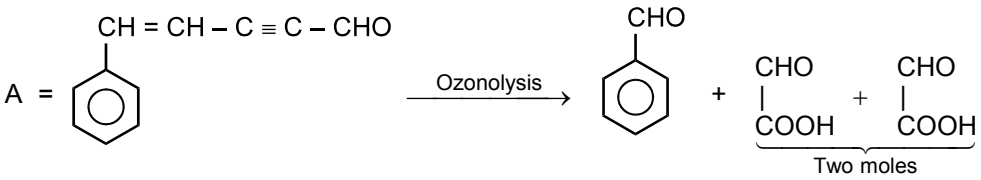
15.

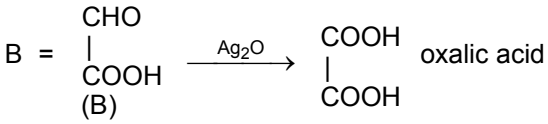


16.

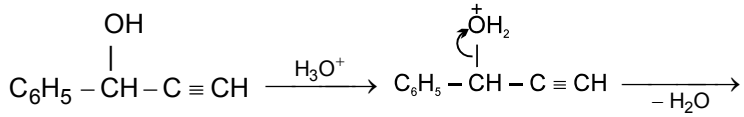


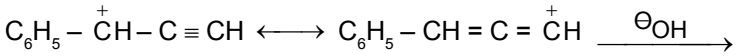
17.





18.

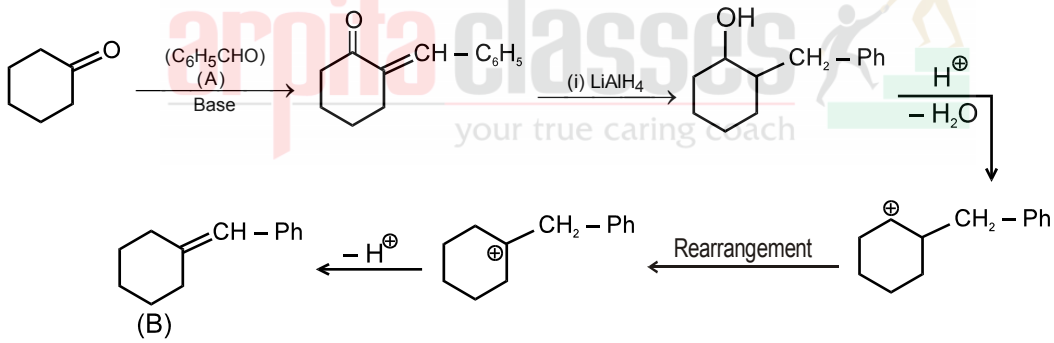




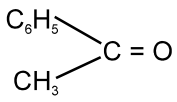
$C_6H_5 - CH = C = CHOH \rightleftharpoons C_6H_5 - CH = CH - CHO$

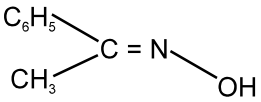
Enol-form (less stable) Keto form (more stable)

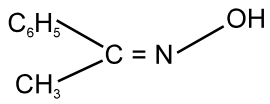
19.

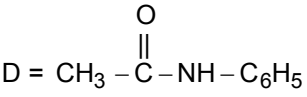


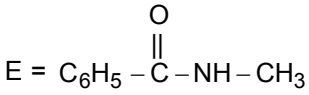
20. So compound are

A = 

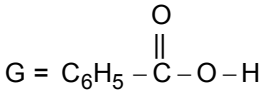
B = 

C = 

D = 

E = 

F = $C_6H_5 - NH_2$

G = 

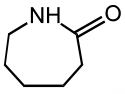
21. $CH_3CH_2C\equiv CH \xrightarrow{Na} CH_3CH_2C\equiv CNa \xrightarrow{CH_3X} CH_3CH_2C\equiv CCH_3 \xrightarrow[H_2O_2,OH^-]{BH_3/THF} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

or $\xrightarrow[H_2O_2/OH^{\ominus}]{BH_3/THF} CH_3-CH_2-CH_2-CH=O \xrightarrow[(2)\ H^{\oplus}]{(1)\ CH_3MgBr} \xrightarrow{(3)\ CrO_3/H^{\oplus}} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

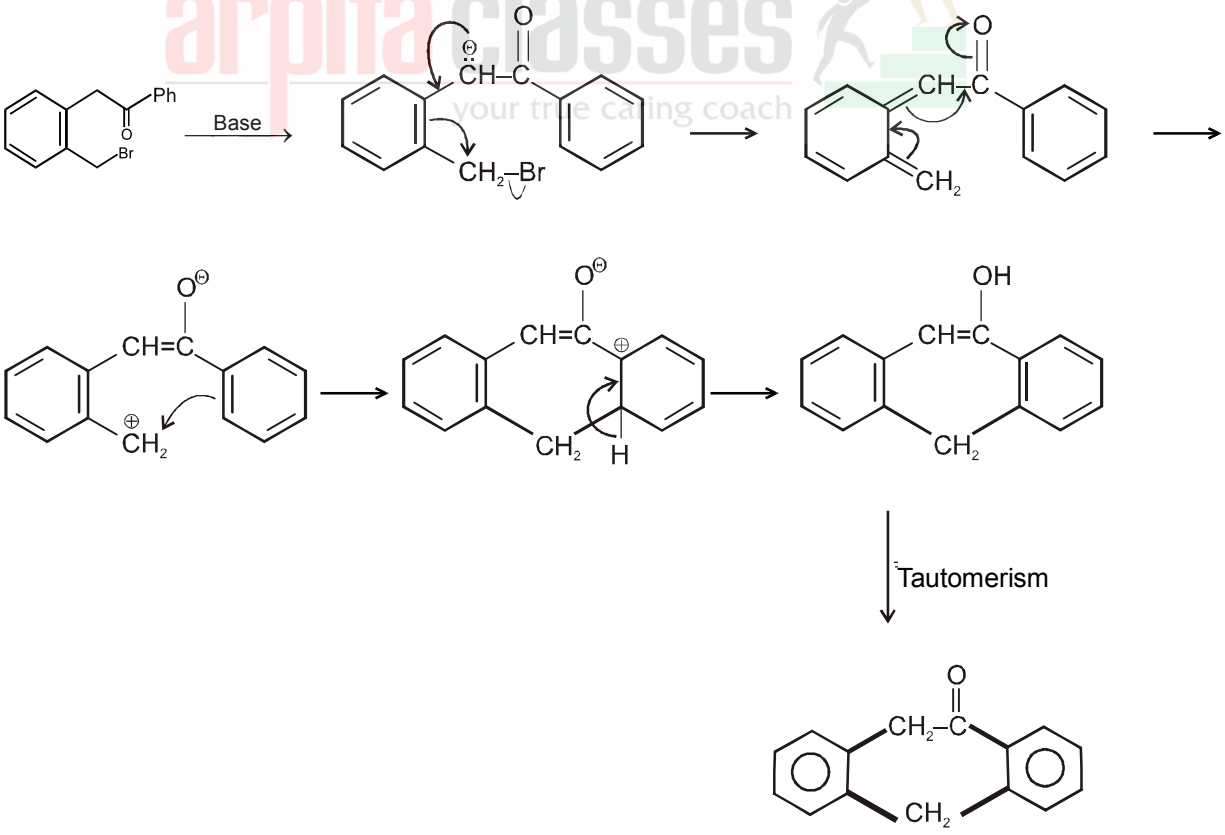
22. **(X)** $C_6H_5CH_2MgX$ **(Y)** CH_3MgX **(P)** $(CH_3)_2C=O$ **(Q)** $C_6H_5CH_2(CH_3)C=O$

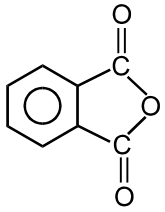
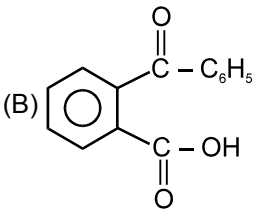
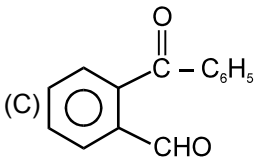
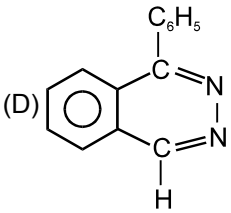
$(CH_3)_2C=O$ (P) + $C_6H_5CH_2MgX$ (X) $\longrightarrow$ $(CH_3)_2C(OMgX)CH_2C_6H_5 \xrightarrow{\text{Hydrolysis}} CH_3-C(CH_3)(OH)-CH_2-C_6H_5$

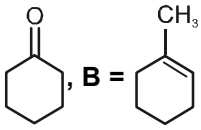
$C_6H_5CH_2(CH_3)C=O$ (Q) + CH_3MgX (Y) $\longrightarrow$ $C_6H_5-CH_2-C(OMgX)(CH_3)_2 \xrightarrow{\text{Hydrolysis}} CH_3-C(CH_3)(OH)-CH_2-C_6H_5$

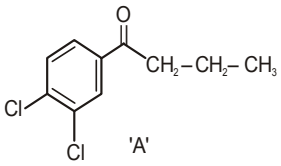
23. (A)  (Beckmann's rearrangement)

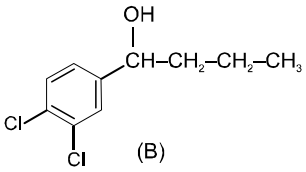
24.

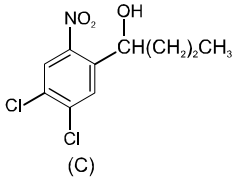


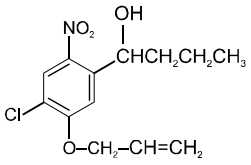
25. (A)  (B)  (C)  (D) 

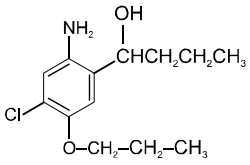
26. **A =**  **, B =**

27. A =  'A'

B =  (B)

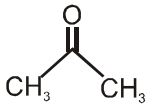
C =  (C)

D =  (D)

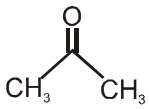
E =  (E)

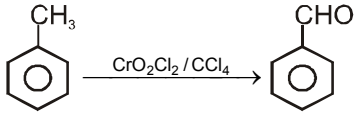
EXERCISE # 1

PART - I

A-1. (a) $2CH_3COOH \xrightarrow{MnO,\ \Delta}$ 

(b) $PhCN + CH_3MgBr \longrightarrow Ph-\underset{CH_3}{\underset{|}{C}}=NMgBr \xrightarrow{H_2O} Ph-\underset{CH_3}{\underset{|}{C}}=O + NH_3 + Mg(OH)I$

(c) $CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3 \xrightarrow{O_3/Zn} 2$ 

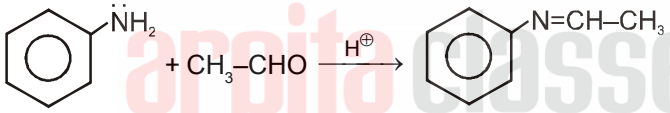
(d) 

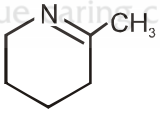
B-2. Rate of nucleophilic addition reactions depends on the amount of +ve charge present at carbonyl carbon.

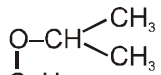
B-3. Rate of nucleophilic addition reactions depends on the amount of +ve charge present at carbonyl carbon.

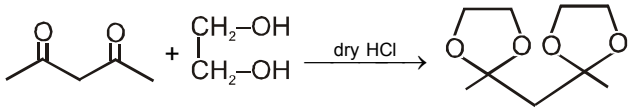
B-4. Rate of nucleophilic addition reactions depends on the amount of +ve charge present at carbonyl carbon.

B-5. Rate of nucleophilic addition reactions depends on the amount of +ve charge present at carbonyl carbon.

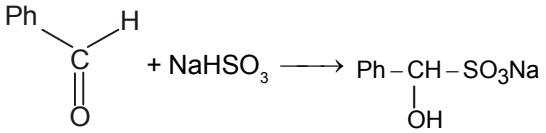
B-8. (a) 

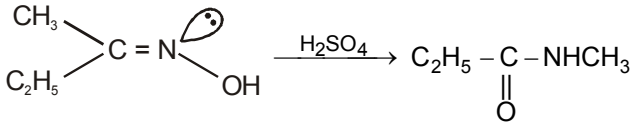
(b) $H_2N-CH_2-CH_2-CH_2-CH_2-CO-CH_3 \xrightarrow{H^\oplus}$ 

B-9. (a) $CH_3-CHO + \underset{CH_3}{\overset{CH_3}{\diagdown\!\diagup}}CH-OH \xrightarrow{\text{dry HCl}} CH_3-\underset{O-CH(CH_3)_2}{\underset{|}{C}}-H$ 

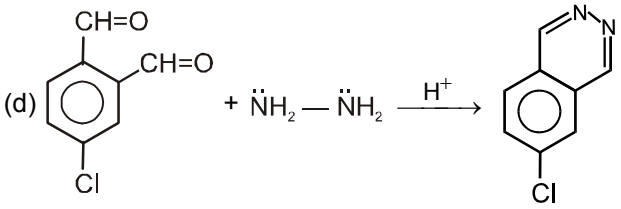
(b) 

excess

B-10. (a) 

(b) 

(c) $CH_3-\underset{\underset{O^{16}}{\|}}{C}-CH_3 \xrightarrow{D_2O^{18}} CH_3-\underset{\underset{O^{18}}{\|}}{C}-CH_3$

(d) 

C-1. (a) $CH_3-CH_2-CHO \xrightarrow[-H_2O]{OH^-/\Delta} CH_3-\overset{\ominus}{\underset{\cdot\cdot}{C}}H-CHO \xrightarrow{CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H} CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{-H_2O} CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO$

C-2. (a) $CH_3CH_2CH_2CHO \xrightarrow[\text{Aldol}]{OH^-} CH_3-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CH_2-CH_3}{\underset{|}{CH}}-CHO$

(b) $CH_3COCH_3 \xrightarrow[\text{Aldol}]{OH^-} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$

C-3. $Ph-CH=\boxed{O+H_2}-CH-\underset{O}{\underset{\|}{C}}-CH-\boxed{H_2+0}=CH-Ph$

$Ph-CH=CH-\underset{O}{\underset{\|}{C}}-CH=CH-Ph \xrightarrow{NH_2OH} Ph-CH=CH-\underset{:N-OH}{\underset{\|}{C}}-CH=CH-Ph$

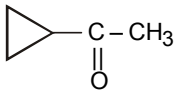
(Phorone)

[X]

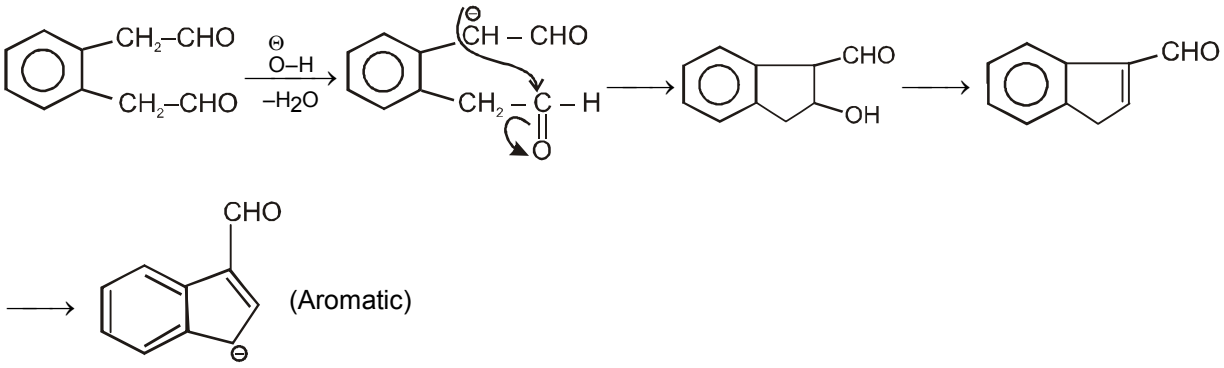
Four stereoisomers are formed.

C-4. (a) $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-\underset{O}{\underset{\|}{C}}-H + CH_3-\underset{O}{\underset{\|}{C}}-H \xrightarrow{OH^\ominus/\Delta} CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH=CH-\underset{O}{\underset{\|}{C}}-H$

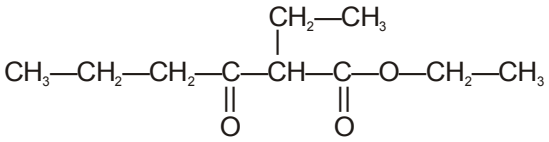
(b) $Ph-\underset{O}{\underset{\|}{C}}-H + CH_3-CH_2-\underset{O}{\underset{\|}{C}}-H \xrightarrow{OH^\ominus/\Delta} Ph-CH=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$

(c) $Ph-\underset{O}{\underset{\|}{C}}-H +$  $\xrightarrow{OH^\ominus/\Delta} Ph-CH=CH-\underset{O}{\underset{\|}{C}}-$ 

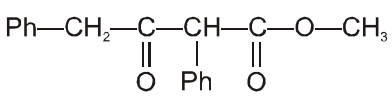
C-5.



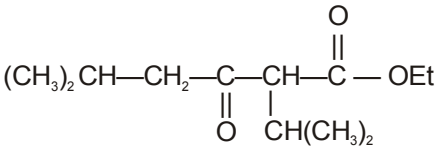
C-6. (a) $CH_3CH_2CH_2COOEt \xrightarrow{\text{claisen condensation}}$



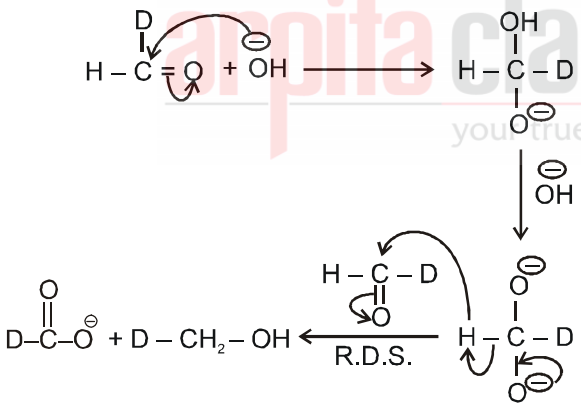
(b) $PhCH_2COOCH_3 \xrightarrow{\text{claisen condensation}}$



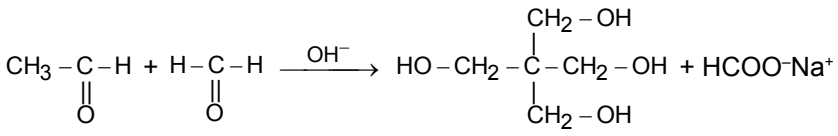
(c) $(CH_3)_2CHCH_2COOEt \xrightarrow{\text{claisen condensation}}$



D-1. Cannizzaro reaction

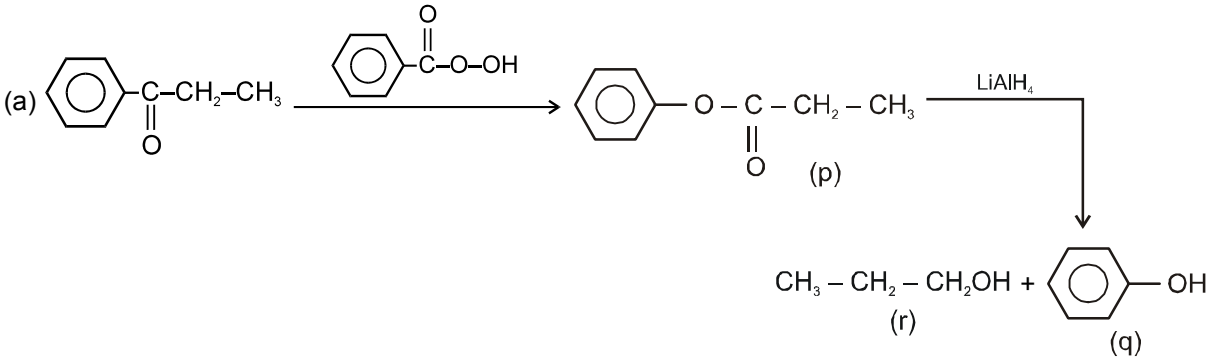


D-2.

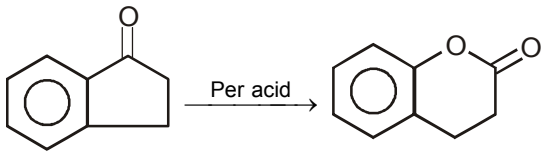


excess

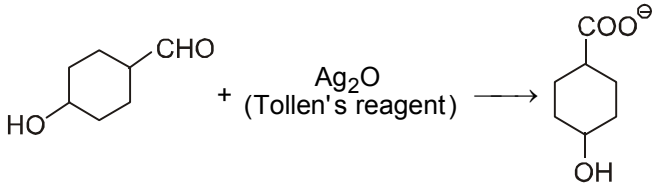
E-1. (a)



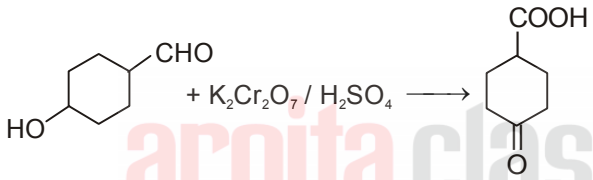
(b)



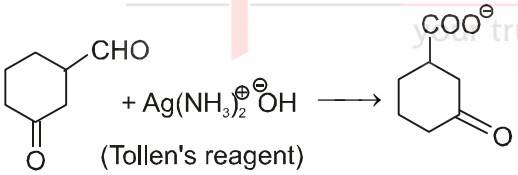
E-2. (a)



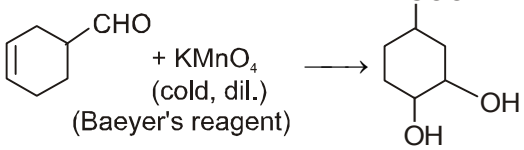
(b)



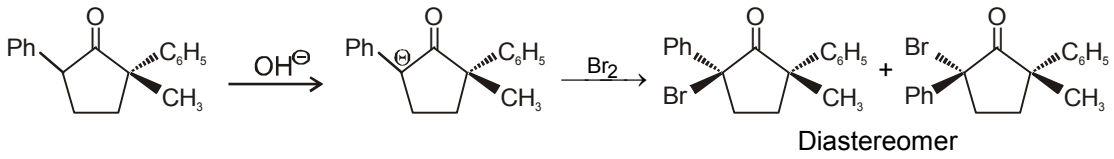
(c)



(d)



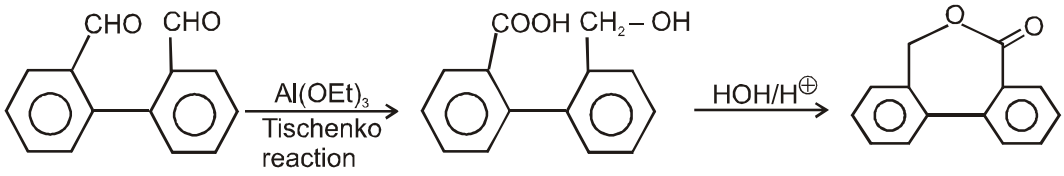
F-1.



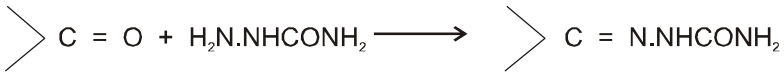
F-2. (a) $CH_3–CH_2–OH \xrightarrow{I_2/KOH} CHI_3 + HCOO^{\ominus}Na^{\oplus}$

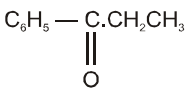
(b) $Ph–CH_2–CO–CH_3 \xrightarrow{I_2/KOH} CHI_3 + PhCH_2COO^{\ominus}Na^{\oplus}$

(c) $(Me)_3C–CO–CH_3 \xrightarrow{I_2/KOH} CHI_3 + (Me)_3C–COO^{\ominus}Na^{\oplus}$

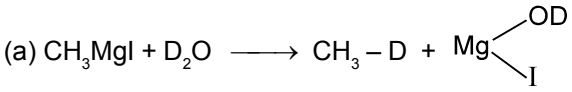
G-2. 

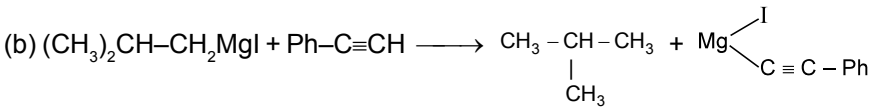
G-3. (i) (X) forms semicarbazone and thus possesses carbonyl group

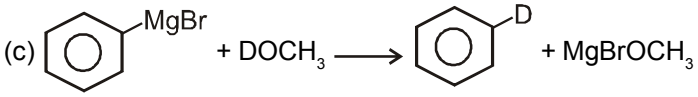


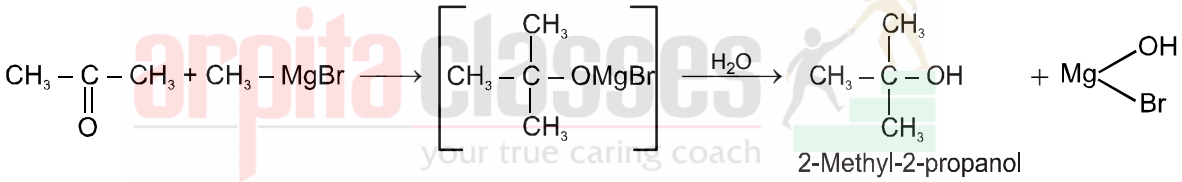
(ii) It does not give Tollen's reagent test and thus it is ketone.
(iii) It does not give iodoform test hence it is not methyl ketone.
(iv) Keeping in view of the above facts and molecular formula; (X) is 

H-1. Ether is suitable solvent for grignard reagent and others solvent are not suitable.

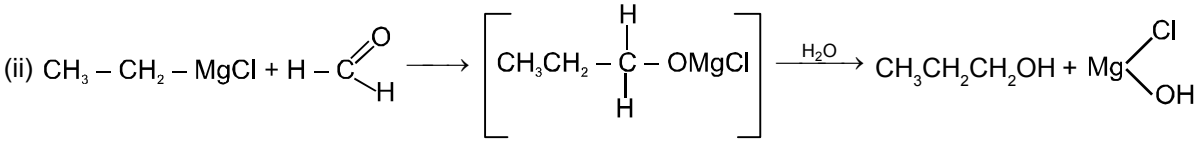
H-2. (a) 

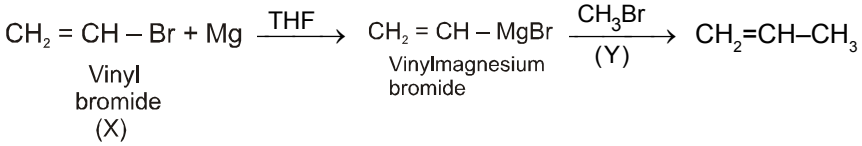
(b) 

(c) 

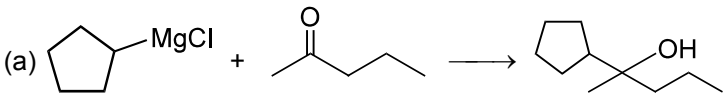
H-4. (i) 

2-Methyl-2-propanol

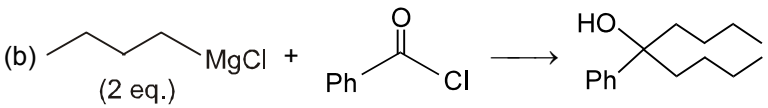
(ii) 

H-5. 

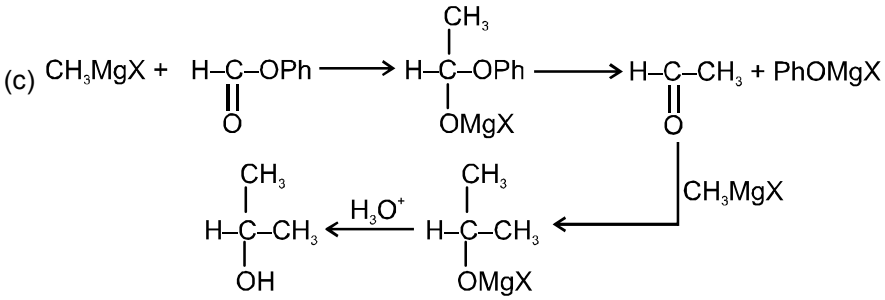
Vinyl bromide (X)
Vinylmagnesium bromide

H-6. (a) 

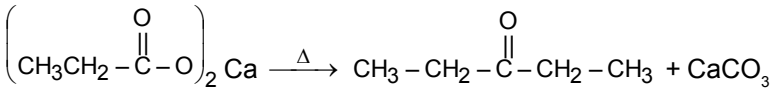
1eq

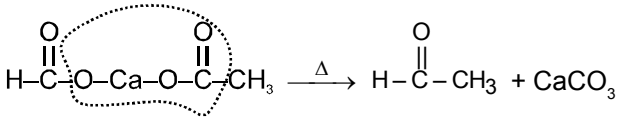
(b) 

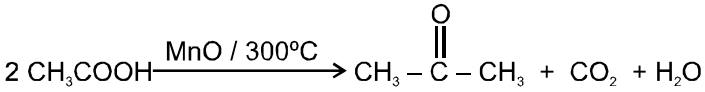
(2 eq.)

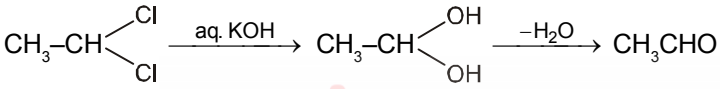
(c) 

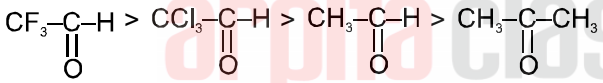
PART - II

A-1. 

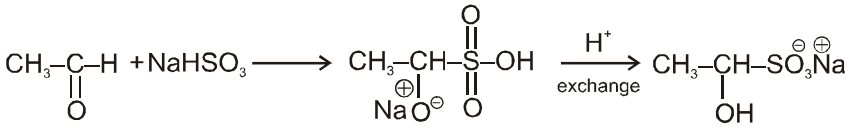
A-2. 

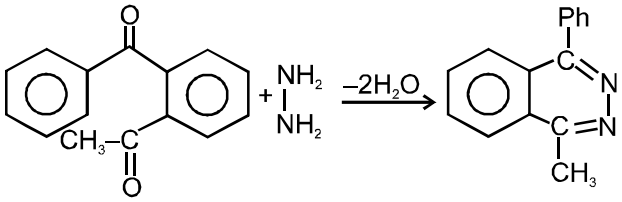
A-3. 

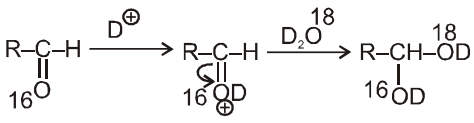
A-5. 

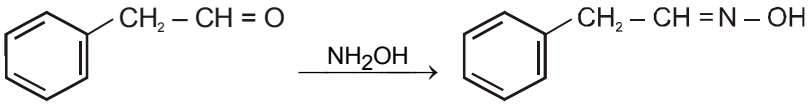
B-1. 

B-2. –I and –M group increase electrophilicity on –CHO group so rate of addition reaction increase and also increases equilibrium constant.

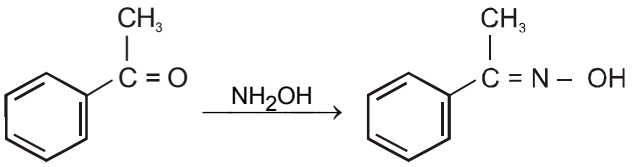
B-3. 

B-4. 

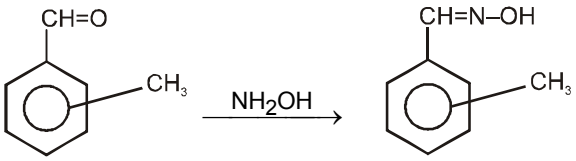
B-5. 

B-6. 

two oximes



two oximes



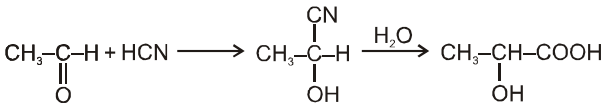
O/M/P

O/M/P
(six isomers)

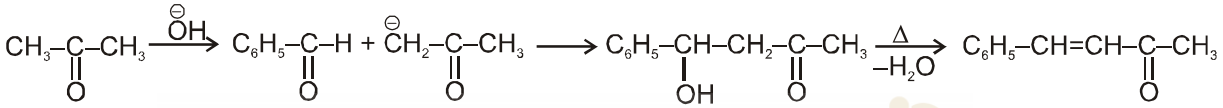
B-7. It is protection of carbonyl compound.

B-8. As the positive charge decreases and steric hinderance increases on carbonyl group the rate of nucleophilic addition reaction decreases.

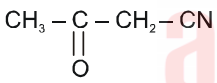
B-9.



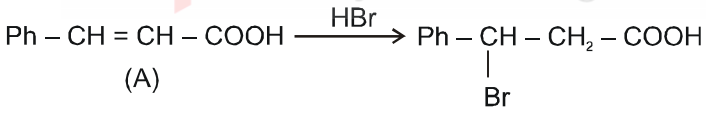
C-2.



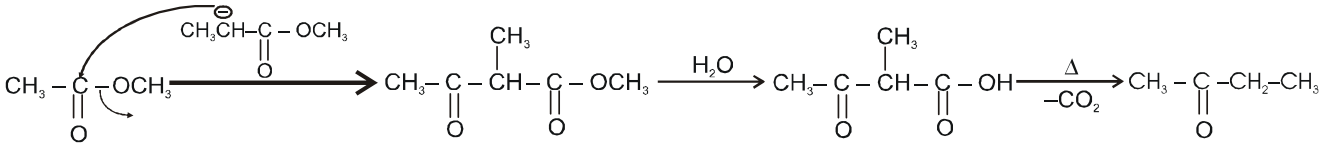
C-3.



C-4. Perkin reaction



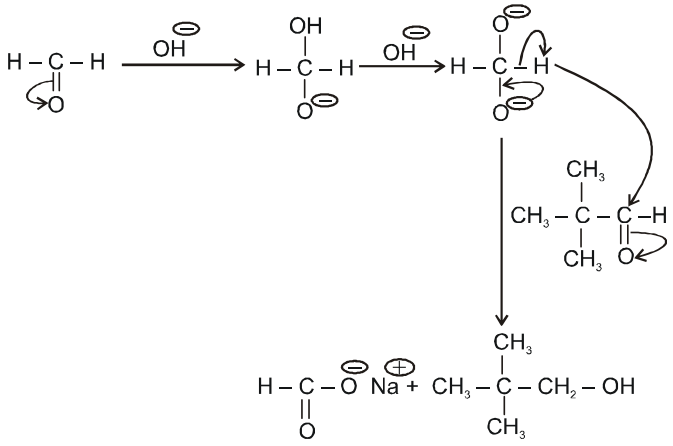
C-5.



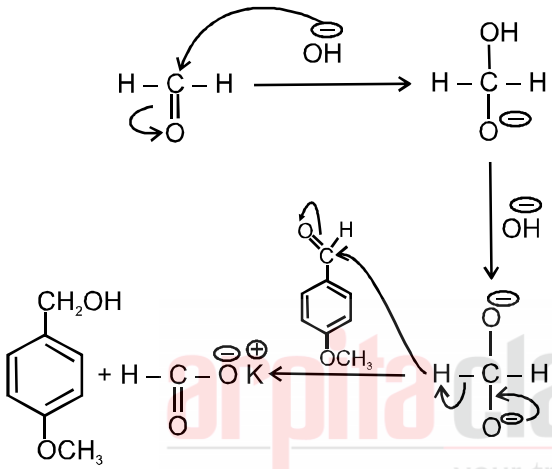
C-6.* Compound which have α-hydrogen gives aldol condensation reaction.

D-1. $CH_3 - CHO$ (α – Hydrogen is present).

D-2.

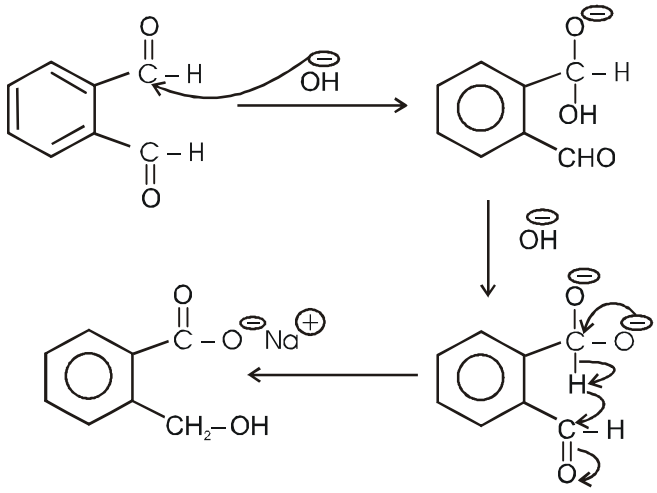


D-3.

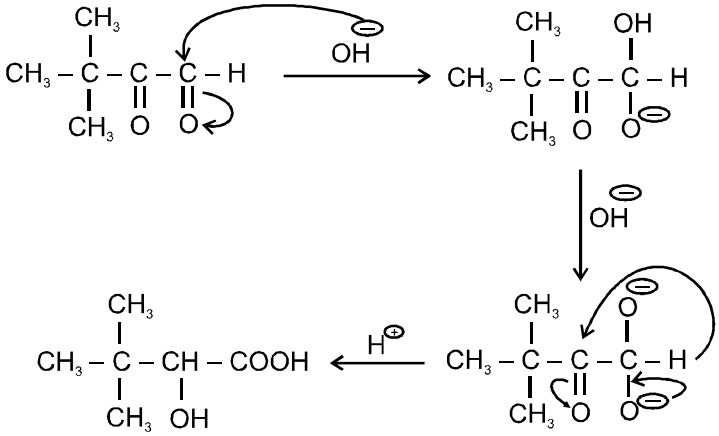


D-4. Dioxide anion is a better hydride donor, and presence of $-OCH_3$ group further increases the electron density.

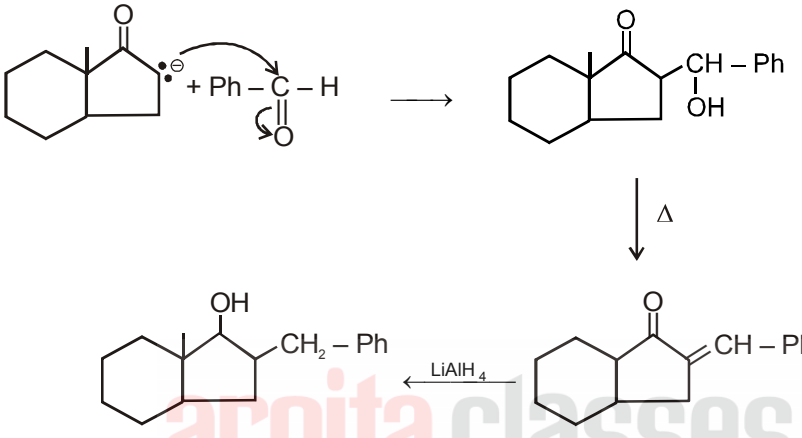
D-5.



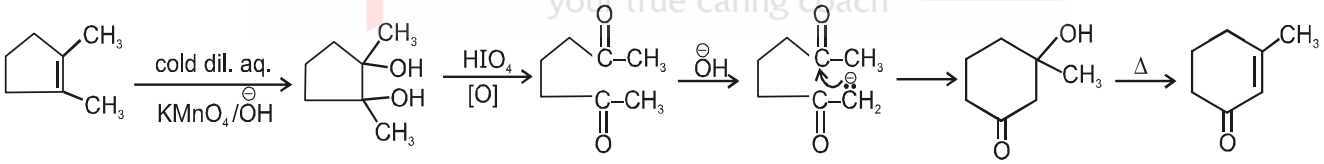
D-6.



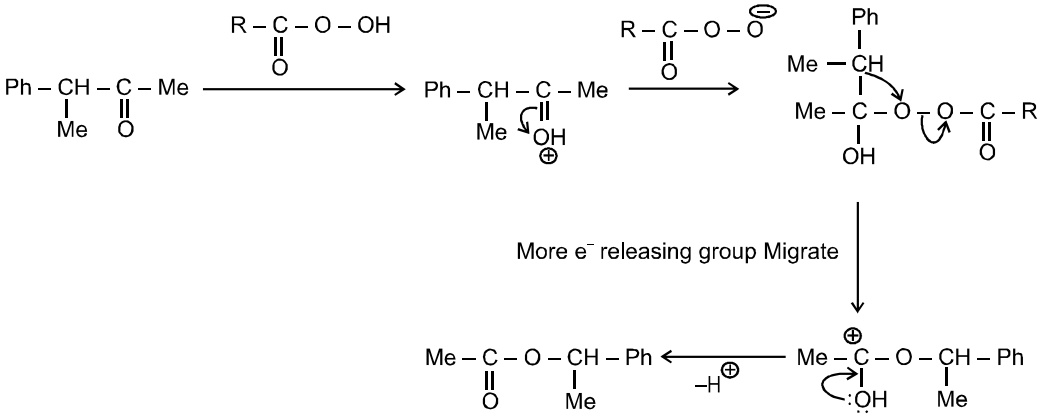
E-1.



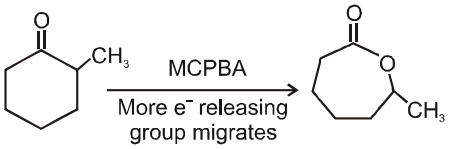
E-2.*



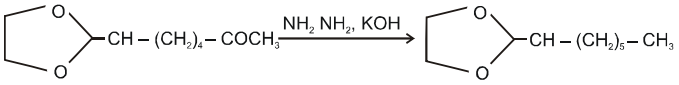
E-3.



E-4.



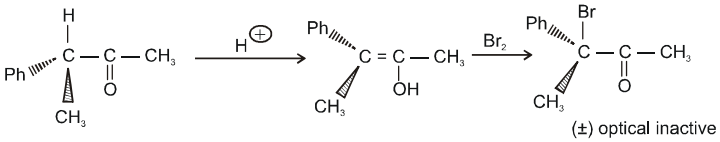
E-5.



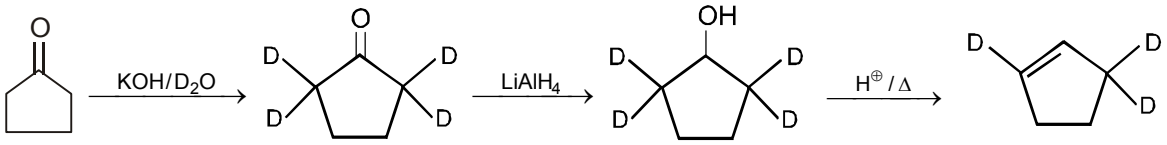
Acetal is hydrolysed in acidic Medium so clemmensen reduction is not used.

E-6. If base sensitive group is present on carbonyl compound then Clemmensen reduction is used.

F-1.



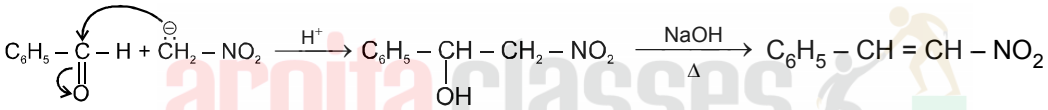
F-2.



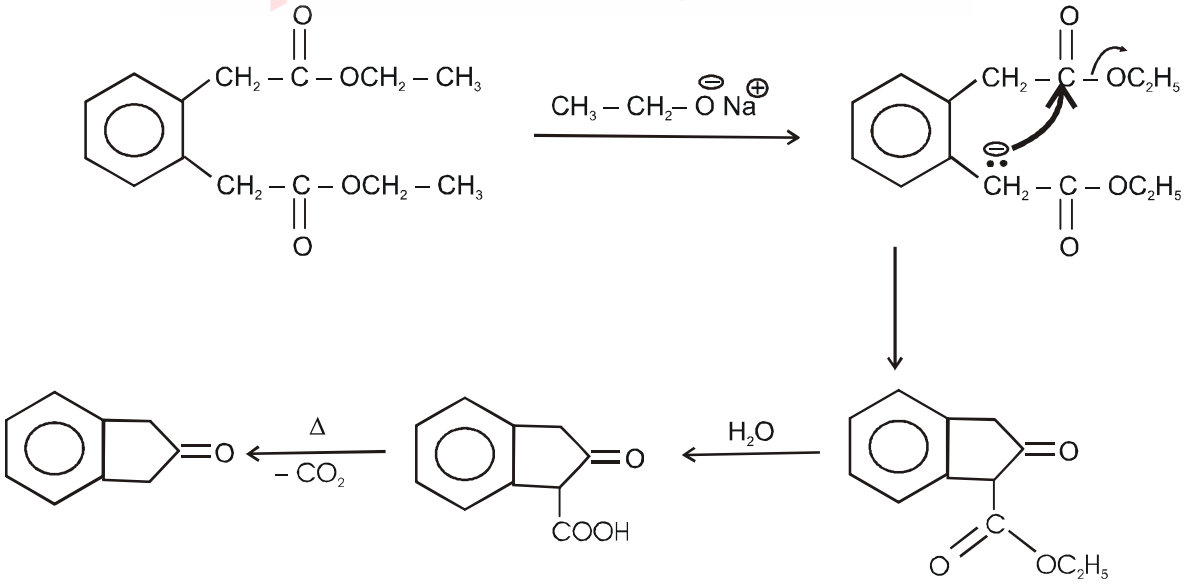
F-4.* Those carbonyl compound in which α – hydrogen is present show deuterium exchange.

F-5.* α – Hydrogen is absent so deuterium exchange is not observed in A and C.

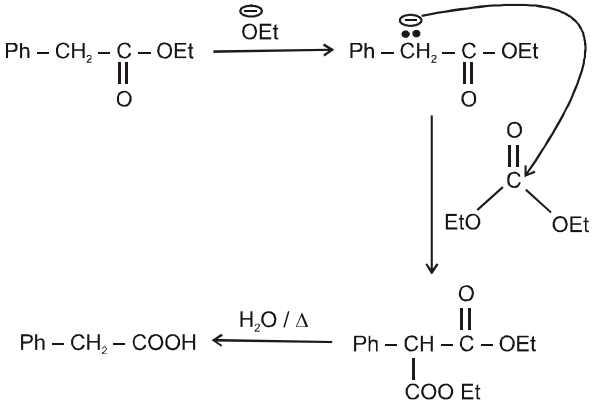
G-1.



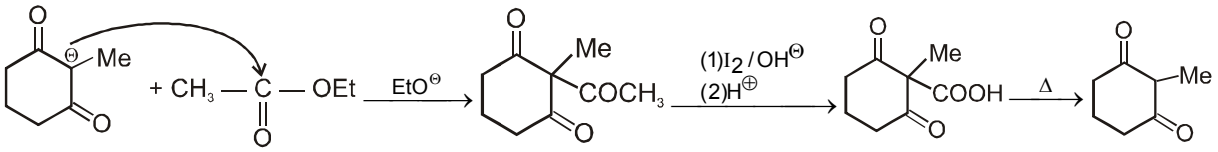
G-2.



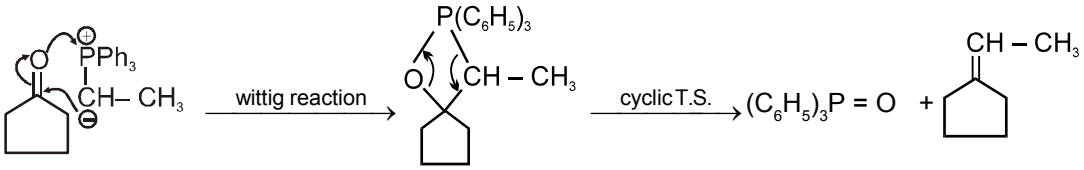
G-3.



G-4.*

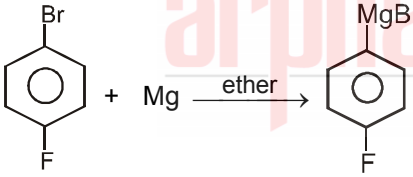


G-6.



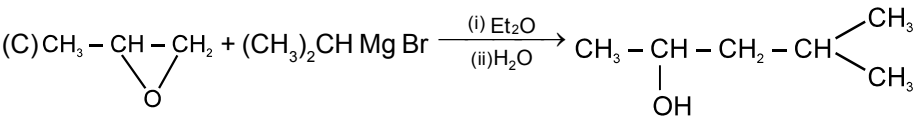
H-1. (A) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COOMgI$

H-2.

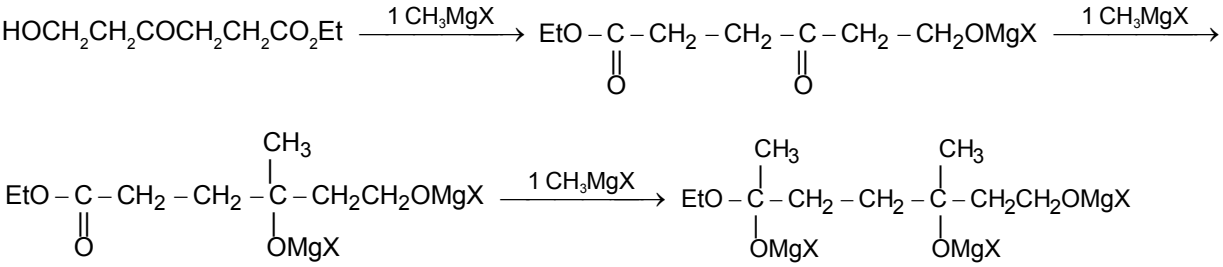


Flourine will not form G.R.

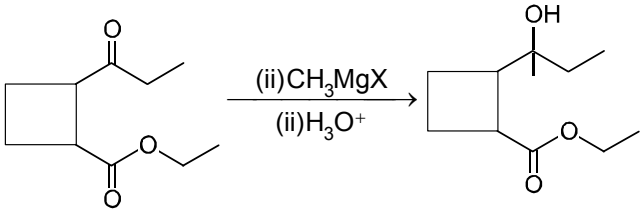
H-3.



H-4.*



H-5.



H-6. $(CH_3)_3CMgCl + D_2O \longrightarrow (CH_3)_3CD$

H-7. $Ph-MgBr + (CH_3)_2CH-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow (CH_3)_2CH-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{Zn-Hg/HCl} Ph-CH_2-\underset{CH_3}{\overset{|}{CH}}-CH_3$

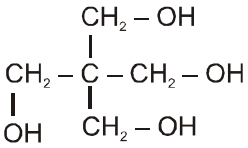
1 mole

H-8. $C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)} C_6H_5-CH_2-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

(Major product)
t-alcohol

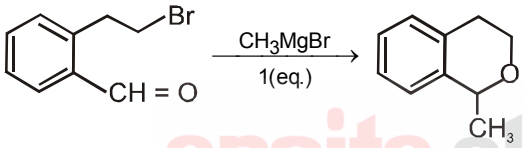
H-9. $C_5H_{12}O_4 \xrightarrow{CH_3MgBr} 4CH_4\uparrow$.

It means compound (X) contains 4 acidic hydrogen. (;kSfxd (X) 4 vEyh ; gkbZ]a ks tu ijek.kq jgrk gS)



H-10. X : $CH_3-(CH_2)_3-CH_2MgBr$ Y : $CH_3-(CH_2)_5-CH_2OH$ Z : $CH_3-(CH_2)_5-CH_2Br$

H-11.



H-12. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr. (i.e. OH, COOH, SO_3H)

PART - III

2. Base will decrease the rate of reaction.

4. $NaHSO_3$ on addition of carbonyl compound forms a salt.

7. Grignard reagent can not be prepared in all nonpolar solvent, it can prepare only in ether solvent.

8._ G.R. can not prepared in aqueous solution due to acid base reaction.

10. Acetals are not hydrolysed in basic medium.

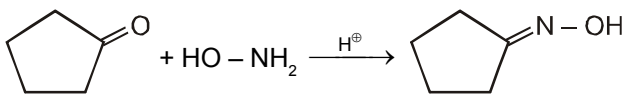
11. Hydrogen of nitromethane is more acidic as $\overset{\ominus}{C}H_2-NO_2$ is more stable.

12. In weakly acidic medium nucleophile is not affected.

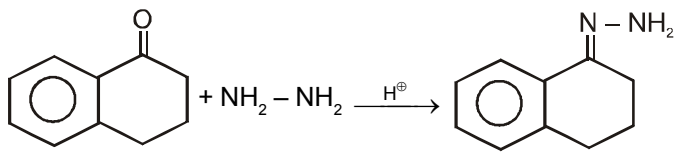
EXERCISE # 2

PART - I

1. (a)

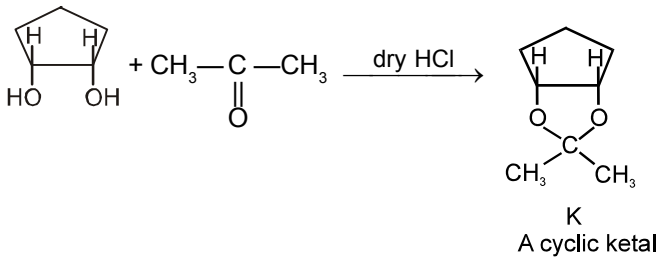


(b)



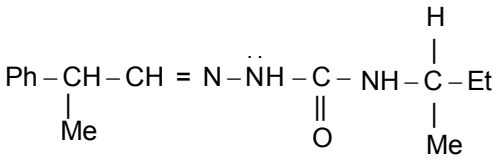
(c) $Ph-CH_2-CH_2-CHO + H_2\ddot{N}-\overset{\overset{O}{\|}}{C}-NH-NH_2 \longrightarrow Ph-CH_2-CH_2-CH=N-NH-\overset{\overset{O}{\|}}{C}-NH_2$

(d) $Ph-\overset{\overset{O}{\|}}{C}-Ph + Ph-NH-NH_2 \longrightarrow Ph-\overset{\overset{N-NH-Ph}{\|}}{C}-Ph$

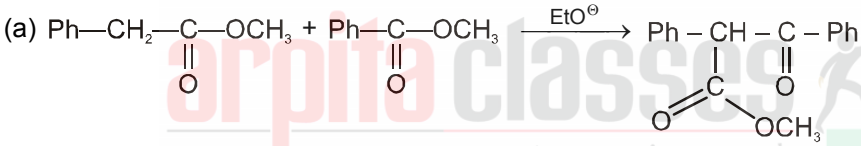
5. (a) 

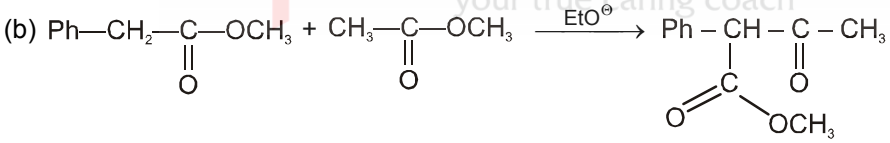
K
A cyclic ketal

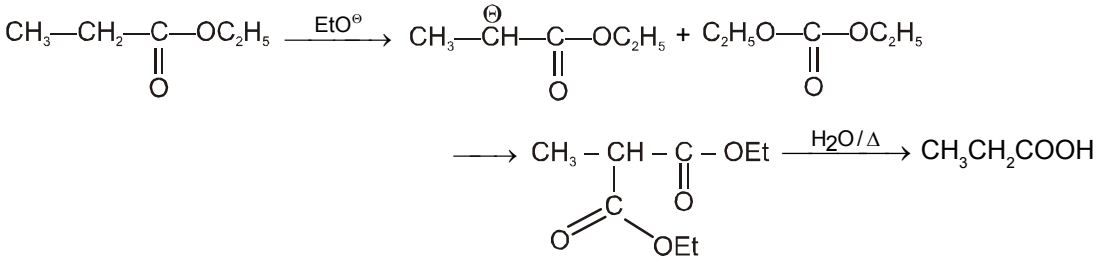
(b) The – OH groups in the trans isomer are too far apart to form cyclic structure.

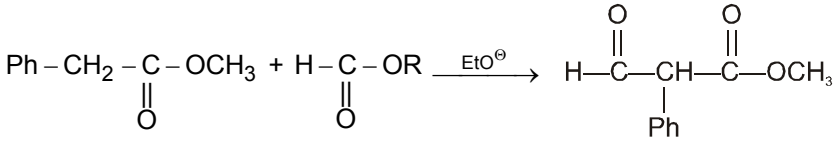
6. (a) 

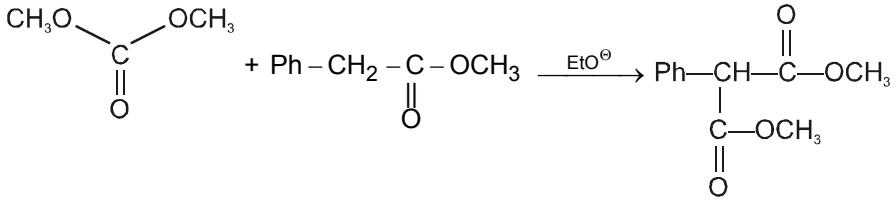
(R, syn)
(R, anti)
(S, syn)
(S, anti)

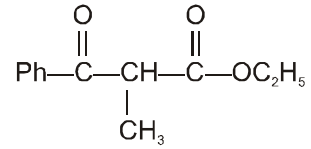
7. (a) 

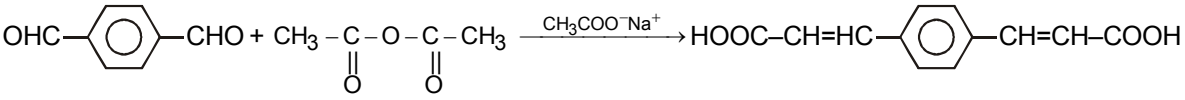
(b) 

(c) 

8. (a) 

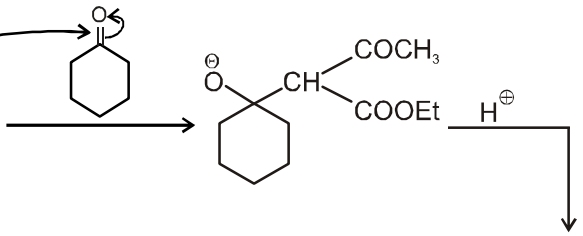
(b) 

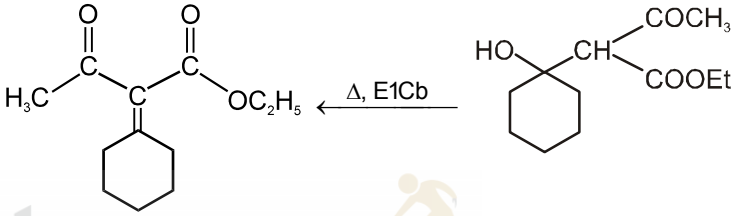
(c) $Ph-\underset{\underset{O}{\|}}{C}-OR + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{EtO^{\ominus}}$ 

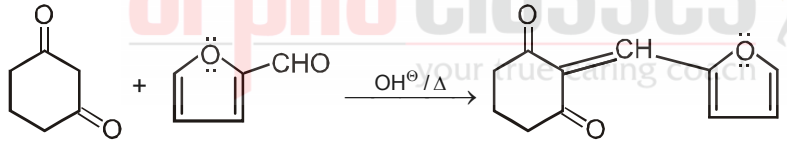
9. (a) 

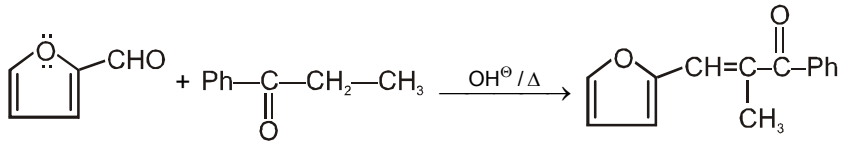
excess

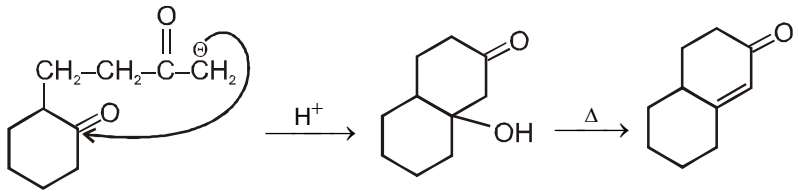
(b) $CH_3CHO + CH_2(CN)_2 \xrightarrow{\text{Pyridine}/\Delta} CH_3-CH=C(CN)_2$

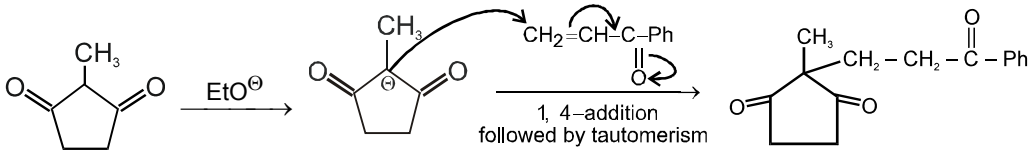
(c) $CH_3COCH_2COOEt \xrightarrow[EtOH]{EtONa/\Delta} CH_3\overset{\ominus}{C}HCOOEt$ 



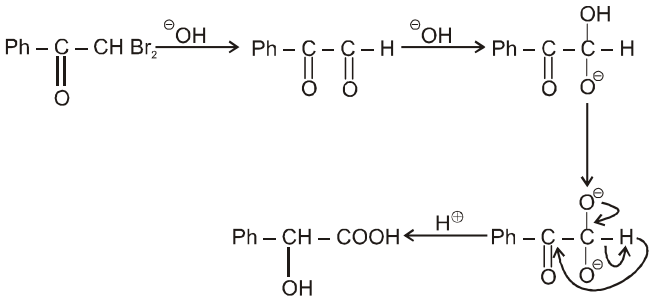
10. (a) 

(b) 

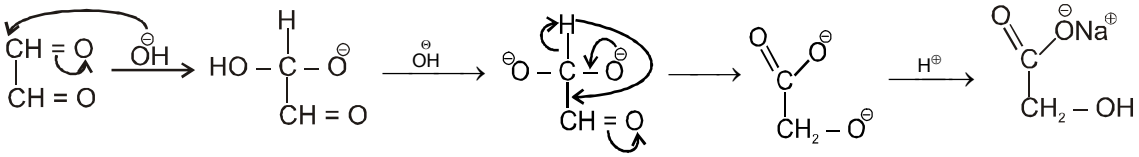
(c) 

11. 

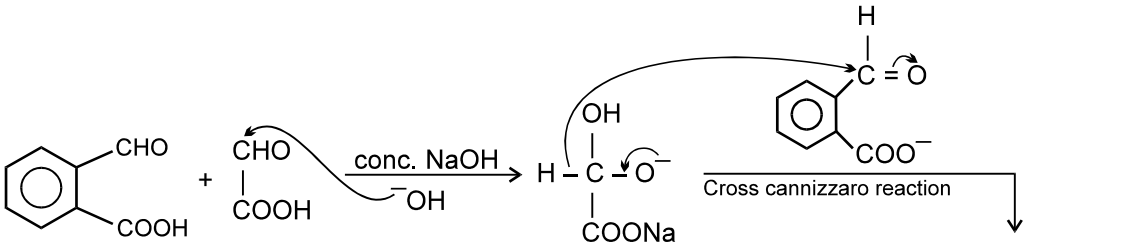
13.



14.



15.



16. (i) (B) reacts with hydroxyl amine and thus (B) has carbonyl group, i.e., > C = O group ketonic or aldehyde (—CH = O) group.

(ii) (B) gives negative test with Tollen's reagent and thus (B) is ketone.

(iii) (B) is obtained by hydrolysis of (A) and thus both Cl atoms should be on same carbon atoms, i.e., (A) must be gem dihalide as well as not on terminals. Thus, only possibility of (A) is $CH_3CCl_2CH_2CH_3$.

(i) $CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_2-CH_3 \xrightarrow{HOH} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

2, 2-Dichlorobutane (A)

(ii) $\begin{matrix}CH_3\\CH_3CH_2\end{matrix}\!\!>C=O + H_2NOH \xrightarrow{\text{Hydroxylamine}} \begin{matrix}CH_3\\CH_3CH_2\end{matrix}\!\!>C=NOH$

(B) Oxime

(iii) $\begin{matrix}CH_3\\CH_3CH_2\end{matrix}\!\!>C=O \xrightarrow{\text{Tollen's reagent}}$ No reaction

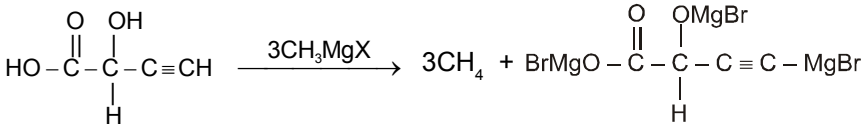
18. $ROH + CH_3MgX \rightarrow CH_4 + ROMgX$

Let molecular mass of alochol is M

$$\frac{56}{22400} = \frac{0.22}{M}$$

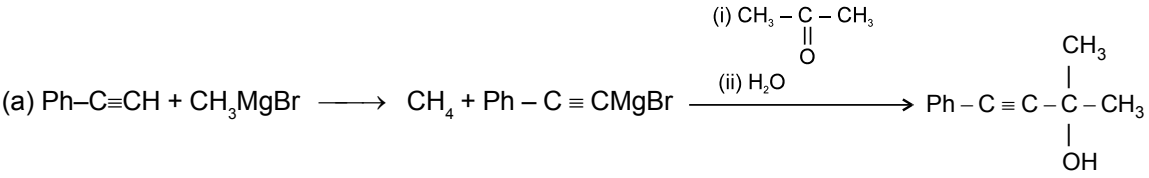
$$M = \frac{22400 \times 0.22}{56} = 88 \text{ gm}$$

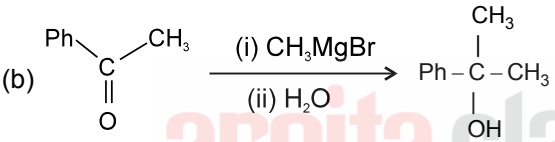
General formula of alcohol is $C_nH_{2n+1}OH$ which correspond to the molecular mass 88. Hence value of n = 5.
So molecular formula of alcohol is $C_5H_{11}OH$.

19. 

20. $CH_3(CH_2)_8CH_2Br \xrightarrow[H_3O^{\oplus}]{Mg} CH_3(CH_2)_8CH_3 \xrightarrow{Cl_2}$ 5 monochloro product.

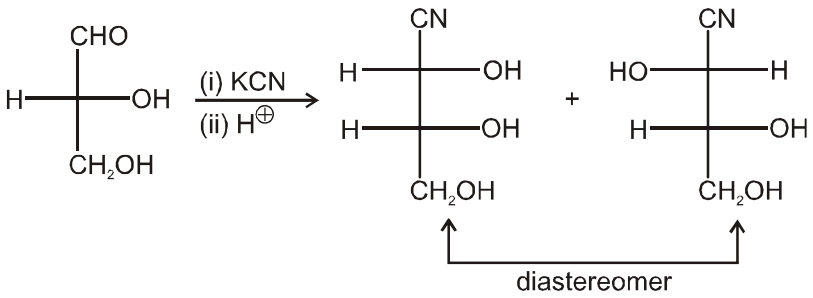
(X) (Y)

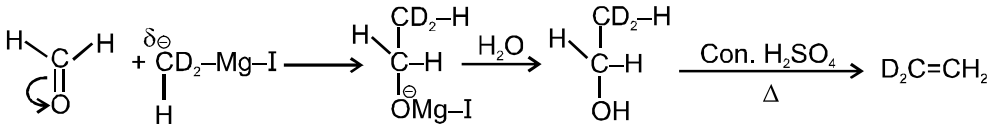
21. (a) 

(b) 

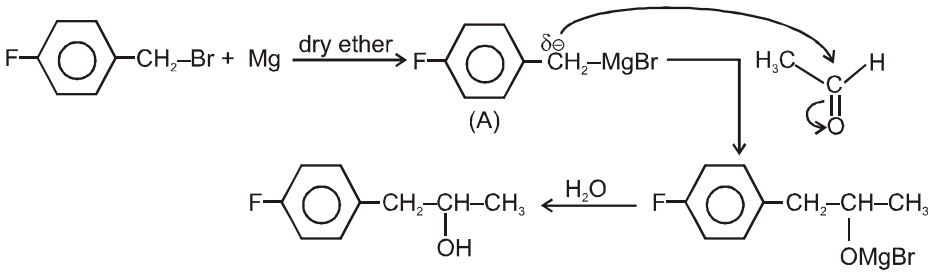
(c) 

PART - II

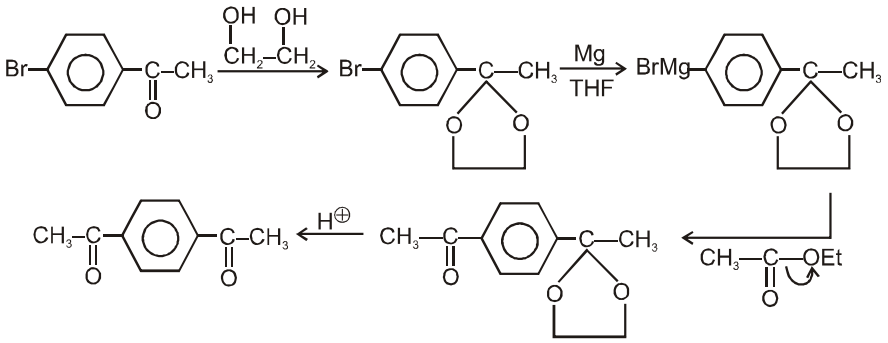
1. 

2. 

3.

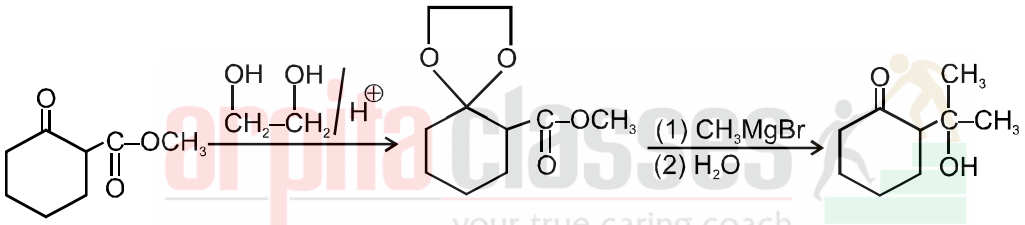


4.

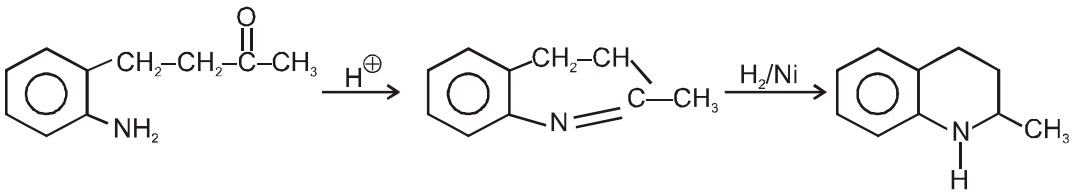


Grignard reagent is stable in THF. Grignard reagent reacts with epoxide hence (B) can't be the answer.

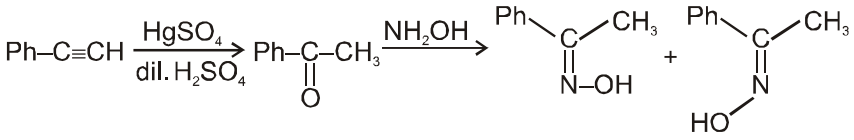
5.



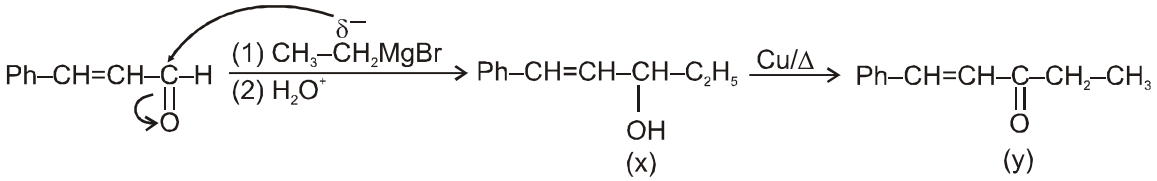
6.



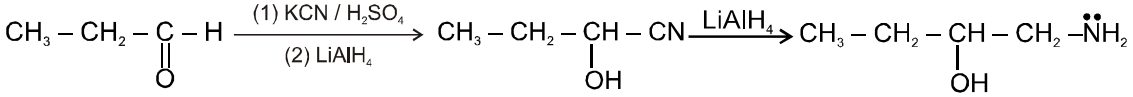
7.



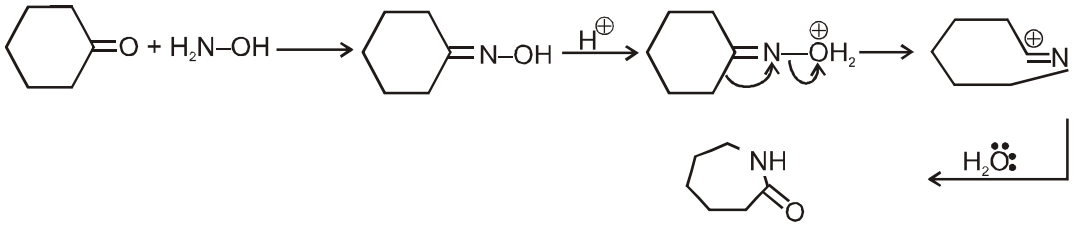
8.



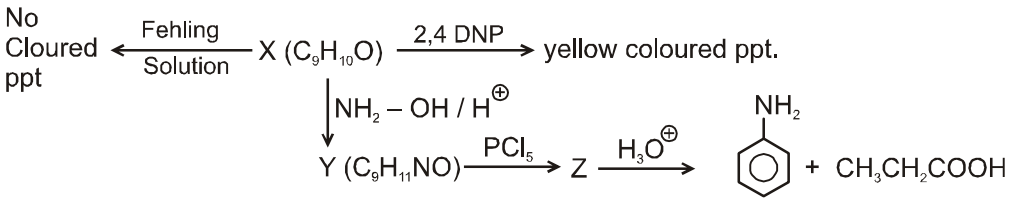
9.

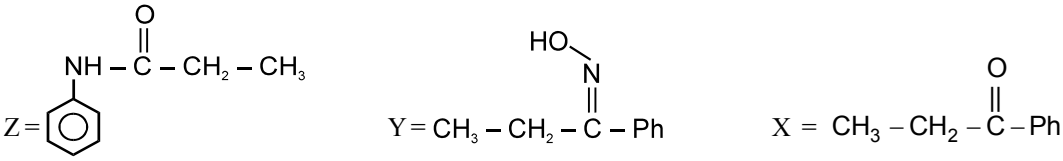


10. Beckmanns rearrangement

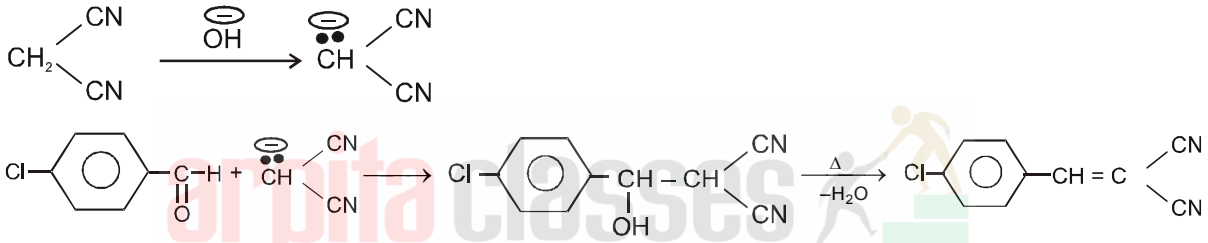


11.

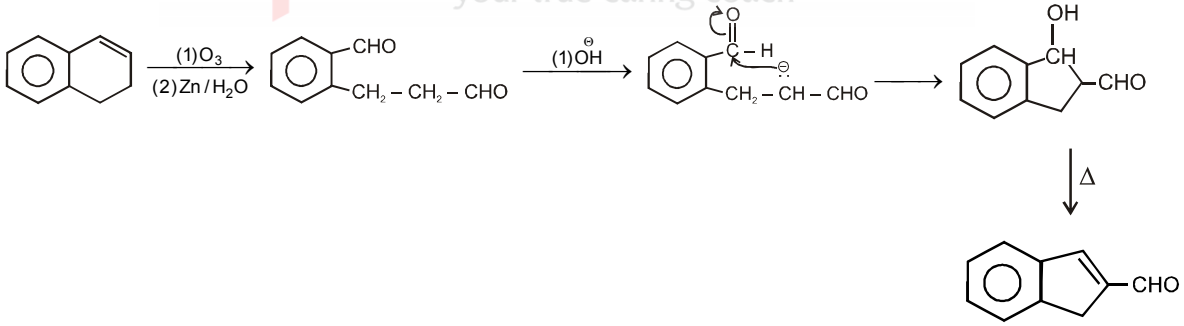




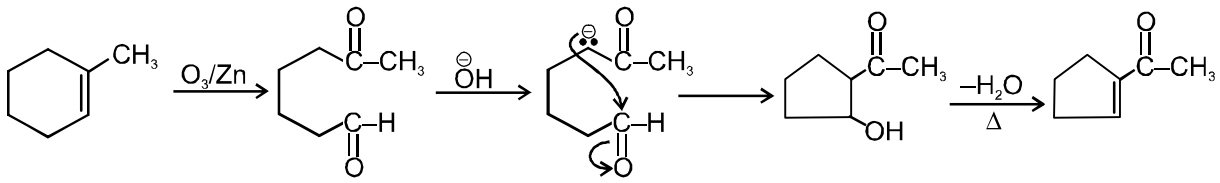
12.



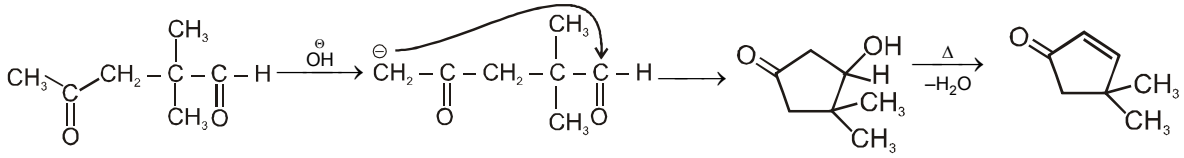
13.



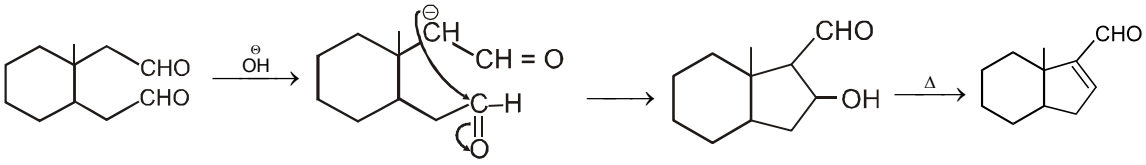
14.



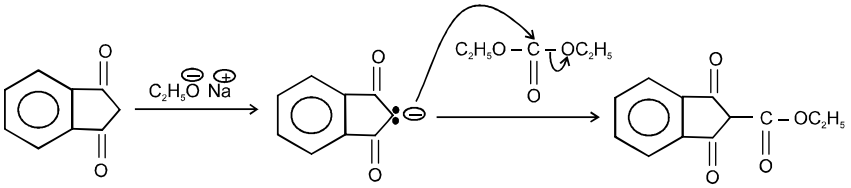
15.



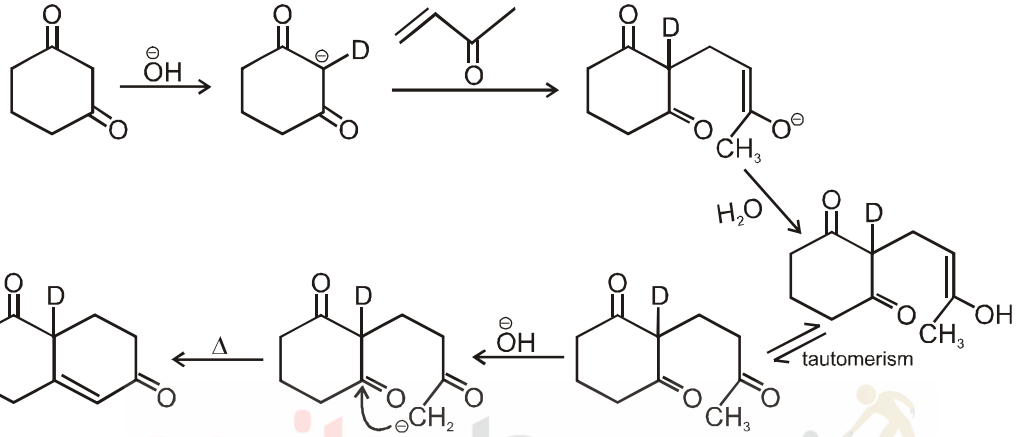
16.



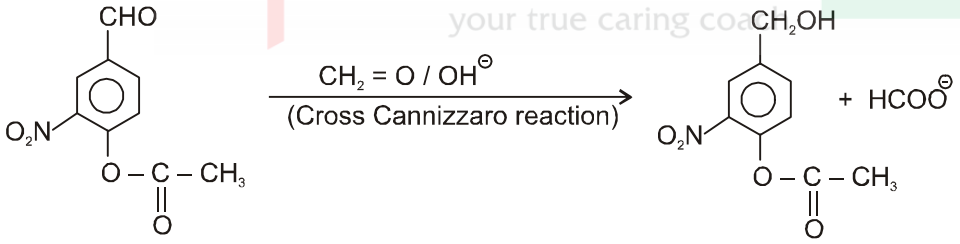
17.



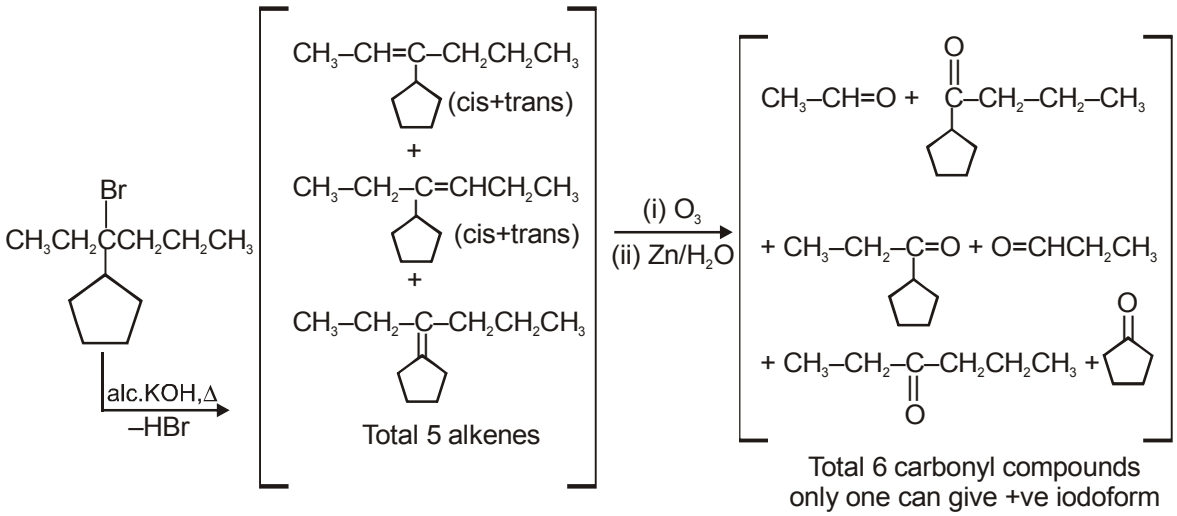
18.



20.

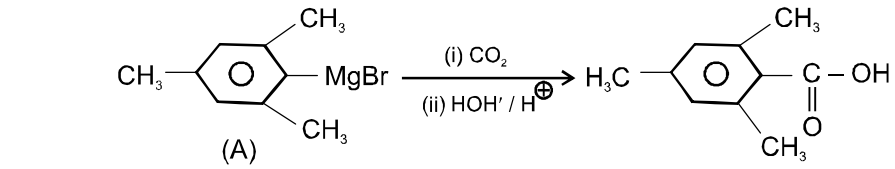


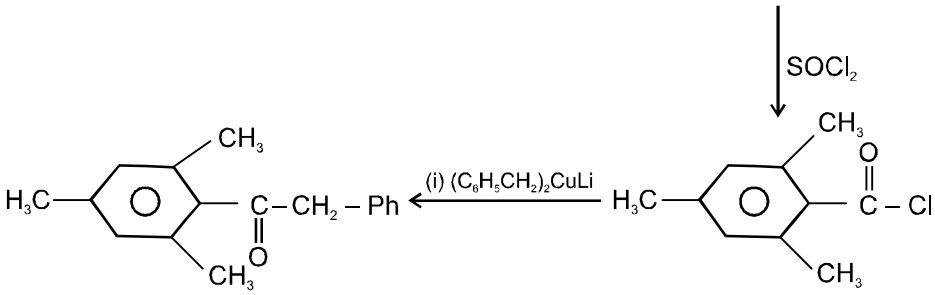
23.



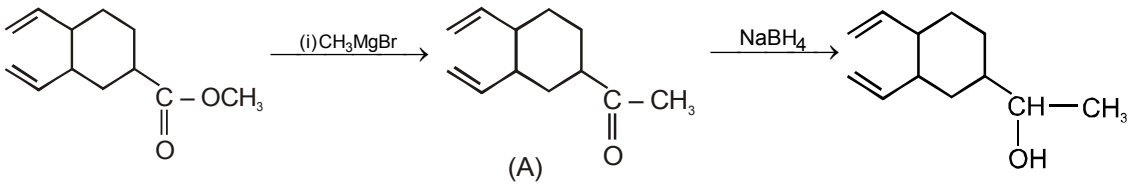
Total 6 carbonyl compounds
only one can give +ve iodoform

24.





25.

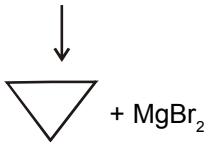


26. (D) $Cl-CH_2-\underset{\underset{O}{\|}}{C}-OEt + 2CH_3MgI \xrightarrow{H_2O} Cl-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

27. (A) $2CH_2=CH-CH_2-Cl \xrightarrow[ether]{Mg} 2\,CH_2=CH-CH_2-MgCl + H-\underset{\underset{O}{\|}}{C}-OC_2H_5$

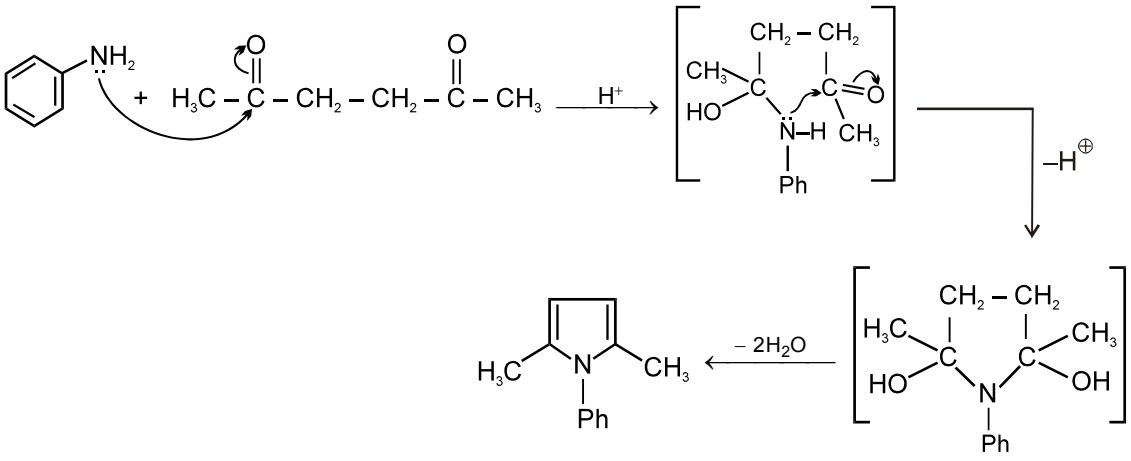
$(CH_2=CH-CH_2)_2\,CH-OH + CH_3-CH_2-OH$

28. (C) $BrCH_2CH_2CH_2Br + Mg \xrightarrow{Et_2O} Br-CH_2-CH_2-CH_2\,MgBr$

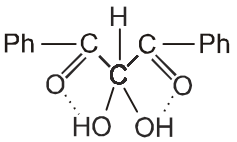


$+ MgBr_2$

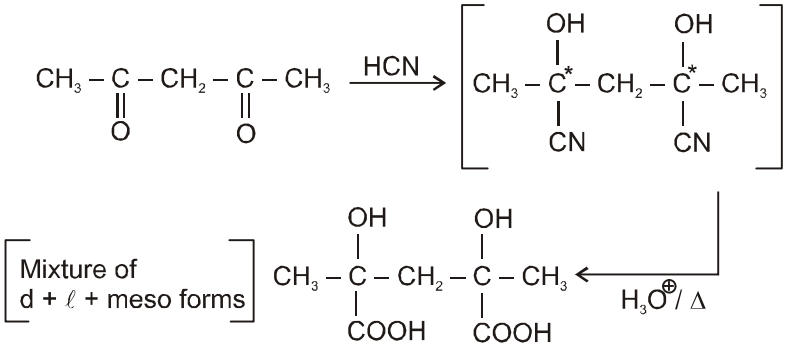
29.



30. (A) Due to substrate (steric factor)

(B) H bonding in 

(C) Cyanohydrin formation is usually reversible

31. 

32. (a) $Ph-CH_2-CH=O \xrightarrow{KCN/H_2O} Ph-CH_2-CH(OH)-CN \xrightarrow{NH_3} Ph-CH_2-CH(NH_2)-CN \xrightarrow{H_3O^{\oplus}} Ph-CH_2-CH(NH_2)-COOH$

(b) $Ph-CH_2-CH=O \xrightarrow{KCN/NH_4Cl} Ph-CH_2-CH(OH)-CN \xrightarrow{NH_3} Ph-CH_2-CH(NH_2)-CN \xrightarrow{H_3O^{\oplus}} Ph-CH_2-CH(NH_2)-COOH$

(c) $Ph-CH_2-CH=O \xrightarrow{HCN/NaOH} Ph-CH_2-CH(OH)-CN \xrightarrow{SOCl_2} Ph-CH_2-CH(Cl)-CN \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ NH_3} Ph-CH_2-CH(NH_2)-COOH$

34. $HC\equiv CH \xrightarrow[dil.\ H_2SO_4]{Hg^{+2}} CH_3-C(=O)-H \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ CH_3MgX} CH_3-CH(OH)-CH_3 \xrightarrow[(2)\ H^{\oplus}]{(1)\ K_2Cr_2O_7} H_3C-C(=O)-CH_3$

(X) (Y) (Z)

35. $CH_3-C(=O)-CH_2-CH_2-CH_3$ and $CH_3-CH(CH_3)-C(=O)-CH_3$ gives positive Iodoform test

36. (A) $(CH_3CH_2COO)_2Ca \xrightarrow{\Delta} CH_3-CH_2-C(=O)-CH_2-CH_3$

(B) $CH_3-CH_2-C\equiv N \xrightarrow{CH_3-CH_2-MgBr} CH_3-CH_2-C(CH_2CH_3)=N\,MgBr \xrightarrow{H_3O^{+}} CH_3-CH_2-C(CH_2CH_3)=NH$

$\xrightarrow{H_3O^{+}} CH_3-CH_2-C(=O)-CH_2-CH_3$

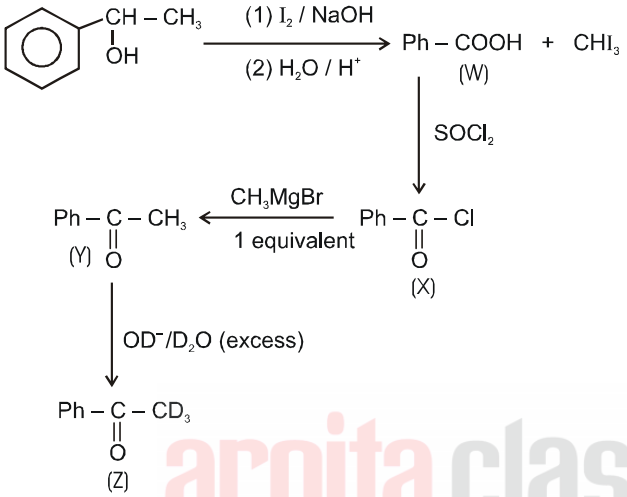
(C) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{H_2O/H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xleftarrow{NaOH/CaO}$

(D) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-CO_2]{\Delta} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

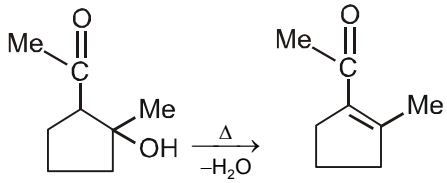
37. (A) Perkin reaction (B) Knoevenagel reaction (D) Reformatsky reaction

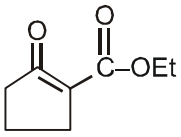
38.



PART - III

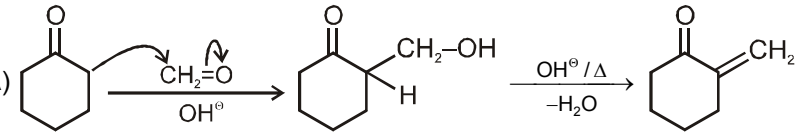
1. (A) $Me-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Me \xrightarrow{OH^{\ominus}}$ intramolecular aldol condensation

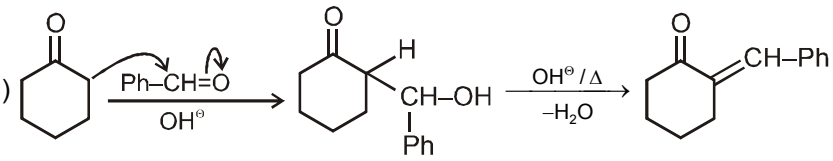


(B) $CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OEt$ / $CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OEt$ $\xrightarrow{\overset{\ominus}{O}Et}$ Dieckmann Reaction (Intra–claisen condensation) → 

(C) Perkin's condensation reaction.

(D) Benzil-Benzilic acid rearrangement.

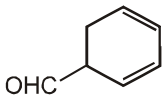
2. (A) 

(B) 

(C) $CH_3CHO \xrightarrow[OH^{\ominus}]{CH_2=O} CH_2-CH_2-CHO \xrightarrow[-H_2O]{OH^{\ominus}/\Delta} CH_2=CH-CHO$

(D) $CH_3CHO \xrightarrow[OH^{\ominus}]{PhCH=O} PhCH-CH_2CHO \xrightarrow[-H_2O]{OH^{\ominus}/\Delta} Ph-CH=CH-CHO$

3. (A) $Ph-CH_2-\overset{\overset{O}{\|}}{C}-CH=CH_2$
- 1, 4-addition.
- Shows tautomerism as it has two α-H.
- Gives +ve 2, 4-DNP test as the carbonyl group is present.

(B) 
- Gives 1, 4-addition.
- Shows tautomerism as it has two α-H.
- Gives +ve tollen's test as it has aldehyde groups.
- +ve 2, 4-dNP test.

(C) $CH_3-CH=CH-CH=CH_2$
- It is a conjugated diene and gives 1, 4-addition.

(D) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$
- Shows tautomerism as it has active methylene group (α-H).
- +ve tollen's test since –CHO group is present.
- +ve 2, 4-DNP test.

5. (A) $RMgI + CH_3-C\equiv N \longrightarrow CH_3-\overset{\overset{R}{|}}{C}=NMgI \xrightarrow{H_3O^+} CH_3-\overset{\overset{O}{\|}}{C}-R$ (Alkanone)

(B) $RMgI + S=C=S \longrightarrow R-\overset{\overset{S}{\|}}{C}-S-MgI \xrightarrow{H_3O^+} R-\overset{\overset{S}{\|}}{C}-SH$ (Dithionic acid)

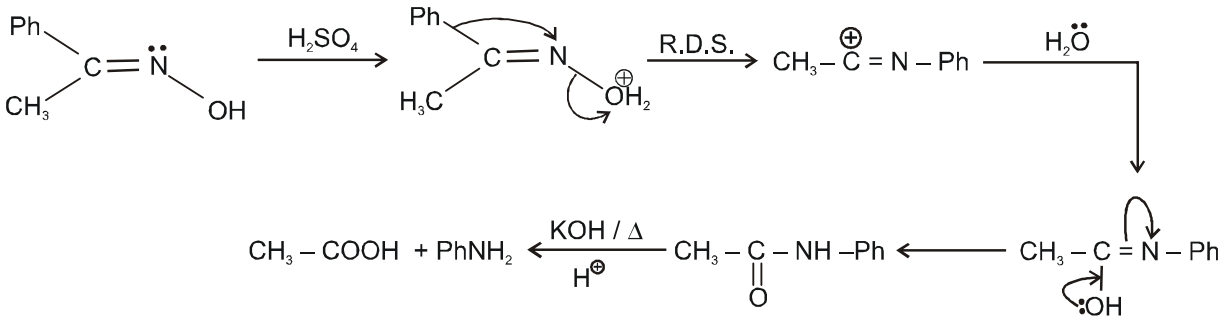
(C) $RMgI + CH_3CH_2O-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow CH_3-CH_2-O-\overset{\overset{R}{|}}{\underset{\underset{OMgI}{|}}{C}}-Cl \longrightarrow CH_3-CH_2-O-\overset{\overset{R}{|}}{\underset{\underset{O}{\|}}{C}} + MgICl$

(Ester)

(D) $RMgI + \underset{\diagdown O \diagup}{CH_2-CH_2} \longrightarrow R-CH_2-CH_2-OMgI \xrightarrow{H_3O^+} R-CH_2-CH_2-OH$ (Alcohol)

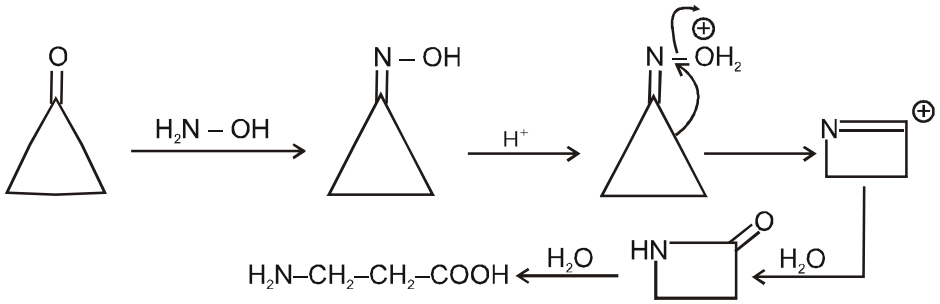
PART - IV

1.



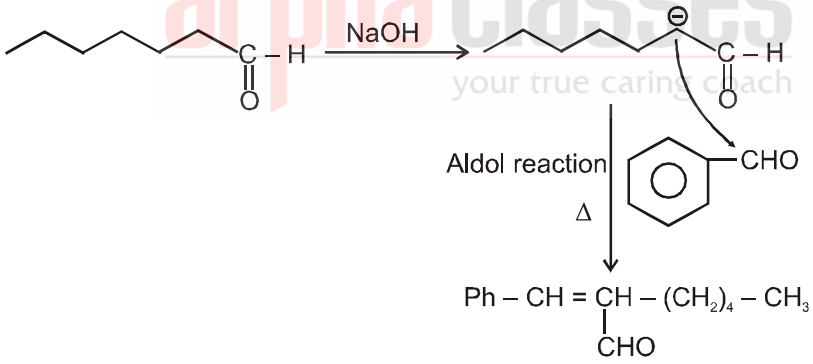
2. Migration of phenyl group is rds. (Step II)

3.



4. α – H hydrogen is present.

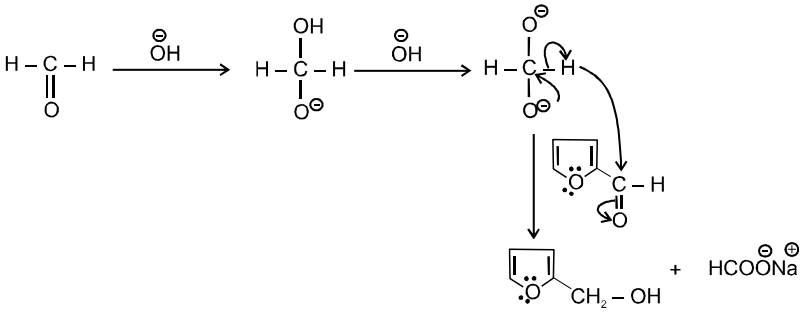
5.



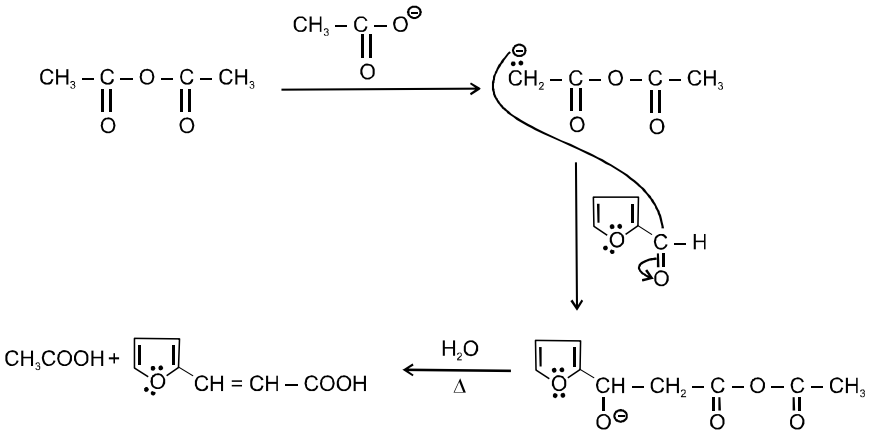
6. Polycarbonyl compound with α hydrogen gives intramolecular aldol condensation reaction in presence of alkaline medium.

7. Transfer of H^- ion is rds.

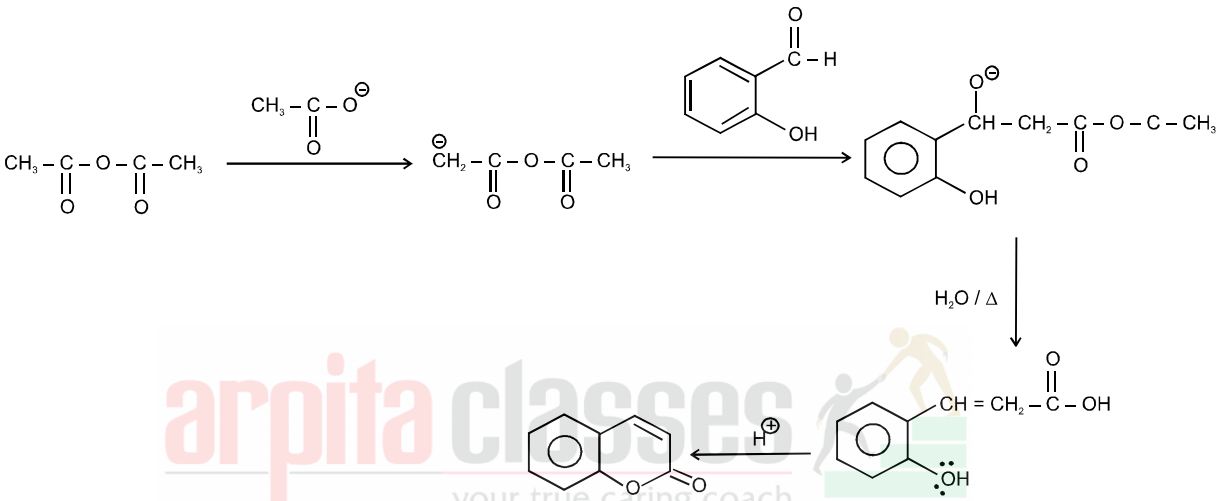
8.



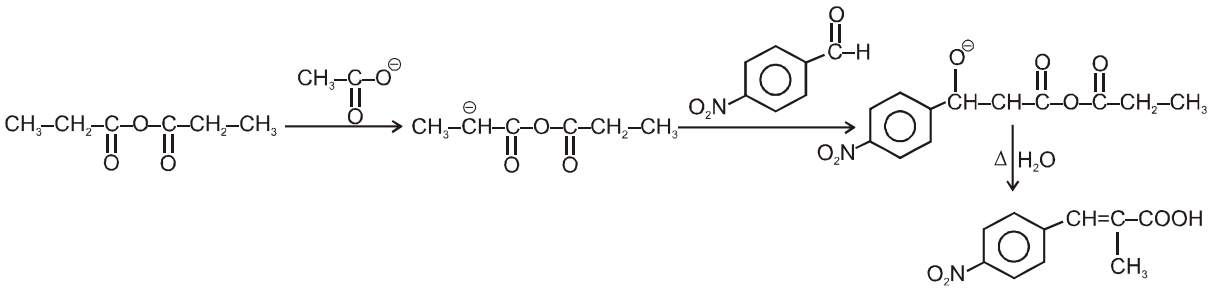
9.



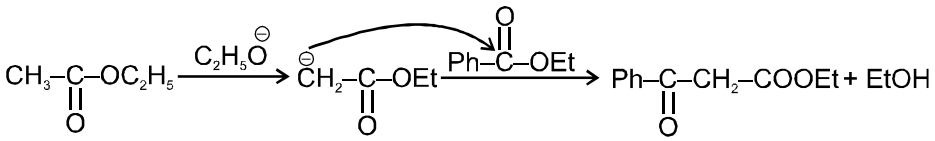
10.



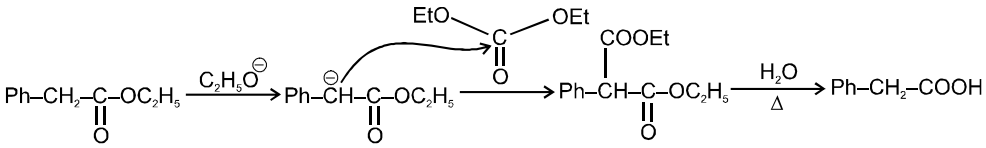
11.



12.



13.



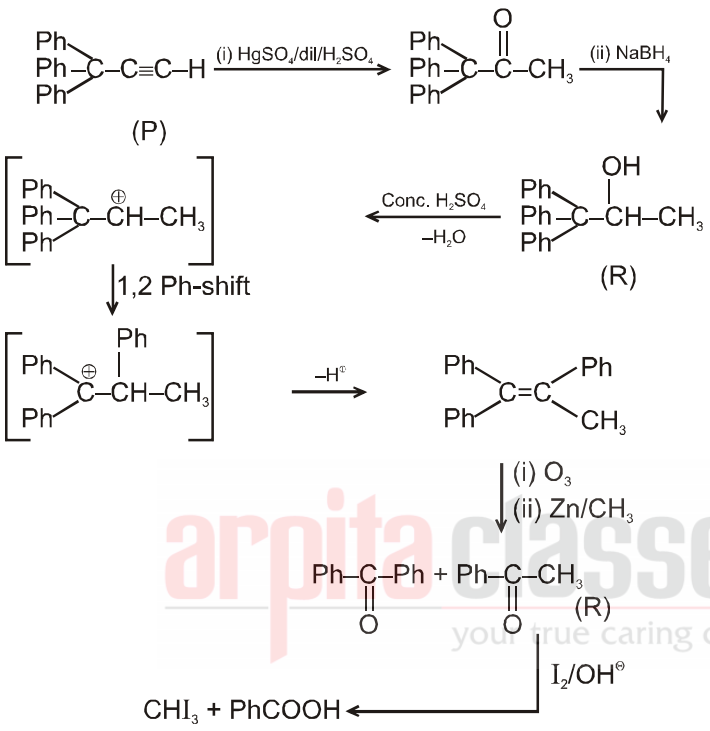
14. $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{C_2H_5O^{\ominus}} CH_3-\overset{\ominus}{\underset{\underset{O}{\|}}{C}}H-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{CH_3I} CH_3-\underset{\underset{O}{\|}}{\overset{CH_3}{\overset{|}{C}}}H-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow[\Delta]{H_2O} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

15. Step 'a' is rds.

16. $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-Ph$ give halloform reaction.

17. Step 'c' produce most acidic hydrogen due to two halogen atom.

(18-20)



21. $CH_3CH_2Cl \xrightarrow[ether]{Mg} CH_3CH_2MgCl \xrightarrow{R-\underset{\underset{O}{\|}}{C}-O-R'} \xrightarrow{H_2O} CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{CH_2-CH_3}{\overset{|}{C}}}-R$

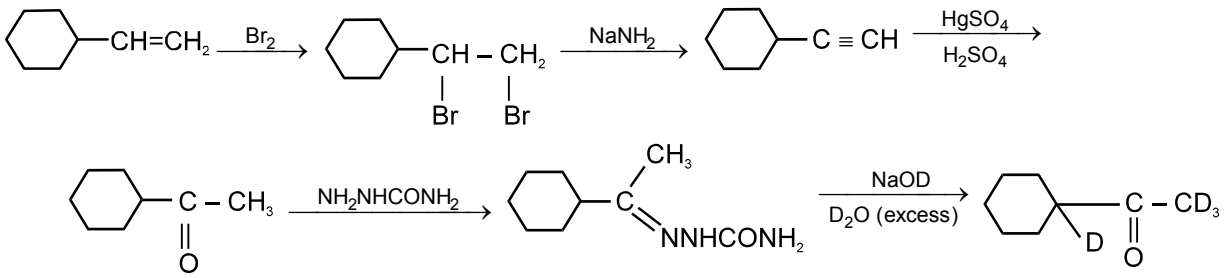
22. $H-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[excess]{RMgX} \xrightarrow{H_2O} H-\underset{\underset{OH}{|}}{\overset{R}{\overset{|}{C}}}-R$ (2^{o} Alcohol)

23. $\underset{excess}{CH_3MgCl} + Ph-\underset{\underset{O}{\|}}{C}-OCH_3 \xrightarrow[(2)\ H_2O]{(1)\ ether} Ph-\underset{\underset{OH}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3$

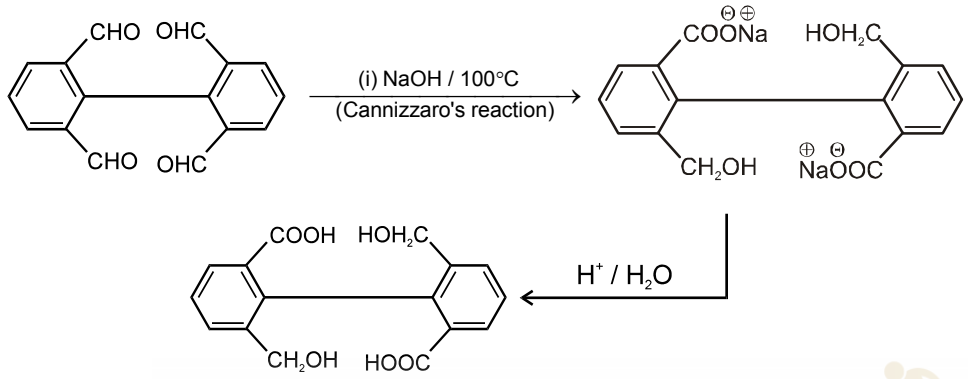
EXERCISE # 3

PART - I

1.

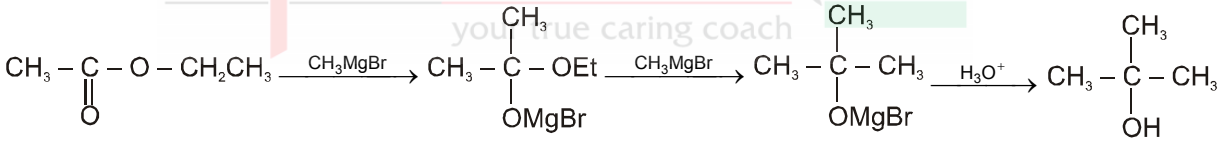


2.

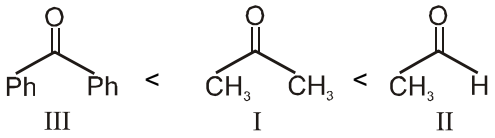


Note : Cannizzaro's reaction is due to the absence of α-hydrogen atom.

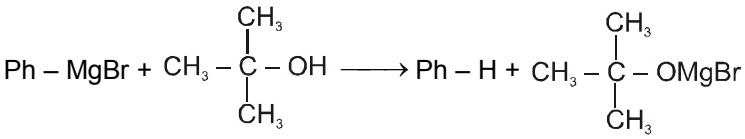
3.



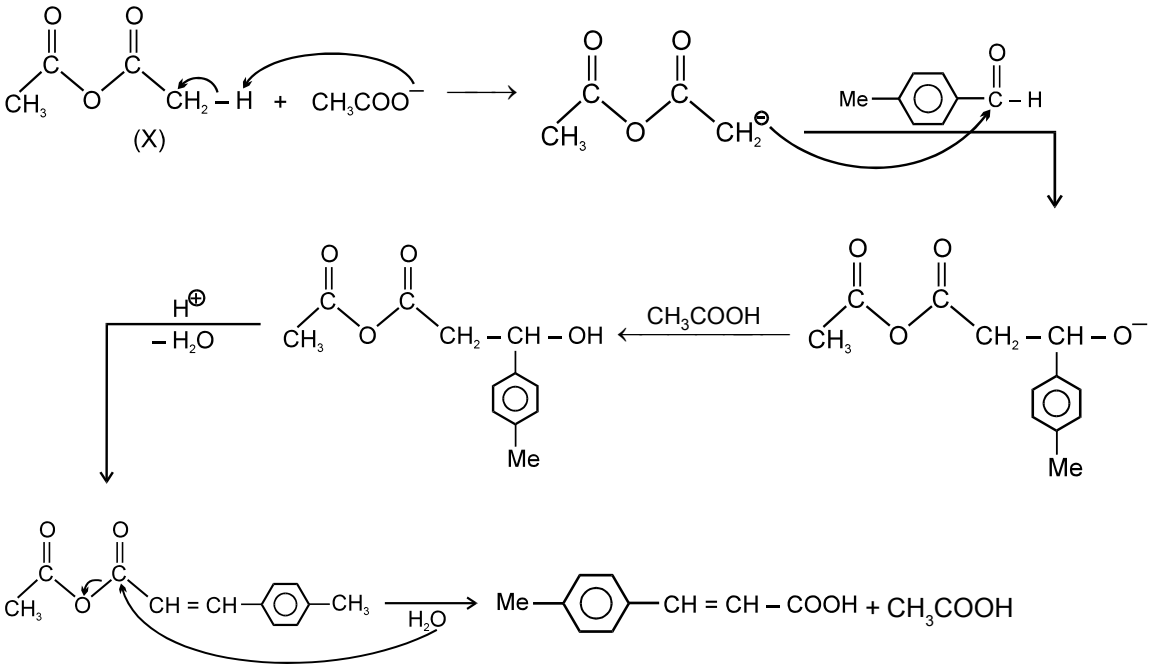
4.



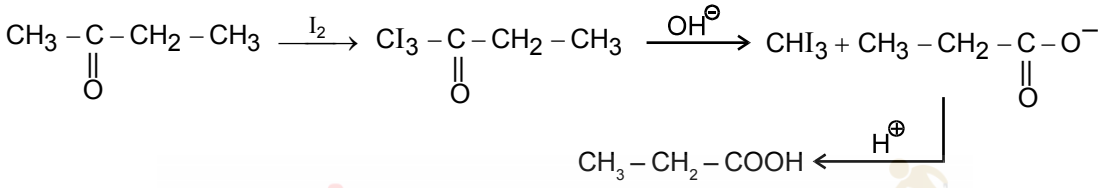
5.



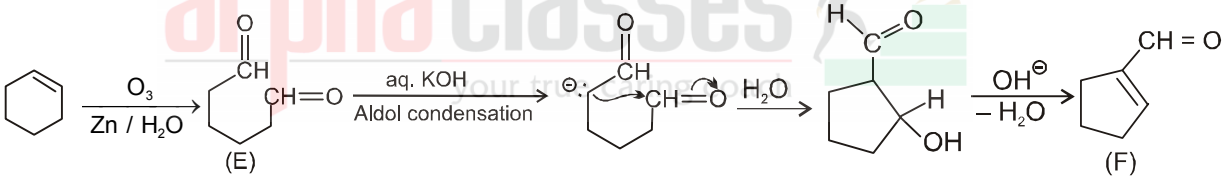
6. This is Perkin reaction



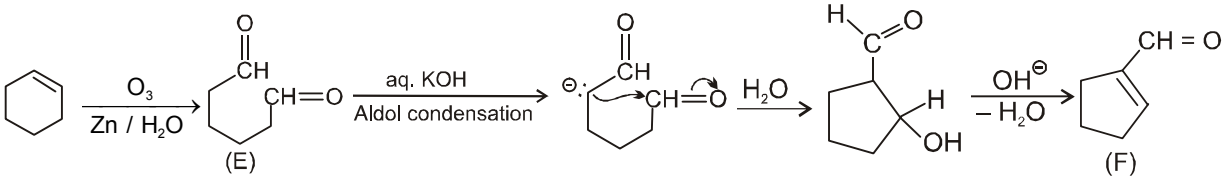
7.



8.



Sol.



Ozonolysis product of cyclohexene will give hexandial and this undergoes intramolecular aldol condensation in presence of alkali to give cyclic α,β-unsaturated aldehyde.

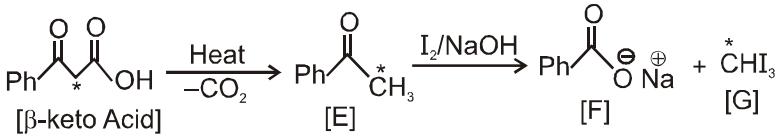
9. **(p)** 2, 4-DNP (2, 4-dinitrophenyl hydrazine) is used to distirguish carbonyl compounds as it gives solid orange precipitate of 2,4-dinitrophenyl hydrazone.

(q) Tollen's reagent (ammonical silver nitrate solution) gives white precipitate with alkyne and silver mirror test with aldehyde.

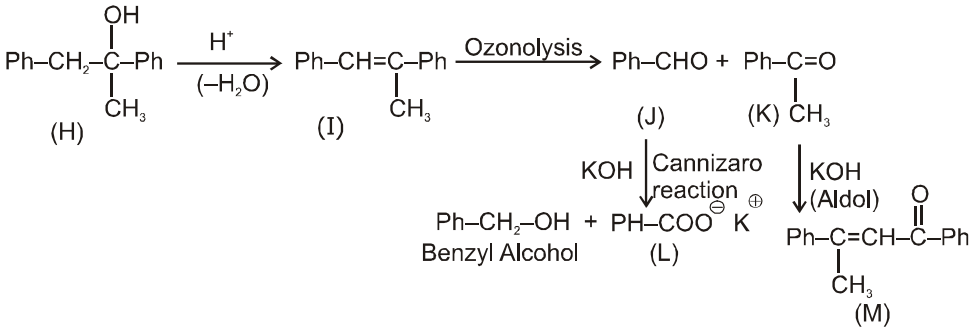
(r) (i) $\overset{\ominus}{C}N$ will gives AgCN with $AgNO_3$ (ii) is nucleophile (iii) forms cyanohydrin

(s) (i) $\overset{\ominus}{I}$ will give AgI with $AgNO_3$ (ii) is nuclophile

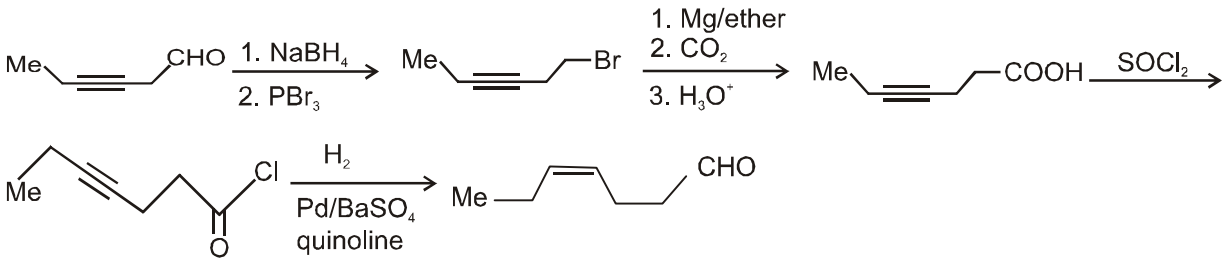
10.



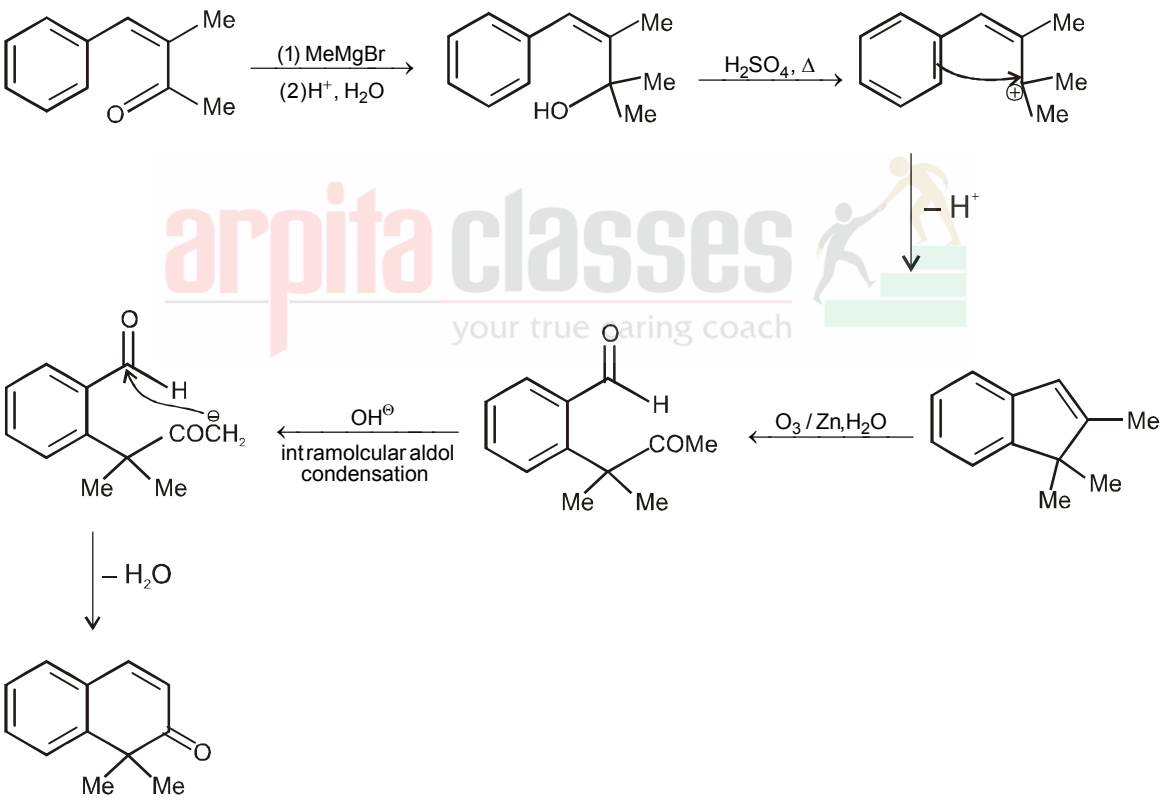
(11-13)



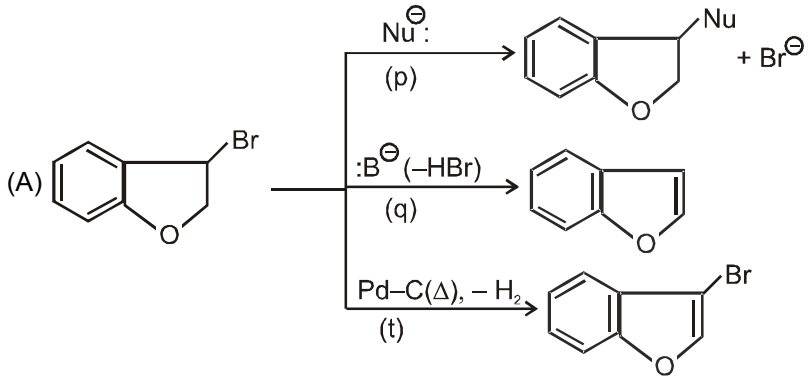
(14-16)

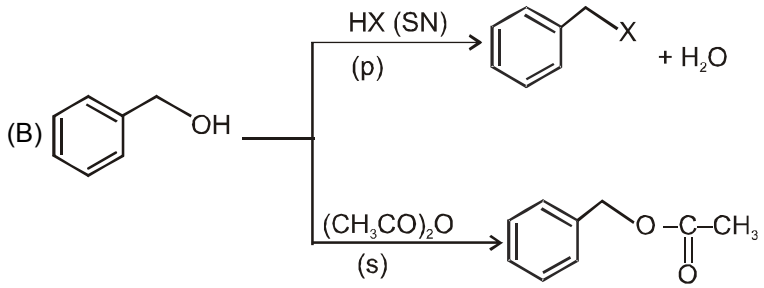


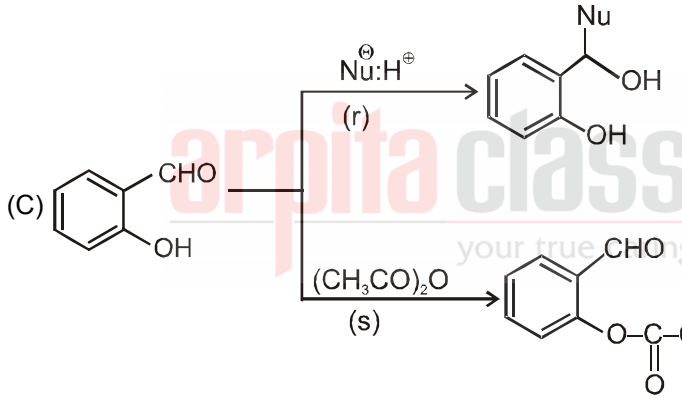
(17-19)

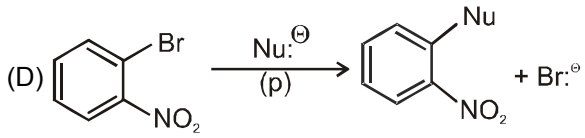


20.

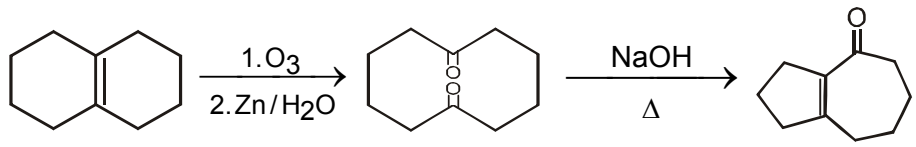




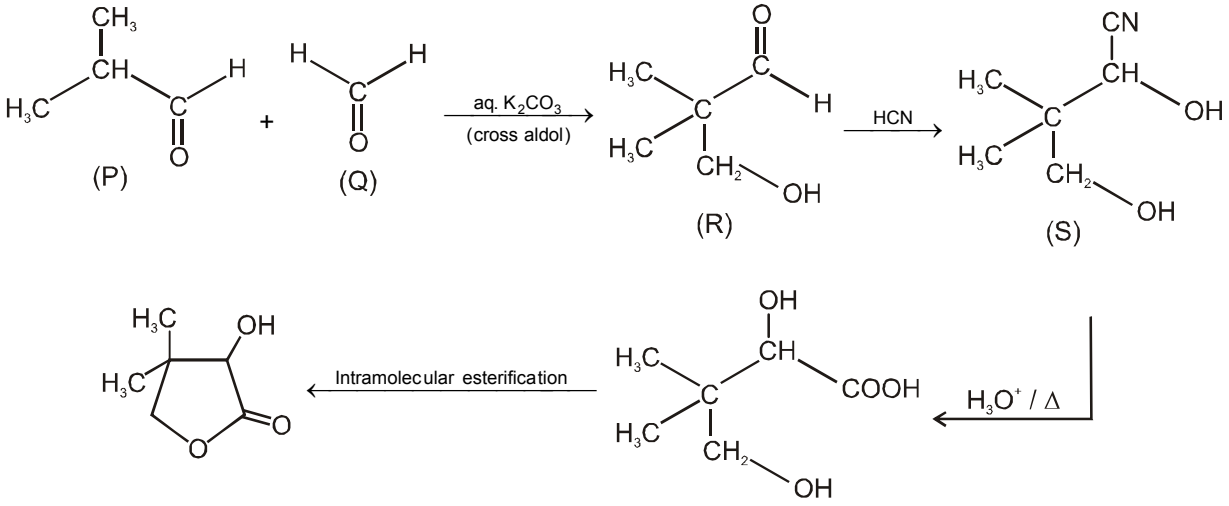




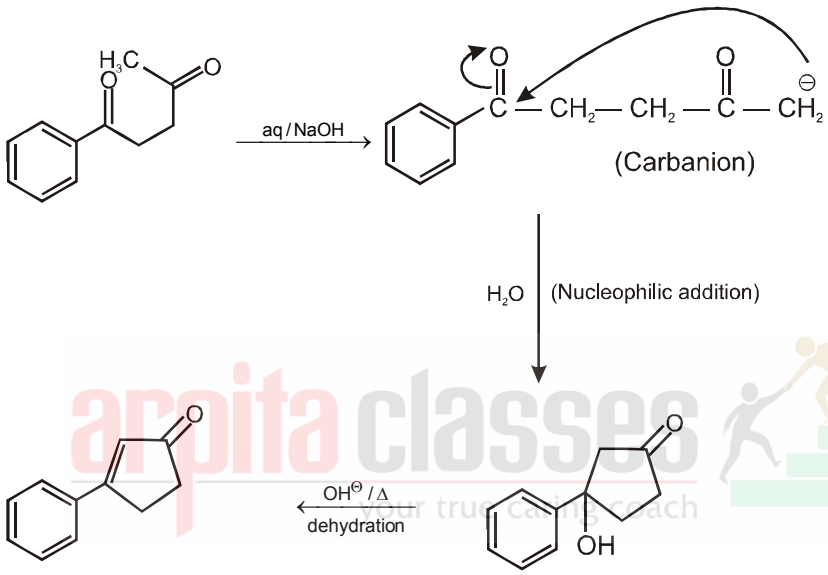
21.



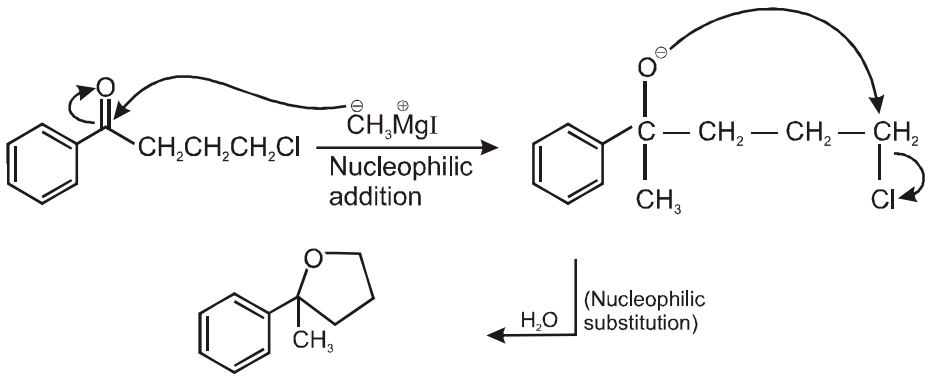
(22-24)



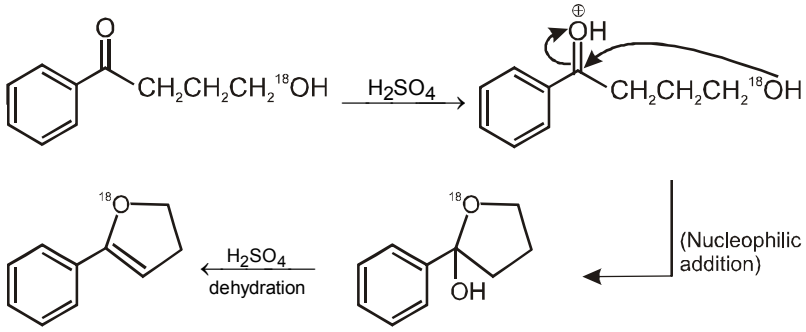
25. (A)

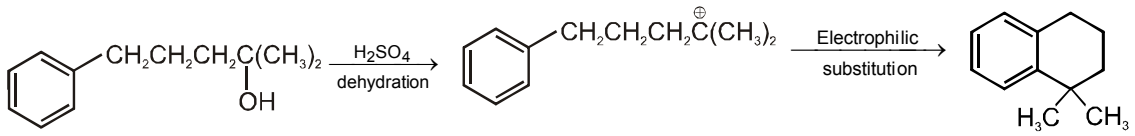


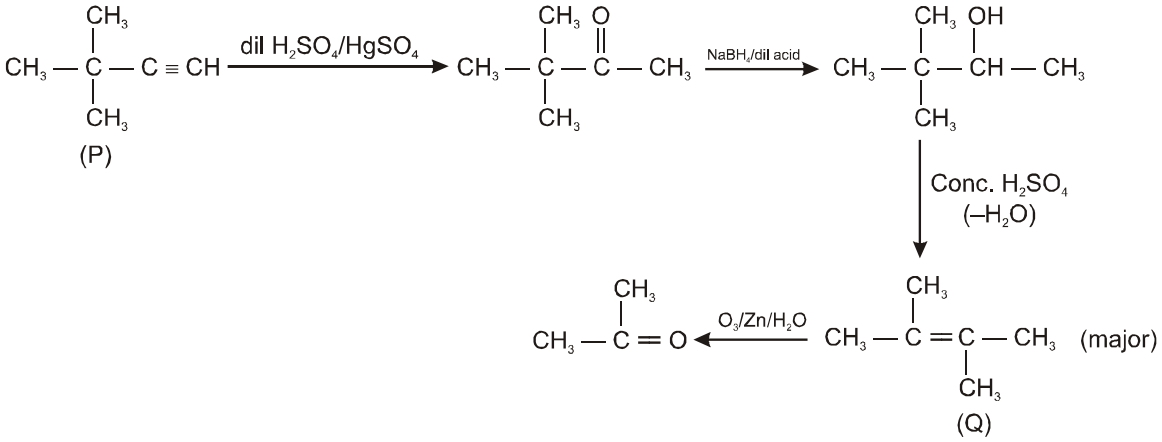
(B)

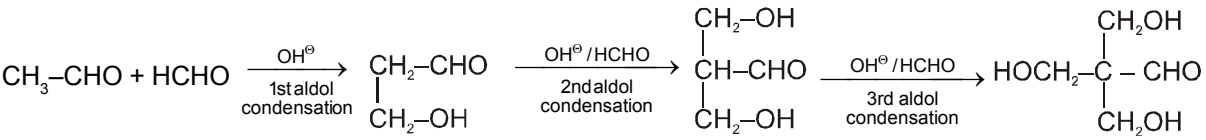


(C)

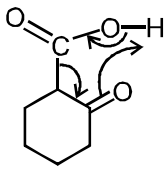


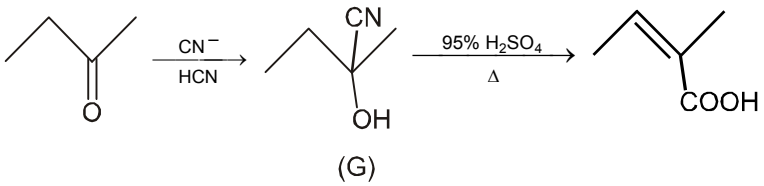
(D) 

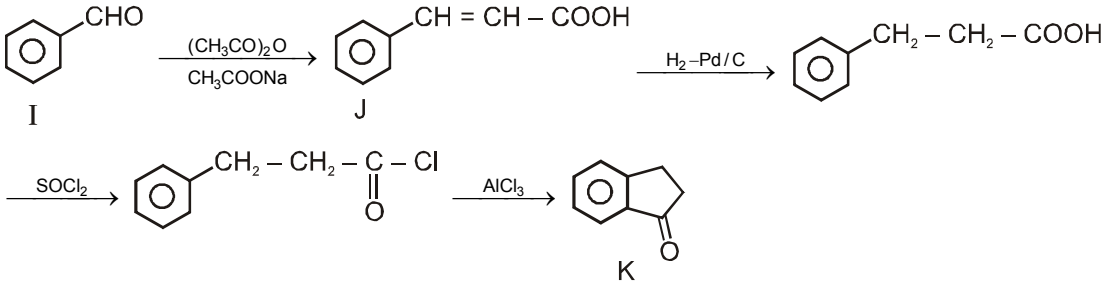
(26-27) 

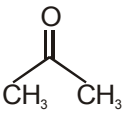
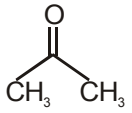
28. 

29. In decarboxylation, β-carbon acquires δ– charge. Whenever δ– charge is stabilized, decarboxylation becomes simple. In (B), it is stabilized by –m & –I of C = O, which is best amongst the options offered,

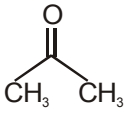
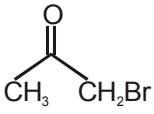


30. 

(31-32) 

33. Reaction I :  (1.0 mol) $\xrightarrow[Na^{\oplus}OH^{\ominus}]{Br_2\ (1.0\ mol)}$ $CH_3COONa + CHBr_3 +$  (Unreacted)

(In basic medium complete haloform reaction takes place since the rate of reaction increases with each α-halogenation)

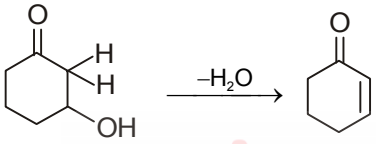
Reaction II :  (1.0 mol) $\xrightarrow[CH_3COOH]{Br_2\ (1.0\ mol)}$ 

(In acidic medium monohalogenation takes place with 1-mol of halogen)

PART - II

1. $H_3C-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CHO \xrightarrow{[O]} H_3C-\underset{\underset{O}{||}}{C}-CH_3 + \underset{\underset{COOH}{|}}{CH_2}-COOH$

2. Dehydration is maximum



3. C – Mg bond

4. $\underset{2-Butanone}{CH_3-\overset{\overset{O}{||}}{C}-C_2H_5} \xrightarrow[HCl]{Zn-Hg} \underset{Butane}{CH_3CH_2CH_2CH_3}$

It refers to as Clemensen's reduction

5. Benzaldehyde undergoes disproportionation with 50% NaOH to given benzyl alcohol and sodium benzoate

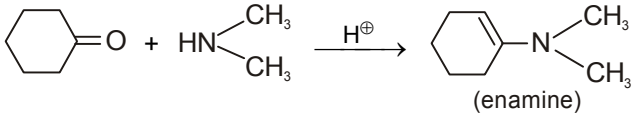
$C_6H_6CHO \xrightarrow{50\%\ NaOH} C_6H_5CH_2OH + C_6H_5COONa$

This is Cannizzaro's reaction.

6. $CH_3-\overset{\overset{O}{||}}{C}-Br + CH_3MgI \longrightarrow CH_3-\underset{\underset{OMgI}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow{CH_3MgI} CH_3-\underset{\underset{OMgI}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{NH_4Cl} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

2-Methyl-2-propanol

7. $H_3C-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_3 \xrightarrow{PCC} H_3C-\underset{\underset{O}{||}}{C}-CH=CH-CH_3$

8. 

(enamine)

9. As increase steric hinderance around carbonyl group then rate of nucleophilic addition reaction decreases.

10. $CH_3CH_2OH \xrightarrow[I_2]{P} CH_3CH_2I \xrightarrow{Mg} CH_3CH_2MgI \xrightarrow{HCHO} H-\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-OMgI \xrightarrow{H_2O} H-\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-OH$

n-propyl alcohol (D)

11. $CH_3-CH=CH-CH_3 \xrightarrow{O_3/Zn} CH_3-CHO$

12. $CH_3MgX + CH_3-C\equiv CH \longrightarrow CH_4 + CH_3-C\equiv C-MgX$

13. $Ph-\overset{\displaystyle O}{\overset{\|}{C}}-H + \overset{\ominus}{O}H \underset{}{\overset{fast}{\rightleftharpoons}} Ph-\underset{\displaystyle OH}{\overset{\displaystyle O^{\ominus}}{\underset{|}{\overset{|}{C}}}}-H \xrightarrow[rds]{Ph-\overset{\displaystyle O}{\overset{\|}{C}}-H} Ph-\overset{\displaystyle O}{\overset{\|}{C}}-OH + Ph-CH_2-O^{\ominus} \xrightarrow[exchange]{H^{\oplus}} Ph-\overset{\displaystyle O}{\overset{\|}{C}}-O^{\ominus} + Ph-CH_2-OH$

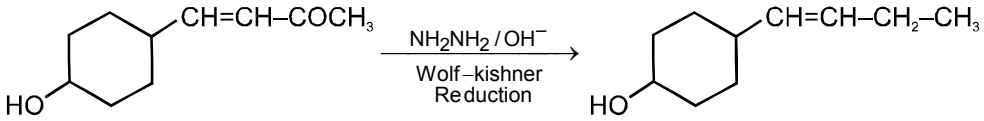
14. The cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.

$Cl_3C-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{NaOH} Cl_3C-\overset{\displaystyle O}{\overset{\|}{C}}-O^{-} + Cl_2C(OH)-CH_2Cl$

15. $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}=CH-CH_2-CH_3 \xrightarrow{O_3/Zn,\ H_2O} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}=O + CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H$

(2-Methyl-2-pentene) (A) — Acetone — Propionaldehyde

16. $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-OH$ isobutyl alcohol does'nt give positive iodoform test.

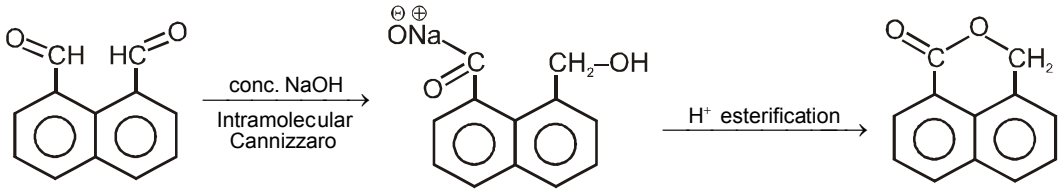
17. 

–OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used.

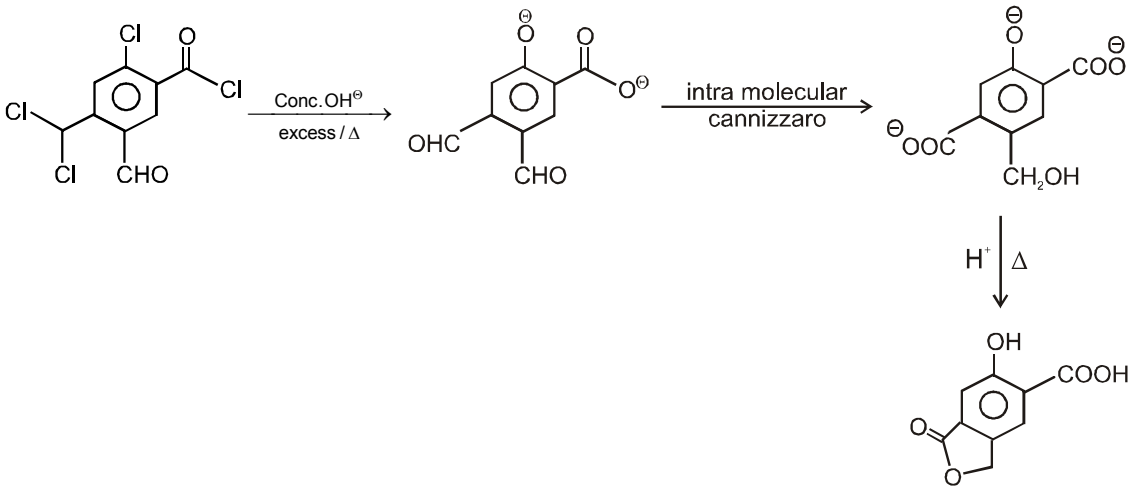
ALP Solutions

PART - I

1. It is a protecion of carbonyl group.

2. 

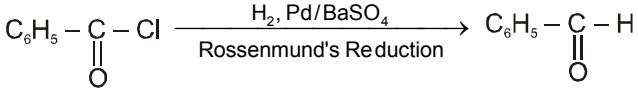
3.



4. It is cazzizzaro reaction.

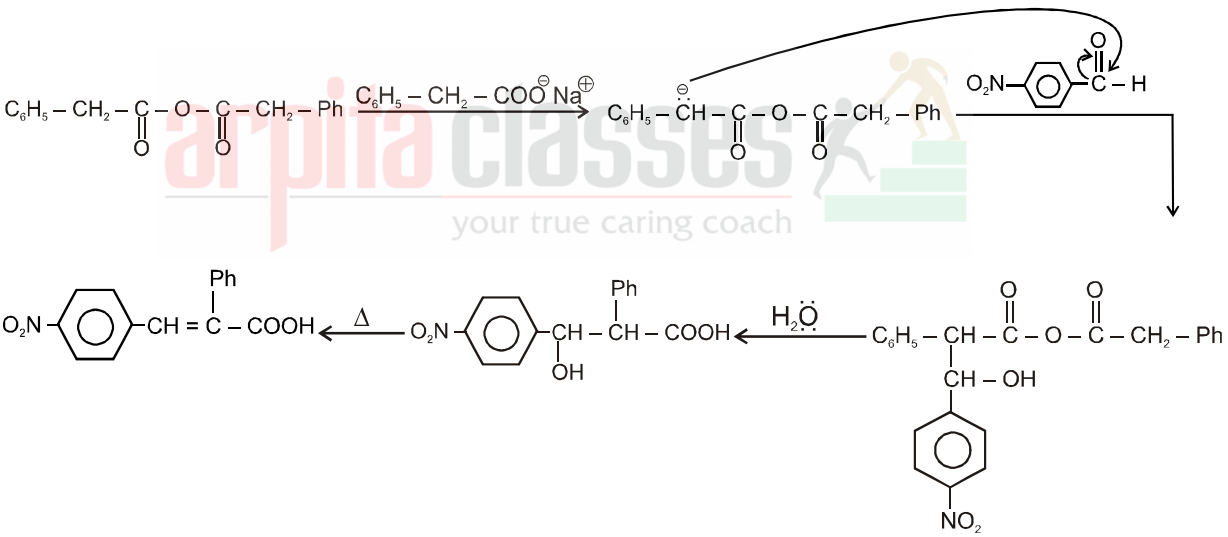
5. In Wolf-Kishner reduction carbonyl compound is converted to hydrocarbon.

6.

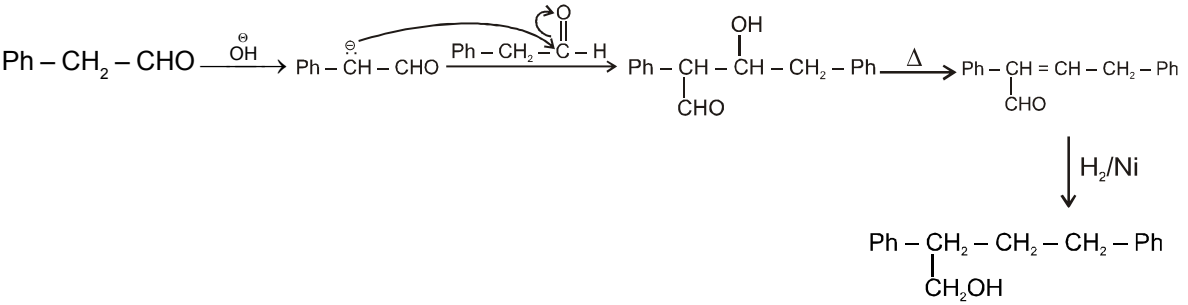


7. Rate of nucleophilic attack $\propto$ amount of +ve charge at carbonyl carbon.

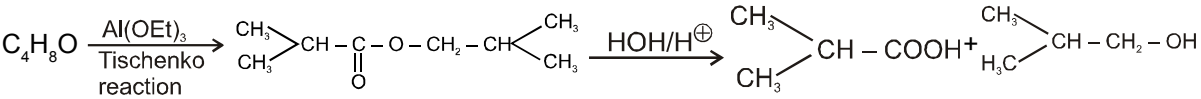
9.



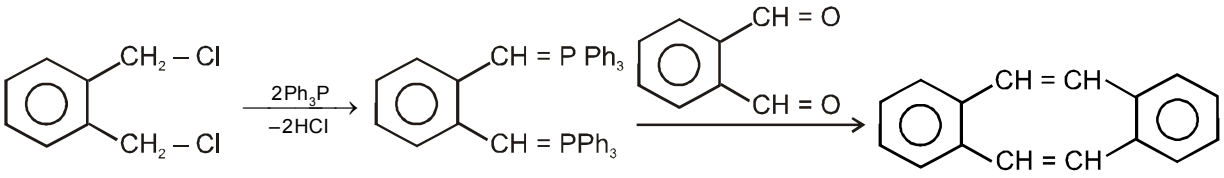
10.



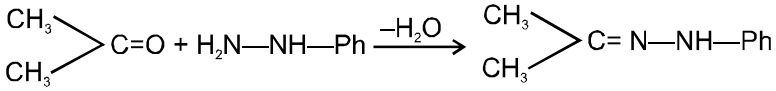
11.



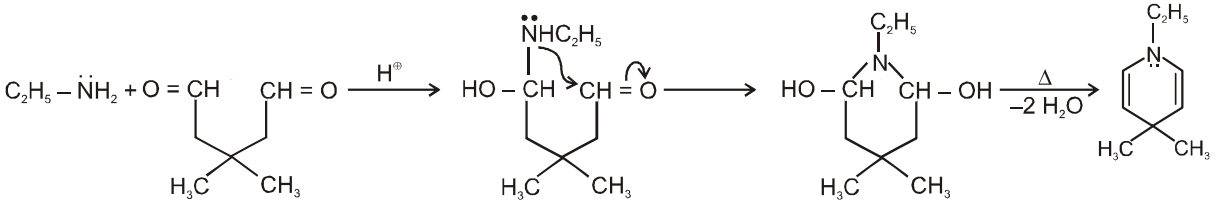
12.



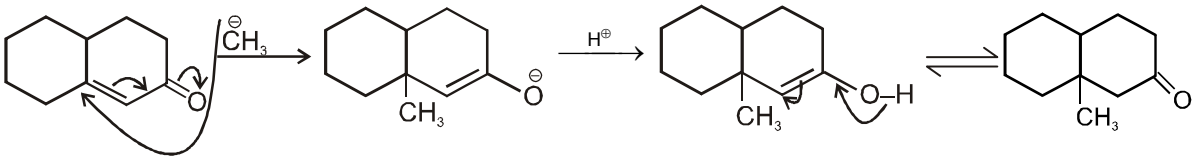
13.



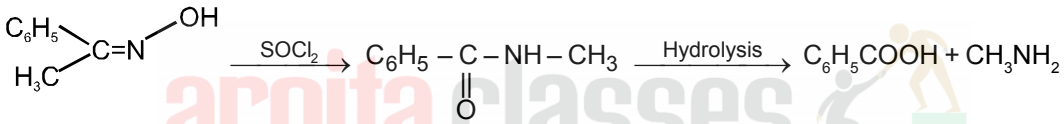
14.



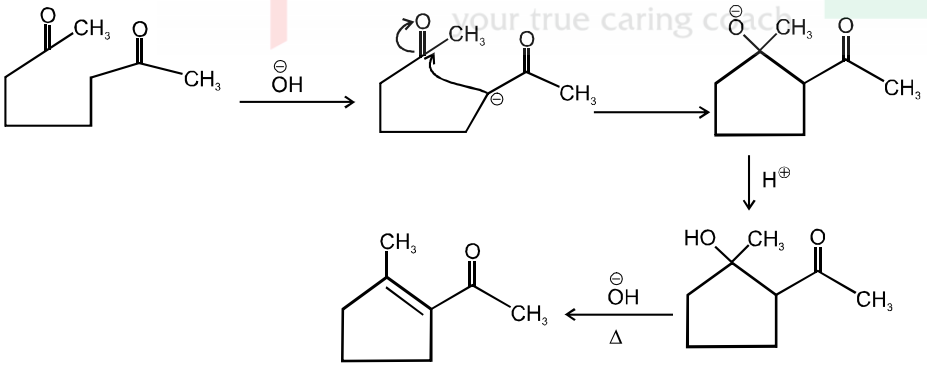
15.



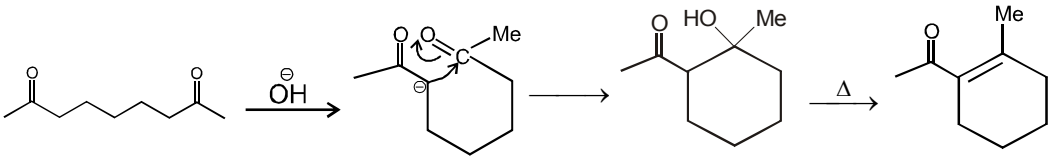
16. Beckamann rearrangement (anti group of –OH migrate)



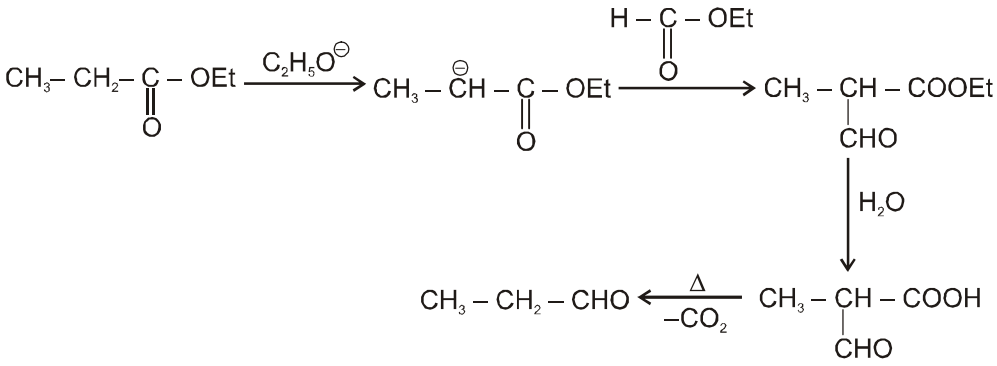
17.



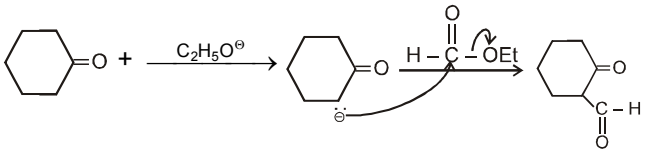
18.



19

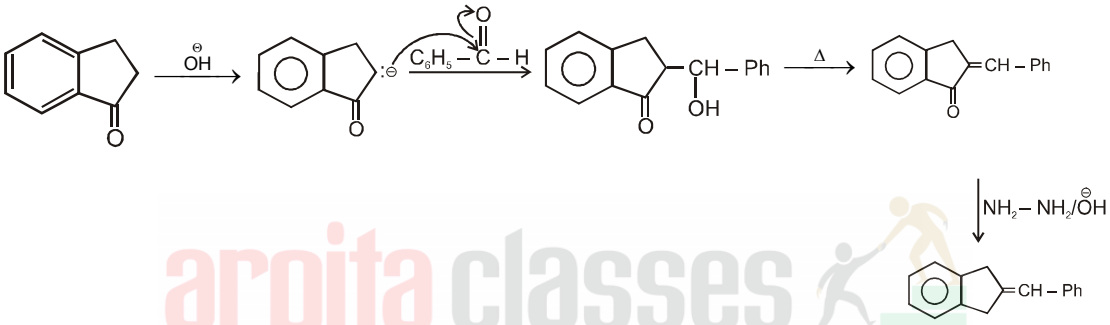


20.



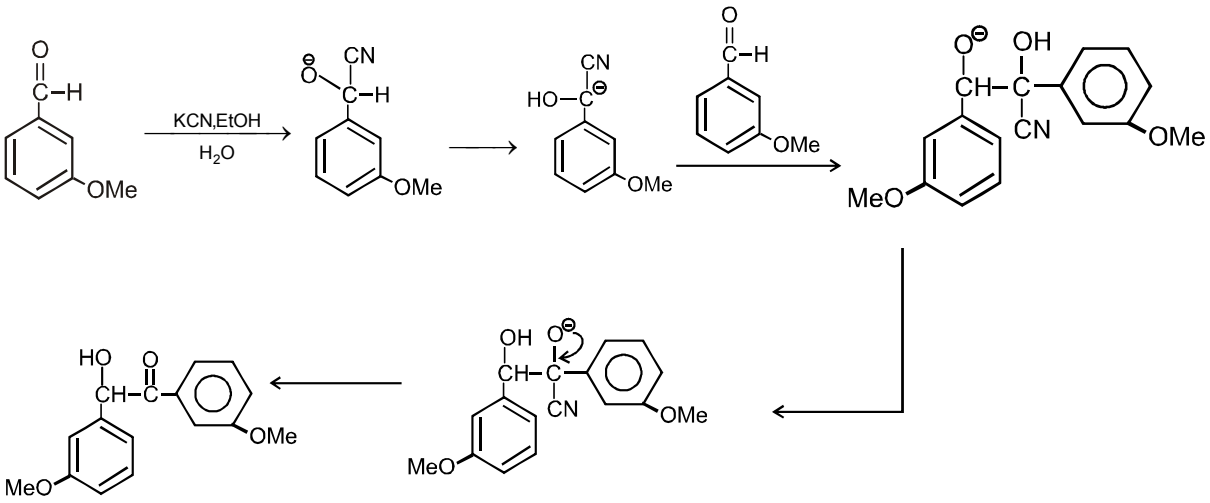
21. $K_2Cr_2O_7$ oxidised secondary alcohol which gives iodoform test.

22.

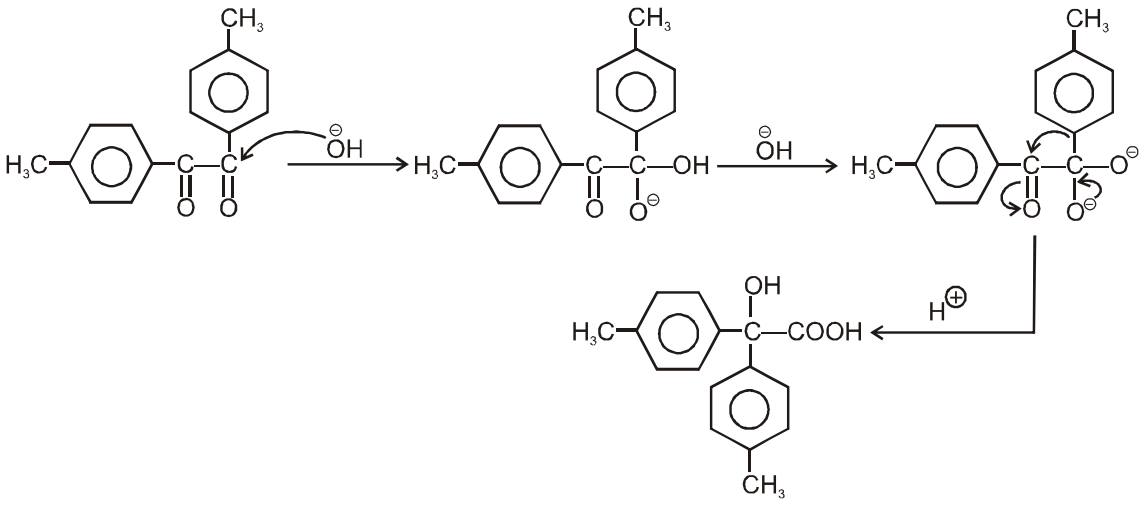


23. –I and –M group increase electrophilicity on carbonyl group so rate of addition reaction increase and also increases equilibrium constant.

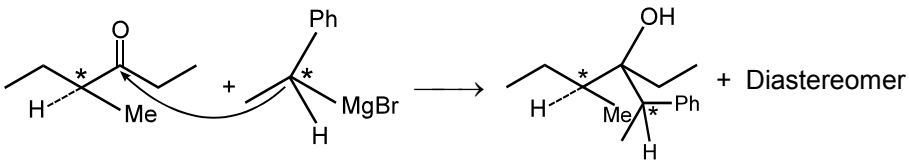
24. Benzoin condensation



25. It is benzil-benzylic acid rearrangement



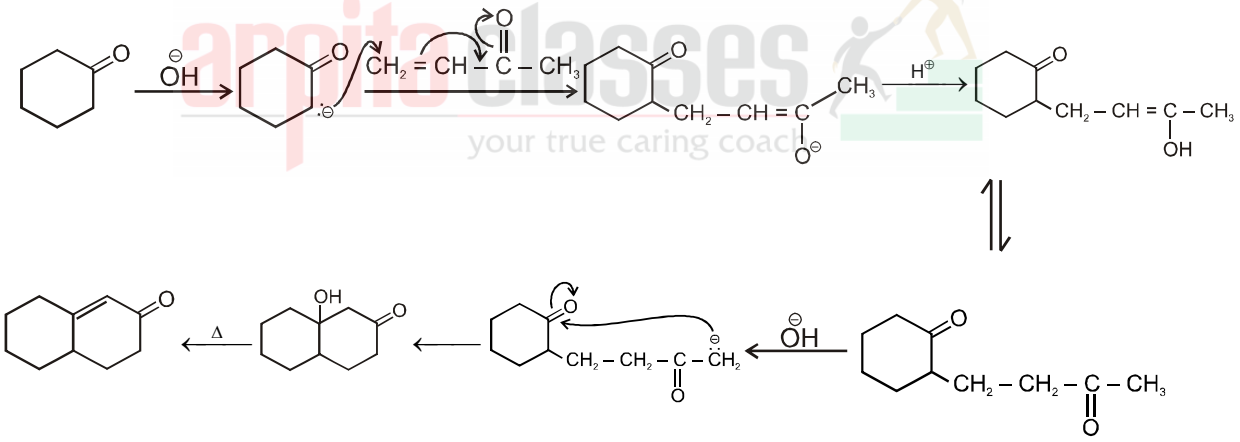
26.



+ Diastereomer

27. Transfer of hydride ion

28.



29. $C_6H_5CHO + HCHO + \underset{(conc.)}{NaOH} \longrightarrow C_6H_5CH_2OH + HCOONa$

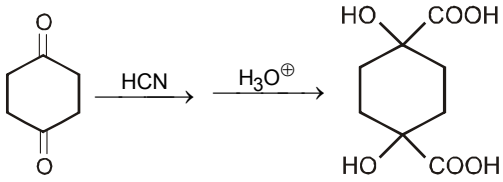
It is crossed Cannizzaro's reaction.

30.

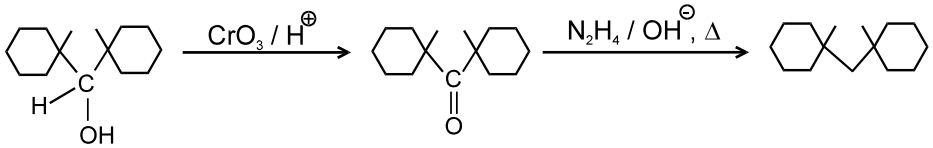
$$\underset{1-\text{propanol}}{CH_3-CH_2-CH_2OH} \xrightarrow[\substack{\text{heat}\\300^\circ C}]{Cu} CH_3-CH_2-CHO \xrightarrow[\text{Fehling Solution}]{2CuO} \underset{\text{red ppt}}{Cu_2O\downarrow}$$

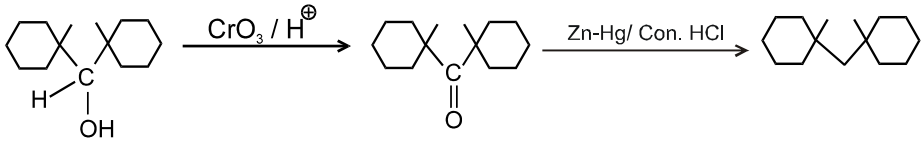
$$\underset{2-\text{propanol}}{CH_3-CHOH-CH_3} \xrightarrow[\substack{\text{heat}\\300^\circ C}]{Cu} CH_3-CO-CH_3 \xrightarrow[\text{Fehling Solution}]{2CuO+CH_3CH_2COOH} \text{No reaction}$$

31.

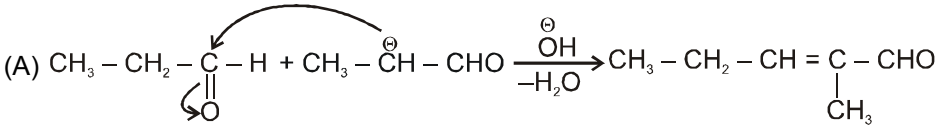


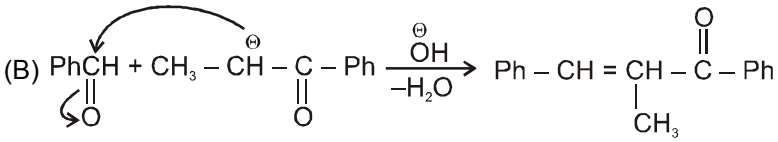
32.

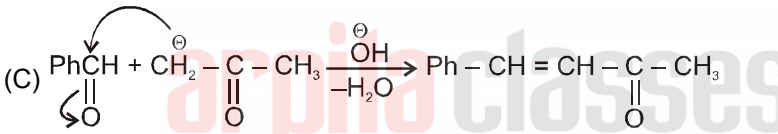




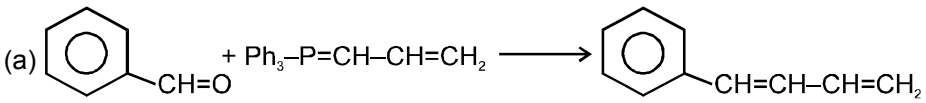
33.

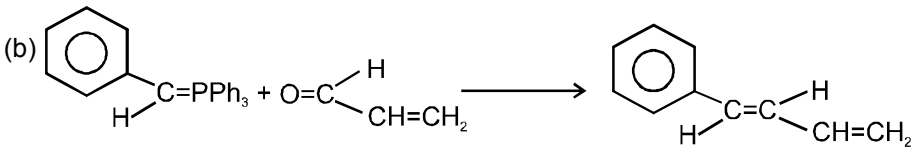






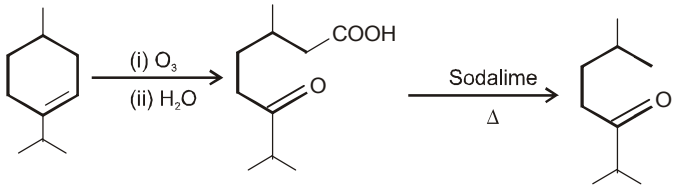
34. Wittig reaction.

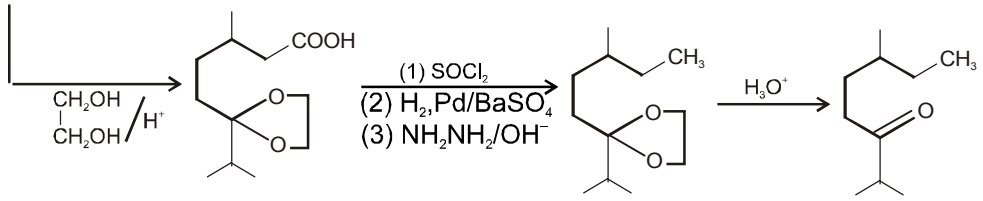




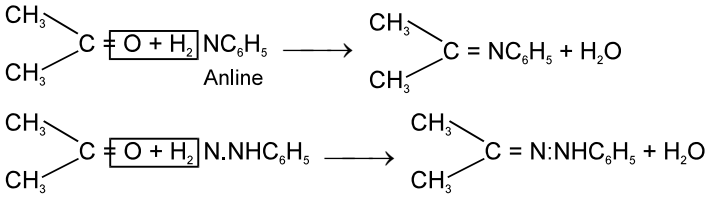
35. Stability of hydrates of carbonyl compound depends on steric hindrance, presence of –I group on gemdiol. intramolecular H-bonding and angle 'strain in carbonyl compound.

36.





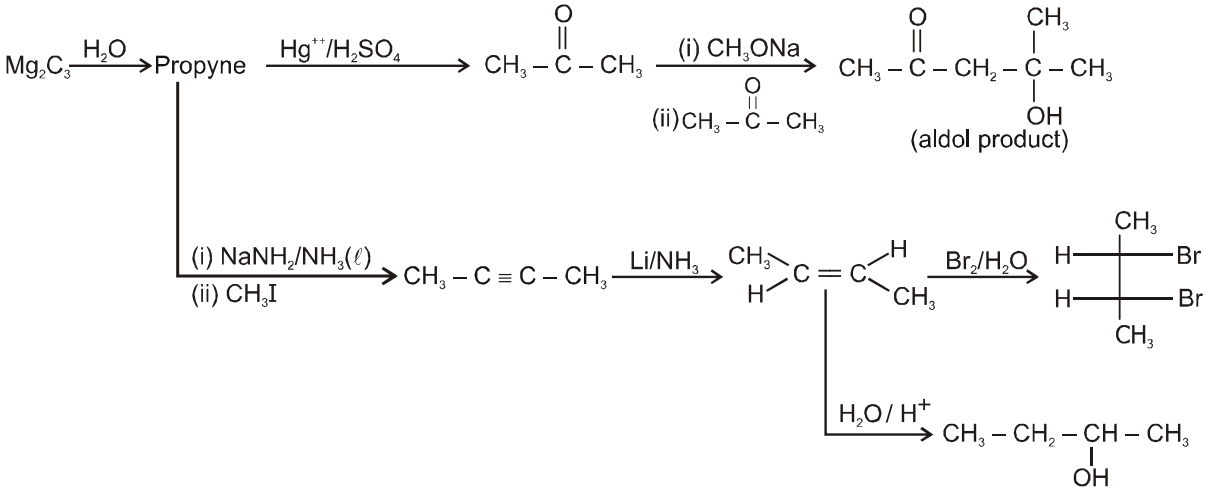
37. Carbonyl compound (acetone) forms condensation product with hydrazine, phenyl hydrazine aniline etc.



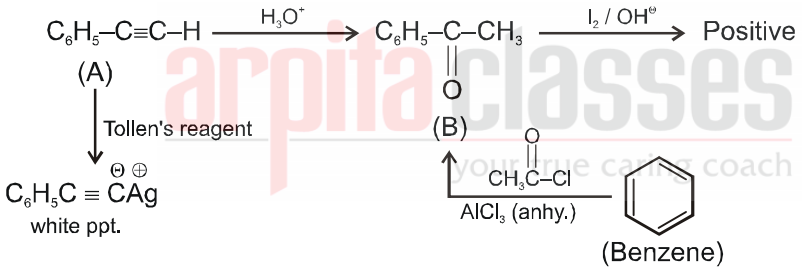
Hence in these reaction > C = N bonds are formed in products.

PART - II

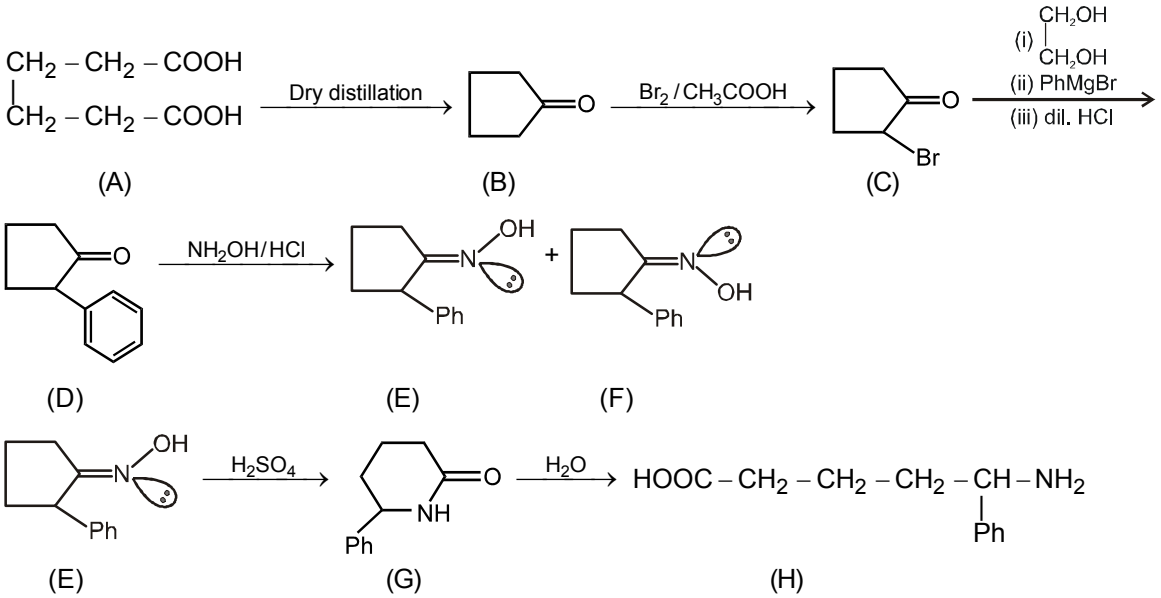
1.

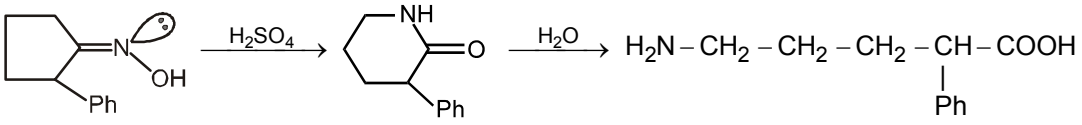


2.



4.





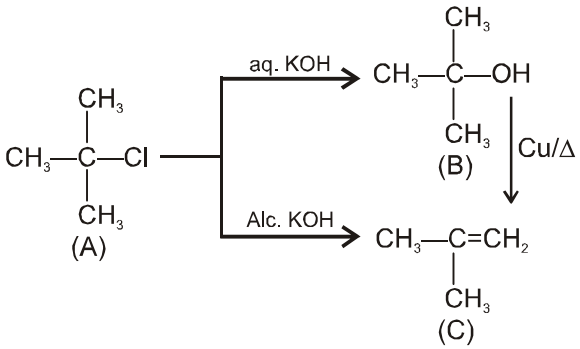
(F) (I) (J)

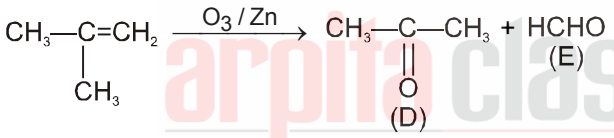
5.

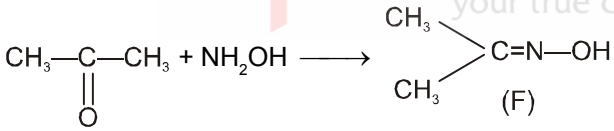
$$CH_3CH=CH_2 \xrightarrow[(2)\ H_2O_2/OH^-]{(1)\ B_2H_6} CH_3CH_2CH_2OH \xrightarrow{HCl,\ ZnCl_2} CH_3CH_2CH_2Cl \xrightarrow{Mg/Et_2O} CH_3CH_2CH_2MgCl$$

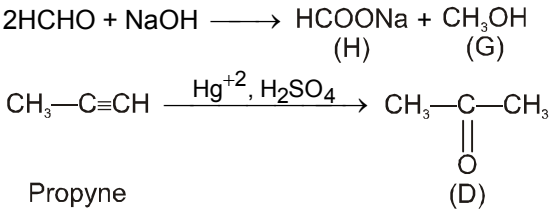
$$CH_3CH_2CH_2MgCl \xrightarrow[(2)\ H_3O^{\oplus},\ \Delta]{(1)\ Ph-CHO} PhCH=CHCH_2CH_3$$

6.









7. Empirical formula of (A) $\Rightarrow CH_2O$
Molecula formula of (A) $\Rightarrow$ HCHO

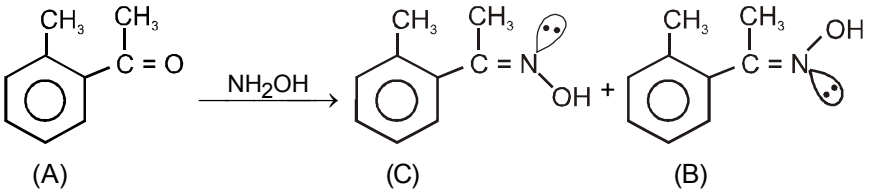
$$2HCHO \xrightarrow{NaOH} CH_3OH + HCOONa \xrightarrow{HCl} HCOOH \xrightarrow{NaHCO_3} HCO\overset{\ominus\ \oplus}{O}Na + CO_2$$
(A) (B) (C) (D)

$$HCOOH \xrightarrow{NH_4OH/AgNO_3} HCO\overset{\ominus\ \oplus}{O}NH_4 + Ag\downarrow$$

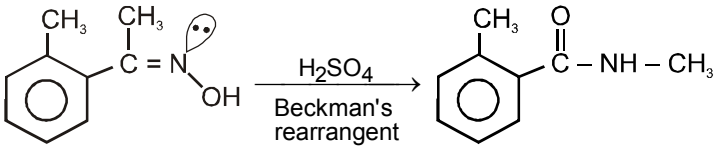
8. $CH_3–CH=CH–CHO \xrightarrow[OH^-]{HCN} CH_3–CH=CH–\underset{\underset{OH}{|}}{CH}–CN \xrightarrow{\text{Alkaline hydrolysis}} \xrightarrow{(H_3O^+)}$

$CH_3–CH=CH–\underset{\underset{OH}{|}}{CH}–COOH$

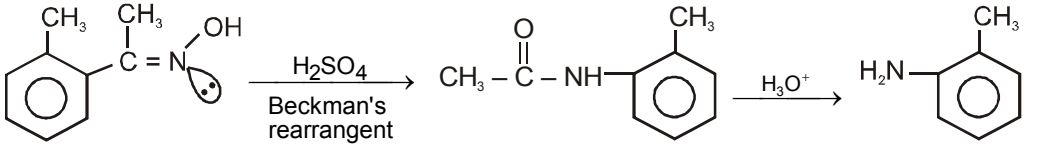
10.



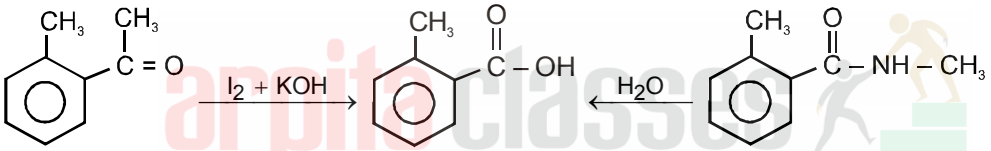
(A) (C) (B)



(C) (D)

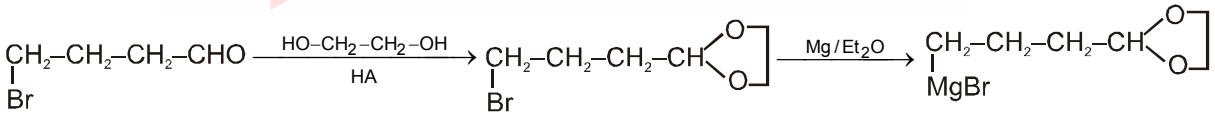


(B) (E) o-methylaniline

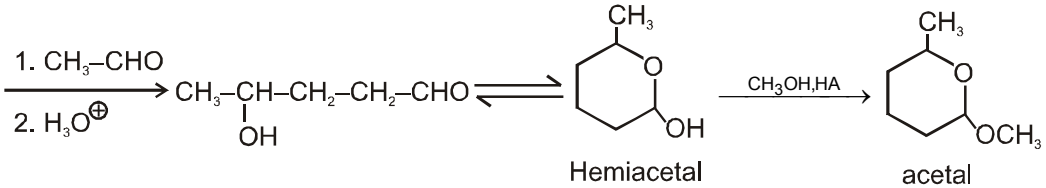


(A) (F) (D)

11.

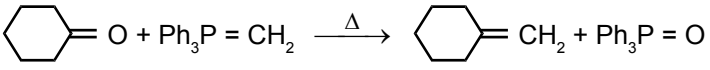


(A) (B)



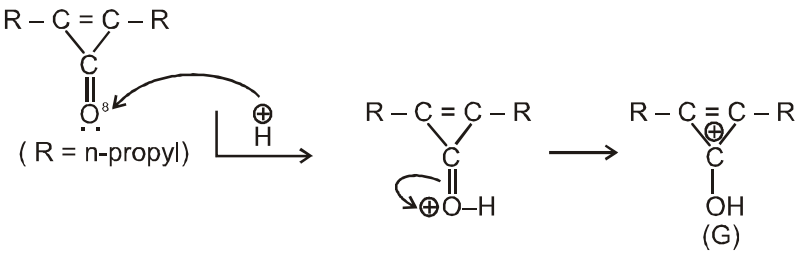
Hemiacetal (C) acetal (D)

13. (a) It is Wittig reaction.

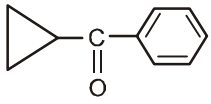


(E)

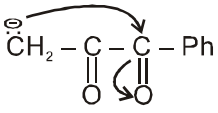
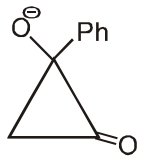
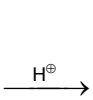
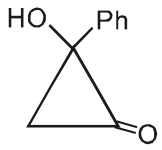
(b)

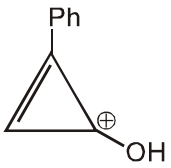
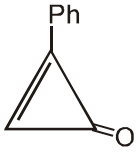


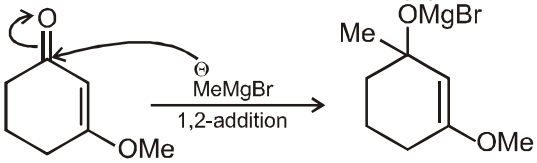
(G)

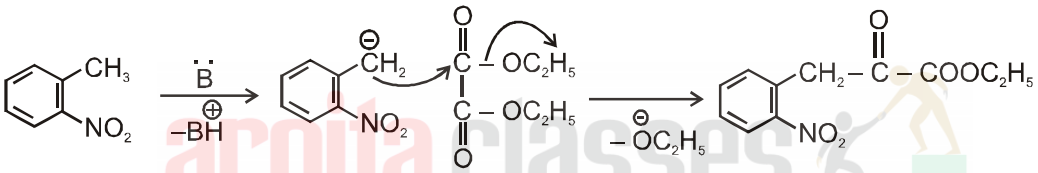
(c) $Cl-CH_2-CH_2-CH_2-COPh \xrightarrow[KOH]{\text{Methanolic}}$  + HCl

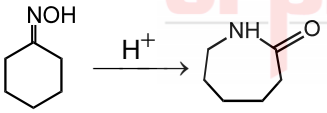
(I)

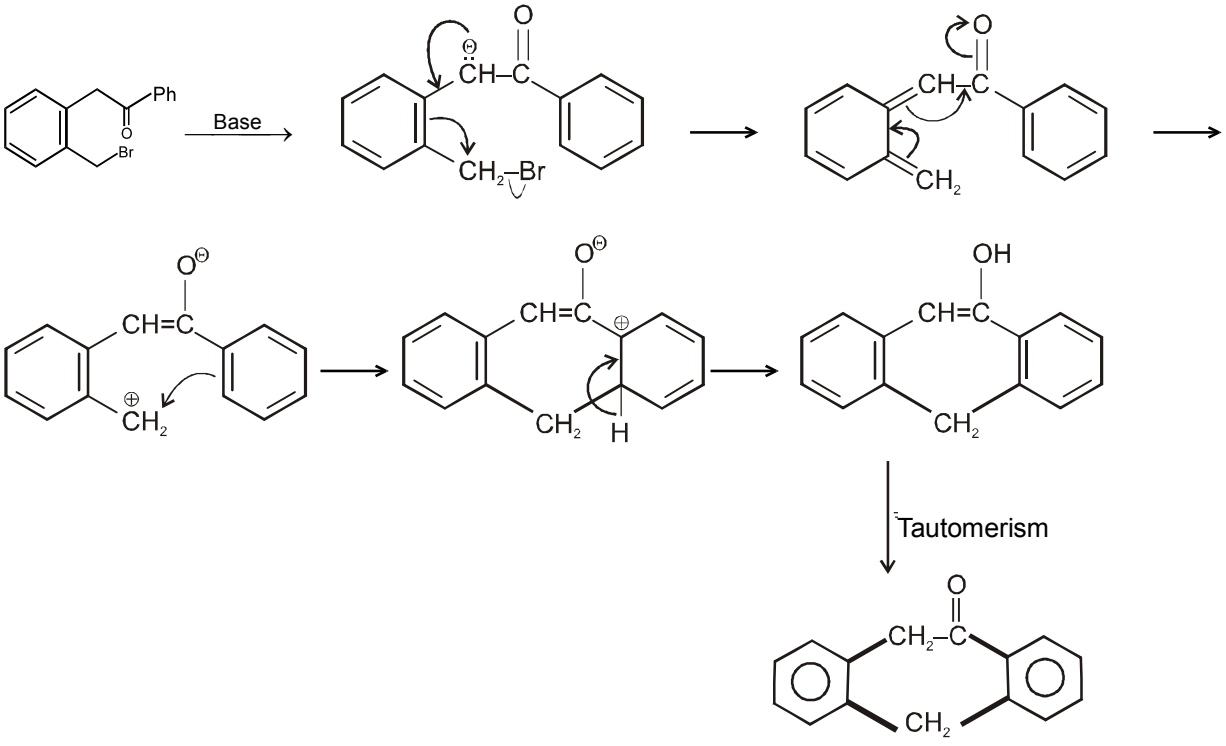
(d) $CH_3-C(=O)-C(=O)-Ph \xrightarrow{\ominus OH}$    

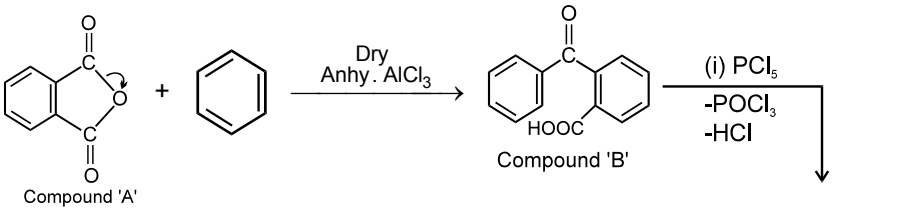
15. 

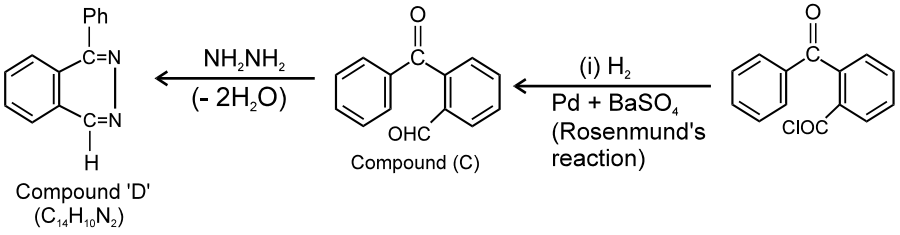
16. 

23.  (Beckmann's rearrangement)

24. 

25.



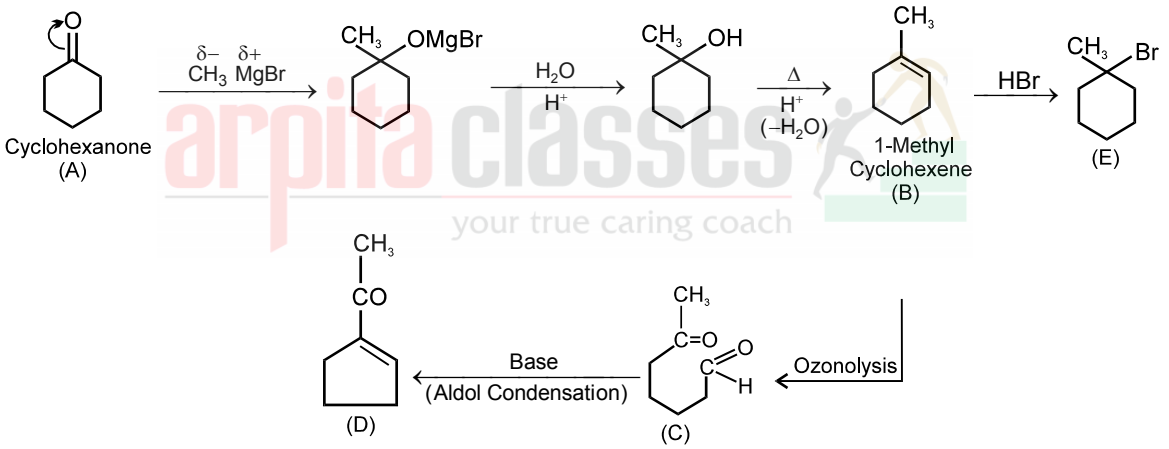


26. Compound 'A' ($C_6H_{10}O$) $\xrightarrow[2.\ H_3O^+]{1.\ CH_3MgBr}$ Compound 'B' $\xrightarrow{\text{Ozonolysis}}$ Compound 'C' $\xrightarrow{\text{Base}}$ Compound 'D'

(1 – acetyl cyclopentene)

Compound 'B' $\xrightarrow{HBr}$ Compound 'E'

Compound 'A' is cyclic canbonyl compound which gives following reaction according to given problem.



27.