

CHAPTER - 20

ALDEHYDES AND KETONES

Syllabus (NCERT)

Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses of aldehydes and ketones.

Detailed Entrance Syllabus

Nomenclature - Electronic structure of carbonyl group-Methods of preparation (i) from alcohols (ii) from acid chlorides (iii) from alkenes by ozonolysis (iv) from alkynes by hydration (v) preparation of acetophenone by Friedel-Crafts acylation.

Physical and chemical properties of aldehydes and ketones (General) formation of paraldehyde and metaldehyde.

Addition of (i) NaHSO_3 (ii) NH_3 and its derivatives (iii) Grignard reagent (iv) HCN and (v) Alcohols.

Oxidation reactions with Tollen's reagent and Fehling's solution.

Oxidation of ketones

Reduction with LiAlH_4 - Clemmensen reduction - Wolff - Kischner reduction - Aldol condensation - Cannizzaro reaction.

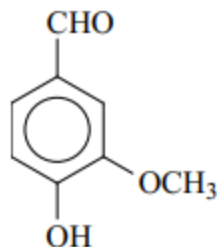
SYNOPSIS

Aldehydes and ketones are organic compounds containing carbon-oxygen double bond, called carbonyl group. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in ketones, it is bonded to two carbon atoms.

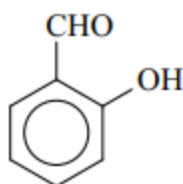
Aldehydes and ketones are wide spread in plants and animal kingdom. They play an important role in biochemical processes of life. They add fragrance and flavour to nature.

Examples are :-

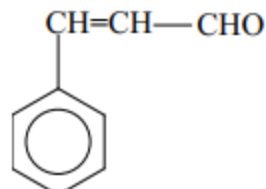
(i) Vanillin (Vanilla beans)



(ii) Salicylaldehyde
(Meadow sweet)



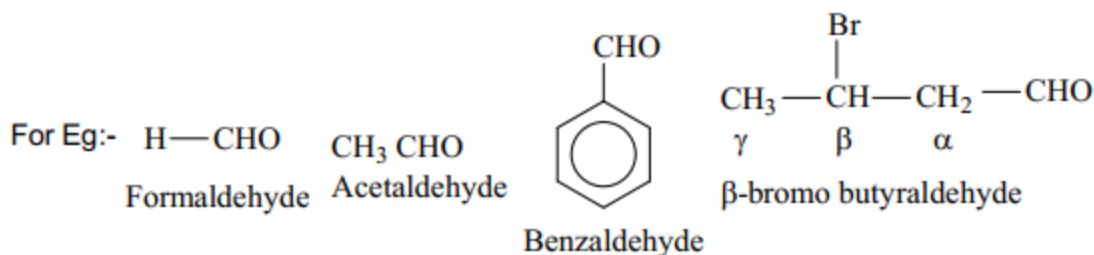
(iii) Cinnamaldehyde
(Cinnamon)



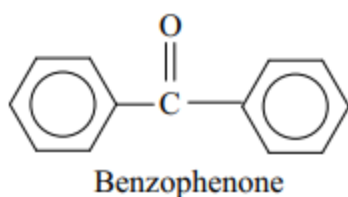
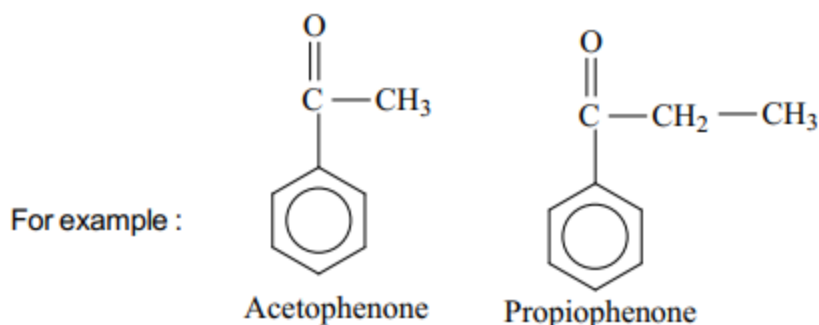
Aldehydes and ketones are used in many food products and pharmaceuticals to add flavours. Some of these are manufactured for use as solvents (Acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics etc

Nomenclature

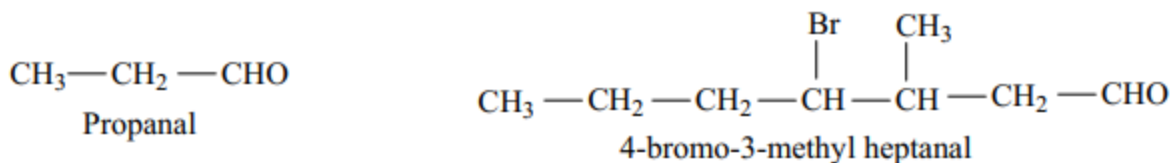
The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending-ic acid with aldehyde. The location of the substituents is indicated by Greek letters α , β , γ , δ etc

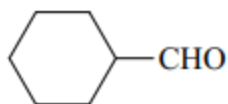


The common names of ketones can be given as follows: The simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the acyl group as prefix to 'phenone'.



The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending 'e' with '-al' and '-one' respectively. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane.

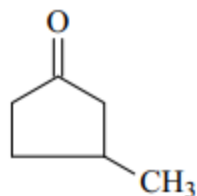




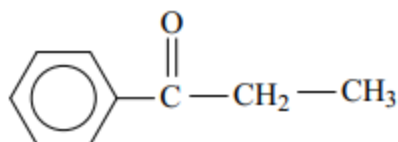
Cyclohexane carbaldehyde



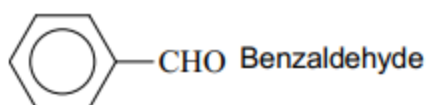
Pent-2-enal



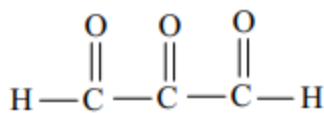
3-methyl cyclopentanone



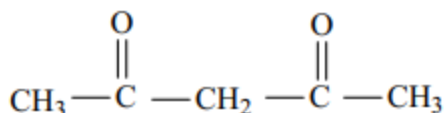
1-Phenyl propan-1-one



Benzaldehyde



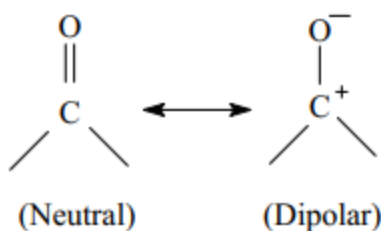
2-Oxo propane-1, 3-dial



Pentane-2,4-dione

Structure of the carbonyl group

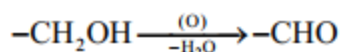
The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence the carbonyl carbon is an electrophilic centre and the carbonyl oxygen, a nucleophilic centre. The polarity of the carbonyl group is explained on the basis of resonance involving its neutral and dipolar structures.



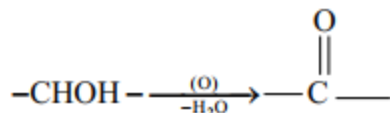
Methods of preparation of Aldehydes and ketones:

1. From Alcohols - by oxidation :

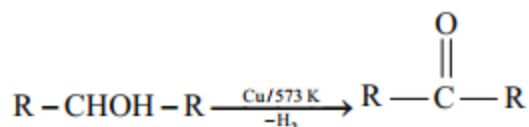
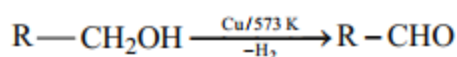
(a) Primary Alcohols are oxidised to Aldehydes



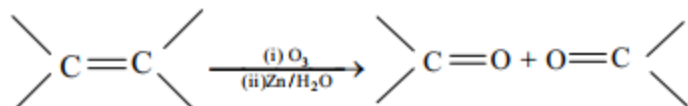
Secondary Alcohols are oxidised to ketones



(b) 1° alcohols are dehydrogenated to aldehydes and 2° alcohols are dehydrogenated to ketones when their vapour is passed over reduced copper (Cu heated to 573 K)



2. From alkenes - by reductive ozonolysis

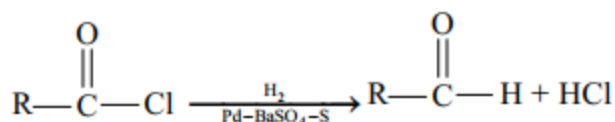


3. From alkynes : by hydration

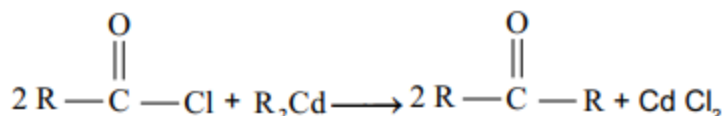
Acetylene produces acetaldehyde, by the addition of water, when it is passed through dil. H_2SO_4 in presence of $HgSO_4$. All other alkynes produce ketones in this reaction.

4. From Acid chlorides:

(a) Acid chlorides are reduced to aldehydes by Rosenmund reduction.

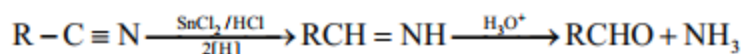


(b) Acid chloride is reduced to ketone by dialkyl cadmium

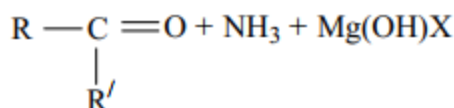
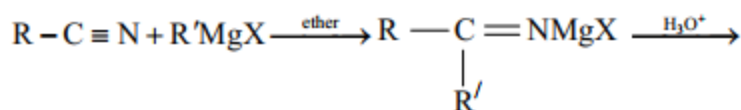


5. From Nitriles ($R-C \equiv N$)

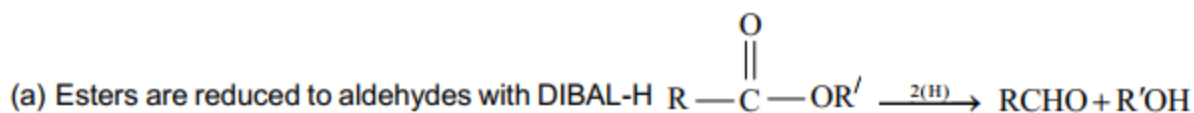
(a) Nitriles are reduced to Aldimine with $SnCl_2$ and HCl . which on hydrolysis give aldehyde (Stephens reaction)



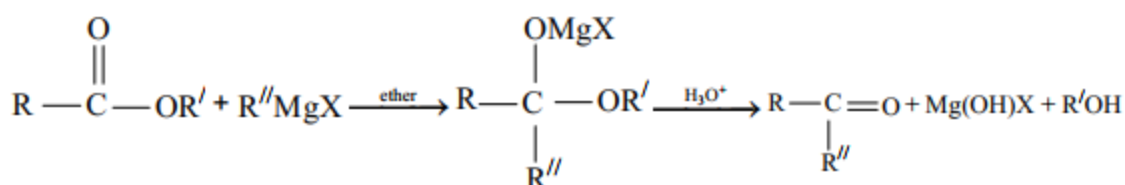
(b) Treatment of a nitrile with Grignard reagent, followed by hydrolysis gives a ketone.



6. From Esters:

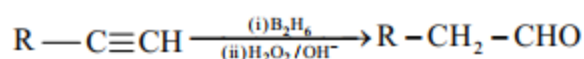


(b) Esters are treated with Grignard reagent and hydrolysed to get ketones



7. Hydroboration - oxidation of alkynes:

(a) Terminal alkynes give aldehydes :



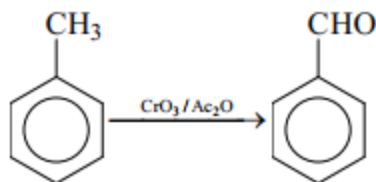
(b) Non-terminal alkynes give ketones : $\text{R}-\text{C}\equiv\text{C}-\text{R} \xrightarrow[\text{(ii) H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{R}$

8. Oxo process $\text{CH}_2=\text{CH}_2 + \text{CO} + \text{H}_2 \xrightarrow[\Delta/\text{pressure}]{\text{cobalt carbonyl hydride}} \text{CH}_3-\text{CH}_2-\text{CHO}$

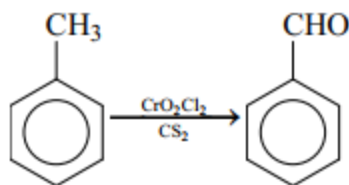
9. Wacker process : $\text{CH}_2=\text{CH}_2 + \frac{1}{2}\text{O}_2 \xrightarrow[\text{(air)}]{\text{PdCl}_2/\text{CuCl}_2, \text{H}_2\text{O}} \text{CH}_3\text{CHO}$

Preparation of Aromatic Aldehydes and Ketones:

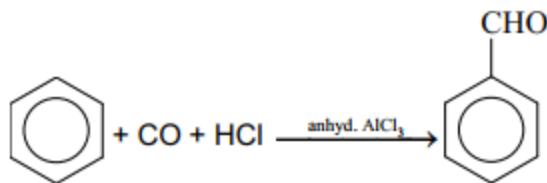
(a) Oxidation of Toluene with CrO_3 and acetic anhydride, followed by hydrolysis gives benzaldehyde.



(b) Etard's reaction : Toluene is oxidised with chromyl chloride to get benzaldehyde :



(c) Gattermann-Koch reaction



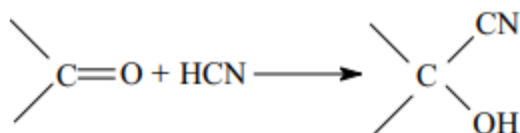
(d) Friedel-Crafts acylation:

**Physical properties**

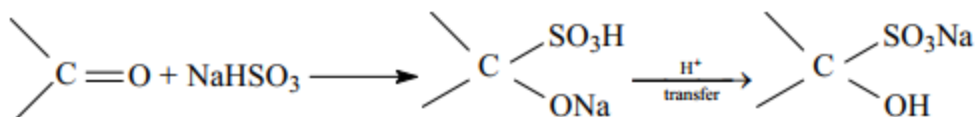
Polar Aldehydes and ketones have higher boiling points than non-polar hydrocarbons and weakly polar ethers as a result of dipole-dipole interaction

Chemical Reactions:

1. **Nucleophilic Addition** is the most characteristic reaction of Aldehydes and ketones. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. Aldehydes are more reactive than ketones due to steric and electronic reasons.

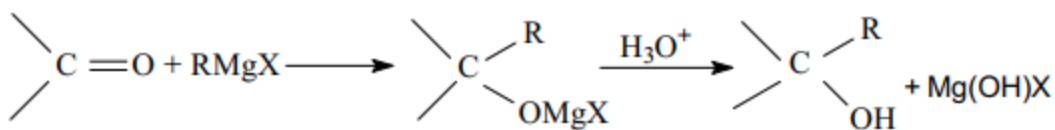
(i) **Addition of HCN**

Cyanohydrins are useful intermediates in the synthesis of hydroxy acids

(ii) **Addition of NaHSO₃**

The crystalline bisulphite addition compound is water-soluble and are useful for separation and purification of aldehydes. This reaction is not given by bulkier ketones.

- (iii) **Addition of Grignard reagents** : Carbonyl compounds add this organo metallic compound to form adducts, which on hydrolysis with dilute acid produce alcohols.



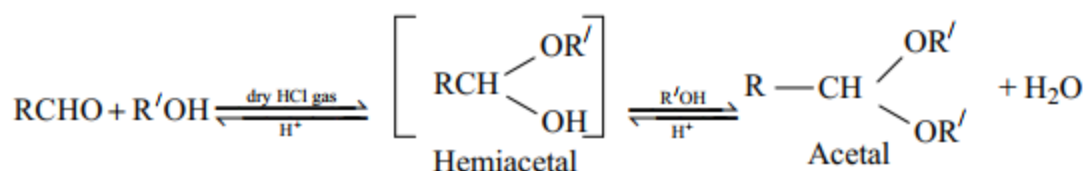
Formaldehyde gives 1° alcohol

Other aldehydes form 2° alcohol

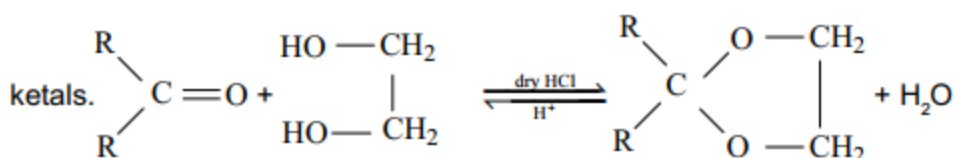
Ketones give 3° alcohol

(iv) **Addition of Alcohols:**

(a) Aldehydes react with one equivalent of monohydric alcohol in presence of dry HCl to form Acetal, through the formation of an intermediate hemiacetal.

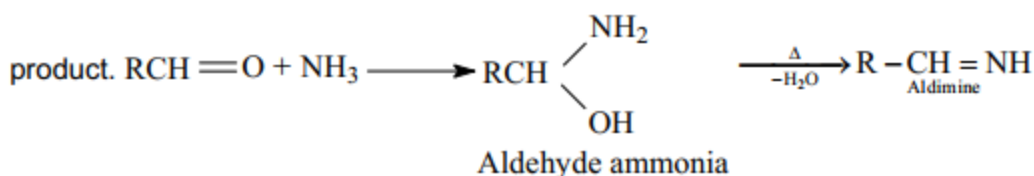


(b) Ketones can react with dihydric alcohols like glycol under similar conditions to form cyclic

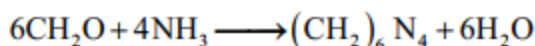


(v) Addition of NH₃

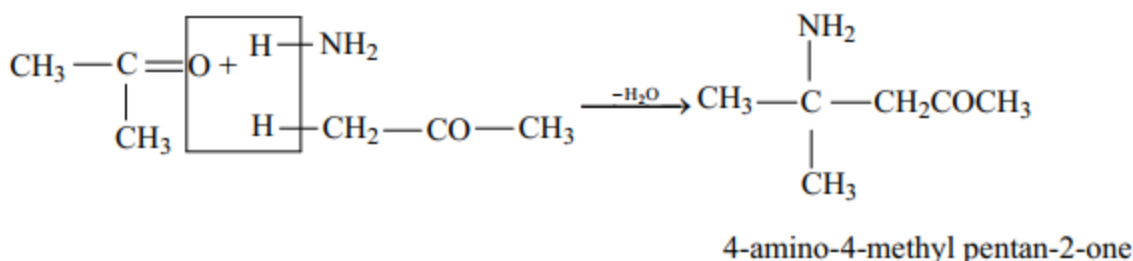
(a) Aliphatic aldehydes except HCHO, react with NH₃ to form Aldehyde ammonia, a nucleophilic add.



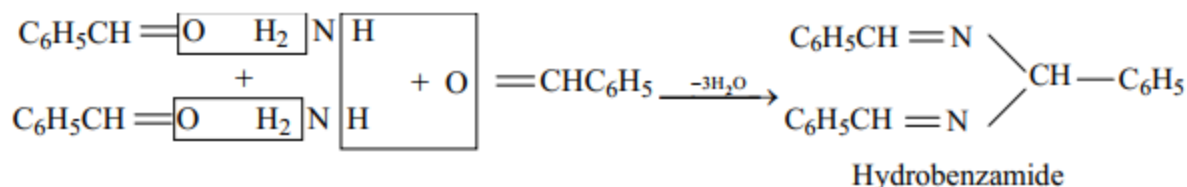
(b) Formaldehyde forms a complex condensation product called Urotropine or Hexamethylene tetramine.



(c) Acetone forms a condensation product, Diacetone amine.

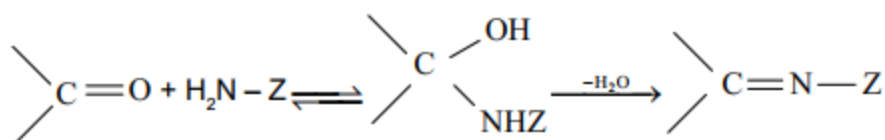


(d) Benzaldehyde forms the condensation product, Hydrobenzamide.

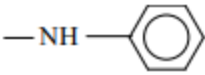
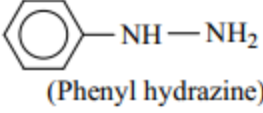
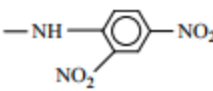
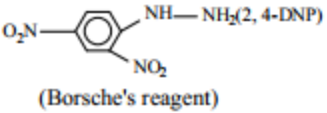
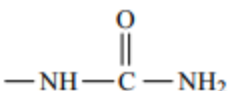


2. Condensation reactions with Ammonia derivatives

Aldehydes and ketones undergo nucleophilic addition with ammonia derivatives (NH₂-Z), followed by elimination of water forming condensation products.

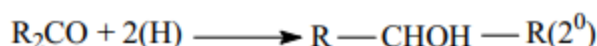


The reaction is reversible and catalysed by acid (pH~4). Due to rapid dehydration, the equilibrium is shifted to right.

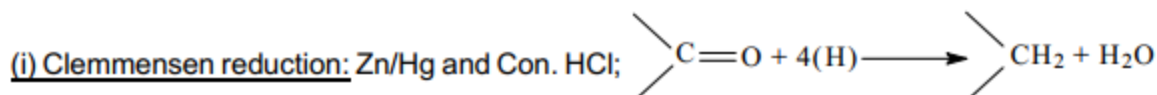
Z	Reagent	Product	Name of product
R	R-NH ₂ (Amine)	>C=NR	Schiff's base
-OH	NH ₂ -OH (Hydroxylamine)	>C=N-OH	Oxime
-NH ₂	NH ₂ -NH ₂ (Hydrazine)	>C=N-NH_2	Hydrazone
	 (Phenyl hydrazine)	$\text{>C=N-NH-C}_6\text{H}_5$	Phenyl hydrazone
	 (Borsche's reagent)	$\text{>C=N-NH-C}_6\text{H}_3\text{(NO}_2)_2$	2,4-dinitro phenyl hydrazone
	NH ₂ -NH-CO-NH ₂ (Semicarbazide)	>C=N-NH-CO-NH_2	Semicarbazone

3. Reduction of Aldehydes and Ketones

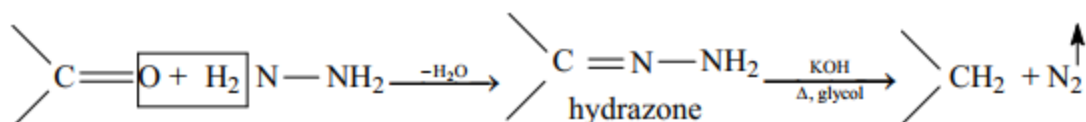
(a) Reduction to Alcohols: NaBH₄, LiAlH₄ and H₂/Ni, Pt or Pd (catalytic reduction) can be used to reduce aldehydes to 1° and ketones to 2° alcohols respectively.



(b) Reduction to Hydrocarbons:



(ii) Wolff-Kischner reduction - Hydrazine/KOH/ Δ in glycol



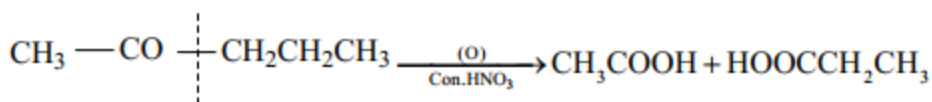
4. Oxidation

Aldehydes differ from ketones in oxidation.

Aldehydes are easily oxidised even with mild oxidising agents to carboxylic acids and hence they can act as reducing agents.

Ketones are oxidised only with strong oxidising agents to carboxylic acids having lesser number of carbon atoms, at elevated temperatures. They cannot act as reducing agents.

Eg : Mixed ketones like 2-pentanone undergoes oxidation forming ethanoic acid and propanoic acid with lesser carbon atoms.

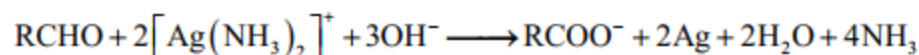


Here, the cleavage takes place according to Popoff's rule.

Mild oxidising agents like Tollen's reagent and Fehling's reagent are used to distinguish aldehydes from ketones.

(i) Tollen's test (Silver mirror test):

On warming an aldehyde with freshly prepared ammoniacal AgNO_3 solution (Tollen's reagent), a bright silver mirror is formed. (in alkaline medium)

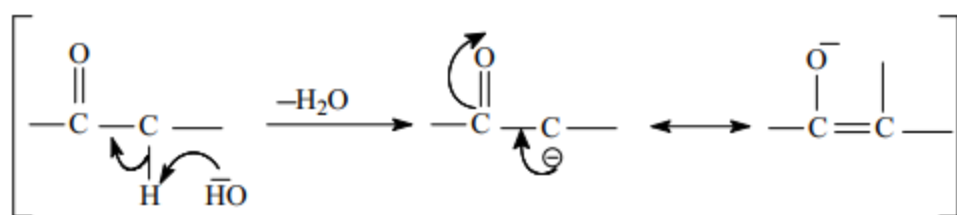


(ii) Fehling's test : On heating an aldehyde with Fehling's reagent a red precipitate of cuprous oxide is obtained.



Aromatic aldehydes do not respond to this test.

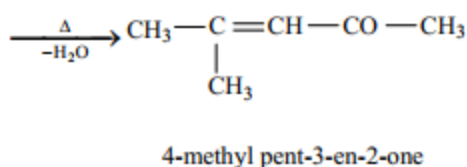
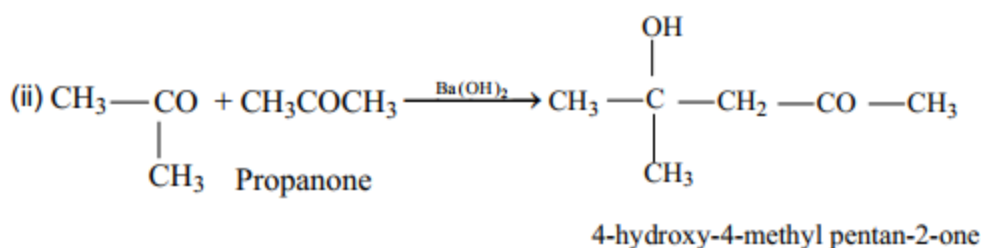
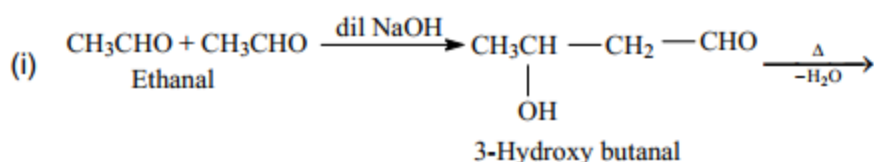
5. **Reaction due to α - H** : **Aldehydes and ketones undergo Aldol reaction** due to the acidic nature of α - H . The acidity of α - H is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



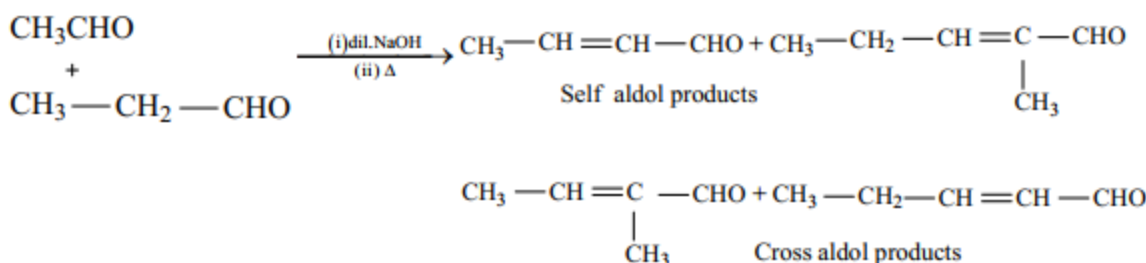
(a) Self Aldol Condensation:

Aldehydes and ketones having at least one α - H undergo a reaction in presence of dilute alkali to form β -hydroxy aldehyde (aldol) and β -hydroxy ketone (ketol). This is called Aldol reaction.

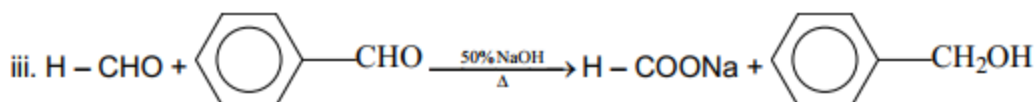
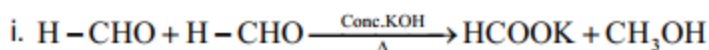
The aldol and ketol readily lose water to give α , β -unsaturated carbonyl compounds and the reaction is called Aldol condensation.

**(b) Cross Aldol Condensation:**

When Aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain α -H, the reaction gives a mixture of four products.

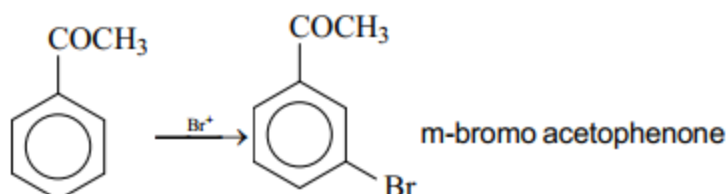
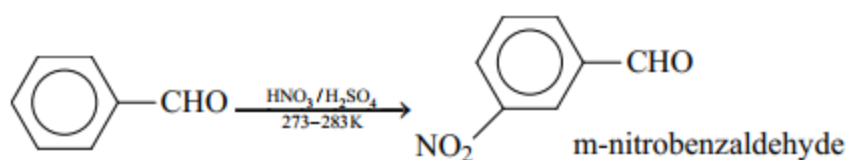
**6. Cannizzaro reaction:**

Aldehydes which do not have α -H atom, undergo simultaneous oxidation and reduction or disproportionation on heating with 50% alkali. In this reaction, one molecule of the aldehyde is oxidised, at the expense of which another molecule is getting reduced.



It is an example of crossed Cannizzaro reaction.

7. Electrophilic substitution reaction in Aromatic aldehydes and ketones. They undergo SE at the ring, in which the carbonyl group acts as a deactivating and meta directing group.



8. **Haloform reaction** (Iodoform test) : Ethanal and methyl ketones (2-ones), on warming with X_2 and alkali (Eg : I_2 and dil. NaOH or aq. Na_2CO_3) form CHX_3 . (Eg : CHI_3 , as yellow ppt. with a characteristic smell).

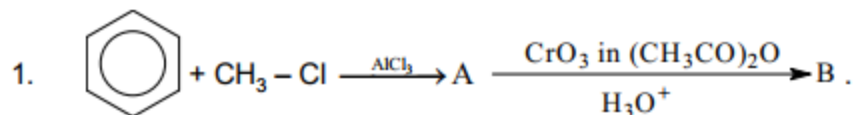
USES

Uses of some aldehydes and ketones:

- 40% solution of formaldehyde called formalin is used as a disinfectant and a preservative for biological specimens
- A trimer of acetaldehyde called paraldehyde is a hypnotic drug
- The tetramer of acetaldehyde called Metaldehyde is a solid fuel
- Acetone and ethyl methyl ketone are important industrial solvents

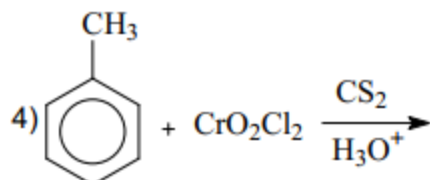
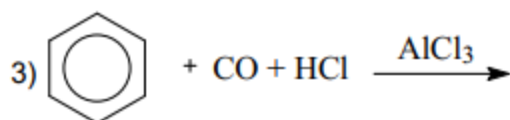
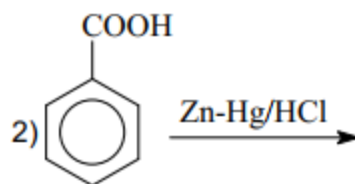
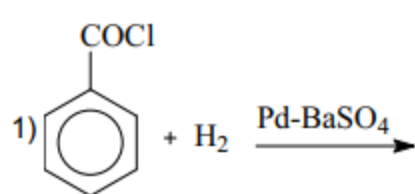
PART-I (JEE MAIN)

SECTION-I- Straight objective type questions



Major product 'B' in the above reaction is

- | | |
|----------------------------|-----------------|
| 1) Acetophenone | 2) Benzaldehyde |
| 3) Cyclohexyl carbaldehyde | 4) Benzoic acid |
2. The reaction by which benzaldehyde cannot be prepared is

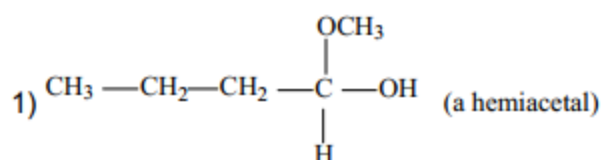


3. **Assertion (A)** : Both Grignard reagent and dialkyl cadmium react with acid chlorides to form tertiary alcohols.

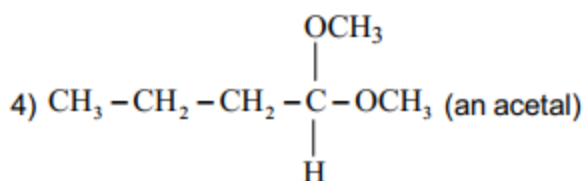
Reason (R) : Dialkyl cadmium is more reactive than Grignard reagent

In the light of the above statements choose the correct option

- 1) Both A and R are true and R is the correct explanation of Assertion
 - 2) Both A and R are true and R is not the correct explanation of Assertion
 - 3) A is true but R is false
 - 4) Both A and R are false
4. Which of the following processes will not yield ethanal?
- 1) Reduction of ethanenitrile with DIBAL-H
 - 2) Oxidation of ethanol by Cu/300°C
 - 3) Oxidation of ethanol by PCC
 - 4) Reaction of ethanenitrile with Grignard reagent
5. What is the final product in the reaction of butanal with excess of methanol and dry HCl?



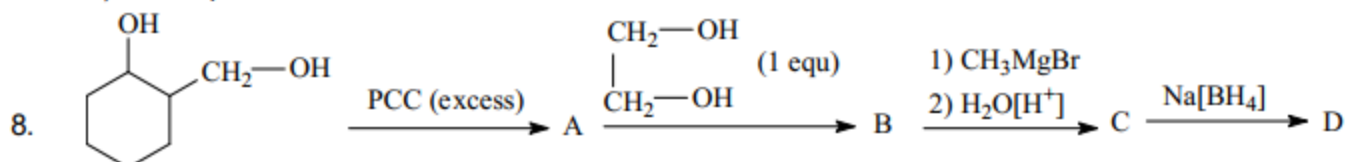
- 2) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOCH}_3$ (an ester)
- 3) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OCH}_3$ (an ether)



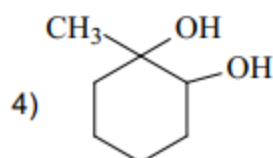
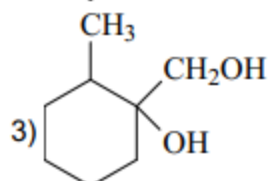
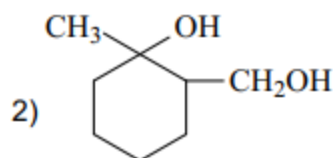
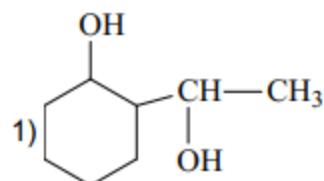
6. The reagent with which both hexanal and pentan-2-one can react is
- 1) Fehling's reagent
 - 2) Sodium hypiododite
 - 3) Tollen's reagent
 - 4) Grignard reagent

7. The reaction, $R-CHO + NH_2-NH_2 \xrightarrow{pH=3.5} R-CH=N-NH_2$, is an example of

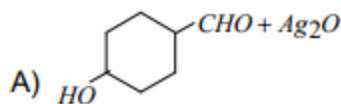
- 1) Electrophilic addition - elimination reaction
- 2) Free radical addition - elimination reaction
- 3) Electrophilic substitution - elimination reaction
- 4) Nucleophilic addition - elimination reaction



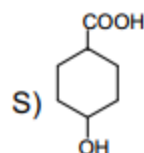
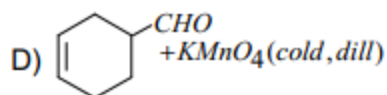
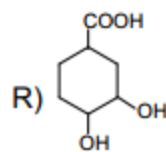
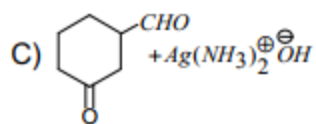
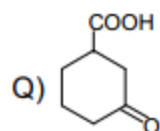
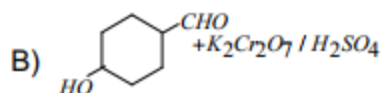
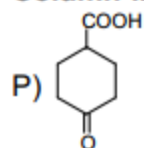
The final product D is



9. Match the following
Column-I (Reaction)



Column-II (Product)



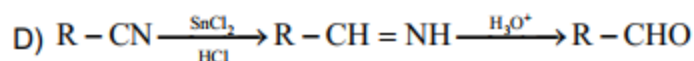
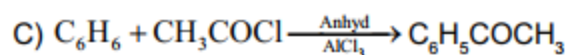
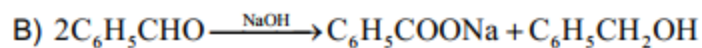
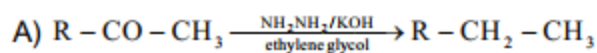
1) A-S, B-P, C-Q, D-R

2) A-P, B-Q, C-R, D-S

3) A-S, B-Q, C-P, D-R

4) A-P, B-P, C-Q, D-R

10. Match the following

Column-I (Reaction)

Column-II (Name)

p) Friedel-Craft's reaction

q) Stephen reaction

r) Wolff - Kishner reduction

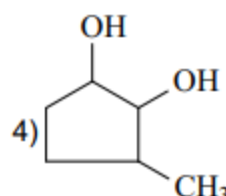
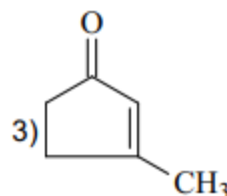
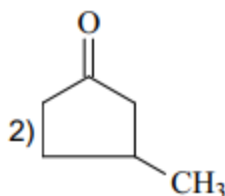
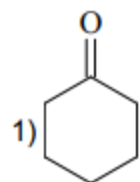
s) Cannizzaro reaction

 1) $A \rightarrow p; B \rightarrow q; C \rightarrow r; D \rightarrow s$

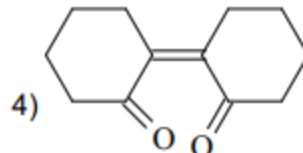
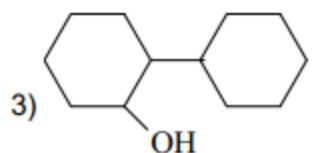
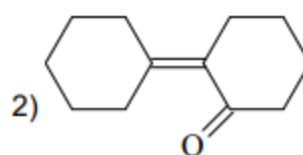
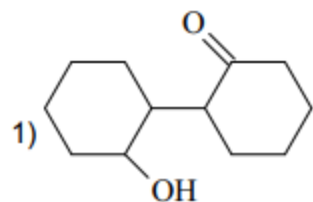
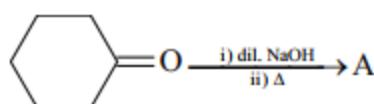
 2) $A \rightarrow q; B \rightarrow p; C \rightarrow r; D \rightarrow s$

 3) $A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q$

 4) $A \rightarrow s; B \rightarrow r; C \rightarrow p; D \rightarrow q$

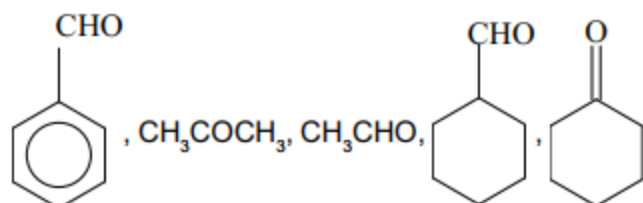
 11. The diketone $CH_3 - \overset{\overset{O}{\parallel}}{C} - (CH_2)_2 - \overset{\overset{O}{\parallel}}{C} - CH_3$ on intramolecular aldol condensation gives the final product


12. Identify the major product (A) in the following reaction

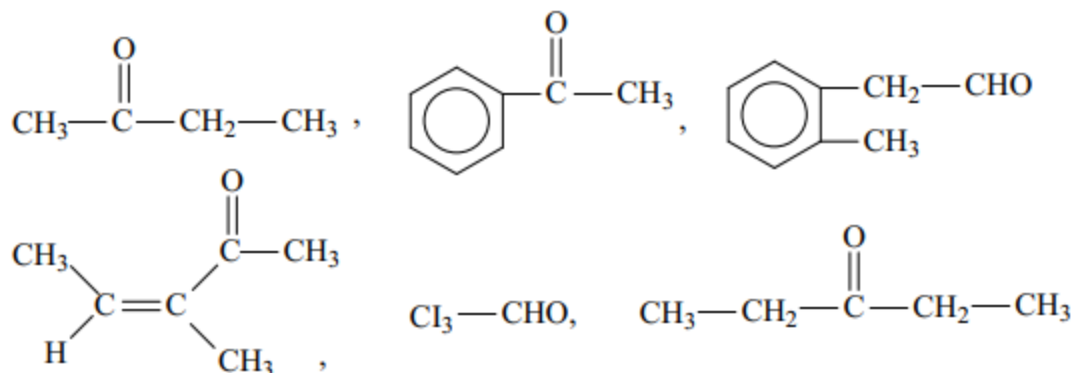


SECTION-II - Numerical Type Questions

13. The number of nitrogen atom(s) present in the semicarbazone molecule of acetone is ____
14. The number of following compound(s) that give(s) positive Tollen's test but negative Fehling's test is ____



15. How many of the following answer(s) iodoform test ?

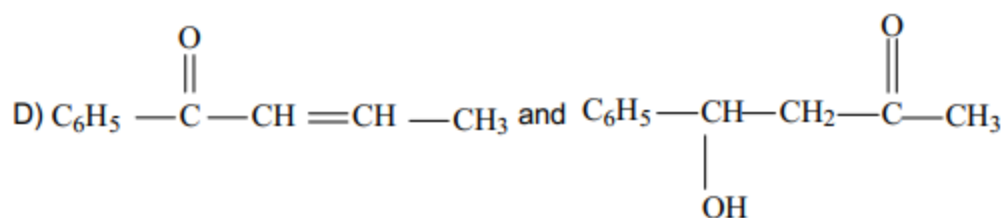
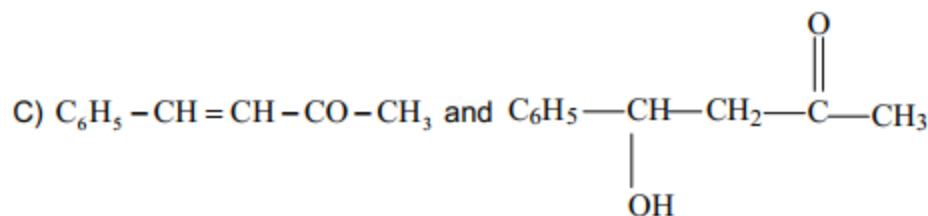
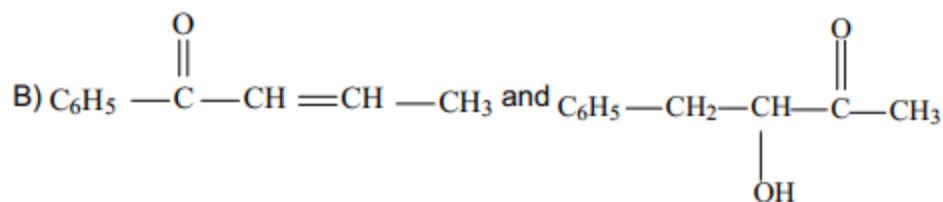
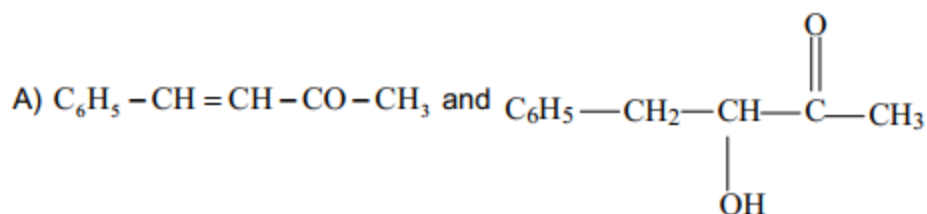


PART-II (JEE ADVANCED)

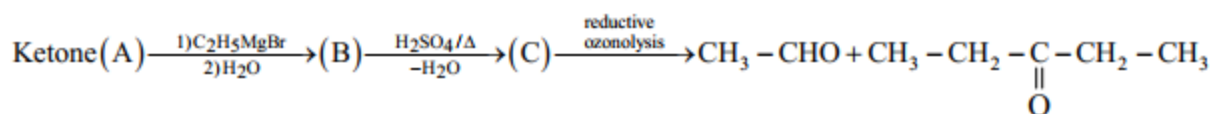
Section-III - Only one option correct type

16. A compound X ($C_4H_{10}O$) on oxidation yields a product Y (C_4H_8O), which gives an oxime and a positive iodoform test. X on treatment with conc. H_2SO_4 gives C_4H_8 . The structure of X is
- A) CH3CH2CH2CH2OH
- B) CH3CHOHCH2CH3
- C) (CH3)3COH
- D) CH3CH2-O-CH2CH3

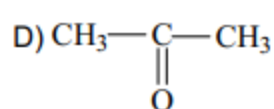
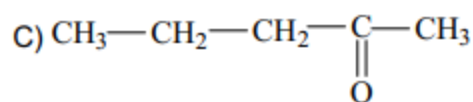
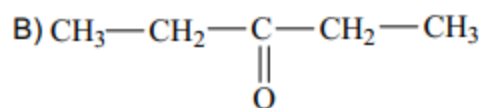
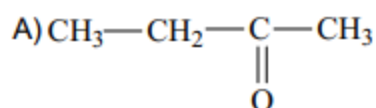
17. Benzalacetone is the aldol condensation product formed between benzaldehyde and acetone. The structure of benzalacetone and the intermediate are, respectively



18. Consider the following sequence of reactions



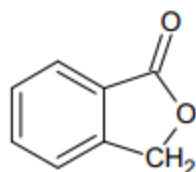
The ketone 'A' is



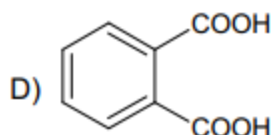
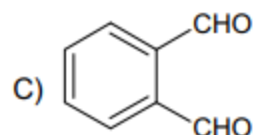
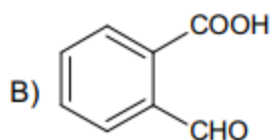
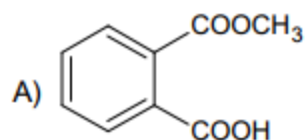
19. The reagent which can be used to distinguish acetophenone from benzophenone is
- A) 2, 4-dinitrophenylhydrazine B) aqueous solution of NaHSO_3
- C) Benedict reagent D) I_2 and Na_2CO_3

Section IV - One or more option correct type

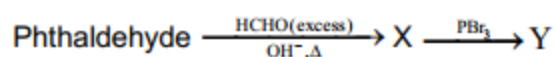
20. Which of the following compounds will give a red precipitate when heated with Fehling's solution?
- A) $\text{C}_6\text{H}_5\text{CHO}$ B) CH_3CHO C) CH_3COCH_3 D) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$
21. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the main product?



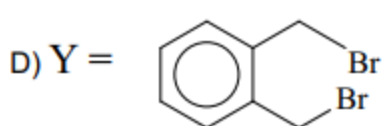
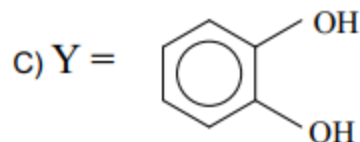
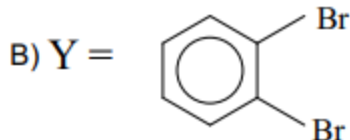
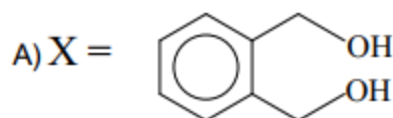
lactone



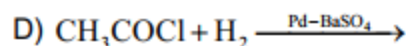
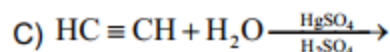
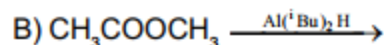
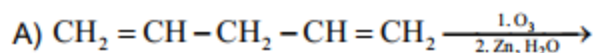
22. X and Y are major products in the following reaction scheme



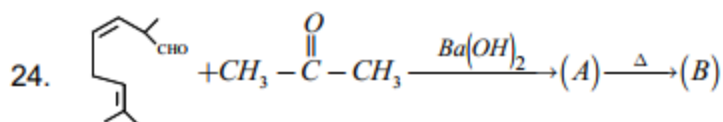
Choose the correct option(s)



23. Which of the following reactions will give acetaldehyde?

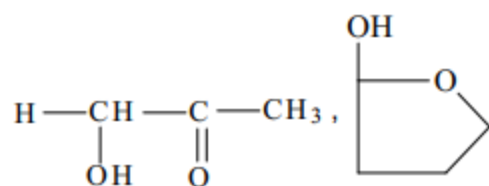
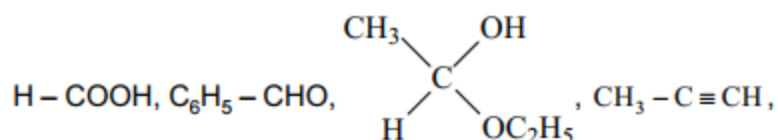
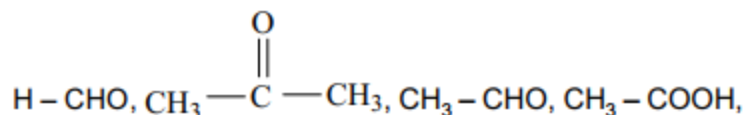


Section V - Numerical type questions

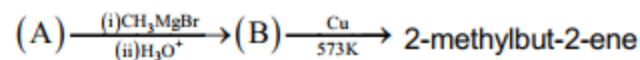


How many double bond equivalents are present in compound (B)?

25. How many of the following compounds would give positive Tollen's test?

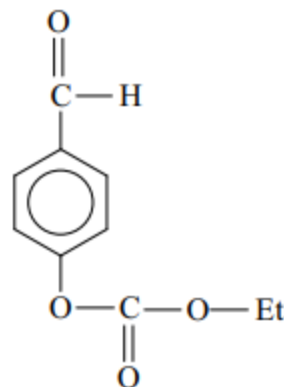
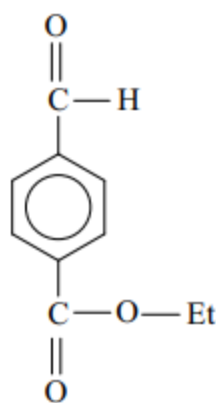
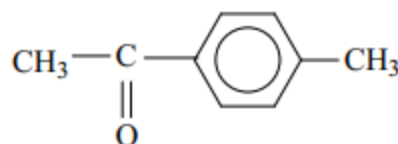
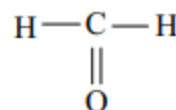
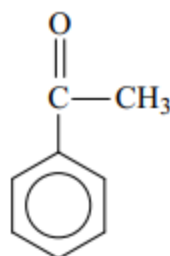
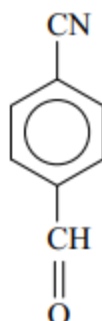
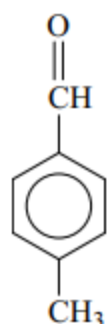


26. Consider the following reaction



The mass percentage of carbon in A is _____

27. How many of the following gives cyanohydrin faster than p-chlorobenzaldehyde?

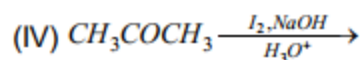
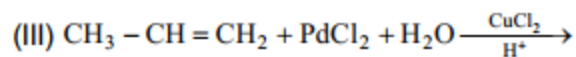
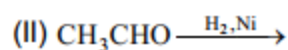
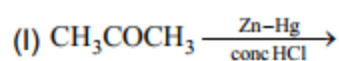


28. The molar mass of 2,4-DNP derivative of benzaldehyde is — gmol⁻¹ (use atomic mass of C = 12, H = 1, N = 14, and O = 16)

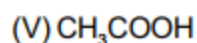
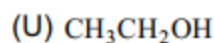
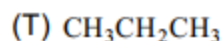
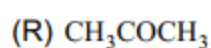
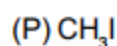
Section-VI - Matrix match type

29. Match the following

Column-I (Reaction)



Column-II (Product)



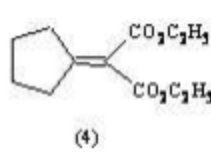
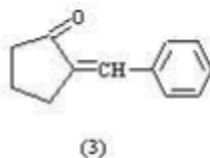
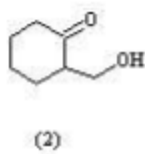
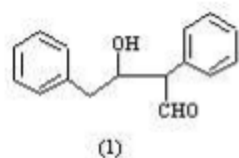
A) I - T, II - U, III - R, IV - PV

C) I - S, II - S, III - T, IV - V

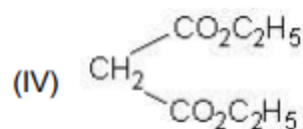
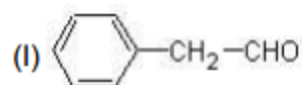
B) I - S, II - S, III - R, IV - PV

D) I - T, II - U, III - R, IV - V

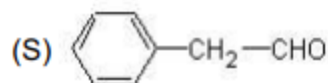
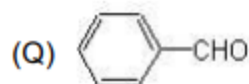
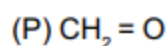
30. Aldol condensation proceeds by carbon-carbon bond formation between an enolate donor and a carbonyl acceptor. For each of the following aldol products (1–4), donor compounds are listed in column I (I–IV). Match them with the correct acceptor compound in column II (P–S)



Column-I (Donor)



Column-II (Acceptor)



A) I - Q, II - P, III - S, IV - R

C) I - Q, II - P, III - Q, IV - R

B) I - S, II - P, III - Q, IV - R

D) I - S, II - Q, III - S, IV - P