

# 12

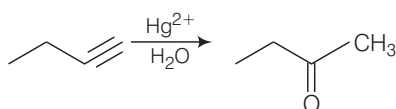
## Aldehyde, Ketones and Carboxylic Acids

### Multiple Choice Questions (MCQs)

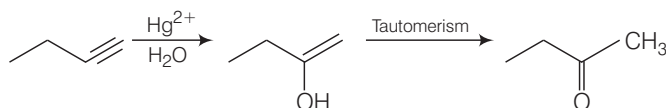
**Q. 1** Addition of water to alkynes occurs in acidic medium and in the presence of  $\text{Hg}^{2+}$  ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?

- (a)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—H}$       (b)  $\text{CH}_3\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$   
 (c)  $\text{CH}_3\text{—CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—OH} + \text{CO}_2$       (d)  $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—OH} + \text{H—}\overset{\text{O}}{\parallel}\text{C—H}$

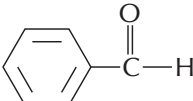
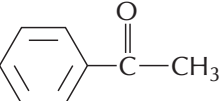
**Ans. (b)** But-1-yne on reaction with water in presence of  $\text{Hg}^{2+}$  ions as a catalyst produces butan-2-one.



**Mechanism**



**Q. 2** Which of the following compounds is most reactive towards nucleophilic addition reactions?

- (a)  $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—H}$       (b)  $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$   
 (c)       (d) 

**Ans. (a)** Reactivity of carbonyl compounds can be decided by two factors

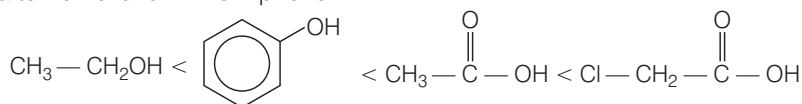
- (i) **Steric factor** Lesser the steric factor greater will be its reactivity.
- (ii) **Electronic factor** Greater the number of alkyl group lesser will be its electrophilicity.

Hence,  $\text{CH}_3\text{—CHO}$  is most reactive towards nucleophilic addition reaction.

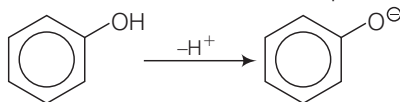
**Q. 3** The correct order of increasing acidic strength is .....

- (a) phenol < ethanol < chloroacetic acid < acetic acid
- (b) ethanol < phenol < chloroacetic acid < acetic acid
- (c) ethanol < phenol < acetic acid < chloroacetic acid
- (d) chloroacetic acid < acetic acid < phenol < ethanol

**Ans. (c)** Phenol is more stable than alcohol due to formation of more stable conjugate base after removal of  $\text{H}^+$  from phenol.

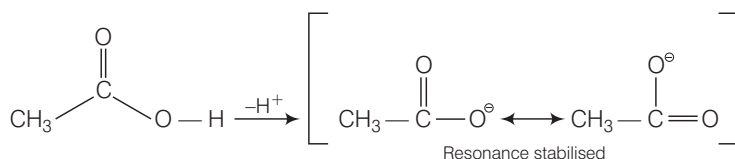


On the other hand, carboxylic acid is more acidic than phenol due to formation of more stable conjugate base after removal of  $\text{H}^+$  as compared to phenol.



Chloroacetic acid is more acidic than acetic acid due to the presence of electron withdrawing chlorine group attached to  $\alpha$ -carbon of carboxylic acid.

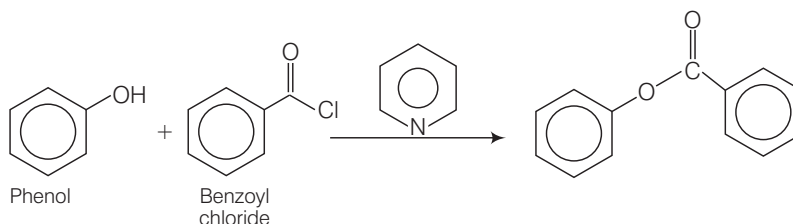
Hence, correct choice is (c).



**Q. 4** Compound  $\text{Ph—O—C(=O)—Ph}$  can be prepared by the reaction of .....

- (a) phenol and benzoic acid in the presence of NaOH
- (b) phenol and benzoyl chloride in the presence of pyridine
- (c) phenol and benzoyl chloride in the presence of  $\text{ZnCl}_2$
- (d) phenol and benzaldehyde in the presence of palladium

**Ans. (b)** Compound  $\text{Ph—COO—Ph}$  can be prepared by the reduction of



This is an example of **Schotten-Baumann reaction**.

**Q. 5** The reagent which does not react with both, acetone and benzaldehyde?

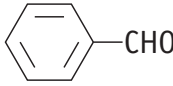
- (a) Sodium hydrogen sulphite                      (b) Phenyl hydrazine  
(c) Fehling's solution                              (d) Grignard reagent

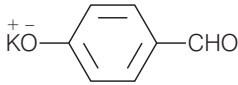
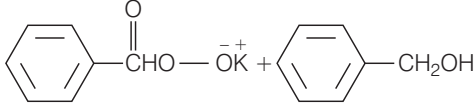
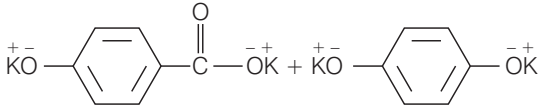
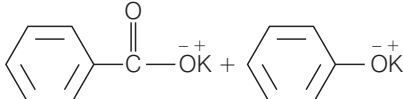
**Ans. (c)** Acetone and benzaldehyde both do not react with Fehling's solution. Fehling's solution react with ketone as acetone is an ketone while benzaldehyde is an aromatic aldehyde having absence of  $\alpha$ -hydrogen.

**Q. 6** Cannizzaro's reaction is not given by ..... .

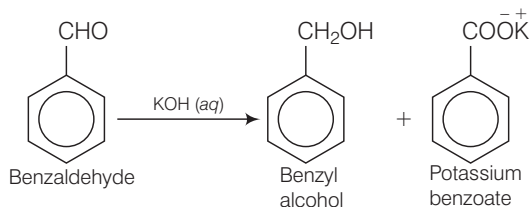
- (a)                       (b)   
(c) HCHO    (d) CH<sub>3</sub>CHO

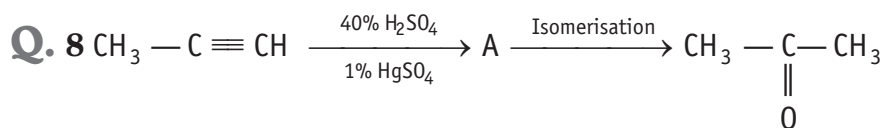
**Ans. (d)** Necessary condition for Cannizzaro reaction is absence of  $\alpha$ -hydrogen atom. So, CH<sub>3</sub>CHO will not give Cannizzaro reaction while other three compounds have no  $\alpha$ -hydrogen. Hence, they will give Cannizzaro reaction.

**Q. 7** Which products is formed when the compound  is treated with concentrated aqueous KOH solution?

- (a)   
(b)   
(c)   
(d) 

**Ans. (b)** Benzaldehyde is an aromatic aldehyde having no  $\alpha$  hydrogen. So, on reaction with aqueous KOH solution it undergo Cannizzaro reaction to produce benzyl alcohol and potassium benzoate.

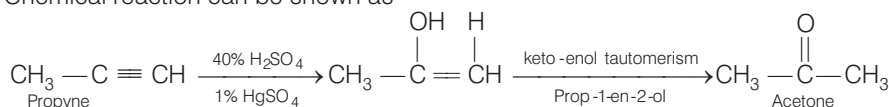




Structure of 'A' and type of isomerism in the above reaction are respectively

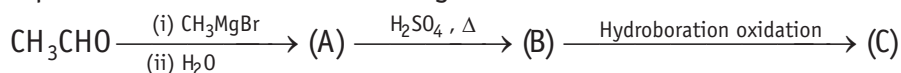
- (a) Prop-1-en-2-ol, metamerism
- (b) Prop-1-en-1-ol, tautomerism
- (c) Prop-2-en-2-ol, geometrical isomerism
- (d) Prop-1-en-2-ol, tautomerism

**Ans. (d)** Chemical reaction can be shown as



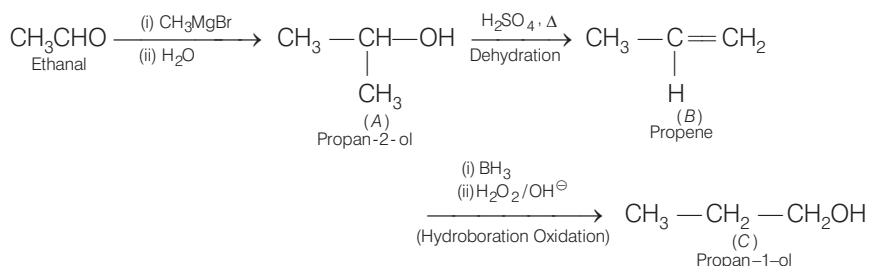
[A] is prop-1-en-2-ol, which undergo tautomerism to form acetone.

**Q. 9** Compounds A and C in the following reaction are .....



- (a) identical
- (b) positional isomers
- (c) functional isomers
- (d) optical isomers

**Ans. (b)** Chemical reaction can be shown as

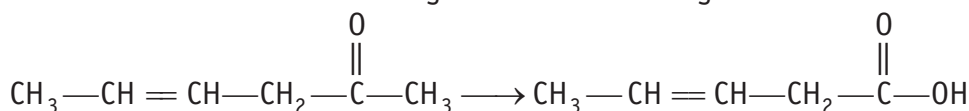


Thus,  $\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{OH}$  and  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH}$  are positional isomers.



Hence, option (b) is correct.

**Q. 10** Which is the most suitable reagent for the following conversion?



- (a) Tollen's reagent
- (b) Benzoyl peroxide
- (c)  $\text{I}_2$  and NaOH solution
- (d) Sn and NaOH solution

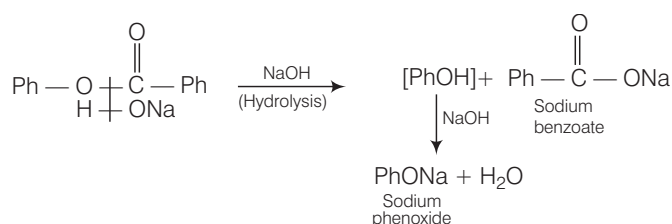


**Q. 14** Treatment of compound  $\text{Ph}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{Ph}$  with NaOH solution yields

- (a) phenol
- (b) sodium phenoxide
- (c) sodium benzoate
- (d) benzophenone

**Ans. (b, c)**

Treatment of compound  $\text{Ph}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{Ph}$  with NaOH yields sodium phenoxide and sodium benzoate by means of nucleophilic substitution reaction as follows



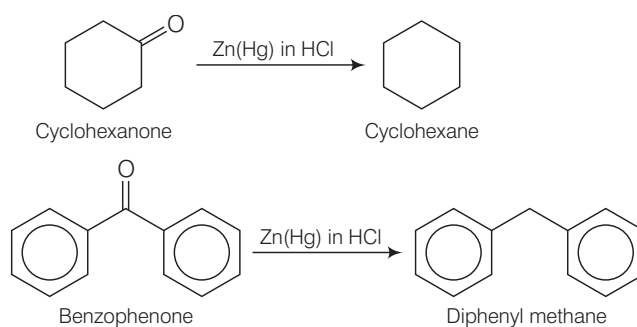
**Q. 15** Which of the following conversions can be carried out by Clemmensen reduction?

- (a) Benzaldehyde into benzyl alcohol
- (b) Cyclohexanone into cyclohexane
- (c) Benzoyl chloride into benzaldehyde
- (d) Benzophenone into diphenyl methane

**Ans. (b, d)**

Clemmensen reduction is used to convert cyclohexanone into cyclohexane and benzophenone into diphenyl methane as follows

Reagent used in Clemmensen reduction is zinc amalgam in hydrochloric acid, *i.e.*, Zn(Hg) in HCl.



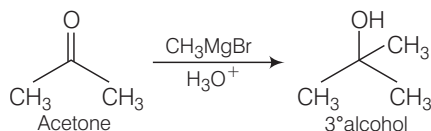
**Q. 16** Through which of the following reactions number of carbon atoms can be increased in the chain?

- (a) Grignard reaction
- (b) Cannizzaro's reaction
- (c) Aldol condensation
- (d) HVZ reaction

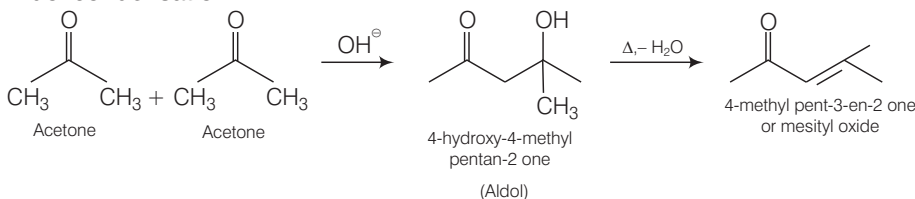
**Ans. (a, c)**

Grignard reaction and aldol condensation is used to increase the number of carbon atom in the chain as follows

**Grignard reaction**



**Aldol condensation**



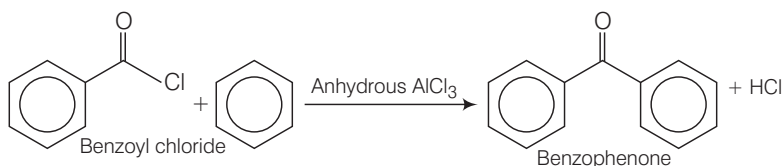
While other two reactions Cannizzaro reaction and HVZ reaction don't lead to increase in number of carbon atom.

**Q. 17** Benzophenone can be obtained by .....

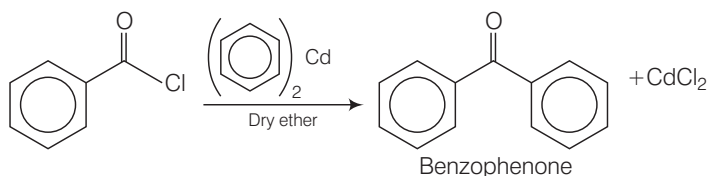
- (a) benzoyl chloride + benzene +  $\text{AlCl}_3$
- (b) benzoyl chloride + diphenyl cadmium
- (c) benzoyl chloride + phenyl magnesium chloride
- (d) benzene + carbon monoxide +  $\text{ZnCl}_2$

**Ans. (a, b)**

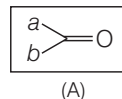
(a) Benzophenone can be obtained by Friedel-Craft acylation reaction. The reaction is shown as



(b) Benzophenone can also be obtained by the reaction between benzoyl chloride and diphenyl cadmium.



**Q. 18** Which of the following is the correct representation for intermediate of nucleophilic addition reaction to the given carbonyl compound (A)?



- (a)

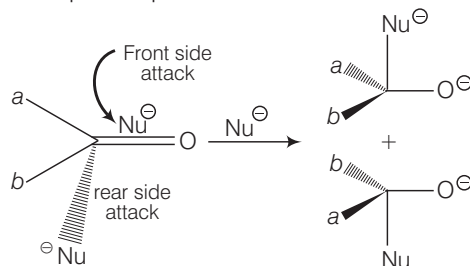
(b)

(c)

(d)

**Ans. (a, b)**

Since, carbonyl compound is a planar molecule hence two orientation of molecule regarding attack of nucleophile is possible as follows



Since, the product contains a chiral carbon, therefore, attack of nucleophile can occur either from front side attack or rear side attack giving enantiomeric products. Hence, (a) and (b) are the correct choices.

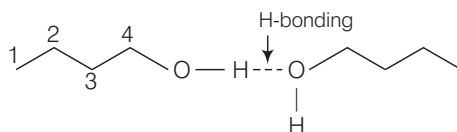
## Short Answer Type Questions

**Q. 19** Why is there a large difference in the boiling points of butanal and butan-1-ol?

### 💡 Thinking Process

*This problem based upon the concept of H-bonding which is used in determination of boiling point.*

**Ans.** Butan-1-ol has intermolecular H-bonding as shown below



Intermolecular H-bonding in butan-1-ol

Butanol has polar O—H bond due to which it shows intermolecular H-bonding which is not possible in case of butanal due to absence of polar bond. Instead of it has only weak dipole-dipole interactions. Hence, butanal has higher boiling point than butan-1-ol.

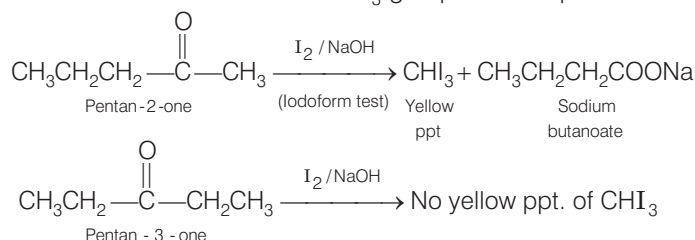
**Q. 20** Write a test to differentiate between pentan-2-one and pentan-3-one.

### 💡 Thinking Process

*This problem is based on the concept of iodoform test. The organic compound*

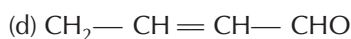
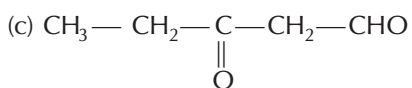
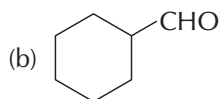
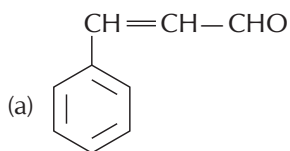
*containing  $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_3 \end{array}$  or  $\text{CH}_3\text{CH}(\text{OH})$  group which produces  $\text{CH}_3\text{CO}$  group on oxidation undergoes iodoform test.*

**Ans. Iodoform test** (yellow ppt. formed when heated with sodium hypohalite) Pentan-2-one gives positive test as it contains  $-\text{COCH}_3$  group whereas pentan-3-one does not.

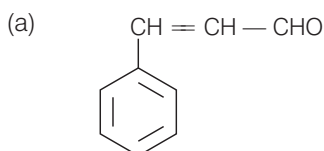




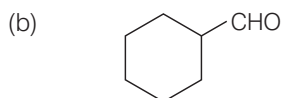
**Q. 21** Give the IUPAC names of the following compounds.



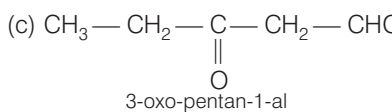
**Ans.** Following are the IUPAC names of the compounds



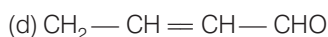
3-phenylprop-2-en-1-al



Cyclohexanecarbaldehyde



3-oxo-pentan-1-al



But-2-en-1-al

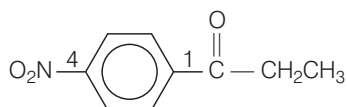
**Q. 22** Give the structure of the following compounds.

(a) 4-nitropropiophenone

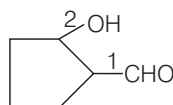
(b) 2-hydroxycyclopentanecarbaldehyde

(c) Phenyl acetaldehyde

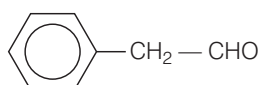
**Ans.** (a) 4-nitropropiophenone



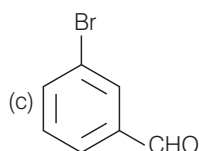
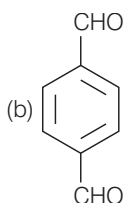
(b) 2-hydroxycyclopentanecarbaldehyde



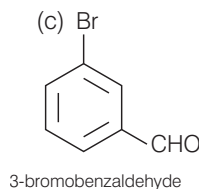
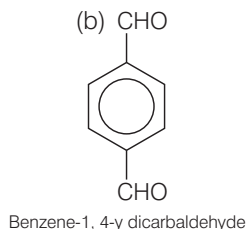
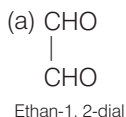
(c) Phenyl acetaldehyde



**Q. 23** Write IUPAC names of the following structures

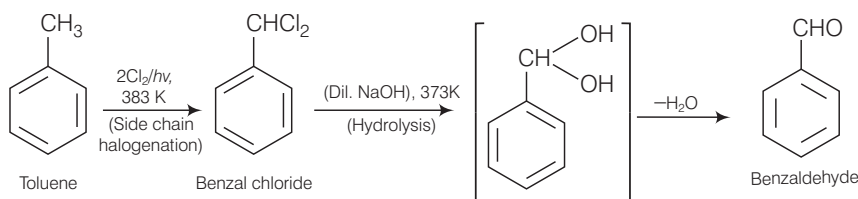


**Ans.** The IUPAC names of the following structures are



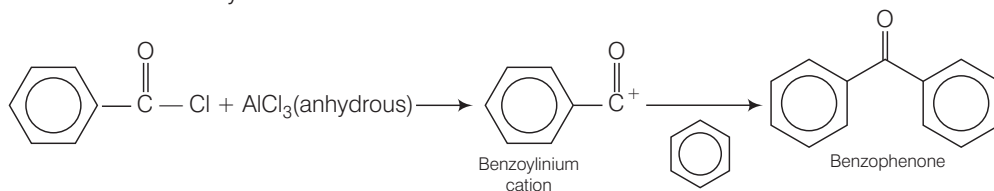
**Q. 24** Benzaldehyde can be obtained from benzal chloride. Write reactions for obtaining benzal chloride and then benzaldehyde from it.

**Ans.** It is the commercial method for preparing benzaldehyde. Benzal chloride can be obtained by photochlorination of toluene *i.e.*, chlorination of toluene in presence of sunlight. Then, benzal chloride on heating with boiling water produces benzaldehyde as shown below.



**Q. 25** Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous  $\text{AlCl}_3$ . Name the reaction also.

**Ans.** Benzene, on reaction with benzoyl chloride undergo formation of benzophenone through intermediate benzoylium cation.



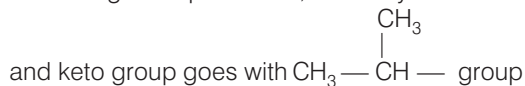
This is an example of Friedel-Craft acylation reaction.

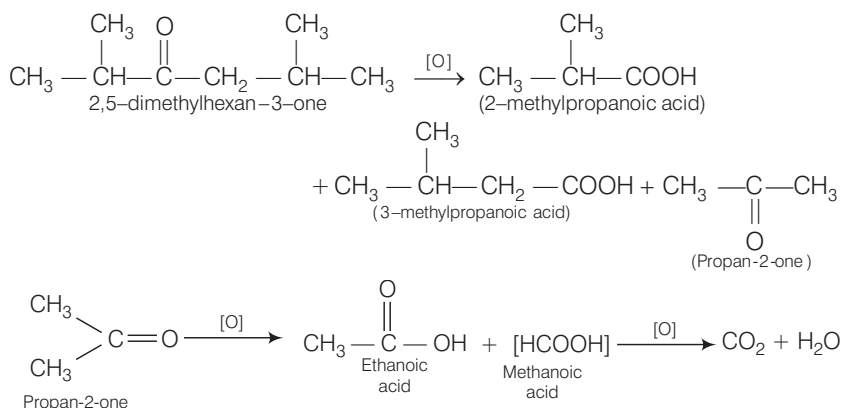
**Q. 26** Oxidation of ketones involves carbon-carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.

**Thinking Process**

This problem is based on concept of cleavage of C—C bond. According to **Popoff's rule**, during cleavage of unsymmetrical ketone, keto group stays preferentially with the smaller group.

**Ans.** According to Popoff's rule, the unsymmetrical ketone on oxidation, C—C bond cleavage





**Q. 27** Arrange the following in decreasing order of their acidic strength and give reason for your answer.



**Thinking Process**

This problem based on the concept of acidic strength, inductive effect and conjugation.

- Presence of + I group decreases acidic strength.
- Presence of – I group increases acidic strength.

**Ans.**  $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{OH}$

**Reasons**

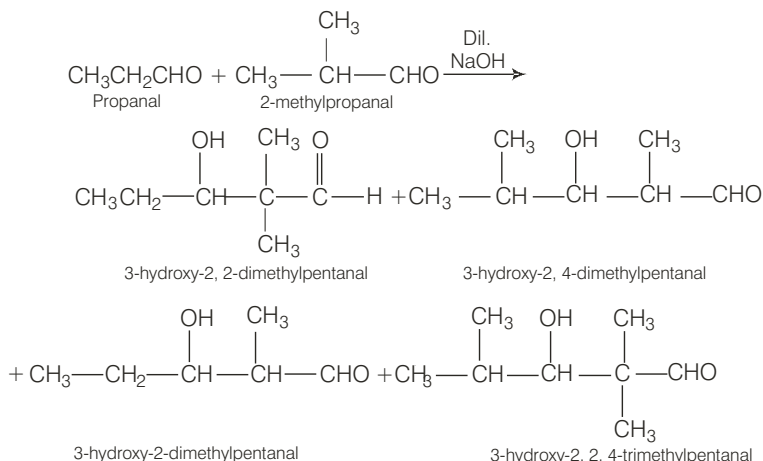
- More the electron withdrawing nature of substituent, more is the acidic strength.
- Direct attachment of  $\text{C}_6\text{H}_5$  group increases acidity due to resonance and  $sp^2$  hybridisation.
- Alcohols are weakly acidic than carboxylic acids.

**Q. 28** What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? What products will be formed? Write the name of the reaction also.

**Thinking Process**

This problem based on the concept of cross aldol condensation.

**Ans.** It is an example of cross aldol condensation.

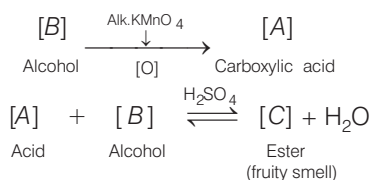


- Q. 29** Compound 'A' was prepared by oxidation of compound 'B' with alkaline  $\text{KMnO}_4$ . Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound 'A' is heated with compound B in the presence of  $\text{H}_2\text{SO}_4$  it produces fruity smell of compound C to which family the compounds 'A', 'B' and 'C' belong to?

**💡 Thinking Process**

*This problem includes conceptual mixing of preparation and properties of carboxylic acid and ester. Try to catch the key point of the process.*

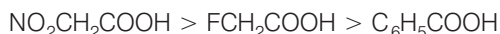
**Ans.** Since, B and A on heating together in the presence of acid produces ester (a fruity smell).



- Q. 30** Arrange the following in decreasing order of their acidic strength. Give explanation for the arrangement.



**Ans.** The decreasing order of their acidic strength



Acidic strength decreases as the number of electron withdrawing substituent(s) linked to  $\alpha$ -carbon atom or carboxylic group of carboxylic acid decreases. Electron withdrawing ability of  $\text{NO}_2$ , F and  $\text{C}_6\text{H}_5$  are as follows



- Q. 31** Alkenes  $\text{>C=C<}$  and carbonyl compounds  $\text{>C=O}$  both contain a  $\pi$  bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

**Ans.** Nature of chemical reaction occurring on  $\text{>C=C<}$  bond or  $\text{>C=O}$  bond can be explained on the basis of nature of bond between  $\text{>C=C<}$  and  $\text{>C=O}$ .

$\text{>C=C<}$   
Non-polar covalent  
compound

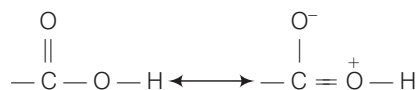
$\text{>C=O}$   
Polar covalent  
compound

- Due to electronegativity difference between carbon and oxygen

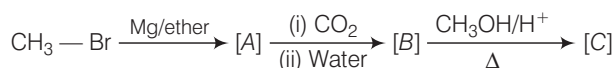
Thus, in  $\text{>C=O}$  carbon acquires partially positive charge and O acquires partially negative charge and show nucleophilic addition reaction to the electrophilic carbonyl carbon. On the other hand,  $\text{>C=C<}$  undergo electrophilic addition reaction due to nucleophilic nature of  $\text{>C=C<}$  which contains  $\pi$  bond.

**Q. 32** Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why?

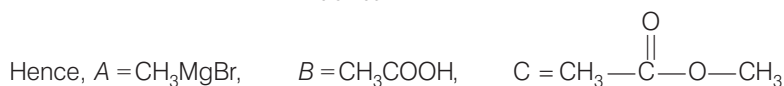
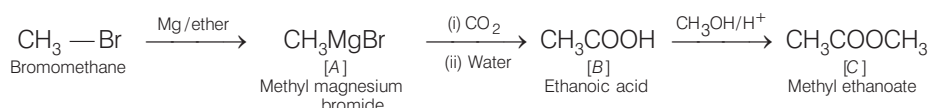
**Ans.** Carboxylic acid contain carbonyl group but do not show nucleophilic addition reaction like aldehyde and ketone. Due to resonance as shown below the partial positive charge on carbonyl carbon atom is reduced.



**Q. 33** Identify the compounds A, B and C in the following reaction.

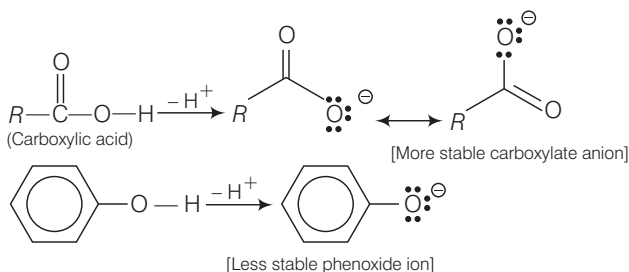


**Ans.** Complete chemical conversion can be done as



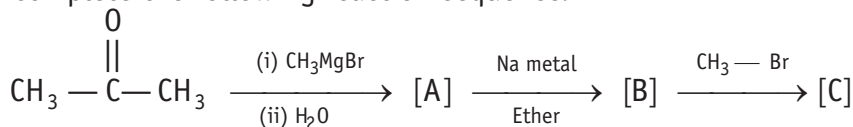
**Q. 34** Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to a oxygen atom (—O—H)?

**Ans.** Carboxylic acids are more acidic than alcohol or phenol, although all of them have O—H bond. This can be explained on the basis of stability of conjugate base obtained after removal of  $\text{H}^+$  from acid or phenol.

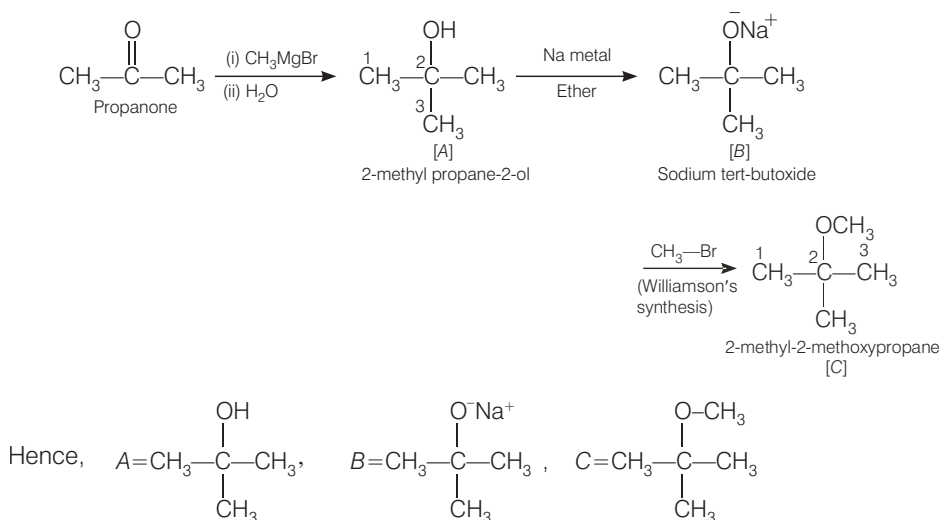


Hence, dissociation of O—H bond in case of carboxylic acid become easier than that of phenol. Hence, carboxylic acid are stronger acid than phenol.

**Q. 35** Complete the following reaction sequence.

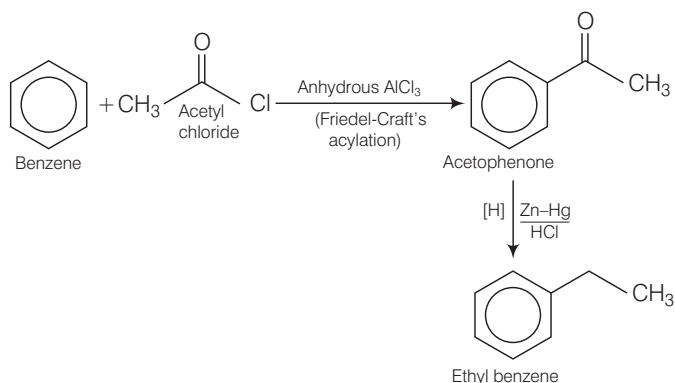


**Ans.** The complete chemical transformation can be shown as



**Q. 36** Ethyl benzene is generally prepared by acetylation of benzene followed by reduction and not by direct alkylation. Think of a possible reason.

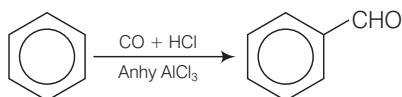
**Ans.** Preparation of ethyl benzene from acylation of benzene and reduction can be shown as



The direct alkylation can not be performed because there is polysubstitution product is formed. Due to disadvantage of polysubstitution that Friedel-Craft's alkylation reaction is not used for preparation of alkylbenzenes. Instead of Friedel-Craft's acylation is used.

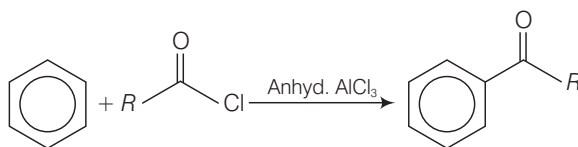
**Q. 37** Can Gatterman-Koch reaction be considered similar to Friedel-Craft's acylation? Discuss.

**Ans.** In Gatterman-Koch reaction, benzene or its derivative is treated with CO and HCl in presence of anhydrous aluminium chloride to produce benzaldehyde.



While in Friedel-Craft acylation, acyl group is transferred to carbon of benzene and acyl benzene is obtained as a result.

This can be done by reaction of benzene with acyl chloride in the presence of anhydrous  $\text{AlCl}_3$ .



Formyl chloride is unstable in nature. So, it can be transferred by only Gattermann-Koch reaction not by Friedel-Craft reaction.

## Matching The Columns

**Q. 38** Match the common names given in Column I with the IUPAC names given in Column II.

Column I (Common names)	Column II (IUPAC names)
A. Cinnamaldehyde	1. Pentanal
B. Acetophenone	2. Prop-2-en-al
C. Valeraldehyde	3. 4-methylpent-3-en-2-one
D. Acrolein	4. 3-phenylprop-2-en-al
E. Mesityl oxide	5. 1-phenylethanone

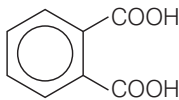

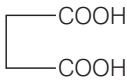
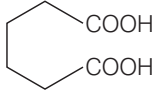
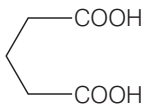
**Ans.** A. → (4)    B. → (5)    C. → (1)    D. → (2)    E. → (3)

Common names	Structure	IUPAC names
A. Cinnamaldehyde		3-phenylprop-2-en-al
B. Acetophenone		1-phenylethanone
C. Valeraldehyde		Pentanal
D. Acrolein		Prop-2-en-al
E. Mesityl oxide		4-methyl pent-3-en-2-one

**Q. 39** Match the acids given in Column I with their correct IUPAC names given in Column II.

Column I (Acids)	Column II (IUPAC names)
A. Phthalic acid	1. Hexane- 1, 6-dioic acid
B. Oxalic acid	2. Benzene-1, 2-dicarboxylic acid
C. Succinic acid	3. Pentane-1, 5-dioic acid
D. Adipic acid	4. Butane-1, 4-dioic acid
E. Glutaric acid	5. Ethane-1, 2-dioic acid

**Ans.** A. → (2)    B. → (5)    C. → (4)    D. → (1)    E. → (3)

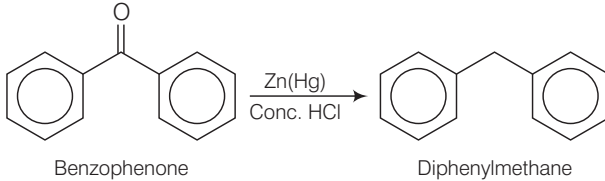
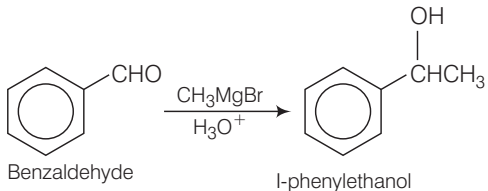
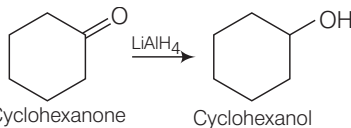
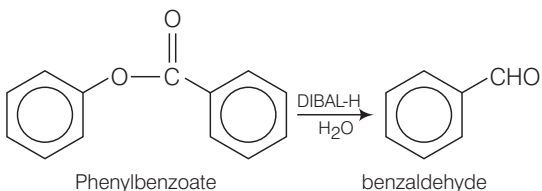
Acids	IUPAC names	Structure
A. Phthalic acid	Benzene-1, 2-dicarboxylic acid	
B. Oxalic acid	Ethane-1, 2-dioic acid	
C. Succinic acid	Butane-1, 4-dioic acid	
D. Adipic acid	Hexane- 1, 6-dioic acid	
E. Glutaric acid	Pentane-1, 5-dioic acid	

**Q. 40** Match the reactions given in Column I with the suitable reagents given in Column II.

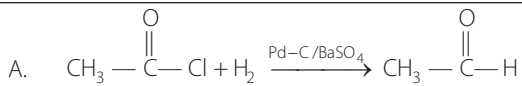
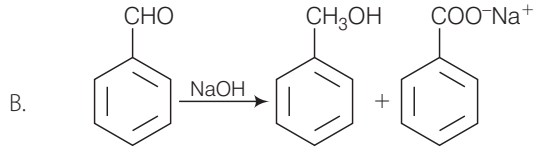
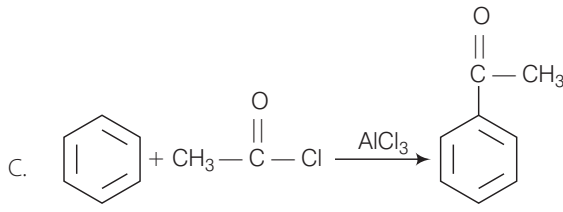
Column I (Reactions)	Column II (Reagents)
A. Benzophenone → Diphenylmethane	1. $\text{LiAlH}_4$
B. Benzaldehyde → 1-phenylethanol	2. DIBAL-H
C. Cyclohexanone → Cyclohexanol	3. $\text{Zn(Hg)/Conc. HCl}$
D. Phenyl benzoate → Benzaldehyde	4. $\text{CH}_3\text{MgBr}$



Ans. A. → (3)    B. → (4)    C. → (1)    D. → (2)

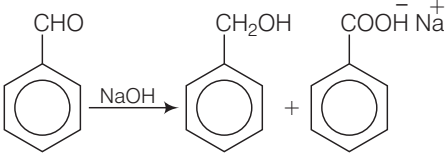
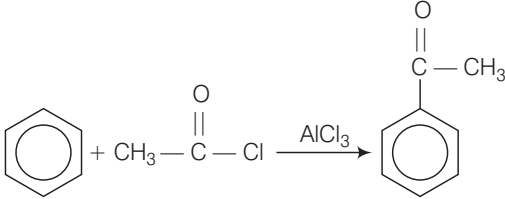
Reactions		Reagents
A.	 <p>Benzophenone → Diphenylmethane</p>	Zn(Hg)/Conc. HCl
B.	 <p>Benzaldehyde → 1-phenylethanol</p>	CH <sub>3</sub> MgBr
C.	 <p>Cyclohexanone → Cyclohexanol</p>	LiAlH <sub>4</sub>
D.	 <p>Phenylbenzoate → benzaldehyde</p>	DIBAL-H

**Q. 41** Match the example given in Column I with the name of the reaction in Column II.

Column I (Example)	Column II (Reaction)
A. 	1. Friedel-Crafts acylation
B. 	2. HVZ reaction
C. 	3. Aldol condensation

Column I (Example)	Column II (Reaction)
D. $R-CH_2-COOH \xrightarrow{Br_2 / \text{Red P}} R-\underset{\text{Br}}{\text{CH}}-COOH$	4. Cannizzaro's reaction
E. $CH_3-CN \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } SnCl_2/HCl} CH_3CHO$	5. Rosenmund's reduction
F. $2CH_3CHO \xrightarrow{NaOH} CH_3-CH=CHCHO$	6. Stephen's reaction

**Ans. A. → (5)    B. → (4)    C. → (1)    D. → (2)    E. → (6)    F. → (3)**

Example	Name of the reaction
A. $CH_3-\overset{\text{O}}{\parallel}{C}-Cl + H_2 \xrightarrow{Pd-C / BaSO_4} CH_3-\overset{\text{O}}{\parallel}{C}-H$	Rosenmund's reduction
B. 	Cannizzaro's reaction
C. 	Friedel-Crafts acylation
D. $R-CH_2-COOH \xrightarrow{Br_2 / \text{Red P}} R-\underset{\text{Br}}{\text{CH}}-COOH$	HVZ reaction
E. $CH_3-CN \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } SnCl_2/HCl} CH_3CHO$	Stephen's reaction
F. $2CH_3CHO \xrightarrow{NaOH} CH_3-CH=CHCHO$	Aldol condensation

## Assertion and Reason

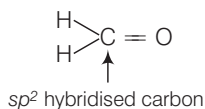
*In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.*

- (a) Assertion and reason both are correct and reason is correct explanation of assertion.
- (b) Assertion and reason both are wrong statements.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- (e) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

**Q. 42 Assertion (A)** Formaldehyde is a planar molecule.

**Reason (R)** It contains  $sp^2$  hybridised carbon atom.

**Ans. (a)** Assertion and reason are correct and reason is the correct explanation of assertion.  
Formaldehyde is planar molecule due to  $sp^2$  hybridised carbon atom.



**Q. 43 Assertion (A)** Compounds containing  $\text{—CHO}$  group are easily oxidised to corresponding carboxylic acids.

**Reason (R)** Carboxylic acids can be reduced to alcohols by treatment with  $\text{LiAlH}_4$ .

**Ans. (e)** Assertion and reason both are correct but reason is not the correct explanation of assertion.

Compounds containing  $\text{—CHO}$  group are easily oxidised to corresponding carboxylic acids. Correct reason is due to electron withdrawing nature of  $\text{C}=\text{O}$  group,  $\text{C—H}$  bond in aldehydes is weak and easily oxidised to the corresponding carboxylic acids even with mild oxidising agent like Fehling's solution and Tollen's reagents.

**Q. 44 Assertion (A)** The  $\alpha$ -hydrogen atom in carbonyl compounds is less acidic.

**Reason (R)** The anion formed after the loss of  $\alpha$ -hydrogen atom is resonance stabilised.

**Ans. (d)** Assertion is wrong statement but reason is correct statement.

Correct assertion is the  $\alpha$ -hydrogen atom in carbonyl compounds is acidic in nature due to presence of electron withdrawing carbonyl group. The anion formed after loss of  $\alpha$ -hydrogen atom is resonance stabilised.

**Q. 45 Assertion (A)** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

**Reason (R)** Aromatic aldehydes are almost as reactive as formaldehyde.

**Ans. (c)** Assertion is the correct statement but reason is the wrong statement.

Aromatic aldehyde and formaldehyde undergo Cannizzaro reaction due to absence of  $\alpha\text{-H}$ -atom lead to formation of carboxylic acid and alcohols of corresponding aldehyde.

**Q. 46 Assertion (A)** Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

**Reason (R)** Both, aldehydes and ketones contain a carbonyl group.

**Ans. (d)** Assertion is wrong statement but reason is the correct statement.

Aldehydes but not ketones react with Tollen's reagent to form silver mirror. Reason is correct statement as aldehyde and ketone both contain carbonyl group.

## Long Answer Type Questions

**Q. 47** An alkene 'A' (molecular formula  $C_5H_{10}$ ) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with  $I_2$  and  $NaOH$ . Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.

### Thinking Process

*This problem is based on conceptual mixing of preparation and properties of carbonyl compound including ozonolysis, iodoform test.*

*Only aldehyde (not ketone) undergo Fehling test.*

Compound containing  $\begin{array}{c} O \\ || \\ -C-CH_3 \end{array}$  group undergo iodoform test.

*Draw all possible structures of A using degree of unsaturation calculations then choose the correct structure using information provided above in the question.*

**Ans.** Molecular formula =  $C_5H_{10}$

$$\text{Degree of unsaturation} = (C_n + 1) - \frac{H_n}{2}$$

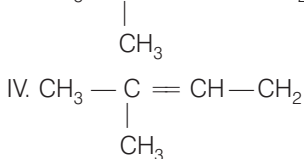
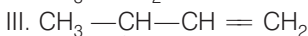
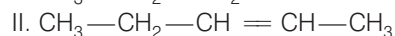
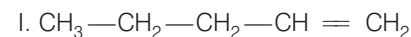
where,  $C_n$  = number of carbon atoms

$H_n$  = number of hydrogen atoms

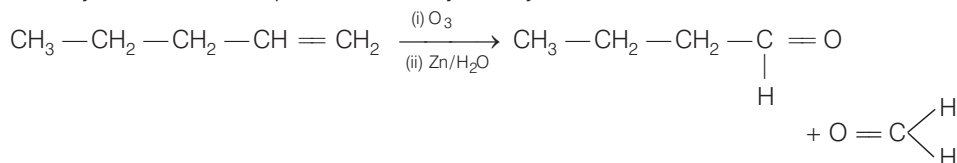
$$= (5 + 1) - \frac{10}{2} = 1$$

Compound A will be either alkene or cyclic hydrocarbon. Since, A is undergoing ozonolysis hence A must be an alkene.

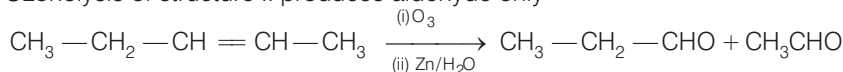
**Possible structures of alkene are**



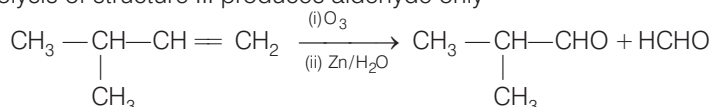
Ozonolysis of structure I produces aldehyde only



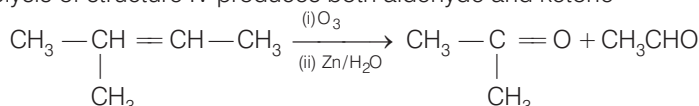
Ozonolysis of structure II produces aldehyde only



Ozonolysis of structure III produces aldehyde only

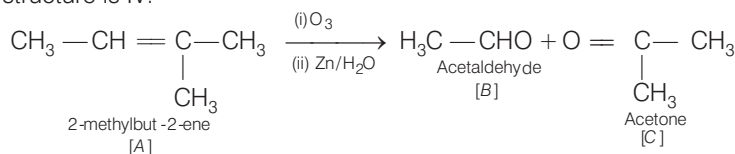


Ozonolysis of structure IV produces both aldehyde and ketone

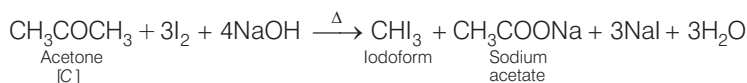


After ozonolysis of each of structures I, II and III produces only aldehydes as both components. But as given in the question one compound doesn't give Fehling test but must

give iodoform test. Hence, compound must be a ketone with  $\text{CH}_3 - \overset{\text{O}}{\underset{\text{||}}{\text{C}}} -$  group. Hence, correct structure is IV.



Formation of iodoform from 'B' and 'C' may be explained as follows



- Q. 48** An aromatic compound 'A' (molecular formula  $\text{C}_8\text{H}_8\text{O}$ ) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (molecular formula  $\text{C}_7\text{H}_6\text{O}_2$ ), which is also formed alongwith the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

### Thinking Process

This problem is based on conceptual mixing of 2, 4-DNP test, iodoform test and oxidation reactions. Search the key point by using by which this question can be answered easily. Follow the following stepwise approach to solve this question.

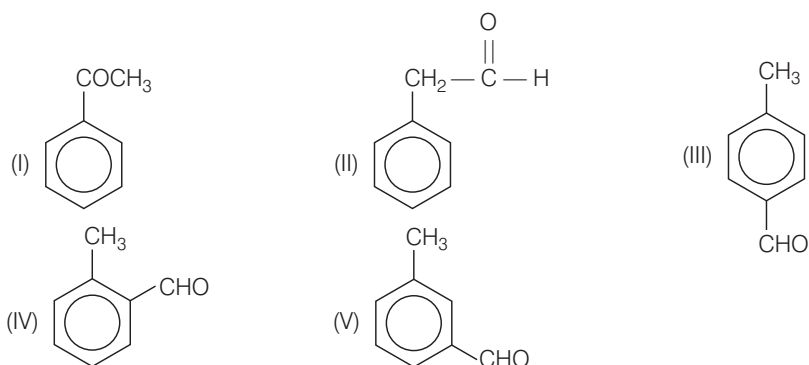
- Determine all possible structures of molecule using degree of unsaturation.
- Use the concept of chemical test given by aldehyde and ketone to identify the correct structure.
- After choosing any predicted structure complete the sequence of reaction.

**Ans.** Molecular formula =  $C_8H_8O$

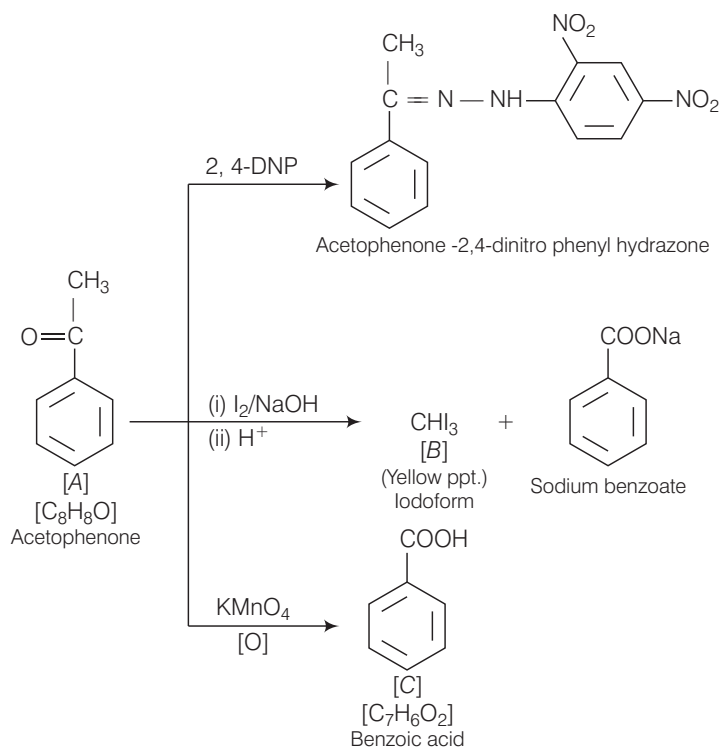
$$\begin{aligned}\text{Degree of unsaturation} &= (C_n + 1) - \frac{H_n}{2} \\ &= (8 + 1) - \frac{8}{2} = 9 - 4 = 5\end{aligned}$$

Degree of unsaturation  $> 5$  i.e., it may contain benzene ring having degree of unsaturation equal to 4 and one degree of unsaturation must be carbonyl group.

Thus, possible structures are

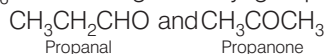


According to question, compound 'A' does not respond to Tollen's or Fehling's test, So, it is a ketone not aldehyde. Therefore, structure I is correct. Complete reaction sequence is as follows

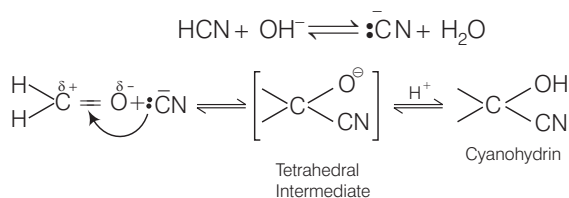


**Q. 49** Write down functional isomers of a carbonyl compound with molecular formula  $C_3H_6O$ . Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

**Ans.** Functional isomers of  $C_3H_6O$  containing carbonyl group are



- (a) Propanal,  $CH_3CH_2CHO$  will react faster with HCN because there is less steric hindrance and electronic factors, which increases its electrophilicity.  
 (b) The reaction mechanism is as follow

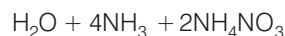
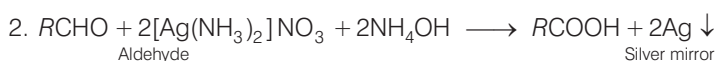
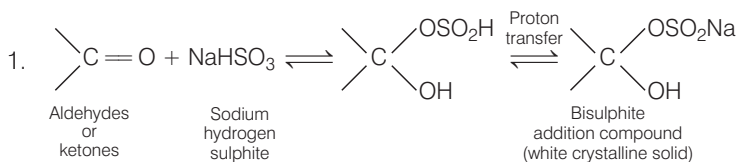


The reaction does not lead to completion because it is a reversible reaction. Equilibrium is established.

- (c) If a strong acid is added to the reaction mixture, the reaction is inhibited because production of  $\cdot\bar{C}N$  ions is prevented.

**Q. 50** When liquid 'A' is treated with a freshly prepared ammoniacal silver nitrate solution it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogen sulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogen sulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions also.

**Ans.** Since the liquid A reduces ammoniacal silver nitrate, (Tollen's reagent), it 'A' is aldehyde.



**Note** Aldehyde and ketone both give white crystalline solid with sodium hydrogen sulphite but this is only aldehyde which gives Tollen's test and Fehling's test.