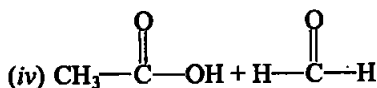
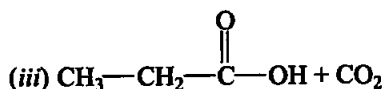
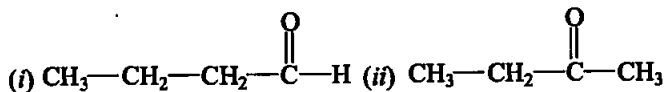


12 ■ ■ ■ Aldehydes, Ketones and Carboxylic Acids

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

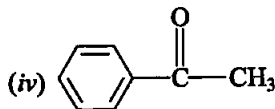
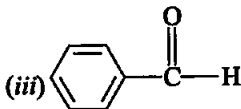
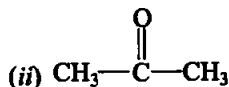
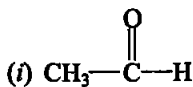
1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?



Ans. (ii)

Explanation: Addition of water to ethyne in the presence of H_2SO_4 and HgSO_4 gives acetaldehyde. Addition takes place by Markovnikoff's rule.

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



Ans. (i)

Explanation: Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former. In benzaldehyde also, it is difficult for the nucleophile to attack on the substrate molecule.

3. The correct order of increasing acidic strength is _____.

- (i) Phenol < Ethanol < Chloroacetic acid < Acetic acid
 (ii) Ethanol < Phenol < Chloroacetic acid < Acetic acid
 (iii) Ethanol < Phenol < Acetic acid < Chloroacetic acid
 (iv) Chloroacetic acid < Acetic acid < Phenol < Ethanol

Ans. (iii)

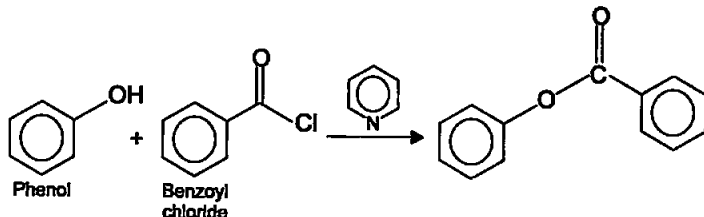
Explanation: Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion. That is why carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Thus, the order of increasing acidic strength is — Ethanol < Phenol < Acetic acid < Chloroacetic acid.

4. Compound $\text{Ph}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$ can be prepared by the reaction of _____.

- (i) Phenol and benzoic acid in the presence of NaOH
 (ii) Phenol and benzoyl chloride in the presence of pyridine
 (iii) Phenol and benzoyl chloride in the presence of ZnCl_2
 (iv) Phenol and benzaldehyde in the presence of palladium

Ans. (ii)

Explanation: Compound $\text{Ph}-\text{COO}-\text{Ph}$ can be prepared by the reaction of



This is an example of Schotten-Baumann reaction.

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

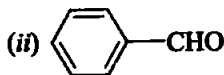
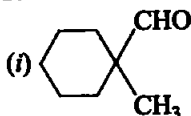
- (i) Sodium hydrogensulphite (ii) Phenyl hydrazine
 (iii) Fehling's solution (iv) Grignard reagent

Ans. (iii)

Explanation: **Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are

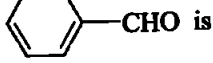
oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

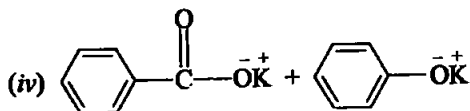
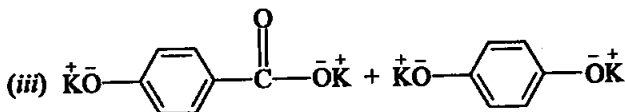
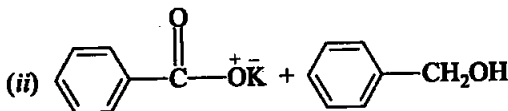
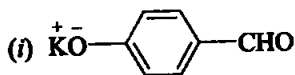
6. Cannizzaro's reaction is not given by _____.



Ans. (iv)

Explanation: Cannizzaro reaction: Aldehydes which do not have an alpha hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt. CH₃CHO has one alpha hydrogen that is why it will not give Fehling's test.

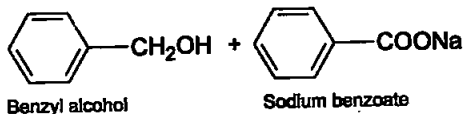
7. Which product is formed when the compound  is treated with concentrated aqueous KOH solution?



Ans. (ii)

Explanation: $2 \text{C}_6\text{H}_5\text{CHO} + \text{Conc. NaOH} \rightarrow$

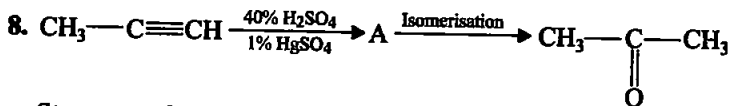
Benzaldehyde



Benzyl alcohol

Sodium benzoate

Similar reaction will occur with KOH.

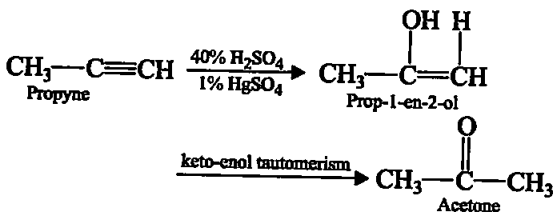


Structure of 'A' and type of isomerism in the above reaction are respectively.

- (i) Prop-1-en-2-ol, metamerism
- (ii) Prop-1-en-1-ol, tautomerism
- (iii) Prop-2-en-2-ol, geometrical isomerism
- (iv) Prop-1-en-2-ol, tautomerism

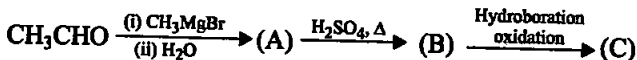
Ans. (iv)

Explanation: Chemical reaction can be shown as



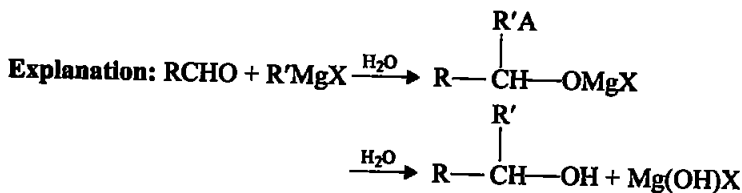
A is prop-1-en-2-ol, which undergo tautomerism to form acetone.

9. Compounds A and C in the following reaction are _____.



- (i) identical
- (ii) positional isomers
- (iii) functional isomers
- (iv) optical isomers

Ans. (ii)

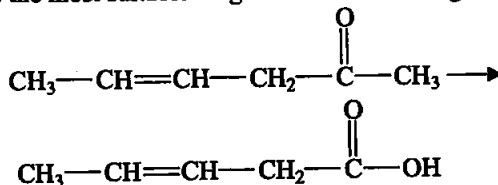


From the above reaction, it is clear that acetaldehyde on treatment with Grignard reagent followed by hydrolysis will give propane-2-ol as the product.

Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4 now the product B will be propene which on hydroboration oxidation will give propane-1-ol.

Thus, propane-2-ol and propane-1-ol are position isomers.

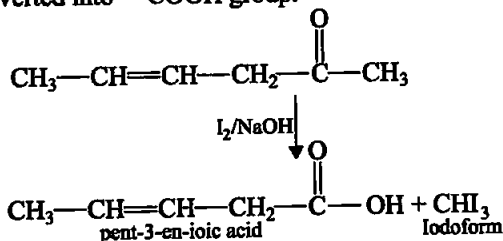
10. Which is the most suitable reagent for the following conversion?



- (i) Tollens' reagent (ii) Benzoyl peroxide
 (iii) I₂ and NaOH solution (iv) Sn and NaOH solution

Ans. (iii)

Explanation: Iodoform test is used for $-\text{COCH}_3$ group which is converted into $-\text{COOH}$ group.

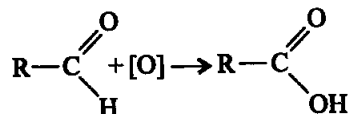


11. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution?

- (i) Butan-1-ol (ii) Butan-2-ol
 (iii) Both of these (iv) None of these

Ans. (ii)

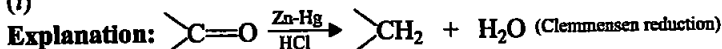
Explanation: Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc.



12. In Clemmensen Reduction carbonyl compound is treated with _____.

- (i) Zinc amalgam + HCl (ii) Sodium amalgam + HCl
 (iii) Zinc amalgam + nitric acid (iv) Sodium amalgam + HNO_3

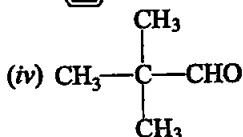
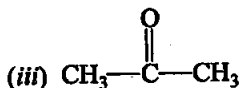
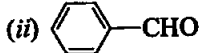
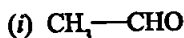
Ans. (i)



II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

13. Which of the following compounds do not undergo aldol condensation?



Ans. (ii) and (iv)

Explanation: *Aldol condensation:* Aldehydes and ketones having at least one alpha-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form beta-hydroxy aldehydes (aldol) or beta-hydroxy ketones (ketol), respectively. This is known as Aldol reaction. In (ii) and (iv) alpha hydrogen is absent.

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

(i) Phenol

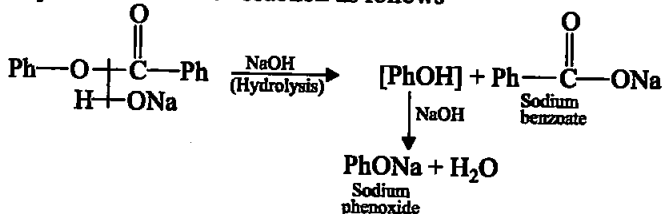
(ii) Sodium phenoxide

(iii) Sodium benzoate

(iv) Benzophenone

Ans. (ii) and (iii)

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



15. Which of the following conversions can be carried out by Clemmensen Reduction?

(i) Benzaldehyde into benzyl alcohol

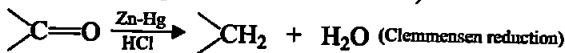
(ii) Cyclohexanone into cyclohexane

(iii) Benzoyl chloride into benzaldehyde

(iv) Benzophenone into diphenyl methane

Ans. (ii) and (iv)

Explanation: The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction]



In (ii) and (iv) only the carbonyl compound is converted into hydrocarbon.

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

(i) Grignard reaction

(ii) Cannizzaro's reaction

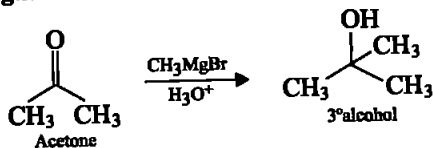
(iii) Aldol condensation

(iv) HVZ reaction

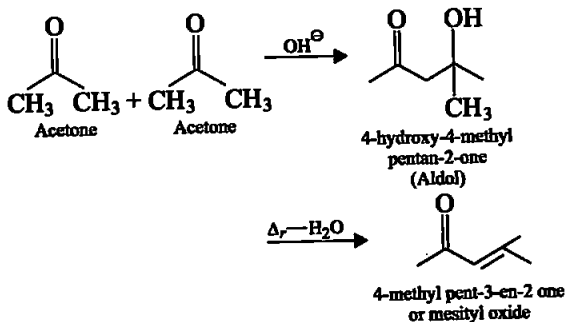
Ans. (i) and (iii)

Explanation: 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 atoms.

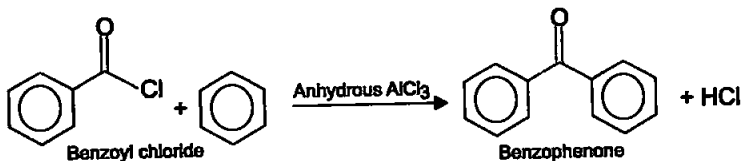
17. Benzophenone can be obtained by _____.

- (i) Benzoyl chloride + Benzene + AlCl_3
- (ii) Benzoyl chloride + Diphenyl cadmium
- (iii) Benzoyl chloride + Phenyl magnesium chloride
- (iv) Benzene + Carbon monoxide + ZnCl_2

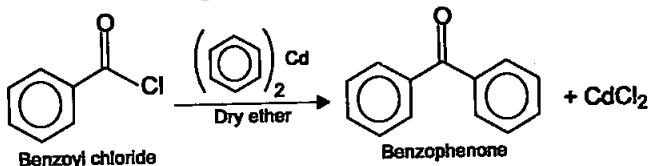
Ans. (i) and (ii)

Explanation:

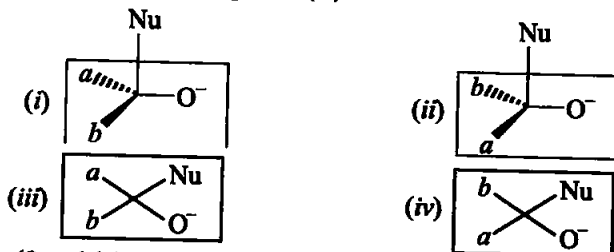
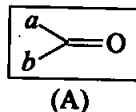
- (a) Benzophenone can be obtained by Friedel-Craft acylation reaction. The reaction is shown as



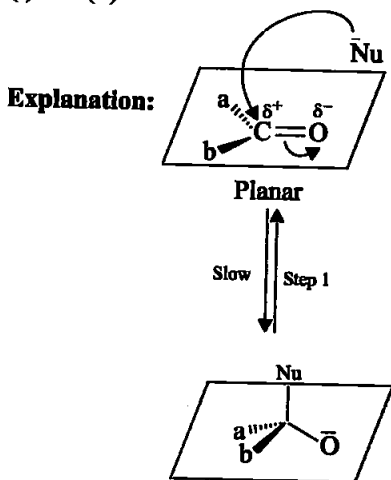
- (b) Benzophenone can also be obtained by the reaction between benzoyl chloride and diphenyl cadmium.



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



Ans. (i) and (ii)



III. SHORT ANSWER TYPE

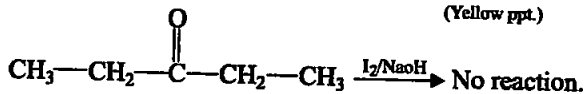
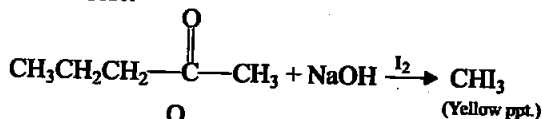
19. Why is there a large difference in the boiling points of butanal and butan-1-ol?

Ans. Boiling points of aldehydes are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

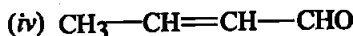
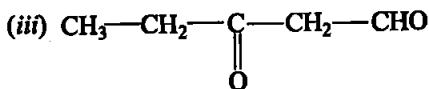
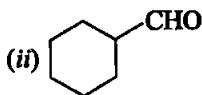
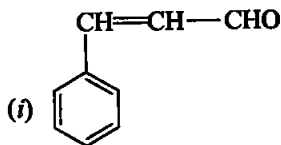
20. Write a test to differentiate between pentan-2-one and pentan-3-one.

Ans. 2-pentanone has a CH_3CO -group, hence gives positive iodoform test. 3-pentanone does not have a CH_3CO -group, hence does not give positive iodoform test.

Iodoform Test:



21. Give the IUPAC names of the following compounds.



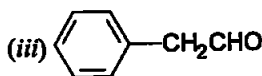
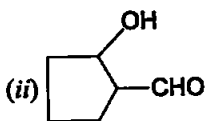
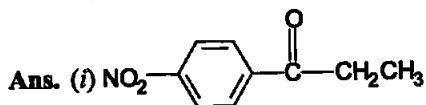
Ans. (i) 3-Phenylprop-2-enal (ii) Cyclohexanecarbaldehyde
 (iii) 3-oxopentanal (iv) But-2-enal

22. Give the structure of the following compounds.

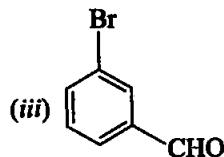
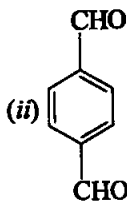
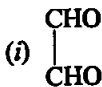
(i) 4-Nitropropiophenone

(ii) 2-Hydroxycyclopentanecarbaldehyde

(iii) Phenyl acetaldehyde



23. Write IUPAC names of the following structures.



Ans. (i) Ethane-1, 2-dial

(ii) Benzene-1, 4-dicarbaldehyde

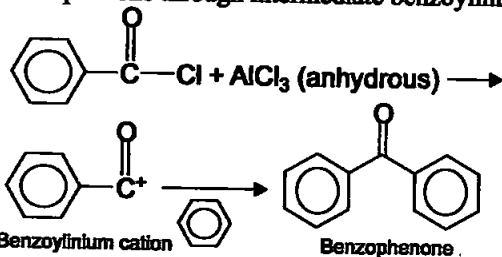
(iii) 3-Bromobenzaldehyde

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



25. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous AlCl_3 . Name the reaction also.

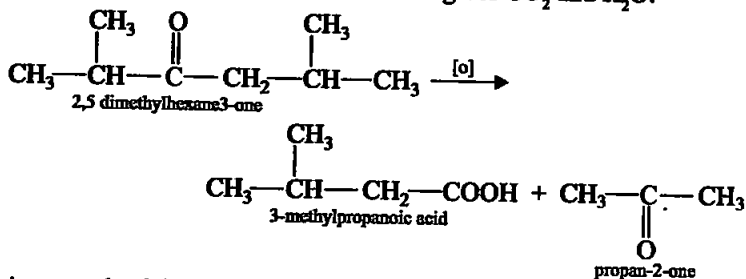
Ans. Benzene, on reaction with benzoyl chloride undergo formation of benzophenone through intermediate benzoylium cation.



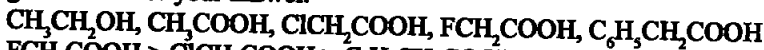
This is an example of Friedel-Craft acylation reaction.

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

Ans. Being an unsymmetrical ketone, oxidation occurs on either side of the $\text{C} = \text{O}$ group giving a mixture of 2-methyl propanoic acid, 3-methylbutanoic acid and propan-2-one. Propan-2-one on further oxidation gives a mixture of ethanoic acid and methanoic acid. Subsequent oxidation of methanoic acid gives CO_2 and H_2O .



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



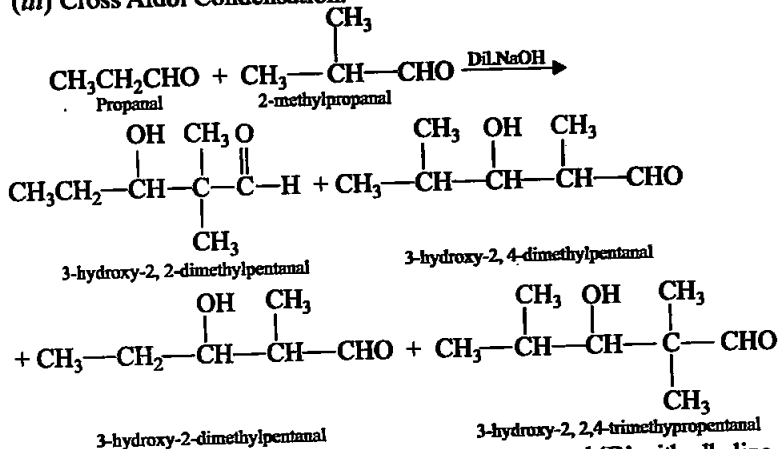
Ans. $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{OH}$

Explanation: Effect of substituents on the acidity of carboxylic acids:

Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

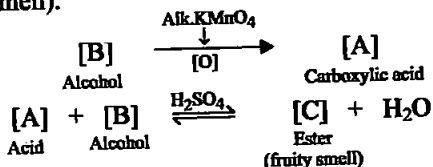
28. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH ? What products will be formed? Write the name of the reaction also.

- Ans. (i) A mixture of two aldehydes or ketones, atleast one of these must contains α -hydrogen undergo cross-aldol condensation.
 (ii) A mixture of four product is formed.
 (iii) Cross Aldol Condensation.

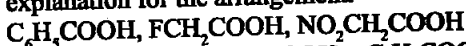


29. Compound 'A' was prepared by oxidation of compound 'B' with alkaline KMnO_4 . Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound 'A' is heated with compound B in the presence of H_2SO_4 it produces fruity smell of compound C to which family the compounds 'A', 'B' and 'C' belong to?

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



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

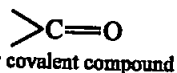
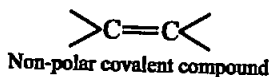


Ans. $\text{NO}_2\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH}$

Explanation: Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects.

31. Alkenes ($>\text{C}=\text{C}<$) and carbonyl compounds ($>\text{C}=\text{O}$), both contain a π bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

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

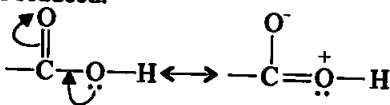


* Due to electronegativity difference between carbon and oxygen

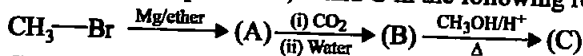
Thus, in $>C=O$ carbon acquires partially positive charge and O acquires partially negative charge and show nucleophilic addition reaction due to the electrophilic carbonyl carbon. On the other hand, $>C=C<$ undergo electrophilic addition reaction due to nucleophilic nature of $>C=C<$ which contains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

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

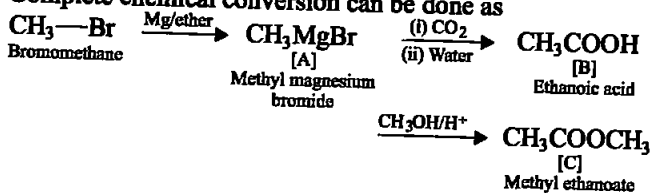
Ans. Due to resonance as shown below the partial positive charge on carbonyl carbon atom is reduced.



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



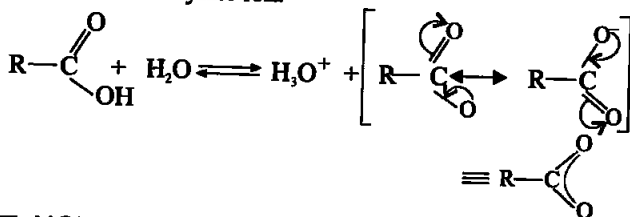
Ans. Complete chemical conversion can be done as



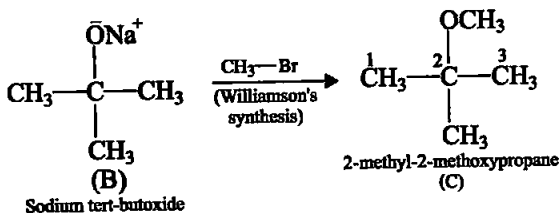
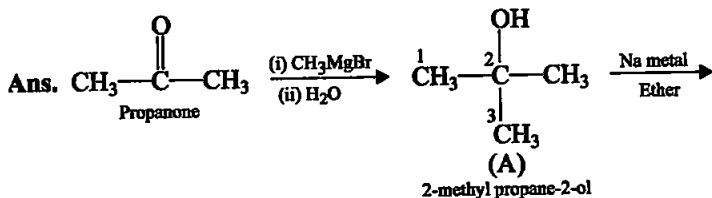
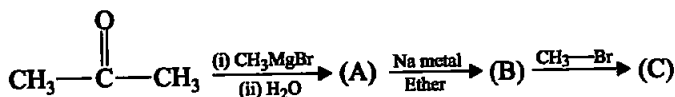
Hence, A = CH_3MgBr , B = CH_3COOH , C = $CH_3-C(=O)-O-CH_3$

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

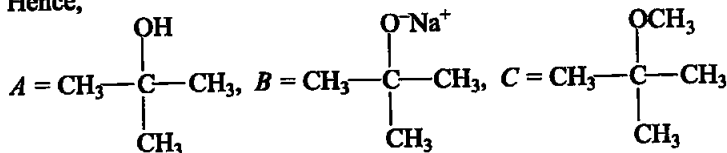
Ans. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion.



35. Complete the following reaction sequence.

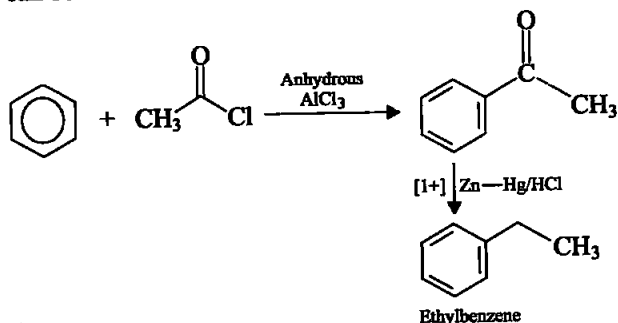


Hence,



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

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



37. Can Gattermann-Koch reaction be considered similar to Friedel Craft's acylation?

Ans. Yes. The reason being that in F.C. acylation reactions, benzene (or any other arene) is treated with an acid chloride in presence of anhyd. AlCl_3 . Since HCOCl (Formyl Chloride) is not stable. Therefore, in Gattermann-Koch reaction, it is prepared in situ by reacting CO with HCl gas in presence of anhydrous AlCl_3 . Thus, Gattermann-Koch "action is similar to F.C. acylation reaction".

IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

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)
(i) Cinnamaldehyde	(a) Pentanal
(ii) Acetophenone	(b) Prop-2-enal
(iii) Valeraldehyde	(c) 4-Methylpent-3-en-2-one
(iv) Acrolein	(d) 3-Phenylprop-2-enal
(v) Mesityl oxide	(e) 1-Phenylethanone

Ans. (i) \rightarrow (d) (ii) \rightarrow (e) (iii) \rightarrow (a) (iv) \rightarrow (b) (v) \rightarrow (c)

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

Column I (Acids)	Column II (IUPAC names)
(i) Phthalic acid	(a) Hexane-1,6-dioic acid
(ii) Oxalic acid	(b) Benzene-1,2-dicarboxylic acid
(iii) Succinic acid	(c) Pentane-1,5-dioic acid
(iv) Adipic acid	(d) Butane-1,4-dioic acid
(v) Glutaric acid	(e) Ethane-1,2-dioic acid

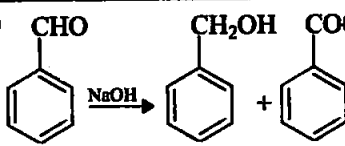
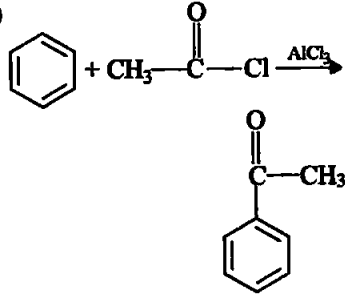
Ans. (i) \rightarrow (b) (ii) \rightarrow (e) (iii) \rightarrow (d) (iv) \rightarrow (a) (v) \rightarrow (c)

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

Column I (Reactions)	Column II (Reagents)
(i) Benzophenone \rightarrow Diphenylmethane	(a) LiAlH_4
(ii) Benzaldehyde \rightarrow 1-Phenylethanol	(b) DIBAL-H
(iii) Cyclohexanone \rightarrow Cyclohexanol	(c) Zn(Hg)/Conc. HCl
(iv) Phenyl benzoate \rightarrow Benzaldehyde	(d) CH_3MgBr

Ans. (i) \rightarrow (a) (ii) \rightarrow (b) (iii) \rightarrow (c) (iv) \rightarrow (d)

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

Column I (Example)	Column II (Reaction)
(i) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} + \text{H}_2 \xrightarrow{\text{Pd-C/BaSO}_4}$ $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	(a) Friedel-Crafts acylation
(ii) 	(b) HVZ reaction
(iii) 	(c) Aldol condensation
(iv) $\text{R}-\text{CH}_2-\text{COOH} \xrightarrow{\text{Br}_2/\text{Red P}}$ $\text{R}-\underset{\text{Br}}{\text{CH}}-\text{COOH}$	(d) Cannizzaro's reaction
(v) $\text{CH}_3-\text{CN} \xrightarrow[\text{(ii) H}_2\text{O/H}^+]{\text{(i) SnCl}_2/\text{HCl}} \text{CH}_3\text{CHO}$	(e) Rosenmund's reduction
(vi) $2\text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}}$ $\text{CH}_3-\text{CH}=\text{CHCHO}$	(f) Stephen's reaction

Ans. (i) → (e) (ii) → (d) (iii) → (a) (iv) → (b) (v) → (f) (vi) → (c)

V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct and reason is correct explanation of assertion.
- Assertion and reason both are wrong statements.

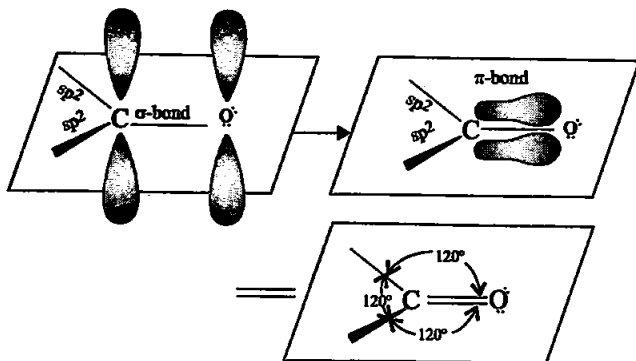
- (iii) Assertion is correct statement but reason is wrong statement.
 (iv) Assertion is wrong statement but reason is correct statement.
 (v) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

42. **Assertion** : Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

Ans. (i)

Explanation:



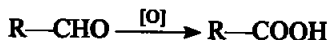
Orbital diagram for the formation of carbonyl group.

43. **Assertion** : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with LiAlH_4 .

Ans. (v)

Explanation: Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehling's reagent also oxidise aldehydes.

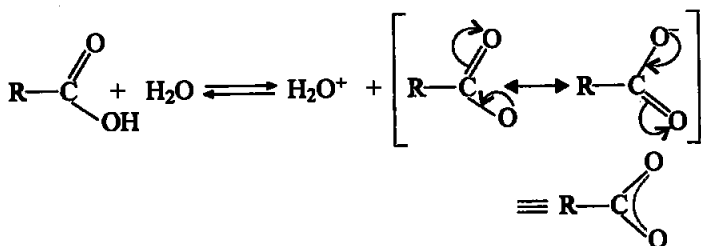


44. **Assertion** : The α -hydrogen atom in carbonyl compounds is less acidic.

Reason : The anion formed after the loss of α -hydrogen atom is resonance stabilised.

Ans. (iv)

Explanation: Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



45. **Assertion** : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

Ans. (iii)

Explanation: Aldehydes which do not have an alpha α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

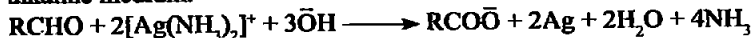
46. **Assertion** : Aldehydes and ketones, both react with Tollens' reagent to form silver mirror.

Reason : Both, aldehydes and ketones contain a carbonyl group.

Ans. (iv)

Explanation: Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage. The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) **Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



VI. LONG ANSWER TYPE

47. An alkene 'A' (Mol. 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.

Ans. Molecular formula = C_5H_{10}

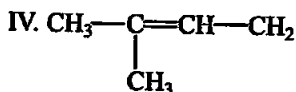
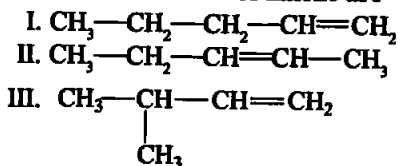
$$\text{Degree of unsaturation} = (\text{C}_n + 1) - \frac{\text{H}_n}{2}$$

where, C_n = number of carbon atoms

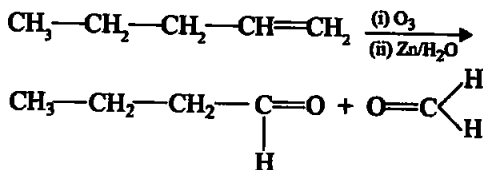
$$H_n = \text{number of hydrogen atoms} = (5 + 1) - \frac{10}{2} = 1$$

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

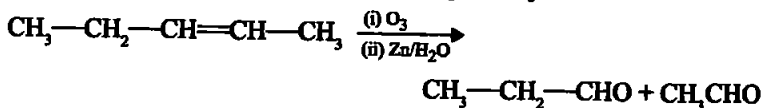
Possible structures of alkene are



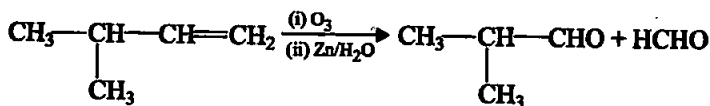
Ozonolysis of structure I produces aldehyde only



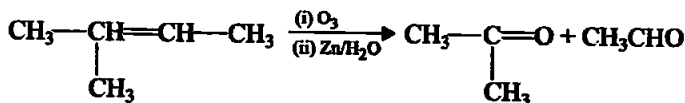
Ozonolysis of structure II produces aldehyde only



Ozonolysis of structure III produces aldehyde only

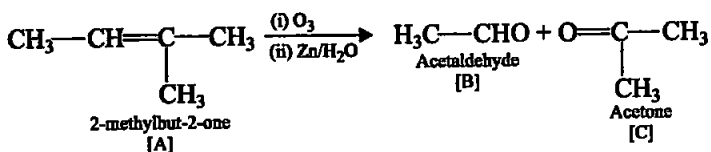


Ozonolysis of structure IV produces both aldehyde and ketone



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's test but must give iodoform test. Hence, compound must

be a ketone with $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{—C—} \end{array}$ group. Hence, correct structure is IV.



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



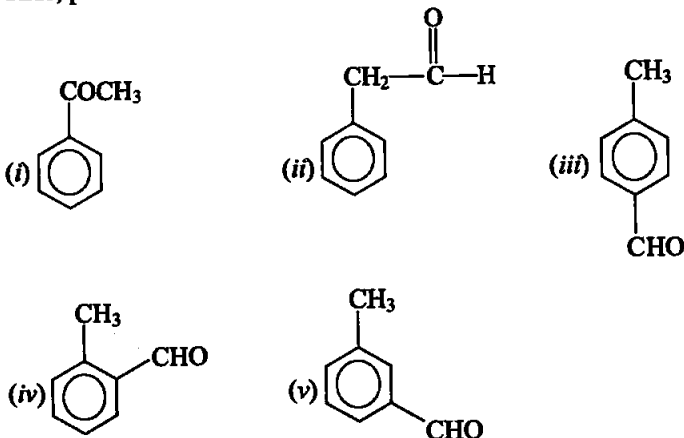
48. An aromatic compound 'A' (Molecular formula $\text{C}_8\text{H}_8\text{O}$) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium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

Ans. Molecular formula = $\text{C}_8\text{H}_8\text{O}$

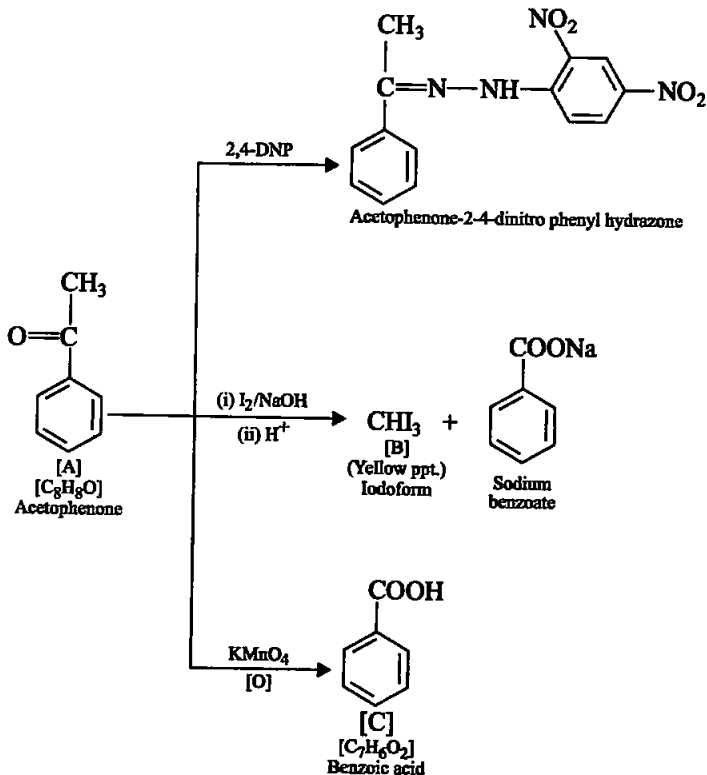
$$\text{Degree of unsaturation} = (\text{C}_n + 1) - \frac{\text{H}_n}{2} = (8 + 1) - \frac{8}{2} = 9 - 4 = 5$$

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

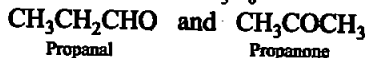


According to question, compound 'A' does not respond to Tollens' or Fehling's test, so, it is a ketone, not aldehyde. Therefore, structure I is correct. Complete reaction sequence is as follows:



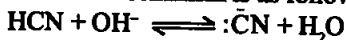
49. Write down functional isomers of a carbonyl compound with molecular formula $\text{C}_3\text{H}_6\text{O}$. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

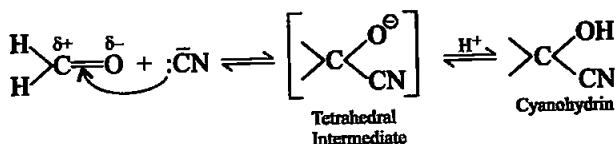
Ans. Functional isomers of $\text{C}_3\text{H}_6\text{O}$ containing carbonyl group are



(a) Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$ will react faster with HCN because there is less steric hindrance and electronic factors, which increases its electrophilicity.

(b) The reaction mechanism is as follows:



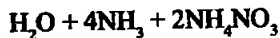
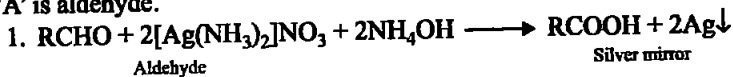


The reaction does not lead to completion because it is a reversible reaction. Equilibrium is established.

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

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 hydrogensulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogensulphite 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), 'A' is aldehyde.



Note: Aldehyde and ketone both gives white crystalline solid with sodium hydrogensulphite but this is only aldehyde which gives Tollens' test and Fehling's test.

□□□